A SPECTROSCOPIC STUDY OF

SOME FREE RADICALS

A thesis presented for the
Degree of Doctor of Philosophy in Chemistry
in the University of Canterbury,
Christchurch, New Zealand.

by

B.M. PEAKE

1971

with 2 accompanying binders
in back pocket.
To

Margaret and my Parents
This thesis contains the results of an original spectroscopic study of some free radicals. Previous work in this field is reviewed and acknowledged. The experimental results are the work of the author except where stated. This thesis is not substantially the same as any which has already been submitted to any other university.
ACKNOWLEDGEMENTS

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I am indebted to BP (N.Z.) Ltd. for the provision of a postgraduate scholarship during the course of this study.
The following papers relating to research described in this thesis have been published:

1) 'A re-interpretation of the EPR Spectrum of the 1,2,3,6,7-hexahydrophenyl Anion Radical'. R.F.C. Claridge, B.M. Pakes, Molecular Physics 18 137 (1970).


Copies of the first two papers are enclosed in the envelope at the end of this thesis.

Papers on this work were also presented at the following conferences:


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(c) TITLE, PLOT: ESR Plotting Program Package.

(2) LIMSHAPE: Calculation of Linewidth Alternation effects in First Order ESR Spectra of Radicals in Solution.

(3) LSTOR: Least Squares Fit of Data to a Linear Function of the form \( Y = DX + A \).

(4) HUCKEL, MOCALC: Simple Huckel, Omega, McLachlan, and Ion Pair MO Calculations.

(5) SCFMO: Semi-Empirical Self Consistent Field MO Calculations.

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ABSTRACT

A spectroscopic study of the radical ions of two series of alkyl substituted naphthalene compounds has been made using ESR techniques. The temperature dependence of the spectra of these species was theoretically simulated and was found to be markedly dependent upon the size and shape of the aliphatic substituents. In some cases chair and boat forms of the molecule could be resolved at low temperatures and the activation energy for the interconversion between these forms was calculated from spectra. Ion pairing effects were observed in certain solvents and predictions regarding the possible structure of these species were made. Simple Huckel and its modifications and Semi-Empirical SCF MO theory have been used to calculate spin densities and the relation of these to observed hyperfine coupling constants was discussed.
CHAPTER ONE

INTRODUCTION AND REVIEW

1.1 Introduction to Free Radicals and Methods of Detection

A free radical is an atom, molecule, or complex which contains one or more unpaired electrons. This project is concerned with the study in the liquid phase of such species that have a single unpaired electron, are stable, have either a positive or negative charge, and are organic in origin.

Historically, Comberga,2 in 1900 was the first to discover an authentic free radical when he observed that hexaphenylethane in various solvents reacted with paramagnetic gases to give the corresponding triphenylmethane derivatives. Later Wood3 separated atomic hydrogen from an electrical discharge tube and Paneth and Holéditz4 in 1929 deduced that the species formed upon heating lead tetramethyl was the free neutral methyl radical, CH3. Since then, a large number of radicals have been prepared and extensively studied.

The presence of unpaired electrons in a free radical, gives it a very high chemical reactivity and an inherent magnetic moment.

As a consequence, these two properties form the basis of the main methods of detection of free radicals and a brief review of some of the techniques used in these methods is as follows:
(1) Mirror: First used by Paneth (see above), this technique has been extended to a large number of organometallic compounds. It involves heating a sample of the compound in a flow tube such that the decomposition products are swept past a 'mirror' of the parent metal. If the mirror disappears then this is considered as evidence for radical formation. It has been used extensively to detect short lived gaseous radicals.

(2) Abnormal Chemical Reactivity: Free radicals may be detected by the unusual products they form by initiating what would otherwise be forbidden reactions. A study of reaction rates for reactions such as polymerisation indicate that the presence of free radicals is necessary to initiate the reaction. The recombination of gaseous free radicals may be detected by the heat evolved when they recombine on the surface of platinum wire which is part of an electrical bridge circuit (7).

(3) Mass Spectrometry: A radical ion has a much lower appearance potential than the same ion produced from the parent molecule within the ion source. Thus the two may be distinguished in mass spectra and molecular weights and cracking pattern differences measured for the radicals.

(4) Absorption Spectroscopy: The presence of the unpaired electrons in a free radical causes a change in the energy levels of the highest occupied orbitals. This, combined with the fact that it is much eas-
ier to promote a single unpaired electron rather than one in a doubly
occupied orbital, causes a shift in the frequency of light absorbed by
such a molecule. As a result many radicals are highly coloured rela-
tive to their parent compounds (for example, the olive green colour of
the naphthalene anion prepared from colourless naphthalene) and thus
show marked differences in their UV and visible spectra.

The UV spectra of radicals also differ from those of their parent
compounds not only because in many cases, a bond has disappeared and
therefore its vibrational frequency no longer exists, but also because
shifts in the frequencies of other vibrations occur through the absence
of coupling between the vibrations of the 'broken' bond and those from
the remaining bonds in the molecule. The absorption spectra of radic-
als in the gas phase produced by flash photolysis may be readily
measured using a second flash some fraction of time after the primary
one. In cases of unstable radicals it is often necessary to trap them
in some sort of inert matrix at low temperatures before the above
spectroscopic methods of detection can be used.

(5) Magnetic Susceptibility: The presence of a magnetic moment in
free radicals makes them paramagnetic and so when a sample is placed
in a static magnetic field it tends to be drawn into it, whereas a
diamagnetic sample is pushed out. A quantity known as the paramag-
netic susceptibility may be calculated from experimental measure-
ments of this effect made using equipment such as a dewy balance
or by NMR spectroscopy. From this quantity, the concentration of
the paramagnetic species may be calculated.

(6) Nuclear Magnetic Resonance: The paramagnetic character of free radicals causes lines in the NMR spectra of these species to be
(1) broadened because the magnetic moment of an electron is $10^3$ times greater than that of a nucleus and thus the spin-lattice relaxation time is promoted, and (2) shifted according to the sign and magnitude of the electron-nuclear coupling constant. Thus radicals may be detected by this method and considerable structural and electronic information obtained. For example, a series of fluorinated phenoxy radicals have been studied by NMR.

(7) Microwave Spectroscopy: Two distinct techniques may be considered for this method viz., resonant absorption at microwave frequencies in
(1) the absence and, (2) the presence of large perturbing fields such as that provided by a static magnet. The former of these, is similar to IR spectroscopy except that rotational rather than vibrational information about the radical is obtained from the spectra. It has not been used extensively at all, mainly because of practical difficulties.

The latter technique, involving application of a large magnetic field, has been used far more extensively and successfully in the detection and identification of free radicals. It is this technique which is known as Electron Spin Resonance* (abbreviated to ESR) and it is the

* The term Electron Paramagnetic Resonance (abbreviated to EPR) is sometimes used to describe this same technique but it will not be used in this report.
spectroscopic technique used exclusively in this project to study a series of stable organic free radicals. A brief outline of the theory of ESR will be given in the next section.

1.2 Theory of ESR and its Applications to the Study of Radical Ions in Solution.

As well as being a branch of microwave spectroscopy, ESR is also included in the subject known as Magnetic Resonance Spectroscopy. This subject is concerned with the observations of transitions induced by the absorption of electromagnetic radiation in the presence of an external magnetic field. In ESR, these transitions are between states of different energy arising from interaction of the unpaired electron spin with the magnetic field.

In more detail, the unpaired electron of a free radical has an inherent magnetic moment, \( \mu \), given by

\[
\mu = -\beta g S
\]

where \( hS \) is the spin angular momentum of the electron,
\( g \) is the Landé g factor,
\( \beta \) is the electron Bohr magneton.

Interaction of this magnetic moment with the external magnetic field \( H \) (known as Zeeman interaction) causes it to align itself either parallel or antiparallel to the field. These two situations, designated by the ket vector \( |M_s\rangle \) where \( M_s \) (the electron magnetic quantum
number) is equal to $-1/2$ and $+1/2$ respectively, are normally degenerate but in a magnetic field they are separated by an energy difference of $g\beta H$ as shown below:

Transitions between the two levels can be induced by application of an oscillating magnetic field, $H_\perp$, perpendicular to $H$ and with a frequency $\nu$ such that

$$h\nu = g\beta H$$

This is known as the Resonance Condition. And for a magnetic field $H$ of 3500 Gauss, assuming a $g$ value of 2, $\nu$ is calculated from this equation to be about 10,000 Mc/s for resonance to occur, and this is in the microwave region of the electromagnetic spectrum.

As well as interacting with the external field, the unpaired electrons magnetic moment also interacts with the magnetic moment of nearby nuclei of atoms in the radical which are encompassed by the molecular orbital of the unpaired electron. This is known as Hyperfine interaction and may be of two types: (1) Anisotropic
(or Dipolar) Coupling: this is entirely analogous to the classical coupling between two bar magnets and because of the random motion of radicals in solution this splitting is averaged to zero in most circumstances; (2) Isotropic Coupling: this arises from the Fermi contact term* and does not average to zero for radicals in solution. The effect of this hyperfine interaction on the energy level diagram given above, is to split each of the two states arising from Zeeman interaction into two or more states whose number depends upon the number of nuclei and their nuclear spin. The interaction with a proton \((M_I = \pm 1/2)\) is shown in this diagram. It is the scanning of the magnetic field over the complete range of possible transitions that is known as an ESR spectrum.

In practice, hyperfine interaction with a proton causes the single line previously observed to be split into two lines separated by a distance known as the Hyperfine Coupling Constant. Theoretically this quantity designated by the symbol \(A\), is given by the Fermi term

\[
A = \frac{8\pi/3}{\varepsilon B_N} \beta_H \left| \Psi(0) \right|^2
\]

* This interaction was first introduced by Fermi to account for Hyperfine structure in atomic spectra, and it represents the energy of the nuclear moment in the magnetic field produced at the nucleus by electric currents which are associated with the unpaired electron.
where the subscript \( N \) refers to the nucleus. Thus for a non zero value of \( A \), there must be a finite probability of the electron wave function at the nucleus, and thus the magnitude of \( A \) is a valuable source of information regarding the chemical and electronic structure of the radical. The above condition also raises some interesting problems with regard to the mechanism of this hyperfine interaction but these will be discussed in more detail in Chapter 5.

These ideas may be extended to hyperfine interaction with other nuclei in the radical and if more than one atom has the same coupling constant then the atoms of this type are said to be magnetically equivalent and usually occupy geometrically equivalent positions in the molecule. It can be shown to first order that the interaction of an unpaired electron with an equivalent nucleus with spin \( I \) will give \( 2M \times 1 \) lines spaced at a distance apart equal to the hyperfine coupling constant and whose relative intensities are proportional to the coefficients in the binomial expansion of \((1 + x)^n\). Second order effects are discussed in Appendix III. It should be noted that deuterium \((I = 1/2)\) gives a different splitting pattern to hydrogen \((I = 1/2)\) and thus by selectively deuterating one set of equivalent atoms in a radical, it is possible to identify the coupling constant arising from this set, as all the other constants will remain the same and give the same number of lines as in the undeuterated species. \(^{15}N\) and \(^{13}C\) nuclei have also been used for this purpose.
Apart from the position of the resonance lines in the ESR spectrum of a radical in solution, which from the resonance condition can be seen to be determined by the value of $g$ and hyperfine interaction, the width and shape of lines are also of interest and can provide useful information. The width of a line can be expressed in terms of frequency from the Heisenberg Uncertainty principle as

$$\Delta \omega = \frac{1}{2 \tau}$$

where $\tau$ is the relaxation time. This is made up of two parts: the spin-spin or transverse, and the spin-lattice or longitudinal, relaxation times. In ESR, the major contribution to the linewidth is from the former of these effects and thus for radicals in solution it is markedly dependent upon the concentration of the radical species, the nature of the solvent, and various other inter- and intra-molecular processes such as electron transfer and conformational interconversion. In this way considerable kinetic information can often be obtained from a study of linewidths of free radicals in solution (11). Linewidth effects can also arise for instrumental reasons such as modulation broadening and magnetic field inhomogeneity where resonance will occur over a wide range of applied fields and thus broaden the absorption lines.

Up until this point, the discussion has been restricted to free radicals with only one unpaired electron, but ESR spectra may also be
observed for radicals in solution with two or more unpaired electrons under certain conditions, dependent upon the proximity of the electrons to each other in the molecule. For example, an extensive study of some nitroxide biradicals has been made\textsuperscript{12}.

Finally, some ESR lines are broadened by the presence of hyperfine coupling which the conventional spectrometer cannot resolve. By using Electron Double Resonance (abbreviated to ENDOR) these very small hyperfine coupling constants can be resolved\textsuperscript{13}, because this technique gives only one absorption line for each group of nuclei with a particular hyperfine coupling constant, whereas the ESR spectrum would have $\sim 2^n$ lines for $n$ nuclei and these would probably overlap.

1.3 Summary of ESR Studies of the Radical Ions of Naphthalene and its Derivatives.

In order to provide a background to the naphthalene compounds studied with ESR techniques in this project, a review will be given in this section of some of the studies that have been made, up until the time of commencement of this project, on the radical ions of naphthalene and its derivatives and, in particular, those relating to alkyl-substituted naphthalenes.

Since the initial study by Weissman et. al.,\textsuperscript{14} of the naphthalene (abbreviated to N) anion in 1,2-dimethoxyethane (DME), this species had been extensively studied by a large number of groups. Included
in these were Tuttle and Weissman\textsuperscript{15} who observed C\textsuperscript{13} satellite hyperfine coupling in the spectrum\textsuperscript{8} of the N anion of C\textsuperscript{13} enriched naphthalene, and Lawler et. al.\textsuperscript{16} who analysed the deuterium isotope effects in the spectra of ten different deuterium-substituted naphthalenes. Ion pairing effects for the N anion in other solvents such as tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) with Na as counterion were first noted by Atherton and Weissman\textsuperscript{17}. This work was extended by Hirota\textsuperscript{18} who considered the temperature dependence of the alkali metal splitting for N anion pairs produced by reduction with all the alkali metals in a wide variety of solvents. Very recently, Fraenkel et. al.\textsuperscript{19} considered the effect of ion pairing on the g value of the N anion in different solvents.

The positive ion of N prepared by oxidation with concentrated H\textsubscript{2}SO\textsubscript{4} was reported as a monomer by Carrington et. al.\textsuperscript{20} but in later reports had been found by Lewis and Singer\textsuperscript{21} and Howarth and Fraenkel\textsuperscript{22} to exist as a dimer when produced by oxidation with SbCl\textsubscript{5} in CH\textsubscript{2}Cl\textsubscript{2}.

Of the derivatives of naphthalene that have been studied with ESR, those with alkyl groups and, in particular, methyl groups, as substituents have received most attention. This is because they provide a relatively simple series of radical ions in which the perturbing effects of a substituent can be readily and successfully correlated with valence.

* Unless specifically referred to, the term 'spectrum' will hereafter be used to denote an ESR spectrum.
theory predictions. The spectra of the anions of the symmetric dimethly- 
naphthalenes (DMN) viz. 1,1-; 1,5-; 1,8-; 2,3-; 2,6-; and 2,7- iso-
mers (see structure I in Figure 1.1 for the numbering system) was first 
reported by de Waard and Henning 23 who prepared them by reduction with 
K in dioxane. Soon after this Gerson et al. 24 reported spectra of the 
same species but prepared with Na in DME. Both groups correlated the 
observed hyperfine coupling constants with spin densities calculated by 
simple Hückel Molecular Orbital (MO) theory. The spectrum of the 
2,3-DMN anion only, in liquid NH3, was reported by Maximadsky 25 but no 
analysis was made. Of the other methyl substituted naphthalenes only 
the 2,3,6,7-tetramethylnaphalene (TN) anion had been studied, by 
Bolton who apparently also studied the symmetric DMNs, but whose work 
is unpublished apart from in his thesis 26, copies of which are unattain-
able (the values he obtained for the coupling constants in the 2,3,6,7 
TN anion have been published by Howarth and Fraenkel 27 ).

No ion pairing effects had been observed for the DMN anions but the 
alkali metal splitting in the anion of 2,6-di-t-butyl naphthalene pre-
pared with Na in THF had been reported by Hirota and Kriedich 23. No 
studies of the unsymmetric DMNs appeared to have been made nor of any 
of the DMN cations. However, results for the 2,3,6,7-TN cation prepared 
by oxidation with SbCl5 in CH2Cl2 were reported by Howarth and Fraenkel 26.

Of the other alkyl-substituted naphthalenes, the ions of the peri-
FIGURE 1.1 Structural formulae for Naphthalene and some derivatives
substituted compoundsacenaphthene (ACN),acenaphthylene (AYN),pyracene (PYC), and hexahydropyrene (H) (II,III,IV, and V in Figure 1.1) had been studied with ESR. The ACN anion and its ion pairs had been studied extensively by a number of groups. It did not appear that the ACN cation had been prepared. The spectrum of the AYN anion and its ion pair was first observed by de Boer and Weissman and had since been studied by a number of groups. In both cases of the ACN and AYN anions, theoretical calculations of the ion pairing effects had been made. Attempts to observe the spectrum of the cation appear to have been unsuccessful.

The spectrum of the PYC anion was first reported by de Boer and Mackor and showed linewidth alternation effects (see later for an explanation of this term) dependent upon the nature of the solvent and counterion. Possible structures for the PYC ion pairs considered responsible for these effects, were considered in these reports. Second order effects were observed by de Boer in the spectrum of the PYC cation prepared by oxidation with concentrated H₂SO₄. Similar effects were observed by de Boer and Praat for the spectra of the HP cation prepared with BF₃ in liquid SO₂. They also interpreted the spectrum of the HP anion with Na⁺ as counterion in DME as being due to the presence of boat and chair forms of this molecule. Shortly afterwards, Iwaizumi and Isobe confirmed this analysis and also reported possible ion pair-
FIGURE 1.2 Structural formulae of the Peri-alkynaphthalenes studied in this project.
ing effects for the HF anion in THF similar to what had been observed for PYC. Studies of the acepleiadiylene anion (VI) and cation were made by Gorson and Heinzer.\textsuperscript{38}

Apart from the above alkyl-substituted compounds, the only other naphthalene derivatives that appeared to have been studied with ESR were the 1,8-dinitronaphthalene and 1,4,5,8-tetranitronaphthalene anions as reported by Gorson and Adams.\textsuperscript{39} Ion pairing effects were observed for the former of these two compounds only.

Further details of these studies will be given in later sections.

1.4 Introduction to the Present Study

In this project it was planned to extend previous studies made on the alkyl-substituted naphthalene compounds reviewed in the previous section, and to look at the radical ions of two new series of compounds of this type, using ESR techniques. It was hoped then to perform some theoretical studies and compare results calculated with MO theory with those obtained from spectra.

The first of these series, was the four peri-substituted naphthalene compounds shown in Figure 1.2. As indicated in Section 1.3, the only one of these whose radical ions have been studied with ESR, was

* The formal chemical names for the compounds I-IV are respectively
2,3-dihydrophenalene; 7,8,9,10-tetrahydrocycloheptadecahydrodicyclonaphthalene; 1,2,3,6,7,8-hexahexahydrophenalene; and 1,2,3,4,7,8,9,10-octahydrodicyclo-
(1,2,3,6,7,8-hexahexahydrophenalene. For brevity, these will be referred to in this
project by the names perinaphthalene, pleiadane, hexahexahydrophenalene and
dipleiadane, with the abbreviations PN, P, HP, and DP respectively.
FIGURE 1.3 Classical Molecular Structures of

(a) HEXAHYDROPYRENE

Chair

Boat

(b) DIPELIADANE

Chair

Boat
the HP molecule and it will be shown in this thesis, that at least in
the case of the HP anion, the original spectra analysis made by de
Boer\textsuperscript{36} and Iwalami and Isobe\textsuperscript{37} was incorrect. The interest in this
series from the ESR point of view was fourfold.

Firstly, there was the effect of the aliphatic substituents on
the coupling constants of the ring protons and also the extent of trans-
fer of unpaired spin density from the \( \pi \) system on the aromatic ring
into the side chains. It was thought that interesting comparisons might
be able to be made between these results for the mono- and di-peri-sub-
stituted compounds.

Secondly, there seemed a definite possibility that the DP molecule
might exist in a number of conformations including the chair and boat
forms shown in Figure 1.3 (a) in much the same way as had been observed
for HP\textsuperscript{36,37}. Molecular models of both these forms for DP indicated that
considerable repulsion effects existed between the \( \beta \) axial protons in
either of the two forms, and that a third 'twisted' configuration was
possible, which would destroy the planarity of the aromatic ring but
relieve this proton-proton interaction. Further, comparison of models
of DP and HP (Figure 1.3 (a) and (b)) tended to indicate that it was
more difficult to bring about interconversion of boat and chair forms
of DP than in HP. Although this may not have been necessarily true for
the actual molecules in solution, it did suggest that the energy of act-
ivation for this interconversion should be larger for DP than for HP.
FIGURE 1.4 Classical Molecular Structures of

(a) PERINAPHTHANE

(b) PLEIADANE
It was thought that a detailed temperature dependence study of the spectra of the radical ions of both molecules should confirm some of the above suggestions regarding conformational effects. Although PN and P (Figure 1.4 (a) and (b)), could obviously not have occurred in chair and boat forms, the same motion should have been observed in the spectra of the radical ions of these species.

Thirdly, it had already been proposed\textsuperscript{37}, that the HP anion produced by reduction with K in THF existed as an ion pair and the spectrum at $-90^\circ\text{C}$ had been analysed in terms of the motion of the alkali metal cation between the two symmetric positions of the carbon atoms at either end of the molecule in the same way as had been proposed for the FIC anion\textsuperscript{34}. If this was correct, then it was thought that these ion pairing effects should also have been evident in the spectra of the HP anion in more polar solvents such as MTHF, and also for the radical ions of DP, DN, and P in these solvents. Thus from an ESR study of the radical ions of all four molecules in a variety of solvents and with different counterions, it was hoped to obtain further information regarding the formation of ion pairs.

Fourthly, it was planned to undertake theoretical calculations using MO theory and try to simulate the above three features and thus gain further insight into the electronic structures of these four molecules.

The second series of compounds that it was planned to study with
ESR techniques was the ten DMN isomers. As indicated in Section 1.3, only the radical ions of the six symmetric isomers had been extensively studied\textsuperscript{23,24,25}. In view of this, it was proposed to look at the radical cations of all the DMN isomers and the radical anions of the unsymmetric ones. From these results and the correlation of the observed hyperfine coupling constants with spin densities predicted by MO theory, it was hoped that further information would be obtained regarding the effect of the two methyl groups on the aromatic naphthalene ring. Also no ion pairing effects for these species had been reported and so it was proposed to investigate this aspect of the series.

Unfortunately during the later half of this project, an extensive study of the radical anions of the symmetric DMNs as well as the 1 and 2-methylnaphthalene and 1,1,5,8-tetramethylnaphthalene anions was reported by Fraenkel et al.\textsuperscript{1,10}. This contained results that had already been obtained in this project but were unpublished at the time, as well as other work which we had proposed to do. Comparisons of results from this project with those reported by Fraenkel will be made at appropriate places. As far as is known, no work has been published on the first series of compounds during the course of this project.

Finally, there have been a number of recent reports of ESR studies of miscellaneous compounds related to both series of compounds and again these will be discussed where appropriate.
CHAPTER TWO

EXPERIMENTAL APPARATUS AND TECHNIQUES

2.1 Preparation of Radicals

2.1.1 Introduction and Review

The main methods of production of free radicals involve chemical, photolytic, radiative, and electrolytic techniques. Of these the former is the most common and was used almost entirely in this project. The details of the various chemical methods available are best discussed in terms of the type of radical that they produce as follows:

(1) Radical Anions: Easily the most widely used method to produce these species is by reduction with an alkali or alkaline earth metal, as first reported by Beckmann in 1891 when he noted the dark blue compounds formed by reaction of alkali metals with aromatic ketones in the absence of air. Later Schlenk recognized these products as radical anions and investigated the formation of dianions from unsaturated hydrocarbons and alkali metals. However, no real progress was made until Scott et al. in 1936 showed that anions could be easily prepared if a suitable solvent was used. The first of what
has become a large number of ESR studies of radical anions produced by this method was by Weissman et. al.\textsuperscript{14} in 1953, when they observed the ESR spectra of the naphthalene and trimesitylboron negative ions.

The mechanism of this process involves simple electron transfer from the metal (M) to the parent material (R):
\[
R + M \rightleftharpoons R^- + M^+.
\]
It should be distinguished from reactions such as
\[
RX + 2M \rightarrow RM + MX
\]
where actual chemical replacement by the metal is occurring. In view of this mechanism certain conditions are necessary including:

(a) The parent compound must have under the experimental conditions a suitably large electron affinity; in terms of MO theory this means it must have an occupied orbital of low energy. Thus aromatic and unsaturated organic compounds are well suited to this reaction.

(b) The metal should not only have a high standard electrode potential but also a low photoselectric work function. Thus Na, K, and Cs (\(\Phi = 2.3, 2.2, \) and 1.81 e.v. respectively) give rapid reduction, while Ca, Ba, and Mg (\(\Phi = 2.7, 2.5, \) and 3.7 e.v. respectively) will reduce only with difficulty and normally only in the form of the amalgam. Li (\(\Phi = 2.3 - 2.4\) e.v.) reduces more slowly than any of the other alkali metals (see later).

(c) All solvents used must be pure and dry. This is related to the
unstable nature and high reactivities of the anions to possible impurities such as water and CO$_2$. This also means that all reductions must be done under a vacuum or at least under an inert atmosphere. The most suitable solvents have been found to be those containing ether groups e.g. 1,2-dimethoxyethane, dioxane, and tetrahydrofuran. Some reductions have also been performed in liquid NH$_3$ and dimethylformamide.

Once formed in this system the radical anion may undergo polymerisation, and further reduction such as

$$\text{R}^- + \text{M} \rightarrow \text{R}^{2-} + \text{M}^+$$

or disproportionation to the dinegative ion

$$2\text{R}^{2-} \rightarrow \text{R} + \text{R}^{2-}.$$ 

Often these are diamagnetic and hence give no ESR signals.

(2) Radical Cations: The two major methods used to produce these species and the ones used in this project are:

(I) Oxidation with strong Oxidising Agents: This method was first used by Hirshon et. al. in 1953 who observed ESR signals from sulphuric acid solutions of some thio compounds. Carrington et. al. have suggested the following mechanism for such an oxidation of a parent compound R which does not involve direct transfer of charge (c.f. alkali metal reduction):
\[
R + H_2SO_4 \rightleftharpoons RH^+ + HSO_4^- \quad (2.1)
\]

\[
R + RH^+ \rightleftharpoons RH + R^+ \quad (2.2)
\]

\[
RH + 3H_2SO_4 \rightleftharpoons R^+ + 2H_2O + SO_2 + HSO_4^- \quad (2.3)
\]

Thus a necessary condition for the radical cation \( R^+ \) to be observed is that the parent compound \( R \) should be able to be readily protonated. In terms of MO theory, this means that a small localisation energy is more important than a low ionisation potential. Again the electronic structure of many aromatic and unsaturated organic compounds satisfy this condition.

Aalbersberg et al. have suggested that in any strong oxidising acid an equilibrium such as 2.2 exists between the protonated form and the cation radical as follows:

\[
R^+ + A^- + H^+ \xrightleftharpoons{K} RH^+ + A
\]

The following expression may be deduced for the equilibrium constant \( K \):

\[
\log_{10} K = \log_{10} K_b + 16.95 \epsilon_{ox} + \text{const.} \quad (2.4)
\]

where \( K_b \) is the basicity constant for \( R \), \( \epsilon_{ox} \) is the standard oxidation potential of \( R \), \( \text{const.} \) is a constant whose value is dependent upon the nature and concentration of \( R^+ \) and \( A \).
Concentrated sulphuric acid has also been used in conjunction with a variety of organic solvents; with traces of H₂O₂, FeCl₃, and KMnO₄; and as oleum to produce cation radicals. No ion pairing effects have been observed which suggests that the cation is quite separate from the HSO₄⁻ anion.

Of the other strong oxidising acids available only methane sulphonic acid in nitrobenzene and trifluoroacetic acid in nitromethane have been used with any success to prepare cation radicals for ESR work.

(II) Oxidation with Lewis Acids: The reaction of SbCl₅ with hydrocarbons in CCl₄ to give paramagnetic species was first noted by Hilpert and Wolf in 1913. Weissman et al. in 1957 were the first to use this method for preparing radical cations for ESR studies when they observed spectra from the solid compounds formed from the reaction of perylene and tetracene with SbCl₅. Since then a large number of Lewis acids (see ref. 21 for a review of these) such as BF₃ in CF₃COOH, SbCl₅ in CH₂Cl₂, AlCl₃ in CH₃NO₂, and BF₃ in liquid SO₂ have been used.

Aalbersberg et al. have also considered the mechanism of this type of oxidation and have postulated the formation of two different species when aromatic hydrocarbons react with strong Lewis acids. These are (1) covalent complexes formed by the addition of the Lewis acid to the same carbon atom of the molecule that would undergo protonation with strong oxidising acids, and (2) monopositive ions formed by
electron transfer from the parent compound to the Lewis acid (cf. alkali metal reductions) as follows

\[ R + A \overset{\text{t}}{\rightleftharpoons} R^+ + A^- \]

The equilibrium between these two species may be written as

\[ R^+ + A^- \overset{\text{RA}}{\rightleftharpoons} \]

Monopositive Lewis Covalent
ion acid complex

and a similar expression to 2.1 may be derived for the equilibrium constant of this reaction. Aalbersberg et al. have used this to explain the relative tendencies of a number of hydrocarbons such as perylene, tetracene and benzopyrene to form positive ions.

The most suitable solvents to form the radical cations have been found to be those with a high dielectric constant probably because the cation is more stabilized by solvation in these circumstances. The apparent low rate of formation of cations in some solvents may be due to the fact that the negative counter ions must be stabilized e.g.

\[ 2\text{AlCl}_3^- \overset{\text{RA}}{\rightleftharpoons} \text{Al}_2\text{Cl}_6^{2-} \]

In the same way that mononegative ions may react further to give dianions, some monopositive ions form dimers but those still have single positive charges.\(^7,\!^5\!^2\)

A comparison of the two methods (I) and (II) shows that although the oxidising acid method is very simple (in many cases samples do not
need degassing or preparation under vacuum), it does suffer from dis-
advantages. In conc. H₂SO₄, many aromatic compounds readily sulphon- 
ate, others are not soluble in the acid, and because it freezes at 
approx. 3°C, analysis of low temperature spectra in this solvent is
very difficult. Conversely, Lewis acid oxidations are generally carried
out in solvents such as CH₂Cl₂ or CH₃NO₂ in which most organic compounds
are soluble and these all have freezing points sufficiently low to enable
well resolved spectra to be observed at low temperatures. The efficiency
of production of the radical cations in the Lewis acid method is very
much greater than with conc. H₂SO₄ e.g. the efficiency of the reaction
of 1,4-dimethoxybenzene in AlCl₃ in CH₃NO₂ is about 100% whereas in conc.
H₂SO₄ it is less than 1% (50). Reactions with CP₃COH and CH₃SOH do
increase the efficiency but it is still not as great as that obtained
by Lewis acids.

To summarise, the requirements for a suitable system for the form-
ation of cation radicals using chemical methods are⁵₃ that the oxidation
potential of the organic compound be relatively small, the electron aff-
finity of the oxidising agent be relatively large and the solvent should
have maximum polarity in order to stabilise both ionic species formed.

(III) Neutral Radicals: There are a large number of chemical methods
available to produce these species and these are normally specific to
the particular type of radical produced. In view of this, and the fact
that no neutral radicals were considered in this project, only a few examples will be given.

(1) t-Butyl hydrogen peroxide and Titanium(III) Chloride: this method pioneered by Dixon and Norman\(^5\) involves reaction of the above two compounds in a flow system to give CH\(_3\) radicals

\[
\text{Ti(III)} + \text{t-BuOOH} \rightarrow \text{Ti(IV)} + \text{t-BuO}^+ + \text{OH}^-
\]

\[
\text{t-BuO}^+ \rightarrow (\text{CH}_3)_2\text{CO} + \text{CH}_3
\]

and these radicals can then react with other species to form secondary radicals. Within the last two years, the t-butoxy radical prepared by photolysis of di-t-butyleroxide, has been used extensively\(^55\) to abstract labile protons from a variety of organometallic compounds to give the corresponding radicals. These later species and, in particular, the (Et)_\(_3\)Si radical, have in turn been used to extract halogens from compounds of the form RX to give R^+ radicals.

(2) Oxidation of Phenols with aqueous alkaline K\(_3\)Fe(CN)\(_6\) in the absence of air: this is a method used to prepare radicals from a large number of substituted phenols\(^56\).

(3) Gomberg's reaction of Triarylmethyl Chloride with a Metal:

\[
\text{Ar}_3\text{Cl}^- + \text{M}^+ \rightarrow \text{Ar}_3\text{C}^+ + \text{MCl}^-
\]

These radicals, which are in equilibrium with their dimers were among the first neutral radicals to be studied in solution by ESR methods.

(4) Oxidation of N, N-diisubstituted hydroxylamines with Tollen's
Reagent:

This method produces nitroxide radicals and a large number of these have also been studied by ESR methods.12

From this brief review it can be seen that there are a number of well developed chemical methods available to produce a given type of radical. The next sections will deal with details of experimental techniques, apparatus, and chemicals based on the same methods and used for the preparation of radicals in this project.

2.1.2 Chemicals

Solvents

(a) 1,2-Dimethoxyethane (BDH Laboratory Reagent): This was purified according to the method described by Bolton and Fraenkel57 as follows: 250 ml. of DME was placed in a 500 ml. flask and 20 gm. of CaH2 (BDH lab reagent) added and then stirred continuously for 2-3 days. The DME was distilled off (b.pt. 81-82°C) using a steam bath and LiAlH4 (Koch-Light laboratory grade) cautiously added until effervescence ceased. The contents of the flask were frozen, and the flask evacuated. Upon warming up to room temperature the DME was degassed and this freeze-pump-thaw cycle repeated until no visible signs of gas appeared on warming up. The DME was distilled over into a storage bulb which was fitted with a Teflon needle valve. This bulb had previously been prepared by
flaming out under vacuum and then forming a K/Anthracene mirror in the bulb by heating a small piece of clean K metal together with 100 mgm. of anthracene.

Upon completion of the distillation of the DME (about 2/3 only was brought over) the solvent was warmed up to room temperature and it was found to turn an olive green due to the formation of the anthracene anion. This, according to Bolton and Fraenkel, is a very sensitive test of the absence of impurities such as water and air in the DME. The storage bulb was then enclosed by Al foil to reduce photo-decomposition of the solvent. DME kept in this way was found to remain pure for at least six months, after which some sort of decomposition occurred which led to broadening of lines in spectra of species produced in the solvent. Attempts to remove these impurities by distillation on the vacuum line were unsuccessful.

