X-RAY INVESTIGATIONS OF STEREOCHEMICAL PROBLEMS:

AN X-RAY CRYSTAL-STRUCTURE ANALYSIS

of

2α,10-DIBROMO-10β-PINAN-3-ONE

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

by

M.B. JAMESON

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Special thanks are also due to New Zealand Universities Research Committee for the award of a Research Fund Fellowship.

Finally I thank my wife for her constant support which helped me through many disappointments and frustrations in the course of this work.
ABSTRACT

The crystal structure of 2,10-dibromo-10β-pinane-3-one, a bromo derivative of the naturally occurring β-pinane, has been determined by x-ray analysis. The compound crystallized in the unusual trigonal space group $P3_1$ with three molecules in the unit cell of dimensions $20.3 \times 20.3 \times 7.00 \lambda$. The structure has confirmed the distorted nature of the pinane skeleton compared with cyclohexanone, the buckled cyclobutane ring, and the correctness of the structure assignment made by Wallis. An essentially planar conformation has been found rather than the more usual up or down conformations expected in six-membered hydrocarbons. The molecular geometry is discussed and compared with other recent structures which have been reported in the previously unexplored pinane field.

The thesis also describes an examination of the effect of anomalous dispersion and in an appendix the development of a computer program to handle and process both densitometer and visually estimated reflection data from Weissenberg photographs.
CONTENTS

ACKNOWLEDGEMENTS

ABSTRACT

CHAPTER I  INTRODUCTION  1

CHAPTER II  EXPERIMENTAL  7
  1. Crystal preparation and characteristics  7
  2. Density of Crystals  8
  3. X-ray photography  10
     Comparison of densitometer and visual
     measurements.  14

CHAPTER III  SPACE GROUP DETERMINATION AND UNIT CELL
     DIMENSIONS  18
     1. Space group determination  18
     2. Unit cell dimensions  21

CHAPTER IV  THE TRIGONAL SYSTEM  22
  1. Trigonal symmetry and indexing of
     the photographs.  22
  2. Correction of indexing errors  25
  3. Explanation of the pseudosymmetry  26
### CHAPTER V  STRUCTURE DETERMINATION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>28</td>
</tr>
<tr>
<td>2. Data preparation</td>
<td>31</td>
</tr>
<tr>
<td>3. Calculation of the Patterson function</td>
<td>33</td>
</tr>
<tr>
<td>4. Solution of the three-dimensional Patterson function.</td>
<td>34</td>
</tr>
<tr>
<td>5. Electron density maps</td>
<td>44</td>
</tr>
<tr>
<td>6. Location of light atoms</td>
<td>48</td>
</tr>
<tr>
<td>7. Refinement of the structure</td>
<td>52</td>
</tr>
<tr>
<td>8. Final isotropic refinement of the structure</td>
<td>57</td>
</tr>
</tbody>
</table>

### CHAPTER VI  DISCUSSION OF THE STRUCTURE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>59</td>
</tr>
<tr>
<td>2. Molecular geometry</td>
<td>64</td>
</tr>
<tr>
<td>3. Discussion of geometry</td>
<td>68</td>
</tr>
<tr>
<td>4. Discussion of cyclobutane ring geometry</td>
<td>76</td>
</tr>
<tr>
<td>5. Conclusion</td>
<td>81</td>
</tr>
</tbody>
</table>

### CHAPTER VII  ANOMALOUS DISPERSION AND ABSOLUTE CONFIGURATION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>84</td>
</tr>
<tr>
<td>2. Anomalous dispersion in 2,4,0-dibromo-pinane-5-one</td>
<td>87</td>
</tr>
<tr>
<td>3. Anomalous dispersion and structure factor calculations</td>
<td>91</td>
</tr>
</tbody>
</table>
APPENDIX I

REFINEMENT OF THE STRUCTURE OF
3-BROMO-1,8-DIMETHYLPHENANTHRENE

94

APPENDIX II

COMPUTING

1. General discussion
   96
2. Programs written by the author
   98
3. Computer programs used in the
   structure analysis
   102
4. Program listings
   105

APPENDIX III

FINAL COORDINATES AND STRUCTURE FACTOR
LISTING

106

APPENDIX IV

COMPARISON OF THE MEASUREMENT OF
INTENSITY DATA BY DENSITOMETER AND BY
EYE.

110

REFERENCES

113
LIST OF FIGURES

Fig. 3.1(a) Reciprocal lattice diagram for the trigonal system...

3.1(b) hk5 photograph

4.1 Okl and 1kl photographs

4.2 hk4 photographs correctly and incorrectly indexed

4.3(a) Space group symmetry of P3_12 and P3_21

4.3(b) Heavy atom positions in projection down the c axis

5.4(a) Marker section, z = .33 of Patterson

5.4(b) Section z = 0 of Patterson

5.4(c) Section z = .50 of Patterson

5.6 View of the contents of the unit cell projected down the c axis

5.7 Bond lengths and angles of 2,10-dibromo-pinan-3-one after anisotropic refinement

6.2(a) Bond lengths and angles of 2,10-dibromo-pinan-3-one after isotropic refinement

6.2(b) Bond lengths and angles of 2,4-dibromo-pinan-3-one, 3-bromo- and 3-chloro-nopinone

6.2(c) Bond lengths and angles of "average" molecule of 2,10-dibromo-pinan-3-one

6.2(d) Bond lengths and angles of "chemically averaged" molecule of 2,10-dibromo-pinan-3-one

6.2(e) Torsion angles in 2,10-dibromo-pinan-3-one

7.1 Structure factor amplitudes under normal and anomalous scattering conditions

7.2 Conditions for maximum and minimum differences in a Bijvoet pair

Molecular reference diagram (fold-out figure)
LIST OF TABLES

1.1 Infrared and ultraviolet spectral shifts of pinan-3-ones (fold-out table)
2.3 Dimensions of crystals used in the analysis p 12
3.1 Trigonal space groups p 19
3.2 Crystal constants p 21
5.4 Patterson vector peaks p 43
6.2(a) Bond lengths and individual standard deviations in 2,10-dibromo-pinan-3-one p 61
6.2(b) Statistical analysis of chemically similar bonds in 2,10-dibromo-pinan-3-one p 63
6.2(c) Planarity of conformation in the pinane series p 66
6.2(d) Buckling of the cyclobutane ring in the pinane series p 67
6.2(e) Intramolecular contacts under 3.75 Å in 2,10-dibromo-pinan-3-one p 67
6.4 Effect of buckling on bond angle in cyclobutane rings p 78
8.1 Comparison of reflection data measured by eye and by densitometer p 111

Fold-out tables and diagrams are located at end of the thesis.
CHAPTER I

INTRODUCTION

Examination of a model of pinane reveals a highly strained molecule consisting of a cyclobutane ring, surmounted by a gem dimethyl group fused to a cyclohexane ring by the addition of a 1:3-methylene bridge. A further methyl group is substituted at the 2 position.

A flexible model shows that while the molecule as a whole appears rigid, two possibilities exist for the C3 atom which can adopt either an up or down conformation, relative to C6, rigidly held at the other end of the cyclohexane ring. When the methylene group at C3 becomes replaced by a carbonyl group, further strain is expected due to the increased bond angle at C3 and a third planar conformational
possibility arises.

In his examination of the properties of the α-bromo derivatives of these pinan-3-ones, Wallis found that the physical methods at his disposal especially infrared and ultraviolet spectra along with nuclear magnetic resonance and optical rotatory dispersion, offered conflicting evidence for the precise assignment of structures to these compounds, though conformational analysis showed that certain conformations were more likely than others. In his investigations Wallis made use of the weak absorption band in the ultraviolet spectra associated with saturated ketones at ca. 290 μ. Cookson states that the absorption band is shifted to larger wavelengths and becomes more intense when bromine in an axial position is introduced adjacent to the carbonyl group in cyclohexanones. The intensity may be enhanced from \( \varepsilon = 20-30 \) to \( \varepsilon = 120-180 \), for an axial bromine in the α position, but bromine in the equatorial conformation is said to affect the position and intensity of the absorption maximum to a negligible extent. Examination of Wallis' table of ultraviolet absorptions (see foldout table 1.1) of α-bromo substituted pinan-3-ones shows in all cases substantial shifts in the absorption maximum of 21-47 μ, and associated enhancement of the intensity from \( \varepsilon = 19 \).
to \( \epsilon = 115-240 \), relative to the unsubstituted isopinocamphone. 10-Bromo-pinan-3-one however, though only having a bromine atom \( \beta \) to the carbonyl group, still shows a shift of 14 \( \text{cm}^{-1} \) but a much smaller intensity enhancement \( \epsilon = 50 \). Although the theory is restricted to cyclohexanones in the "chair" conformation, and the pinane skeleton cannot be described as having an orthodox chair conformation, it is clear that the deduction of axial conformations for the bromine atoms in these compounds cannot be made with certainty.

Further if the table of infrared stretching frequencies of the carbonyl group in these compounds is now examined (see foldout table 1.1), an opposite conclusion is arrived at. Jones and his coworkers\(^{b}\) state after examining the effect of bromination at the \( \alpha \) position to a carbonyl group, that the carbonyl band in the infrared spectrum is displaced by about 20 \( \text{cm}^{-1} \) to a higher frequency, when bromine is in an equatorial conformation. When the bromine is an axial conformation the effect is apparently very small. This criterion of conformation is again limited to the chair form of cyclohexanones. If the criterion is applied to Wallis' results, all of the \( \alpha \) substituted pinan-3-ones show shifts in the carbonyl stretching frequency, relative
to isopinocamphone, in the range $14-19 \text{ cm}^{-1}$, while
the effect of the $\beta$ substituent, as in
10-bromo-pinane-3-one, is as expected small, ($4 \text{ cm}^{-1}$).
The opposite conclusion is therefore reached, that the
conformation of the bromines is predominantly equatorial
in contradiction to the results obtained from the
ultraviolet spectra; in fact 2,4-dibromo-pinane-3-one
which shows the largest effect in the infrared, also
shows the largest effect in the ultraviolet.

In the series of 4-bromo- substituted pinane-3-ones,
Wallis$^5$ was able to associate a very small increase in
the chemical shift of the $\text{-CHBr-}$ proton signal with
increasing equatorial character of the $\text{CH}$ proton and
therefore increasing axial character of the $\text{CH}$ bromine
atom. The reason for this shift is said to be due to
the fact that axial protons in $\alpha$-halogenoketones are more
deshielded than equatorial protons so that as the protons,
become more axial, a greater chemical shift occurs.

From the optical rotatory dispersion measurements
correlations with qualitative predictions were made but
Wallis was unable to make definite pronouncements on
whether the bromine substituents in these compounds were
mainly axial or equatorial.

The physical evidence quoted by Wallis was thus
to some extent contradictory and the most reasonable
interpretation of it was to assume the pinane-3-ones
adopted an approximately planar conformation with the bromine substituents at positions C2 and C4, having a conformation midway between axial and equatorial as in fact a "Drydeen" model suggests. It also appears that the criteria used for interpreting the infrared and ultraviolet spectra are not strictly applicable to these α-bromo-pinane-3-ones in view of the conflicting conclusions possible. In order to elucidate these problems and test the validity of the conformational analysis in describing these compounds and their behaviour and properties, the author determined the x-ray crystal-structure of 2α,10-dibromo-10β-pinane-3-one. In addition there were no known crystal-structure determinations involving a pinane derivative, and only a small number involving a cyclobutene ring had been reported.

2α,10-dibromo-10β-pinane-3-one was chosen for the investigation because it happened to be one of only two compounds which were reasonably stable crystalline solids. The alternative 2α,4α-dibromo-10β-pinane-3-one was investigated by the author and its cell dimensions and space group determined but owing to its reputed instability attention was directed to the 2,10-dibromo compound which had the advantage of only one substituent at the 2 position instead of two as in the 2,4- compound.
The structure of the 2,4-dibromo compound was subsequently determined by Dr P.P. Williams whose results are compared with those in the present work.
CHAPTER II

EXPERIMENTAL

1. CRYSTAL PREPARATION AND CHARACTERISTICS

2,4,10-Dibromo-pinane-3-one was prepared by Dr A.F.A. Wallis of this department in a two step synthesis from the naturally occurring \( \beta \)-pinene. Optically pure \( \beta \)-pinene was oxidised with selenium dioxide to give pinocarvone which on reaction with one mole of bromine gave the required compound after careful chromatographic separation and crystallization from ethereal solution.

The compound crystallized as colourless, chunky crystals, elongated in what proved to be the unique short axis direction. The crystals melted at 73 - 74\(^\circ\)C and showed an optical rotation in benzene solution of \([\alpha]_D = -159^\circ\), indicating at least substantial retention of configuration in the synthesis from the optically active starting material \( \beta \)-pinene \([\alpha]_D = -20^\circ\). A micro-analysed sample of the compound gave Br = 52.1\% and \( \text{C}_{20}\text{H}_{44}\text{Br}_2\text{O} \) requires Br = 51.6\%. No error is quoted but it is expected that the agreement is well within experimental error for a micro-analysis of a stoichiometric, pure compound. Careful purification of the starting material was essential if any crystalline product at all was to be obtained. In an attempt to obtain further crystals from a supplied sample of impure compound in
solution which had been prepared as an intermediate for another synthesis, the author was unable to separate the desired compound from its impurities using a chromatographic column and no further crystals were obtained.

As it was suspected that the compound was unstable to light, the crystals were kept away from the light. The crystals were somewhat volatile, possessing a distinctive camphor-like odour, but their usefulness was limited principally by their gradual chemical decomposition and change to a red colour when exposed to the X-ray beam. The red colour presumably indicated some loss of bromine. Actual crystals used in the structure determination seldom lasted more than 50 hours exposure to the X-ray beam before becoming quite useless for diffraction purposes. A powder sample photographed at intervals up to 72 hours total cumulated exposure showed no obvious changes in the powder line pattern, though the sample rapidly turned red in colour. This observation indicated that the decomposition was probably a surface effect but still sufficiently serious to spoil intensity photographs on the Weissenberg camera with most crystals after 50 hours exposure, if not well before this time.

2. DENSITY OF CRYSTALS

Initially the crystal density was measured by flotation in sulphuric acid using a hydrometer graduated to .001 gm.
cm.\(^{-3}\). This method gave a value, averaged over several crystals of 1.61 ± 0.05 gm. cm.\(^{-3}\). Using a Berman density balance a figure of 1.69 gm. cm.\(^{-3}\) was obtained corresponding to eight molecules in the unit cell, but the method was not regarded as very satisfactory owing to the fact that water had to be used as the immersion liquid, instead of the usual volatile organic liquids in which the compound is soluble. The use of water resulted in difficulties in drying as well as marked surface tension effects. Since unit cell measurements later suggested that the density was more likely to be 1.84 gm. cm.\(^{-3}\) for nine molecules in the unit cell respectively, a re-determination was carried out.

Saturated silver nitrate solution has a density of 2.392 gm. cm.\(^{-3}\) at 25°C and proved to be a far more suitable (and less reactive) immersion liquid than sulphuric acid and adequately covered the desired range of densities. Again using several crystals a figure of 1.85 ± .05 gm. cm.\(^{-3}\) was obtained, which was a much more plausible value than obtained previously. The large estimated error is a consequence of the large surface tension effect and the effects of occluded air in some hollowed out crystals. These effects also probably account in part for the lower values of the density obtained in the earlier determinations. The measurements thus confirmed that there were nine molecules in the crystallographic unit cell.
For the isomeric terpene 2,4-dibromopinan-3-one Williams also reported a lower observed density, 1.7 gm. cm.\(^{-3}\) than calculated density, 1.8 gm. cm.\(^{-3}\) but still in good agreement with the figures reported above, as would be expected for such chemically similar compounds.

3. X-RAY PHOTOGRAPHY

All diffraction data were recorded photographically using X-rays from a fine focus copper target and Philips generator type PW 1009. The X-ray tube was run at 35 k.V. and 20 m.a. but lacked specific stabilization equipment. Though some fluctuations in the tube current were occasionally observed, no serious errors in the resulting photographic intensities are believed to have arisen from this cause as all reflections would have been affected approximately equally with the exposure times used.

Crystals for X-ray photography were selected after examination under the polarizing microscope and were readily aligned along the most prominent axis which it was found corresponded with the shortest axis, the unique threefold axis of the crystallographic unit cell. The crystals used for photography were generally cut from larger chunky crystals to give approximately cuboid crystals lengthened along the short axis direction.

All intensity photographs were taken with nickel
filtered CuKα radiation (λ = 1.5418 Å) using a Nonius integrating Weissenberg camera. The full intensity range of all reflections was covered by using multiple film packs of no more than six films. Some additional supplementary intensity photographs were also taken using a non-integrating Unicam Weissenberg camera and a Supper precession camera was also used to obtain accurate cell dimensions.

Several different crystals had to be used to collect all the required intensity data, as the crystals seldom lasted longer than the time to collect more than two intensity layers. Many crystals which were photographed were rejected immediately and a number of other crystals, initially acceptable, deteriorated so rapidly that intensity photographs were ruined by heavy powder lines and streaky spots. Approximately five months of continuous photography were necessary before an adequate set of intensity data was collected. This was achieved using six different crystals which varied in cross-section from 0.2 x 0.2 mm.s to 0.4 x 0.45 mm.s for the cross-section perpendicular to the X-ray beam. The crystals which had an average length of 0.45 mm.s were fully bathed in the X-ray beam.

