P. S. Robertson

STUDIES

RELATED TO

THE CHEMISTRY AND STRUCTURE

of

THE TETRAMER OF HYDROGEN CYANIDE
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Abstract of Thesis

Investigations were made of the chemical behaviour and ultra-violet absorption spectra of the crystalline tetrarner of hydrogen cyanide (and derivatives) in an attempt to establish whether the tetrarner normally exists as aminoisocaproic acid or diaminomaleic acid. Chemical studies including partial hydrolysis, ozonolysis, attempted replacement of a possible labile hydrogen and condensation of a second aldehyde molecule were all inconclusive. Although other workers have established the existence of aminoisocaproic acid, the spectroscopic measurements indicate that the tetrarner normally exists as diaminomaleic acid. These apparently conflicting results may be explained by the tautomeric relationship between the two forms, which in turn explains the inconclusive chemical results which have arisen in so many investigations of the tetrarner.
SECTION I

INTRODUCTION AND HISTORICAL RESUMÉ

OF THE KNOWN CHEMISTRY OF THE CRYSTALLINE

POLYMER OF HYDROGEN CYANIDE

In the 80 years since the only crystallizable polymer of hydrogen cyanide was first isolated there have been considerable changes and some conflicts in the concepts of its constitution and chemistry. That the polymer is a tetramer of hydrogen cyanide is now definitely established by the analysis of a large range of derivatives. For an understanding of the objects of the present work the following review of previous work is given.

The possibility of the presence of different polymeric forms in the amorphous black "azulmic acid", polymerization product of hydrocyanic acid, was first suggested by Gautier. This was confirmed in 1874 when Wippermann extracted, with ether, a white crystalline "trimer" from the dark coloured "azulmic acid" produced by base-catalysed polymerization of hydrogen cyanide.

A year prior to this Lange had isolated a red-brown crystalline compound of empirical formula (HCN)\(x\), from the solid body unexpectedly formed in an attempt to condense hydrocyanic acid and epichlorhydrin. This solid body was undoubtedly the "azulmic acid" formed by Gautier.

TRIMERIC NATURE OF POLYMER

Lange suggested that the crystalline polymer was a trimer \((\text{HCN})_3\) since on baryta hydrolysis, ammonia, barium

---

*He did not suggest that the trimer may be amino-malononitrile as Hinkel, Richards and Thomas' claim.
carbonate and glycine were identified as products. The trimeric nature of the polymer was later supported by Wippermann\textsuperscript{62}, Leascoeur and Rigaut\textsuperscript{37}, Bamberger and Rudolph\textsuperscript{3}, Grischkevitsch - Trochimovski\textsuperscript{16, 17, 22}.

Wippermann indicated that whereas weak acids inhibit, bases, such as epichlorohydrin, catalyse the formation of the "tripolymer" and "azulmic acid". (In this connection see also Girard\textsuperscript{14} and Lewcock\textsuperscript{36}) "Azulmic acid" always accompanies its formation owing to further reaction. He repeated Lange's hydrolysis semi-quantitatively and from the results was able to formulate the equations -

\[(\text{HCON})_3 + 2\text{Ba(OH)}_2 + 3\text{H}_2\text{O} \rightarrow \text{NH}_2\text{-CH}_2\text{-COOH} + 2\text{NH}_3 + \text{BaCO}_3\]

\[(\text{HCON})_3 + 2\text{HCl} + 4\text{H}_2\text{O} \rightarrow \text{NH}_2\text{CH}_2\text{COOH} + \text{CO}_2 + 2\text{NH}_4\text{Cl}\]

thereby supporting the trimeric nature of the polymer.

The formation of glycine led Wippermann to the conclusion that the polymer must be a nitrile, which in turn led to the only logical possibilities,

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{NH}_2 & \\
\text{C} \equiv \text{N} - \text{C} - \text{C} \equiv \text{N} & \text{NH}_2 \\
\text{H} & \\
\text{and} & \\
\text{N} \equiv \text{C} - \text{C} - \text{C} \equiv \text{N} & \\
\text{H} &
\end{align*}
\]

I was rejected as it did not yield the expected formic acid. Aminomalonalonitrile, II, was accepted because the observed products, glycine and carbon dioxide were known (Bayer) to be decomposition products of the expected hydrolysis product aminomalonic acid.