(b) Tetrahydrofuran (Fluka Purum): purified as above.
(c) 2-Methyltetrahydrofuran (Eastman Organic Chemicals White Label): purified as above.
(d) Nitrobenzene (Analar): used without further purification.
(e) Sulphur Dioxide (DDH): this was used without further purification and was distilled into a storage bulb by connecting the SO₂ cylinder directly to the vacuum line.

Solutes
(a) Methanesulphonic acid (Fluka A.G., Buchs Technical Grade): This was used without further purification.
(b) Boron Trifluoride (Matheson Co., Inc.): this was used without further purification and was stored in a similar manner to SO₂ except that a trap containing glass wool was placed between the gas cylinder and the line in order to remove any of the tar-like impurities which had been observed to be present in the BF₃ in the past.

(c) Conc. Sulphuric acid (Riedel-de-Haen): used without further purification.

(d) Alkali Metals:

(i) Sodium, Potassium, Lithium (BDH): apart from purification within the reaction cells (see later) these were cut up in the atmosphere and washed in dry diethylether.

(ii) Caesium: this was prepared by the method suggested by Casson and Tabner, viz., reduction of CsCl (Analar) with calcium turnings (Riedel-de-Haen). Details will be given later.

(e) Antimony Pentachloride (Riedel-de-Haen): used without further purification.

(f) Aluminium Chloride: this was prepared by passing HCl gas over heated Al turnings.

(g) Peri-Alkylinaphthalenes: samples of pleiadane and perinaphthane were obtained from M. Opie of this department and had been prepared by the methods reported by Gilmore and Horton and Lewis and Topson respectively. The perinaphthane was brown in colour rather than the white that it is when first prepared but this did not seem to affect the purity as determined by GLC, nor the NMR spectrum. This fact had
FIGURE 2.1 Vacuum line for preparation of Radical Ions.
also been noted by Lewis and Topsoe.

Dipleiadane was prepared by D. Leonard\textsuperscript{61} and hexahydropyrene was obtained from K and K laboratories. Both were used without further purification. Of the ten dimethylnaphthalene isomers, the 1,8-DMN was obtained from M. Opie and had been prepared by the reduction of naphthalic anhydride\textsuperscript{62}. The 1,6-; 2,2-; and 2,6- DMNs were obtained from L. Light and Co. Ltd.; the 1,1-; 1,3-; and 1,5-DMNs from the Fluka Co., and the 2,7-; and 1,2-DMNs from K and K laboratories. The purity of all compounds was checked with NMR and GLC. Although in some cases (in particular the 1,2-isomer) there were small impurities, no attempt was made to purify them further, because of the difficulties reported in the literature\textsuperscript{63} for separation of these isomers even on analytical columns. Attempts made in this study to purify the liquid samples on an Autoprep were unsuccessful.

2.1.3 Apparatus and Techniques

(a) Vacuum Line: As mentioned in section 2.1.1, cation and anion radicals are rather unstable and reactive towards impurities such as O\textsubscript{2} and water. Thus a high vacuum line of design shown in Figure 2.1 was constructed to prepare these species in the absence of any traces of air, and also for the storage of purified solvents and gases.

The whole system was designed so as to allow both lines to be used
independently of each other although using common pumps. In practice, one side was used exclusively to prepare cation radicals while the other was used for anions. A Hitachi mechanical pump was used in conjunction with a Hg diffusion pump. Pressure measurements on the anion side were made using a Pirani gauge (Edwards High Vacuum) and a vacuum meter (C.H. Rowe and Co. Ltd., Model A). On the cation side, a Hg manometer with silicone oil as protective fluid was used to read pressures of corrosive gases such as BF$_3$ and SO$_2$.

Apeizon grease (Type M) was used for all joints on the anion side while KEL-F No. 90 grease was used on the cation side. Although this latter grease is not as satisfactory as Apeizon it was found necessary to use it in order to avoid reaction with the BF$_3$ and the SO$_2$.

As mentioned in Section 2.1.2, all the other solvents were stored in bulbs fitted with Fischer teflon needle valves. A number of other types of valves were tried but they all reacted with the solvents.

(b) Anion Preparation: A number of different designs of reaction cell for alkali metal reductions were tried and the most suitable one was found to be that shown in Figure 2.2 (a). There are no greased joints in this assembly other than where it is connected to the vacuum line and this feature was found to give a marked improvement in radical stability over previous designs which involved at least one joint at E. Apart from the quartz sample tube, all of the cell was constructed from pyrex glass. Modifications to this cell for caesium and lithium reductions are shown in Figure 2.2 (b).
FIGURE 2.2 Reaction Cells for Alkali Metal Reductions.
A typical reduction with Na or K is as follows: the whole assembly was placed in an annealing oven and baked out at 500°C for several hours. This had the effect of cleaning the cell thoroughly and in particular, burning out any organic material. Upon cooling, about 1 - 2 mg. of the organic compound was placed in B through the open end A. A small piece of alkali metal was washed in dry ether several times to remove any traces of the kerosene over which the metal had been stored, and then placed in the side arm at position D. The open end at A was sealed off and the whole assembly attached to the vacuum line and evacuated. The alkali metal was gently heated by placing a flame under A until it had vaporised and condensed on the cooler surfaces in the region of C. Care was found to be necessary at this stage to avoid overheating of the metal and thus 'bumping' which caused it to travel up the tube and over into B without losing its oxide coating. This procedure was repeated several times until a bright, clear, 'mirror' was formed in the vicinity of E. The lower portion of the tubes containing the impurities was sealed off each time and removed.

All steps up until this stage were done under continual pumping. The cell was then shut off from the pump and solvent admitted to the system by opening the respective needle valve. About 2-3 ml. was distilled over and frozen down in B by placing a liquid N₂ trap around it. The solvent was then warmed up to RT to remove any last traces of air,
frozen down again and pumped for 5 mins, until a pressure of $10^{-2}$ mm. Hg. was reached. At this stage it was found advantageous to reform the alkali metal mirror by gentle heating as it appeared that the solvent vapour (or more likely traces of air in it) had oxidised and removed the reactive surface of the alkali metal during the distillation of the solvent. The cell was then sealed off from the line at F and allowed to warm up to RT.

By careful tipping, the solution of the organic compound was brought into contact with the alkali metal mirror in E. Rapid reaction normally occurred as indicated by the appearance of the intense colour of the anion formed. The resulting solution was then tipped through the fritted glass disc (used to stop any pieces of metal passing into the ESR tube) into the quartz sample tube at G. The concentration of the radical anion in this part could be adjusted by distillation of more or less solvent over from B by placing a cold trap momentarily around G or B respectively.

A number of designs of side arms were tried which it was hoped would enable the anions to be produced at low temperatures but, although there have been numerous reports in the literature of this method, none of these was found to be successful in this project. It would appear that apart from immersing the whole assembly in a large dewar, there is no simple design of cell that has even part of it at low temperatures. Any side arms that could be rotated for tipping required some sort of joint which in turn required grease which as stated above, was
found to be unsatisfactory.

If the parent organic compound was a liquid then a teflon valve was placed at H and the sample admitted through this. The liquid was then thoroughly degassed and pumped down in the frozen state before the valve at H was closed. This isolated B and its contents from the rest of the assembly during preparation of the metallic mirror. When this was complete, the valve was opened again and solvent distilled directly onto the frozen liquid. From then on the preparation proceeded as normal for solid compounds.

For calcium reductions, the side arm A was extended by adding the piece shown in Figure 2.2(b). About 200 mgms. each of CsCl and Ca turnings were placed in I and a cap placed over J. The whole assembly was then evacuated and after thorough degassing of the Ca turnings, the top part J was removed by sealing off at K. Gentle heating caused a reaction between the Ca and the CsCl leading to the formation of a bright gold mirror of Cs metal in the upper part of the side arm at C. The other products in I were removed by sealing off at A. The preparation then proceeded as before.

This proved to be an extremely convenient method for preparation of Cs mirrors and alleviated any of the problems normally associated with the handling of this metal in air. Because of the small quantity produced no problems were experienced when the tube was finally opened up to the atmosphere. This method was also considered for the production
of rubidium but was discarded because RbCl melts at 770°C and reacts with Ca at even higher temperatures, and hence the section of Pyrex tubing at I would probably have melted with disastrous effects. If this section were to be made from quartz with a graded seal at L then this apparatus could probably be used for preparation of Rb mirrors as well.

A large number of frustrating attempts were made to make suitable modifications to the basic cell shown in Figure 2.2(a) for use of lithium metal as reducing agent. A search through the literature showed that either no special techniques were used over and above that used for Na or K, or the metal was used in the form of finely cut pieces, or as an amalgam. The difficulties with the first of these approaches are that Li melts (even under vacuum) at a temperature higher than that at which pyrex glass melts and thus the ordinary reaction cell could not be used, and also a protective layer of oxide forms immediately upon cutting a fresh surface on the metal in air.

Thus attempts were made to design apparatus that enabled the metal to be cut under an inert atmosphere and then evacuated without contact with air, but these were unsuccessful except for 1,6-DMN in DME which took several days for any appreciable radical concentrations to form. Attempts were made to prepare the amalgam but this was found not to produce radicals. Winkler et al. had reported the generation of Li salts of radical ions by photolysis in an inert atmosphere of the corresponding hydrocarbon in the presence of phenyl lithium. Attempts
were made in this project to prepare anions by this method using butyl lithium, but again these were unsuccessful.

From the above, it may be concluded that lithium reductions are certainly not easy and for consistent results they require some other design of apparatus from those considered in this project. Also because Li has a much higher photoelectric work function than either Na or K, it will reduce organic species more slowly than these latter two metals. Recently, Fraenkel et al.\textsuperscript{19} have noted these difficulties with Li reductions and they have recommended cutting the metal under methanol and then rapidly transferring it to the reaction cell followed by pumping off the methanol. This apparently left the metal with a clean surface.

No attempts were made to obtain quantitative estimates of the concentration of radical ions produced by these methods but from a consideration of the resolution and linewidth obtained in spectra these were $\sim 10^{-3}$ M.

(c) Cation preparation:

(1) Concentrated H$_2$SO$_4$: Although this method does not normally require that preparations be carried out under vacuum, it was considered that a vacuum might enhance the stability and increase the concentration of the actions considered in this project. With this in mind the reaction cell shown in Figure 2.3(a) was designed and used successfully.

All glass is pyrex and due to the high dielectric constant of
**FIGURE 2.3** Reaction Cells for Radical Cation Preparations.
The usual 3 mm quartz sample tube was replaced by a 0.5 mm pyrex capillary tube. 1-5 mgms. of the organic compound was placed in A together with 2-3 ml. of conc. H₂SO₄ and radicals began to form at this stage. The reaction cell was then connected to the vacuum line and evacuated. When the acid was completely degassed the cell was sealed off at C and by careful tipping, the solution containing the radicals was moved into the capillary side arm B which in turn was placed in the cavity of the ESR spectrometer.

(2) SO₂/BF₃: In designing apparatus to prepare cations by this method, precautions had to be taken to allow for the large increase in volume that occurs when 2-3 ml. of liquid SO₂ at -80°C is brought up to room temperature. Several designs were considered and the most successful was found to be that shown in Figure 2.3(c). All glass other than the ESR sample tube was Pyrex and all stopcocks (Vao Seal) were used with Kel-F Grease. The volumes of the measuring bulbs were calculated by filling with water.

A typical preparation is as follows: The key at stopcock D was removed and 1-5 mgms. of organic compound was placed in the bottom of the sample tube G. The key was then replaced and the whole assembly was connected to the vacuum line and evacuated. Stopcock F was closed and SO₂ from the storage bulb on the line was admitted to A. By closing E and opening F, it was then trapped in the finger C by placing a liquid N₂ trap around C. A similar procedure was used to transfer BF₃ into the cell. Pressures of gases were read from the mercury manometer.
Typical amounts of gases used were \( \text{SO}_2 \): 370 ml at 69 cm, \( \text{Hg} \), and \( \text{BF}_3 \): 123 ml at 40 cm, \( \text{Hg} \). Stopcock D was then closed and the assembly (i.e., from D down) was removed from the line. At this stage the \( \text{SO}_2 \) and \( \text{BF}_3 \) were still frozen in the finger C. It should be noted that the gases were not distilled directly into C because it was found that ice tended to form on the outside of the sample tube if this was done and if the tube was then inserted directly into the cavity of the ESR spectrometer then tuning problems occurred. Instead, the sample tube C was placed in the precooled cavity at \(-110^\circ\text{C}\) and the trap removed from around C which was allowed to warm up to room temperature. In this way the gases were slowly distilled from C into A where radical reaction took place with the organic material to give the corresponding cation radical. Because this part was all ready in the cavity then the radical could be detected immediately. It should be noted that because \( \text{SO}_2 \) has a very low viscosity at low temps (\( \eta = 1 \text{ cp., at } -70^\circ\text{C} \)) and has no nuclear moment, then very narrow hyperfine lines may be observed in the spectra of radicals prepared in this solvent.

(3) \( \text{CH}_3\text{SO}_2\text{H/C}_8\text{H}_5\text{NO}_2 \): The preparative technique used here followed closely that described in ref. 46: 10-15 mgm. of the organic compound was dissolved in 1-2 ml. of methanesulphonic acid. The solution was stirred for 5 minutes by bubbling \( \text{N}_2 \) gas through it. Radicals formed during this time and spectra were observed by tipping the resulting solution into a capillary tube. No precautions were taken to exclude air.
FIGURE 2.4 Block Diagram of the X Band Spectrometer
(b) \( \text{AlCl}_3/\text{CH}_3\text{NO}_2 \): 5 mgm. of the organic compound was placed in the sample tube shown in Figure 2.3 (b). 10 mgm. of anhydrous \( \text{AlCl}_3 \) was then placed in the tube in a dry box and the whole reaction cell was then quickly attached to a vacuum line and 5 ml. of \( \text{CH}_3\text{NO}_2 \) distilled into it. It was then sealed off at \( A \) and allowed to warm up to room temperature.

2.2 ESR Equipment and other Instruments

The ESR spectrometer used in this project was a 100 kHz X-band spectrometer constructed by Dr. T. J. Seed of the Physics Department, University of Canterbury. In view of the fact that it is not a commercial model a block diagram of its design is shown in Figure 2.4.

The magnet was a Varian V3503 12 in. one with a Fieldial Mark II to control the field. A Varian 1530 Klystron was used in conjunction with a Hewlett-Packard Microwave Frequency converter (Type 2590B) and Electronic counter (Type 525L) to monitor the microwave frequency. Spectra were recorded as the first derivative on a Mosely (Model 7005B) X-Y recorder. The cavity was a Varian General Purpose one and a Varian V-4557 Variable Temperature accessory was used to obtain temperatures in the range from -180°C up to +200°C. The remainder of the equipment was constructed within the Physics Department. The details of this equipment and its operation are very similar to those described by Ingram" for any general purpose high-frequency modulation.
spectrometer and hence will not be discussed here.

The magnetic field was calibrated with the Hewlett-Packard counter and a proton resonance probe. The variable temperature accessory was calibrated using a chromel-constantan thermocouple and the temperature indicated on the dial of this device were found to be accurate to within \( \pm 2^\circ C \).

Other instruments used in this project included a Varian A60 NMR spectrometer and a Varian Aerograph 1200 Gas Chromatograph.

The SCFMO calculations were performed on an IBM 360 Model 50 (250 K word core storage) computer at the University of New South Wales, Australia. All other calculations and the plotting were performed on an IBM 360 Model 44 (32 K word core storage) computer and an IBM 1627 plotter respectively, at the University of Canterbury.

2.3 Methods of Measurements and Calculation of Results

(1) Observation of Spectra

Once a sample of the radical had been prepared, the cavity of the spectrometer was tuned and a standard sample of plasticene which gave strong Mn\(^{2+}\) signals run to check modulation connections etc., and that the cavity was tuned to the best klystron mode. The quartz sample tube containing the radical solution was inserted into the cavity and the latter retuned. A number of spectra were then run to determine whether any signals were present, and if so, the scan rate, modulation
filtering, gain, microwave power, and radical concentration were adjusted so as to get maximum resolution and minimum linewidth. A check was made on the microwave power to make sure that saturation of the sample was not occurring. A recorder scale of $2 \text{G}_0 = 1^\circ$ was normally used so that observed spectra could be directly compared with theoretical spectra produced later on the $X-Y$ plotter. The temperature of the sample was then raised or lowered depending upon the nature of the radical and the solvent. Typical operating conditions were as follows:

- **Modulation Amplitude**: $0.03 \text{ G}_0$
- **Microwave Power**: $2 \text{ mW}_0$
- **Magnetic Field Sweep**: $25 \text{ G}_0$ in 10 mins, centred at $\sim 3260 \text{ G}_0$
- **Amplifier Gain**: $60 \text{ dB}$ with reference to the amplifier.
- **Integration Time**: 2 secs.

Upon completion of a run the reaction cells were cut open. Normally the intense colour of the radical disappeared immediately upon exposure to the air. Any unreacted alkali metal in the case of radical anions, was destroyed by reaction with ethanol, glycerol, water, and air for Na, K, Li, and Cs respectively. The whole cell was then washed out with ethanol to remove any traces of organic material, concentrated HNO$_3$ to remove any inorganic material such as alkali metal hydroxides (formed during decomposition of the metal), water and finally acetone. It was then placed in an annealing oven at $500^\circ\text{C}$ for several hours before
joining a new BIO connection ready for the next preparation.

It should be noted that the value of the $g$ factor, which determines the position of the centre of the spectrum in the magnetic field, is for most hydrocarbon radicals within $0.1\%$ of the free electron value of $g = 2.0023$. Although a recent study by Fraenkel et. al.\(^1\) of the variation of the $g$ value for the naphthalene anion with different counterions in a variety of solvents, has shown that considerable structural information can be obtained from such measurements, the precision and stability of the spectrometer required for this type of work precluded any similar studies being made with the spectrometer used in this project.

(2) Calculation of Hyperfine Coupling Constants

Observed spectra were measured up on a board similar to that described by Bolton and Fraenkel\(^5\). Trial values for the hyperfine coupling constants (measured to within $1/1000$) together with information regarding the nuclear spin and number of atoms giving rise to this hyperfine splitting, were then used as input for the computer program SIMESER (see separate volume for details). The theoretical spectrum was laid over the observed one on a light box and the two compared. Adjustments were made to the trial values of the coupling constants and the above process repeated until visual agreement was obtained between observed and calculated spectra. Unless otherwise stated, all lineshapes were taken to be $100\%$ Lorentzian in character. The sets of coupling constants determined in this way are in no way the only set that could fit the
spectra i.e. they are not unique, but chemical evidence and MO calculations have been used to confirm these splittings.

In the cases of the DMNs, the best hyperfine coupling constants obtained by the above methods were used as input for the computer program STICK which produced a stick absorption spectrum with each line labelled with the angular momentum quantum numbers given rise to it. These lines were then identified in the observed spectrum and their positions measured relative to a fixed point. This information was used as input for the program HYPLST* which calculates the least squares refined values of the coupling constants together with their standard deviations.

Details of the use of the other computer programs used in this project will be given in later sections.

(3) Miscellaneous: The diagrams for the peri-alkynaphthalenes (Figures 1, 3 and 11) were produced using the Canterbury University version of the crystallographic program, ORTEP, using Cartesian coordinates calculated by hand for the classical structures of these compounds i.e., aromatic angles 120°, aliphatic angles 109.5°, C-C aromatic bond length 1.39 Å, C-C aliphatic bond length 1.54 Å, and C-H bond length 1.09 Å.

* This program is a modified version of the program DATA REDUCTION V written by M. Kaplan and to whom the author is grateful for a listing.
FIGURE 3.1 ESR SPECTRA OF THE PERINAPHTHANE ANION

(a) K/DMF Experimental

(b) Computer Simulated (Linewidth is 0.1 G.)

(c) K/THF

(d) K/MTHF
1-2 mgm. of the parent compound in 2-3 ml. of other solvent was found to be readily reduced by sodium or potassium at room temperature using the procedures outlined in Section 2.1.3. The colourless solution turned a yellow colour immediately upon contact with the metal mirror and within minutes, as the concentration of the radical increased, this changed to the olive green colour characteristic of the naphthalene anion itself. Details of the spectra for this species in a variety of systems are as follows:

3.1.1 1',2-Dimethoxyethane

PN/Na,K/DME: The PN anion prepared in this system was stable for at least 24 hrs. at RT. Spectra were observed at 10° intervals over the range from -95° to +100°C. A typical spectrum for the Na reduced species at -95°C is shown in Figure 3.1 (a). Reduction with K gave identical results.

* The symbolism R/M/S refers to a system in which R is the parent organic compound, M is the reducing (or oxidising) agent, and S is solvent.
spectra over the range from -95° to +30°C.

The interesting feature about this spectrum is the absence of a strong central line thus indicating that there must be a hyperfine splitting arising from an odd number of protons or from the alkali metal cation (I = \( \frac{3}{2} \) for Na and K giving rise to four lines of intensity 1:1:1:1). The latter possibility was discounted because of the nature of the solvent not lending itself to ion pairing effects and there being no obvious groups of four lines of equal intensity. Further, a consideration of the classical model of PN shown in Figure 1.4 (a) indicated that the \( \beta \) protons were in different environments and thus could each give rise to a separate coupling constant. With this in mind a number of trial spectra were considered and finally the theoretical one shown in Figure 3.1 (b) was obtained using the hyperfine coupling constants given in Table 3.1.

<table>
<thead>
<tr>
<th>Table 3.1</th>
</tr>
</thead>
</table>

Hyperfine Coupling Constants for the Perinaphthene Anion in 1,2-dimethoxyethane at -95°C (Gauss)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta ) ax</td>
<td>8.68</td>
</tr>
<tr>
<td>( \beta ) eq</td>
<td>2.30</td>
</tr>
<tr>
<td>( \gamma ) ax</td>
<td>0.53</td>
</tr>
<tr>
<td>( \gamma ) eq</td>
<td>0.36</td>
</tr>
<tr>
<td>4,9</td>
<td>1.54</td>
</tr>
<tr>
<td>5,8</td>
<td>1.92</td>
</tr>
<tr>
<td>6,7</td>
<td>4.54</td>
</tr>
</tbody>
</table>
This spectrum was found to give best agreement with the observed one although it was very sensitive to small changes in the $\gamma$ coupling constants.

The assignment of the coupling constants to specific positions in the PN molecule was made on qualitative grounds and from a knowledge of the relative magnitudes of the coupling constants in related compounds such as acenaphthene. Also as the temperature was raised, it would be expected that the splittings arising from the aromatic protons should remain constant while the others should give rise to linewidth effects (see Section 3.5 for details). Thus it was possible to readily identify the aromatic splittings from the spectrum at $+23^\circ C$ but this did not allow the aromatic splittings to be distinguished within themselves. This was done using simple Hückel MO theory and an Inductive model for the naphthalene ring with the coulomb integrals of the $C$ atoms at the 1 and 8 positions changed to allow for the effect of the aliphatic substituents in these positions (for details see Section 5.2.2). By comparing the changes in spin densities at the 2, 3, and 1C atoms then the assignments given in Table 3.1 for the aromatic protons could be made. However, the only way to confirm these positively would be to obtain spectra from samples of PN that had been selectively deuterated in each of these positions as discussed in Section 1.2.

3.1.2 Other Solvents

(1) Tetrahydrofuran

(a) PN/H$_2$/THF: The PN anion prepared in this system was stable for
FIGURE 3.2 Comparison of spectra of the PN anion in (a) THF and (b) DME at various temperatures with Na⁺ as counterion.

-70°C
-10°C
+30°C

(a) THF

-95°C
-70°C
-10°C
+30°C

(b) DME

-90°C
-60°C
-20°C
+30°C
several days and finally decayed to a brown species that disappeared upon exposure to air. The spectrum of the anion at -95°C was identical to that of the PN anion produced by reduction with Na in DME at the same temperature. However, upon raising the temperature to +30°C marked differences were observed between the two sets of spectra as can be seen from a comparison of the spectra in THF (Figure 3.2 (a)) with those in DME (Figure 3.2 (b)) at the same temperature. These changes were quite reversible with temperature in both solvents.

No detailed analysis of these spectra in THF was made but in view of their similarity with those observed for the 2,3-dimethylnaphthalene and naphthalene anions also produced by reduction with Na in THF (see Chapter Four), it was concluded that ion pairing was occurring and the extra lines apparent in the spectrum at +30°C were due to the hyperfine splitting from the Na⁺ cation. As the temperature is lowered, this ion pair dissociates into the free ion such that at -95°C this is the only species present.

(b) PN/K/THF: Spectra were observed for the PN anion prepared in this system over the temperature range from -125°C to +50°C. Comparison of a typical spectrum at -95°C (Figure 3.1 (c)) with that observed for the PN anion with either Na⁺ or K⁺ as counterion in DME (Figure 3.1 (a)) indicates some marked differences at this temperature.

There is still no strong central line but the ratios of intensities
of the lines associated with the $M_{\beta_{ax}} = \pm 1$ components (indicated by arrows) relative to the $M_{\beta_{ax}} = 0$ lines is much more than the ratio observed for the same groups of lines in the spectra of the PN anion in DME. Possibly for the same reason, the total spectrum width in THF seems less than in DME. Also the hyperfine splitting pattern associated with the $M_{\beta_{ax}} = 0$ lines is not repeated at the $M_{\beta_{ax}} = \pm 1$ positions and each is different from that observed in DME. From $-95^\circ$ to $-125^\circ$C there was a slight change in the hyperfine pattern with all lines becoming less well resolved. This can probably be attributed to the increasing viscosity of the solvent as the temperature is lowered and thus causing an increase in linewidth. Above $-100^\circ$C, the spectra in THF were identical to those in DME at the same temperatures.

A large number of theoretical spectra were calculated and although no spectra were obtained that were in particularly good agreement with the observed one, it was found that by assuming the presence of two species in a 1:1 ratio and increasing the $\beta_{ax}$, $\beta_{eq}$, $\gamma_{ax}$, and $\gamma_{eq}$ coupling constants by a small amount such that the $\beta_{ax}$ and $\beta_{eq}$ values for the two species were slightly different, then the observed intensity ratio and hyperfine pattern of the central groups of lines could be well matched. No exact values of the hyperfine coupling constants were found.

*This symbol refers to the total $z$ component of the nuclear spin angular momenta of the axial protons at the $z$ position.*
stants could be obtained because of the difficulty experienced in manually varying 14 parameters (at one time).

As will be seen later, this suggestion of there being two species present at -95°C is not unreasonable and although no alkali metal splitting is apparent in the spectra, this may be accounted for by an ion pairing effect which becomes appreciable at temperatures below -40°C.

(2) 2-Methyltetrahydrofuran
(a) PN/K/MTHF: Rapid reaction of PN with K in MTHF occurred at RT and a typical spectrum of the species formed is shown in Figure 3.1 (d). It can be seen that this is different from that observed in DME and again from that in THF. The intensity ratio of the M\(\beta_{ax} = \pm 1\) and 0 groups of lines in the spectrum in MTHF is similar to that in DME rather than in THF. However, the hyperfine patterns of these groups of lines are different and indeed the M\(\beta_{ax} = 0\) lines are very similar (allowing for a possible increase in linewidth in the MTHF solvent) to those observed in THF. Spectra from -40°C upwards were identical to those observed in DME at the same temperatures.

Unfortunately all attempts to simulate this spectrum with either one or two species were unsuccessful.

(b) PN/Na/MTHF: Attempts to prepare the PN anion in this system resulted in only a weak green solution which rapidly turned yellow and gave no ESR signals. Reforming the Na mirror had no effect.
1-2 mgm. of the parent compound was found to react with an alkali metal mirror in ether solvents at RT using procedures outlined in Section 2.1.3. The characteristic olive green colour of the radical anion appeared immediately upon contact of the colourless solution containing the dissolved HP with the metal mirror. The intermediate yellow colour observed in the reduction of PN was not observed possibly because of more rapid reaction. Details of spectra of the HP anion observed in various systems are as follows:

3.2.1 1,2-Dimethoxyethane

(a) HP/Na/IME: The anion prepared in this system was found to be stable at RT for days. However, at temperatures >470°C, it decomposed within minutes to an orange red species (presumably this was the dianion as it gave no ESR signals but disappeared rapidly upon opening the sample to the air). Spectra were observed over the temperature range from
FIGURE 3.3  EPR SPECTRUM OF HEXAHYDROPYRENE ANION IN 1,2 DIMETHOXYETHANE WITH K$^+$ AS COUNTER-ION

Experimental

TEMP. = -95°C

5 G.

Computer Simulated (Linewidth is 0.1 G.)

H
-93°C to +83°C at 20°C intervals. A typical spectrum at -93°C is shown in Figure 3.3.

As mentioned in the introduction to this project, the HP anion had been previously prepared and its spectra observed by de Boer and Praat, and Iwaizumi and Isobe. The spectrum observed in this project (Figure 3.3) was found to be identical to that reported by these two groups for reduction of HP with Na in DME and K in DME. This provided a valuable check that the ESR and preparative techniques used in this project were at least as good as those of the above two groups.

Both of these reports had interpreted the spectrum in terms of a single \( \gamma \) coupling constant, even at temperatures several degrees below the freezing point of the solvent. An examination of molecular models of the HP molecule (Figure 1.3 (b)) indicated that the \( \gamma \) protons were in two different environments in exactly the same way as they are for the PN molecule. This, together with the fact that two different \( \gamma \) coupling constants had been resolved in the spectrum of the PN anion, suggested that a re-examination of the analysis of the spectrum of the HP anion made by the above two groups, might well be worthwhile.

It was found that computer simulation using the values previously given (Columns (1) and (2) of Table 3.2) gave spectra whose lines agreed in position but not in intensity with those of the observed spectrum.
However, by using the set of five coupling constants including two separate $\gamma$ values (Column (3) in Table 3.2) a theoretical spectrum (Figure 3.3) was obtained which was in perfect agreement with the observed one. The simulated spectrum was found to be markedly dependent upon the value of this second $\gamma$ coupling constant: spectra computed for $\gamma_{eq} = 0.35$ G and $0.37$ G gave different intensity patterns from that observed. As before it appears that the difference between the coupling constants of the boat and chair forms in $\text{LM}^2$ is too small.
to allow separate spectra to be observed for these two species.

The assignment of the larger $\gamma$ coupling constant of 0.50 G to the axial position and the smaller to the equatorial position has been made on the following qualitative grounds: the contribution to the spin density at the two pairs of $\gamma$ protons due to spin polarisation along the aliphatic side chains will presumably be the same, but as the axial $\gamma$ protons are in a more favourable position to allow hyperconjugation with the $\pi$ orbitals of the aromatic rings than the equatorial $\gamma$ protons, then it would be expected that the former should have a higher spin density and hence a larger hyperfine coupling constant. The other assignments were made from a study of the high temperature spectra (see Section 3.5). Again the only positive way to confirm all of these assignments would be to obtain spectra from species of the HP anion that had been selectively deuterated. This would be difficult, if not impossible, because the axial and equatorial protons in both the $\beta$ and $\gamma$ positions interconvert at high temperatures.

Confirmation of the presence of two $\gamma$ coupling constants came from an examination of the temperature dependence of the spectra. This will also be discussed in Section 3.5.

(b) HP/CS/DME: Very rapid reduction of HP occurred in this system at temperatures $< 0^\circ$C to produce the HP anion which was stable at RT for about half an hour.
FIGURE 3.4  ESR Spectra of the HP Anion in DME with Cs⁺ as counter ion.

(a) -90°C

(b) -40°C

(c) 0°C

FIGURE 3.5  ESR Spectrum of the HP Anion in a 2:1 DME/THF mixture with K⁺ as counter ion.

-90°C
A typical spectrum at -95°C is shown in Figure 3.4 (a). It can be seen from this that there is a broad asymmetric signal upon which is superimposed the hyperfine splitting pattern. This was thought to have been due to exchange between the anion and parent compound as this sample was prepared with excess HP, but another one prepared with excess Cs metal gave similar asymmetry. Diluting the sample with fresh solvent caused this signal to lessen considerably but also changed the hyperfine pattern slightly which, with the obvious increase in the number of lines compared with the spectrum in DME, suggested that some sort of ion pairing equilibrium was present in the system.

Although no detailed analysis of this spectrum was made, some approximate values for the hyperfine coupling constants may be determined as follows: there is no central line in the spectrum which indicates that Cs alkali metal splitting is present as this metal will cause each line of the free ion to be split into eight lines of equal intensity and no central line. The size of this Cs metal splitting is estimated to be 0.4 G. The five groups of lines associated with the largest splitting may be easily detected and gave a value of 8.3 G for the $\beta_{ex}$ coupling constant. The distance between the smaller groups is 2.0 G which may be associated with either the $\alpha$ or $\beta_{eq}$ splittings. The lack of resolution (or linewidth broadening) was reproducible and reversible.
with temperature and thus may well be due to some sort of intramolecular motion of the Cs cation near the HP molecule.

The effect on the spectrum of raising the temperature is shown in Figure 3.4 (b,c). It can be seen that a linewidth broadening effect is still present at -40°C but the position of this corresponds to that observed for conformational interconversion in the free ion and thus probably arises from this cause rather than motion of the cation. Above 0°C the spectrum decayed rapidly. Within this range there were no temperatures at which the Cs metal splitting was zero and thus causing the spectrum to consist solely of that for the free ion, as de Boer had observed for the Pyracene/Cs/DME system at -49°C.\(^3\)

Because of the complexity of this spectrum in DME, no attempts were made to prepare the HP anion by reduction with Cs in other solvents such as THF and MTHF where ion pairing effects should have been more marked.

### 3.2.2 Tetrahydrofuran

(a) **HP/K/THF**: The HP anion prepared in this system was the usual olive green in colour and was stable for at least 24 hrs. at RT. Spectra were observed at 10°C intervals over the range from -120°C to +60°C and these were found to be identical in all respects to those previously reported by Iwaizumi and Isobe\(^3\) for this system. A typical spectrum at -100°C is shown in Figure 3.6(a).
FIGURE 3.6 ESR Spectrum of the HP Anion in THF with $K^+$ as counterion

(a) Experimental

(b) Computer Simulated (Linewidth is 0.12 G.)
A comparison of this with the spectrum observed for the HP anion in DME at -95°C (Figure 3.3 (a)) shows that marked differences are present. From an examination of the spectra taken over the complete temperature range a number of features were apparent: At +23°C the linewidth alternation effect arising from conformational interconversion as observed in DME at this temperature, was also observed for this system in THF and the values of the coupling constants were the same and indeed all spectra in the range from +60°C to -40°C were identical to those observed in DME at the same temperatures. However, below -40°C, marked divergences were noticeable and the linewidth effect apparent in Figure 3.6 (a) began to appear. Below -90°C there was no change in the spectrum until the freezing point of the solvent was reached, other than the expected small increase in linewidth. No alkali metal splitting was observed over the complete temperature range. Finally, as well as the hyperfine pattern of the $M/\beta_{ax} = \pm 1$ lines having changed, so had that of the unbroadened $M/\beta_{ax} = 0$ lines relative to the spectrum in DME.