The linear absorption coefficient, μ, for C₁₀H₁₄O₃Br₂ with CuKα radiation is 93.0 cm⁻¹9(c) and absorption corrections were made treating the crystals as cylinders of radius \( r = \left( \frac{b}{\pi} \right)^{\frac{1}{2}} \) where a and b are the cross-sectional
TABLE 2.3

TABLE OF CRYSTALS USED IN STRUCTURE ANALYSIS

<table>
<thead>
<tr>
<th>Crystal Number</th>
<th>Crystal size in microscope graticule units</th>
<th>Weissenberg layers Photographed</th>
<th>Radius for Absorption Corrections</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0 x 2.0 x 2.0</td>
<td>hk0</td>
<td>.170 mms.</td>
</tr>
<tr>
<td>2</td>
<td>4.5 x 1.5 x 2.5</td>
<td>hk1</td>
<td>.155</td>
</tr>
<tr>
<td>3</td>
<td>3.0 x 1.0 x 1.5</td>
<td>hk2</td>
<td>.103</td>
</tr>
<tr>
<td>3</td>
<td>3.0 x 1.0 x 1.5</td>
<td>hk3</td>
<td>.103</td>
</tr>
<tr>
<td>4</td>
<td>3.0 x 2.0 x 2.0</td>
<td>hk4</td>
<td>.169</td>
</tr>
<tr>
<td>5</td>
<td>2.5 x 1.5 x 1.5</td>
<td>hk5</td>
<td>.127</td>
</tr>
<tr>
<td>6</td>
<td>3.0 x 2.0 x 2.0</td>
<td>hk6</td>
<td>.170</td>
</tr>
<tr>
<td>7</td>
<td>3.0 x 2.0 x 2.0</td>
<td>0kl</td>
<td>.170</td>
</tr>
<tr>
<td>7</td>
<td>3.0 x 2.0 x 2.0</td>
<td>1kl</td>
<td>.170</td>
</tr>
</tbody>
</table>

Calibration of the microscope showed each graticule unit = 0.15 mms.
dimensions. The optimum radius of a cylindrical crystal is about 1.5 \mu which in this case is 0.15 mm. and most of the crystals used were about this thickness or a little less as indicated in table 2.3. Owing to the substantial scattering of the heavy bromine atoms in the crystal, exposure times of about 20 hours were usually sufficient to obtain a good photograph. This time corresponded to the time taken to complete one cycle of integration on the Nonius camera. Following Wiebenga\textsuperscript{10} the integration limits were chosen so that the spots on the integrated film were spread out at least twice their own unintegrated breadth and depth to give a central "plateau" area with contributions from all parts of the original spot. Despite the extra care and longer exposure times needed for integrated photographs, depending on the chosen integration limits, the reward in improved quality made integration well worth while.

Integration was particularly successful in overcoming the problem of contracted and to a lesser extent the problem of extended spots encountered in the upper level photographs using the Weissenberg equi-inclination method.

Calculation from the unit cell dimensions indicates that using CuKα radiation 3825 independent reflections are accessible and of these 2,600 independent reflections were photographed or 68\%, some 280 of which were too weak to be
observed by instrument or eye. A substantial number of the outer reflections were only just observable and were too weak to be measured densitometrically. Unobserved reflections were recorded at 2/3 the minimum observable intensity for the appropriate layer. All reflections whose intensities were used in the structure analysis, were collected by rotation about the c axis. The reciprocal lattice layers hkl to hkl inclusive were recorded in this manner though the hkl photographs, being very weak and of rather poor quality, were not measured. This data represents the maximum number of layers obtainable by the equi-inclination Weissenberg method since the equi-inclination angle required for the hkl photograph was $44.3^\circ$, just under the instrumental limit of $45^\circ$.

Correlation data about the long axes was obtained from Weissenberg photographs of the 0kl and 1kl layers. These were of rather lower quality, especially the 1kl photographs, owing to the time necessary to align the crystal along the rather elusive long 20.3 Å axes, during which the crystal had markedly deteriorated. Negligibly few reflections of 1 index greater than 5 were observed on either the 0kl or 1kl photographs and therefore contributed no additional data. Both the 0kl and 1kl reflection intensities were measured but were used principally for correlation of the c axis data. In addition however the 0kl and 1kl photographs proved invaluable in solving some rather subtle problems
of indexing associated with the rather unusual symmetry and pseudo-symmetry of the diffraction pattern.

4. MEASUREMENT OF X-RAY INTENSITIES. COMPARISON OF DENSITOMETER AND VISUAL MEASUREMENTS.

Since it was likely that the successful determination of the structure, especially as far as the location of carbon and oxygen atoms was concerned, would depend on the availability of accurate intensity data, the author decided to investigate more sophisticated means of measurement than the usual visual estimation with an intensity strip. An Adam-Hilger microdensitometer employing a photo-electric cell to measure changes in transmission of light from a constant source through a photographic film, as recorded by a sensitive galvanometer, was found to give reasonably reproducible results under constant conditions. The integrated intensity films were held flat between two thin glass plates. By means of a wedge and variable slit only the central plateau region of the integrated spot was allowed to transmit light to the photo-electric cell. This transmission area was kept constant for any layer set of intensities. Care was taken to ensure that extraneous light was excluded by surrounding the light path to the photo-electric cell with black paper, excluding direct daylight and avoiding use of nearby artificial light
sources. The apparatus was allowed to warm up over a period of twenty minutes, during which time most of the light-source variation and detector drift occurred.

Measurements were made by recording the average transmission of the immediate background, \( t_B \), of the reflection spot compared with the minimum transmission of the spot itself, \( t_s \). The galvanometer deflection is assumed to be a linear function of transmission and the zero of the scale is set for zero transmission i.e. with the light beam shut right off. Small fluctuations in the reading for zero transmission frequently occurred and this was checked after each reading of film transmission and adjusted if necessary. A graph of \( \log_{10} \frac{t_B}{t_s} \) against exposure time gave a straight line using all the spots on a standard visual intensity strip. Since the exposure times and therefore the degree of blackening of the spots on the intensity strip are a direct measure of X-ray intensity, the linearity of the graph showed that both the intensity strip and densitometer were measuring the same quantity. Later remeasurements of the photographic data showed in fact that the visual and densitometer measurements gave almost identical results in the structure analysis, though the author had anticipated rather better results using the densitometer. Improved densitometers and other similar instruments now available commercially undoubtedly would yield more accurate
intensity measurements than obtainable by visual estimation.

Initially all intensity data, including the \( a/h \)
correlation data, were measured by densitometer except
where the intensities were too weak to give changes in
the transmission appreciably different from the adjacent
background of the reflection on the film. The remaining
weaker reflections, to which the human eye is noticeably
more sensitive than most instruments, were measured by
the usual intensity strip and correlated with the
densitometer data by using reflections measured by both
methods. For many purposes in the structure analysis
as indicated later, only the stronger, densitometer
measured, reflections were used, as these were considered
to be more accurate. At a much later stage all the data
were completely remeasured by visual estimation using a
standard intensity strip, in order to verify that the
densitometer measurements had been accurately made but as
indicated both sets of data gave very similar results.
The author believes that while the densitometer can
differentiate the blacker spots more readily and accurately
than the human eye, the advantage is lost in the measure-
ments of weaker spots which of course includes the second
and third measurements generally possible with intense
reflections on the underlying films. In addition the
densitometer measurement proved to be a frustratingly
slow process partly due to the time taken to identify in the darkness the required reflection for measurement correctly, and partly the difficulty in obtaining a reliable reading of the average background for each reflection.

An analysis and comparison of the two methods of intensity measurement is made and discussed in Appendix IV.
Fig. 3.1(b)

hk5 PHOTOGRAPH

(showing the breakdown of the pseudosymmetry)
CHAPTER III

SPACE GROUP DETERMINATION AND UNIT CELL DIMENSIONS

1. SPACE GROUP DETERMINATION

On taking a single crystal rotation photograph with a crystal mounted parallel to the most prominent morphological axis, it was found that the crystal was readily aligned along a short 7.0 Å crystallographic axis. Transfer of the crystal to the Weissenberg camera with rotation about the same axis gave zero layer photographs showing two central point rows with equal spacing 60° apart and two-dimensional Laue symmetry 6mm characteristic of both hexagonal and trigonal crystals. There were no systematic absences and close visual inspection showed no observable departure from this symmetry so that all pairs of reflections of the form h00 and kh0 were apparently equal.

Higher layer equi-inclination photographs about the same c axis also showed no systematic absences and all the higher layer photographs appeared to conform to $\overline{3}m$ (3-â) Laue symmetry. On close examination of good quality photographs of the outermost layers in particular (see fig 3.1(b) showing a reproduction of the hk05 photograph) it became apparent that the photographs possessed only pseudo mirror symmetry since a number of obvious exceptions
### TABLE 3.1

#### TABLE OF POSSIBLE TRIGONAL SPACE GROUPS

<table>
<thead>
<tr>
<th>Space Group Number</th>
<th>Symbol</th>
<th>Point Group</th>
<th>Space Group</th>
<th>General Multiplicity</th>
<th>Conditions limiting possible Reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>143</td>
<td>P3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>None</td>
</tr>
<tr>
<td>144</td>
<td>P3₁</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0001:1=3n</td>
</tr>
<tr>
<td>145</td>
<td>P3₂</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0001:1=3n</td>
</tr>
<tr>
<td>149</td>
<td>P31₂</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>None</td>
</tr>
<tr>
<td>150</td>
<td>P32₁</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>None</td>
</tr>
<tr>
<td>151</td>
<td>P3₁₂</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>0001:1=3n</td>
</tr>
<tr>
<td>152</td>
<td>P3₂₁</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>0001:1=3n</td>
</tr>
<tr>
<td>153</td>
<td>P3₂₁₂</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>0001:1=3n</td>
</tr>
<tr>
<td>154</td>
<td>P3₂₂₁</td>
<td>32</td>
<td>3₂</td>
<td>6</td>
<td>0001:1=3n</td>
</tr>
</tbody>
</table>

**Note:** All other trigonal space groups, which involve either inversion or mirror symmetry or which are based on a rhombohedral lattice, have been excluded from this table.
to the requirement for the hk0 and kh0 reflections to be equal, were clearly observable. The symmetry is illustrated in the reciprocal lattice diagram fig. 3.1(a) and is discussed further in the following chapter.

From this information it followed that the rotation axis was threefold and further since the photographs of all layers were superimposable, it was deduced that the threefold symmetry was based on a hexagonal lattice rather than a rhombohedral lattice, if a primitive unit cell was to be chosen. The space group therefore had to be trigonal based on a hexagonal lattice.

Since the compound was known to be optically active, it followed that all trigonal space groups involving inversion or mirror symmetry could be immediately eliminated together with all rhombohedral space groups. In addition, since density measurements indicated nine molecules in the unit cell, those remaining space groups (see table 3.1) with general multiplicity six, were extremely improbable.

The only trigonal space groups remaining after these exclusions were P3, P31, and P32 and a zero layer photograph about one of the other equal, non-unique axes was therefore required to determine the presence or absence of a screw axis. The 001 photograph (fig. 4.1) however showed 001 reflections present only for l = 3n, n an integer, confirming the existence of a threefold screw axis. There was a
rather faint indication of a "forbidden" 004 reflection on one set of integrated photographs but not on a longer exposed set of unintegrated photographs. This was considered to be either spurious since it was not quite in the expected position, or else an example of the Remlinger 11 effect and in view of the solution of the structure assuming the threefold screw axis, there is little doubt that a right choice was made. Having verified the existence of a screw axis it was possible to choose quite arbitrarily one of the enantiomorphous space group pairs $P_3_1$ or $P_3_2$, which differ only in that the first has an anticlockwise screw axis and the second a clockwise axis, with respect to the same origin. Rigorous assignment to one or other can be made only by determination of the absolute configuration of the molecule, which is discussed further in Chapter VII. Thus of the enantiomorphous pair $P_3_1$ and $P_3_2$, $P_3_1$ was arbitrarily chosen and all calculations have been made assuming that symmetry.

Space group $P_3_1$ (and $P_3_2$) has no special positions and hence all atoms must lie in general positions of multiplicity three and the number of molecules in the unit cell must therefore be an integral multiple of three, if the rather unlikely possibility of disordering is excluded.
2. UNIT CELL DIMENSIONS

There are only two independent unit cell parameters to be determined in trigonal space groups, the length of the two equal axes at $120^\circ$ to each other and the length of the unique threefold axis perpendicular to these. Accurate dimensions were obtained from zero layer precession photographs by measuring the separations of all the various parallel rows of reflections and averaging the results which are tabulated below with the other crystal constants.

\begin{table}
\centering
\caption{Table of Crystal Constants}
\begin{tabular}{ll}
\hline
a = 20.35 \pm 0.05 & a$^*$ = 0.876 \pm 0.002 (dimensionless) \\
c = 7.00 \pm 0.03 & b$^*$ = 2.103 \pm 0.009 (dimensionless) \\
v = 2510.4 & v$^*$ = 0.0003963 \, \text{Å}^{-3} \\
D_x = 1.85 \pm 0.05 & D_c = 1.84 \, \text{g.m. cm}^{-3} \\
FW. \quad 10H\cdot Br_2 & = 310 \\
\mu & = 99.0 \, \text{cm}^{-1} \\
\hline
\end{tabular}
\end{table}

The number of molecules in the unit cell $z$ is given by

$$z = \frac{D_x \cdot V \cdot N}{FW}$$

where $N$ is the Avogadro number.

Hence $z = 9.02$ and the number of molecules in the unit cell is nine which on substitution back in the equation gives $D_c$ as tabulated above.
CHAPTER IV

THE TRIGONAL SYSTEM

1. TRIGONAL SYMMETRY AND INDEXING OF THE PHOTOGRAPHS.

In any non-orthogonal crystal system one of the most vexing problems encountered is that of indexing the X-ray reflections in a rigorous and unambiguous manner. Particularly is this so when only Weissenberg data is available, and the situation is aggravated even further when the available data has been collected from a number of different crystals of unknown, relative orientations. All of these problems, together with that of pseudo-symmetry occurred in the indexing of the photographs of the trigonal crystal 2,10-dibromo-pinac-3-one.

In space group $P3_1$, as in all trigonal space groups based on a hexagonal lattice, the non-unique axes $a$ and $b$ are equal. Thus on the first set of $hk0$ photographs it is quite arbitrary which of the identically spaced row of axial spots will be given index $h$ and which $k$; but in any succeeding layer, e.g. $hk1$, $hk2$ etc., the axes must be correctly labelled so that all the layers have the same relative orientation, even though the $h$ and $k$ axial rows are again identical in spacing (but not in intensity). This correlation is relatively straightforward where the same crystal is used for all photographs, since by keeping
Fig. 3.1(a)

RECIPROCAL LATTICE DIAGRAM FOR THE TRIGONAL SYSTEM

(The threefold 1 axis passes through the origin perpendicular to the diagram.)

- $x = \text{Mirror set of reflections } hkl$
- $x = \text{General set of trigonal equivalent reflections } hkl$
- $x = \text{Mirror set of reflections } hkl$
- $x = \text{Approximately equal to the above set}$
- $x = \text{Reflections before index change}$
- $x = \text{Reflections after index change (} hkl \uparrow\text{)}$
the crystal and camera oscillating over the same range and increasing the equi-inclination angle in the same sense, no ambiguity need arise. In this investigation, owing to crystal deterioration, almost every layer set had to be collected with a different crystal so that unambiguous correlation, and with it correct indexing, of the photographs was only possible by reference to the 0kl and 1kl photographs taken about one of the non-unique axes.

In the trigonal system and all hexagonal lattices, it is often convenient to introduce a fourth index \( i \) such that

\[ h + k = -i \]

and the reflection hkl is now written hkil, in which only two of the three indices \( h, k \) and \( i \) are independent. With this convention the general threefold equivalence of trigonal reflections can be expressed by

\[ \text{hkil} = \text{ihkl} = \text{kihl}. \]

The inter-relationship of \( h, k \) and \( i \) is shown in the reciprocal lattice diagram fig. 3.1(a).

If Friedel's law, from which it follows that \( \text{hkil} = \overline{\text{hkil}} \), can be assumed (and strictly speaking as elaborated in Chapter VII this is not exactly true), then each reflection can be given six equally valid sets of
Fig. 4.1: Okl and 1kl Photographs (showing the pseudosymmetry)
Miller indices. Further confusion arises from the fact that these six reflections are very similar in intensity to the six mirror related reflections given by

$$hkl = ikl = hikl$$

see fig. 3.1(a) and as has been already pointed out, the initial choice of $h$ or $k$ is quite arbitrary.

By making an arbitrary assignment of positive and negative $k$ and $l$ values on the $0kl$ photographs, the author was able to label consistently the various $h$ and $k$ axes on the $hko$, $hkl$, ..., $hk5$ photographs. It was believed that this in itself was sufficient to enable all the indexing to be made on a thoroughly consistent basis. It was only at a considerably later date when a solution of the Patterson function was being tested, that it became apparent that it was also very relevant which of the alternative $h$ and $k$ axes were taken together to define the $h + k + l$ zone of reflections. This was eventually resolved in an entirely satisfactory manner by reference to the previously unused, unindexed $1kl$ photographs, which were however of somewhat poorer quality.

It was found convenient for various reasons such as computer program restrictions, to choose the indices such that $k$ and $l$ were always positive or zero for the $c$ axis Weissenberg photographs. Thus in a general layer $c$ axis photograph the two adjacent independent $60^0$ zones of reflections were described by $hkl$ and $\bar{h}kl$. To distinguish
Fig. 4.2

hk$^1$ Photographs correctly and incorrectly indexed

hk$^1$ incorrectly indexed  hk$^1$ correctly indexed
these two adjacent zones for all layers, reference was made to the 1kl photographs, where it was readily observed that all the hkl reflections were found on one half of the Weissenberg film and the hkl reflections on the other half of the film. Only in this way was it possible to assign unambiguous indices to all reflections in a completely consistent and rigorous manner, since both halves of the 0kl photographs were identical. The correctly indexed 0kl and 1kl photographs are shown in fig. 4.1.

2. CORRECTION OF INDEXING ERRORS

In fig. 4.2 the correctly indexed hkl Weissenberg photographs are compared with the wrongly indexed photographs and it can be seen that the error in choosing the wrong h axis to go with a particular k axis, was one of correlation rather than identification, since the two h axial rows are equivalent in every respect. The effect of the wrong indexing was rectified by applying the conversion

\[ \bar{h}k\bar{l} = hkl, \]

which as can be seen from the reciprocal lattice diagram fig. 3.1(a) effects the desired change and produces the correctly indexed reflection or one exactly equivalent to it. Thus for example, the reflection indexed 1234 should have been indexed as \( \bar{1} \bar{3} \bar{2} \bar{1} \) and the conversion
above produces the reflection $\overline{2} \overline{1} 3 1$ but

$$\overline{2} \overline{1} 3 1 = 3 \overline{2} \overline{1} 1 = \overline{1} \overline{3} 2 4,$$

as shown in fig. 3.4(a), which also shows how on account of the repetition every 120°, an h axis is exactly equivalent to a -h axis and k axis to a -k axis.

3. EXPLANATION OF THE PSEUDOSYMMETRY

Following the solution of the Patterson function it was found that the eighteen bromine atom positions all closely approximated to either $P3_1 12$ or $P3_1 21$ symmetry. Six bromine atoms were lying approximately in general positions of multiplicity six, and the remaining twelve in special positions of multiplicity three as shown in fig. 4.3(b) which shows the bromine atom arrangement in projection. The arrangement may be compared with the exact requirements of space groups $P3_1 12$ and $P3_1 21$ as shown in fig. 4.3(a).