Preparation of a black hydrochloride of apparent composition \((\text{HCON})_3\). 3 HCl + 3 H\text{O} from the crystalline polymer led Leascoeur and Rigaut\textsuperscript{37} also to postulate its being a trimer. (The existence of this trihydrochloride is doubtful as subsequent workers have only been able to
form a white crystalline monohydrochloride.)

Further evidence for the formula aminomalononitrile (II) was obtained when Johnson and Nicolet\textsuperscript{29} used the crystalline polymer as a starting material in a synthesis of 2-thio-6-oxy-4,5-diaminopyrimidine which they explained thus:

\[
\begin{align*}
\text{NH}_2\text{CH} + \text{C}=\text{S} & \rightarrow \text{NH}_2\text{C}=\text{N}\text{H}_2 \\
\text{CS} & \rightarrow \text{CS} + \text{NH}_2\text{H}_2
\end{align*}
\]

In view of the currently accepted tetrameric nature of the polymer it is difficult to explain this synthesis, as they did not specify the by-products of the reaction. The highly basic conditions of the reaction make it probable that it is a hydrolysis product of the tetramer which actually condenses with thiourea.

Substitution reactions as a method of elucidating the structure of the tripolymer were attempted by Grischkevitsch-Trochimovski and co-workers.\textsuperscript{16,17,21,22} They condensed aldehydes, such as benzaldehyde, salicylaldehyde and anisaldehyde and obtained derivatives of the type \( R - \text{CH} = \text{N} - \text{CH(CH)}\text{CN} \), thus confirming the presence of an amino-group. But no evidence was given that these derivatives had been analysed. More recently Hinkel, Richards and Thomas\textsuperscript{26} showed by analysis that derivatives of the type \( R - \text{CH} = \text{C}_4\text{H}_2\text{N}_4 \) are formed with aldehydes. The close agreement between the melting points of the corresponding derivatives of the two schools, indicates that Grischkevitsch-Trochimovski had in fact prepared the same compounds but had interpreted his results in terms of a tripolymer.
TETRAMERIC NATURE OF THE POLYMER

Determinations of the molecular weight of the polymer led Bedel to conclude that it was actually a tetramer and not a trimer as earlier workers had thought. He also found that acid hydrolysis gave, amongst other products, one mol. per mol. of hydrogen cyanide; and that baryta hydrolysis gave a large amount of barium oxalate. Both these were undetected by earlier workers. From these facts and from the fact that the polymer gave a carbylamine reaction he concluded that the tetrapolymer was probably the hydrocyanide of aminomalononitrile. This work still shows the influence of the trimer concept.

DIAMINOMALONONITRILE

Considering the polymer to be a tetramer Grischkevitich-Trochimovski was now able to explain the formation of 4, 5 dicyano - 1, 2, 3 - triazole, by reaction with nitrous acid, thus

$$\text{NC} - \text{C} - \text{NH}_2 \rightarrow \text{NC} - \text{C} - \text{N} = \text{NOH} \rightarrow \text{NC} - \text{C} - \text{NH}_2$$

Formerly, assuming the polymer to be a trimer, he had developed the far more complicated explanation of the condensation as outlined below.

$$\text{NC} - \text{CH-NH}_2 \rightarrow \text{NC} - \text{CH-N} = \text{NOH} + \text{NC} - \text{CH-NH}_2 \rightarrow \text{NC} - \text{CH-N} = \text{N} - \text{NH} - \text{CH}_2$$

The constitution of the triazole was established by hydrolysis to 1, 2, 3 - triazole - 4, 5 - dicarboxylic

*Hinkel, Richards and Thomas incorrectly give the earlier reference for this work.
acid (Bladin\textsuperscript{2}). The existence of two isomeric forms of 4,5 - dicyano - 1, 2, 3 - triazole was suggested by Grischkevitsch - Trochimovski\textsuperscript{16,21} and supported, on doubtful evidence, by Fainkov\textsuperscript{10} Hinkel, Richards and Thomas\textsuperscript{26} have been able to disprove this, using absolutely pure tetramer.

Condensation of glyoxal with the tetramer to yield dicyanopyrazine (characterized by hydrolysis to the dicarboxylic acid, (Gabriel and Sohn\textsuperscript{12} ), was further evidence for both the tetrameric nature of the polymer and its behaviour as a diamine\textsuperscript{16}.