In view of these features it appeared that the lack of resolution of the $M/\beta_{ax} = \pm 1$ lines may have been caused by (a) formation of an ion pair such that intramolecular motion of the cation at these temperatures gave rise to a linewidth alternation effect (as had been previously postulated by Iwaizumi and Isobe\textsuperscript{37} for this system) and/or (b) the presence of two species such that the $\beta_{ax}$ coupling constants
were just sufficiently different to cause cancellation effects at the
\(M\beta_{\text{ax}} = \pm 1\) but not the \(\pm 2\) positions (obviously the \(M\beta_{\text{ax}} = 0\) lines
would be unaffected by the values of the \(\beta_{\text{ax}}\) coupling constants).

For a number of reasons (see discussion in Section 3.6) including the
fact that the observed effect did not change with temperature in the
range \(-90^\circ\text{C} \text{ to } -120^\circ\text{C}\) (cf. pyracene ion pair\(^{58}\)), and that the lines
at the \(M\beta_{\text{ax}} = \pm 1\) positions were irregular in pattern rather than the
symmetric shape expected, cause (a) was discounted and an analysis of
the spectra was made in terms of two species with slightly different
\(\beta_{\text{ax}}\) coupling constants.

A number of different coupling constants were considered for each
of the two species and it was found that the computed spectra changed
dramatically with a small change in these values. It appeared at first
that species (1) was in fact the free ion in equilibrium with an ion
pair (species (2)) but the spectrum computed on this basis for a
number of different models of the ion pair gave poor agreement with
the observed spectrum and it was found necessary to make the \(\beta_{\text{eq}}, \gamma_{\text{ax}},\)
and \(\gamma_{\text{eq}}\) coupling constants in both species different from that of the
free ion in DME. Finally, using the values given in Table 3.3, the
spectrum shown in Figure 3.6 (b) was obtained and it can be seen that
this is in very good agreement with the observed spectrum (Figure 3.6(a)).
In order to obtain further information about the two species that appeared to be present in THF, the HF anion was prepared by reduction with K in a mixture of 2 vols. DME: 1 vol. THF and the spectrum shown in Figure 3.5 was obtained at -90°C. This was again different from that observed for the free ion and so it seemed reasonable in view of the mixture of solvents that it may have arisen from the presence of three species: the free ion and the two species observed in THF. However, simulation of spectra with various ratios of these three species gave very poor agreement. Finally it was found that by increasing the linewidth form 0.1 G to 0.12 G and using the same coupling constants as the free ion except for small changes of the $\gamma_{eq}$ and $\gamma_{ax}$ coupling constants to 0.35 and 0.505 G respectively, a good fit to the observed spectrum was obtained.
FIGURE 3.7 ESR Spectrum of the HP Anion in MTHF with K⁺ as counterion

(a) Experimental

(b) Computer Simulated (Linewidth is 0.1 G.)
(b) \( \text{HP/Li}_2\text{Na/THF} \): A large number of attempts were made to prepare the HP anion in these two systems but in all cases they were unsuccessful with no reaction occurring. In the case of Na reduction, it had been found that the same sample of metal and solvent had successfully reduced the closely related compound, PN, to its anion (see Section 3.1.2) and thus the difficulty of reduction of HP is concluded to lie in the actual reaction (or lack of it) of the Na with the HP molecule, rather than in the purity of the chemicals or the design of the apparatus used in the reduction.

3.2.3 2-Methyltetrahydrofuran

(a) \( \text{HF/K/THF} \): The HP anion prepared in this system was not very stable and decomposed to a bright red diamagnetic material after 6-8 hrs. at RT. The spectrum of the anion at \(-80^\circ \text{C}\) is shown in Figure 3.7.

(a) Apart from the obvious change in phase of the signal, this spectrum can be seen to be quite different from that observed in either DME or THF. A temperature dependence study was made from \(-110^\circ \text{C}\) up to \(+20^\circ \text{C}\) and this indicated drastic changes in that not only was the expected linewidth alternation effect arising from conformational interconversion observed, but also as the temperature was lowered from \(-80^\circ \text{C}\) to \(-110^\circ \text{C}\) certain parts of the spectrum became less well resolved and this can be clearly seen from the spectra at various temperatures shown in Figure 3.8.

Examination of these spectra indicated a number of features as
FIGURE 3.8 ESR Spectra of the HP Anion in MTHF at low temperatures with $K^+$ as counter ion

(a) $-80^\circ C$

(b) $-90^\circ C$

(c) $-100^\circ C$

(d) $-110^\circ C$
follows: the hyperfine coupling constants were identical to those of the free ion in DME over the range $-10^\circ$ to $+20^\circ$C. At temperatures below this, departures from the spectra of the free ion were observed. The hyperfine pattern associated with the $M_{\beta \text{ax}} = 0$ group of lines was different from that of the $M_{\beta \text{ax}} = \pm 1$ group whereas these were identical in the spectra of the free ion. As the temperature was lowered both patterns changed and the $\beta_{\text{ax}}$ coupling constant as measured from the centre line of the $M_{\beta \text{ax}} = 0$ group to that of the $M_{\beta \text{ax}} = \pm 1$ groups, increased appreciably. The lines that became less well resolved as the temperature was lowered, appeared to be at the positions where the $M_{\beta \text{eq}} = \pm 2$ components of each of the $M_{\beta \text{ax}} = \pm 2$, $\pm 1$, and 0 groups overlapped. All these changes were quite reversible with temperature and no alkali splitting was observed at any temperature.

In view of these features and in particular the nature of the solvent, it appeared that ion pairing effects were occurring. By considering only those spectra observed below $-80^\circ$C any linewidth effects arising from conformational interconversion were eliminated, and from the analysis of the free ion spectra in DME it was known that the chair and boat forms of the HP molecule were present in a 1:1 ratio at these temperatures. Attempts to simulate the spectrum at $-80^\circ$C assuming only one species with one or two different $\beta_{\text{ax}}$ coupling constants were unsuccessful because both cases led to identical hyperfine patterns for
the \( \beta_{ax} = 0, \pm 1, \) and \( \pm 2 \) positions and this clearly was not apparent in the observed spectrum. Thus although the characteristic decrease in intensity that had been observed in the wings of the spectra of the HF/K/THF and FN/K/THF systems, where two species had been observed, was not present in these spectra in WTHF, a model involving two different species with different \( \beta_{ax} \) constants was considered.

Using the values given in Table 3.4, the theoretical spectrum shown in Figure 3.7 (b) was obtained.

**TABLE 3.4**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \beta_{ax} ) (Species 1)</th>
<th>( \beta_{ax} ) (Species 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-30^\circ C)</td>
<td>8.08</td>
<td>8.10</td>
</tr>
<tr>
<td>(-90^\circ C)</td>
<td>8.13</td>
<td>8.15</td>
</tr>
<tr>
<td>(-100^\circ C)</td>
<td>8.18</td>
<td>8.20</td>
</tr>
<tr>
<td>(-110^\circ C)</td>
<td>8.21</td>
<td>8.24</td>
</tr>
</tbody>
</table>

As shown in this table, by increasing the values of both the \( \beta_{ax} \) coupling constants the observed spectra at \(-90, -100, \) and \(-110^\circ C\)
were successfully simulated. Although it would be expected that if the \( \beta_{ax} \) coupling constants had changed relative to the free ion, then so would the \( \beta_{eq} \) and \( \gamma \) constants as well, it was difficult to see what effect small changes in these quantities had on the spectrum. However, it was clear that the \( \alpha \) splitting was invariant over this temperature range as would be expected.

A more detailed discussion of these results and their implications with regard to the possible structure of these two species will be given in Section 3.6.

### 3.3 Pleiadane Anion

![Diagram of Pleiadane Anion]

1-2 mgm of pleiadane was found to react moderately fast with an alkali metal in several ether solvents using procedures outlined in Section 2.1.3., to give an olive green solution of the P anion. Details of the spectra observed in various systems are as follows:

#### 3.3.1 1,2-Dimethoxyethane

(a) \( \text{P/Na/DME} \): The P anion in this system was stable for several days at RT before decaying to a brown diamagnetic material. Spectra were
FIGURE 3.9 ESR SPECTRA OF THE PLEIADANE ANION

(a) Na/DME  Experimental  -95°C

(b) Computer Simulated  (Linewidth is 0.1 G.)

(c) K/THF  -80°C

(d) K/MTHF  -90°C
observed over a temperature range from $-95^\circ$ to $+60^\circ$ C and marked changes were observed.

A typical spectrum of the P anion at $-95^\circ$ C is shown in Figure 3.9 (a). There are no particularly notable features of this spectrum and an analysis of it was carried out in the usual manner. Using the hyperfine coupling constants given in Table 3.5, the theoretical spectrum shown in Figure 3.9 (b) was obtained. It was found to be very sensitive to small changes in the $\gamma$ coupling constant.

**TABLE 3.5**

| Hyperfine Coupling Constants for the Pleiadane Anion in DME at $-95^\circ$ C (Gauss) |
|---------------------------------|-----------------|
| $\beta_{ax}$                    | 6.79            |
| $\beta_{eq}$                    | 1.22            |
| $\gamma$                       | 0.22            |
| 5,10                            | 1.58            |
| 6,9                             | 1.80            |
| 7,8                             | 4.64            |

The assignment of the coupling constants to various symmetric positions in the molecule was made in much the same way as was done for the PN anion. The aromatic proton coupling constants would be expected to be independent of temperature change and could in practice
be identified from the spectrum at high temperatures (see Section 3.5). Within this group of aromatic proton coupling constants, assignments were made to specific positions using Simple Huckel MO predictions (see Section 5.2 for details). Again, selective deuteration would confirm these assignments.

The temperature dependence of the spectra will be discussed in detail in Section 3.5.

(b) F/K/DME: The P anion prepared in this system gave identical spectra to the Na reduced species but did not appear to be as stable as the latter anion.

3.3.2 Other Solvents

(1) Tetrahydrofuran

(a) F/Na/THF: The P anion prepared in this system was only stable for 10-12 hrs. before decaying to a brown diamagnetic material. The spectrum observed at -90°C for this species was identical to that observed in DME at this temperature. However, upon raising the temperature, differences between the two sets of spectra appeared in the same way as had been observed for the PN/Na/THF system. Because of the poor signal to noise ratio in these spectra no detailed analysis was made.

(b) F/K/THF: Reaction of P with a K mirror in THF gave a more concentrated solution of the anion than that obtained by reduction with Na in the same solvent. Spectra were observed over the range from -100°C to +20°C and a typical spectrum at -80°C is shown in Figure 3.9 (c). This
can be seen to be quite different from that in DME (figure 3.9 (a)) and similar to that observed for the PN/K/THF and HP/K/THF systems (Figures 3.1 (b) and 3.6) in that there is a smaller intensity ratio of the $M\beta_{ax} = \pm 1$ to $M\beta_{ax} = 0$ groups of lines in THF than in DME, and hence the former spectrum appears narrower than the latter.

In view of the previous analyses made for the PN and HP anion systems in THF, attempts were made to simulate this spectrum assuming two species with slightly different $\beta_{ax}$ coupling constants. It was found that by using the values given in Table 3.5 except with $\beta_{ax}$ values of 6.80 and 6.87 G the observed intensity ratio could be simulated, but as for the PN/K/THF system, it was not possible to obtain exact values for the other coupling constants.

Above -60°C the spectra for this species were identical to those observed in DME.

(2) 2-Methyltetrahydrofuran: The P anion prepared in this solvent by reduction with K was unstable at RT and decayed to a bright red diamagnetic material within an hour or so. However, if used immediately after preparation, it gave good spectra at -90°C as shown in Figure 3.8 (d).

This spectrum can be seen to bear a similar relationship to the spectrum of the P anion in DME (Figure 3.8 (a)) as the spectrum of the PN/K/THF system does to the PN/K/DME system at the same temperature (Figures 3.1 (a) and 3.1 (c)). In view of the analyses made for these
latter systems, attempts were made to simulate this P anion spectrum assuming the presence of two species but these were unsuccessful. However, from the general shape of the spectrum and the position of the major peaks and the total spectrum width, it may be concluded that there are probably no large changes in the coupling relative to those observed in DME.

From -60°C to +20°C the spectra in MTHF were identical to those in DME at the same temperature.

3.4 Diphenyldiame Anion

1-2 mgm of diphenyldiame was found to react rapidly with an alkali metal to give the characteristic olive-green coloured solution that had been previously observed for the PN, P, and HP radical anions. Details of the spectra observed for a variety of systems are as follows:

3.4.1 1,2-Dimethylxylene

(a) DF/Na/DME: The DP anion prepared in this system was stable for days at RT but above +60° C it decayed within 10 minutes to a red diamagnetic material. Spectra were obtained over the temperature range from -100° C up to +60° C and as expected showed drastic changes.
FIGURE 3.10

ESR Spectrum of the Dipleiadane Anion in DME with K⁺ as counterion

Experimental

-95°C

Computer Simulated (Linewidth is 0.1 G.)
A typical spectrum at -95°C is shown in Figure 3.10. This exhibits some interesting features and perhaps the most notable of these is the lack of resolution of the two groups of lines indicated by arrows. This feature was present up to -60°C when all splitting due to the smallest coupling constant disappeared. Accompanying this feature is the small ratio of $\sim 1:4$ of the intensities of the groups of lines marked with arrows to the central group of lines compared with the expected 2:3 ratio for hyperfine interaction with $4\alpha$ equivalent protons. Another feature is the asymmetry of the spectrum, the high field side being less resolved than the low field one.

An initial analysis of this spectrum indicated the presence of three coupling constants but spectra simulated on this basis were in very poor agreement. Thus in view of the similarity of this spectrum with that observed previously for the HF/K/THF system (Figure 3.6) which had been analyzed in terms of two species, it was considered that two species of the DF anion with slightly different $\beta_{ax}$ coupling constants may be present in this spectrum. Also from a consideration of the structure of the DF molecule it was obvious that there must be at least four coupling constants. Finally using the values of the hyperfine coupling constants given in Table 3.6 the theoretical spectrum shown in Figure 3.10 was obtained.
TABLE 3.6

Hyperfine Coupling Constants for the Dipleiadene
Anion in DMF at -95°C (Gauss)

<table>
<thead>
<tr>
<th></th>
<th>Species(1)</th>
<th>Species(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>1.57</td>
<td>1.57</td>
</tr>
<tr>
<td>$\beta_{\text{ax}}$</td>
<td>6.28</td>
<td>6.16</td>
</tr>
<tr>
<td>$\beta_{\text{eq}}$</td>
<td>1.35</td>
<td>1.57</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Variation of the $g$ values and the relative amount of each species indicated that they were present in an approximate ratio of 1:1 and had identical $g$ values. The anisotropy in the spectrum has been observed in other spectra of similar species, e.g., the pyracene anion, and has been attributed to the combined influence of the intramolecular anisotropic dipolar and $g$ tensor interactions with the magnetic field.

The possibility that the lack of resolution in parts of this spectrum might be due to a linewidth alternation effect arising from movement within the molecule was considered unlikely in view of the temperature of measurement, and also because no such effects had been observed for the structurally related HP molecule at this temperature.

Ion pairing effects were also rejected for several reasons including:

(a) The identity of the spectra when either Na$^+$ or K$^+$ was used as counterion.
(b) The dielectric constant of DME is such as to discourage ion pairing, and indeed no such effects had been observed for the radical ions of any other peri-substituted naphthalenes in this solvent with Na$^+$ or K$^+$ as counterion.

(c) No alkali metal splitting was present and attempts to simulate the spectrum using reasonable values for such a metal splitting were unsuccessful. If the smallest splitting in the spectrum i.e. 0.22 G was in fact an alkali metal splitting, then it would be expected to change in value with temperature but it was found to be invariant over the range from -100$^\circ$C to -100$^\circ$C.

The assignments of the coupling constants to specific positions within the DP molecule were made from an inspection of the groupings and intensities of the lines within the spectrum and also from the assignments made previously for the HF anion in DME.

Confirmation of the presence of two species of the radical ion at low temperatures was obtained from the temperature dependence of the spectra. At high temperatures the well known phenomenon of linewidth alternation was observed and it was found that the spectra could only be satisfactorily simulated if it was assumed that conformational interconversion was occurring between two species. This will be discussed in more detail in Section 3.5.

Further confirmation was obtained when the radical anion of $1,2,3,6,7,8,9$-hexahydro-1H-cyclohepta(gh)phenalene of structure
was prepared by reduction with K in DME. This species did not give particularly good spectra but they were well enough resolved to see that at low temperatures a similar phenomenon to that observed for the DP anion was also occurring for this species. Unfortunately only a very small amount of the material was available and only two sets of spectra could be obtained.

(b) **DF/K/DME**: As mentioned above, the DP anion produced in this system gave identical spectra over the temperature range from -100° to +30° to those observed for the Na reduced species in DME and hence will not be discussed further.

(c) **DF/Cs/DME**: The bright green colour of the DP anion appeared immediately upon contact of a solution of DP in DME with a Cs mirror. The anion was found to be rather unstable and decayed within 15 mins. at RT to a purple and then deep brown diamagnetic material.

A typical spectrum at -90° C is shown in Figure 3.11. Comparing this with the spectrum observed for the HF/Cs/DME system (Figure 3.4
FIGURE 3.11
ESR Spectrum of the DP Anion in DME with Cs⁺ as counterion

FIGURE 3.12
ESR Spectra of the DP Anion in (a) THF and (b) MTHF with K⁺ as counterion
(a) it can be seen that the broad asymmetric signal is still present. However, there is very little fine structure in the DP anion spectrum and it is not possible to identify any Cs metal splitting if ion pairing was occurring. Examination of the center of this spectrum relative to the wings tends to show that the $J_{\beta ax} = 0, \pm 2$ groups of lines are better resolved than the $J_{\beta ax} = \pm 1$ ones and this of course, was the feature which was so obvious in the spectra of the Na and K reduced species in DME. The distance between the groups of lines is about 1.5 C which is comparable to the same splitting in the other spectra in DME.

3.4.2 Other Solvents

(1) Tetrahydrofuran

(a) DP/K/THF: The DP anion prepared in this system was stable for at least 24 hrs. Spectra were observed over a temperature range from $-120^\circ$ to $+70^\circ$C. A typical spectrum at $-120^\circ$C is shown in Figure 3.12(a).

In comparison with the spectra observed in DME, this spectrum is similar except that the smallest hyperfine splitting is not nearly as well resolved as in DME. However, as has been noted for the spectrum of the DP/Cs/DME system at this temperature, there is still a slight lack of resolution of the $J_{\beta ax} = \pm 1$ groups of lines, but the pronounced drop off in intensity of these lines previously observed in the PN, P, and HF/K/THF systems is not present and in fact the intensity ratio
is very similar to the expected 2:3 value. This fact obviously does not preclude the possibility of there being two species present at low temperatures as has been found for these other systems.

In all other respects, the spectra of the DP anion in THF were identical to those observed in DME.

(b) DP/Na/THF: Attempts to prepare the DP anion in this system were unsuccessful which was not surprising in view of the previous failure to prepare the HF anion by reduction with Na in THF.

(2) 2-Methyltetrahydrofuran

Only K was used to produce the DP anion in this solvent and it was found to give good spectra over the temperature range from -120° to 0°C. A typical spectrum at -115°C is shown in Figure 3.12 (b) and in comparison with the spectrum in THF, it shows no fine structure at all but in other respects was identical at all temperatures to that observed in THF. Again no alkali metal splitting was resolvable.

3.5 Temperature Dependence of the Spectra

A consideration of the structures of the perinaphthene, pleiadane, hexahydropyrane, and dipleiadane molecules (Figures 1.3 and 1.4) suggested that in solution the aliphatic parts of these compounds should be capable of moving backwards and forwards through the plane of the aromatic naphthylene ring. As mentioned in the introduction to this
project (Section 1.4) this would constitute interconversion between the chair and boat forms in the case of DP and HP. In all four molecules, the extent of this motion would be dependent upon the temperature and this feature should have been detectable from the temperature dependence of the spectra of the ions of these four compounds. As noted in the previous sections, all spectra did show drastic changes as the temperature was raised and it is proposed in this section to show that this is in fact related to movement of the aliphatic substituents in these molecules.

The $\beta$ protons having hyperfine coupling constants at least an order of magnitude greater than the $\gamma$ proton constants, would be expected to give rise to the major effects. Although the $\gamma$ protons will also be in motion and thus give rise to smaller effects, it was not possible to extend the theory to allow both effects at once and so the $\gamma$ protons were made equivalent using an average value for the $\gamma$ hyperfine coupling constant. As a result, some of the simulated low temperature spectra were not in particularly good agreement, but at higher temperatures this approximation seemed quite acceptable. Further, the $\gamma$ protons should be much more mobile than the protons attached to the $\beta$ C atoms which in turn are directly attached to the rigid naphthalene ring and thus the former would be expected to become equivalent at much lower temperatures, and this view was supported by studies of the $\gamma$ lineshapes on their own.
Temperature Dependence of the ESR Spectra of the HP Anion in DME with K⁺ as counterion

<table>
<thead>
<tr>
<th>Observed</th>
<th>Computed</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60°C</td>
<td>$T = 1.43 \times 10^{7}$ Sec.</td>
</tr>
<tr>
<td>-40°C</td>
<td>$5.34 \times 10^{8}$</td>
</tr>
<tr>
<td>-20°C</td>
<td>$1.78 \times 10^{9}$</td>
</tr>
<tr>
<td>0°C</td>
<td>$3.56 \times 10^{9}$</td>
</tr>
<tr>
<td>+23°C</td>
<td>$8.91 \times 10^{10}$</td>
</tr>
<tr>
<td>+73°C</td>
<td>$2.49 \times 10^{10}$</td>
</tr>
</tbody>
</table>
Considering first the spectra of the HP anion observed at various temperatures, the region in which the most drastic changes occurred was from -60° to +30° C and a sample of these is shown in Figure 3.13 (only one half of the spectra are shown as they are symmetric about their centre). It can be seen that as the temperature was raised certain groups of lines broadened right out until at +23° C, the spectrum may be described in terms of 5 major groups of lines separated by a distance of 9.68 G and each of these is split into another two sets of five lines with splitting values of 1.69 and 0.42 G. These later two values may be reconciled respectively with the \( \alpha \)-splitting, which would be unaffected by the movement of the aliphatic substituents, and an average value of the two \( \gamma \) coupling constants observed at -93° C. As mentioned earlier, this value of 0.42 G was confirmation of the presence of two \( \gamma \) coupling constants at low temperatures for the HP anion in DME. The large coupling constant is approximately equal to the sum of the \( \beta_{ax} \) and \( \beta_{eq} \) coupling constants and in fact the five major groups of lines may be shown to correspond to \( M_\beta \) values of ± 4, ± 2, and 0 where \( M_\beta \) is the total \( z \) component of both the \( \beta_{ax} \) and \( \beta_{eq} \) protons. Those groups of lines with \( M_\beta \) values of ± 3, and ± 1 were broadened right out at this temperature and so the term linewidth alternation is used to describe this effect.

It had been previously observed in the spectra of the HP anion by de Boer and Prest, \(^{26}\) and Inaiami and Isobe, \(^{37}\) and had been explained in
in terms of the boat and chair forms of the HF molecule present at low
temperatures (region of slow exchange) interconverting at an increasing
rate as the temperature was raised. When the rate of interconversion
is comparable to the hyperfine frequency (region of medium or interme-
diate exchange) around +20°C then the alternating linewidth effect occurs
giving only five groups of lines rather than the expected nine. At
higher rates of interconversion, the \( \beta_{ax} \) and \( \beta_{eq} \) protons become
equivalent (Fast exchange limit) and give rise to nine groups of lines
separated by the average value of the \( \beta_{ax} \) and \( \beta_{eq} \) coupling constants.
The spectrum at +73°C is approaching this situation. The fact that at
+23°C the major groups of lines are separated by a distance of
\( |a_{ax}| + 2|a_{eq}| \) rather than \( |a_{ax} - 2|a_{eq}| \) has been interpreted
to indicate that the \( \beta_{ax} \) and \( \beta_{eq} \) coupling constants have the same
sign.36

Using the theory developed in Appendix I for the linewidth alterna-
tion effect, the temperature dependence of the observed spectra of the
HF anion was simulated as follows: it is possible to draw four conforma-
tions, two boat and two chair, for the HF molecule and these may inter-
convert as shown in Figure 3.14 (a). This situation corresponds to the
four jump model discussed in Appendix I and the equations developed
there for this model were used as follows:

The hyperfine contributions \( \omega_A, \omega_B, \omega_C, \) and \( \omega_D \) to the res-
FIGURE 3.14

(a) Four Jump Model

\[
\begin{align*}
\delta \omega_1 & \quad \delta \omega_2 \\
1 & \quad 2 & \quad 4 \\
5 & \quad 6 & \quad 8 \\
\end{align*}
\]

\[\iff\]

\[
\begin{align*}
\delta \omega_3 & \quad \delta \omega_4 \\
1 & \quad 2 & \quad 4 \\
5 & \quad 6 & \quad 8 \\
\end{align*}
\]

A (CHAIR) \iff C (BOAT)

B (BOAT) \iff D (CHAIR)

(b) Two Jump Model

\[
\begin{align*}
\delta \omega_1 & \quad \delta \omega_2 \\
1 & \quad 2 & \quad 4 \\
5 & \quad 6 & \quad 8 \\
\end{align*}
\]

\[\iff\]

\[
\begin{align*}
1 & \quad 2 & \quad 4 \\
5 & \quad 6 & \quad 8 \\
\end{align*}
\]

A \iff B

\[\text{refers to } \beta_x \text{ protons} \quad \cdot \beta_{ax} \quad \cdot\]
onance frequency from the $\beta$ protons were calculated for each of the 256 spin wavefunctions assuming that the changes occur without change in nuclear spin. These functions can be classified into groups of 1, 8, 26, 56, 70, 56, 26, 8 and 1 corresponding to $M_\beta$ values of $-4, -3, -2, -1, 0, +1, +2, +3,$ and $+4$ respectively. Thus for $M_\beta = +4$, only one spin state is possible viz. $\alpha(1)\alpha(2)\alpha(3)\alpha(4)\alpha(5)\alpha(6)\alpha(7)\alpha(8)$ where $\alpha$ and $\beta$ refer to the spin up ($M_\alpha = +\frac{1}{2}$) and spin down ($M_\alpha = -\frac{1}{2}$) orientations of the nuclei. The hyperfine contributions for this state are

$$\omega_A = \omega_D = 2\omega_1 + 2\omega_2 \text{ and } \omega_B = \omega_C = 2\omega_3 + 2\omega_4$$

where $\omega_1$ and $\omega_3$ are the $\beta_{eq}$ coupling constants and $\omega_2$ and $\omega_4$ the $\beta_{ex}$ coupling constants of the two forms. Similarly the value for the spin state $\alpha(1)\beta(2)\alpha(3)\beta(4)\beta(5)\beta(6)\alpha(7)\beta(8)$ corresponding to $M_\beta = 0$ is

$$\omega_A = 2\omega_1 = 2\omega_2, \quad \omega_B = \omega_C = 0, \quad \text{and} \quad \omega_D = -2\omega_1 + 2\omega_2$$

(In the case of the HP anion where two forms could not be distinguished at low temperatures $\omega_1 = \omega_3 = 2.02$ and $\omega_2 = \omega_4 = 7.96 \text{ G}$.) Further examples of the method of calculation of these hyperfine contributions will be given later for the simpler two jump cases of P and PM.

Having evaluated the 1024 contributions for all the states of the four forms, these values were substituted in eqn. 1 of Appendix I together with an $\alpha$ coupling constant of 1.69 and an averaged value of 0.49 G for the $\gamma$ coupling constant. A transverse relaxation time
FIGURE 3.15
Temperature Dependence of the ESR Spectra of the DP Anion in DME with Na⁺ as counterion

Observed

Computed

(a) -40°C

(b) -20°C

(c) 0°C

(d) +20°C

(e) +40°C

(f) +60°C

(g) +80°C

T = 2.14 x 10⁻⁷ Sec

7.12 x 10⁻⁹

1.88 x 10⁻⁸

9.91 x 10⁻⁷

4.46 x 10⁻⁸

2.95 x 10⁻⁹

8.91 x 10⁻¹⁰
$T_2$ of 10 sec. was used and spectra were then calculated and plotted for a range of $T$ values assuming that $T = T_A = T_B = T_C = T_D$. These spectra were then compared with the experimental spectra and the process repeated for new $T$ values until good agreement was obtained. The simulated spectra found to give best fit at various temperatures are shown in Figure 3.13 together with their respective $T$ values.

The spectra of the DP anion were found to show the most marked changes in the region from $-10^\circ$C to $+60^\circ$C and a selection of these is shown in Figure 3.15. It can be seen from these that the linewidth alternation effect occurs at much higher temperatures than for the HP anion. As mentioned earlier the small $\gamma$ splitting of 0.22 G disappeared at temperature $-40^\circ$C and this is probably accounted for by the extra width of the lines above this temperature. At $+70^\circ$C the distance between the main groups of lines was 7.70 G which is comparable to the quantity $|a/\beta_3| \times |a/\beta_{eq}|$, and the smaller splitting of 1.57 G which did not change over the complete range from $-95^\circ$C to $+60^\circ$C may be reconciled with the $\alpha$ splitting constant. Using the same four jump model as proposed for the HP anion, except that $6\omega_1$, $6\omega_2$, $6\omega_3$, and $6\omega_4$ were now distinguishable and were given values of 6.16, 1.57, 6.26, and 1.35 G respectively, the theoretical spectra shown in Figure 3.15 were obtained.

In the cases of P and PN, the boat and chair forms of these molecules are not distinguishable and so motion of the aliphatic substituents would be expected to lead to a simple two jump system involving
FIGURE 3.16
Temperature Dependence of the ESR Spectra of (a) PN and (b) P Anions in THF with K⁺ as counterion

(a) (1) -40°C
H
τ = 3.66 x 10⁻⁶ sec

(b) (1) -30°C

(2) +20°C

(3) +20°C

8.81 x 10⁻⁹
8.91 x 10⁻⁹
1.42 x 10⁻⁹
two species as shown in Figure 3.14 (b). The observed spectra for these
two anions, reflected this reduced symmetry of the P and PN molecules
compared with DP and HP and the effect of temperature on the spectra was
not nearly as marked as in the latter two cases. A selection of the
spectra at various temperatures is shown in Figure 3.16. The P anion
gave rather weak signals at higher temperatures and hence the signal to
noise ratio in the spectra of this species is quite low.

The spectrum of the PN anion at +20°C clearly shows the three
lines arising from the two equivalent $\gamma$ protons with a coupling con-
stant of 0.44 G, as well as the three aromatic proton splittings of
1.54, 1.93, and 1.54 G. Similarly the spectrum of the P anion at
+20°C shows a $\gamma$ splitting of 0.30 G and the three aromatic proton
splittings of 1.58, 1.79, and 1.63 G. As mentioned earlier, both these
sets of spectra at high temperatures confirmed the assignments of some
of the splittings made for the PN and P anions at lower temperatures.

The hyperfine contributions to the resonance frequency are consid-
erably less in number for a two jump model and they were calculated
using the scheme shown in Figure 3.14 (b) and are listed in full in
Table 3.7 (obviously the contributions for the $M_I = -2$, -1 states will
be the same as for $M_I = +2$, +1). These were substituted in eqn. I-3
of Appendix I and using the appropriate values for $\gamma \omega_1$ and $\gamma \omega_2$,
the theoretical spectra shown in Figure 3.16 were obtained. Because
there was no marked change in the observed spectra with moderate changes
in temperature due to the overlap of lines whose linewidth did not
change with temperature, it was found that a range of \( T \) values could be used without any apparent change in the theoretical spectrum. Thus the values given in Figure 3.16 for various temperatures have much larger errors than those given for the DF and HP anions.

### Table 3.7

<table>
<thead>
<tr>
<th>( M/\beta )</th>
<th>Spin State</th>
<th>( A )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \alpha(1)\alpha(2)\alpha(3)\alpha(h) )</td>
<td>( 26\omega_1 + 26\omega_2 )</td>
<td>( 26\omega_1 + 26\omega_2 )</td>
</tr>
<tr>
<td>1</td>
<td>( \alpha(1)\alpha(2)\alpha(3)\beta(h) )</td>
<td>( 26\omega_2 )</td>
<td>( 26\omega_1 )</td>
</tr>
<tr>
<td></td>
<td>( \alpha(1)\alpha(2)\beta(3)\alpha(h) )</td>
<td>( 26\omega_2 )</td>
<td>( 26\omega_2 )</td>
</tr>
<tr>
<td></td>
<td>( \alpha(1)\beta(2)\alpha(3)\alpha(h) )</td>
<td>( 26\omega_1 )</td>
<td>( 26\omega_2 )</td>
</tr>
<tr>
<td></td>
<td>( \beta(1)\alpha(2)\alpha(3)\alpha(h) )</td>
<td>( 26\omega_2 )</td>
<td>( 26\omega_1 )</td>
</tr>
<tr>
<td>0</td>
<td>( \alpha(1)\alpha(2)\beta(3)\beta(h) )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( \alpha(1)\beta(2)\alpha(3)\beta(h) )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( \beta(1)\alpha(2)\alpha(3)\beta(h) )</td>
<td>( -26\omega_1 + 26\omega_2 )</td>
<td>( 26\omega_1 - 26\omega_2 )</td>
</tr>
<tr>
<td></td>
<td>( \alpha(1)\beta(2)\beta(3)\alpha(h) )</td>
<td>( 26\omega_1 - 26\omega_2 )</td>
<td>( -26\omega_1 + 26\omega_2 )</td>
</tr>
<tr>
<td></td>
<td>( \beta(1)\alpha(2)\beta(3)\alpha(h) )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>( \beta(1)\beta(2)\alpha(3)\alpha(h) )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

If the interconversion between the various forms is considered as a first order rate process then the first order rate constant, \( k \), may be identified with \( 1/T \) and using the Arrhenius Expression
LEAST SQUARES CALCULATION FOR ARRENHIUS PLOT OF HP, DP ANIONS

FIGURE 3.17
\[ k = A \exp \left( -\frac{E}{RT} \right) \]

the frequency factor, \( A \), and the energy of activation, \( E \), for this process may be calculated. This method has been used extensively in the literature to obtain rate constants for linewidth alternation processes (e.g. Ref 65). In practice a plot of \( \log(1/\tau) \) versus \( 1/RT \) was constructed for a variety of values of \( T \) and then a straight line was fitted to these points by least squares methods.