Thus even though the molecules themselves could not possibly be described by the higher symmetry involving a twofold axis, the principal diffracting components could be so described by the higher 3m symmetry, despite the fact that two space groups were involved. The near-perfect, higher symmetry observed on the hk0 photographs is not surprising, since the z coordinates of the bromine atoms, which differed slightly from the higher symmetry requirements, would not be relevant.
Fig. 4.3(a)

Space group symmetry of P₃₁̄₂ and P₃₂₁

Coordinates of equivalent positions

**P₃₁̄₂**

- \( x, y, z \)
- \( y, x - y, \frac{1}{3} + z \)
- \( y - x, x, \frac{2}{3} + z \)
- \( y, x, \frac{2}{3} - z \)
- \( x, y, \frac{5}{6} \)
- \( x, 2x, \frac{1}{6} \)
- \( 2x, -x, \frac{1}{2} \)
- \( x, x, \frac{1}{3} \)
- \( x, 2x, \frac{2}{3} \)
- \( 2x, -x, 0 \)

**P₃₂₁**

- \( x, y, z \)
- \( y, x - y, \frac{1}{3} + z \)
- \( y - x, x, \frac{2}{3} + z \)
- \( y, x, \frac{2}{3} - z \)
- \( y, x, \frac{5}{6} \)
- \( 0, x, 1/6 \)
- \( x, x, \frac{1}{3} \)
- \( x, 0, \frac{1}{2} \)
- \( 0, x, \frac{2}{3} \)
- \( x, x, 0 \)
HEAVY ATOM POSITIONS IN PROJECTION
DOWN THE C AXIS

(showing the origin of the pseudosymmetry observed on the photographs)
because the $hk0$ intensities are independent of the $z$
coordinates. As the magnitude of $l$ increases, any
discrepancies from the higher symmetry in terms of $z$
coordinates are magnified and become more obvious in
the photographs. The pseudo-symmetry is clearly
observed in fig. 4.1 showing the $0kl$ and $1kl$ photographs,
where the differences between the $0kl$ and $0\bar{k}l$ ($= k0l$)
reflections and the similarly related $1kl$ reflections,
are hardly discernible. In fig. 4.2 the $h\bar{k}l$ and $k\bar{h}l$
reflections are also seen to have virtually undistinguish-
able intensities.
CHAPTER V

STRUCTURE DETERMINATION

1. INTRODUCTION

It is immediately apparent from consideration of the formula \( \text{C}_{10} \text{H}_{14} \text{OBr}_2 \), that for X-ray diffraction purposes 2,4-dibromo-pinacolone-3-one is very heavily dominated by the two bromine atoms in the molecule. The heavy-atom factor \( r \), is defined by

\[
r = \left[ \frac{x(f_H^2)}{\sum x(f_L^2)} \right]^{\frac{1}{2}},
\]

where \( f_H \) is the number of electrons in the heavy atom and \( f_L \) the number in the light atoms, and the summations are over all the heavy and light atoms respectively. For \( \text{C}_{10} \text{H}_{14} \text{OBr}_2 \) \( r = 2.4 \).

It is generally considered\(^1\)\(^2\) that the ratio of heavy-atom to light-atom contribution should be not less than 1.0 if heavy-atom, Patterson function methods are to be employed successfully in the structure analysis.

In the present case where \( r = 2.4 \), the heavy-atom contribution to the structure factors is on the average very large and thus it can be assumed that in principle the heavy-atom locations can be determined with some precision by Patterson methods. Unfortunately it is also true that the positions of the light atoms, which
in this case are carbon, oxygen and hydrogen atoms, can not be determined with anything approaching the same degree of precision, on account of their relatively small contributions to the structure factors. For these reasons a mono-bromo derivative would have been preferable for this analysis especially if the main interest had centred on the precise geometry of the pinane skeleton alone. Since no stable, crystalline, mono-bromo derivatives were available and of the dibromo derivatives the 2,10-compound was the most stable and also had interest in its own right as a dibromo compound, there was little alternative other than the reputedly less stable 2,4-dibromo compound, which was subsequently investigated by Dr P.P. Williams.

When it was found that 2,10-dibromo-pinane-3-one had a rather large unit cell containing nine molecules, it became apparent that the only practicable method of structure solution available under conditions of limited computer facilities, (an IBM 1620 with 40K storage) was the Patterson heavy-atom method. No Patterson superposition programs were available but it was thought there was still a reasonable chance, using analytical techniques, of solving the three-dimensional Patterson function for the 18 bromine atoms in the unit cell, from which the remaining light atom positions could be located using standard Fourier techniques.
Sim $^{12}$ has shown that for $r = 2.4$, $99\%$ of the reflections have their phase angles determined with an error of less than $60^\circ$, and $73\%$ of the phase angles are determined with an error of less than $20^\circ$. Thus provided the heavy-atom positions could be located accurately, it appeared likely that, given good intensity data, the light-atom positions would follow fairly readily from standard electron density Fourier analysis. Regrettably not only did the Patterson function prove particularly difficult to solve, as was partly anticipated, but also the light-atom positions did not immediately follow once the bromine atoms had been located, which was not as expected. The reasons, as far as can be determined, for these difficulties are discussed in the subsequent sections.
2. DATA PREPARATION

To prepare the intensity data for structure determination, full use was made of a comprehensive collection of computer programs which have been built up around the University of Canterbury's IBM 1620 computer. Many of these programs have already been described by this author and others\textsuperscript{13, 14, 15} or else are of a relatively trivial nature. Programs falling within either of these categories will not be discussed further in this work. This author was concerned in the writing and modification of a number of programs some of which were peculiar to the needs of this investigation of a trigonal structure. In Appendix II these are elaborated further, together with the author's major program addition, CAXR\textsuperscript{16}, an intensity data processor and error assignment program. The latter program though considerably modified by Elder\textsuperscript{17}, was invaluable in assisting the author to handle the very large quantities of both densitometer and visually estimated photographic intensity data involved in this analysis and the program has been extensively used in this department in both the earlier and present versions by a number of users.

All intensity data was recorded directly onto data coding sheets, punched and processed through CAXR 13 which produced output suitable for use by the L.P. and
absorption corrections program CAXR2. The absorption corrections were made as for cylindrical crystals, which was a reasonable approximation for the c axis intensity data used in the analysis, as the crystals were somewhat elongated in the c direction, but a rather rough approximation for the 0kl and 1kl data, which were however only used for correlation purposes.

Correlation of the intensity sets was carried out using program CAXR4 which sorted out reflections common to any two sets of data and calculated the average ratio of intensities for all ratios within any specified range. A satisfactory correlation was obtained with both the 0kl and 1kl reflection data. The data was converted to a common scale after correlation by means of the author's own CAXR4 L.P. output scalar and index conversion program. At this stage it was also possible to rectify any systematic indexing errors as occurred with the 0kl intensities (see previous Chapter IV.2).
3. CALCULATION OF THE PATTERSON FUNCTION

The coefficients for the calculation of the three-dimensional Patterson function were prepared using CAXR 5\textsuperscript{20}, a program which prepares sharpened Fourier coefficients with origin peak removal as required. "Normal" sharpened coefficients were used using an overall artificial temperature factor of $3.0^9 A^2$ and 93\% removal of the large origin peak. CAXR 5 required a plot of local average intensity for the various zones of reflections zoned by $\sin \theta/\lambda$ values and this was carried out by means of the intensity statistics program CAXR 9\textsuperscript{21}.

Once the Patterson coefficients had been calculated as desired for all the 2,600 reflection data, it was necessary to generate all the equivalent data using a small program written by the author, since the Fourier summation program ICO\textsuperscript{22} effectively treats all space groups as $P\bar{1}$ or $P\bar{1}$ and requires as input on the one punched card the four (or eight for a non-centrosymmetric Fourier) terms arising from combinations of the amplitudes of the reflections $hkl$, $\bar{h}k\bar{l}$, $hk\bar{l}$ and $h\bar{k}\bar{l}$ which in general in the trigonal system as in the triclinic system are quite independent. Thus the 2,600 independent data plus the 5,200 equivalent data generated by the threefold symmetry, were all required before the Patterson Fourier input deck could be prepared. The
task of condensing the large data deck as outlined above, was carried out by program CAXR 6\textsuperscript{23}, which produced a Fourier input deck of approximately one quarter the size.

\textbf{4. SOLUTION OF THE THREE-DIMENSIONAL PATTERTSON FUNCTION}

As is well known, the function defined by Patterson\textsuperscript{21,25} is

\[ P(u, v, w) = \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} p(x, y, z) p(x + u, y + v, z + w) \, dx \, dy \, dz, \]

represents a variable vector which sweeps out the whole of the unit cell of volume \( V \) and which takes finite values only when both ends of the vector are points of positive electron density. The larger the electron density \( p \) at the points \( (x, y, z) \) and \( (x + u, y + v, z + w) \), the larger is the product of the electron density, and the larger the value of the Patterson function \( P(u, v, w) \).

In a heavy atom structure such as the present one, the quantity \( P(u, v, w) \) is largest for bromine-bromine vectors where \( 35 \times 35 = 1225 \) electrons are involved compared with 280 electrons for a bromine-oxygen vector, the next largest vector peak. Thus 18 atoms gave rise to \( 18^2 \) vector peaks of which 18 peaks arising from vectors between an atom and itself are coincident at the origin to form the large origin peak. To enable a more useful scale to be used in the output from the calculation, as
indicated previously, the origin peak was largely removed.

The calculation was performed using Lipson and Beevers reformulation of the Fourier series representation of the Patterson more commonly stated as

\[ P(u,v,w) = \frac{1}{V} \sum_{h,k,l=0}^{+\infty} |F|^{2}(hkl) \cos 2\pi(hu + kv + lw) \]

where the \(|F|^{2}(hkl)\) were the appropriately sharpened, modified coefficients calculated from the intensities \(I(hkl)\) of the various hkl reflections.

In 2,4,6-dibromo-pinene-3-one there are two independent bromine atoms in each molecule and three independent molecules in the unit cell, giving a total of 18 heavy atoms in the unit cell of which six are strictly independent. From this it follows that in the Patterson there will be

\[ \frac{18 \times 17}{3 \times 2} = 51 \]

strictly independent, non-origin vector peaks. The factors of three and two in the denominator allow respectively for the trigonal symmetry and the inevitable centrosymmetry of the Patterson function. The space group symmetry of the Patterson vector set is \(P3\) which is derived by adding a centre of symmetry to the translation-free residue.
of the actual space group $P3_1$ in real space. Thus all peaks in the Patterson occur in sixes, three at the level $w$ and three centrosymmetrically disposed at the level $-w$.

It therefore followed that any valid solution of the Patterson would predict the position of 54 independent vector peaks and that all of these must be accounted for by actual observable peaks of the correct height in the Patterson vector map, allowance being made for any peaks which might by chance be doubled or tripled etc. In general all vector peaks would be expected to be single weight peaks in this non-centrosymmetric structure and double weight or higher peaks would only arise by chance caused by other pairs of bromine atoms lying in very similar orientations or an accumulation of equally oriented light-atom vectors. The chance of light-atom vectors such as those between bromine and oxygen or bromine and carbon seriously altering the height of a bromine-bromine vector peak was felt to be very remote as in general the separations and orientations in this un-symmetrical compound would be very different; the likelihood of bromine-bromine vectors being approximately coincident however was much greater and to be expected, as was indeed found.

In view of the infinitesimal chance of resolving
the 51 independent peaks in projection, no attempt was made to solve the Patterson in projection. In three dimensions however providing that the Patterson can be calculated at sufficiently fine intervals, almost all heavy-atom heavy-atom peaks should be well resolved. It has been shown that for CuKa radiation where all reflections up to Bragg angle $\pi/2$ are observed the limit of resolution of the X-ray goniometer is $0.6\lambda/2$ or $0.45 \AA$. In the present case the data used for the Patterson did include a large number of high angle reflections so that an interval as fine as $0.2 - 0.3 \AA$ would have been justified to enable vector peaks to be adequately and meaningfully resolved. The finest interval possible with the available computer program was $1/100$ of the unit cell edge but owing to practical limitations of the computer, intervals of $1/50$, $1/50$ and $1/20$, in the $x$, $y$ and $z$ directions respectively, were taken corresponding to intervals of $0.40 \AA$ in the $x$ and $y$ directions and $0.35$ in the unique axis direction. Though finer intervals would have been preferable, those chosen gave adequate resolution to enable the analysis to proceed. Since the Patterson function is always centrosymmetric, it was calculated only for the unique half of the unit cell. It was found neither practical nor particularly desirable to separate out as well the unique portion of the vector
map without the other equivalent areas generated by the trigonal symmetry, which cannot be simply specified using normal coordinates with program IGR 1.

The analytical solution of the three-dimensional Patterson function is greatly simplified using the approach of Barker 26, later elaborated by Buerger 27. Barker pointed out that in space groups containing certain symmetry elements, certain planes or lines within the Patterson unit cell will have concentrations of vector peaks with these planes as lines. Buerger 27 has further shown how these may be used as a rapid means of distinguishing many space groups. In space groups P312 and P3121 by which the bromine atoms were later found to be approximately described Buerger 28 has shown planar concentrations also occur respectively for x, x, z and x, 2x, z and the planes at 120° to these. Examination of the Patterson (see figs. 5.4(a) and 5.4(b)) showed that these planes (or lines with respect to sections on z) showed a considerable concentration of peaks.

In space group P31 the presence of the 31 screw axis leads to a Barker section at z = 1/3 where z is the unique axis direction. This is readily seen from the coordinates of the equivalent positions:

\[ x, y, z; \bar{y}, x-y, z + 1/3; \quad y-x, \bar{x}, z + 2/3; \]

which shows the vectors between atoms related by the
screw axis will all lie on the Harker section \( z = \frac{1}{3} \) and will be duplicated centrosymmetrically on section \( z = \frac{2}{3} \). If the screw axis had been a pure threefold axis, the Harker section would have occurred on section \( z = 0 \) and there would have been no reason for there being any concentration of peaks on section \( z = \frac{1}{3} \) except by chance. Examination of the \( z = \frac{1}{3} \) Harker section, fig. 5.4(a), showed it to have a large concentration of peaks, as would be expected if it were in fact a true Harker section. Since the number of peaks was considerably greater than the eighteen required for the Harker section, it was evident that a number of bromine atoms apart from those related by the screw axis had \( z \) coordinates which accidentally, i.e. in a manner not required by the symmetry of the space group, differed by \( z = \frac{1}{3} \).

The problem of deriving the fundamental set of six independent atoms from the 54 independent peaks in the Patterson which they generate, is considerably complicated by the fact that each of the 54 sets of peaks in the Patterson has in general six equally valid solutions. Three of these solutions are sets within space group \( \text{P}3_1 \) and the other three, centrosymmetrically related, are necessarily in space group \( \text{P}3_2 \). This arises simply from the inherent centrosymmetry of the Patterson leading to solutions in centrosymmetric pairs and the fact that the operation of inversion of a
Fig. 5.4(a)

HARKER SECTION, z = .33 OF PATTERSON

(Numbers refer to true Harker peaks)
set of points in space group $P_3_1$ leads to a set in $P_3_2$ and vice versa.

Since space group $P_3_1$ was arbitrarily chosen to work in, half of the solutions could therefore be rejected as they were incompatible with the chosen space group. The problem was thus slightly reduced to that of determining the six correct sets from the 30 solutions obtained from the ten independent sets of peaks observed on the Barker section. Any random or unsystematic selection process was clearly quite impossible since an enormously large number of choices were available. The ten sets of peaks occurring on or very close to the Barker section $z = \frac{1}{2}$, are shown in Fig. 5.4(a). Of these only four (numbered accordingly) proved to be genuine Barker peaks, although one of these, the largest peak on the section, was three peaks merged into one.

The nine molecules in the unit cell may be considered conveniently in terms of three groups of three molecules symmetrically disposed about the three independent screw axes in the unit cell. It was deduced that the three groups would all have rather similar arrangements within themselves from the fact that some peaks on the Barker section appeared to have been at least doubled in height. In addition some very high peaks had also occurred on section zero. If the peaks were genuinely doubled, then it was quite possible that
more than one of the solutions, or perhaps all three, from one independent set of Barker peaks would be required for the bromine atom positions. The large peaks on section zero suggested that some otherwise unrelated bromine atoms had similar z coordinates and the fact that these peaks occurred near to the threefold axes passing through the points \((\frac{1}{4}, \frac{3}{4}, 0)\) and \((\frac{3}{4}, \frac{1}{4}, 0)\), was highly suggestive of similar arrangements of atoms about two or more of the screw axes.

Consideration of the various possible bromine-bromine vectors suggested that the intramolecular vectors, joining the two bromine atoms within the three independent molecules would be among the shortest vectors. These vectors should be readily identified from those which occurred closest to the origin and within the range \(2.3 - 4.5\) Å, corresponding to the minimum and maximum separation possible of two bromine atoms joined to each other through a carbon-carbon bond. Since the two atoms within any one molecule could not be related by the screw axis, an intramolecular vector peak could lie on the Barker section by chance only, and this reduced the possibilities even further. In addition the three independent intramolecular vectors were expected to be of very similar length. If all the molecules were similarly oriented then coincidences
of the vectors would be expected with correspondingly higher peaks in the Patterson.

Examination of the Patterson, showed that only three sets of peaks at (0.22 0.11 0.20), (0.11 0.22 0.20) and (0.09 0.045 0.50) could account for the intramolecular vector, the first two sets giving peaks 4.1 Å from the origin, and the second 3.9 Å from the origin. The shortest vector was most likely to correspond to the intramolecular vector, (although all were equal to or greater than two Van der Waals bromine radii 3.9 Å) while the others were more likely to relate bromine atoms in different molecules.

Having made these assumptions, it next remained to test systematically the various solutions to find which pair of solutions could account for these prominent key vectors. Initially the largest Barker section peaks labelled 1 in Fig. 5.4(a) were taken to provide one set and other sets tested with it. Those peaks on the Barker section which lay on or near the special symmetry lines (x, x) (x, 2x) etc., and which included the set 1 above, were investigated first since they were characteristic of the pseudo higher symmetry.