Orthophenylene diamines, although not strictly analogous with aliphatic diamines, are known (Hinsberg\textsuperscript{28}, Richards\textsuperscript{49}) to condense readily with glyoxal to yield quinoxaline.

On the basis that the tetrapolymer also condenses readily to yield a dicyanopyrazine, Grischkevitsch - Trochimovski concluded that it must be a dicyano-, diamino- compound. This made cis-diaminomaleonitrile the only possible configuration.

\[
\begin{align*}
\text{H} - \text{C} = \text{O} &+ \text{NH}_2 - \text{C} - \text{CN} \\
\text{H} - \text{C} = \text{O} &\quad \text{NH}_2 - \text{C} - \text{CN} \quad \rightarrow \\
\quad &\quad \quad \quad \text{diaminomaleonitrile}
\end{align*}
\]

This was further confirmed by the formation of a dicyanotriazole from the tetramer, for under similar conditions o-phenylenediamine was known to form a triazole (Ladenburg\textsuperscript{32,33}).

Under the guidance of L.E. Hinkel work was begun in Britain on the nature of the tetrapolymer in 1927.

In his thesis Thomas\textsuperscript{52} reinvestigated the ebulliometric molecular weight determinations and obtained results varying between (HCH)\textsubscript{3} and (HCH)\textsubscript{5}; analysis of aldehyde and acetyl derivatives led, however, to the definite
establishment of the tetrameric nature of the polymer. As the tetramer would only form a mono-aldehyde derivative Thomas concluded that only one amino group was present. He considered the constitution to be:

\[
\begin{align*}
\text{CH} & = \text{NH} \\
\text{NH}_2 & \quad \text{O} \quad \text{CN} \\
\text{CN}
\end{align*}
\]

Formation of a monohydrochloride definitely disproved Bodel's suggested constitution (the cyanide of aminomalononitrile), and indicated the existence of an amino, or isocyanide group. The presence of the latter was disproved by the failure of the hydrochloride to undergo a Friedel Craft's reaction with benzene to yield benzaldehyde.

\[
\text{H} + \text{C} + \text{HCl} \rightarrow \text{Cl} + \text{C}_6\text{H}_5\text{AlCl}_3 \rightarrow \text{NH}_2 + \text{C}_6\text{H}_5\text{CHO}.
\]

**AMINOMINOSUCINONITRILE**

Richards and Hinkel, Richards and Thomas suggest that the polymerization of hydrogen cyanide to the tetramer proceeds through an intermediate triopolymer of structure III or IV which adds a further molecule of hydrogen cyanide to form V or VI

\[
\begin{align*}
\text{CN} & \quad \text{NH}_2 - \text{CH} - \text{CN} \\
\text{NH}_2 & \quad \text{CH} - \text{CN} \\
\text{NH}_2 & \quad \text{CH} - \text{CN} \\
\text{NH} & = \text{C} - \text{CN} \\
\text{CN} & \quad \text{NH}_2 - \text{CH} - \text{CN} \\
\text{VI} & \quad \text{VII}
\end{align*}
\]

Hinkel, Richards and Thomas continue: "The diamino- maleinonitrile structure VII cannot be considered in this
connection since it necessitates the migration of a hydrogen atom during the addition of the last molecule of hydrogen cyanide and there seems no valid reason for this supposition, nor is there any evidence that the polymer acts tautomERICALLY." Having disposed of the possibility of the \(N-C=N-C\) chain present in VI, by its formation of a pyrazine and not a pyrimidine on condensation with glyoxal, these workers interpreted all behaviour of the tetramer in terms of aminominosuccinonitrile, V. They consider that the tetramer cannot be \(\text{amine}^2\) since it does not react with aldehydes in the same manner as \(o\)-phenylenediamine. But they overlooked the fact that the behaviour of glyoxal and nitrous acid with the tetramer was entirely analogous with the behaviour of \(0\)-phenylenediamine with these same reagents.