The results for the HP and DP anions are shown in Figure 3.17 and gave the following values:

<table>
<thead>
<tr>
<th>Anion Species</th>
<th>( A (\text{sec}^{-1}) )</th>
<th>( E (\text{Kcal/mole}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>( 10^{14.0} \pm 0.9 )</td>
<td>7.08 \pm 0.8</td>
</tr>
<tr>
<td>HP</td>
<td>( 10^{13.5} \pm 0.8 )</td>
<td>6.37 \pm 0.6</td>
</tr>
</tbody>
</table>

Estimates of these quantities were also made for the P and PH anions, but because of the relative insensitivity of these spectra to changes in temperature, no accurate estimates of \( A \) and \( E \) could be obtained other than to say that the energy of activation for interconversion in both species was \( \sim 7.5 \pm 1.5 \) Kcal/mole which is certainly within the experimental error of the values obtained for the DP and HP anions.

Attempts were made to observe this interconversion from the temperature dependence of the NMR spectra of the parent diamagnetic compounds but spectra observed over the range from \(-30^\circ\) to \(+60^\circ\) C in \( CD_2Cl_2 \) showed only one species and hence it was concluded that the rate of intercon-
version is too great for the NMR technique to detect i.e., the NMR fast exchange limit is reached at temperatures < -30°C. This is in agreement with the findings of Oko, Iwaizumi, and Hayakawa who attempted to use NMR techniques to determine the rate of inversion of o,o'-bridged biphenyls.

A discussion of the values of these activation energies in relation to the values observed for other compounds will be given in Chapter Six.

3.6 Discussion of Ion Pairing Effects

Although no alkali metal hyperfine splitting was observed in any of the spectra described in previous sections for the anions of FN, P, HP, and DP (with the exception of the Pn/Ns/THF and HP/Gs/DME systems), it may be deduced from the effect of changing the solvent and counterion on the temperature dependence of the spectra, that ion pairs of some sort are formed by all four compounds in certain systems.

The formation of these is favoured by lower dielectric solvents and larger radius of the cation. For example, all the anions produced by reduction with Na or K in DME showed no ion pairing effects and hence were considered to be free ions, whereas the HP anion produced by reduction with Cs in DME did show these effects. Similarly, changing the solvent from DME to THF (both with dielectric constants ~6.0)
and then to MTIP (D = 1.63) causes an increase in ion pairing effects for the HP anion. These trends are in agreement with the general rules for ion pairing formation as postulated by Aten et. al. 68.

From the temperature dependence of the spectra of the free ions of all four compounds in DME, it can be seen that any effects due to conformational equilibria of the aliphatic substituents will be eliminated by restricting attention to only those spectra observed at temperatures < -50°C. Further, in the case of DP and HP the ratio of chair and boat forms will be approximately 1:1 in this region. However, there are still changes in the spectra of all four compounds observed at temperatures < -50°C and thus it may be concluded that these must arise from ion pairing and/or possibly solvent effects.

As far as the structures of these ion pairs is concerned, it would seem reasonable that the cation should occupy a symmetric position with respect to the anion molecule. Hence possible positions for the cation in the di- and mono-alkylphenanthrene molecules are respectively:

and

\[ \text{I} \quad \text{II} \quad \text{III} \quad \text{IV} \quad \text{V} \quad \text{VI} \]
It should be noted that in all the models the cation may be above or below the plane of the aromatic ring and in III and VI it may also lie in this plane.

Models such as these have been used in the past to explain ion-pairing effects in a number of other alkynaphthalenes and related compounds. For example, the pyrazone (PYC) anion (Structure III in Figure 1.1) was found to show two different alternating linewidth effects depending upon the solvent and the counterion. The spectrum with $K^+$ in THF was interpreted in terms of a model similar to III above in which the cation was oscillating between the two ethylene bridges at positions C. The spectrum with $Na^+$ in MTHF at temperatures $<-30^\circ C$ indicated that the cation was fixed at one end of the molecule and was oscillating between the two pairs of protons in that bridge. From these results for the PYC anion, it was suggested that the observed linewidth effect in the spectrum of the HP ion with $K^+$ in THF might be explained by an ion pair such that the cation is situated at either C positions and a dynamic equilibrium existing between these two possible conformations. Recently, an alternative model for this species has been proposed in which it was suggested that the cation was in position A and the alternating linewidth effect was considered to arise from movement of the cation between the two equivalent A positions and above and below the aromatic plane.

From this it can be seen that there is considerable doubt as to the exact structure and nature of the HP ion pair, so for the moment
it is proposed to consider the HP anion alone and the three possible models (I - III) for this species and compare predicted effects in spectra with those that have been observed in this project (Section 3.2).

Unfortunately the aliphatic substituents in the HP molecule make it non planar, and so, as previously noted, boat and chair forms configurations are possible (Figure 1.3 (b)) and this complicates the possible positions of the cation in HP ion pairs. Also the spin distribution of the anion will be polarised by the electric field of the cation depending on its size, nature, and distance from the molecule. This will reduce the magnetic symmetry of the molecule as shown by certain atoms no longer being magnetically equivalent as they are in the free ion and thus extra hyperfine splittings are resolvable in the spectra if the cation is stationary, or if it is in the region of intermediate exchange then linewidth effects may occur (in the fast exchange limit the atoms will retain their equivalence but the hyperfine splittings will be the average of the two in the stationary state and no linewidth broadening will occur).

For model I there are four possible structures for the ion pair when the cation is stationary above or below the plane in position A as follows:
Structures (2) and (h) are obviously indistinguishable so in effect there are three distinct forms. In all four models the four \( \alpha \) protons will lose their equivalence and will be split into two sets of two equivalent protons, as will the \( \beta_{ax} \) and \( \beta_{eq} \) protons also. The \( \gamma \) protons will be unaffected.

If the cation is moving between the two symmetric \( \Lambda \) positions in Model I then out-of-phase modulations of the \( \beta_{ax} \) and \( \beta_{eq} \) splittings would occur and this should lead to observable linewidth alternation effects in the spectra. This movement will be temperature dependent and again this should be evident in the temperature dependence of the linewidth in the observed spectrum. Movement of the cation above and below the plane will correspond to interconversion between (1) and (3), and (2) and (h). In the latter case this will be out-of-phase modulation and it will give the normal alternating linewidth effects, while in the former case it will be in-phase and the effect of this on the spectra would be much more difficult to predict.

The situation for Model II is very similar to that of I in that the three structures (1), (2) and (3) are possible. However, when the
cation is stationary at position B, the molecule will not lose any symmetry and so none of the groups of equivalent protons will be split up and hence only one coupling constant would be observed for the $\alpha$, $\beta_{ax}$, $\beta_{eq}$, $\gamma_{ax}$, and $\gamma_{eq}$ groups of protons. Motion of the cation above and below the plane at position B is most unlikely.

There are four possible ion pair structures (1) - (4) for Model III as follows:

When the cation is stationary, it would be predicted for each of these forms that two different hyperfine coupling constants would be observed for the $\beta_{ax}$, $\beta_{eq}$, $\gamma_{ax}$, $\gamma_{eq}$, and $\alpha$ groups of atoms. When the cation is moving from one C position to the other, the
structures (5)-(8) would be obtained and it can be seen that this will
give rise to inphase modulation of the hyperfine coupling constants
wheras in (3) and (h) it will be out-of-phase. A second movement is
possible above and below the aromatic plane i.e. (1) ⇔ (2) and
(3) ⇔ (h). Finally, a third movement specific to this model is possi-
ble in which the cation is stationary at one end of the molecule but
is moving symmetrically from side to side between the two atoms as has
been postulated for the pyreanone ion pair with Na⁺ or K⁺ in MTHF. The
effects on the spectral linewidths of these latter two movements
are again difficult to predict.

Considering now the experimental results observed for the HP
anion and summarised in Table 3.8, it can be seen that as the solvent
becomes more polar, ion pairing effects increase as shown by the
polarising influence of the cation on the spin density distribution
in the anion.

**TABLE 3.8**

<table>
<thead>
<tr>
<th>Posit-</th>
<th>IME -95°C</th>
<th>DME/THF -90°C</th>
<th>THF -100°C</th>
<th>MTHF -80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>on</td>
<td>S(1)</td>
<td>S(2)</td>
<td>S(1)</td>
<td>S(2)</td>
</tr>
<tr>
<td>β ax</td>
<td>7.96</td>
<td>7.97</td>
<td>6.03</td>
<td>6.06</td>
</tr>
<tr>
<td>β eq</td>
<td>2.02</td>
<td>2.06</td>
<td>2.06</td>
<td>2.06</td>
</tr>
<tr>
<td>α</td>
<td>1.69</td>
<td>1.70</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>γ ax</td>
<td>0.50</td>
<td>0.54</td>
<td>0.61</td>
<td>0.61</td>
</tr>
<tr>
<td>γ eq</td>
<td>0.36</td>
<td>0.39</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>
## FIGURE 3.18
Calculation of Overlap of Alkali Metal Cation with Alkyl Protons of HF

| Overlap Atoms | Na Position A | | | | Position B | | | |
|---------------|--------------|---|---|---|---------------|---|---|---|---|
|               | 1*           | 2 | 3 | 4 | 5 | 1 | 2 | 3 | 4 |
| M-γ ax        | 0.063        | 0.077 | 0.059 | 0.029 | 0.009 | 0.105 | 0.125 | 0.106 | 0.064 | 0.02 |
| M-γ eq        | 0.006        | 0.002 | 0.002 | 0.029 | 0.009 | 0.105 | 0.125 | 0.106 | 0.064 | 0.02 |
| M-β ax        | 0.031        | 0.031 | 0.179 | 0.008 | 0.002 | 0.055 | 0.061 | 0.043 | 0.020 | 0.00 |
| M-β eq        | 0.004        | 0.010 | 0.005 | 0.029 | 0.009 | 0.105 | 0.125 | 0.106 | 0.064 | 0.02 |
|               |              |    |    |    |    |    |    |    |    |
| M-γ ax        | 0.012        | 0.063 | 0.234 | 0.201 | 0.056 | 0.057 | 0.102 | 0.114 | 0.202 | 0.11 |
| M-γ eq        | 0.032        | 0.026 | 0.008 | 0.002 | 0.009 | 0.105 | 0.125 | 0.106 | 0.064 | 0.02 |
| M-β ax        | 0.096        | 0.282 | 0.179 | 0.060 | 0.014 | 0.083 | 0.190 | 0.201 | 0.108 | 0.03 |
| M-β eq        | 0.037        | 0.085 | 0.046 | 0.014 | 0.003 | 0.026 | 0.094 | 0.088 | 0.034 | 0.01 |

* Values given are the absolute differences between the overlaps for structures 1 and 2 for a given type and height of cation.

* Refers to height above the aromatic planes (Å).
This may be reconciled with the decreasing solvation of the cation by
the solvent and hence it is able to move closer to the anion. Thus
the first protons to be affected will be the \( \gamma \) ones followed by the
\( \beta_{ax} \) and \( \beta_{eq} \) as the cation–anion distance decreases even further.

From this Table and the results in Section 3.2, it can be seen
that the spectra of the HP anion in THF and n-THF solvents at temperat-
ures \(-80^\circ C\), has been analysed in terms of two species, neither of
which is the free ion, rather than linewidth effects arising from intra-
molecular motion of the cation as suggested by Iwaisumi and Isobe\(^{37}\),
and Iwaisumi and Bolton\(^{69}\). Calculations have been made using the pro-
gram \( \text{MKY} \) of the overlap between a Na 2p and Rb 5s orbital and the
\( \beta_{ax} \) and \( \beta_{eq} \) proton 1s orbitals for the two species

[Diagrams showing the overlap between orbitals]

arising from the chair and boat configurations of the molecule. The
results of these calculations shown in Figure 3.18 indicate consider-
able differences between the two forms depending upon the position of
the cation.
Although the unpaired spin density giving rise to the observed hyperfine coupling constants for the $\beta_{ax}$ and $\beta_{eq}$ protons probably arises mainly from spin polarisation and hyperconjugative effects from the naphthalene ring, the presence of an alkali metal in their vicinity will lead to some direct transfer of spin density from the alkali metal outer $s$ orbital into these proton orbitals and this will be indicated by small changes in the $\beta_{ax}$ and $\beta_{eq}$ coupling constants relative to those observed in the free ion. The extent of this transfer of charge will obviously be dependent upon the amount of overlap of the orbitals and from the results shown in Figure 3.18, it can be seen that the greatest difference between the overlaps for the two forms occurs for the $\beta_{ax}$ protons rather than for the $\beta_{eq}$ or $\gamma$ positions. This agrees qualitatively with the observation that the only detectable difference between the two species observed in THF and DMF is in the values of the $\beta_{ax}$ hyperfine coupling constant. The constants associated with the protons in the other positions in the molecule are also changed but because the cation-anion overlap between the two forms is smaller than that calculated for the $\beta_{ax}$ protons, then there is no detectable difference between the values for the $\beta_{eq}$, $\gamma$, and $\alpha$ positions in the two species. This is similar to the situation of the free ion in DME, where the difference between the overlaps of the $\gamma_{ax}$ and $\gamma_{eq}$ protons is also small in the chair and boat forms and this shows itself in spectra
by both configurations having identical coupling constants. Also as
the cation moves closer to the anion with decreasing dielectric con-
stant of the solvent, then interaction with the $\beta$ ax protons becomes
greater and hence the difference between the coupling constants for
these protons in the two forms becomes greater.

As far as the exact position of the cation is concerned (Models
I - III above), the apparent absence of linewidth alternation effects
at temperatures $-80^\circ C$ would suggest that the cation is either station-
ary or in the region of fast exchange. Considering the effects on the
spectra predicted above for each of these two situations in each of
the models, it is difficult to decide from the observed spectra whether
the cation is stationary and if so where it is, nor whether it is
moving and its path of motion. Although the increasing lack of res-
olution in parts of the spectra of the HF/K/MTHF system could be
reasonably well simulated by increasing the two $\beta$ ax coupling const-
ants, this effect may also be a linewidth effect arising from oscilla-
ation of the cation within a potential well at one end of the molecule
as had been suggested for the FJC/K/MTHF system at these temperatures.
Also the marked changes in the aliphatic coupling constants compared
with the aromatic ones would suggest that the cation is closer to the
former groups than the aromatic rings i.e. position C rather than A
or B. This position would also be favoured on energetic grounds (see
later). However, better spectra would be necessary to elucidate the
exact position of the cation.

Much of what has been discussed above for the HP molecule also holds for the other three compounds. Unfortunately the complexity of the spectra arising from the P and PH anions did not allow even as detailed an analysis as that made for the HP anion systems. From the shape of the PH/K/THF and P/K/THF spectra it would appear that ion pairing effects similar to that analyzed in the HP/K/THF system are also occurring. Again, in terms of Models IV, V, and VI, it is not possible to come to any definite conclusions as to the most likely position for the cation, but from the apparent change in the $\beta_{ax}$ coupling constants it would appear that the cation is either in positions E or F, rather than D.

As discussed in Section 3.4, the spectra of the DP anion in THF and MTHF were not well enough resolved at low temperatures to make any predictions regarding ion pairing effects in this molecule.

Lastly, in an attempt to confirm the predictions that the cation in the ion pairs of these perialkylinsaphthalene anions is in position C or E rather than over the aromatic rings, calculations of the theoretical interaction energies between the cation and anion were made using the theory outlined in Appendix II. Unfortunately the model used in these calculations is restricted to $\pi$ systems only and thus the unsaturated equivalents of pyrene, hexahydropyrene and diplop-pene, were used rather than the actual compounds themselves.
FIGURE 3.19
Calculation of Ion Pair Interaction Energies for some aromatic radical anions

(a) Naphthalene

(b) 1458-Tetramethylinaphthalene

(c) Pyracylene

(d) Pyrene

(e) Dipleiadene
The results for the following compounds

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

are shown in Figure 3.19. In this diagram the quantities represented by the symbol, \( E \), are the interaction energies of the cation and anion and are in units of the standard resonance integral for the benzene ring, \( \beta_{CC} \). The energy maps show the variation of \( E \) as the cation moves in a plane 3 Å above the naphthalene ring. This corresponds to a reasonable distance for a Potassium ion with an ionic radius of 1.33 Å to be above the plane of the anion. The graphs show the variation in \( E \) as the cation moves symmetrically along the line through the centre of each compound (as shown by dotted lines in the structures above) and at various distances above the ring.

From these results it can be seen that as the rings attached to the naphthalene ring become larger, then the most likely position for the cation (as given by the highest value of the interaction energy) also tends to move out over the attached rings. Thus although
the saturated analogues studied in this project of these compounds

do not have such extensive \( \pi \) systems in these positions, this trend

for the unsaturated compounds would probably occur to a lesser extent

for the \( \text{PC}, \text{HP}, \) and \( \text{DP} \) molecules. This is a further indication that

cation in the ion pairs observed in this project is probably asso-

ciated more with the aliphatic rings than the naphthalene ring. The

importance of obtaining the \( \text{Li}^+ \) and \( \text{Na}^+ \) ion pairs of HP in order to
determine the position of the cation, can be seen from the graphs for

dication-anion distance of 2 Å. However, as mentioned in Section 2.2,
all attempts to prepare the HP anion in these systems were unsuccessful.

3.7 Cation Radicals

Attempts were made to prepare the cation radicals of all four
compounds using the methods outlined in Section 2.1.3 and the following
results were obtained:

(1) Pleiadene and Perimaphthene:

Attempts to prepare the cations of these two species were
unsuccessful. Both compounds were insoluble in conc. \( \text{H}_2\text{SO}_4 \) even with
the addition of \( \text{K}_2\text{S}_2\text{O}_8 \) and hence gave no signals. Reaction of \( \text{P} \) with
\( \text{CH}_3\text{NO}_2 \) and \( \text{AlCl}_3 \) led to a purple solution which immediately changed
to a sea green colour that gave no signals until 15 mins. later, when
a broad line probably due to a charge transfer complex, was observed.
Similarly \( \text{P} \) in \( \text{CH}_3\text{SO}_3\text{H}/\text{C}_3\text{H}_5\text{NO}_2 \) gave no colour change and no signals.
FIGURE 3.20  ESR Spectra of some Radical Cations.

(a) HP/BF$_3$/SO$_2$

(b) DP/BF$_3$/SO$_2$

(c) DP/H$_2$SO$_4$
Finally, in view of the failure to observe spectra for 1,8-DMN using the BF$_3$/SO$_2$ method (see later), no attempts were made to use this method for preparing the P and PN cations.

(2) Hexahydroxyprylene:

Although the spectrum of the HP cation had been observed before in conc. H$_2$SO$_4$ 36, all attempts in this project to prepare the cation by this method were unsuccessful. However, the BF$_3$/SO$_2$ method of preparation was used with moderate success. The sample on warming up to -110°C was an olive green in colour and this rapidly decayed to a bright red diamagnetic material at temperatures above -60°C. A portion of the spectrum at -95°C is shown in Figure 3.20 (a). Unfortunately at the time of running this sample, difficulties were being experienced in tuning the spectrometer and some of the dispersion mode of the signal as well as the absorption mode was being recorded and hence only the top half of the spectrum appears to be present. Although in subsequent runs this fault was corrected, the spectra were not nearly as well resolved.

The total spectrum consisted of five major groups of lines each split into a number of overlapping groups of lines. The distance between the major groups was ~ 14.80 C and thus as noted by de Boer and Praat 36, second order effects become appreciable in view of the magnitude of this splitting constant. Using the theory developed by Fraenkel 70 and outlined in Appendix III, the second order shifts
downfield for these five major groups of lines are given in Table 3.9 (see Appendix III for symbolism).

<table>
<thead>
<tr>
<th>$M_{\beta_3}$</th>
<th>$I$</th>
<th>Degeneracy (Intensity)</th>
<th>$\Delta P_+^{H^+}$</th>
<th>$\Delta P_+^{DP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0.066</td>
<td>0.046</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>0.165</td>
<td>0.115</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.033</td>
<td>0.023</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0.199</td>
<td>0.139</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>0.165</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

The effect of allowing for this second order shift on the positions of the five major groups of lines is shown in the stick diagram below:
From this it would be predicted that the distance between the $M_{\beta_{ax}} = +1$ and 0 groups should be slightly greater than that between the $M_{\beta_{ax}} = 0$ and -1 groups whereas in the first order spectrum these distances are the same. In practice, a difference of 0.06 G was observed compared with the predicted value of 0.046 G, and this confirmed the presence of second order effects in the observed spectrum of the HP cation.

Theoretical spectra were calculated using the values given by de Boer and Pratt (Table 3.10) and they were not found to give particularly good agreement with the observed spectra. Using the values given in the second column of this table, a simulated spectrum was obtained which gave better agreement. Unsuccessful efforts were made to resolve two different $\gamma$ splittings as had been done in the HP anion spectrum in DME. It appeared that if two different $\gamma$ coupling constants do exist, then they must have nearly the same values and the difference between them would probably be comparable to the second order shifts and hence would be masked in the spectra by these latter effects.

(3) Dipoleiadene:

Use of the CH$_3$NO$_2$/CH$_2$Cl$_2$ method of cation preparation gave no reaction at RT and hence no signals were observed. The SOCl$_2$/CH$_2$Cl$_2$ method gave a sample which, on warming up to -77°C in a dry ice acetone bath, turned a bright red colour but spectra observed at -95°C, -50°C, and -20°C showed only a broad asymmetric signal.
The DF/SD$_2$ method was much more successful and upon warming the sample up to -110°C it turned an olive green colour and gave good spectra. A typical one observed at -95°C is shown in Figure 3.20 (b) and an enlarged section of the central portion is shown below it.

As observed for the HF cation in this system, the spectrum consists of five major groups of lines separated by a distance of \(~12.25\,\text{G}\). Thus second order effects will also be appreciable and these were calculated and are listed in Table 3.9. Measurement of the distance between the $M/\beta_{ax} = \pm 1$ and 0 groups and the 0 and -1 groups indicated that the latter distance was greater than the former which is the opposite to what would be predicted from second order effects and to what had been observed for the HF cation. This may be partly due to the difficulty in determining the precise centre of each group of lines. However, the difference between the hyperfine pattern of the central lines of the $M/\beta_{ax} = 0$ group compared with the $M/\beta_{ax} = \pm 1$, and \(\pm 2\) groups would suggest that some sort of second order effects were present. Attempts to simulate the observed spectrum were not very successful but they did indicate that two species were present and an estimate of the values of the coupling constants are given in Table 3.11.
TABLE 3.10

Hyperfine Coupling Constants (Gauss) for the
BP Cation in BP/SCl at -90°C.

<table>
<thead>
<tr>
<th>Species(1)</th>
<th>Species(2)</th>
<th>Present Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>de Boer and Praat*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta_{ax} )</td>
<td>14.70</td>
<td>14.63</td>
</tr>
<tr>
<td>( \beta_{eq} )</td>
<td>3.64</td>
<td>3.90</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>( \delta )</td>
<td>0.40</td>
<td>0.40</td>
</tr>
</tbody>
</table>

* ref. 36.

TABLE 3.11

Hyperfine Coupling Constants (Gauss) for
the BP Cation

<table>
<thead>
<tr>
<th>Species(1)</th>
<th>Species(2)</th>
<th>II.20°C at +20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_{ax} )</td>
<td>12.11</td>
<td>12.22</td>
</tr>
<tr>
<td>( \beta_{eq} )</td>
<td>3.62</td>
<td>3.03</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>( \beta_{ax} + eq )</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Approximate only
It should be noted that there appeared to be no resolvable \( \gamma \) splitting and this may be accounted for by the increase in the observed linewidth in the spectra shown in Figure 3.17 (b) compared with that observed for the lines in the spectrum of the HF cation in the same system and temperature.

Use of conc. \( H_2SO_4 \) to prepare the DP cation was also found to be quite successful: 10 mg of DP was reacted in 3-lul, of conc. \( H_2SO_4 \) and gave a weak pink colour over a 5 min. period, although the DP crystals were not very soluble at all. A typical spectrum at \( +20^\circ C \) is shown in Figure 3.20 (c).

It can be seen from this that the linewidth alternation effect observed in the spectrum of the DP anion is also present for the cation. The spectrum consists of five major groups (the two outermost ones are not shown) and each of these is split into another five lines. Attempts to narrow the linewidth by decreasing the modulation were unsuccessful because of the low concentration of the cation species.

The two coupling constants that may be measured from this spectrum are given in Table 3.11. The smaller of these may be assigned to the \( \alpha \) position, while the larger value of 13.78 G may be explained by the fact that at \(+20^\circ C\) the DP system is still in the region between slow and intermediate exchange and hence this distance is midway between the value of \( a_{\beta_{ax}} \) at the slow exchange limit (12.11 G) and the predicted value of \( |a_{\beta_{ax}}| + |a_{\beta_{eq}}| \) for intermediate exchange.
(15.5 o). If the temperature had been raised to +80°C then it would be expected that this distance would increase to the predicted value.

It is interesting to note that at low temperatures the DP cation in the DP₃/SO₂ system is green in colour, while in conc H₂SO₄ at +20°C it has a pink colour and this is the same as that observed for the cations of the octamethyl- and the two hexamethylnaphthalenes in conc. H₂SO₄ at RT. 71.

Finally, it should be noted that there was no tendency for dimer formation in any of the spectra of these cation species. Dimers had been observed for other cations such as pyrene, naphthalene and 2,3,6,7-tetramethylnaphthalene 22.
**FIGURE 4.1**

ESR Spectra of the Naphthalene Anion in DME

(a) N/K/DME

-85°C

(b) N/Cs/DME

(i) -85°C

(ii) -50°C

(iii) -30°C

5 G.
CHAPTER FOUR

RESULTS FOR THE NAPHTHALENE AND DIMETHYLNAPHTHALENE

RADICAL IONS

4.1 Naphthalene Anion

As a check on the methods of preparation and observation of spectra used for the radical ions in this project and also as a basis for comparison of the coupling constants of the DMN anions, the naphthalene negative ion was prepared and spectra observed of this species as follows:

4.1.1 1,2-Dimethoxyethene

(1) N/K/E/E: Rapid reaction occurred at RT to give the olive green colour of the naphthalene anion. This was stable for weeks and gave excellent spectra throughout this period. Least squares fitting of theoretical spectra to a typical observed one at -85°C (Figure 4.1 (a)) gave the two coupling constants of value 1.93 ± 0.02 G and 1.86 ± 0.02 G. These were assigned from simple Hückel results to the protons at the α (1,4,5,8) and β (2,3,6,7) positions in the naph-
thulium molecule respectively. There appeared to be no change in these values over the temperature range from $-95^\circ$C to $+10^\circ$C. Spectra of the $\text{N}$ anion produced by reduction with $\text{Na}$ were identical to the above.

(2) $\text{N/Ca/DMF}$: The $\text{N}$ anion prepared in this system was stable for several hours at RT and spectra were observed over the temperature range from $-95^\circ$ to $0^\circ$C. A sample of these spectra is shown in Figure 1.1 (b), (c), and (d). Apart from the obvious decrease in intensity with an increase in temperature, these spectra show changes in hyperfine pattern with change in temperature and are quite different from those observed for the $\text{N/Na,K/DMF}$ systems.

As noted by Hirota $^{72}$, there appears to be a linewidth effect as the temperature is lowered and the lines associated with the Cs metal splitting show increasing broadening in the order of their $M_\parallel$ components i.e. $1/2$, $3/2$, $5/2$, and $7/2$. This can best be seen in the wings of the spectra although it is not nearly as clear in these spectra as in those shown by Hirota. This has important consequences with regard to the nature of the ion pairs present at these temperatures (see Section 4.5). The Cs metal splitting at $-95^\circ$C was measured as $1.30$ G and this value together with its relative insensitivity to change in temperature (see Figure 4.9), is also in agreement with the results obtained by Hirota for the same system.
FIGURE 4.2

ESR Spectra of the N anion in THF with Na⁺ as counterion

(a) -90°C

(b) -70°C

(c) -50°C

(d) -30°C

(e) -10°C

(f) +25°C
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1.2 Other Solvents

The only other system considered for the N anion was reduction with Na in THF. A sample of the spectra observed over the temperature range from -90° to +25°C is shown in Figure 1.2. It can be seen that the observed spectrum at -90°C is identical to that observed for the N/Na,K/TME systems. (Figure 1.1 (a)). As the temperature is raised, the lines begin to broaden and there is a resultant drop in intensity which may be related to the appearance of a second species with a Na metal coupling constant. As the temperature is increased further, the relative amount of this second species increases as does the value of the metal coupling constant, and this is shown in the graph in Figure 1.9. There did not appear to be any marked variation in linewidths of the lines arising from the metal splitting as had been observed for the N/Ca/TME system.
FIGURE 4.3
ESR Spectra at -85°C of the (a) 1,4- and (b) 1,5-DMN Anions in DME with Na⁺ as counterion

(a) Experimental

Computer Simulated

(b) Experimental

Computer Simulated
As mentioned in the introduction to this project, these species had been previously observed\textsuperscript{23,24,27} but there seemed to be a considerable variance in results mainly because different methods of preparation and observation temperatures had been used. Hence in order to obtain a consistent set of coupling constants for these species, they were all prepared using the same method viz., reduction with Na in DME at RT and spectra were observed at −35°C.

\textbf{1,2-Dimethoxythane}

All six compounds were found to readily react with the Na mirror and gave olive green coloured solutions of the anions that were stable for weeks. Typical spectra for some of these are given in Figures 1, 2, and 3. The linewidths were \( \sim 0.1 \text{ G} \) and hence the spectra were not as well resolved as those reported by Gerson et. al.\textsuperscript{24} but all attempts to narrow these lines by dilution of the sample and reduction of the modulation, were unsuccessful probably due to magnet inhomogeneity.

Least squares fitting of theoretical spectra to the observed ones gave the coupling constants and their standard deviations given in Table 1. The accuracy specified here is probably greater than that justified by the width of the observed lines. The assignments to specific positions were made from simple Hückel theory (see Section 5.2).
FIGURE 4.4
ESR Spectra at -85°C of the (a) 2,6- and (b) 2,7-DMN Anions in DME with Na⁺ as counterion

(a) Experimental

5 G.  H

Computer Simulated

(b) Experimental

Computer Simulated
FIGURE 4.5
ESR Spectra of the 2,3-DMN Anion in DME with Na$^+$ as counterion

(a) $-70^\circ$C

(b) $-40^\circ$C

(c) $-10^\circ$C

(d) $+20^\circ$C
The theoretical spectra calculated from these values are given below each of the observed ones and it can be seen that there is excellent agreement. A discussion of these results compared with those observed in other reports will be given in Chapter Six.

When the temperature was raised, most of the spectra became less well resolved and disappeared completely at +30°C. Allowing for this fact, there did not appear to be any large changes in the hyperfine patterns over the range from -95°C to +10°C and hence it was concluded that the couplings are not markedly dependent on temperature and that the ions exist as free ions and not ion pairs in this system. A notable exception to this was the 2,3-DIM anion which underwent some marked changes in the region from -40°C to +20°C as shown in Figure 1.5. The spectrum at +20°C is quite different from that observed at lower temperatures. This change was reversible and suggested that some sort of ion pairing effect was occurring at high temperatures. To a lesser extent similar changes were observed for the 1,3-DIM anion spectra as well.

Reduction of all six compounds with K in IME gave identical spectra but those were not as well resolved as those produced by reduction with Na.

The 1,8- and 2,6-DIM anions were the only species prepared by reduction with Cs in IME and each gave good spectra over the temper-
Observed Hyperfine Coupling Constants (Gauss) for the Symmetric DMN Anions in DMN with Na as Counterion at -85°C.

<table>
<thead>
<tr>
<th>Species</th>
<th>Position</th>
<th>Hyperfine Coupling Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4</td>
<td>1</td>
<td>3.361 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.439 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.672 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.853 ± 0.001</td>
</tr>
<tr>
<td>1,5</td>
<td>1</td>
<td>4.378 ± 0.0007</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.666 ± 0.0018</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.119 ± 0.0014</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.111 ± 0.0015</td>
</tr>
<tr>
<td>1,8</td>
<td>1</td>
<td>4.535 ± 0.0004</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.666 ± 0.0009</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.678 ± 0.0004</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.678 ± 0.0004</td>
</tr>
<tr>
<td>2,3</td>
<td>1</td>
<td>4.729 ± 0.0025</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.002 ± 0.0020</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.701 ± 0.0015</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.736 ± 0.0026</td>
</tr>
<tr>
<td>2,6</td>
<td>1</td>
<td>4.675 ± 0.0032</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.911 ± 0.0032</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.223 ± 0.0013</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.702 ± 0.0030</td>
</tr>
<tr>
<td>2,7</td>
<td>1</td>
<td>4.386 ± 0.0014</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.215 ± 0.0014</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.195 ± 0.0005</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.764 ± 0.0013</td>
</tr>
</tbody>
</table>

...ature range from -95°C to -10°C. A typical spectrum for the 1,8-DMN anion at -85°C is shown in Figure 4.6. The value of the
FIGURE 4.6

ESR Spectra of the 1,8-DMN Anion in different systems

(a) Na/DME

(b) Cs/DME

(c) Cs/THF
metal coupling constants for both species was measured as 1.22 G and it was found to be invariant with temperature.

2.2 Other Solvents

(1) Tetrahydrofuran

(a) 1,8-DMN/K/TIF: The 1,8-DMN anion prepared in this system gave good spectra over the temperature range from -90° to +40° C. This is in contrast to the spectra obtained in DME where all hyperfine structure had disappeared by RT. The spectra showed no change with temperature and could be successfully analysed in terms of the coupling constants given in Table 1.1 for the same species in DME at -85° C.

(b) 1,8-DMN/Li/TIF: This was one of the few successful reductions made with Li in this project. The anion formed was stable for days and gave good spectra over the range from -90° to RT. These were analysed in terms of the coupling constants $a_{CH_3} = a_{H_5} = 6.60$ G and $a_{2.7} = a_{3.6} = 1.63$ G.

(c) 1,8-DMN/Li/TIF: Spectra prepared for the 1,8-DMN anion prepared in this system were observed over the temperature range from -90° to +40° C. At -90° C the spectrum of this species was identical to that of the free ion in DME except that the coupling constants had changed slightly: $a_{CH_3} = a_{H_5} = 58$ G and $a_{2.7} = a_{3.6} = 1.63$ G. As the temperature was raised the lines began to broaden at around -60° C, and at -50° C definite lines due to hyperfine coupling with the alkali
metal cation were observed. As the temperature was raised further the metal coupling constant increased in magnitude as shown in the graph in Figure 4.9. These changes were quite reversible with temperature.

(d) 1,3-DMN/Ca/THF: The anion species prepared in this system was emerald green in colour and was stable for several hours at RT before decaying to a bright red diamagnetic species. Spectra observed from -90°C to +40°C indicated a definite asymmetric signal (cf. the asymmetric signal obtained for the HF/Ca/DME system shown in Figure 3.4) but as the temperature was raised this disappeared and the lines became well resolved and symmetric (Figure 4.6 (b)). At -90° a value of 1.20 G was obtained for the Ca coupling constant and this was found to decrease only slightly with temperature (Figure 4.9). The small change in this value would not explain the marked change in the spectra from -90°C to +40°C, and thus it is presumed that a linewidth effect comparable to that observed for the N/Ca/DME system is also present in this system. Another possibility would be the presence of another species, such as the free ion, in equilibrium with the ion pair at low temperatures. Unfortunately the wings of the spectrum were not well enough resolved to check these conclusions.