After a great many possibilities had been tested analytically and by large numbers of structure factor calculations, using the hko reflection data, a two-dimensional solution was finally found which rapidly
### Table 5.4

**Independent Patterson Vector Peaks**

#### Heavy Atom Coordinates

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>y</th>
<th>x-y</th>
<th>z+1/3</th>
<th>y-x</th>
<th>x</th>
<th>z+2/3</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>0.958</td>
<td>0.894</td>
<td>0.135</td>
<td>0.106</td>
<td>0.063</td>
<td>0.468</td>
<td>0.937</td>
<td>0.042</td>
<td>0.302</td>
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<tr>
<td>B</td>
<td>0.996</td>
<td>0.813</td>
<td>0.680</td>
<td>0.157</td>
<td>0.153</td>
<td>0.013</td>
<td>0.947</td>
<td>0.004</td>
<td>0.347</td>
</tr>
<tr>
<td>C</td>
<td>0.591</td>
<td>0.226</td>
<td>0.530</td>
<td>0.772</td>
<td>0.363</td>
<td>0.863</td>
<td>0.638</td>
<td>0.409</td>
<td>0.197</td>
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#### Marker Peaks

<table>
<thead>
<tr>
<th></th>
<th>BR511</th>
<th>0.148</th>
<th>0.169</th>
<th>0.333</th>
<th>BR531</th>
<th>0.164</th>
<th>0.310</th>
<th>0.333</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>BR521</td>
<td>0.162</td>
<td>0.155</td>
<td>0.333</td>
<td>BR311</td>
<td>0.164</td>
<td>0.310</td>
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#### Other Peaks Occurring Near Section \( z = 0.333 \)

<table>
<thead>
<tr>
<th></th>
<th>0.508</th>
<th>0.357</th>
<th>0.318</th>
<th>0.196</th>
<th>0.540</th>
<th>0.349</th>
<th>0.848</th>
<th>0.438</th>
<th>0.340</th>
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<tr>
<td></td>
<td>0.190</td>
<td>0.663</td>
<td>0.314</td>
<td>0.502</td>
<td>0.163</td>
<td>0.353</td>
<td>0.307</td>
<td>0.505</td>
<td>0.323</td>
</tr>
<tr>
<td></td>
<td>0.990</td>
<td>0.480</td>
<td>0.329</td>
<td>0.184</td>
<td>0.386</td>
<td>0.358</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

#### Peaks Occurring Near Section \( z = 0 \)

<table>
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<tr>
<th></th>
<th>0.347</th>
<th>0.017</th>
<th>-0.015</th>
<th>0.029</th>
<th>0.353</th>
<th>-0.049</th>
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<td>0.333</td>
<td>0.007</td>
<td>0.692</td>
<td>0.306</td>
<td>-0.004</td>
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</table>

"Internal" Peaks Occurring Near Sections \( z = 0.11, 0.20 \) and \( 0.47 \)

#### A

<table>
<thead>
<tr>
<th></th>
<th>0.301</th>
<th>0.714</th>
<th>0.122</th>
<th>0.162</th>
<th>0.894</th>
<th>0.134</th>
<th>0.210</th>
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<td>0.800</td>
<td>0.780</td>
<td>0.212</td>
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<td>0.209</td>
<td>0.199</td>
<td>0.098</td>
<td>0.217</td>
<td>0.209</td>
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<tr>
<td></td>
<td>0.090</td>
<td>0.038</td>
<td>0.455</td>
<td>0.059</td>
<td>0.087</td>
<td>0.167</td>
<td>0.036</td>
<td>0.091</td>
<td>0.857</td>
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TABLE 5.4 (cont.)

REMAINING VECTOR PEAKS FROM ATOMS IN GROUPS A AND B

<table>
<thead>
<tr>
<th></th>
<th>.633</th>
<th>.334</th>
<th>.395</th>
<th>.186</th>
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<th>.272</th>
<th>.680</th>
<th>.515</th>
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<tr>
<td>.454</td>
<td>.694</td>
<td>.137</td>
<td>.342</td>
<td>.499</td>
<td>.196</td>
<td>.261</td>
<td>.398</td>
<td>.471</td>
<td></td>
</tr>
<tr>
<td>.405</td>
<td>.615</td>
<td>.150</td>
<td>.776</td>
<td>.520</td>
<td>.183</td>
<td>.358</td>
<td>.434</td>
<td>.483</td>
<td></td>
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</tbody>
</table>

REMAINING VECTOR PEAKS FROM ATOMS IN GROUPS A AND C

<table>
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<tr>
<th></th>
<th>.319</th>
<th>.667</th>
<th>.402</th>
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<th>.265</th>
<th>.326</th>
<th>.829</th>
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<tbody>
<tr>
<td>.772</td>
<td>.383</td>
<td>.441</td>
<td>.536</td>
<td>.786</td>
<td>.192</td>
<td>.638</td>
<td>.080</td>
<td>.475</td>
<td></td>
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<tr>
<td>.719</td>
<td>.282</td>
<td>.443</td>
<td>.443</td>
<td>.673</td>
<td>.190</td>
<td>.712</td>
<td>.120</td>
<td>.477</td>
<td></td>
</tr>
</tbody>
</table>

REMAINING VECTOR PEAKS FROM ATOMS IN GROUPS B AND C

<table>
<thead>
<tr>
<th></th>
<th>.595</th>
<th>.273</th>
<th>.464</th>
<th>.097</th>
<th>.548</th>
<th>.203</th>
<th>.729</th>
<th>.586</th>
<th>.130</th>
</tr>
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<tbody>
<tr>
<td>.227</td>
<td>.639</td>
<td>.464</td>
<td>.065</td>
<td>.484</td>
<td>.128</td>
<td>.780</td>
<td>.523</td>
<td>.205</td>
<td></td>
</tr>
</tbody>
</table>
converged on least-squares refinement to give an
R factor of 0.25. As anticipated the solution was a
rather symmetrical arrangement of the bromine atoms
in three basically similar groups of six atoms, two
groups of which were orientated one way and the third
group the opposite way as shown in fig. 4.3(b).
Again applying analytical methods and examining a
large number of possibilities, many of which were very
similar, z coordinates were derived which satisfied
all the requirements of the Patterson. Since the
origin is not otherwise defined in space group P3₁,
one bromine atom z coordinate served to define the
origin, so that only five of the z coordinates were
strictly independent, and on account of the symmetry,
it was possible to take initially three z coordinates
to be zero, deducing the remainder from the Patterson
requirements.

The most exhaustive test of the uniqueness of the
solution found was to calculate the positions of the
54 independent vector peaks generated by the six atoms
and to verify their existence in the Patterson in the
right location and of the right peak height. This
was done and the predicted positions of the 54 vector
peaks are tabulated opposite, table 5.4. These may
be compared with the actual positions of the peaks
observed in the three-dimensional Patterson itself as
Fig. 5.4(b)  
SECTION z = 0 OF PATTERSON
SECTION $z = 0.50$ OF PATTERSON
shown in Fig. 5.4(a) (b) and (c). A thorough investigation showed that all the 51 independent vector peaks could be located and no other major peaks remained which could possibly be described as representing a bromine-bromine vector. The likelihood of another solution existing which could not only exhaustively account for all the 51 predicted vector peaks but also give such a low \( R \) factor was remote indeed. It was reasonable to assume that a unique solution had been obtained and to continue the structure analysis on this assumption.

5. ELECTRON DENSITY MAPS

In the introduction to this chapter, it was stated that once the heavy-atom positions were known it was believed that the remaining light atoms would be located by standard Fourier procedures. Before any electron density maps were computed however, the bromine atom positions were refined by block-diagonal least squares, using Mair's SFLS program. Convergence was attained at an overall \( R = 0.28 \). For this and all subsequent structure factor calculations, the scattering factors used for bromine were those based on the T.F.D.9(c) model, corrected for the real part of the anomalous scattering effect. The scattering factors, used later in the analysis, for
carbon and oxygen were those obtained by the self-consistent field method with exchange effects taken into account.9(c)

Although it was believed very unlikely that the pinane skeletons would be fully resolved in projection, an electron density Fo synthesis was calculated in projection down both the short c and long a axes. Though the c axis projection revealed a substantial number of likely atom peaks, it proved uninterpretable. The a axis projection was even less promising. In the analysis of non-centrosymmetric structures by Fourier methods, considerable errors may arise if difference Fouriers are used, since the phase angle effectively used, \( \tan^{-1}(B_o/A_o) - \tan^{-1}(B_c/A_c) \), is the difference of two angles, each of which will be in error, and may be quite different from the correct phase angle. In the calculation the signs of \( A_c \) and \( B_c \) are invariably applied to \( A_o \) and \( B_o \), before taking the difference. By contrast in a centrosymmetric heavy-atom structure a large percentage of the phases are exactly correct since only signs (±1), need be determined, whereas in a non-centrosymmetric structure, all phases are in error, and a number in quite considerable error. Einstein33 described how the use of electron density difference maps in the non-
centrosymmetric structure $P_2\overline{3}Br_2$, led to confusing results. For these reasons most of the earlier work in this analysis was carried out using $F_o$ syntheses, where the effect of wrong phase angles is not quite so marked. At a later stage electron density difference maps were used and gave good resolution of the light atom peaks, owing to the fact that the trial structure, based on bromines alone, was sufficiently accurate to determine most of the phases with only small errors.

As indicated previously, to carry out Fourier summations using program ICR 1 22, it was necessary to prepare (in the case of triclinic non-centric functions), eight combinations of the terms $A(hkl)$ and $B(hkl)$ from the group of four reflections $hkl, \bar{h}kl, h\bar{k}l, \bar{h}\bar{k}l$, where $F(hkl) = A(hkl) + iB(hkl)$ etc. Owing to an error in the usual program, ICR 6, in handling the triclinic non-centric case, Peinfield and Elder 31 wrote a new triclinic Fourier input conversion program to prepare the terms correctly for ICR 1, and this program was used to prepare all input data for all Fourier summations calculated in this structure analysis.

In order to have a completely independent check of the new conversion program, a test calculation was made on a CDC 3600 machine using Blount's "Fourier" program 35.
Identical values of the electron density were obtained over a large range of points in the unit cell which confirmed that the new system at Canterbury calculated electron density maps for space group \( P1 \) correctly.

Because of the IBM 1620 limitations, it was not possible to generate the equivalent reflections from the independent data, sort them, and combine them correctly, all in a single program to fit into a 40K storage machine. The requirements in terms of both storage and speed are enormous, and the only practicable method was to first generate the equivalent reflections and then sort the 3,000 cards using a mechanical card sorter. This method was undoubtedly quicker than using the 1620 to sort the cards, but still a lengthy and at times a hazardous process with a sorter which was prone to jam and mutilate the cards.

Despite the fact that no advantage could be taken of the threefold symmetry of the space group in the Patterson calculations, or in preparing the electron density Fourier input, it was possible to calculate the electron density for the unique area only, since the screw axis causes all the independent atoms to be found in any third of the unit cell taken perpendicular to the unique axis. Sections were therefore taken on \( z \) from 0 to 0.35 at intervals of 0.05 and the full cell
evaluated in the x and y directions at intervals of 0.02. The intervals corresponded to $0.140 \times 0.140 \times 0.35 \AA$ for the x, y and z directions respectively.

6. LOCATION OF THE LIGHT ATOMS

Initially the three-dimensional $p_c$ map, assuming only isotropic bromine atom positions, was thought to be quite uninterpretable. There appeared to be a considerable number of likely atom peaks within bonding distance of each bromine atom or else having the same x and y coordinates of bromine atoms. For these reasons the bromine atoms were allowed to vibrate anisotropically, but after several cycles of least-squares refinement, there was negligible improvement in the $R$ factor, and the resulting electron density maps looked equally uninterpretable.

In order to obtain a plausible arrangement of the light atoms, it was decided to search the electron density map for the two carbon atoms C2 and C10 known to separate the two bromine atoms within each molecule and to have normal tetrahedral symmetry. Examination of the heavy-atom positions showed that symmetry restrictions and actual distance apart implied that any one bromine atom could be bonded in one of only two possible ways to other bromine atoms. Thus any two bromine atoms related by the threefold symmetry,
could not be part of the same molecule and of the remaining 15 bromine atoms in the unit cell, 13 were much too distant (see fig. 4.3(b)).

On reexamination of the electron density map, disregarding this time the misleading regions of positive electron density within 1.5 Å of any bromine atom, it was possible to identify peaks which could account for atoms C2 and C340 in each molecule. A later difference map in fact showed that the peak taken to be C340 at (.72, .28, .00) was the largest peak on the map. This atom could only be bonded to Br 53 at (.77, .35, -.13) which in turn required this bromine atom to be in the same molecule as Br 320 at (.80, .30, .33). The only alternative bromine atom at (.70, .50, .66) was now impossibly distant, unless the large peak assumed to be C340 was to be completely ignored. To have done this would have been crystallographically unreasonable and the search therefore continued on the basis that the large peak was C340.

By systematic analysis it was possible using only peaks found on the electron density map, eventually to place all atoms. 28 of the 33 light atoms were placed on quite prominent peaks on the ρ₀ map, while the remaining five had to be placed on rather weaker peaks. In the difference map the atoms were rather better resolved, including the five which showed up
Fig. 5.6
VIEW OF CONTENTS OF THE UNIT CELL PROJECTED DOWN THE C AXIS
rather weakly in the $F_0$ map.

A significant feature of the solution was that the peaks assigned as oxygen atoms included the largest peaks observable, which is as expected for atoms with a third more electrons than carbon atoms. One noteworthy feature of the light-atom arrangement was the very similar packing of the three molecules around the screw axes through $(\frac{1}{2}, \frac{2}{3}, 0)$ and $\frac{2}{3}, \frac{1}{2}, 0)$. The three remaining molecules around $(0, 0, 0)$ were similarly packed but were rotated $180^\circ$ with respect to the other six molecules. The resulting molecular arrangement in projections is shown in Fig. 5.6.

The structure deduced was thus chemically reasonable, explained the principal features of the electron density map and filled the unit cell in a symmetrical manner, in keeping with the pseudo-symmetry of the X-ray photographs. There were no unusually short inter-molecular contacts. Subsequent detailed examination of the observed and difference electron density maps, based on phases calculated with isotropic bromine atoms, failed to indicate any other possible arrangement of the light atoms. It was evident from the analysis that the structure is so dominated by the bromine atoms that the light atoms appeared only just above the general background. Using Cruickshanks relation $h_0, h_1, h_2$ for
the error in a non-centric Fourier map, which Ibers\textsuperscript{13} has shown to be generally applicable at all stages of structure determination, the estimated standard error in the electron density map used to locate the light atoms, was found to be $0.9 \ e/A^3$. The error $\sigma(p)$ given by

$$
\sigma(p) = \frac{2}{\nu} \left[ \sum_{hkl} (\Delta p^2) \right]^{\frac{1}{2}},
$$

was calculated using a computer program written by the author. We may assume that a background fluctuation of up to three times the standard error or $2.7 \ e/A^3$ is possible. This value may be compared with the "large" peaks assigned as oxygen atoms which appeared at an average height of only $3.6 \ e/A^3$ and the carbon atom peaks which occurred mainly in the range $2.0 - 3.4 \ e/A^3$ or only marginally above the random fluctuations expected in the background. The inclusion of the five atoms which appeared on very low peaks in the range $1.0 - 2.0 \ e/A^3$ can only be justified on chemical grounds, since it is clear that these peaks were not significantly greater than the standard error of the map.

The final difference map calculated after placing all 39 independent atoms had an estimated standard error of $0.7 \ e/A^3$. Apart from positive residual peaks at the bromine positions of up to $3.4 \ e/A^3$, which were at least partly due to the fact that $2|F_o|$ was about 8%
higher than $2|F_0|$ when the calculations were made, there were no other residual peaks higher than $1.4 \ e/\AA^3$, which was much less than three times the standard error in the map. Most of the remaining peaks were considerably less than this and in view of the error no significance can be attached to them. There were no negative troughs of electron density at positions where atoms were placed and negative regions generally corresponded to regions remote from atom positions.

7. REFINEMENT OF THE STRUCTURE

Once all the expected 33 light atoms had been located in chemically plausible positions, refinement was carried out using Mair's SFLS\textsuperscript{36}. Owing to the maxima in the electron density map observed near the bromine atoms, all bromine atoms were initially treated anisotropically but all other atoms were invariably treated isotropically. Only reflections where $\sin \theta/\lambda < 0.5$, were used at this stage of the refinement, because of the enormous amount of computing time, which was not always readily available on the IBM 1620 (see Appendix II). On account of the inefficient block-diagonal least-squares method, convergence was attained only slowly. After four cycles of refinement
by which time the \( R \) factor was 0.16 for data of
\[ \sin \frac{0}{\lambda} < 0.5, \]
negligible improvement could be obtained
and atom shifts were of no apparent significance.

The weighting scheme at this stage was one of those
given by Rollett\(^{37}\) where

\[
\begin{align*}
\text{for } kF_o &< F^a & (w)_{k}^{\frac{1}{2}} &= 1 \\
\text{and for } kF_o &> F^a & (w)_{k}^{\frac{1}{2}} &= F^a/kF_o 
\end{align*}
\]

The value \( F^a \), which was not scaled by the factor \( k \),
was chosen so that unobserved and weak reflections were
given less weight in the refinement.

Apart from an early misplaced atom, which was
rapidly removed and replaced in its correct position,
refinement proceeded smoothly and at no stage did any
atoms show tendencies for large positive increases in
their temperature factors, indicating a seriously
misplaced atom. It was also clear that despite the fall
in the usual \( R \) factor and weighted \( R \) factor, indicating
gradual convergence, these quantities were relatively
insensitive to large shifts in individual light-atom
positions.

At this stage with the availability of funds for
high speed computing in Australia, it was decided to
attempt further least squares refinement using Blount's
ORFLS A\(^{38}\), which employs the full matrix of normal
equations, rather than the less sophisticated and much
less efficient, block-diagonal approximation. Initially all data were used, the six independent bromine atoms treated anisotropically, and all the remaining atoms isotropically to give a total of 192 variables. Before computing could proceed, modifications to ORFLS A were required, since the problem already exceeded the maximum number of both variables and atoms allowed, 166 and 38 respectively. Since the dimensions for scale factors, symmetry operations and scattering factor tables were larger than necessary, it was possible to increase the number of atoms allowed beyond the 39 minimum required in this problem, but the number of variable parameters could be increased to only 176.