Consideration of the conflicting interpretations proposed by Grischkevitsch - Trochimovski and Hinkel leads to a possible explanation of the chemistry of the tetrapolymer: that it is an example of a prototropic tautomeric system.

\[
\begin{array}{c}
\text{H} \\
\text{NH}_2-C=C=\text{N} \\
\text{NH}=C=\text{N} \\
\text{NH}=C=\text{N} \\
\end{array}
\xrightleftharpoons{H^+ \text{ or } NH_2^+} \xrightarrow{\text{H}^+} \xrightarrow{\text{H}^+} \xrightarrow{\text{H}^+} \xrightarrow{\text{H}^+} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

aminomimino-
diamino-
succinonitrile

On this basis all the observed chemistry would be satisfactorily explained. Although the aminominosuccinonitrile has a slightly lower internal energy it will be shown later that from optical activity and ultraviolet absorption spectra, it is probable that the main contributing form is diaminomaleonitrile.
Further consideration must now be given to the work of Kinkel, Richards and Thomas and to their contention that aminociminoacrylonitrile is the only possible form.

Formation of a monohydrochloride is, they consider, evidence for the tetramer being a mononamine compound as all aliphatic diamino compounds are highly basic. From electronic considerations the formation of a monohydrochloride of an α-β unsaturated diamine should, very markedly, reduce its basicity.

\[
\begin{align*}
\text{NH}_2 - & \begin{array}{c} \text{C} \end{array} & \text{R}_1 & Cl \\
\text{NH}_2 - & \begin{array}{c} \text{C} \end{array} & \text{R}_1 & Cl, \\
\text{NH}_2 - & \begin{array}{c} \text{C} \end{array} & \text{R}_2 & \text{NH}_2 - \begin{array}{c} \text{C} \end{array} & \text{R}_2
\end{align*}
\]

The last equilibrium form will make a significant contribution and therefore formation of a dihydrochloride would be unlikely. Furthermore ketamines are known to form relatively stable hydrochlorides (Moreau\textsuperscript{43} etc.) and the behaviour of the imino group of aminociminoacrylonitrile may be compared with these ketamines, though there may be some reduction in activity due to the effect

\[
\text{NH} = \text{C} \rightarrow \text{C} = \text{N}.
\]

Consequently, formation of a monohydrochloride does not provide definite evidence for either V or VII.

As was mentioned earlier, Richards\textsuperscript{49} made a complete reinvestigation of the condensation of the tetramer with glyoxal. He found that the red intermediate, isolated in neutral conditions was not CHO -- CH = N\textsubscript{4} C\textsubscript{4} H\textsubscript{2} as Thomas\textsuperscript{52} had suggested, but was 2 : 3 - dicyano - 5 - hydroxyhydro- pyrazine VIII as it gave no reaction with phenylhydrazine.

\[
\begin{align*}
\text{CHO} & + \text{NH}_2 - \text{CH-CN} \rightarrow \text{CHO} \begin{array}{c} \text{NH} \end{array} = \text{C} - \text{CN} \\
\text{CHO} & \begin{array}{c} \text{NH} \end{array} = \text{C} - \text{CN} \rightarrow \text{CHO} \begin{array}{c} \text{NH} \end{array} = \text{C} - \text{CN}
\end{align*}
\]

VII
The final product 2,3-dicyanopyrazine, IX was definitely established, by Richards, and independently by Linstead Nobel and Wright, not only by conversion to the corresponding acid as Grischkevitsch - Trochimovski had done, but also by conversion to the parent base, and comparison of these with authentic specimens prepared from quinoxaline (Gabriel and Sohn). Richards then investigated the reaction of C-phenylenediamine with glyoxal, and found that its behaviour was "completely analogous with the corresponding reaction of glyoxal with the tetrapolymer of hydrocyanic acid". In both cases a hydroxy-intermediate was isolated. In view of this close analogy it appears that the preceding equation might equally well be written in terms of the diamine, thus:

\[
\begin{align*}
\text{CHO} \quad &\text{HN} - \text{C} - \text{CN} \\
\text{CHO} \quad &\text{HN} - \text{C} - \text{CN} \\
\text{CHO} \quad &\text{HN} - \text{C} - \text{CN} \\
\text{CHO} \quad &\text{HN} - \text{C} - \text{CN} \\
\end{align*}
\]

\[
\text{CH} = \text{N} - \text{C} - \text{CH} \rightarrow \text{CH} = \text{N} - \text{C} - \text{CN} \rightarrow \text{CH} = \text{N} - \text{C} - \text{CN} + \text{H}_2\text{O}
\]