(e) 2,3-DMN/K/THF: The spectra of the 2,3-DMN anion prepared in this system were observed over the temperature range from -90° to +40°C. The spectrum at -85°C was quite different from that observed for the
FIGURE 4.7

ESR Spectra of the 2,3-DMN Anion in THF with Na⁺ as counterion

(a) -90°C

(b) -80°C

(c) -60°C

(d) -30°C

(e) -10°C

(f) +10°C
2,3-DMN anion DME and was analysed in terms of the coupling constants: 

\[ a_{\text{CH}_3} = a_{6,7} = 1.78 \text{ G, } a_{1,4} = 4.16 \text{ G and } a_{5,8} = 5.38 \text{ G.} \]

There was no change in these values with temperature.

(1) 2,3-DMN/Na/TIF: The 2,3-DMN anion prepared in this system gave identical spectra at -95°C to those observed for this species produced by reduction with Na in DME. At -80°C all lines broadened and at -60°C lines attributable to hyperfine splitting with the Na\(^{+}\) cation began to appear. As the temperature was increased further the value of this coupling constant increased markedly (see graph in Figure 4,9). These effects can be clearly seen from the sample spectra shown in Figure 4,7. All changes were reversible with temperature.

(g) 2,6-DMN/Cs/TIF: Spectra of the 2,6-DMN anion in this system could be analysed in terms of a Cs metal coupling constant of 1.20 G at -90°C. The value of this constant was more dependent on temperature than the other Cs splittings.

(2) 2-Methyltetrahydrofuran:

The only species prepared in this solvent was the 1,8-DMN anion by reduction with K. The spectrum of this species at -100°C could be analysed in terms of the coupling constants \[ a_{\text{CH}_3} = a_{1,8} = 1.64 \text{ G, and } a_{2,7} = a_{2,6} = 1.70 \text{ G.} \]

There was no change in these values over the temperature range from -120°C to -80°C.
FIGURE 4.8

ESR Spectra of some Unsymmetric DMN Anions in DME at -90°C with Na⁺ as counter ion

(a) 1,2-

(b) 1,3-

(c) 1,6-

Computer Simulated
1.3 Unsymmetric Dimethyl-naphthalene Anions

The three unsymmetric anions from 1,2-; 1,3-; and 1,6-DMe were found to be readily prepared by reduction with Na in DME. They were the characteristic olive green in colour and were stable at RT for several days. Reduction with K in DME gave the same species but with less well resolved spectra.

Typical spectra for these three anions at -90°C are shown in Figure 1.8. Spectra observed at higher temperatures although less well resolved and reduced in intensity, did not appear to show any major changes from the hyperfine pattern observed at -90°C. All attempts to reduce the linewidth and hence improve the resolution in these spectra by dilution of the sample and reduction of the modulation were unsuccessful.

These spectra can be seen to be very complex due to the lack of symmetry in the parent molecules. Because of this and the poor signal/noise ratio, it was not possible to analyse these spectra directly by measurement of line positions and intensities as is normally done. Instead two alternative approaches were used as follows:

(a) Simple Huckel MO theory was used to calculate theoretical spin densities for these species assuming the usual Inductive-Hyperconjugative model for the methyl groups with standard values for the coulomb
and resonance integrals (details will be given in Chapter Five).

Coupling constants were then calculated from these spin densities using McConnell's relation with $q_{CH}^H$ and $q_{CCCH}^H$ values of 2h, 7h and 19h G respectively as determined by Gerson et al. 2h for the symmetric DMN anions.

(b) Frankel's Additivity Relationship (see Chapter Six) was used to predict the aromatic proton coupling constants while the methyl proton constants were calculated as above from NO predictions of the spin density at these positions.

The values predicted for the coupling constants using these two methods are given in Table 4.2. It can be seen that there is quite good qualitative agreement between the sets of values.
<table>
<thead>
<tr>
<th>Species</th>
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<th>Hyperfine Coupling Constant (Gauss)</th>
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<td></td>
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<td>Simple Racah Method Additivity</td>
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<tr>
<td></td>
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<td>Relationship</td>
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<tr>
<td>$1,2^-$</td>
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</tr>
<tr>
<td></td>
<td>8</td>
<td>4.82</td>
</tr>
</tbody>
</table>

Spectra calculated for these sets of coupling constants with one exception, gave very poor agreement with the observed spectra shown in Figure 4.8. The exception was the theoretical spectrum shown in Figure 4.9 (c) for the $1,6$-DMN anion and simulated from coupling constants.
FIGURE 4.9 Variation of the metal Coupling Constants with Temperature in DMN Ion Pairs
ants calculated with method (b). Small changes in any of the coupling constants caused marked changes in all the spectra.

It would appear from these results that in order to successfully analyse the spectra of the unsymmetric DNN anions it is necessary to obtain spectra with better resolution particularly in the region of the spectral wings.

4.4 Discussion of Ion Pairing Effects in the Symmetric Dimethylanthalamene Anions

As discussed in the results for these species in Section 4.2, alkali metal splitting was observed in many of the spectra of these anions depending upon the nature of the solvent, counterion and temperature. These results are summarised in the graph shown in Figure 4.9. These are in good agreement with those previously obtained by Hirota for the 2,6-di-t-butylanthalamene/Na/THF, N/Cs/DMF, and N/Cs/THF systems.

From this graph it can be seen that there is little difference between the Cs metal coupling constants for the DNNs and Na, and all show little variation with temperature. On the other hand, the Na coupling constants are markedly dependent upon the species and the temperature. The results for the 1,8-DNN/Na/THF system are in good agreement with Bolton's observations for the 1,5-DNN/Na/THF system.
in which he noted that the value of $a_{Na}$ was about 0.1 G less than that for the N ion pair at the same temperature. In this respect the results for the 2,3-DMN ion pair are somewhat unusual and this combined with the appearance in DME of a 2,3-DMN anion species different from that observed at low temperatures (see Figure 4.5), may well suggest an ion pairing effect related to the proximity of the two methyl groups is occurring in all solvents. This is supported by the observation by Ricko et al. that the spectra of the 2,3-DMN/K/DME system may be interpreted in terms of an ion pair with coupling constants of $a_{1,4} = 1.32$, $a_{5,8} = 5.25$, $a_{6,7} = 1.75$, and $a_{6,7} = 1.75$ G at +25°C, and this species dissociates to the free ion at low temperatures with coupling constant values of 4.7, 5.0, 1.7, and 1.75 G respectively.

Unfortunately the complexity of all spectra showing metal hyperfine splitting, did not enable any detailed study to be made of the extent of perturbation of the proton coupling constants arising from the polarising effect of the metal cation. Such effects had been reported to be quite marked in the spectra of the ion pairs of acenaphthene, acenaphthylene, and anthracene. However, from the variation in the proton coupling constants with solvent and cation in spectra that did not show metal splitting e.g. the 1,8-DMN ion, it may be concluded that these perturbations are present in all the DMN anion systems.
Hirota has interpreted the temperature dependence of the alkali metal splitting of the N and 2,6-di-t-butyl-naphthalene ion pairs in terms of a rapid equilibrium between different ion pairs and this concept appears to satisfactorily explain the results observed for the DMN anions in this project as follows:

At high temperatures a tight ion pair i.e. one that shows alkali metal hyperfine coupling, is considered to be present while at low temperatures there exists a loose ion pair i.e. one which shows no metal coupling and the cation is only loosely associated with the anion. This later species is to be distinguished from the free ion which, from the effect of dilution on the intensity of the lines in the spectra, was considered to be also present at low temperatures. Thus the following equilibrium scheme may be drawn up for these three species:

\[ \text{Tight Ion Pair} \quad \text{Loose Ion Pair} \]

\[
\begin{align*}
R^- M^+ & \rightleftharpoons K \\ 
\rightleftharpoons R^- H^+ \\
\rightleftharpoons R^- + M^+ & \rightleftharpoons \text{Free Ion}
\end{align*}
\]

Hirota deduced from the linewidth variation of the alkali metal components of the spectra that a second tight ion pair was also present but as this variation was not detected in the DMN spectra (mainly because of the poor signal to noise ratio in the wings) it will not be consid-
ered further in this discussion. From such a study of the linewidth variation with temperature, an estimate of the lifetime of each of the ion pair species would have been obtained.

It is the equilibrium between the tight (TIP) and loose (LIP) ion pairs that is considered to give rise to the rapid change in the magnitude of the alkali metal coupling constants with temperature as follows:

If $K$ is the equilibrium constant then

$$K = \frac{[\text{LIP}]}{[\text{TIP}]}$$

If $P_{\text{LIP}}$ and $P_{\text{TIP}}$ are the fractions of each ion pair then

$$P_{\text{LIP}} = \frac{[\text{LIP}]}{[\text{TIP}]} = \frac{K}{K + 1}$$

$$P_{\text{TIP}} = \frac{[\text{TIP}]}{[\text{TIP}]} = \frac{1}{1 + K}$$

and if $a_{\text{LIP}}$ and $a_{\text{TIP}}$ are the metal coupling constants for the LIP and TIP species respectively, then the observed metal coupling constant $a_{\text{obs}}$ will be given by
\[ \text{obs} = a_{\text{TIP}}^\text{TIP} + a_{\text{LIP}}^\text{LIP} \]

\[ = a_{\text{TIP}} + K a_{\text{LIP}} \]

\[ \frac{1}{1 + K} \]

Thus if the values of \( a_{\text{TIP}}, a_{\text{LIP}}, \) and \( \text{obs} \) are known then the equilibrium constant \( K \) may be calculated. A plot of \( \log_\text{o}(K) \) versus \( 1/RT \) should then give a straight line a gradient of \( \Delta H \) and intercept of \( \Delta S \) for the equilibrium (\( \Delta G = RT \log_\text{o} K = \Delta H - \Delta S \)).

Above about 0°C, it can be seen that the metal coupling constants for the 1,8- and 2,3-DMN/Na/THF systems were approximately constant with values of 0.95 and 1.10 G respectively. Thus assuming these values for \( a_{\text{TIP}} \) for the tight ion pairs and a value of \( a_{\text{LIP}} = 0 \) (this comes from the definition given above for a loose ion pair), a plot of \( \log_\text{o} K \) versus \( 1/RT \) was made for the 1,8- and 2,3-DMN/Na/THF systems and it gave the results

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta H ) (Kcal/mole)</th>
<th>( \Delta S ) (Kcal/mole degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,8-</td>
<td>(-6.6 \pm 0.7)</td>
<td>(-25.3 \pm 3)</td>
</tr>
<tr>
<td>2,3</td>
<td>(-6.8 \pm 0.7)</td>
<td>(-26.3 \pm 3)</td>
</tr>
</tbody>
</table>

which are comparable to the values of \(-5.6\) Kcal/mole and \(-25.6\) Kcal/mole degree obtained by Hirota for the N/Na/THF system. The high \( \Delta S \) values for this type of ion pair equilibrium have been reconciled with the decrease in solvation and hence ordering of the Na\(^+\) as it changes from the loose to the tight ion pair.
This calculation may be repeated for the Cs DMN ion pairs but from the invariance of $a_{\text{us}}$ with change in temperature, these give a value for $\Delta H$ of $\sim 0.0$. This would suggest that there is no equilibrium between loose and tight ion pairs for this cation and any ion pairing effects are interpreted in terms of a static tight ion pair. This conclusion was also reached by Hirota for the N/Cs/DME,THF,MTHF systems.

In order to determine the most likely position for the cation in relation to the naphthalene ring, calculations were performed similar to those described for the peri-alkynaphthalenes in Section 3.6 and based on the theory described in Appendix II. The usual Inductive-Hyperconjugative model was used for the methyl groups with standard values for the coulomb and resonance integrals (see Section 5.2). The methyl groups were assumed to lie in the plane of the naphthalene ring and calculations repeated for non planar CH$_3$ groups indicated that this approximation was reasonable.

From cation-anion interaction energy maps for the 1,5-, 1,8-, 2,3-, 2,6-, 1,2-, and 1,6- DMN ion pairs and for cation distances of 2 and 3\text{Å} above the naphthalene ring, it could be seen that a distance of 2\text{Å}, at least two potential maxima appear and that the position of these varies with the position of the substituent CH$_3$ groups. As the cation-anion distance
increases, then these maxima become shallower until at 1 Å and above, only one maxima situated directly over the centre of the naphthalene ring is predicted (see diagram for naphthalene in Figure 3.19).

It would be reasonable to conclude that for the Li⁺, Na⁺, and K⁺ cations with ionic radii of 0.68, 0.97, and 1.33 Å respectively, there are several positions for these to be situated and movement between them would give rise to linewidth effects in the spectra of the DMN anions prepared by reduction with these metals in certain solvents. As mentioned above, it was not possible to detect these effects in practice. Conversely Cs has an ionic radius of 1.67 Å and hence would be expected to occupy the one position viz. over the centre of the naphthalene ring, and hence no movement other than within this maxima would be possible. Thus little change would be predicted in the Cs hyperfine coupling constant with temperature and this is in good agreement with the observed results for the Cs DMN ion pairs.

Finally by using a similar model for the 2,3-DMN ion pair and placing the cation midway between the positions of the interaction energy maxima at a cation-anion distance of 3 Å, the following results were predicted for the aromatic proton coupling constants:
\begin{center}
\begin{tabular}{ccc|ccc}
  \textbf{Position} & \textbf{Calculated (Causa)} & \textbf{Observed (Causa)*} \\
  & \textbf{Free Ion} & \textbf{Ion Pair} & \textbf{Free Ion} & \textbf{Ion Pair} \\
  \hline
  6.7 & 1.66 & 1.81 & 1.76 & 1.75 \\
  5.8 & 4.15 & 6.11 & 5.00 & 5.0 \\
  1.4 & 3.91 & 1.52 & 4.72 & 4.32 \\
\end{tabular}
\end{center}

* Values from this project

It can be seen from these that the model overemphasises the effect of the cation but it does predict, at least qualitatively, the observed trends and thus gives support to the suggestion of Rieke et al. \cite{7h} that the 2,3-DMN anion species exits as an ion pair at high temperatures and this dissociates into the free ion at lower temperatures.

4.5 Dimethylnaphthalene Cation Radicals

Unsuccessful attempts were made to prepare the cation radicals of the DMNs. This is not altogether surprising as these species would seem to be the obvious choice to study after the DMN anions and hence if they could have been prepared using standard techniques then it would be expected that this would have been reported in the literature long ago.

Some of the methods of cation preparation tried and results obtained are as follows:
(1) Conc. H\(_2\)SO\(_4\): The DMNs were generally insoluble in this medium and hence no reaction and no signals were observed. Exceptions to this were the unsymmetric 1,2-; 1,3-; and 1,6-DMNs which dissolved to give light green solutions and these were found to give spectra consisting of a single line with a trace of hyperfine structure superimposed upon it. The addition of H\(_2\)SO\(_4\) to the H\(_2\)SO\(_4\) did not improve the situation. The 1- and 2- methylnaphthalenes also gave no spectra when dissolved in this acid.

(2) BF\(_3\)/SO\(_2\): This method was used for samples of the 2,6-; 2,7-; and 1,8-DMNs and in all cases the sample turned a yellowish green colour on warming to ~90\(^\circ\)C but gave no signals. On warming to higher temperatures this colour changed to red, presumably due to the formation of some sort of charge transfer complex.

(3) CH\(_3\)CO\(_2\)/CH\(_3\)NO\(_2\): No colour change was observed when a small sample of each of the DMNs was dissolved in this system. The resulting solutions gave no signals.

In terms of the conditions given in Section 2.1.1 for successful cation formation it would appear that in the case of the DMNs even though their oxidation potentials are lower than that of naphthalene (average of 1.08 v. compared with 1.23 v. respectively versus SCE\(^{75}\)), they cannot be as readily protonated as naphthalene, and hence do not form cation radicals in strong oxidising acids, whereas naphthalene does. Alternatively if the protonated species is readily formed, then
the equilibrium between it and its positive ion

$$R^+ + A^- + H^+ \rightleftharpoons RH^+ + A$$

as suggested by Aalbersberg\(^{15}\) (see Section 2.1.1) must lie much more to the right for the DMNs than for naphthalene. In terms of the expression derived for the equilibrium constant for this reaction (Eqn. (2.4) in Section 2.1.1) this would mean that the DMNs have much larger basicity constants than naphthalene. Unfortunately no data was available in the literature to check these predictions.

Similarly the failure to observe spectra using the $BF_3/\text{SO}_2$ technique may be due to the formation of covalent complexes with the Lewis acid rather than undergoing direct electron transfer to form the positive ion.

Finally, it has been reported that preparations of the radical cations of the tetra-alkyl substituted naphthalenes BP and HP (this project); the $1,4,5,8$- and $2,3,6,7$- TMNs\(^22,27\); the $1,2,3,4,5,8$- and $1,2,3,4,6,7$-hexamethyl naphthalenes; and octamethylnaphthalene\(^71\) have been successful using conc H$_2$SO$_4$ and/or $BF_3/\text{SO}_2$ methods, while attempts to prepare the cations of $2,3,6$-trimethylnaphthalene\(^71\) and the di- and mono-methylnaphthalenes (this project) were unsuccessful. This may be rationalized in terms of the electron donating effect of one, two, or three methyl groups making the naphthalene ring more electrophilic to sulphonation. However, when four or more methyl groups are present
then although the electrophilic character of the naphthalene ring is enhanced even more, steric effects become important and ortho substitution through sulphonation is not possible. Thus structures of the form

\[
\begin{align*}
\text{[Diagram of structures]} & \\
\end{align*}
\]

cannot be sulphonated. Protonation leading to the formation of the cation is not dependent upon steric effects and hence occurs in preference to sulphonation for these species. An interesting test of this hypothesis would be the compound

\[
\begin{align*}
\text{[Diagram of structure]} & \\
\end{align*}
\]

where although there are four methyl groups present it should undergo sulphonation, in preference to protonation and subsequent formation of the positive ion.
CHAPTER FIVE

COMPARISON OF THEORETICAL SPIN
DENSI TIES WITH OBSERVED HYPERFINE COUPLING CONSTANTS

5.1 Introduction

ESR techniques may be used to obtain much useful information regarding the electronic structure of free radicals. As discussed in Section 1.2, variables such as hyperfine coupling constants, g values and linewidths may be shown to be related to the distribution of unpaired electrons in the radicals, and thus 'experimental' spin densities at various positions in the molecules may be obtained. The usefulness of obtaining these values lies in the fact that theoretical estimates of spin densities may be readily calculated using Molecular Orbital (MO) and Valence Bond (VB) theories and by comparison of these values with the experimental ones, the validity of approximations.

The term electron spin density (abbreviated to spin density) at a point \((x, y, z)\) is defined as the difference in electron density between electrons of \(\alpha\) spin and those of \(\beta\) spin at that point and is thus a many electron function. By convention free radicals are considered to have an overall spin orientation of although there may be regions where there is a local excess of \(\beta\) spin over \(\alpha\) spins and thus spin densities at these positions are negative.
imations made in these two types of calculation may be tested.

Unfortunately the quantitative relation of the variables in the spectra to spin densities is not always straightforward. For example, as discussed in Section 1.2, isotropic proton hyperfine coupling arises from spin density at the nuclei of atoms. Thus it is surprising to observe coupling from the aromatic protons in the naphthalene anion since these lie in the nodal planes of the $\mathcal{W}$ system in which the unpaired electron is considered to reside and hence they should have no spin density. There have been a number of theories (see Ref. 53b for a review of these) proposed to explain some of these apparent anomalies and it is proposed in this section to discuss some of these and, in particular, those relating hyperfine coupling constants at aromatic, methyl and methylene proton positions to theoretical spin densities at those points.

McConnell\textsuperscript{76} introduced the term spin polarisation to account for the above paradox as follows:

Consider a CH radical fragment in a conjugated hydrocarbon:

![Diagram of a CH radical fragment]

Here $\mathcal{W}$ is the $2p_z$ orbital on C, $\sigma$ is a $sp^2$ hybrid orbital.
pointing towards the H atom, and $S$ is a 1s orbital of hydrogen. The VB wavefunctions constructed for this situation must obey the following conditions:

(a) Each orbital holds only one electron.

(b) Wavefunctions must be eigenfunctions of

(i) $S_z$ with eigenvalues of $\pm \frac{1}{2}$

(ii) $S^2$ with eigenvalues of $\frac{3}{2}$

(c) One of the wavefunctions must approximate the ground electronic state of the CH fragment in which there is a chemical bond between the C and H atoms.

Two spin eigenfunctions that obey these conditions are

\[
\frac{1}{\sqrt{2}} \left[ \alpha(1) \beta(2) \alpha(3) = \alpha(1) \alpha(2) \beta(3) \right]
\]

and

\[
\frac{1}{\sqrt{6}} \left[ \alpha(1) \alpha(2) \beta(3) + \alpha(1) \beta(2) \alpha(3) - 2 \beta(1) \alpha(2) \alpha(3) \right]
\]

corresponding to the complete wavefunctions i.e., with normalisation, spatial, and spin parts:

\[
\Psi_1 = \frac{1}{\sqrt{1 + S_o^2}} \frac{1}{\sqrt{6}} \left\| \mathbf{\Pi} (1) \sigma(2) S(3) \right\| \frac{1}{\sqrt{2}} (\alpha \beta \alpha \alpha \alpha \beta)
\]

and

\[
\Psi_2 = \frac{1}{\sqrt{1 - S_o^2}} \frac{1}{\sqrt{6}} \left\| \mathbf{\Pi} (1) \sigma(2) S(3) \right\| \frac{1}{\sqrt{6}} (\alpha \beta \alpha \beta \alpha \alpha \beta)
\]

where $S_o$ is the overlap integral between the $\sigma^*$ and $S$ orbitals and $\left\| \cdots \right\|$ represent a Slater determinantal wave function.
Of these, \( \psi_1 \) represents a bonding orbital but gives no spin density on the hydrogen \( \text{H} \) orbital. In order to get this it is necessary to mix in a little of the excited state \( \psi_2 \) and so the improved wavefunction may be written as

\[
\psi = \psi_1 + \lambda \psi_2 \quad \text{where} \quad \lambda \ll 1.
\]

A value for \( \lambda \) may be obtained using first order perturbation theory such that

\[
\lambda = \frac{\sqrt{3}}{2(1 - S_0) \frac{1}{2}} \left[ J_{\pi \sigma} - J_{\pi \delta} \right]
\]

where \( J_{\pi \sigma} \), \( J_{\pi \delta} \) are exchange integrals and \( E_2^0 \), \( E_1^0 \) are the energies of the wavefunction \( \psi_1 \) and \( \psi_2 \) respectively. The value of the spin density at the proton in the CH fragment, \( \rho_{\text{H}}(0) \) may be shown to be

\[
\rho_{\text{H}}(0) = \frac{1}{3} \frac{1}{1 - S_0} \lambda^2 \left| s(0) \right|^2
\]

where \( \left| s(0) \right|^2 \) is the probability density of the hydrogen \( \text{H} \) orbital.
at the proton.

If the proton isotropic coupling constant for unit spin density in the \( \pi \) orbital is \( Q_{\text{CH}}^H \) (in this expression the superscript refers to the nucleus giving rise to the hyperfine splitting, the first subscript to the atom in which the spin density originates and the two subscripts together to the bond through which it is transmitted), then using the expression given in Section 1.2 for the Fermi contact hyperfine interaction,

\[
Q_{\text{CH}}^H = \frac{8\pi}{3} \frac{\mu^H}{I} \rho^H(o)
\]

\[
= - \frac{8\pi}{3} \frac{\mu^H}{I} \frac{1}{(1-S^o)} \frac{J_{\pi\varphi} - J_{\pi\sigma}}{E_2 - E_1} |s(o)|^2
\]

An estimate of the value of \( |s(o)|^2 \) may be made if it is assumed that the proton in the CH fragment is similar to that of a free hydrogen atom. Hence

\[
\alpha^H = \frac{8\pi}{3} \frac{\mu^H}{I} |s(o)|^2
\]

where \( \alpha^H \) is the isotropic hyperfine splitting constant for the free hydrogen atom. Thus

\[
Q_{\text{CH}}^H = \frac{1}{(1-S^o)} \frac{J_{\pi\varphi} - J_{\pi\sigma}}{E_2 - E_1} \alpha^H
\]

In words, this means that the observed hyperfine coupling constant
for the proton in a CH fragment will be the same fraction of that observed for the free hydrogen atom. This fraction will be principally dependent upon the value of the exchange integral $J_{\pi\sigma}$ i.e. the extent of penetration of the $\pi$ spin density into the $\sigma$ system.

So far it has been assumed that the $\pi$ orbital has unit spin density, but it may be shown that if the unpaired electron is shared over a number of $\pi$ centres, then the observed isotropic proton coupling constant $a_i^H$ for a proton attached to a carbon atom $i$ with spin density $\rho_i^\pi$, will be given by the linear relation

$$a_i^H = Q CH \rho_i^\pi$$

This is McConnell's Relation for isotropic proton hyperfine interaction as first derived by McConnell.

In qualitative terms, this transfer of spin density via an exchange mechanism may be easily seen from a consideration of the two possible arrangements for the 3 electrons:

![Diagram](a) ![Diagram](b)

Energetically, arrangement (b) is slightly favoured over (a) and hence there is a slight excess of $\beta$ spins at the proton nucleus and hence
a small negative hyperfine coupling constant is observed for this proton.

It should be noted that $Q_{CH}^H$ has a negative sign and this has been confirmed experimentally by Gutowsky et al. Thus the observed hyperfine coupling constants also have a negative sign for positive $\rho T$, although this cannot be determined from ESR spectra. In subsequent results, for convenience all coupling constants will be considered to be positive in sign.

Using this relationship, it is possible to obtain experimental spin densities from observed coupling constants but this requires a known value of $Q_{CH}^H$ and herein lie some major difficulties. For example in the methyl radical, $a^H = -23.03$ G and thus since $\rho T = 1$, $Q_{CH}^H = -23.03$ G whereas in the benzene ion where $\rho T = 1/6$, $a^H = -3.75$ G and thus $Q_{CH}^H = -22.5$ G. From these two examples it can be seen that $Q_{CH}^H$ is by no means constant for every type of molecule and indeed Bolton has pointed out that it is only constant with a value of 27.0 $\pm$ 1 G for a restricted group of neutral free radicals where two C atoms and a hydrogen atom are bonded to the trigonal carbon atom of interest. In spite of this, a large number of correlations have been made in the literature for a variety of types of radicals assuming different $Q$ values.

Two approaches have been used to extend McConnell's relation to the case of proton hyperfine coupling constants in radical ions.
Colpa and Bolton observed that for a given alternant hydrocarbon ion, the proton hyperfine splittings were greater in the cation than in the anion. Since the pairing theorem derived from simple Hückel MO theory predicts the same value of $\rho^1 \pi$ for both species, then application of McConnell's relation would suggest that either the pairing theorem was in error or the value of $Q_{CH}^H$ changed with excess charge, $\xi_1^\pi$, on the C atom to which the proton was attached. For a variety of reasons they considered the latter cause to be the most likely and proposed the relation

$$\alpha_1^H = \left[ Q_{CH}^H (o) + K_{CH}^H \xi_1^\pi \right] \rho_1^\pi$$

where $Q_{CH}^H (o)$ is the value of $Q_{CH}^H$ appropriate for neutral free radicals and $K_{CH}^H$ is a constant. Using data derived from spectra of the positive and negative ions of some polyacenes they showed that there is a significant improvement between calculated and observed spin densities compared with McConnell's relation.

Giacometti, Nordio, and Pavan proposed the relation

$$\alpha_1^H = Q_1 \rho_{11}^\pi + Q_2 \xi_j^\pi \rho_{1j}^\pi$$

where $\rho_{1i}^\pi$ and $\rho_{ij}^\pi$ are elements of the $\pi$ atomic orbital spin density matrix, atom $i$ is assumed to be bonded to atom $j$ and $Q_1$ and $Q_2$ are constants. This expression has also been found
to give better agreement than McConnell’s relation but not as good as that derived by Colpa and Bolton.

McConnell’s relation has also been extended to the calculation of experimental spin densities from observed proton splittings in methyl groups attached to aromatic pi-electron radicals. The splitting constants \( \varepsilon_{\text{CH}_3}^H (i) \) may be related to either the \( \rho^\pi \) value at the carbon atom to which the methyl groups is attached:

\[
\varepsilon_{\text{CH}_3}^H (i) = Q_{\text{CCH}_3}^H / \rho^\pi
\]

or to the \( \rho^\pi \) value of the pseudo \( \pi \) orbital formed by the three hydrogen atoms in the inductive-hyperconjugative model of the methyl group (see Section 5.2):

\[
\varepsilon_{\text{CH}_3}^H (i) = Q'_{\text{CCH}_3}^H / \rho \times \rho
\]

Values ranging from 18.4 to \( \sim 38 \) G have been determined for \( Q_{\text{CCH}_3}^H \). The predicted value of \( Q'_{\text{CCH}_3}^H \) is 169 or 220 G depending upon whether overlap between the 1s H orbitals is neglected or allowed for, the former value is obtained simply by taking 1/3 of the free hydrogen atom coupling constant. In practice a wide range of \( Q'_{\text{CCH}_3}^H \) values from 169 to 220 G have been obtained.

The main reason for the large variation in both constants is because the mechanism of transfer of spin density into the \( \text{CH}_3 \) proton orbitals involves not only spin polarisation but also hyperconjugation.
and McConnell's relation allows for only the former of these.
Levy has pointed out that in the few cases where the above two
equations have been found to give good agreement then it is just
coincidence that the hyperconjugation part of the spin density is
roughly proportional to the spin polarisation part. In general both
effects are present but hyperconjugation has been shown by Colpa and
de Boer to be the principal coupling mechanism.

Levy derived the two formulae

$$a_{\text{CH}_2} = 327 \, C_H^2 + 19.8 \, C_c^2 + 161 \, C_c \, C_H$$

$$+ (5.95 \, C_H^2 + 1.60 \, C_c) \, (C_c^I + C_c^II)$$

$$- 3.09 \, (C_c^I)^2 + (C_c^II)^2$$

and

$$a_{\text{CH}_3} = 219.8 \, C_H^2 + 13.17 \, C_c^2 + 107.7 \, C_H \, C_c$$

$$+ 3.997 \, C_H \, C_c^I + 0.973 \, C_c \, C_c^I$$

$$- 3.09 \, C_c^I$$

for the hyperfine coupling constants (Gauss) of a methylene and methyl
group attached to aromatic radicals. In these formula the C terms
refer to the coefficients obtained from simple Huckel theory allowing
for overlap for the following position: $C_H$ to the pseudo $H_3$ (or $H_2$)
orbital, \( C \) to the methyl (methylene) atom, and \( C', C'' \) to the two (one) carbon atoms to which the methyl (methylene) groups are attached. These two relations have been used recently by a number of workers\(^{22,40,86}\) to predict proton hyperfine coupling constants at methyl or methylene positions in aromatic radical ions.

To summarise, there are a number of relations that may be used to obtain experimental spin densities from observed coupling constants or to predict coupling constants from theoretical spin densities. In the next two sections, it is planned to use these relations to predict coupling constants from theoretical spin densities calculated using simple Hückel theory and its extensions and Self Consistent Field MO theory.

5.2 Results from Simple Hückel MO Theory and its Extensions

5.2.1 Theory

In order to describe a system completely it is necessary to find wavefunctions, \( \psi \), which are solutions of the Schrödinger equation

\[
\hat{H} \psi = E \psi
\]

where \( \hat{H} \) is the Hamiltonian operator for all interaction terms. For polyelectronic systems, no exact analytical expression for \( \psi \) is
possible and thus the approximation is made that $\psi$ is a linear combination of the atomic orbitals of a system (LCAO). In simple Hückel theory for unsaturated hydrocarbons only the $\pi$ electron system is considered and thus these atomic orbitals (AO) are of one type only: carbon $\psi_z$. The $i$-th molecular orbital (MO) may then be written as

$$\psi_i = C_{1i} \phi_1 + C_{12} \phi_2 + \cdots + C_{1n} \phi_n$$

$$= \sum_{r=1}^{n} C_{ir} \phi_r \quad (5.2.1)$$

where $\phi_r$ is the $\psi_z$ AO of the $r$-th carbon atom and $C_{ir}$ is the coefficient of the $r$-th AO in the $i$-th MO.

Use of the Variational Principle leads to the following condition for there to be non-zero coefficients $C_{ir}$:

$$\det \left| H_{rm} - E S_{rm} \right| = 0 \text{ for all } r, m$$

where $H_{rm} = \int \psi_r \mathcal{H} \psi_m \, d\tau$

and $S_{rm} = \int \psi_r \psi_m \, d\tau$

This is known as the Secular Determinant and it yields $n$ values of $E$ which represent the energy levels of the system. Substitution of these values for $E$ into the equation
\[ \sum_{r=1}^{n} C_{rt} (H_{rt} - E S_{rt}) = 0 \]

will give the coefficients \( C_{rt} \).

In order to simplify the secular determinant, Hückel \(^{87}\) made certain approximations:

1. The Coulomb integral, \( H_{rr} \), represents the energy of an electron in the 2p\(_z\) orbital of carbon \( r \). In view of only the \( \pi \) electron system being considered, these are set equal to a constant value of \( \alpha a_v \).

2. The Resonance integral, \( H_{rs} \), represents the energy of interaction of two AOs centred on atoms \( r \) and \( s \). This clearly depends upon the distance between the two atomic centres and thus the approximation is made that if atoms \( r \) and \( s \) are bonded to each other, then \( H_{rs} \) is set equal to a constant, \( \beta \), otherwise they are set to zero.

3. The Overlap integral, \( S_{rs} \), represents the extent of overlap of the 2p\(_z\) orbitals on atom \( r \) with that on atom \( s \). Obviously \( S_{rr} = 1 \) and the approximation is made that \( S_{rs} = 0 \) for \( r = s \), although this certainly is not true in practice.

Once the coefficients and energies have been obtained by solution of 5.2.4 and 5.2.5, the latter are arranged in order of increasing energy, and the electrons fed into these energy levels starting with the lowest energy first and allowing for a maximum of 2 electrons per
level (Pauli Principle). A number of other electronic properties may be determined including bond orders, electron densities, atom-atom polarisabilities, total energy and, if the \( \pi \) system has an unpaired electron then the spin density of this electron at various atoms in the molecule. For atom \( r \), the spin density \( \rho_r \), is defined as

\[
\rho_r = c_{kr}^2
\]

where \( \psi_k \) is the highest occupied MO. It is this latter quantity which is used in conjunction with McConnell's relation to give an estimate of theoretical coupling constants for aromatic radical ions.