In the first cycle all positional parameters, scale factors, anisotropic temperature factor parameters and 18 isotropic temperature factors were varied. In the second cycle the same positional parameters were allowed to vary with the substitution of the unvaried temperature factors for the 18 varied in the first cycle. The weighting scheme employed the actual errors in the measured intensities determined in program CAXR 13. Because the origin in space group P31 is not defined in the z direction by the symmetry elements, it was necessary to hold constant one of the bromine atom z coordinates to prevent a singular matrix being obtained.
Fig. 5.7

BOND LENGTHS AND ANGLES AFTER ANISOTROPIC REFINEMENT

(Bond length errors are ≤ those in table 6.2(a) (p 61))

Molecule 1 around (0,0,0)

(Bond lengths in angstroms)

Molecule 2 around (1/2,2,0)

(Bond angles in degrees)

Molecule 3 around (3/4,1,0)

(Bond lengths in angstroms)
After two cycles of refinement the structure had evidently converged to give the best structure factor agreement possible with the data available and the structure model used. Only two of the 176 parameters varied showed a greater shift than the standard error and of the remainder a further 29 had shifted by half the standard error. The shifts indicated for the remaining 145 parameters were less than one half their standard errors. The $R$ factor had decreased to 0.197 for all 2,595 reflections or 0.189 if the 278 unobserved data were omitted. The weighted $R$ factor omitting unobserved data was 0.255 before the second cycle but that based on the output parameters was predicted to drop to only 0.254. For these reasons there seemed little justification in continuing further expensive refinements in Australia.

The bond lengths and angles obtained from the second cycle of the anisotropic refinement are shown in Fig. 5.7. It is evident that there are a number of substantial differences between what must be considered chemically identical bonds in the three independent molecules. None of these, even so, are statistically significant.

Some very unsatisfactory features of the refinement were the large interactions, greater than $+0.80$, between the scale factors and the bromine anisotropic
temperature factors as indicated by the correlation matrix put out at the end of this refinement. These indicated highly dependent variables which should not have been varied simultaneously. It was realized that there is in fact no justification for carrying out anisotropic refinement unless a fully correlated set of data on one common scale is available, which certainly did not pertain to the present situation, where separate layer scale factors were used. For these reasons it appeared desirable to attempt another refinement using isotropic temperature factors for the bromine atoms. In addition there was no evidence that the introduction of the anisotropic parameters had significantly improved the structure factor agreement.

At this stage when all possible sources of error were being exhaustively investigated, it was decided to completely remeasure all the 2,600 intensity data and correlation data as an independent check on the reliability of the densitometer data. This lengthy task was carried out but structure factor calculations for the various layers using the remeasured data gave almost identical agreement with what had been obtained before with the exception of one layer where a slight improvement was noted. A comparison of a portion of the data measured by the two methods is made and discussed in Appendix IV.
9. FINAL ISOTROPIC REFINEMENT OF THE STRUCTURE

For the final fully isotropic refinement of the structure, the remeasured visually estimated data were used, since these appeared to give very slightly improved structure factor agreement in the preliminary calculations. 1,623 data were used, of which 127 were unobserved, and all had \( \sin \theta/\lambda < 0.5 \), which meant that a nearly complete inner sphere of data was used. The weighting scheme was again based on the actual errors determined by CAXR 13. 39 of the most intense inner reflections where \( |F|_{\text{OBS}} < |F|_{\text{CALC}} \), and therefore possibly subject to extinction, were assigned large errors to weight them effectively right out of the refinement. With the removal of all the anisotropic thermal parameters it was now possible to refine all 161 variable parameters simultaneously in one cycle.

After two cycles of refinement the \( R \) factor, omitting unobserved data, was reduced to 0.160 from 0.164, and the weighted \( R \) factor predicted from the output parameters, also omitting unobserved data, was 0.208 a drop of only .003 having been indicated. Only 7 parameters had shifted by more than their standard errors and a further 15 had shifts greater than half their standard errors. No significant changes could therefore be expected to warrant further refinement. Examination of the correlation matrix after the second
cycle of isotropic refinement revealed a much more satisfactory situation than had the previous anisotropic refinement. The largest correlation coefficients (up to \( \pm 0.54 \)) were between the \( x \) and \( y \) coordinates of all atoms, caused by the non-orthogonality of the trigonal unit cell, \( (\gamma = 120^\circ) \). As a consequence of defining the origin by fixing one of the bromine atom \( z \) coordinates, there were interactions between all the remaining bromine \( z \) coordinates. The largest remaining correlation coefficients were between the bromine isotropic temperature factors and the six layer scale factors but none of these was greater than \( \pm 0.48 \).
CHAPTER VI

DISCUSSION OF THE STRUCTURE

1. INTRODUCTION

In his thesis Wallis\(^{39}\) was able to assert on purely mechanistic grounds that the compound Schmidt\(^{14}\) had earlier obtained by the addition of bromine to pinocarvone, was 2α,10-dibromo-10β-pinan-3-one implying a specific stereochemistry. He also made quite clear\(^{45}\) that many of the generalisations made concerning the pinane skeleton, though probably soundly based, were supported by no definite physical evidence. We may now say as a result of this investigation and the closely related one 2α,βα-dibromo-pinan-3-one carried out by Dr Williams\(^7\), together with the two fairly closely related 3-bromo- and 3-chloro-nopinone structures, reported by Miss. Barrans\(^{46}\), that Wallis' structure assignment is correct and the mechanism he has suggested is entirely consistent with the structure reported here.

Of the broad features that emerge from the structure, one of the most obvious is that of the two most favoured orientations of the C10-Br dipole, the one assumed by the structure is the one in which the very electronegative bromine atom is furthest from the even
more electronegative oxygen atom of the carbonyl group. For this reason we may expect that this bromine atom, C=O, will have negligible effect on either the infrared stretching frequency of the carbonyl group, or the ultraviolet absorption of the carbonyl group, since the dipoles are too distant to interact to any significant extent. It is not surprising therefore that the spectra of 2-bromo-pinan-3-one and 2,10-dibromo-pinan-3-one show almost the same shifts, compared with the reference compound isopinocamphone as shown in (foldout) table 1.1.

A further obvious deduction from the structure analysis, which will be elaborated below, is that as Wallis predicted\(^7\) from his spectral data, the structure of this compound and also the 2,4-dibromo compound, can be ascribed an approximately planar conformation, with a tendency towards the up conformation predicted on conformational analysis grounds.
molecule 1
round (0,0,0)

molecule 2
round (1,2,0)

molecule 3
round (2,4,0)

(Bond lengths in Angstroms)
(Bond angles in degrees)
**Fig. 6.2(b) Bond Lengths and Angles of Pinane Derivatives**

2,4-Dibromo-pinane-3-one

\[ \sigma(C-C) = 0.035 \text{ Å} \]
\[ \sigma(\theta) = 2^\circ \]

3-Bromo-pinonone

\[ \sigma(C-C) = 0.015 \text{ Å} \]

3-Chloro-pinonone

\[ \sigma(C-C) = 0.015 \text{ Å} \]

(Bond lengths in Angstroms) (Bond angles in degrees)
TABLE 6.2(a)

BOND LENGTHS AND STANDARD DEVIATIONS OF

2,10-DIBROMO-PINAR-3-ONE

<table>
<thead>
<tr>
<th>Bond</th>
<th>Molecule 1</th>
<th>Molecule 2</th>
<th>Molecule 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-C2</td>
<td>1.92</td>
<td>.05</td>
<td>1.80</td>
</tr>
<tr>
<td>Br-C10</td>
<td>1.85</td>
<td>.05</td>
<td>1.96</td>
</tr>
<tr>
<td>C0-C3</td>
<td>1.27</td>
<td>.10</td>
<td>1.40</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.42</td>
<td>.09</td>
<td>1.55</td>
</tr>
<tr>
<td>C1-C6</td>
<td>1.83</td>
<td>.14</td>
<td>1.56</td>
</tr>
<tr>
<td>C1-C7</td>
<td>1.59</td>
<td>.09</td>
<td>1.63</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.76</td>
<td>.10</td>
<td>1.63</td>
</tr>
<tr>
<td>C2-C10</td>
<td>1.56</td>
<td>.07</td>
<td>1.43</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.37</td>
<td>.15</td>
<td>1.54</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.45</td>
<td>.14</td>
<td>1.73</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.66</td>
<td>.13</td>
<td>1.56</td>
</tr>
<tr>
<td>C5-C7</td>
<td>1.63</td>
<td>.08</td>
<td>1.49</td>
</tr>
<tr>
<td>C6-C8</td>
<td>1.43</td>
<td>.15</td>
<td>1.56</td>
</tr>
<tr>
<td>C6-C9</td>
<td>1.59</td>
<td>.14</td>
<td>1.49</td>
</tr>
</tbody>
</table>
2. MOLECULAR GEOMETRY

In fig. 6.2(a) the bond lengths and angles for the three independent molecules found in this analysis are shown and compared in fig. 6.2(b) with the corresponding results obtained by Williams for 2,4-dibromo-pinane-3-one and Barrans for 3-chloro- and 3-bromo-nopinone. In table 6.2(a) below the bond lengths for the three independent molecules are tabulated in parallel columns with their standard deviations.

The errors given are derived using the relationship,

\[ \sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2) \]

where \( \sigma(d_{12}) \) is the standard error in the bond between atoms 1 and 2 of individual coordinate errors \( \sigma(x_1) \) and \( \sigma(x_2) \) in the direction \( d_{12} \). The much smaller unit cell dimension errors have not been included since they made negligible difference to the overall bond length errors.

In view of the rather large standard errors in many individual bond lengths, a fairer representation of the molecular structure is obtained by either averaging the corresponding bonds in the three molecules and noting the maximum deviation from the mean for each bond, or alternatively averaging all bonds expected to be chemically identical, and determining a statistically significant standard deviation for bonds of like
BOND LENGTHS AND ANGLES OF "AVERAGE" MOLECULE OF
2,10-DIBROMO-PINAN-3-ONE

(Bond lengths in Angstroms)

(Bond angles in degrees)
character. The "average" molecule is shown in fig. 6.2(c). This has been obtained simply by averaging the three independent measurements of every bond length and bond angle without consideration of the individual standard errors. The "chemically averaged" molecule fig. 6.2(d) has been obtained by considering all bonds in the three independent molecules to fall within one of the mutually exclusive classes (i) carbon-bromine, (ii) carbon-oxygen, (iii) cyclobutene carbon-carbon, (iv) carbon-methyl (including Cl$_2$Br), (v) sp$^3$-sp$^3$ carbon-carbon and (vi) sp$^3$-sp$^2$ carbon-carbon bonds. The standard deviations for each of these classes are tabulated below in table 6.2(b) and are corrected for small samples. The values represent the mean standard deviation divided by $\sqrt{n-1}$, where $n$ is the number of bonds in the particular group.

In calculating the standard deviations quoted in table 6.2(b), it has been assumed that all measurements are strictly independent which of course is only very approximately true, even for bonds measured in crystallographically independent molecules, since all atoms make some contributions, however small, to most structure factors and therefore directly or indirectly affect the positions of all other atoms. In the
analysis of the 12 cyclobutane bonds, a more realistic figure for the average length of a cyclobutane bond in the compound may be obtained by excluding two bonds which gave very large positive deviations from the mean. If this is done the average falls to 1.68 \( \AA \), \( \sigma = 0.03 \) \( \AA \), for the remaining ten measurements.

### TABLE 6.2(b)

**STATISTICAL ANALYSIS OF CHEMICALLY SIMILAR BONDS IN 2,10-DIBROMO-PYRAN-3-ONE**

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Mean ( \bar{r} ) ( \AA )</th>
<th>( \sigma ) ( \AA )</th>
<th>No. Bonds</th>
<th>No. of Bond Deviations &gt; 2 ( \sigma )</th>
<th>No. of Bond Deviations &gt; ( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Br</td>
<td>1.88</td>
<td>0.03</td>
<td>6</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>C=O</td>
<td>1.27</td>
<td>0.09</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>1.63*</td>
<td>0.03</td>
<td>12</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>C-He</td>
<td>1.50</td>
<td>0.05</td>
<td>9</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>sp(^3)-sp(^3) C-C</td>
<td>1.56</td>
<td>0.05</td>
<td>6</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>sp(^3)-sp(^2) C-C</td>
<td>1.58</td>
<td>0.05</td>
<td>6</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

In order to determine more precisely the nature of the distortions which occur in the pinane system, a detailed examination of the torsion angles about the various carbon-carbon bonds which comprise the basic cyclohexanone and cyclobutane rings was made. The angles between the
Fig. 6.2(c) TORSION ANGLES IN 2,4-DIBROMO-PINAN-3-ONE

View down C3-C2 bond

View down C3-C4 bond

View down C2-C1 bond

View down C2-C3 bond

View down C1-C6 bond

View down C1-C7 bond

View down C5-C6 bond

View down C5-C7 bond
various planes are given in fig. 6.2(e) which gives the views looking down each of the bonds in the two rings in turn. The angles quoted represent the average of the values obtained from the three independent molecules in the structure. Since it was not possible to locate hydrogen atoms in this structure, and it was difficult to predict with any certainty their position in this highly strained molecule, where regular tetrahedral symmetry is exceptional, no calculations could be made of torsion angles involving hydrogen atoms. This information would have been of considerable interest in predicting the nature of the fine structure of the nuclear magnetic resonance spectra (n.m.r.).

It has been shown that the $J$ coupling constant for two vicinal protons in a substituted ethane depends on the dihedral angle $\phi$ between them according to the relation,

$$ J = 4.22 - 0.5 \cos \phi + 4.5 \cos 2\phi $$

and this has been shown to be applicable to substituted cyclohexanes. It is known that axial and equatorial protons absorb differently in the n.m.r. spectrum to give predictable spectral patterns. The spectrum of 2,10-dibromo-pinane-3-one showed a number of readily identifiable features but it was not possible to unravel the spectrum of the C5 proton, which owing to coupling
with the two protons at both C4 and two others at C7, gave a rather complicated five structure consisting probably of either two quartets or two quintets. Although it is beyond the scope of this investigation, it is to be hoped that the geometrical information contained in this thesis may assist in the interpretation of the n.m.r. spectra of the compound and those of related compounds so that meaningful predictions can be made of the main structural feature, as far as is possible with n.m.r. data alone.

Of particular interest in this work was the determination of the extent to which the molecule actually attains the planar conformation referred to in the introduction. In table 6.2(c) the planarity of the atoms C1, C2, C4 and C5 in each of the three independent molecules is compared with that observed in the other reported pinane structures. The table also indicates the elevation of the carbonyl groups towards C9 i.e. the degree to which the molecule moves from the planar to the up conformation, and the actual extent to which the atoms in the carbonyl group are out of the C1, C2, C4, C5 plane. In the case of the nopolinene the corresponding depression from the C1, C2, C4, C5 plane of the C3 atom to which the halogen atom is attached is given.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Max. Dev. from C1, C2, C4, C5 Plane</th>
<th>Dev. of C3 towards C9</th>
<th>Dev. of Oxygen atom towards C9</th>
<th>Elevation of C2, C3, C4 (°) Plane towards C9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule 1, 2,10 D.B.P.</td>
<td>.023 °</td>
<td>+.089 °</td>
<td>+.038 °</td>
<td>10.5°</td>
</tr>
<tr>
<td>&quot; 2</td>
<td>.026 °</td>
<td>+.274 °</td>
<td>+.056 °</td>
<td>15.9°</td>
</tr>
<tr>
<td>&quot; 3</td>
<td>.052 °</td>
<td>-.015 °</td>
<td>+.057 °</td>
<td>2.3°</td>
</tr>
<tr>
<td>2,4-D.B.P.</td>
<td>.042 °</td>
<td>+.064 °</td>
<td>+.033 °</td>
<td>6.7°</td>
</tr>
<tr>
<td>Bromo-nopinone</td>
<td>.015 °</td>
<td>-.427 °</td>
<td>( - )</td>
<td>-29.9°</td>
</tr>
<tr>
<td>Chloro-nopinone</td>
<td>.013 °</td>
<td>-.419 °</td>
<td>( - )</td>
<td>-30.6°</td>
</tr>
</tbody>
</table>

The final geometrical aspect of particular interest in the pinane series is the extent to which the cyclobutane ring is buckled and this is most conveniently measured by the two dihedral angles measured across the C1-C5 and C6-C7 diagonals denoted by C1-X-C5 and C6-Y-C7 respectively. These angles are expressed as the supplement of the true dihedral angle and measure the departure from planarity, for which on this convention the dihedral angle is zero. The angles are tabulated and compared as before with the other pinane structures and cyclobutane itself in table 6.2(d).

A view of the structure in projection showing the contents of one unit cell is given in fig. 5.6. (facing p 59)
TABLE 6.2(d)

BUCKLING OF THE CYCLOBUTANE RING IN THE PINANE SERIES

<table>
<thead>
<tr>
<th>Compound</th>
<th>C1-X-05</th>
<th>C6-Y-C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule 1, 2,10-B.P.</td>
<td>38.3°</td>
<td>36.0°</td>
</tr>
<tr>
<td>&quot; 2 &quot;</td>
<td>27.0°</td>
<td>31.0°</td>
</tr>
<tr>
<td>&quot; 3 &quot;</td>
<td>38.6°</td>
<td>41.5°</td>
</tr>
<tr>
<td>2,4-B.P.</td>
<td>40.3°</td>
<td>39.2°</td>
</tr>
<tr>
<td>3-bromo-nopinone</td>
<td>35.2°</td>
<td>34.5°</td>
</tr>
<tr>
<td>3-chloro-nopinone</td>
<td>35.0°</td>
<td>35.3°</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>20°</td>
<td>20°</td>
</tr>
</tbody>
</table>

The structure revealed no significantly short intermolecular contacts and as the diagram shows, the nine molecules in the unit cell are well resolved from each other. Some of the shorter contacts are tabulated below and only one bromine-oxygen contact of 3.20 Å is less than the sum of the Van der Waals' radii \(^{50}\) (3.35 Å for bromine plus oxygen).

TABLE 6.2(e)

<table>
<thead>
<tr>
<th>Molecule 1</th>
<th>Molecule 2</th>
<th>Molecule 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>04-BR511</td>
<td>020h-BR 521</td>
<td>030h-BR 531</td>
</tr>
<tr>
<td>3.11 Å</td>
<td>3.20 Å</td>
<td>3.34 Å</td>
</tr>
<tr>
<td>04-C307</td>
<td>020h-07</td>
<td>030h-G205</td>
</tr>
<tr>
<td>3.18 Å</td>
<td>3.36</td>
<td>3.49</td>
</tr>
<tr>
<td>04-C305</td>
<td>020h-05</td>
<td></td>
</tr>
<tr>
<td>3.70 Å</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>04-C9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.69 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BR311-C305</td>
<td></td>
<td>3.67</td>
</tr>
</tbody>
</table>
3. DISCUSSION OF GEOMETRY

Despite the fact that there are substantial errors in most of the bond lengths, as would be expected in a structure of this kind, which failed to refine below \( R = 0.16 \), a number of generalizations and deductions can be made. An examination of the errors in the bond lengths of chemically identical bonds shows that with one exception all bonds are within three standard deviations of the mean, and the means are themselves well within one standard deviation of the accepted values for the particular type of bond.