VII IX

Grischkevitsch - Trochimovski interprets the condensation of the tetramer with nitrous acid by analogy with the behaviour of C-phenylene diamine with this reagent. But Hinkel, Richards and Thomas suggest that it is also possible to consider that the condensation proceeds thus:

\[
\begin{align*}
\text{CN} - \text{CH} - \text{NH}_2 \quad &\text{HNO}_2 \\
\text{CN} - \text{CH} - \text{NH}_2 \quad &\text{HNO}_2 \\
\end{align*}
\]

\[
\text{CN} - \text{CH} - \text{NH}_2 \quad \rightarrow \quad \text{CN} - \text{CH} - \text{N} = \text{NCH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH}
\]

V

\[\text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \]

\[\text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \]

\[\text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \quad \rightarrow \quad \text{CN} - \text{C} = \text{NH} \]

Hinkel, Richards and Thomas imply that Grischkevitsch Trochimovski's suggestion, that formation of 2,3 dicyanopyrazine is evidence for diaminomaleinimide, is not acceptable because his characterisation of the pyrazine was not very thorough.
Although the tetramer's rapid reaction with dialdehydes and diketones such as glyoxal, benzil, and diacetyl, to yield the corresponding dicyanopyrazines, lent some support to Grischevitsch-Trochimowski's contention that it is a diamine, its behaviour with monoaldehydes was found to be incompatible with that of O-phenylenediamines. Richards points out that Ladenburg\textsuperscript{34} and later Veil and Marcinkowska obtained heterocyclic condensation products from O-phenylenediamine with aldehydes.

\[
\begin{array}{c}
\text{NH}_2 \text{NH}_2 \\
\text{2 RCHO} \\
\end{array}
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{R} \\
\text{N} \\
\text{CH}_2 \text{R} \\
\end{array}
\]

It was found impossible to form more than a mono-aldehyde derivative of the tetramer however, and then only an open chain derivative was formed. Richards further showed that acetic anhydride yields first a monoacetyl derivative X and then a diacetyl derivative XI,

\[
\begin{array}{c}
\text{NH}_2 \text{CH-CN} \\
\text{Ac}_2 \text{O} \\
\text{CH}_3 \text{CO-NH-CN} \text{CH-CN} \\
\text{Ac}_2 \text{O} \\
\text{NH=CH-CN} \\
\text{CH}_2 \text{CO-N=CH-CN} \\
\end{array}
\]

\[
\begin{array}{c}
\text{V} \\
\text{X} \\
\text{XI} \\
\end{array}
\]

with no evidence of heterocyclic derivatives such as O-phenylenediamine would form

\[
\begin{array}{c}
\text{NH}_2 \text{NH}_2 \\
\text{HO-C-R} \\
\end{array}
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{R} \\
\end{array}
\]

The reliability of this information in establishing the presence of only one amino group is debatable, for the behaviour of an \(\alpha-\beta\) unsaturated \(\alpha,\beta\)diamine cannot be strictly compared with that of resonance-stabilized O-phenylenediamine. Comparison with aliphatic diamines would be preferable. Aliphatic diamines can form monoderivatives with aldehydes(Weiner\textsuperscript{58}) and monoderivatives of both aliphatic and heterocyclic diamines are known to
be fairly stable (Truque,$^{53, 54, 55}$ Gabriel and Coleman,$^{11}$ Baddiley and coworkers,$^{1}$ Zahloré,$^{64}$ Hill and Aspinall,$^{24}$).

Evidence which Hinkel, Richards and Thomas present as conclusive for the presence of but one amino group is that the benzylidene derivative will not react with nitrous acid but is oxidized by nitrous fumes to 4: 5- dicyano-2-phenyliminozole XII which they characterized by hydrolysis and subsequent decarboxylation (Maquenne$^{40, 41}$)

\[
\begin{align*}
\text{CH} & \equiv \text{N} - \text{CH} - \text{CN} \\
\text{NH} & \equiv \text{O} - \text{CN}
\end{align*}
\]

XII

In contrast with this the monoacetyl tetramer reacts with nitrous acid yielding a mixture of 4: 5 dicyano-1; 2; 3-triazole, and its partial hydrolysis product 4 (or 5) cyano-1; 2; 3- triazole-5 (or 4) carboxamide.