The original Huckel method involving the above approximations is referred to as simple Huckel theory as it has been extended by a number of other workers since it was first proposed. Wheland and Mann proposed that the value of the coulomb integral at carbon atom \( r \) is linearly related to the charge at the atom:

\[
\alpha_r = \alpha_0 + (1 - q_r) \beta_0 \omega
\]

where \( \omega \) is a dimensionless parameter whose value is chosen so as to give best agreement with experiment, and \( \alpha_0 \) and \( \beta_0 \) are the coulomb and resonance integrals for benzene, and \( q_r \) is the charge on atom \( r \).

In applying this method which has become known as the Omega technique, a simple Huckel calculation is made to get an initial estimate of the charges, \( q_r \), and these are then used to calculate new coulomb integrals,
\[ \alpha_{r} \], using the above expression. The new charge distribution is then calculated and the process repeated until the electron densities no longer change from one cycle to the next. The value of \( \omega \) is chosen initially so as to speed this convergence and hence takes a small value of 0.2 for the first few cycles and this is gradually increased to 1.0.

From the definition given above for the unpaired spin density, it can be seen that all these values must be \( > 0 \). In practice, many ESR spectra can only be explained by negative values of spin densities and thus McLachlan developed an MO theory based on simple Hückel methods and which allowed for mixing of the ground state wavefunctions with excited state configurations. In practice a simple Hückel calculation is performed to give the MOs \( \psi_{1}^{\prime} \ldots \psi_{n}^{\prime} \psi_{o}^{\prime} \), where the unpaired electron occupies \( \psi_{o}^{\prime} \). The calculation is repeated then for the same resonance integrals but with new coulomb integrals

\[ \alpha_{r} = \alpha_{r} + 2 \lambda \beta_{o}^{2} \]

where \( \beta_{o} \) is the coefficient of the AO \( \phi_{r} \) in the MO \( \psi_{o} \), and \( \lambda \) is a constant that normally takes the value of 1.2. This gives the new MO's \( \psi_{1} \ldots \psi_{n} \). The unpaired spin density is then calculated as

\[ \rho_{r} = \beta_{o}^{2} + \sum_{i=1}^{n} (c_{ir}^{2} - c_{ir}^{2}) \]
and thus there exists the possibility, if the second term in this expression is sufficiently negative, that \( \rho_r \) may also be negative.

The methods of calculation for the simple Hückel, McLachlan and Omega techniques described above, have been incorporated in the computer programs, HUCKEL and MOCALC.

5.2.2 Results

(a) Symmetric Dimethylnaphthalene Radical Anions

Three models have been used in the literature to describe the methyl groups in unsaturated systems using simple Hückel methods (see Ref. 90 for details) as follows:

(1) Inductive Model: Substitution of a methyl group for a hydrogen atom in an aromatic hydrocarbon produces a change in the coulomb integral at the aromatic carbon atom to which the methyl group is attached. This is allowed for by assigning a small negative value, \( h_x \), to the coulomb integral for this carbon atom i.e.

\[ \alpha_r = \alpha_0 + h_x \beta_0 \]

Values used for this \( h_x \) in the literature have range from \(-0.3\) to \(-0.5\).

(2) Heteroatom Model: The methyl group is regarded as a heteroatom, \( X \), which contributes a pair of electrons to the \( \pi \) system. Thus two new parameters are necessary to describe (a) the resonance integral of the \( C_{Ar} - X \) bond \( (k_X) \) and (b) the coulomb integral of the hetero atom itself \( (h_X) \). These have been given the values \( 0.7 - 0.8 \) and \( 1.3 - 3.3 \) respectively.
(3) Hyperconjugative Model: The methyl group is treated as a modified vinyl group

\[ C_{Ar} - C_{Me} - H_3 \]

in which the three hydrogen is A0s are combined in such a way as to form a pseudo atom which is capable of overlapping with the aromatic \( \pi \) system. This type of interaction of appropriately orientated \( \sigma \)-bonds with \( \pi \) systems is known as Hyperconjugation. In this model, there are three coulomb integral parameters, \( h_{Ar} \), \( h_{Me} \), and \( h_{H_3} \); and two resonance integral parameters, \( k_{ArMe} \), and \( k_{MeH_3} \), which must be considered. Values used in the past for these are 0 to 0.1, 0 to -0.1, 0 to -0.5, 0.7 to 1.0, and 2 to 2.5 respectively.

These three models were used to calculate spin densities for the radical anions of the unsubstituted- and dimethyl-naphthalenes. These were compared with the observed coupling constants as follows:

**Aromatic Ring Protons**

(1) Inductive Model (I): The value of the parameter, \( h_p \), for the coulomb integral was varied over the range from -0.05 to -0.35 at 0.05 intervals. The best value for \( h_p \), as determined by the minimum standard deviation of the gradient of the straight line fitted by least squares methods to a plot of \( a_H^{(Obs)} \) versus the calculated spin density at the C atom to which the proton is attached, \( \rho_{Ar}^{(Calc)} \), was found to be -0.15 and this corresponded to a \( ^1H_{\text{CH}} \) value of 27.18.\( \pm \).
FIGURE 5.1
Plots of Aromatic proton Coupling Constants versus Spin Densities for the Symmetric DMN anions.

(a) Inductive

(b) Hyperconjugative
0.79 G. The plot of $a_H$ versus $p_{AR}$ for this case is shown in Figure 5.1 (a). It can be seen that there is quite a spread of values about this line, and that the $\alpha$ splittings (larger coupling constants in upper group of points) give better agreement than the $\beta$ splittings (smaller coupling constants in the lower group) although the accuracy of fitting a straight line to two groups of points such as these is debatable. The spin densities calculated for $h_\alpha = 0.15$ and the coupling constants calculated from them for the seven axions using McConnell's Relation and the above $Q^H_{CH}$ value, are given in columns 1 and 3 respectively, of Table 5.1.

(2) Heterocaton Model (HET): The value of the resonance integral parameter, $k_\alpha$, was kept constant at 0.7 and the coulomb integral parameter, $h_\alpha$, was varied over the range from +1.5 to +3.5 at 0.5 intervals. The best fit to the observed coupling constants was obtained for an $h_\alpha$ value of 3.0 corresponding to a $Q^H_{CH}$ value of 23.53 ± 3.1 G. It can be seen that this value is quite different from that obtained using the inductive or hyperconjugative models (see later) and from the large standard deviation it is not a particularly good fit. The values of the spin densities and the coupling constants calculated from them using McConnell's relation and the above $Q^H_{CH}$ value, are given in columns 2 and 4 of Table 5.1.
TABLE 5.1

Calculated Spin Densities and Coupling Constants for the
Aromatic Protons of Naphthalene and Dimethylnaphthalene Anions

<table>
<thead>
<tr>
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<th>Spin Densities</th>
<th>Coupling Constants (Gauss)</th>
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<td>(3) HYPO</td>
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<tr>
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<td>3</td>
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<td>0.1647</td>
</tr>
</tbody>
</table>

* See Figure 1.2 for number system
(3) Hyperconjugative Model (HYPO): The parameters used for this model were those used by Lamidin9 for calculations on the toluene anion assuming this model for the methyl group. These were

\[ h_{He} = -0.05, \quad k_{HeHe} = 0.86 \]

\[ h_{He} = -0.5, \quad k_{HeHe} = 2.5 \]

and the inductive parameter, \( h_{Ar} \), for the aromatic carbon atoms to which the methyl groups were attached was varied from 0.0 to -0.35 at 0.05 intervals. The best value for this parameter was found to be -0.15 corresponding to a \( Q^H \) value of 27.41 ± 0.60 G.

A plot of \( a_\parallel \) versus \( \rho_\parallel \) for this case is shown in Figure 5.1(b). Compared with the similar plot for the inductive model in Figure 5.1(a), there is again better agreement for the \( \alpha \) splittings than for the \( \beta \) ones. The overall fit, as determined by the standard deviation of the \( Q^H \) value, is marginally better for the hyperconjugative than inductive models. The coupling constants predicted using McConnell's relation with the above \( Q^H \) value and the theoretical spin densities predicted with this model, are given in columns 3 and 6 of Table 5.1 respectively.

Comparing the predicted coupling constants for the three models with the observed values in column 7 of Table 5.1, it can be seen that the hyperconjugative model with \( h_{Ar} = -0.15 \) gave the best agreement.
### TABLE 5.2

Calculation of Coupling Constants Using Different Relations and the Spin Densities Calculated from Hyperconjugative Model of the Dimethylanilines Aromes

<table>
<thead>
<tr>
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<td></td>
<td>4</td>
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<td>4.630</td>
<td>4.656</td>
<td>4.656</td>
<td>4.663</td>
</tr>
<tr>
<td>2,3-</td>
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<td>4.622</td>
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<td>5.120</td>
<td>5.249</td>
<td>5.253</td>
<td>5.215</td>
</tr>
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</table>
In order to see what effect changing the relation used to calculate the coupling constants from the theoretical spin densities would have, the results from the hyperconjugative model were used in conjunction with the McConnell, Colpa-Bolton, and Giacometti relations (see Section 5.1 for a definition of the latter two) and the predicted coupling constants are given in Table 5.2. The values for $Q_{CH}^H(0)$ and $K_{CH}^H$ were chosen to be 31.2 and 17.0 G respectively as determined by Colpa and Bolton in their original derivation of this expression. Similarly, the values for $Q_1$ and $Q_2$ were chosen to be 31.5 and 7.0 G as determined by Giacometti, Nordio, and Pavan.

A qualitative comparison of these results would indicate that the Colpa-Bolton and Giacometti relations give slightly better agreement than McConnell's relation. This has been noted before for other systems, but in this case it is difficult to decide which is the better of the two. Again discrepancies between values of predicted and observed coupling constants for the $D_5$ ring are greater for the $\beta$ splittings than the $\alpha$ splittings.

In an attempt to improve the agreement between calculated and observed coupling constants, the hyperconjugative model with $h_\kappa = 0.15$ was used in conjunction with the McLachlan and Omega extensions to simple Hückel theory. The value of the $\lambda$ parameter in McLachlan's method was set equal to 1.1 and the value of the $\omega$ parameter in the Omega method was taken to be 0, 0.8, 1.0 and 1.4 in the first four
\begin{table}
\centering
\caption{McLachlan and Omega technique Calculations of Spin Densities and Coupling Constants for the Dimethylphenalen Radical Anions}
\begin{tabular}{|l|l|l|l|l|l|l|l|l|}
\hline
\textbf{Compound} & \textbf{Position} & \textbf{(1) Huckel} & \textbf{(2) McLachlan} & \textbf{(3) Omega} & \textbf{(4) Huckel} & \textbf{(5) McLachlan} & \textbf{(6) Omega} & \textbf{(7) Obs.} \\
\hline
Unsubstituted & 1 & 0.1809 & 0.2267 & - & 4.958 & 5.186 & - & 4.93 \\
 & 2 & 0.0691 & 0.0511 & - & 1.594 & 1.067 & - & 1.86 \\
1,4 & 2 & 0.0568 & 0.0517 & 0.0533 & 1.560 & 0.810 & 1.11 & 1.679 \\
 & 5 & 0.1952 & 0.2359 & 0.1617 & 5.350 & 5.951 & 3.638 & 5.133 \\
 & 6 & 0.0706 & 0.0519 & 0.0536 & 1.935 & 1.067 & 1.205 & 1.858 \\
1,5 & 2 & 0.0591 & 0.0335 & 0.0363 & 1.620 & 0.811 & 1.357 & 1.119 \\
 & 3 & 0.0676 & 0.0458 & 0.0568 & 1.853 & 1.108 & 1.278 & 2.141 \\
 & 4 & 0.1732 & 0.2175 & 0.1733 & 4.747 & 5.284 & 3.999 & 4.664 \\
1,6 & 2 & 0.0522 & 0.0611 & 0.0373 & 1.431 & 0.511 & 1.601 & 1.677 \\
 & 3 & 0.0706 & 0.0590 & 0.0372 & 2.053 & 1.428 & 1.362 & 1.677 \\
 & 4 & 0.1639 & 0.2063 & 0.1813 & 4.630 & 5.024 & 4.079 & 4.663 \\
2,3 & 1 & 0.1663 & 0.2097 & 0.1659 & 4.572 & 5.074 & 4.108 & 4.729 \\
 & 5 & 0.1823 & 0.2296 & 0.1615 & 4.997 & 5.555 & 4.051 & 5.002 \\
 & 6 & 0.0660 & 0.0537 & 0.0582 & 1.664 & 1.108 & 1.399 & 1.767 \\
2,4 & 1 & 0.1733 & 0.2174 & 0.1828 & 4.682 & 5.261 & 4.113 & 4.674 \\
 & 3 & 0.0732 & 0.0720 & 0.0278 & 2.390 & 1.742 & 0.671 & 2.702 \\
 & 4 & 0.1590 & 0.2215 & 0.1612 & 4.405 & 5.360 & 4.077 & 4.914 \\
2,5 & 1 & 0.1614 & 0.2059 & 0.2049 & 1.079 & 4.913 & 1.610 & 4.386 \\
 & 3 & 0.0756 & 0.0522 & 0.0533 & 2.072 & 1.263 & 1.199 & 1.723 \\
 & 4 & 0.1868 & 0.2370 & 0.1722 & 5.120 & 5.735 & 3.874 & 5.215 \\
\hline
\end{tabular}
\end{table}
cycles respectively, and then kept at the normal value of 1.4 for all subsequent cycles. The spin densities and the coupling constants predicted using McConnell's relation and $Q_{HI}$ values of 24.2 and 22.5 G respectively (as used by other workers for the McLachlan$^{89}$ and Omega$^{71}$ methods of calculation of spin densities for the radical ions of substituted naphthalenes) are given in columns 5 and 6 of Table 5.3.

A comparison of these coupling constants with those predicted using simple Hückel theory (column h) shows that they do not improve the agreement with the observed coupling constants and, in fact, in many cases make it worse.

It appears that the effect of the McLachlan approximation is to increase the value of the spin densities at the $\alpha$ positions and decrease those at the $\beta$ positions. This conclusion had also been reached by Gerson et. al$^{21}$ for the D&M anions and McLachlan$^{89}$ for the unsubstituted naphthalene anion. A possible reason for this effect is that the bond lengths in the naphthalene ring are not all equal and thus the resonance integrals for these bonds should be different. However, McLachlan found that even allowing for the variation in values with bond length according to the formula$^{92}$:

$$\beta(r) = \beta_0 \exp \left[ -\frac{(r - 1.40 (\AA))}{a} \right]$$

where $a = 0.311$ \(\AA\) and using bond lengths found from X-ray data, the
agreement between the predicted and observed coupling constants for
the unsubstituted naphthalene anion was little better than before.

The discrepancies in the coupling constants derived using the
Omega technique did not seem to follow any trend although, in general,
the predicted coupling constants seemed to be smaller than those
obtained from simple Huckel theory and this may be due to the value
of $Q_{CH}^H = 22.5$ G used to derive them from the spin densities, being
too small. The spin densities themselves do not seem to show any
marked trends either.

Methyl Protons

Estimates of the values of the methyl proton coupling constants,
$a_{CH_3}^H$ were made using the same models and range of coulomb and reson-
ance integrals as were used for the aromatic protons. Details are as
follows:

(1) Inductive Model: In this model the observed $a_{CH_3}^H$ values were
correlated with the spin densities calculated at the aromatic C atoms
to which the methyl groups were attached. The best value of $h_x^C$ was
found to be 0.20 corresponding to a $Q_{CCH_3}^H$ value of $21.3 \pm 1.4$ G.

(2) Heterocatom Model: A similar correlation to that used in the
inductive model was used here and the best value for $h_x^C$ was found to
be 3.0. This gave a $Q_{CCH_3}^H$ value of $15.7 \pm 5$ G.

(3) Hyperconjugative Model: The spin densities at two different
atoms were used in this model to correlate the observed $a_{CH_3}^H$ values:
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<th>2.6</th>
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<td>2.506</td>
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<td>1.104</td>
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<td>Hyperconjugative</td>
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<td></td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>3.265</td>
<td>4.091</td>
<td>4.214</td>
<td>1.771</td>
<td>1.077</td>
<td>1.162</td>
</tr>
<tr>
<td>$\alpha_2$ - (1)</td>
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<td>4.068</td>
<td>4.044</td>
<td>1.771</td>
<td>0.967</td>
<td>1.400</td>
</tr>
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<td>4.295</td>
<td>5.118</td>
<td>1.342</td>
<td>1.056</td>
<td>1.093</td>
</tr>
<tr>
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<td>5.834</td>
<td>5.604</td>
<td>1.957</td>
<td>3.077</td>
<td>2.113</td>
</tr>
<tr>
<td>Levy</td>
<td>3.650</td>
<td>4.324</td>
<td>4.210</td>
<td>1.591</td>
<td>1.341</td>
<td>1.605</td>
</tr>
<tr>
<td>Experimental</td>
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<td>4.378</td>
<td>4.535</td>
<td>1.701</td>
<td>1.223</td>
<td>2.195</td>
</tr>
</tbody>
</table>

**TABLE 5.4**

Predicted Methyl Proton Coupling Constants
for Dimethylcarbazole Radical Anions

<table>
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<th>Methyl Proton</th>
<th>Hyperfine Coupling Constant (Gauss)</th>
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</thead>
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<td>1.4</td>
</tr>
<tr>
<td>Heterocatal</td>
<td>3.077</td>
</tr>
</tbody>
</table>
| Hyperconjugative | | | | | | }
| $\alpha_2$ | 3.265 | 4.091 | 4.214 | 1.771 | 1.077 | 1.162 |
| $\alpha_2$ - (1) | 3.070 | 4.068 | 4.044 | 1.771 | 0.967 | 1.400 |
| McLachlan | 4.090 | 4.295 | 5.118 | 1.342 | 1.056 | 1.093 |
| Omega | 6.156 | 5.834 | 5.604 | 1.957 | 3.077 | 2.113 |
| Levy | 3.650 | 4.324 | 4.210 | 1.591 | 1.341 | 1.605 |
| Experimental | 3.361 | 4.378 | 4.535 | 1.701 | 1.223 | 2.195 |
(a) the $\rho_{ax}$ value at the aromatic C atom to which the modified vinyl group was attached, and (b) the $\rho_{H_3}$ value at the pseudo atom $H_3$. The best fit was for $h_{ax}$ values of $-0.25$ and $-0.30$ corresponding to values of $Q_{CH_3}^H = 22.6 \pm 1.6$ G and $Q_{CH_3}^H = 180.2 \pm 13$ G for methods (a) and (b) respectively.

The methyl proton coupling constants predicted from the spin densities calculated in these three models and using McConnell's relation with the appropriate $Q_{CH_3}^H$ values are shown in Table 5.h.

McLachlan and Omega calculations were also performed using the above hyperconjugative model and assuming a $\lambda$ value of $1.14$ and an $\omega$ value of $1.14$. The $a_{CH_3}$ values were calculated in both cases from the spin densities at the $H_3$ pseudo atom and the above value of $Q_{CH_3}^H$.

Finally, Levy's formula for methyl proton splittings (see Section 5.1) was used in conjunction with the molecular orbital coefficients determined from the hyperconjugative model. The predicted $a_{CH_3}$ values for all the latter three methods are given in Table 5.h.

A comparison of the predicted and observed $a_{CH_3}$ values, indicates that many of the discrepancies noted for the aromatic protons are also present for the methyl protons. Thus in all models, the $\alpha$ methyl splittings are predicted much more closely than the $\beta$ ones. Of the three simple Hückel methods, the hyperconjugative model gives the best agreement and it is interesting to note that the two possible methods of calculation of $a_{CH_3}$ values in this model give similar results.
The poor agreement of the heteroatom model is reflected in the large standard deviation in the $Q^H_{CH_3}$ value.

As has been observed for the aromatic proton coupling constants, the McLachlan method tends to increase the $\alpha$ splittings and decrease the $\beta$ splittings. Use of the Omega technique gives even worse results.

Finally, it can be seen that Levy's formula probably gives best agreement of all the models, with the observed $Q^H_{CH_3}$ values. This point has been noted by Valenzuela and Bard, who used Levy's formula to calculate similar values for the DNB anions as part of a study of some methyl-substituted anthracene radical anions.

(b) Polycyclicnaphthalene Radical Anions

Simple Hückel theory and the McLachlan and Omega modifications to it are restricted to planar $\pi$ electron systems (or pseudo $\pi$ such as the hyperconjugative model for the methyl group). Hence these methods cannot be used to calculate spin densities on the aliphatic substituents in the radical ions of the peri-alkynaphthalenes considered in this project. However, an attempt has been made to simulate the inductive effect of these substituents on the naphthalene system by using the inductive model previously used for the DNB's and changing the coulomb integrals of the aromatic C atoms to which these substituents are attached. The predicted changes in the aromatic proton coupling constants (relative to unsubstituted naphthalene) were
Figure 5.2 Plot of predicted Aromatic Proton Coupling Constants versus the Inductive parameter.
then compared with those observed from spectra of the anions of these species.

In detail, the two systems

were considered and the coulomb integral parameter, \( h_0 \), for the 1,8- and 1,4,5,8- positions was varied from 0.0 to -0.50 at 0.10 intervals. The aromatic proton coupling constants predicted from these spin densities for the A1, A2, A3, and A4 positions using McConnell's relation and a \( q_{CH}^H \) value of 27.2 G are plotted in Figure 5.2 along with the corresponding values of \( h_0 \). The values for the observed coupling constants for these positions in the perialkynaphthalene anions are given in Table 5.5 in order of increasing size of the aliphatic substituents.

Considering the observed values it can be seen that alkyl substitution causes a decrease in the \( \alpha \) splitting and gives two values for the \( \beta \) splitting, one less and one greater than the value in the
unsubstituted naphthalene anion. From Figure 5.2 it can be seen that the inductive model also predicts a similar effect and indeed the assignments made in Section 3.1 and 3.3 of the observed aromatic coupling constants for PN and P to the A1, A2, and A3 positions were made from these NO predictions. However, the observed values for the di-substituted compounds do not show any obvious trends and thus they cannot be related to the systematic changes predicted with the inductive model by changing the n value. The tetra-substituted compounds do show an approximate increase in the A1 splitting as the size of the substituent increases and this could possibly be reconciled with a decreasing inductive effect of the substituent.

### Table 5.5

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<th>Acenaphthene*</th>
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<th>P</th>
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</table>

* Ref 29  † Ref 31  †† Ref 10
5.3 Results from Semi-Empirical Self Consistent Field MO Theory

5.3.1 Introduction

As discussed in the previous section, simple Hückel theory and its extensions cannot be used to calculate spin densities in the aliphatic substituents of the peri-alkynaphthalene anions studied in this project. Thus it was necessary to use an MO theory which took into account both the $\sigma$ and $\pi$ type valence electrons as well as the geometry of these molecules. To this end a Self Consistent Field (SCF) modification to Hoffmann's Extended Hückel (EH) method was developed and used for calculations on these radical ions.

The basic equation to be solved in MO theory is that given by eqn. 5.2.4 in Section 5.2 and this may be rewritten in matrix notation as

$$ H = E S C $$

(5.3.1)

In simple Hückel theory this eqn. is solved by assuming that $S_{ij} = \delta_{ij}$ (Kronecker delta function) and considering only the $\pi$ system. In EH theory, all valence orbitals are considered and the $S_{ij}$ elements are calculated from Slater orbitals. A separate program, OVERLAP, was written to calculate these elements $S_{ij}$ of the overlap matrix $S$ and details of the calculation method used are given in Appendix IV.

The Hamiltonian matrix elements in eqn. 5.3.1 were calculated in terms of a one electron Hamiltonian operator by a simple extension
of the method used in simple Hückel theory. The diagonal elements, $H_{ii}$, were considered to be a measure of the energies of the valence electrons in AO $i$ and therefore were approximated by the negative of the valence state ionisation potential (VSIP) of the orbital. The values of these VSIP quantities may be determined experimentally and were found to be dependent upon the net charge on the atom, $q_k$, and the number of electrons in the AO $i$ centred on atom $k$, $d_{ik}$, as follows:

$$H_{ii} = A d_{ik} + B q_k + C$$

where $A$, $B$, and $C$ were constants obtained from emission spectral tables.

For the particular calculations performed in this project, $H_{kk} = 1$ and $h$ for hydrogen and carbon respectively, and $A$, $B$, $C$ were given the values $-1.5$, $11.9$ and $12.9$ ev. for the $2p_x$, $2p_y$ and $2p_z$ AOs of carbon and $-1.7$, $11.9$, and $23.9$ ev. for the $2s$ AO of carbon. The $H_{ii}$ elements for the hydrogen atoms were taken to be

$$H_{ii} = -13.6 q_i^2$$

This relation may be derived from the solution of the Schrödinger equation for the hydrogen atom and had been previously used for similar calculations.

The off diagonal elements, $H_{ij}$, were calculated according to the formula:

$$H_{ij} = 0.5 k (H_{ij} + H_{ji}) s_{ij}$$
where \( k \) is some constant normally taken to be 1.75. It is the fact that the values of \( H_{ii} \) and \( H_{ij} \) elements are calculated from experimental VSIPs that gives rise to this type of MO calculation being known as Semi-Empirical.

The eqn. 5.3.1 was easily solved in simple Hückel theory because of the approximation that \( S_{ij} = 6_{ij} \) and hence reducing down to the standard eigenvalue-eigenfunction problem of Hückel. However, as mentioned above, this approximation is no longer valid in the EH method and thus eqn. 5.3.1 must be solved making full allowance for the overlap matrix. The most convenient way of doing this is outlined in Appendix V.

To reduce the computer time involved in the diagonalisation step (for an average 60 x 60 symmetric matrix this is of the order of 6.8 mins, using the Jacobi method), a symmetry matrix was constructed for each molecule from its point group symmetry and this was used to transform the \( H \) and \( S \) matrices into two or more smaller blocks of square matrices and in doing so, drastically reducing the computational time required for diagonalisation. Details of this procedure are given in Appendix VI.

Having obtained the energies, \( E_i \), and the coefficients of the \( \zeta \)s, \( C_{ij} \), in the \( \psi \)s, \( \psi_j \), a Mulliken population analysis was undertaken as follows:
(1) The net atomic population (NAP) in AO $\phi_s$ is defined as

$$\text{NAP}_s = \frac{n}{i=1} n_i C_i s$$

where there are $n$ MOs and $n_i$ is the number of electrons in MO $\phi_i$.

(2) The overlap population (OP) between the AOs $r$ and $s$ is

$$\text{OP}_{rs} = \frac{n}{i=1} n_i C_i r C_i s$$

(3) The net overlap population (NOP) in AO $\phi_s$ is

$$\text{NOP}_s = \frac{n}{i=1} \text{OP}_{rs}$$

(4) The gross atomic population (GAP) for AO $\phi_s$ is

$$\text{GAP}_s = \text{NAP}_s + \text{NOP}_s$$

Obviously this quantity can never exceed the value of 2. The GAP value for an AO i of atom k is the same as the quantity, $d_{ik}$, defined above for the calculation of the $N_{ii}$ elements.

(5) The net charge ($q$) on the k-th atom is defined as

$$q_k = n_k - \frac{1}{t} \sum_{s=1} GAP_s$$

where $n_k$ is the number of valence electrons on atom k. The summation is taken over all t AOs centered on atom k.

The above theory involving one cycle of calculation and with the exception of the symmetry transformation is the basis of the Extended Huckel method as first proposed by Hoffmann. This method may be
extended itself to further cycles by comparing the net charge on each atom with the initial value used to evaluate the \( H_{ij} \) matrix elements. If they are not the same (within a present tolerance), then new \( H \) matrix elements are calculated from the new charges and the cycle repeated until a self consistent set of wavefunctions is obtained that predicts the same net charges as those used in the calculation of them. This is known as the Self Consistent Field (SCF) method and it has been used extensively in the literature for the calculation of many different electronic properties and is the basis of the calculations described in this section.

The criterion for self consistency used in this project was actually based on the GAP values rather than the charges, \( q_k \), as follows:

\[
\text{if } \left( \sum_{i=1}^{n} (\text{GAP}_{i(\text{OUT})} - \text{GAP}_{i(\text{IN})})^2 \right)^{1/2} \ll 0.003n \text{ where } n
\]

is the total number of orbitals, then self consistency was considered to have occurred. If it was greater than the test value, then the GAP values for the next cycle (and hence charges for calculation of the new \( H_{ij} \) elements) were calculated from the previous ones using the expression:

\[
\text{GAP}_{i(\text{NEW})} = \text{GAP}_{i(\text{IN})} - \lambda (\text{GAP}_{i(\text{IN})} - \text{GAP}_{i(\text{OUT})})
\]

where \( \lambda \) is a damping factor chosen to optimize the rate of converg-
ence of the calculation to self consistency. Values for $\lambda$ of 0.1 were used for the first few cycles and this was gradually increased to 0.25. Use of $\lambda$ values greater than 0.25 at any stage led to divergence of the calculation.

A computer program SCFMO was written to perform these Semi-Empirical SCF MO calculations and a listing of this is given in a separate volume.

So far in this discussion, the spins of the valence electrons have been neglected but it can be shown that electrons must obey Fermi-Dirac statistics and hence the wavefunctions for several electrons must be antisymmetric on interchanging any two of them. Thus the complete wavefunction is more correctly written as the product of a space part and a spin part:

$$\psi = \left| a_1 a_2 \ldots \ldots a_n \right| m_{s_1} m_{s_2} \ldots m_{s_n}$$

where the $\left| \ldots \right|$ term refers to the Slater determinant which provides the antisymmetric requirement. This has important consequences in MO theory and leads to the concept of open and closed shell structures as follows: if the electronic configuration being considered has each MO completely filled then it is said to be a closed shell structure. The converse is true for open shell structures. Most molecules have a closed shell structure although notable exceptions are the oxygen molecule and free radicals.
Roothaan has developed an NO method for closed shell structures by using Hartree Fock Self Consistent Field methods and allowing the NOs to consist of linear combinations of AO's. He derived the equation

$$ F C = \mathcal{E} SC $$

where \( \mathcal{E}, S, \) and \( C \) are the same matrices as defined in EH theory, and \( F \) is the Hartree Fock operator consisting of two parts

$$ F = H + C $$

where \( H \) is the one electron Hamiltonian and \( C \) is the two electron operator containing Coulomb and exchange terms (see ref. 97 for a discussion and derivation of these terms).

Peake and Heilbronn extended Roothaan's method to open shell structures by assuming that the electrons with \( \alpha \) spin may be treated separately from those with \( \beta \) spin. They showed that an equation similar to that given above for the closed shell structures, may be derived for each of these cases. This method was incorporated into the program SCFMO.

The spin densities are calculated according to whether the calculation is for open or closed shell structures as follows:

(a) Closed Shell: The radicals considered in this project have open shell structures in the strict sense, but initially the Semi-Empirical SCF method described in the first part of this section was used and
this does not distinguish between $\alpha$ and $\beta$ spins. Although these calculations are not strictly closed shell in the sense that Roothaan has defined the term, they will be referred to by this name. Spin densities were calculated for these calculations as follows:

The $m$-th MO $\psi_m$ is in general, a linear combination of AOs

$$\psi_m = \sum_{K} c_{km} \phi_K$$

and hence the unpaired spin density on the $i$-th orbital of the $m$-th MO is given by

$$\rho_i = c_{im} \int \phi_i^* \psi_m \, d\tau = c_{im} \sum_{K} c_{km} \phi_K \, d\tau = c_{im} \sum_{K} c_{km} \int \phi_i^* \phi_K \, d\tau = c_{im} \sum_{K} c_{km} S_{iK}$$

where $S_{iK}$ is the overlap integral for AOs $i$ and $K$. If the Hückel approximation that $S_{iK} = \delta_{iK}$ then the above expression simplifies down to

$$\rho_i = c_{im} c_{im}$$

$$= c_{im}^2$$
which is the expression used in simple Hückel MO theory to calculate spin densities.

In practice the MOs were arranged in increasing order of energy and electrons fed into these orbitals two at a time until the last orbital, \( \psi_m \), contained only one electron; it is the coefficients \( C_{lm} \) of the MOs in this MO which were used in the expression above to calculate spin densities.

(b) Open Shell:

In this type of calculation it was necessary to define charge density-bond order matrices \( P^\alpha \) and \( P^\beta \) for the \( \alpha \) and \( \beta \) electrons as follows

\[
P_{tu}^\alpha = \sum_{m}^N C_{tm}^\alpha C_{um}^\alpha
\]

\[
P_{tu}^\beta = \sum_{m}^M C_{tm}^\beta C_{um}^\beta
\]

where there are \( M \) \( \beta \) electrons and \( N \) \( \alpha \) electrons. The electron density in an orbital \( t \) is then defined as

\[
\rho_t = \sum_{u=1}^N \frac{1}{2} P_{tu}^\alpha - \sum_{u'=1}^M \frac{1}{2} P_{tu}^\beta
\]

This is the difference between the \( \alpha \) and \( \beta \) electron densities which is precisely the definition given for this quantity in the introduction to this chapter.
5.3.2 Results

Closed shell calculations were made for naphthalene and all the peri-alkynaphthalene anions studied in this project. Open shell calculations were then performed for both the chair and boat forms of the DP and HP anions. Some approximations were necessary in this later work because many of the exchange and coulomb integrals required for complete open shell calculations on these compounds could not be evaluated. This, combined with the fact that the bulk of the spin density was expected to reside on the naphthalene ring, led to the inclusion of coulomb repulsion elements between the naphthalene $2p_z$ orbitals only. The numerical values for these matrix elements were taken from the estimates made by Pariser and Parr.39

The $S$ matrix elements were calculated using the program OVERLAP, and assuming the standard bond lengths and angles given at the end of Section 2.3 for the classical structures given in Figures 1.3 and 1.4. Slater exponents of 1.625 and 1.0 were used for the H and C atoms respectively. The $H$ matrix elements were calculated using the values given above for the parameters $A$, $B$, and $C$ for Carbon and Hydrogen and assuming an initial configuration in which the unpaired electron was shared equally between the Carbon $2p_z$ orbitals on the naphthalene ring.

Results of the closed shell calculations for the naphthalene,
perinsaphthene, and pleiadene anions are given in Table 5.6; and of
both the open and closed shell calculations for the boat and chair forms
of the dipleiadene and hexahydropryrene anions, are given in Table 5.7.
Listed are the spin densities in the H atoms at the various positions
and the total spin densities in the C atoms to which they are attached.

A number of important points may be noted by comparison of these
calculated spin densities with the observed coupling constants. In
both types of calculation there is effectively no spin density on the
protons attached to the naphthalene ring (e.g. 0.0000006 for the
protons in the boat form of the HP anion). This point has been noted
by People et al.\textsuperscript{100}. Thus it is necessary to invoke a spin polariza-
tion mechanism as was done in the simple Hückel calculations for the
dimethylnaphthalenes (Section 5.2) in order to account for the observed
spin densities at these aromatic proton positions. Evidence for this
type of mechanism is provided by the good qualitative agreement between
the spin densities in the $2p$ orbitals of the aromatic C atoms to which
the aromatic protons are attached and the proton coupling constants
at these positions.