The six carbon-bromine bonds in the three molecules gave an average length of 1.88 Å with a standard deviation of 0.03 Å and appeared to have refined noticeably better in the final isotropic refinement than in the earlier refinement when the bromines were allowed to vibrate anisotropically. Since the errors in the bromine atom positions were quite small the errors in the bond lengths are consistently smaller than for the other bonds involving only light atoms. The C-3r bond length varied from 1.80 Å to 1.96 Å which may be compared with the values of 1.97 Å and 2.06 Å \((c = \pm 0.03 \text{ Å})\) found by Williams\(^7\) in 2,4-dibromo-pinane-3-one, which was better refined \((R = 0.127)\) and where both bromines were in very similar environments unlike 2,10-dibromo-pinane-3-one. Though the bromine atom attached to C10 is obviously
less sterically restricted than bromine atoms substituted at C2 or C3, there seems little reason to suppose that significant differences in the bond lengths will occur since in all three positions approximately normal tetrahedral symmetry and sp³ hybridization may be expected. There is certainly no evidence of any such difference from this investigation.

Carbon-bromine bond lengths of quite different and often incompatible values have been reported for quite similar compounds and we may note the value 1.88 Å, \( \sigma = 0.03 \) Å obtained in the determination of 2-bromo-3, 3,5,5-tetramethylcyclohexanone\(^{51} \), the values 1.98 Å and 1.95 Å, \( \sigma = 0.03 \) Å in 2,4-dibromoethane\(^{52} \), a terpene, 1.970 Å, \( \sigma = 0.015 \) Å in 3-bromo-nopinone\(^{46} \), 1.97 Å and 2.06 Å, \( \sigma = 0.03 \) Å in 2,4-dibromo-pinane-3-one\(^{7} \) and 1.88 Å, \( \sigma = 0.03 \) Å in the present investigation.

The carbonyl bond length in the compound which was found to be 1.27 Å with a rather large error, \( \sigma = 0.09 \) Å, is nevertheless quite consistent, within the limits of error, of other values which have been reported. These values also show a substantial variation in the literature which is difficult to explain adequately.

Coenen and Grant\(^{51} \) report values of 1.23 Å and 1.49 Å in two similar bromo-cyclohexane compounds, Bossel and Romers\(^{53} \) 1.208 Å and 1.213 Å in a very accurate (\( \sigma = 0.009 \) Å) low temperature determination of
cyclohexane-1,3-dione and Romers' a value 1.24 Å, 
\( \sigma = 0.02 \) Å in an electron diffraction study of cyclohexan-
one. Other measurements in the terpene series show a 
trend to rather lower values of the length of the 
carbonyl group with 1.16 Å, \( \sigma = 0.04 \) Å in 
2,4-dibromomenthone reported by Wunderlich and Lipscomb and 
the same value 1.16 Å, \( \sigma = 0.04 \) Å obtained by 
Williams in 2,4-dibromo-pinane-3-one. An exception 
is provided by the measurements of Barrans who reported 
values of 1.24 Å and 1.20 Å, \( \sigma = 0.015 \) Å in her 
determinations of the structures of 3-bromonopinone and 
3-chloronopinone respectively. It may be observed for 
instance that Wunderlich and Lipscomb's value of 1.16 Å 
is not within three standard errors of Barrans more 
accurate determination of 1.24 Å in 3-bromonopinone.

The mean values of the carbon–carbon bonds of all 
kinds except cyclobutane bonds are all consistent within 
the limits of error for the corresponding accepted value of 1.54 Å for ordinary carbon–carbon bonds. Some 
variation in the length of carbon–carbon bonds can be 
expected where one atom is \( sp^2 \) hybridized, instead of 
both being \( sp^3 \) hybridized, and a carbon–methyl bond is 
often shorter than a carbon–carbon bond where both atoms 
have at least one non-hydrogen atom substituent.

In this analysis the carbon–methyl distances which 
include C-CH\(_2\)Br, appear to be considerably less than the
other carbon-carbon bonds, but no definite statistical significance can be attached to this apparent shortening, since the mean distance is still within one standard deviation of a normal carbon-carbon bond.

Analysis of the data given in table 6.2(c) shows that the conformation of 2,10-dibromo-pinan-3-one is best described as planar, though the evidence points to a slightly up conformation, with the carbonyl group elevated by an average amount of $10^\circ$ towards the C9 methyl group. In at least two of the molecules the oxygen atom appears to be significantly out of the C1, C2, C4, C5 plane by a factor of 15 to 20 times the maximum deviation of any of the four atoms in the plane. In the third independent molecule, which is possibly more significant, since the bond lengths appear more "normal" in length, the elevation of the carbonyl group is only $2.3^\circ$ and the oxygen atom is certainly within three standard deviations of the mean displacement from the reference plane. The evidence is definitely against the carbonyl group being in a down conformation, in agreement with conformational analysis based on normal steric requirements. In 2,4-dibromo-pinan-3-one the C1, C2, C4, C5 group of atoms is closely planar and the carbonyl group also shows a definite inclination of $6.7^\circ$ towards the C9 methyl group. The oxygen atom lies $0.234 \text{ \AA}$ above the plane towards C9, whereas the
maximum departure from planarity of the four atoms is only 0.012 Å. It is apparent in this instance that the elevation of the carbonyl group is definitely significant, and the conformation, though still not far from planar, is significantly in the up conformation by the small amount of 6.7°. Whether the elevation of the carbonyl group in this compound is significantly different from that in 2,4-dibromo-pinan-3-one is uncertain. Steric considerations suggest that owing to the greater repulsion between the bromine atoms attached to C2 and CH4, compared with a single bromine atom at C2 only, and the smaller repulsion between the methyl group at C9 with the methyl group at C10 compared with a CH2Br group, 2,4-dibromo-pinan-3-one should have a flatter or even a down conformation compared with 2,10-dibromo-pinan-3-one. Both the steric factors mentioned above suggest this, but the evidence of the two structure analyses suggests that the repulsion of the bromine atoms in the C2 and CH4 positions is not significantly different from a single bromine and a hydrogen atom, and similarly the repulsion between the non-bonded methyl atoms at C9 and C10 is not significantly increased by the addition of a bromine atom attached to C10. These deductions are reinforced by the fact that even in the slightly up conformation, the bromine atoms at C2 and CH4 are still widely separated, being 4.27 Å.
apart, whereas the C9 and C10 separation is only 3.30 Å in the 2,4-compound. In the 2,4 compound the bromine atom at C10 is 4.25 Å from C9 and evidently has a very small effect on the C9 - C10 separation, which is only increased to an average figure of 3.45 Å.

The steric factors operating in the nopinones are quite different since the carbonyl group is now situated at C2 and the halogen atoms are attached at C3. The two structures reported by Barrans indicate that the molecules are in the down conformation with the halogen atom substituted in the equatorial position at C3 in contrast to the two compounds described above but in agreement with the assignment of Lalande et. al. based on infrared spectra and dipole moment measurements.

Since the only major difference between the nopinones and the pinen-3-ones is the presence of the C10 methyl group in the latter series, we may conclude in agreement with the preceding paragraph that the carbon atom at C10 is primarily responsible for determining the conformation of the molecule. In the absence of C10 in the 3 position it may be inferred from the nopinone results that the skeleton prefers a down conformation.

From the preceding argument we may say therefore in the pinene series that where a methyl or bromomethyl group is in the 10β position as in isopinocamphone, 2α-bromo-, 2α,10-dibromo-, 2α, 4α-dibromo-, and
2α,4α,10-tribromo-pinan-3-one, the pinane conformation is governed by the non-bonded repulsion between C9 and C10 and tends toward the planar or slightly up conformation; where C10 is absent, as in the nopinones, or certain to be 10α, as in pinocamphone and probably in 4α-bromo-, 10-bromo- and 4α,10-dibromo-pinan-3-one, the down conformation is preferred. We may deduce further that where the planar or up conformation is preferred as in the first group of compounds, the shift in the ultraviolet absorption maxima will be greatest per bromine atom α to the carbonyl group, and the infrared shift least per a bromine atom since the bromine atoms are more axial than in a down conformation. For the second group of pinane bromoketones the reverse is true and reference to foldout table 1.1 shows that the relative magnitude of the ultraviolet and infrared shifts is in accord with these predictions. It is worth noting however that the terms "axial" and "equatorial" in reference to pinane substituents, have very little meaning since in the essentially planar conformations adopted in the two dibromo compounds discussed, it is quite arbitrary which substituents are labelled axial and which equatorial. It is clear that these terms have only a precise meaning when referred to standard compounds such as cyclohexane or cyclohexanone and should only be used in such contexts, contrary to the present
practice of some authors.

There have been a number of predictions of the nature of the geometry of the pinane skeleton and it is noteworthy that those based on conformational analysis have been proved correct. In the course of his work Wallis\textsuperscript{56} predicted that the dihedral angle $\alpha$ in the diagram would be reduced compared with cyclobutane i.e. the cyclobutane ring would be more buckled, and that angles $\beta$, $\gamma$ and $\delta$ would be reduced compared with cyclohexanone. On the other hand Shatt\textsuperscript{57} concluded from a study of the strain energies of cyclobutane and the four-membered ring in pinane, that "the four-membered ring in pinane is not buckled to any great extent, if at all", whereas the evidence presented here shows this prediction to be in error.
4. DISCUSSION OF THE CYCLOBUTANE RING GEOMETRY

Examination of the table 6.2(d) shows that contrary to Bhatt's prediction, in 2,10-dibromo-pinane-3-one and in all the other pinanes whose structures have been reported, the cyclobutane ring is buckled to an extent of 35° - 40°, or at least 15° more than in cyclobutane itself, where electron diffraction measurements have shown that the buckling is only 20°. Since a planar cyclobutane ring already represents a severely strained system, with bond angles 19° 28' less than the ideal tetrahedral angle for normally bonded carbon atoms, it is somewhat surprising that the ring can be buckled to an extent of 35° - 40° as in the pinanes, but this can be rationalized on a number of grounds.

In planar cyclobutane it can be readily observed from a model that all the hydrogen atoms or other ring substituents are eclipsed, whereas in a buckled ring these non-bonded interactions can be considerably reduced. A search of the literature has shown that of the cyclobutane derivatives whose structures have been reported, the majority crystallize in space groups which permit a buckled ring.

Buckled cyclobutane rings in systems not involving fused rings include octafluorocyclobutane dihedral angle θ = 20°, octachlorocyclobutane, θ = 22°, methycyclobutane, θ = 20-30°, 1,2-dibromo-
1,2-dicarbomethoxycyclobutane, θ = 27° trans form,
30° cis form 63, bromocyclobutane, θ = 29° 64, and
cyclobutane itself, θ = 20°. The exceptions, which
are planar, are tetracyanocyclobutane, (p2_1/a, Z = 2) 65,
cetahydroxycyclobutane, (p2_1/n, Z = 2) 66 and
1,2,3,4-tetraphenylcyclobutane, (p2_1/a, Z = 2) 67,68.

In cyclobutane derivatives where the ring is
fused onto one or more other hydrocarbon ring systems,
as in the pinacene, it is much less surprising that the
cyclobutane ring is buckled though there are instances
again where the cyclobutane ring is planar as in
cyclopent-2-eneone dimer, (p2_1/n, Z = 2) 69 and cubane,
(R3, Z = 1) 70.

The author is aware of no instances where cyclo-
butane rings are planar in space groups where both
planar and non-planar conformations are possible.
Where the cyclobutane ring is found to be planar, the
symmetry is invariably used by the space group. It is
possible therefore that where the ring is planar in a
non-fused system, it is as a result of packing require-
ments, rather than any inherent preference for the
planar conformation. It is also very significant that
cyclobutane itself in the gaseous phase is known from
electron diffraction measurements 58,59 to be buckled
indicating that this is the preferred conformation.

Geometrical considerations show that cyclobutane
can be severely buckled with very little effect on the bond angles. If it is assumed that all bonds and angles in the cyclobutane ring remain equal, then it is possible to derive the relation that

\[ \tan \frac{\varphi}{2} = \cos \frac{\theta}{2} \]

where \( \varphi \) is the C-C-C bond angle of the cyclobutane ring, and \( \theta \) is the dihedral angle, defined previously. Substitution for various values of \( \theta \), gives the following table.

### TABLE 6.4

**EFFECT OF BUCKLING ON BOND ANGLE IN CYCLOBUTANE RINGS**

<table>
<thead>
<tr>
<th>Dihedral Angle, ( \theta )</th>
<th>Bond Angle, ( \varphi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>90°</td>
</tr>
<tr>
<td>30°</td>
<td>88.1°</td>
</tr>
<tr>
<td>45°</td>
<td>85.5°</td>
</tr>
<tr>
<td>60°</td>
<td>81.7°</td>
</tr>
<tr>
<td>90°</td>
<td>70.5°</td>
</tr>
</tbody>
</table>

The table shows that large distortions of the cyclobutane ring can occur by buckling with only very small increases in strain due to reduction of the bond angles below 90°.
Simple geometry also shows that despite the strain of $10^\circ 28'$ in the cyclobutane ring, the external bond angles need only be increased to $113^\circ$, i.e. a strain of $3^\circ 32'$, to fulfill the requirement that the three remaining bonding angles be equal, assuming $\varphi = 90^\circ$. In accordance with this mathematical theory it is found in 2,10-dibromo-pinane-3-one and in the other pinane structures that there is only a small decrease in the cyclobutane bond angles below $90^\circ$, and the bond angles external to the atoms in the cyclobutane ring, are only slightly increased beyond the tetrahedral angle.

Thus not only does substantial buckling of the cyclobutane ring in the pinane series reduce non-bonded interactions, but in so doing it also causes negligible changes in bond angle from the "ideal" planar values. There would therefore be little justification for believing with Bhatt that the strain energy is increased to any significant extent, or that most of the strain is taken up in the six-membered ring.

It has been known for some time that the bonds in a cyclobutane ring are significantly larger than normal carbon-carbon bonds. The "best" averaged value obtained in this investigation was $1.60 \text{ Å}$, $\sigma = 0.03 \text{ Å}$ which is more than one standard deviation greater than the accepted value$^{50}$ of $1.54 \text{ Å}$. Williams$^{7}$ obtained an average value of $1.56 \text{ Å}$, $\sigma = 0.04 \text{ Å}$, while Barrans$^{16}$ found
the ring bonds to be \( 1.61 \, \AA \), \( \sigma = 0.015 \, \AA \) in both the
naphinones. Cyclobutane itself was found by electron
diffraction to have carbon-carbon bonds of length
\( 1.548 \, \AA \), \( \sigma = 0.003 \, \AA \) but these and other X-ray analyses
generally have found the bonds to be increased in length
relative to the accepted carbon-carbon single bond value.

The reasons for an increased carbon-carbon bond
length in a cyclobutane ring, if in fact the increase
is real, have been ascribed to such causes as the extra
strain in the ring, requiring bent bonds, or non-bonded
repulsion across the ring diagonals. Bent bonds have
also been predicted on theoretical grounds. Although
neither this investigation nor any of the other which
have been discussed were sufficiently accurate to locate
hydrogen atoms or bonding electrons, recent very accurate
X-ray investigations have shown that even bonding electrons
are detectable. In his investigation into the structure
of the terpene 2,5-dimethyl-7,7-dicyanonorcaradiene,
Fritchie\(^7\) claims to have located bent bonds in the
cyclopropane ring. In another extremely accurate
structure (\( R = 0.023 \)) reported recently by Hartman and
Hershfeld\(^7\), bent bonds of about \( 22^\circ \) were found in
cis-1,2,3-tricyanocyclopropane. These results were in
agreement with Fritchie's estimate of the bending \( 26^\circ \pm 10^\circ \)
and also in agreement with Coulson's\(^8\) theoretical
predictions. We may therefore justly speculate on
whether X-ray evidence for bent bonds in cyclobutane rings may be produced in the future.

6.5 CONCLUSION

It is evident from an examination of the results obtained in this crystal structure analysis that despite intensive and exhaustive analysis of all possible sources of error, the structure has failed to refine to the extent that might reasonably have been expected. Although other workers in this field working with much smaller unit cells and without the complications of trigonal symmetry, have also experienced difficulties in refinement, the result in this instance was nevertheless rather unexpected. It may be noted however that in the X-ray analysis of the related terpene 2,4-dibromomenthone, Wunderlich and Lipscomb\textsuperscript{52} were only able to obtain a wR factor of 0.17, after omitting reflections suffering from extinction, despite the fact that there was only one molecule in the orthorhombic unit cell of size 13.6 x 13.8 x 6.3 Å, which was much less than half the size of the unit cell in 2,10-dibromopinene-3-one.

In the previous chapters evidence has been adduced to justify not only the solution of the Patterson function, but also the determination of the structure as a whole. There was no evidence to suggest either
any alternative heavy-atom or any alternative light-atom arrangement. The intensity data has been unambiguously indexed after overcoming subtle problems of indexing and has been shown to be reliably measured in two completely independent measurements of the entire 2,600 data. Although some of the X-ray photographs undoubtedly display pseudo-symmetry corresponding to a higher symmetry space group, there is no doubt the space group has been correctly chosen and the reproductions of the photographs contained in the thesis, clearly refute any contrary suggestion. In addition an explanation has been given for the apparent higher symmetry observed in some of the photographs.

The author believes that the most reasonable explanation of the poor refinement of the structure, is provided by the fact that the data used in the analysis was obtained from such a variety of crystals. It has been stated previously that the crystals were relatively highly absorbing, $\mu = 99.0 \text{ cm}^{-1}$, moderately large, and subject to gradual decomposition under the X-ray beam. As is discussed further in the following chapter it was also not possible to ensure that all crystals had the same absolute orientation and this could have led to further inaccuracies in the data. Any or all of these factors may account for the failure of the structure to refine to the extent normally anticipated with accurately
measured photographic data, but only a complete redetermination of the structure using a single crystal and counter measured data, if this were possible, could finally verify these explanations.
CHAPTER VII

ANOMALOUS DISPERSION AND ABSOLUTE CONFIGURATION

1. INTRODUCTION

For a variety of reasons, it is often of interest to determine the absolute configuration of optically active compounds. 2,4,6-dibromo-pinane was known to be optically active and although prepared by Wallis from (-) β-pinene, there was some doubt as to the absolute configuration of the crystals. As pointed out in chapter III, it was not possible by ordinary crystal-structure analysis to make a rigorous assignment of the compound to either space group P3₁ or P3₂ without determination of the absolute configuration. Quite arbitrarily space group P3₁ was chosen and the structure solved in that space group, although P3₂ could equally well have been chosen.