Richards strongly criticised the explanation of the hydrolysis, which Grischkevitsch-Trochimovski$^{13}$ proposed

\[
\begin{align*}
\text{CN} - \text{C} - \text{NH}_2 + \text{HOH} & \rightarrow \text{HO-C-NH}_2 \xrightarrow{\text{HOH}} \text{HO-CO-NH}_2 \rightarrow \text{CO}_2 + \text{NH}_3 \\
\text{CN} - \text{C} - \text{NH}_2 & \xrightarrow{\text{CN} - \text{C} - \text{NH}_2} \text{HO-CO-CH}_2\text{NH}_2 + \text{NH}_3
\end{align*}
\]

as attack at the double bond is contrary to the behaviour of methyl-, amino-, and hydroxymaleic acids. These are all stable to boiling alkali. Furthermore, Grischkevitsch-Trochimovski did not explain the formation of oxalic acid.

Richards carried out quantitative hydrolysis experiments. He found that on baryta hydrolysis $\geq 2$ but $\leq 3$ mols. of ammonia were evolved; one mol. of glycine and fractions of a mol. of oxalic, hydrocyanic, and carbonic acids were also produced. Acid hydrolysis gave similar results but one mol. of hydrocyanic acid and no oxalic acid were formed. He explained these results thus.
\[
\begin{align*}
\text{NH}_2 - \text{CH} - \text{CN} & \rightarrow [\text{NH}_2 - \text{CH} - \text{CN}] + \text{NH}_3 (1 \text{ mol.}) \\
\text{NH} & \rightarrow \text{C} - \text{CN} \\
+ \text{H}_2\text{O} & \rightarrow \text{acid hydrolysis} \rightarrow \text{CO}_2 + \text{HCN} (1 \text{ mol.}) \\
[\text{NH}_2 - \text{CH}_2 - \text{CN}] & \rightarrow [\text{CH} - \text{C-OOH}] \\
\text{alkaline hydrolysis} & \rightarrow \text{CO}_2 + \text{HCN} (1.52 \text{ mol.})(1.15 \text{ mol.}) \\
\text{NH}_2 - \text{CH}_2 - \text{COOH} + \text{NH}_3 & \rightarrow (\text{COOH})_2 + \text{NH}_3 (1 \text{ mol.}) (1 \text{ mol.}) (0.65 \text{ mol.})(0.3 \text{ mol.})
\end{align*}
\]

It should be noted, however, that if the final step from XVI was correct there should be produced equal proportions of oxalic acid and ammonia; and also equal proportions of carbon dioxide and hydrogen cyanide.

Grishkevitsch - Trochimowski\(^{19}\) replied to the criticism of Hinkel, Richards and Thomas suggesting that while the tautomeric relationship of the two structures, diaminomaleinonitrile and aminominosuccinonitrile renders all evidence inconclusive the main arguments which they put forward are,

"...(i) that the tetrapolymer behaves as a monoacid base and (ii) that it reacts with only one molecule of benzaldehyde; but they entirely ignore the fact that two cyanogroups would diminish the basic properties of the two aminogroups and that many other amines.... react with only one molecule of an aldehyde forming iminazole derivatives."

Hinkel\(^{25}\) in reply again claimed that there is no evidence for tautomerism and that the presence of a cyanogroup does not inhibit the basic properties of the aminogroup. He further stated that in view of the evidence of Ladenburg\(^{34,35}\); Hinsberg\(^{23A}\); Finnow and Wiskott\(^{47}\)

"O- dimines with aldehydes give rise to the substituted iminazoles XIII and XIV of which XIV predominates
Furthermore in those isolated cases where c-diamines react with only one molecule of an aldehyde, compounds of the type XV result, and these compounds react with a second molecule of an aldehyde...

Although, according to Hinkel, the basicity of the amino group is not inhibited by the presence of a cyano-group in aminoacetonitrile it will have some effect for in the analogous example of cyanoacetic acid the dissociation constant is substantially greater than that of acetic acid.