In general, non-zero spin densities are predicted for the all-
phatic protons but multiplication of these by the hyperfine coupling
constant for a single hydrogen atom ($509 \text{ G}$) was done by Colpa and
de Boer\textsuperscript{29} for similar types of calculations on pyracene and aceanaph-
## Table 5.6

Calculated Spin Densities for Closed Shell Configurations of Naphthalene, Perinaphthalene, and Pheianthane Radical Anions

(a) Naphthalene:

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Observed Proton Coupling Constant (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 1, 5, 8</td>
<td>0.0</td>
<td>0.18561</td>
<td>4.93</td>
</tr>
<tr>
<td>2, 3, 7, 6</td>
<td>0.0</td>
<td>0.064140</td>
<td>1.86</td>
</tr>
</tbody>
</table>

(b) Perinaphthalene:

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Observed Proton Coupling Constant (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, 7</td>
<td>0.0</td>
<td>0.22721</td>
<td>4.54</td>
</tr>
<tr>
<td>5, 8</td>
<td>0.0</td>
<td>0.08760</td>
<td>1.92</td>
</tr>
<tr>
<td>4, 9</td>
<td>0.0</td>
<td>0.07433</td>
<td>1.58</td>
</tr>
<tr>
<td>$\beta_{ax}$</td>
<td>0.0056</td>
<td>0.00237</td>
<td>0.68</td>
</tr>
<tr>
<td>$\beta_{eq}$</td>
<td>0.0011</td>
<td>0.00237</td>
<td>2.30</td>
</tr>
<tr>
<td>$\gamma_{ax}$</td>
<td>0.0</td>
<td>0.00635</td>
<td>0.50</td>
</tr>
<tr>
<td>$\gamma_{eq}$</td>
<td>0.0</td>
<td>0.00635</td>
<td>0.36</td>
</tr>
<tr>
<td>1a, 3a</td>
<td>0.0</td>
<td>0.23271</td>
<td>-</td>
</tr>
</tbody>
</table>

(c) Pheianthane:

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Observed Proton Coupling Constant (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7, 8</td>
<td>0.0</td>
<td>0.22163</td>
<td>4.64</td>
</tr>
<tr>
<td>6, 9</td>
<td>0.0</td>
<td>0.02489</td>
<td>1.80</td>
</tr>
<tr>
<td>5, 10</td>
<td>0.0</td>
<td>0.06103</td>
<td>1.22</td>
</tr>
<tr>
<td>$\beta_{ax}$</td>
<td>0.00331</td>
<td>0.01007</td>
<td>6.79</td>
</tr>
<tr>
<td>$\beta_{eq}$</td>
<td>0.00008</td>
<td>0.01007</td>
<td>1.22</td>
</tr>
<tr>
<td>$\gamma_{ax}$</td>
<td>0.0</td>
<td>0.00913</td>
<td>0.22</td>
</tr>
<tr>
<td>$\gamma_{eq}$</td>
<td>0.0</td>
<td>0.00913</td>
<td>0.22</td>
</tr>
<tr>
<td>1a, 1a</td>
<td>-</td>
<td>0.23323</td>
<td>-</td>
</tr>
</tbody>
</table>
**TABLE 5.7**

Calculated Spin Densities for Open and Closed Shell Configurations of Hexahydropyrrole and Diplediane Anions

(a) Hexahydropyrrole

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Open</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Observed Proton Coupling Constants (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.08765</td>
<td>0.0</td>
<td>-0.1851</td>
<td>1.69</td>
</tr>
<tr>
<td>$\beta_{ex}$</td>
<td>0.00303</td>
<td>0.00303</td>
<td>0.00187</td>
<td>0.00187</td>
<td>-0.00282</td>
<td>7.96</td>
</tr>
<tr>
<td>$\beta_{eq}$</td>
<td>0.0077</td>
<td>0.00681</td>
<td>0.00187</td>
<td>0.00187</td>
<td>-0.00282</td>
<td>2.92</td>
</tr>
<tr>
<td>$\gamma_{ex}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00629</td>
<td>0.00629</td>
<td>-0.00282</td>
<td>0.50</td>
</tr>
<tr>
<td>$\gamma_{eq}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00629</td>
<td>0.00629</td>
<td>-0.00282</td>
<td>0.35</td>
</tr>
<tr>
<td>1a,3a</td>
<td>-</td>
<td>-</td>
<td>0.2318</td>
<td>0.2318</td>
<td>-0.7090</td>
<td>-</td>
</tr>
</tbody>
</table>

(b) Diplediane

<table>
<thead>
<tr>
<th>Position</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Open</th>
<th>$\rho_H$</th>
<th>$\rho_C$</th>
<th>Observed Proton Coupling Constants (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.05535</td>
<td>0.05535</td>
<td>-0.1912</td>
<td>1.57</td>
</tr>
<tr>
<td>$\beta_{ex}$</td>
<td>0.00156</td>
<td>0.00156</td>
<td>0.00156</td>
<td>0.00156</td>
<td>-0.00150</td>
<td>6.16, 6.19</td>
</tr>
<tr>
<td>$\beta_{eq}$</td>
<td>0.00001</td>
<td>0.00001</td>
<td>0.00001</td>
<td>0.00001</td>
<td>-0.00160</td>
<td>1.15, 1.35</td>
</tr>
<tr>
<td>$\gamma_{ex}$</td>
<td>0.0078</td>
<td>0.0078</td>
<td>0.00238</td>
<td>0.00238</td>
<td>0.00264</td>
<td>0.22</td>
</tr>
<tr>
<td>$\gamma_{eq}$</td>
<td>0.00001</td>
<td>0.00001</td>
<td>0.00238</td>
<td>0.00238</td>
<td>0.00264</td>
<td>0.22</td>
</tr>
<tr>
<td>1a,4a</td>
<td>-</td>
<td>-</td>
<td>0.17714</td>
<td>0.17714</td>
<td>0.67837</td>
<td>0.67387</td>
</tr>
</tbody>
</table>
there and by other workers\textsuperscript{100} gives values which are very much less than the observed coupling constants. This would suggest that the calculation does not allow (at least not to any extent) hyperconjugation and spin polarisation mechanisms for transferring the spin density into the aliphatic side chains. These two mechanisms would undoubtedly occur in practice and from the values of the spin densities at the aromatic C atoms to which the aliphatic substituents are attached (these values are given in the columns labelled $\rho_c$ in Tables 5.6 and 5.7), it can be seen that allowance for these two factors would account for the large coupling constants observed in spite of the low spin densities calculated. It is difficult to see from the theory of the SCF MO methods used here just how much allowance is made for spin polarisation and hyperconjugation. It is possible that the neglect of the exchange and coulomb integrals for the aliphatic substituents in the open shell calculations may be responsible for the low spin densities in these positions. Obviously the inclusion of these elements for the naphthalene ring has caused a marked redistribution in the spin densities in the open shell case compared with the closed shell one.

In general, the trends of the spin densities at the aliphatic protons are the same as those of their coupling constants although it should be noted that the $\gamma_{ax}$ and $\gamma_{eq}$ spin densities in the open shell calculation for both forms of the HP anion are in the reverse
order to the assignments given to the experimental coupling constants at these positions. Again this may be a real effect or by allowing
for spin polarisation and hyperconjugation, the calculated order may
be reversed. It is interesting to note that the spin densities at
the $\beta_{\text{ax}}$ and $\beta_{\text{eq}}$ positions in both forms of the HP anion have
the same sign which is what had been predicted from the linewidth
alternation effects observed in the spectra of these species.

Finally, it should be noted that neither the open nor closed
shell calculations on the HP and DP anions show that there is any
significant difference in spin densities between the boat and chair
forms. In view of these calculations being made in terms of standard
bond lengths and angles for the classical structures of these two
compounds, and since two species were resolved in the spectra of the
DP anion but not in that of the HP anion, then it may be concluded
that the actual structures of both forms of the HP molecule are very
similar to the classical structures, whereas for DP they are dist-
orted each in a different way so as to make their coupling constants
slightly different.
FIGURE 6.1
Hyperfine Coupling Constants for some Peri- Alkynaphthalene Anions in DME (Gauss).

1,3-DIMETHYL-ACENAPHTHENE

PERINAPHTHANE

PLEIADANE

1,4,5,8 TETRAMETHYL- PYRACENE

HEXAHYDROPYRENE

DIPLEIADANE
CHAPTER SIX

SUMMARY OF RESULTS AND CONCLUSION

As discussed in the introduction in Section 1.4, it was planned in this project to use ESR techniques to study the radical ions of two series of alkyl-substituted naphthalene compounds. The results for the radical anions of the first series are summarized in Figure 6.1 together with results for the related compounds,acenaphthene, pyrene, and 1,1,5,8-tetramethylnaphthalene.

These nine compounds form a very interesting series in which the effects of increasing size of the aliphatic substituents can be readily seen. For the mono-perialkyl compounds, the effect on the naphthalene aromatic proton coupling constants is to split the two constants observed for the unsubstituted naphthalene anion into three. The relative magnitude of these can be predicted by increasing the inductive effect of the alkyl substituents in simple Huckel calculations on the 17 electron system of the naphthalene ring. For the di-perialkyl compounds, the single aromatic proton coupling constant is considerably decreased relative to that observed for the same positions in the unsubstituted naphthalene anion.

In all compounds it can be seen that there is considerable transfer of unpaired spin density into the aliphatic side chains as shown
by the large values observed for the aliphatic proton coupling constants. The magnitude of these was found to be dependent upon (1) the orientation of the protons relative to the aromatic ring, which suggests some sort of hyperconjugative mechanism, and (2) the distance out along the chain: the further out the smaller the coupling constant. Golding and Bailey have predicted theoretically this decrease in spin density in moving out along such aliphatic chains in terms of a spin polarization effect, and thus it is reasonable to suggest that this effect is also present in these compounds.

The SCFMO calculations made on these compounds supported this view that it is necessary to invoke hyperconjugation and spin polarization to account for the transfer of spin density from the naphthalene ring out into the aliphatic substituents.

As far as the geometry of these compounds is concerned, it can be seen from the number and magnitude of the aliphatic coupling constants that when the aliphatic rings are six or seven C atoms in size, then the molecules are no longer planar and in the case of the diperalkyl compounds these exist at low temperatures in chair and boat forms in the approximate ratio of 1:1. As the temperature was raised then these aliphatic substituents began to move backwards and forwards across the plane of the aromatic ring. From the theoretical simulation of the alternating linewidth effects arising from this motion,
activation energies for this chair-boat interconversion were calculated
to be 6.37 and 7.88 Kcal/mole for the hexahydropryrene and dipladiadane
anions respectively.

From a study of the literature, these values would appear to be
the first experimental estimates that have been made for this type
of interconversion in these compounds. When de Boer and Praat\textsuperscript{36} first
reported the spectrum of the HP anion they mentioned that a detailed
kinetic study was in progress at the time, but to the best of the au-
thor's knowledge, no subsequent reports have appeared on this topic.
Both values compare favourably with the value of 10.1 Kcal/mole which
has been determined by NMR methods for the boat-chair interconversion
in cyclohexane\textsuperscript{102}. The decrease on this value observed for the HP
anion in this project may be explained by the presence of the naphth-
alene ring separating the two aliphatic substituents and thus elimi-
inating any interactions that are present between the two ends of the
cyclohexane molecule.

Further information regarding the geometry of the $\beta$ protons
in the PM, P, HP and DP molecules may be obtained by using the expression
derived by McConnell and Chestnut\textsuperscript{10h} for the magnitude of the
proton coupling constant in a fragment of the form

\[
\begin{array}{c}
\text{C}_x \\
\text{CH}_2 \\
\beta \\
\text{CH}_2 \ldots \quad \ldots
\end{array}
\]
Here $C_{C\alpha}$ is part of a $\pi$ electron system; $C_{\beta}, C_{\gamma} \ldots$ are carbon atoms belonging to an aliphatic substituent directly bonded to the electron system. Heller and McConnell proposed the relation

$$a_{\beta}^H = (B_0 + B_1 \cos^2 \theta) f_{\pi}$$

where $a_{\beta}^H$ are the hyperfine coupling constants for the $\beta$ protons.

$B_0$ and $B_1$ are constants.

$\theta$ is the angle between the axis of the $p_\beta$ orbital of the aromatic C atom and the $C_{\beta} – H$ bond.

$f_{\pi}$ is the spin density of the aromatic C atom.

Using the two values observed for the $\beta_{eq}$ and $\beta_{eq}$ proton coupling constants for the DP, and HP anions, and defining the two angles $\theta_{eq}$ and $\theta_{eq}$ as below:

![Diagram of DP and HP](image)

the above equation may be used to calculate values for $\theta_{eq}$ and $\theta_{eq}$.
and these are given in Table 6.1. Calculations for PN and P gave similar values. From this table, it can be seen that the calculated values compare well with those observed for the classical structures of these four compounds (figures 1.3 and 1.4). Hence it is concluded that the geometry of all four compounds in solution differs little from that of their classical structures.

| Table 6.1 |
|---|---|---|---|
| Calculated and Observed Values for $\theta_{\text{ax}}$ and $\theta_{\text{eq}}$ for the Protons in the DP and HP anions |  |
|  | Obs. $\theta_{\text{ax}}$ | Calc. $\theta_{\text{ax}}$ | Obs. $\theta_{\text{eq}}$ | Calc. $\theta_{\text{eq}}$ |
| Diploeiadane | $45^\circ$ | $45^\circ$ | $72^\circ$ | $78^\circ$ |
| Hexahydropropylene | $0^\circ$ | $2^\circ$ | $12^\circ$ | $16^\circ$ |

The larger discrepancy between calculated and observed values for the DP anion compared with HP may indicate that there is more distortion, although it may be small, in the DP molecule than in HP. This would be confirmation of the suggestion that the reason for two species being resolved for the DP anion at $-95^\circ$C whereas they are identical for HP, is because the distortion from the classical structure for the boat form of DP is different from the corresponding distortion for the chair form, while in HP this distortion is not large enough to distinguish the two forms (or alternatively both forms are distorted the same way for HP but not for DP). Further evidence for this distortion comes from the SCF MO calculations on the DP anion which showed that the $\beta_{\text{ax}}$ proton coupling constants were almost indistinguishable if the classical structures were used. This distortion for DP would arise from the
necessity to relieve the large repulsive interactions of the \( \beta_{ax} \) protons which in the classical structures of both the chair and boat forms are at a distance of 0.8 A apart.

The increase in activation energy of 1.5 kcal/mole for interconversion in going from HP to DP, confirms initial predictions made from stick models for the two compounds that DP should be more strained than HP.

The observation of only one \( \gamma \) coupling constant in the DP and P anion spectra whereas two were resolved for the HP and PN anions, may be due to the difference between the two \( \gamma \) coupling constants in DP and P being too small to allow them to be separately observed, or there may be some motion of the \( \text{C}_2-C_3 \) bond even at -95\(^\circ\)C which causes broadening of the \( \gamma \) resonances and makes them indistinguishable.

In certain solvents and with certain metals as counterions, ion pairing effects were observed. Many of these spectra could be analysed in terms of two species which, as discussed at length in Section 3.6, arise from the non planarity of the aliphatic substituents. Where alkali metal hyperfine coupling was resolvable then the magnitude
of the metal coupling constant was comparable to that observed in the unsubstituted naphthalene anion systems. The complexity of these spectra made it difficult to decide upon a definite structure for the ion pairs but MO calculations based upon an electrostatic model for the cation-anion interaction indicated that the cations would probably lie over the aliphatic substituents rather than the naphthalene ring. This latter position had recently been postulated for the HP/K/THF system by Iwaizumi and Bolton.

Although the spectra of the DP and HP cation radicals were not analysed completely they did show second order effects due to the large values of the $\beta_{\text{ax}}$ coupling constants of 12.22 and 11.70 G respectively. It did not appear that the $\gamma$ protons in the HP cation could be resolved into two values as had been done for the HP anion. The spectra of the DP cation at low temperatures also indicated the presence of two species and this was confirmed by the observation of an alternating linewidth effect in the high temperature spectra of this species.

The second series of compounds that it was planned to study in this project were the dimethylnaphthalene radical ions. Attempts to prepare the cation species using a variety of methods were unsuccessful probably due to the presence of the two methyl groups making the naphthalene ring more susceptible to sulphonation and formation of covalent complexes with Lewis acids. The unsymmetric 1,2-, 1,3-, and 1,6- DMW anions were
<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th>Present Study</th>
<th>Gerson</th>
<th>deWaard</th>
<th>Bolton</th>
<th>Siew</th>
<th>Cassion</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>1 2</td>
<td>1.93 1.88</td>
<td>1.95 1.83</td>
<td>1.94 1.87</td>
<td>1.95 1.83</td>
<td>1.94 1.83</td>
<td>1.94 1.83</td>
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</tr>
<tr>
<td>1,4-</td>
<td>1 5</td>
<td>3.38 5.59</td>
<td>3.25 5.17</td>
<td>3.03 5.05</td>
<td>3.32 5.05</td>
<td>3.31 5.05</td>
<td>3.31 5.05</td>
<td>3.31 5.05</td>
</tr>
<tr>
<td>1,5-</td>
<td>1 5</td>
<td>4.375 5.64</td>
<td>4.37 5.50</td>
<td>4.37 5.50</td>
<td>4.37 5.50</td>
<td>4.37 5.50</td>
<td>4.37 5.50</td>
<td>4.37 5.50</td>
</tr>
<tr>
<td>1,8-</td>
<td>1 5</td>
<td>4.535 5.02</td>
<td>4.55 5.05</td>
<td>4.55 5.05</td>
<td>4.55 5.05</td>
<td>4.55 5.05</td>
<td>4.55 5.05</td>
<td>4.55 5.05</td>
</tr>
<tr>
<td>2,3-</td>
<td>1 5</td>
<td>5.729 5.02</td>
<td>5.67 5.05</td>
<td>5.72 5.05</td>
<td>5.72 5.05</td>
<td>5.72 5.05</td>
<td>5.72 5.05</td>
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</tr>
<tr>
<td>2,6-</td>
<td>1 5</td>
<td>6.67 6.02</td>
<td>6.55 5.75</td>
<td>6.60 5.88</td>
<td>6.65 5.82</td>
<td>6.65 5.82</td>
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</tr>
<tr>
<td>2,7-</td>
<td>1 5</td>
<td>5.365 5.21</td>
<td>5.32 5.12</td>
<td>5.26 5.09</td>
<td>5.21 5.17</td>
<td>5.21 5.17</td>
<td>5.21 5.17</td>
<td>5.21 5.17</td>
</tr>
<tr>
<td></td>
<td>2 5</td>
<td>2.195 2.16</td>
<td>2.18 2.18</td>
<td>2.18 2.18</td>
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<td>2.18 2.18</td>
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<tr>
<td></td>
<td>3 5</td>
<td>1.765 1.76</td>
<td>1.81 1.81</td>
<td>1.81 1.81</td>
<td>1.81 1.81</td>
<td>1.81 1.81</td>
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</tr>
</tbody>
</table>
successfully prepared but they gave very complex spectra that could not be analysed directly or by using simple Hückel MO predictions.

The results for the symmetric DMN anions are given in Table 6.1 along with the results obtained previously by Gerson et al., de Waard, Bolton, Slow and Campion. A comparison of the results obtained in this project with these others, indicates good agreement particularly with those obtained by Campion who used similar least squares refinement procedures to that used in this project. Differences between the results are probably due to the use by the other groups of different solvents and cations to prepare the anions whereas a standard system viz. DMN/Na/DME at RT was used for the preparation of all the DMN anions in this project.

The predicted values for the coupling constants of these species were calculated using results obtained by Fraenkel et al. for the 1- and 2- methylnaphthalene anions and an Additivity relationship as follows: "Substitution of groups at positions i and j produces a change in the splitting at position k which is equal to the sum of the effects observed at k in radical ions which are substituted only at i or j". This relationship is expected to hold only when the substituent effects are small and the groups do not interact. Fraenkel et al. showed
this situation holds for the methyl naphthalenes.

In practice the hyperfine splittings for the 1-methylnaphthalene anion are considered and the changes in the proton splittings at the 2, 3, 4, 5, 6, 7, and 8 positions relative to the unsubstituted naphthalene anion are calculated and labelled b, c, d, e, f, g, and h respectively.

In a similar way, the changes at the 1, 3, 4, 5, 6, 7, and 8 positions in the 2-methylnaphthalene anion are calculated and labelled a', c', d', e', f', g', and h' respectively. The actual values for these quantities are given in Table 6.2 using Fraenkel's results for the two anions.

\[
\begin{array}{l|l|l}
\text{Position} & \text{Value} & \text{Position} \\
\hline
a & 0 & a' & -0.35 \\
b & -0.14 & b' & - \\
c & 0.03 & c' & 0.05 \\
d & -0.50 & d' & 0.12 \\
e & 0.07 & e' & 0.12 \\
f & -0.32 & f' & -0.51 \\
g & 0.04 & g' & 0.43 \\
h & 0.10 & h' & -0.16 \\
\end{array}
\]
The coupling constants for the aromatic protons of the dimethyl-
naphthalene anions may be readily predicted from the same values. For
example, the structure of the 1,8-DMN anion may be regarded as the sum
of two 1-methylnaphthalene anions with the orientation shown below

![Diagram of dimethyl-naphthalene anions]

Hence the aromatic proton coupling constants at the 2,7; 3,6;
and 4,5 positions would be predicted to have values of $\beta + g + h$,
$\beta + c + f$, and $\alpha + d + e$ respectively where $\alpha$ and $\beta$ refer to the
unsubstituted naphthalene anion hyperfine splittings. In this way all
the aromatic proton coupling constants for the symmetric and asymmetric
DMNs may be predicted and these are given in Tables 6.1 and 6.2 respectively. A similar analysis may be made for the methyl proton splittings
for the symmetric DMNs only and these are also given in Table 6.1.
A comparison of the observed and values predicted using this model
indicates good agreement.

Ion pairing effects were observed in the spectra of the symmetric
DMN anions in solvents other than DME, and when Cs⁺ was present as counterion in any of the solvents. These effects have been discussed in detail in Section 4.5 and it remains only to say that these effects correspond closely to those observed previously by other workers for the unsubstituted- and 2,6-di-t-butylnaphthalene systems¹⁸,¹², with the possible exception of the 2,3-DMN anion where the proximity of the methyl groups appears to lead to unusual ion pairing effects. MO calculations based on an electrostatic model for the cation-anion interaction in these ion pairs gave information regarding the most likely position for the cation.

Simple Hückel MO theory has been used for the DMN's to predict the coupling constants from theoretical spin densities using a variety of expressions. The α splittings gave better agreement than the β ones as had been noted by Gerson et. al.²¹ and Fraenkel.¹⁰ There appears to be a difference between the value of the inductive parameter that gave the best fit for the aromatic and methyl proton splittings (βₓ = -0.15 and -0.25 respectively). For the aromatic protons the Colpa-Bolton relation appeared to give better overall agreement than the usual McConnell relation. Values of Qⁿᶜʰ and Qⁿᶜᶜᶜ‴ obtained from these calculations are in agreement with those obtained in a much more detailed analysis made by Fraenkel et. al.¹⁰ The McLachlan and Omega techniques gave no better agreement between the observed and calculated results.
To conclude, the results from this project and summarised in this chapter, show that considerable structural and electronic information may be obtained by using ESR techniques to make a spectroscopic study of the radical ions of alkyl-substituted naphthalene compounds.

From these results it is considered that there are a number of aspects of this work which could well be investigated further. Perhaps foremost of these, is the necessity to obtain spectra of many of these species with a better signal to noise ratio such that the wings of the spectra may be clearly observed. It is the opinion of the author that the spectra described in this project were the best that could be produced from the particular spectrometer used but with the availability of better equipment many of the spectra could be improved. This may well lead to the successful analysis of the unsymmetric DMN anion spectra. The ion pairing effects observed in all these systems could be extended by using other metals as reducing agents and other solvents. In this respect, development of a successful method for Li reduction would be very useful in checking some of the conclusions already reached about the presence of ion pairs in certain systems. Use of a very recently reported method of oxidation of aromatic hydrocarbons to their radical cations with Co$^{2+}$ may well lead to the successful preparation of the DMN radical cations. Finally, theoretical calculations using more sophisticated MO theories such as CNDO and INDO with less approximations could well give more information regarding the mechanism of transfer of spin density from the naphthalene ring into the aliphatic substituents attached to it.
APPENDIX I

Theory of Linewidth Alternation in ESR Spectra

The Linewidth Alternation effect in ESR spectra was first reported by Bolton and Carrington\textsuperscript{105} for the temperature dependence of the spectrum of the durosemiquinone cation. Since then a large number of examples and theoretical interpretations have appeared in the literature. In a review of these, Hudson and Luckhurst\textsuperscript{106} point out that relaxation theory has advantages in that a wide variety of dynamical models may be used but it is restricted to the fast exchange region. For the slow and intermediate regions of exchange such as observed in the spectra described in Chapter Three, it is necessary to use a modified form of the Bloch equations in order to simulate the alternating linewidth effect. Such a theory has been developed by Carrington\textsuperscript{107} and it forms the basis of the calculations described in Section 3.5.

In order to calculate the shape of an electron resonance line it is necessary to calculate the electron magnetisation and one method of doing this is to use the Bloch equations. Thus if a complex moment, \( G \), is defined as
\[ \mathbf{G} = \mathbf{U} + i \mathbf{V} \]

where \( \mathbf{U} \) and \( \mathbf{V} \) are the in-phase and out-of-phase magnetizations of the electron, then the Bloch equation for \( \mathbf{G} \) is

\[ \frac{d\mathbf{G}}{dt} + \eta \mathbf{G} = -i \omega_1 \mathbf{M}_0 \quad (I.1) \]

In this eqn. \( t \) is time, \( \omega_1 = \gamma \mathbf{H}_1 \) where \( \gamma \) is the gyromagnetic ratio, \( \mathbf{H}_1 \) is the intensity of the applied microwave field and \( \mathbf{M}_0 \) in the high field approximation is equal to \( \mathbf{M}_z \) assuming no saturation \( \eta \) is given by

\[ \eta = \frac{1}{T_2} - i (\Delta \omega + \omega_\|) \]

where \( T_2 \) is the transverse relaxation time, \( \Delta \omega = \omega_0 - \omega \) where \( \omega_0 \) is the Larmor precession frequency in the absence of hyperfine interaction and \( \omega_\| \) represents the shift in resonance due to the hyperfine interaction.

Eqn. I-1 may be solved to give

\[ \mathbf{G} = -i \omega_1 \mathbf{M}_0 \frac{1 - \exp (-\eta t)}{\eta} + \mathbf{G}^0 \exp (-\eta t) \]

where \( \mathbf{G} = \mathbf{G}^0 \) at time \( t = t_0 \).

If the molecular environment of the electron changes, the average value of \( \mathbf{G} \) before the change is
\[ G(t) = \int_0^\infty \exp \left( -\frac{t}{\tau} \right) G(t') \, dt' \]

\[ = \frac{i \omega \mu_0}{1 + \eta \tau} + \frac{G^0}{1 + \eta \tau} \quad (I-2) \]

where \( \tau \) is the lifetime of the environment.

To obtain the true average value of \( G \) one must average over all possible values of \( G^0 \) and these will depend on the immediate past history of the system. Hence at this point it is necessary to consider the exact nature of the change of the molecular environment and for the particular examples considered in this project, two cases may be distinguished:

1. Two Jump Model:

This model involves two nuclei or groups of equivalent nuclei, interchanging their hyperfine coupling constants. Thus there exists the equilibrium

\[ A \rightleftharpoons B \]

and an expression of type \( I-2 \) may be written for each of the two forms. The value of \( \langle G_A^0 \rangle \) will depend on the immediate past history and thus is equal to \( \langle G_B^0 \rangle \). Hence assuming

\[ \tau_A = \tau_B = \tau \]

\[ \langle G_A^0 \rangle = \frac{i \omega \mu_0}{1 + \eta A \tau} \times \frac{\langle G_B^0 \rangle}{1 + \eta_A \tau} \]

\[ = \frac{1}{\gamma_A} \left( \langle \bar{G}_B^0 \rangle = i \omega \mu_0 \tau \right) \]

where \( \gamma_A = 1 + \eta_A \tau \)
Similarly \[ \langle \gamma_B \rangle = \frac{1}{\gamma_B} (\langle \gamma_A \rangle = i \omega_1 M_0 \tau) \]

Solving these two expressions gives

\[ \langle \gamma_A \rangle = -i \omega_1 M_0 \tau \quad (\gamma_B = 1) \]

\[ \langle \gamma_B \rangle = -i \omega_1 M_0 \tau \quad (\gamma_A = 1) \]

and

The net magnetisation is

\[ \langle \gamma_{\text{net}} \rangle = \langle \gamma_A \rangle + \langle \gamma_B \rangle \]

\[ = -i \omega_1 M_0 \tau \quad (\gamma_A \gamma_B = 1) \]  

This is comparable to the expression derived by Hudson and Luckarst. The absorption lineshape is obtained by taking the imaginary part of this expression.

(2) **Four-Jump Model:**

This model involves a system in which a nucleus, or group of equivalent nuclei, can exist in four different states and these may interconvert according to the scheme

\[
\begin{array}{c}
A \iff C \\
| \quad \downarrow \quad \uparrow \\
D \iff B
\end{array}
\]
and subject to the restriction that \( A \Rightarrow B \) and \( C \Rightarrow D \). Cis-trans interconversion is a classic example of this model.

As before, four expressions of type I=2 may be written down for each of the four states. Considering the situation for state \( A \), the molecule may arrive at \( A \) from either \( C \) or \( D \) with equal probability and thus

\[
\langle a_{A}^{C} \rangle = \frac{1}{2} \left[ \langle a_{C} \rangle + \langle a_{D} \rangle \right]
\]

and assuming \( \tau_{A} = \tau_{B} = \tau_{C} = \tau_{D} = \tau \)

\[
\langle a_{A} \rangle = \frac{-I \omega_{1} M_{0}}{1 + \eta_{A} \tau} \times \frac{\langle a_{C} \rangle + \langle a_{D} \rangle}{2 (1 + \eta_{A} \tau)}
\]

Similar expressions may be obtained for \( \langle a_{B} \rangle \), \( \langle a_{C} \rangle \), and \( \langle a_{D} \rangle \) and solving all four gives

\[
\langle a_{A} \rangle = -I \omega_{1} M_{0} \times 2 \gamma_{B} \left\{ \tau (2 \gamma_{C} \gamma_{D} + \gamma_{C} + \gamma_{D}) \right\} / (\gamma_{A} \gamma_{B} \gamma_{C} \gamma_{D} (\gamma_{A} + \gamma_{B}) (\gamma_{C} + \gamma_{D}))
\]

where \( \gamma_{A} = 1 + \eta_{A} \tau \)

with corresponding expressions for \( \langle a_{B} \rangle \), \( \langle a_{C} \rangle \) and \( \langle a_{D} \rangle \).

The net magnetization is
\[ \langle \bar{u}_{\text{Net}} \rangle = \langle \bar{u}_A \rangle + \langle \bar{u}_B \rangle + \langle \bar{u}_C \rangle + \langle \bar{u}_D \rangle \]

\[ = -i \omega_1 \mu_0 \tau \left\{ \left( \gamma_A + \gamma_B \right) \left( \gamma_C + \gamma_D + 2 \gamma_C \gamma_D \right) \left( \gamma_C + \gamma_D \right) \right. \]

\[ \left. \left( \gamma_A + \gamma_B + 2 \gamma_A \gamma_B \right) \right\} \]

\[ = \hbar \gamma_A \gamma_B \gamma_C \gamma_D - \left( \gamma_A + \gamma_B \right) \left( \gamma_C + \gamma_D \right) \]

(I-l)

As before, the imaginary part of this expression will give the resonance absorption lineshape for a four jump model.

Rather than undertake the complicated manual analysis made by Carrington\textsuperscript{107} eqns. I-3 and I-4 were incorporated in a computer program LINSHAPE as complex functions and their imaginary part calculated within the program. The details of the hyperfine contributions \( \omega_A, \omega_B, \omega_C, \) and \( \omega_D \) for the specific cases of DP, HP, PN, and P are given in Section 3.5.
APPENDIX II

Calculations of Ion Pairing Effects
in Hydrocarbon Radical Ions

The calculation of these effects has, in the main, been made using an Electrostatic model first proposed by McClelland\textsuperscript{108}. (For a review of other methods see Ref. 73). In this model, the effect of the cation is considered in terms of point charge electrostatic attractive forces operating on the $\pi$ electron system of the radical ion. This is an inductive effect and any resonance and repulsive effects arising from electron sharing between the radical ion and the alkali metal cation are neglected.

In detail, simple Huckel MO theory is used to describe the $\pi$ electron system but the one-electron Hamiltonian (see Section 5.2) is modified by adding a term to allow for the perturbation of the $\pi$ electron system by the cation as follows

$$\hat{H} = \hat{H}^0 - \frac{\epsilon^2}{r}$$

where $\hat{H}^0$ is the Hamiltonian for the free ion and $r$ is the distance between the centre of the cation and the electron. As before, the MOs have the form

$$\psi_i = \sum_{\mu=1}^{2N} C_{i\mu} \phi_{\mu} \quad (i = 1, 2, \ldots, 2N)$$

where $\phi_{\mu}$ are the $2p_z$ AO$s$ of the C atoms of the $\pi$ system. The
coefficients, $c_{i\mu}$, are obtained from the solution of the secular eqn.

$$\det \left| H_{\mu\nu} - E S_{\mu\nu} \right| = 0$$

where

$$H_{\mu\nu} = \int \phi_\mu \mathcal{H} \phi_\nu \, d\tau$$

$$= H_{\mu\nu}^0 + \beta^2 \int \left( \frac{\phi_\mu \phi_\nu}{\tau} \right) \, d\tau$$

and

$$S_{\mu\nu} = \int \phi_\mu \phi_\nu \, d\tau$$

McClendon made the approximation that

$$\int \left( \frac{\phi_\mu \phi_\nu}{\tau} \right) \, d\tau = \frac{2 S_{\mu\nu}}{(r_{\mu} + r_{\nu})}$$

In practice, the usual assumptions that $S_{\mu\nu} = S_{\nu\mu}$ is made and the effect of the perturbation term is then to alter the secular integral of each atom in the $\pi$ electron system to

$$c_{i\mu} = c_{i\mu}^0 + \frac{1\hbar k}{\beta_0} \left( \frac{1}{r_{\mu}} \right)$$

where $r_{\mu}$ is the distance in Å between the cation and atom $\mu$, and the factor $(1\hbar k/\beta_0)$ is used to convert the terms $1/r_{\mu}$ to units of $\beta_0$, where $\beta_0$ is the resonance integral of the C-C bond (usually set = -2.5 eV). The spin distribution in the $\pi$ electron system of the radical ion is then calculated from the coefficients $c_{i\mu}$ for the lowest occupied MO in the usual manner (Section 5.2).
A McLachlan type calculation may also be performed using the same model in order to get negative spin densities.