If the structure determined in space group P3₁ is labelled A, where

\[ A = \sum_{j=1}^{n} (x_j, y_j, z_j) \]

then the enantiomorphous structure B is given by

\[ B = \sum_{j=1}^{n} (\bar{x}_j, \bar{y}_j, \bar{z}_j) \]

and structure B must be described by space group P3₂.
assuming both space groups include conventional right-handed axes. Thus once the structure has been found to be described correctly as $A$ in space group $P3_1$, the determination of the absolute configuration will either confirm this as the true structure or else show it to be structure $B$, the mirror image structure, in space group $P3_2$. There is no possibility of either structure $A$ in space group $P3_2$ or structure $B$ in space group $P3_1$, since these would lead to entirely different Patterson functions.

With non-centric symmetric crystals the sequence of atoms that an X-ray beam strikes for the reflection $hkl$ is opposite to and therefore different from that encountered for the $\bar{h}\bar{k}\bar{l}$ reflection. When the atoms all scatter normally though the phases are opposite, the amplitudes and therefore the intensities of the scattered rays are still equal. Thus in general

$$I_A(hkl) = I_A(\bar{h}\bar{k}\bar{l}) = I_B(hkl) = I_B(\bar{h}\bar{k}\bar{l}) \quad (1)$$

and

$$\sigma_A(hkl) = -\sigma_A(\bar{h}\bar{k}\bar{l}) = \sigma_B(hkl) = -\sigma_B(\bar{h}\bar{k}\bar{l}) \quad (2)$$

where $A$ and $B$ again refer to the enantiomorphous structures. Relation (1) is a statement of Friedel's law.

When the wavelength of the incident X-ray beam becomes near to and just less than the wavelength of one of the absorption edges of the scattering atoms,
the scattering factor becomes a complex number which may be expressed as,

\[ f = f_0 + \Delta f' + i\Delta f'' \]

where \( f_0 \) is the normal scattering factor of the atom for incident wavelengths remote from absorption edges, and \( \Delta f' \) and \( \Delta f'' \) are the correction terms for the anomalous portion of the scattering when the incident wavelengths are near an absorption edge. The quantity \( \Delta f' \) is usually negative and represents the real correction, while \( \Delta f'' \), the imaginary part of the complex number, is always ahead of the real part by \( \pi/2 \) and this advance in phase is independent of the direction of incidence of the X-ray beam and the position of the atoms in the structure. Thus when the quantity \( \Delta f'' \) is non-zero for a particular atomic scatterer, and other atoms which scatter normally are also present, an asymmetry in the phase of scattering occurs for the hkl reflection compared with the \( \overline{hkl} \) reflection and this causes the resultant structure amplitudes of the two reflections in general to differ. Friedel's law is only broken down when both of these conditions are met as illustrated in Fig. 7.4 (see p 89).

It is clear that once an asymmetric structure has been solved, it is possible to calculate the amplitudes \( |\tilde{f}|(hkl) \) and \( |\tilde{f}|(\overline{hkl}) \) for the left and right-handed
forms making due allowance for anomalous dispersion. The calculated differences in intensity can then be compared with the observed differences in intensity for a number of reflections where the effect is most pronounced. Under favourable conditions the observed inequalities of the I(hkl), I(REF) intensities will either be in systematic agreement or equally systematic disagreement with the calculated difference and the absolute configuration can therefore be uniquely determined.

2. ANOMALOUS DISPERSION IN 2,10-DIBROMO-PINAN-3-ONE

For 2,10-dibromo-pinane-3-one reference to tables 9(c) shows that with CuKα radiation, bromine scatters anomalously while carbon and oxygen can be regarded as normal scatterers and no corrections need be made. Af' for bromine with CuKα radiation is 1.5 electrons at sin θ/λ = 0 falling off to 1.3 electrons at sin θ/λ = 0.6. With MoKα radiation, the anomalous scattering of bromine is greater and Af' = 2.6 electrons at sin θ/λ = 0 falling off to 2.3 electrons at sin θ/λ = 1.3.

At the time of investigation only Weissenberg equi-inclination photographs taken with CuKα radiation were available to examine the effects of anomalous
scattering, and all remaining crystals had decomposed. It has been pointed out however by Ramaseshan²⁹ that when Δf" is small, as in this situation, Geiger counter or similar techniques are necessary if significant differences in the pairs of reflections are to be detected. Despite these unfavourable circumstances, it was decided to investigate possible "Bijvoet pairs" using the microdensitometer to compare the intensities. A "Bijvoet pair", named after Bijvoet who first applied these techniques³⁰, consists of two reflections which are of equal intensity under normal scattering, but which become unequal, when anomalous scattering is present and thus any symmetry in the crystal will add considerably to the number of possible Bijvoet pairs.

In space group P3₁ it can be seen from consideration of the reciprocal lattice diagram that Bijvoet pairs only occur on the same film, using the Weissenberg equi-inclination technique, for the h00 and 0kl photographs. There are no Bijvoet pairs in the higher layers about the unique axis and only isolated pairs, two per layer, for photographs taken about one of the non-unique axes. In all these instances the reflections constituting the Bijvoet pairs are recorded on opposite sides of the film, which is always undesirable even when the spots are well integrated, as they were in this investigation.
Fig. 7.1

Structure factor amplitudes
under normal and anomalous scattering conditions

Fig. 7.2

Conditions for maximum and minimum differences
in a Bijvoet pair

Diagrams from "Advanced Methods of Crystallography" 29.
In order to calculate the magnitude of the anomalous effect, it was necessary to calculate separately the contributions of the real part of the bromine atoms, the imaginary part of the bromine atoms, and the real contribution of the carbon and oxygen atoms. These were then added vectorially to give the resultant magnitudes $|F|_{hkl}$ and $|F|_{\overline{hkl}}$ for the assumed arrangement of atoms. Ten reflections, where the light-atom contribution was relatively large and different in phase from the bromines and which were thus likely to show the largest anomalous effect, were plotted out in this manner. In all cases it was found that the calculated difference in the structure factor amplitudes of the $|F|_{(hkl)}$ and $|F|_{(\overline{hkl})}$ was at the most only 5% of the average amplitude and thus of the same order as the usual errors in Weissenberg intensity measurement. Examination of the reflections with the densitometer failed to reveal any significant or systematic difference between the various pairs, from which the absolute configuration could be determined.

Reference to fig. 7.2 shows that even in the most favourable circumstances when $\Delta F''$ is large, it does not necessarily follow that all Bijvoet pairs will show large differences as the difference depends primarily on the relative phases and amplitudes of the normal
and anomalous scattering atoms. Fig. 7.2 shows the conditions for the maximum and minimum effect and it can be seen that even when the relative phases are the most favourable, the maximum effect will be observed only when the light-atom contribution to the resultant structure factor is considerably greater than the real contribution of the anomalous atoms since the former must be the hypotenuse and the latter the side of a right-angled triangle. In 2,10-dibromo-pinan-3-one this was quite impossible since it was found for most structure factors that the bromine atom contributions were at least three times those of the light-atom contributions, so that even in the most favourable cases the anomalous effect, which was already small because $Af''$ was small, was only at the most a rather diminutive effect. It was quite apparent that only counter methods of measurement would be able to detect the small differences in intensity expected, without all the limitations of Weissenberg photography but at this stage neither crystals nor facilities were available to enable further investigations to be carried out.
3. ANOMALOUS DISPERSION AND STRUCTURE FACTOR CALCULATIONS.

Since it has been shown that when anomalous dispersion occurs, the amplitudes of the reflections \( hkl \) and \( \overline{hkl} \) are not generally equal, it is clearly desirable that in structure factor calculations proper corrections be made for anomalous dispersion and that all reflections be given their true absolute Miller indices. In this investigation the only available least-squares structure factor program Mail's SFLS did not have any such provision for the inclusion of anomalous scattering and the program could not be readily modified since it already used the whole of the available storage of the IBM 1620. Blount's program ORFLSA used later in the analysis also had no provision for anomalous scatterers. A correction was made for the real part of the anomalous scattering but no correction could be included for the important imaginary part which leads to any difference in Bijvoet pairs which may occur.

A further difficulty arises from the use of several crystals since it is quite impossible to tell which crystals have the same relative orientation and whether the \( hkl \) or \( \overline{hkl} \) reflections are being measured. If all photographs in the analysis had been taken with
one crystal in a fixed orientation, there would have been no difficulty in measuring consistently all reflections of one form or the other, even though it might not have been known which form was being measured. In this investigation however it is extremely unlikely that all layers which were assumed to be hkl reflections were all hkl reflections and not $\bar{h}\bar{k}\bar{l}$ reflections for some layers. The only way round this impasse in the absence of certain knowledge of the absolute configuration, would be to adopt an empirical approach and calculate structure factors separately for all layers, assuming first that the reflections are hkl and then $\bar{h}\bar{k}\bar{l}$. This approach might be successful but it has been shown$^{31,32}$ that the effect on the $R$ factor of the introduction of anomalous scattering or a change in the absolute configuration is often only very slight.

Although the neglect of the imaginary components of anomalous scattering may have little effect on the $R$ factor, the same authors have shown that quite significant and substantial changes in some bond lengths can occur as in the refinement of the structure of $(S\bar{O}_{2})_{3}^{31}$, where $\Delta f^1$ for sulphur atoms is only 0.6 electrons using copper radiation and negligible for
oxygen atoms. In the absence of an adequate full matrix least-squares program, which made allowance for anomalous dispersion, and in the absence of computing facilities to carry them out, no further investigations of the effect of anomalous dispersion on the structure refinement were possible.
Appendix I

REFINEMENT OF THE STRUCTURE OF
3-BROMO-1,8-DIETHYLNAPHTHALENE

The crystal structure of 3-bromo-1,8-dimethyl-
naphthalene was determined and the results submitted by
the author in a thesis for the degree of Master of Science
and Honours, in the University of Canterbury, 1963. At
the time of presentation of the thesis, the structure had
been solved but not fully refined owing to time limita-
tions and the fact that there was then no computer program
available for carrying out least-squares calculations.
It was evident from the results obtained at that time that
further refinement was required since some anomalies in
the lengths of chemically similar bonds were apparent, and
the overall precision of atomic coordinates was low.

The R factor was 0.147.

During the course of the present work, the author
undertook the refinement of the structure by full matrix
least-squares using the programme of Busing, Martin and
Levy\(^3\), in Australia. After two cycles the R factor had
fallen to 0.106 for all 1,338 observed reflections, and
the structure had fully refined. The whole structure
analysis has been reported\(^7\) and includes a detailed
discussion and analysis of the molecular strain. This
analysis which had not been previously made by the author
is discussed in the paper, a preprint of which is included
in the pocket in the inside back cover of this thesis.
For further details of the structure analysis the reader is referred to the paper.
Appendix II

COMPUTING

1. GENERAL DISCUSSION

In the determination of the crystal structure of compounds crystallizing with large unit cells and therefore involving large quantities of diffraction data, the availability of reliable, high speed, computing facilities is of the greatest importance. Equally important is a comprehensive and completely general set of programs to make full use of the facilities. 2,10-dibromo-pinane-3-one with a unit cell volume of 2510 \( \AA^3 \) must be considered in the category of compounds with large unit cells but the large cell was hardly matched by the available computer, an IBM 4620 with 400K storage, which is at present the only machine at the University of Canterbury. No other faster machines were available in New Zealand which had a comparable or superior set of crystallographic programs, and only at the later stages in this work were funds made available for high speed computations on the CDC 3600 machine at C.S.I.R.O., Canberra, Australia. Despite the existence of a comprehensive efficient set of programs, the author was severely limited in the range of computations which could be conveniently carried out. As has been
previously pointed out, because of program limitations, which were in turn caused by storage and calculating time limitations of the IBM 1620, the calculation of a single electron density map required what would be considered elsewhere to be an enormous amount of computing time. A typical cycle required 15 hours to punch the 7,300 structure factors, 1 hour to sort the cards, 1 hour to prepare the Fourier input and 6 hours to run the Fourier calculation, a total of 23 hours. Least-squares calculations using just the unique inner data, and including all atoms, required approximately 7 hours, despite the fact that the block diagonal approximation was used. Using the full matrix least squares method and all 2,600 data but on the CDC 3600 machine, required only 36 minutes for a much more involved calculation.

In view of the extensive computing time requirements indicated above it was therefore not surprising that the author has used in excess of 1,200 hours of computing time on the IBM 1620, most of which has been spent on running calculations specifically related to the structure investigation and a much smaller amount on program testing and development. All computing required the personal supervision of the author.
2. PROGRAMS WRITTEN BY THE AUTHOR

The author's main contribution to an already quite extensive range of crystallographic programs was to write CAXR13, an intensity data processor and error assignment program. The program was originally written primarily to handle the author's own densitometer-measured intensities, but at an early stage was made quite general, so that all photographic intensity data, whether measured by densitometer or eye, could be accepted. The main purpose of the program was to allow raw X-ray photographic intensity data to be converted into a form acceptable as input to the Lorentz and polarization correction program, CAXR2, to assign errors to individual intensities, and to do all this on a completely rigorous basis.

The program is divided into four main parts the first of which deals only with densitometer measured data, and was used extensively for handling the author's own densitometer measurements. As with visual measurements of intensities, it is assumed that densitometer measurements are entered directly on to data coding sheets so that errors due to the transference of figures from one place to another are eliminated. Once the data were punched and verified (by professional key-punch operators) no further manual intervention was required at any stage since all programs were mutually compatible. The conversion of the densitometer measurements to relative intensities,
equivalent to those obtained by visual estimation, was made using the relationship,

\[ I = K \times \lambda^{3/4} \times 10 \log_{e} \frac{t_{B}}{t_{S}} \]

where \(I\) is the relative intensity obtained from the pair of readings \(t_{B}\) and \(t_{S}\), representing the transmission of the reflection spot, \(t_{S}\), and its background, \(t_{B}\), obtained by the densitometer. \(K\) is a conversion factor found by calibrating a standard visual intensity strip. All the densitometer readings were prechecked by the program to ensure that they were non-zero and in the right order.

Parts 2, 3 and 4 were compiled together in a separate program and accepted as input, either the punched output from part 1 or manually punched visual estimates of intensity. Part 2 calculated the film factors and provision was made to exclude from the average any ratios outside any specified limits. Statistics put out at the end of part 2 enabled the operator to choose scale factors based on either an overall film factor averaged over all pairs of films in the intensity set, or alternatively (as is necessary with precession camera data) based on separate scale factors for each pair of films. There was no reason to suppose that the films in a Weissenberg multiple pack had had different exposure times or
photographic development, the overall film factors were used to calculate the scale factors for use in parts 3 and 4.

In part 3 of the program the data is reread and put on common scale using the scale factors punched in part 1 (or any other scale factors in the appropriate format). Part 4 of the program, which was generally run concurrently with part 3, calculated the best average intensity on the basis of various consistency tests and operator estimated percentage errors. Reflections which were measured on three films gave three consistent readings thus had a smaller percentage error than those measured only once on one film. Provision was also made to assign smaller errors to reflections measured twice, as for example in a zero layer Weissenberg photograph.

The program as described was used by the author, Kistler75, Elder76 and Gainsford77 in the successful solution of a number of crystal structures and undoubtedly saved a large amount of time. In view of the still somewhat arbitrary character of the estimation of percentage errors for the different groups of reflections of varying consistency, Elder77 subsequently made some quite extensive modifications to CAXR13. These enabled the errors in the intensities to be obtained directly
from consideration of the individual film factors of each reflection and the number of standard deviations by which they deviated from the average film factors for the particular pair of films. Listings of CAXR13 part 1, and the author's CAXR13 parts 2, 3 and 4 are given below in section 4.

Another program written by the author which proved to be useful was CAXR14, an L.P. output scaler and index-converter program. Other programs included one to generate the Patterson coefficients of the trigonal equivalent reflections and a similar one to generate the equivalent reflections for input to the structure factor program. Another program was written to list or punch equivalent positions in space group P3₁, given the set of unique positions on the atom parameter cards used for structure factor calculations.

The author also wrote a number of other minor programs, including one to prepare input for Blomnt's "Fourier" program and another to contour alphabetic output from the Fourier summation program and one to calculate errors in Fourier maps. He also modified programs CAXR4 and CAXR5 mentioned below. Apart from a small machine language modification to condense input data for the Fourier program IGR 4, all programs written by the author were in the Fortran II programming language.
3. COMPUTER PROGRAMS USED IN THE STRUCTURE ANALYSES

The following main computer programs were used in the structure analysis and their function is briefly indicated. Further details may be obtained from the authors indicated in the references and have already been discussed by the author\textsuperscript{13}, Robinson\textsuperscript{14}, Einstein\textsuperscript{15} and others.

(a) Programs used on the IBM 1620:

1. CAXR 13/1\textsuperscript{16} - converts densitometer-measured intensities to equivalent visual intensities.

2. CAXR 13/2,3 and 4\textsuperscript{17} - converts either part 1 output or visually estimated intensities to the "best" average intensities on a common scale and assigns errors.

3. CAXR 2/1\textsuperscript{73} - accepts CAXR 13/4 output and applies Lorentz, polarization and either spherical or cylindrical absorption corrections.

4. CAXR 4\textsuperscript{18} - assists in the correlation of reciprocal lattice layers by calculating the ratios of common reflections using CAXR 2 output.

5. CAXR 5\textsuperscript{20} - calculates coefficients, sharpened or otherwise, with or without origin peak removal, for the Patterson function using CAXR 2 output.

6. CAXR 6\textsuperscript{23} - converts the CAXR 5 coefficients to a form appropriate for the Fourier summation program IGR 1.
7. CAXR 9 \( \text{H} \) – calculates the local average intensity as a function of \( \sin \theta \)/\( \lambda \) and other intensity statistics using CAXR 2 output.

8. CAXR 10 \( t \) – converts CAXR 2 output to a form acceptable for Blount’s ORFLS A least-squares program and assigns errors to the intensities.