In a further reply Grischovitsch - Trochimovski claims that the suggested aminociminosuccinonitrile is devoid of convincing experimental data and also that in the reactions of the tetramer with glyoxal and nitrous acid Hinkel, Richards and Thomas are obliged to assume isomerisation with migration of the hydrogen atom and rearrangement of the double bond, when it would be more logical to assume that the grouping $\text{--C--CN}$ already existed.

OPTICAL ACTIVITY

Definite evidence for the existence of the form aminociminosuccinonitrile was obtained by Hinkel and Watkins in 1940 when they succeeded in resolving the $\delta$-camphorsulphonic acid salt of the tetramer. Of the two possible forms
\[ \text{V} \quad \text{and} \quad \text{VII} \]

the former is the only one with an asymmetric carbon and
is therefore the only form capable of being resolved into
optically active isomers.

The diastereoisomeride separated was found to be
hydrolysed by water and also by dilute alkali. The
liberated base was optically inactive, which suggests that
the hydrogen atom on the asymmetric carbon atom is
extremely labile. This is borne out by the mutual inter-
conversion of the diastereoisomeride on simple solution.
The inactivity of the liberated base may be explained by
considering the symmetrical and therefore inactive
diaminomaleinitrile VII as the main contributing form in
the equilibrium of the tautomers.
CHART 1.

THE KNOWN CHEMICAL BEHAVIOR OF THE TETRAMER
BEFORE THE PRESENT STUDIES

\[ \text{Diagram of known chemical reactions involving tetramer compounds.} \]
SECTION II
AIMS AND OBJECTS

The historical resume given in the preceding section has shown that much of the more recent studies have of necessity been reinvestigations of previously "established" results. There has been conflict as to whether the crystalline polymer is a trimer or a tetramer; and following this whether the tetramer is a dimerino- or dimerimino-compound. This latter polemic cannot be said to have ended satisfactorily, and the possibility that these two forms are in equilibrium must not be overlooked.

Questions, such as the following, come easily to mind when considering what is already known of the chemistry of the tetramer and its derivatives.

Is the tetramer mono- or dibasic?

May the carbon-hydrogen bond of the aminomino-formulation be easily broken?

What evidence is there for the presence of a carbon-carbon double bond in the tetramer and its derivatives?

Does the chemical behaviour of the tetramer and its derivatives indicate the presence of a typical imino-group?

Is it possible to condense two molecules of aldehyde with the tetramer?

In Section III these questions are investigated.

The difference in the lengths of the conjugated systems present in the two alternative formulations of the tetramer (and its derivatives) suggests that the absorption spectra of these compounds might establish which form exists in solution. If, as was outlined
earlier, the two forms are actually tautomeric then while the chemical behaviour may give indications of both forms owing to facile interchange, the absorption spectra should indicate the main equilibrium form. The interpretations of the measured absorption spectra of the tetramer and its derivatives is discussed in Section IV.

As a by-product of these investigations several previously unknown derivatives are described.
SECTION III

CHEMICAL INVESTIGATION OF THE
TETRAMER AND DERIVATIVES

I. DISCUSSION OF THE INVESTIGATIONS

A. THE BASICITY OF THE TETRAPOLYMERIC

The basicity of the tetrapolymer has been an important factor in the interpretation of the chemical behaviour of the tetrapolymer since Lescoeur and Rigaut\textsuperscript{37} claimed to have prepared a black, crystalline, trihydrochloride. The preparation of the trihydrochloride has not, however, been supported by subsequent workers who have only been able to prepare a white, monohydrochloride. In fact, Hinkel, Richards and Thomas\textsuperscript{26} suggest that since the tetramer will only form a monohydrochloride, there can only be one amino-group present as in aminoisosuccinonitrile, for "all aliphatic diamines are strongly basic and yield dihydrochlorides". This is, however, not necessarily the case because in dianimomaleonitrile, as has been pointed out in Section I (page 8), formation of the monohydrochloride of a compound with two amino-groups on adjacent, ethylenic-linked carbon atoms, would reduce the basicity of the second amino-group. Furthermore aminoisosuccinonitrile would also be expected to form a dihydrochloride for, by analogy the -NH group of ketimines will also form a relatively stable hydrochloride under similar conditions\textsuperscript{43}. Thus formation of a monohydrochloride is evidence for either form.