The interaction energy, $E$, of the cation with the radical anion is calculated from the relationship

$$E = 2 \sum_{i=1}^{N} \left( E_1 - E_1^0 \right) + E_{N+1}^0 - E_{N+1}$$

$$+ \sum_{\mu=1}^{2N} e^2/\mu$$

for $2N+1$ $T$ electrons, where $E_1^0$ and $E_1$ are the energies respectively of the free ion, and the ion allowing for the perturbing effect of the cation. The final summation in this expression arises from the coulomb repulsion between the $2N$ nuclei (each having an effective charge of $+e$) and the cation. The value of $E$ will normally be in terms of the quantity $\beta_0$ and since this latter term is negative, then the position of the cation with largest $E$ value will correspond to the most favoured energetic position for the cation to be situated in the ion pair.

This theory was incorporated into the computer programs MOCALC and HUCKEL.
APPENDIX XIII

Second Order Hyperfine Splitting in the
ESR Spectra of Free Radicals in
Solution

The zero order spin Hamiltonian for a radical in solution is
given by

\[ \hbar \hat{h} \hat{\mathbf{c}} = g \beta_e \hat{S} \mathbf{B}_0 - \hbar \mathbf{1}_1 \mathbf{I}_1 \mathbf{B}_0 = \hbar \mathbf{1}_1 \mathbf{I}_1 \mathbf{B}_0 = \hbar \gamma_e \mathbf{1}_1 \mathbf{a}_1 \mathbf{I}_1 \mathbf{S} \]

(III-1)

where \( \beta_e \) is the electron Bohr magneton
\( g \) is the Landé g factor
\( \mathbf{B}_0 \) is the external applied magnetic field
\( \gamma_e \) and \( \gamma_i \) are the magnetogyric ratios of the
electron and the \( i \)-th nucleus
\( \mathbf{1}_1 \) and \( \mathbf{S} \) are the nuclear and electron spin operators
respectively
\( \mathbf{a}_1 \) is the isotropic hyperfine coupling constant for
nucleus \( i \).

In general, it is assumed that the applied field is in the Z
direction and that the nuclear Zeeman interaction (second term in
expression above) is small compared to the electron interaction
(first term). Thus eqn. III-1 becomes
\[ \mathcal{H}_0 = \frac{g_e}{\hbar} \mathbf{S} \cdot \mathbf{B}_0 - \gamma_e \mathbf{\hat{I}}_z + \sum_{i=1}^{n} q_i \mathbf{I}_z \mathbf{S}_i \]

\[ = \frac{g_e}{\hbar} \mathbf{S} \cdot \mathbf{B}_0 - \gamma_e \sum_{i=1}^{n} q_i (\mathbf{I}_{iz} \mathbf{S}_z + \mathbf{I}_{ix} \mathbf{S}_x + \mathbf{I}_{iy} \mathbf{S}_y) \]

(III-2)

To first order the cross terms \( \mathbf{I}_{ix} \mathbf{S}_x \) and \( \mathbf{I}_{iy} \mathbf{S}_y \) are neglected.

Thus for interaction with one set of equivalent nuclei (i.e., \( q_1 = a \) for all \( n \) nuclei), eqn. (III-2) becomes

\[ \mathcal{H}_0 = \frac{g_e}{\hbar} \mathbf{S} \cdot \mathbf{B}_0 - \gamma_e a \sum_{i=1}^{n} \mathbf{I}_z \mathbf{S}_i \]

The effect of this operating on the appropriate wave functions is to allow for only the diagonal matrix elements and this gives transitions whose angular frequency is linearly dependent upon \( m \) as follows

\[ \omega (m) = \omega_0 + |\gamma_e| a m \]

(III-3)

where \( \omega_0 = |\gamma_e| B_0 \) where

\( \gamma_e \) is the electron spin Larmor frequency

in the field \( B_0 \) (i.e., the frequency at the centre of the spectrum)

and \( m = \sum_{i=1}^{n} \mathbf{I}_z \) is the total \( z \) component of the nuclear spin angular momentum of the \( n \) nuclei.

Because of the linear dependence on \( m \), these transitions give rise in the ESR spectrum to a multiplet of lines equally spaced a distance apart such that their intensity distribution is given by the coefficients
of the binomial expansion

\[ I(m) = \frac{n!}{(n/2 - m)! (n/2 + m)!} \]

To second order, we may no longer neglect the cross terms in the expansion of \( \mathbf{I}_1 \cdot \mathbf{S} \) and hence the full expression is used:

\[ \mathbf{I}_1 \cdot \mathbf{S} = \mathbf{I}_{1z} \mathbf{S}_z + \mathbf{I}_1 \mathbf{S} + \mathbf{I}_{1y} \mathbf{S}_y \]

\[ = \mathbf{I}_{1z} \mathbf{S}_z + \frac{1}{2} (\mathbf{I}_+ \mathbf{S}_+ + \mathbf{I}_- \mathbf{S}_-) \]

Thus eqn. (III-2) to second order becomes

\[ \mathcal{H}_o = g \gamma_e \mathbf{S}_z \mathbf{B}_0 = \gamma_e a \sum_{1}^{n} \left( \mathbf{I}_{1z} \mathbf{S}_z + \frac{1}{2} (\mathbf{S}_+ \mathbf{I}_+ + \mathbf{S}_- \mathbf{I}_-) \right) \]

and now both diagonal and off diagonal matrix elements are considered. This gives rise to transitions whose frequencies are both linearly and quadratically dependent upon \( m \) as follows:

\[ \omega (m) = \omega_0 + \left( g \gamma_e |m a + \gamma_e| \right) (a^2/2B_0) \left[ I_1 (I_1 + 1) - m^2 \right] \] (III-3)

where \( I_1 \) is the total nuclear spin.

Comparing eqns. (III-3) and (III-4), it can be seen that the latter eqn. is the same as the former except for a quadratic term and this is known as the Second Order correction.

The effect of this on the spectrum is to make it no longer symm-
etic about its centre. Each m value may give rise to one or more values of I and thus each line in the first order spectrum is split into a number of others whose frequency will be given by Eqn. (III-4) and intensity by the statistical weight of I (see Ref. 111 for details of this term). The shifts will be downfield as follows: the usual ESR spectrum is obtained at a fixed frequency with a variable magnetic field. Thus \( B_0 = 2 \pi \omega_0 |\gamma| \) where \( \omega_0 \) is the fixed frequency and (III-4) becomes

\[
\delta B(m) = B_0 - m a - \left( \frac{a^2}{2B_0} \right) (I (I + 1) - m^2) \quad \text{(III-5)}
\]

From eqn. (III-5) it can be seen that for \( B_0 = 3300 \) G and \( a = 5 \) G, the second order correction for \( I = 1 \) and \( m = 0 \) is 0.007 G. Thus second order effects only become appreciable in spectra when \( a > 10 \) G.
APPENDIX IV

Calculation of Overlap Integrals

Using Slater Orbitals

The overlap integral for a pair of atomic orbitals (AOs) \( a \) and \( b \) centred on atoms \( a \) and \( b \) respectively is written as

\[
S_{ab} = \int \phi_a^* \phi_b \, d\tau \tag{IV.1}
\]

where the integration extends over all space. In order to evaluate this expression it is necessary to know the form of the AOs and one of the most convenient analytical expressions is that derived by Slater\,[112].

A Slater type orbital is defined as the product of a radial and angular function:

\[
\psi(n, l, m, k) = R_{n, l, m}(r) \ Y_{l, m}(\theta, \varphi) \tag{IV.2}
\]

where \( n \) is the principal quantum number, \( l \) is the azimuthal quantum number, \( m \) is the magnetic quantum number, and \( k \) is the Slater exponent defined by \( k = Z^*/n \) where \( Z^* \) is the effective nuclear charge as determined by some empirical rules postulated by Slater\,[112].

The radial parts of (IV.2) have the form

\[
R_{n, l, m}(r) = N \ r^{l+1} e^{-kr/a_0}
\]

where \( N \) is a normalizing factor given by
\[ \frac{1}{N^2} = \int_0^{\infty} r^{2n} e^{-2\pi r/a_o} \, dr \]

\[ = (2n)! \left(\frac{a_o}{2\pi}\right)^{2n+1} \]

where \(a_o\) is the Bohr radius.

The angular factors of eqn. (IV-2) express the symmetry of the wavefunctions and thus have explicit expressions depending on the values of \(l\) and \(m\) as follows:

\[ Y_{l,m} = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \]

\[ Y_{p,0} = \left(\frac{3}{\pi}\right)^{\frac{1}{2}} \cos \theta \]

\[ Y_{p,\pm 1} = \left(\frac{3}{\pi}\right)^{\frac{1}{2}} \sin \theta \cos \phi \text{ if } m = \pm 1 \]

\[ = \left(\frac{3}{\pi}\right)^{\frac{1}{2}} \sin \theta \sin \phi \text{ if } m = 0 \]

Using expressions of type (IV-2), the overlap integral in (IV-1) becomes:

\[
S_{ab} = \sum_{a} \sum_{b} \int r_a^n e^{\frac{-k r_a}{a_o}} \, dr_a \int r_b^n e^{\frac{-k r_b}{a_o}} \, dr_b \cdot \]

\[ \times \int Y_{l_a,m} (\theta_a, \phi) Y_{l_b,m} (\theta_b, \phi) \, d\theta_a d\phi d\phi \quad (IV-3) \]

For symmetry reasons \(m_a = m_b = m\) or else the integral is zero. For example, the integral between a \(2\sigma\) orbital on one atom and a \(2\phi\) orbital on a second one is always zero.

The integration in eqn. (IV-3) may be simplified by a trans-
formation from polar coordinates \( r, \theta, \phi \) to elliptical coordinates defined as

\[
\begin{align*}
\xi &= (r_a + r_b)/R \\
\eta &= (r_a - r_b)/R \\
\varphi &= \varphi_a - \varphi_b
\end{align*}
\]

where \( R \) is the internuclear distance.

Defining

\[
\begin{align*}
p &= \frac{1}{2} (k_a + k_b)/R \\
t &= (k_a - k_b)/(k_a + k_b)
\end{align*}
\]

leads to the expressions:

\[
\begin{align*}
\cos \Theta_a &= (1 + \xi \eta)/(\xi + \eta) \\
\cos \Theta_b &= (\xi \eta + 1)/(\xi - \eta) \\
r_a &= (\xi + \eta) R/2 \\
r_b &= (\xi - \eta) R/2
\end{align*}
\]

and

\[
d\tau = (R/2)^3 (\xi^2 - \eta^2) d\xi d\eta d\theta.
\]

Using these expressions, eqn. (IV-3) becomes

\[
S_{ab} = \sum_a \sum_b (R/2)^n_a + n_b + 1 \int_1^\infty \int_{-1}^1 \int_0^2 (\xi + \eta)^n_a (\xi - \eta)^n_b e^{p_\xi} e^{-t\eta} \xi^m \xi^m \left( \varphi_a, \varphi \right) \xi^m \xi^m \left( \varphi_b, \varphi \right) \xi^m \xi^m \left( \varphi_b, \varphi \right) d\xi d\eta d\varphi \quad (IV-4)
\]

In order to proceed further, the \( \sum_{p, m} \) terms must be expressed in terms of \( \xi \) and \( \eta \) and this depends upon the values of \( l_a, l_b \) and \( m \). Mulliken et al. have solved eqn. (IV-4) for specific cases and have given the results in terms of a formual containing the auxiliary integrals

\[
A_\lambda(p) = \int_1^\infty e^{-p\xi} \xi^{\lambda-1} d\xi
\]

and
\[ B_j (p, t) = \int_1^{\infty} e^{-p\eta} \eta^j d\eta \]

As an example consider the \sigma\-type overlap between a 1s and 2p\_x: The Slater functions for these two orbitals are respectively

\[ \phi_{1s} = (\frac{k_a}{a})^2 e^{-k_a r} \]

and

\[ \phi_{2p_x} = (\frac{k_r}{r})^3 r \cos \theta e^{-k_r r} \]

Substitution of these expressions into eqn. (IV-1) gives

\[ S(1s, 2p_x, \sigma) = \frac{1}{2} (p(1 + t))^{3/2} (p(1 - t))^{3/2} (A_1 B_2 - A_2 B_1 + A_3 B_4) \]

Extensive lists of these formulae have been prepared by Mulliken et al. \textsuperscript{112}. To evaluate \( A_1(p) \), the recurrence relation \textsuperscript{11b}

\[ A_1(p) = A_0(p) + 1/p A_{1-1}(p) \]

where \( A_0(p) = 1/pe^{-p} \)

was used. To evaluate \( B_j (p, t) \), a quantity \( q \) was defined as \( q = pt \)

and the following two cases considered

1. If \( q = 0 \)

\[ B_n (0) = 2/_{n+1} \text{ for } n \text{ even} \]

\[ = 0 \text{ for } n \text{ odd} \]
(2) If $q \neq 0$

$$
B_n(q) = 2 \sum_{1 = 1, 3, \ldots, 00}^{q} \frac{2l + 1}{(2l + 1)^\frac{1}{2}} \frac{1}{(2l + n + 2)}
$$

for $n$ odd

$$
= 2 \sum_{1 = 0, 2, 4, \ldots, 00}^{q} \frac{2l}{(2l + 1)^\frac{1}{2}} \frac{1}{(2l + n + 2)}
$$

for $n$ even

These formulae had been used successfully in previous overlap calculations.⁹⁵

A computer program, OVERLAP, was written to calculate $S(1s, 2s, \sigma)$, $S(1s, 2p, \sigma)$, $S(2s, 3p, \sigma)$ and $S(2p, 3p, \pi)$ overlaps for first and second row elements.
APPENDIX V

Lowdin’s Method of Solution of the Secular Equation

Allowing for Overlap

Lowdin proposed that the Secular Equation

\[ HC = ESC \quad (V-1) \]

could be solved for \( C \) and \( E \) in the following way:

Multiplication of both sides of eqn. (V-1) by \( S^{-\frac{1}{2}} \) gives

\[ S^{-\frac{1}{2}} HC = S^{-\frac{1}{2}} ESC \]

Since \( S = S^{-\frac{1}{2}} S^{-\frac{1}{2}} \) then

\[ (S^{-\frac{3}{2}} H S^{-\frac{3}{2}}) (S^{\frac{3}{2}} C) = E (S^{\frac{3}{2}} C) \]

\[ H' C' = E C' \quad (V-2) \]

where \( C' = S^{\frac{3}{2}} C \) \quad (V-3)

\[ H' = S^{-\frac{1}{2}} H S^{-\frac{1}{2}} \]

Eqn. (V-2) is now the standard eigenvalue-eigenfunction problem that is easily solved with diagonalization procedures such as the Jacobi or Householder methods.

In practice, the matrix \( S_{D}^{-\frac{3}{2}} \) was calculated by the method suggested by Colpa and de Boer as follows:

the matrix \( S \) is diagonalised using the transformation

\[ U^{T} S U = S_{D} \quad (V-4) \]
where $U$ is the matrix of eigenfunctions and $U^T$ its transpose. The matrix $S_D^{-\frac{1}{2}}$ is then constructed by taking the reciprocal of the square root of each of the diagonal elements of $S_D$. Writing $S_D^{-\frac{1}{2}}$ for $S_D$ in the above transformation (Eqn. V.14) gives

$$U^T S_D^{-\frac{1}{2}} U = S_D^{-\frac{1}{2}}$$

i.e.,

$$S_D^{-\frac{1}{2}} = U S_D^{-\frac{1}{2}} U^T$$

According to Colpa and deBoer, this method avoids the problem of slow convergence that occurs if Lowdin's series expansion for $S_D^{-\frac{1}{2}}$ is used.

The order of computation then is to diagonalise the $S$ matrix and calculate $S_D^{-\frac{1}{2}}$. The matrix $U$ is formed and diagonalised. This gives the matrix of eigenfunctions $C'$ and its eigenvalues $E$. Using eqn. (V.3) the matrix of true eigenfunctions $C$ can be obtained from $C'$. 
APPENDIX VI

Use of Symmetry Transformation to Simplify the Hamiltonian Matrix

Because of the size of the periselenindanaphthalene molecules being studied in this project and hence the large dimensions of the matrices involved in MO calculations on these species (92 x 92 in the case of diphenylnaphthalene), it was clear that there would be a considerable saving in computer time and an increase in accuracy if the point group symmetry of the molecules could be used to reduce each matrix to a number of smaller matrices. Accordingly the following theory was developed:

If the basis functions are initially chosen as the atomic orbitals on each atom i.e. $\phi_i^1 (i = 1, \ldots, N)$, then the overlap and Hamiltonian matrix elements are respectively defined as

$$ S_{ij} = \langle \phi_i^1 | \phi_j^1 \rangle \quad (VI-1) $$

and

$$ H_{ij} = \langle \phi_i^1 | H | \phi_j^1 \rangle \quad (VI-2) $$

If the basis is changed such that the new basis functions, $\bar{\phi}_j$, are given by

$$ |\bar{\phi}_j\rangle = \sum_k c_{kj} |\phi_k\rangle \quad (VI-3) $$

where $c_{kj}$ is a real constant, then

$$ |\phi_k\rangle = \sum_i d_{ik} |\bar{\phi}_i\rangle \quad (VI-4) $$
for some real constant $d_{ik}$. Substituting (VI-1) in (VI-3) gives

$$\left| \overline{\psi}_j \right> = \sum_{i} \sum_{k} d_{ik} c_{kj} \left| \overline{\psi}_i \right>$$

and

$$\left| \phi_j \right> = \sum_{i} \sum_{k} c_{ik} d_{kj} \left| \phi_i \right>$$

The overlap and Hamiltonian matrices given by (VI-1) and (VI-2) may be rewritten for the new basis functions as

$$\hat{S}_{ij} = \left< \overline{\psi}_i \left| \overline{\psi}_j \right> \right>$$

$$= \left( \sum_{k} c_{ik} \left| \phi_1 \right> \right)^* \left( \sum_{k} c_{kj} \left| \phi_k \right> \right)$$

$$= \sum_{i} \sum_{k} c_{ik}^* c_{kj} \left< \phi_1 \left| \phi_k \right> \right>$$

$$= \sum_{i} \sum_{k} b_{ij} S_{ik} c_{kj} \quad (\text{VI-5})$$

where $S_{ik} = \left< \phi_1 \left| \phi_k \right> \right>$

and $b_{ij} = c_{i}^*$

Similarly

$$\hat{H}_{ij} = \sum_{i} \sum_{k} b_{ij} c_{ik} H_{lk} c_{kj} \quad (\text{VI-6})$$

Eqs. (VI-5) and (VI-6) may be rewritten in matrix notation as

$$\hat{S} = \mathbf{B} \mathbf{S} \mathbf{C} \quad (\text{VI-7})$$

and

$$\hat{H} = \mathbf{B} \mathbf{H} \mathbf{C}$$

A secular equation may be constructed for $\hat{H}$ and $\hat{S}$ as follows:
for some eigenvalue $E_{ji}$ of $H$, there will be an eigenfunction consisting of linear combinations of $\Phi_j$'s such that

$$H \Psi_j = E_{ji} \Psi_j$$

Multiplying both sides by $\langle \Phi_k |$ gives

$$\langle \Phi_k | H \Psi_j = E_{ji} \langle \Phi_k | \Psi_j$$

or in matrix notation

$$H \mathbf{L} = E \mathbf{S} \mathbf{L} \quad (\text{VI-8})$$

This corresponds to the secular equation

$$H \mathbf{C} = E \mathbf{S} \mathbf{C}$$

that would be obtained for the original basis functions of atomic orbitals.

From eqn. (VI-3) it can be seen that

$$\Psi_j = \sum_k c_{kj} \Psi_k$$

and thus the matrix of eigenfunction coefficients, $L'$, in terms of the original basis functions of atomic orbitals, may be obtained from the matrix $L$ by the expression
\[ L' = C L \quad (VI-9) \]

In practice, a symmetry matrix \( C \) is chosen that will block the \( S \) and \( H \) matrices given by eqns. (VI-7) into a number of smaller matrices. Secular eqns. of the form given by (VI-8) are then calculated and solved for each of these blocks in the \( \hat{H} \) matrix to give energies \( E_k \). By using eqn. (VI-9), the coefficients \( l_{ki}' \) of the eigenfunctions are obtained in terms of the original basis functions of atomic orbitals.

In order to construct a symmetry matrix \( C \) that will block the \( H \) and \( S \) matrices, the point group symmetry of the molecule is considered. Combinations of the atomic orbitals are chosen that will transform as one of the irreducible representations of the group. This is best explained by considering the specific example of naphthalene:

This has the structure

![Diagram of naphthalene]

and thus assuming it is planar, it has \( D_2h \) symmetry and the character table corresponding to this is given in Table 5.6. It can be readily seen that there are two general sets of four equivalent positions.
### Table 5.6

Character table for $D_{2h}$ symmetry.

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_{22}$</th>
<th>$C_{2y}$</th>
<th>$C_2$</th>
<th>1</th>
<th>$(xy)$</th>
<th>$(xz)$</th>
<th>$(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$a, b, c, d$ corresponding to the $\alpha$ and $\beta$ positions, and one special set of two equivalent positions $e, f$ at the bridging C atoms.

Considering the carbon 2s and hydrogen 1s orbitals, it is possible to have four different plus and minus combinations of these orbitals at the general $a, b, c, d$ positions that will each transform under the eight symmetry operations given in Table 5.6 as one of the irreducible representations. These combinations are
Thus combination (1) will transform under the eight symmetry operations as the $E$ irreducible representation. Similarly (2) will transform as $B_{2u}$, (3) as $B_{1g}$, and (4) as $B_{3u}$. At the special positions, e and f, there are only two possible combinations

\[
\begin{align*}
(5) & \quad + \quad + \\
(6) & \quad + \quad -
\end{align*}
\]

corresponding to the situations

\[
\begin{align*}
(5) & \quad \begin{array}{c}
\rotatebox{90}{$\times$} \\
\end{array} \\
(6) & \quad \begin{array}{c}
\rotatebox{90}{$\times$} \\
\end{array}
\end{align*}
\]
These can be readily shown to transform as the $B_{1g}$ and $B_{2u}$ representations. A similar analysis may be made for the $p_z$, $p_x$, and $p_y$ carbon atomic orbitals.

All combinations that transform according to the same irreducible representation are collected together in groups. The number of these will equal the order of the symmetry group to which the molecule belongs i.e. 8 for a $D_{2h}$ group.

Each of these groups of combinations is then considered in turn and the symmetry matrix elements, $c_{ij}$, are constructed as follows: considering the first combination of the first group, the reference number of the actual atomic orbitals at the four atoms in one of the two sets of general symmetric positions are identified (say $\phi_i$, $\phi_h$, $\phi_l$ and $\phi_n$). The symmetry matrix elements $c(1,1)$, $c(l,1)$, $c(7,1)$ and $c(11,1)$ are then set equal to +1 if the particular orbital makes a plus contribution and a -1 for a minus contribution. All other elements in the first column are set equal to 0, 0. The second set of general positions in the first combination is then considered and in this way the complete symmetry matrix is built up.

If this matrix is used to construct the $H$ and $S$ matrices according to the equations:

$$\hat{H} = B H C$$

and $$\hat{S} = B H C$$
where $B$ has elements

\[ b_{ij} = c_{ji} \]

then it will be found that $H$ and $S$ will be blocked in the form

\[
\begin{bmatrix}
  [ & ] \\
  [ & ]
\end{bmatrix}
\]

where the elements in each block are non-zero while all others are zero.
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A re-interpretation of the E.P.R. spectrum of the 1,2,3,6,7,8-hexahydropyrene anion radical

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(Received 14 July 1969)

In the course of a study of the radical ions of some peri-substituted naphthalene derivatives we have found it necessary to re-investigate the E.P.R. spectrum of the 1,2,3,6,7,8-hexahydropyrene anion radical.

The anion radical was prepared by reduction of the parent compound with potassium in 1,2-dimethoxyethane.

The spectrum of this species was first reported by de Boer and Praat [1] and later by Iwaizumi and Isobe [2]. Examination of molecular models of the hexahydropyrene molecule shows that the \( \gamma \) protons are in two different geometric environments and should hence give rise to two distinct \( \gamma \) coupling constants. Both reports [1, 2] have interpreted the spectrum of the anion radical in terms of a single coupling constant due to the \( \gamma \) protons, even at a temperature several degrees below the freezing point of the solvent.

The spectrum obtained by us at \(-95^\circ C\) (figure (a)) is identical in all respects to that shown in the previous reports [1, 2]. We find that computer simulation using only four coupling constants gives spectra whose lines agree in position but not intensity with those of the observed spectrum. However by using the set of five coupling constants including the two distinct \( \gamma \) coupling constants given in the table, a theoretical spectrum (figure (b)) which is in perfect agreement with the observed spectrum is obtained. The simulated spectra have been found to be markedly dependent on the value of the fifth coupling constant: spectra computed for \( \gamma_{eq}=0.35 \) and \( 0.37 \) gave different intensity patterns. As before, it appears that the difference between the coupling constants of the chair and boat isomers of the anion in 1,2-dimethoxyethane is too small to allow separate spectra to be observed.
E.P.R. spectrum of hexahydropyrene anion in 1,2-dimethoxyethane with K⁺ as counter ion.

(a) Experimental. (b) Computer simulated (linewidth is 0.1 G).

|         | Low temperature | High temperature ||
|---------|-----------------|-------------------|
|         | -95°C†          | -81°C‡           | -81°C§           | †    | ‡    | §    |
| α       | 1.69            | 1.69             | 1.68             | 1.69 | 1.69 | 1.68 |
| β₁K     | 7.96            | 8.03             | 8.00             | —    | —    | —    |
| βₑα     | 2.02            | 2.02             | 2.02             | —    | —    | —    |
| βₓα+βₑα | —               | —                | —                | 9.88 | 9.86 | 9.87 |
| γₓα     | 0.50            | 0.50             | 0.51             | —    | 0.41 | 0.41 |
| γₑα     | 0.36            | —                | —                | —    | —    | —    |
| γₓᵥ     | —               | —                | —                | 0.42 | —    | —    |

† Present study.
‡ Ref. [1].
§ Ref. [2].
∥ All values at +23°C.

Coupling constants of 1,2,3,6,7,8-hexahydropyrene radical anion in 1,2-dimethoxyethane (values in gauss).
The assignment of the larger $\gamma$ coupling constant of 0.50 G to the axial position and the smaller to the equatorial position has been made on the following qualitative grounds. The contribution to the spin density at the two pairs of $\gamma$ protons due to spin polarization will presumably be the same, but, as the axial $\gamma$ protons are in a more favourable geometric position to allow hyperconjugation with the $\pi$ orbitals of the aromatic rings than the equatorial protons, we would expect a higher spin density and hence a larger coupling constant for the axial protons.

Confirmation of the assignments made comes from the examination of the temperature dependence of the spectrum. The now well-established linewidth alteration effect due to conformational interconversion was observed. At $+23^\circ C$ only three coupling constants are necessary to simulate the spectrum. At this temperature the rate of interconversion of the chair and boat forms is of the order of the hyperfine frequency, and is the rate of the movement of the $\gamma$ carbon atom through the plane of the aromatic system causing the interconversion of the $\beta$ axial and $\beta$ equatorial protons. Under these conditions the coupling constant is $(\beta_{\text{ax}} + \beta_{\text{eq}})$ as previously observed. At this same temperature the $\gamma$ protons at each $\gamma$ carbon atom are rapidly interconverting and are equivalent, giving rise to a single coupling constant $\gamma_{\text{av}}=0.41$ G. This value is in very good agreement with the average of the two low temperature coupling constants (0.43 G).

The assignment of two distinct $\gamma$ coupling constants in this way obviates the need to explain the large change in the coupling constant with temperature.

An investigation of the E.P.R. spectrum of the hexahydropyrene monopositive ion in order to establish whether there are two distinct $\gamma$ coupling constants is in progress.

**References**

An E.P.R. study of the anion radical of diplieadane

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As a continuation of our studies of the radical ions of perisubstituted naphthalenes [1] we have investigated the E.P.R. spectrum of diplieadane(1,2,3,4,7,8,9,10-octahydridicyclohepta[de : ij]naphthalene). This compound was synthesized by one of us (D. R. A. L.) as part of an investigation of the chemistry of substituted naphthalenes [2]. Molecular models indicate that there should be considerable repulsion effects between the βαX protons which may lead to distortion of either the aromatic ring or the aliphatic rings, or both. An E.P.R. investigation was undertaken to determine whether the molecule existed in cis and trans isomers which could interconvert in the same way as has been observed for the hexahydropyrene ions [1, 3, 4], or whether the distortion would be such as to lead to only one form of the molecule.

The anion radical was produced by reduction of the parent compound with either sodium or potassium in 1,2-dimethoxyethane. Attempts at reduction with lithium were unsuccessful.

The spectrum of the anion radical in dimethoxyethane at −95°C is shown in the figure (a).

We have interpreted this spectrum in terms of the superposition of the spectra of two closely similar species which we attribute to the cis and trans forms of the parent molecule ion. Variations of the relative amount and g value of each species was considered, but the theoretical spectrum (figure (b)) computed using the hyperfine coupling constants given in the table and for identical g values and a 1 : 1 ratio of each species gave the best fit with the observed spectrum.

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E.P.R. spectrum of dipleiadane anion in 1,2-dimethoxyethane with K⁺ as counter ion. 

| Coupling constants of dipleiadane(1,2,3,4,7,8,9,10-octahydrohepta[de:ij]napththalene) radical ion in 1,2-dimethoxyethane (in gauss). |
|---|---|---|
| α | 1.57 | 1.57 |
| β<sub>ax</sub> | 6.28 | 6.16 | — |
| β<sub>eq</sub> | 1.35 | 1.57 | — |
| β<sub>ax</sub> + β<sub>eq</sub> | — | — | 7.70 |
| γ | 0.22 | 0.22 | — |

The possibility that the lack of resolution in parts of the spectrum might be due to a line width alternation effect arising from movement within the molecule was considered unlikely in view of the temperature of the measurement. Ion pairing effects were also rejected for several reasons:

(a) The identity of the spectra when either sodium or potassium were used as the counter ion.
(b) The dielectric constant of dimethoxyethane is such as to discourage ion pairing, and indeed no such effects have been observed for the radical ions of any other peri-substituted naphthalenes with sodium or potassium in this solvent.
Attempts to simulate the spectrum using reasonable values for the alkali metal coupling constants were unsuccessful.

The assignments of the coupling constants to the positions within the molecule were made from an inspection of the groupings and intensities of the lines within the spectrum and also from the assignments made for the structurally similar hexahydropyrene anion radical in the same solvent [1, 3, 4]. In this latter compound we have previously observed [1] separate \( \gamma \) coupling constants corresponding to the two separate environments for the \( \gamma \) protons. In diplieadane we can distinguish only one \( \gamma \) coupling constant although two would be expected. Either the difference between the two coupling constants is too small to allow them to be separately observed or there is some motion of the \( C_2 \cdots C_9 \) bond causing broadening of the \( \gamma \) resonances making the two indistinguishable.

The most probable cause of the differences in the \( \beta \) proton coupling constants observed for the two forms of the molecule at \(-95^\circ\text{C}\) is that the distortion from the classical boat structure for the \textit{cis} form of diplieadane will be different from the corresponding distortion for the \textit{trans} form. This will arise from the necessity to alleviate the large repulsive interaction of the \( \beta_{ax} \) protons. In the classical model the distance between these two protons is \( 0.8 \) \( \AA \).

The relation [5]:

\[
\alpha_{p}H = (B_0 + B_1 \cos^2 \theta) \rho_{Ar}^n,
\]

where \( \alpha_{p}H \) are the hyperfine constants for the \( \beta \) protons attached to the \( \beta \) carbon atoms (1, 4, 7, 10); \( B_0 \) and \( B_1 \) are constants and \( \theta \) are the angles between the axis of the \( p_z \) orbital of the adjacent aromatic carbon atoms (1a, 4a, 7a, 10a) and the \( C_\beta - H \) bond, both projected onto a plane perpendicular to the \( C_{Ar} - C_\beta \) bond, has been used to obtain information on the orientation of the axial and equatorial protons at the \( \beta \) carbon atom. Assuming \( B_0 = 0 \) and that the bonds about the \( \beta \) carbon atom retain tetrahedral symmetry (i.e. \( \theta_{ax} = 120 - \theta_{eq} \)) we calculated using the \( \beta \) coupling constants listed in the table that the \( \theta_{ax} \) and \( \theta_{eq} \) angles for both forms are 49° and 71° respectively, to within a degree, compared with 42° and 78° calculated from the classical forms. These values indicate that some distortion of the aliphatic rings has occurred although the difference between the two forms is minor. Distortion of the naphthalene ring is too small to be observed by E.P.R. although it is likely to have occurred to help alleviate the steric interaction of the \( \beta_{ax} \) protons in much the same way as is observed in crystallographic studies of 3-bromo-1,8-dimethyl-naphthalene [6]. Indication that there is some distortion of the naphthalene nucleus is obtained from the value of the spin density at the carbon atoms 1a, 4a, 7a and 10a. A value of \( \rho_{Ar}^n = 0.31 \) is calculated assuming further that \( B_1 = 46 \) gauss [4] and using the above values of \( \theta_{ax} \) and \( \theta_{eq} \) compared with the value of 0.17 for the hexahydropyrene anion and of 0.18 from a simple Hückel calculation for the naphthalene anion for atoms in the equivalent positions.

The larger spin density at the 1a, etc. carbon atoms of the diplieadane anion is consistent with a buckling of the aromatic ring causing an increased \( s \) character in the orbital containing the unpaired spin.

Confirmation of the presence of two species of the radical ion at low temperatures was obtained from the temperature dependence of the spectrum. Line width alternation effects arising from a dynamic equilibrium between the two forms leads to drastic changes in the spectrum. At 55°C the rate of
interconversion becomes comparable to the hyperfine frequency and only five
groups of lines separated by the average value of \( |a_{\beta \chi} + a_{\beta \text{eq}}| \) are observed. These lines are further split by the hyperfine coupling constant arising from the aromatic protons. Because the radical is unstable at this temperature, resulting in a low signal to noise ratio, we were unable to resolve the \( \gamma \) coupling constant nor was it possible to decide whether the two aliphatic groups moved independently or in conjunction.

The activation energy for the interconversion of the two forms of the anion is greater than that for hexahydropyrene anion where the rate of interconversion became comparable with the hyperfine frequency at 23°C which would be expected from the more sterically hindered nature of the molecular motion involved in diplieadane.

We conclude that the diplieadane molecule exists in cis and trans forms which do not differ greatly from the classical boat and chair forms of the molecule.

REFERENCES