9. CAXR 14 \( j \) – scales and or converts the indices of CAXR 2 output.

10. SFLS \( r \) – computes structure factors and optionally performs block-diagonal least-squares calculations.

11. SFLS RESULTS \( r \) – calculates the shifts to the atomic parameters from the SFLS least-squares totals and calculates bond lengths and angles for atoms within the asymmetric unit.

12. TRICLINIC FOURIER INPUT CONVERSION \( \beta \) – converts SFLS output to a form acceptable as input for the Fourier summation program.

13. ICR 1 \( \delta \) – a program to perform all Fourier summations including Patterson, \( F \) observed and difference electron density maps.

14. ICR 13 \( \delta \) – a general bond lengths and angles program which uses SFLS atomic parameter cards as input.

15. ICR 14 \( \delta \) – calculates bond angles using ICR 13 output.

16. LEAST SQUARES PLANES \( \xi \) – calculates the least squares planes through three or more atoms again using SFLS atomic parameter cards, and optionally calculates
the angles between planes.

17. "FOURIER" INPUT \( \text{78} \) - converts SFLS output to a form acceptable for Blount's "FOURIER" program.

(b) Programs used on the CDC 3600 at C.S.I.R.O., Canberra, Australia.

1. ORFLS A \( \text{38} \) - J. Blount's modification of Busing and Levy's ORFLS - a full matrix structure factor least-squares program.

2. FOURIER \( \text{35} \) - a two- and three-dimensional Fourier summation program.
### Appendix III

**Final Atomic Parameters After Isotropic Refinement**

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<th>Atom</th>
<th>x</th>
<th>σ(x)</th>
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<th>σ(y)</th>
<th>z</th>
<th>σ(z)</th>
<th>B</th>
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<tbody>
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<td>0.1062</td>
<td>(4)</td>
<td>0.0647</td>
<td>(4)</td>
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Appendix III (cont.)

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<th>y</th>
<th>o(y)</th>
<th>z</th>
<th>o(z)</th>
<th>B</th>
<th>o(B)</th>
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<td>.4689 (37)</td>
<td>.4823 (37)</td>
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<td>.5331 (38)</td>
<td>.0226 (101)</td>
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<td>.5599 (41)</td>
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<td>-.2324 (87)</td>
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<td>.2711 (28)</td>
<td>-.0036 (79)</td>
<td>1.3 (0.9)</td>
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</table>

* denotes a bromine atom z coordinate kept constant in order to define the origin in the z direction.
* after $|F_0|$ value denotes a reflection given lower weight in the least-squares refinement.
|----|----|----|------|----|----|----|------|----|----|----|------|----|----|----|------|----|----|----|------|----|----|----|------|----|----|----|------|
Appendix IV

COMPARISON OF THE MEASUREMENT OF INTENSITY DATA
BY DENSITOMETER AND BY EYE

It was stated in chapter V that in an attempt to eliminate all possible sources of error in the determination of the structure of 2,10-dibromo-pinan-3-one, all reflection data were remeasured visually. It was found that both densitometer measured data and visually estimated data gave almost identical structure factor agreement for all layers, with the exception of one layer, where a slight improvement was obtained by using the visually estimated data. For this reason only visually estimated data was used in the final isotropic refinement, described previously, although densitometer measured data had been used for all prior calculations.

In order to determine the relative accuracy of the two methods of measurement, an analysis was made of the hk2 structure factors. To enable a fair comparison to be made the two sets of inner data for which \( \sin \theta/\lambda < 0.5 \) were each scaled, so that on using the final set of coordinates obtained from the isotropic refinement, \( x|F_0| = x|F_C| \). It was convenient to sort the data by zones of \( \sin^2 \theta \), so that the \( R \) factor for the various zones of reflections measured by the two methods could be compared.
The results are tabulated below.

**TABLE 8.1**

**COMPARISON OF REFLECTION DATA MEASURED BY EYE AND BY DENSITOMETER**

<table>
<thead>
<tr>
<th>$10^4 \sin^2 \theta$</th>
<th>Visually Estimated Data</th>
<th>Densitometer Measured data</th>
<th>$R_{Vis}/R_{Dens}$</th>
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<tr>
<td></td>
<td>No. of Data</td>
<td>$R$</td>
<td>Factor</td>
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<tr>
<td>0</td>
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<td>.170</td>
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</tr>
<tr>
<td>0.1</td>
<td>68</td>
<td>.094</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>60</td>
<td>.092</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>66</td>
<td>.124</td>
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<tr>
<td>0.4</td>
<td>58</td>
<td>.154</td>
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</tr>
<tr>
<td>0.5</td>
<td>59</td>
<td>.173</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>341</strong></td>
<td><strong>.124</strong></td>
<td></td>
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</table>

The table indicates that although the overall agreement by both methods was very nearly the same, the visually estimated data has appeared to give substantially better agreement for the inner reflections, and the outer reflections, which in the case of the densitometer measured data does not include those too weak to be detected by the instrument. These two zones of data are significant in that they are derived from the
parts of the Weissenberg film where the contrast is poorest. In the case of the inner reflections, there is generally a high background near the film backstop trace, and in the outer regions of the film, the contrast is poorer, simply due to the weakness of the average reflections. In the intermediate zones the R factor ratio given in the table indicates that the densitometer measurements are comparable or of greater accuracy than the visual measurements, the superiority becoming more marked as the contrast improves away from the centre of the film.

Analysis of the reflections showing poorest agreement, showed no significant trends and such reflections were generally common to both sets of data. There is no reason to believe that similar analyses of the other data measured by both methods, would reveal any patterns of agreement different from those indicated above. We may conclude that the evidence points to little, if any, advantage having been gained by measuring the data by the densitometer, but it is highly likely that superior instruments, which now operate accurately under conditions of small photographic contrast, would yield more accurate data in the range of intensities to which they are sensitive.
REFERENCES


   (a) Volume I (1952).
   (b) Volume II (1959).
   (c) Volume III (1962).


44. Schmidt, H., Ber. (1944), 77, 167.


<table>
<thead>
<tr>
<th>Compound</th>
<th>I.R. * (CCl₄)</th>
<th>Δν</th>
<th>U.V. (MeOH) λ max.</th>
<th>Δλ max. μμ</th>
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<tr>
<td>isopinocamphone</td>
<td>1712 cm⁻¹</td>
<td>-</td>
<td>289 μμ (ε, 19)</td>
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<td>2α-bromo-10β-pinan-3-one</td>
<td>1726 cm⁻¹</td>
<td>14 cm⁻¹</td>
<td>312.5 μμ (ε, 130)</td>
<td>23.5 μμ</td>
</tr>
<tr>
<td>4-bromo-pinan-3-one</td>
<td>1727 cm⁻¹</td>
<td>15 cm⁻¹</td>
<td>310 μμ (ε, 220)</td>
<td>21 μμ</td>
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<tr>
<td>10-bromo-pinan-3-ones</td>
<td>1716 cm⁻¹</td>
<td>4 cm⁻¹</td>
<td>298, 308 μμ (ε, 51, 50)</td>
<td>1 μμ</td>
</tr>
<tr>
<td>2α,4α-dibromo-10β-pinan-3-one</td>
<td>1731 cm⁻¹</td>
<td>19 cm⁻¹</td>
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<td>47 μμ</td>
</tr>
<tr>
<td>2α,10-dibromo-10β-pinan-3-one</td>
<td>1724 cm⁻¹</td>
<td>12 cm⁻¹</td>
<td>313 μμ (ε, 115)</td>
<td>24 μμ</td>
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<td>4α,10-dibromo-10α-pinan-3-one</td>
<td>1728 cm⁻¹</td>
<td>16 cm⁻¹</td>
<td>215, 224 μμ (ε, 187, 180)</td>
<td>23 μμ</td>
</tr>
<tr>
<td>2α,4α,10-tribromo-10β-pinan-3-one</td>
<td>1728 cm⁻¹</td>
<td>16 cm⁻¹</td>
<td>336 μμ (ε, 164)</td>
<td>47 μμ</td>
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</tbody>
</table>

* Accurate to ± 0.5 cm⁻¹

MOLECULAR REFERENCE DIAGRAM

2,10-Dibromo-pinane-3-one

2,4-Dibromo-pinane-3-one

3-Halogeno-noninone
THE observed dissociation constants of a number of methylnaphthoic acids as reported by Fischer et al. and in particular, the value for 4,5-dimethyl-1-naphthoic acid, cannot be explained satisfactorily on the assumption that the electronic effects of peri-substituted methyl groups are additive. These observations concerning substituents which must be under severe steric compression or molecular overcrowding, led to the question of just what type of modification of the unstrained molecular structure could be associated with such small but measurable electronic effects. 3-Bromo-1,8-dimethylnaphthalene was chosen as a model for examining the effect on the overall molecular configuration of two methyl groups substituted in peri positions of a naphthalene ring system.

EXPERIMENTAL

Preparation and Crystal Data.—The compound was prepared by the method described by Mitchell, Topsom, and Vaughan in four steps from naphthalic anhydride. It was recrystallized from ethanol and finally appeared as colourless, flattened needles whose direction of greatest elongation corresponded to the shortest crystallographic axis of the chosen triclinic unit cell.

3-Bromo-1,8-dimethylnaphthalene, C_{12}H_{11}Br; M = 235.0; triclinic, a = 8.56 ± 0.02, b = 8.59 ± 0.02, c = 7.71 ± 0.02 Å, α = 118.8 ± 0.1°, β = 97.9 ± 0.1°, γ = 91.2 ± 0.1° (uncertainties are three times the standard errors) assuming λ = 1.5418 Å for Cu-Kα radiation. U = 489.3 Å³, Dm = 1.07 (by flotation), Z = 2, Dc = 1.59, F(000) = 236, linear absorption coefficient for Cu-Kα radiation = 55.4 cm⁻¹ Å⁻¹. A crystallographic centre of symmetry was indicated by Sim’s test using a statistical analysis of the intensity distribution of the hk0 X-ray reflexions, and the space group P1 (C1, No. 2) was confirmed by the structure analysis.

The equi-inclination Weissenberg method was used to record reflexions within the levels hkl · · · 3 and 0 · · · 2kl. 1338 independent reflexions in all, representing 60% of the total Cu-Kα limiting sphere, were accessible in these levels and their intensities were estimated by eye, 54 of them being too weak to observe. Owing to crystal deterioration, three different specimens had to be used. None were large enough to make absorption effects serious and no corrections were made.

Except for the least-squares refinement which is discussed below, all computations were performed on the IBM 4320 computer at the Mobil Computer Laboratory of the University of Canterbury using, in part, programmes supplied by the Institute for Cancer Research (Dr. A. L. Patterson), Philadelphia, U.S.A. Least-squares planes through groups of atoms were evaluated by the method of Schomaker et al.

Structure Determination.—Bromine co-ordinates were located unambiguously from projections of the Patterson function on (001) and (100). A three-dimensional Fourier synthesis based on the bromine signs then revealed all twelve carbon atoms. Preliminary refinement was by six difference Fourier cycles, in the course of which anisotropic thermal parameters for the bromine atom were assigned, using the expression $f = \lambda \exp \left(-\left(h^2a_1^2 + k^2a_2^2 + l^2a_3^2 + 2hka_4 + 2hka_5 + 2hlb_4 + 2lb_5 \right) \right)$. Finally, two three-dimensional least-squares cycles were performed using the programme ORFLS of Busing, Martin, and Levy. All atoms were refined anisotropically but, because of programme limitations, the thermal parameters of only Br, C(11), C(12), and half the remaining carbon atoms could be varied in each cycle. In the first least-squares cycle,
seven scale factors were adjusted and $R$ fell from 0·15 to 0·114. In the second cycle the scale factors were held constant and $R$ fell to its final value of 0·106 for all 1338 observable reflexions, unobserved orders being assigned a value half the minimum observable. The least-squares weighting scheme was based on that of Hughes except for 34 intense inner reflexions which appeared to be suffering from extinction and for which empirical corrections were made from a plot of $F_0/F$ against $F_0$. A 50% error was assigned to each of these reflexions to ensure that they were not unduly weighted in the refinement. The correlation matrix put out by the ORFLS computation showed that there were a number of appreciable interactions between $y$ and $z$ co-ordinates of the same atom (a consequence of the use of non-orthogonal reference axes), the largest correlation coefficient being 0·53 for atom C(5). Atomic scattering factors used were, for carbon, those of Berghuis et al., and for bromine, the Thomas–Fermi–Dirac statistical model values, corrected for anomalous dispersion. A final three-dimensional difference map suggested the positions of most of the hydrogen atoms but these were not included in any structure factor calculations. Final positional parameters for all atoms, referred to a centre of symmetry as origin, are given in Table 1 together with standard deviations derived directly from the least-squares inverse matrix. On account of the interactions already mentioned, values for $\sigma Y$ and $\sigma Z$ are likely to be underestimates. Anisotropic thermal parameters are shown in Table 2. Structure amplitudes for all observed reflexions are listed with the calculated values in Table 3. Standard errors in bond lengths, derived from the listed co-ordinate errors are: for C-C bonds, a maximum of 0·015 Å; for C-Br, 0·011 Å. The corresponding mean standard error for bond angles is 0·8°. Because of the parameter interactions, we shall assume the slightly higher values of 0·17Å, 0·13Å, and 1·0°, respectively, in the subsequent discussion.

**TABLE 1.**

Atomic co-ordinates and standard errors.

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<th>Atom</th>
<th>$x/a$</th>
<th>$\sigma X$ (Å)</th>
<th>$y/b$</th>
<th>$\sigma Y$ (Å)</th>
<th>$z/c$</th>
<th>$\sigma Z$ (Å)</th>
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<td>0·9106</td>
<td>0·001</td>
<td>0·9005</td>
<td>0·001</td>
<td>0·7312</td>
<td>0·002</td>
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**DESCRIPTION OF THE STRUCTURE AND DISCUSSION**

Views of the molecular packing in the crystal structure are shown in Fig. 1. There are no unusually short intermolecular distances, the closest contacts being 3·48 Å for C(1) · · · C(10) and 3·88 Å for Br · · · C(12). The only markedly anisotropic atom is Br whose direction of maximum vibration is approximately normal to the molecular plane.
TABLE 3.
Observed structure amplitudes and calculated structure factors ($\times 10$). Reflections corrected for secondary extinction are marked with an asterisk.

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**Table 3.** (Continued.)

$$d_k = \sum_{j=1}^{m} (d_j)^k$$

$\exists k$
All bond lengths and angles within the molecule are shown in Fig. 2. Although there are differences of up to 0.04 Å within pairs of equivalent bonds, none of these differences rates as being definitely significant. Furthermore no bond within the aromatic nucleus differs significantly from the length of the corresponding bond in naphthalene, the greatest observed difference of this kind being 0.03 Å. Both C-CH₄ bonds have lengths appropriate to the states of hybridisation of the bonded atoms and the C-Br length is not significantly different from other precise values (1.885 and 1.901 Å) for similar environments.

The molecular distortions relative to an unstrained configuration, both within the aromatic rings and external to them are most interesting. The most obvious result of the overcrowding is that the two methyl groups have been pushed apart by 0.42 Å approximately within the mean aromatic plane. This has been achieved mainly by a sideways bending of the C-CH₄ bonds by 4° each, about C(1) and C(8), respectively. There is also however quite considerable in-plane distortion of the naphthalene nucleus itself as indicated
by the inequality of the angles $C(8)C(9)C(1)$ and $C(4)C(10)C(5)$ which in turn leads to the significant difference of $0.12\, \text{Å}$ between the non-bonded distances $C(4)\cdot\cdot\cdot C(5)$ and $C(1)\cdot\cdot\cdot C(8)$. While these in-plane effects together make by far the greatest contribution to the relief of the molecular overcrowding, there are also some smaller but systematic out-of-plane distortions which we shall now consider.

Only one atom, $C(12)$ shows a significant departure ($0.097\, \text{Å}$) from the mean plane of the naphthalene skeleton. However there are definite suggestions that the skeleton itself is non-planar and, as Hirshfeld has recently pointed out, consideration of mean planes through non-planar sets of atoms can be very misleading. A closer examination of ring planarity in the present case shows that the situation is by no means correctly described as
a simple out-of-plane bending of C(8)C(12). Results of a planarity analysis of various portions of the molecule are summarised in Fig. 3. The first important feature to note is that the immediate environment of each of the atoms [C(1), C(3), C(8), C(9), C(10)], which is involved in three bonds with other than hydrogen atoms, is closely planar. Each of the three substituents is therefore coplanar with that portion of the naphthalene skeleton to which it is attached. Inspection of Fig. 3 (c) shows that there is a considerable torsional strain about the bond C(8)–C(9), the angle of twist being 4°. The consequence of this is that one or both of the aromatic rings will be buckled. In fact the six atoms of ring B show no significant departures from planarity so, to a first approximation, the out-of-plane aromatic distortion appears confined to ring A, a consequence evidently of the effect of the heavy bromine substituent in ring B. Figs. 3(c) and (e) help to indicate the precise nature of the distortion of ring A and in Fig. 4 is shown an end-on view of this ring with the out-of-plane displacements exaggerated. Ring B appears to have remained planar only
at the expense of considerable strain in its internal angles $C(1)C(9)C(10)$ and $C(4)C(10)C(9)$, no such strain being apparent in ring A.

![Diagram](image)

**FIG. 4.** End-on view of ring A showing the (exaggerated) displacements from the least-squares plane.

Except for the case of octamethylnaphthalene where considerable buttressing effects come into play, we know of no structure analysis involving two methyl groups in adjacent peri positions. The results reported by Gafner and Herbstein for 1,4,5,8-tetrachloronaphthalene are, however, relevant. Significant out-of-plane displacements in opposite directions were reported for the peri chlorine atoms. An examination of the published displacements shows that here also each chlorine is in fact closely planar with its three nearest carbon atoms and the distortions can be described as twisting about both $C(1)C(9)$ and $C(8)C(9)$ 

$[C(2)C(3)$ and $C(3)C(4)$ in the original paper], buckling occurring in both rings.

It is reasonable to assume that the distortions which are observed for 3-bromo-1,8-dimethylnaphthalene are qualitatively those which occur in 4,5-dimethyl-1- and 2-naphthoic acids. Without attempting a detailed analysis of the consequences of these distortions, we are at least in a position to associate the types of in-plane and out-of-plane molecular strain described, with a small but measurable effect on a physical property of the derived acid, the dissociation constant. Extension of this type of structure analysis to other naphthalene compounds is obviously desirable and further work is planned.

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