Grischkevitch-Trochimovskij\textsuperscript{24} has suggested that the basicity of the amino-group present in the dianimomaleonitrile formulation would be reduced by the two cyano-groups
present. Hinkel\textsuperscript{25} on the other hand, claims that no such effect exists, taking as an example the ready formation of a hydrochloride by aminoacetonitrile.

The importance attributed to the basicity of the tetramer led, in the present work, to the measurement of the pH of an aqueous solution. This gave considerable support to the suggestion that the basicity of the amino-group(s), present in both formulations of the tetramer, will be reduced, for rather than being a weak base it was found that the tetramer was a weak acid.

That the negative inductive effect of the groups is partially responsible for this reduction of basicity is supported by the increased dissociation constant of acetic acid on introduction of a cyano group to give cyanoacetic acid.

It appears that the tetrapolymer is almost completely dissociated in acid solution, for an attempt to detect the presence of an "end point" corresponding to formation of a mono- or dihydrochloride, by measurement of pH during hydrochloride acid titration, was completely unsuccessful. (Graphs 1 and 2)

D. THE LABILE HYDROGEN OF THE AMINOIMINO-
FORMULATION OF THE TETRAPOLYMER

Hinkel and Watkins\textsuperscript{27} have established that the tetramer may exist in the optically active aminoimino-succinonitrile form, in which a hydrogen atom is bonded to the asymmetric carbon atom thus:

\[
\begin{align*}
\text{NH} & \quad \text{C} \quad \text{CH} \\
\text{NH}_2 & \quad \text{C} \quad \text{CH} \\
\text{NH} & \quad \text{C} \quad \text{CN}
\end{align*}
\]

It appears, for reasons outlined in Section I, that this
GRAPH 1

TITRE OF 380c.c. OF AN 0.0096N.
AQUEOUS SOLUTION OF THE TETRABER
WITH 0.1143N. HCL.

c.c. of 0.1143N. HCl →
Graph 2.

Titre of 380 c.c. of an 0.00953N. aqueous solution of the tetramer with 0.02841N. HCl.
hydrogen is possibly capable of shifting to the imino-group. The finding of such a labile hydrogen would thus be a significant addition to the knowledge of the behaviour of the tetramer. The presence of the reactive cyano- and amino-substituents complicates such an investigation, for reagents which will replace a labile hydrogen may also react with these groups. For this reason no attempt was made to replace this hydrogen by use of a Grignard reagent.

Brightly coloured solutions resulted from treatment of the tetramer with metallic sodium powder or sodium ethoxide, but no definite sodio-derivative could be isolated, nor could any methyl-substituted derivative be isolated after treatment of these solutions with methyl iodide.

The failure of these attempts to isolate a sodio-, or methyl- derivative was probably due to decomposition and to side reactions with the amino-group(s) and cannot be interpreted as evidence that such a hydrogen does not exist.

C. THE TETRAPOLYMER WITH ALDEHYDES

The behaviour of the tetrapolymer with aldehydes has in the past received considerable attention. In no instance has it been found possible to couple more than one monosaldehyde with the tetramer, a fact which lends some support to Hinkel, Richards and Thomas's contention that there is only one amino-group present in the tetrapolymer.

Acrolein, cinnamaldehyde, p-hydroxybenzaldehyde and p-nitrobenzaldehyde were successfully condensed with the tetramer to provide suitable derivatives for the spectroscopic investigation (Section IV), and to increase the knowledge of the reactions of the tetrapolymer. The
tetramer in some instances appears reluctant to condense with even one aldehyde molecule. Repeated attempts to condense phenylacetalddehyde, n-butyaldehyde and acetaldehyde with the tetramer were unsuccessful.

Replacement of One Aldehyde by Another

In an endeavour to add a second, different molecule of an aldehyde, Richards\(^4^9\) found that although the desired result was not achieved, there had been a replacement of one aldehyde by the other.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} = \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 + \text{CHO} \\
\text{CH}_3 & \quad \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 + \text{CH}_3 \quad \text{CH} = \text{CHO}
\end{align*}
\]

He claims:

"The double bond between the carbon and nitrogen atoms in the aliphatic aldehyde and ketone derivatives of the tetramer appears to be easily broken. In all cases of competitive condensation between aliphatic and aromatic derivatives with the tetrapolymer, the aromatic polymer derivative is invariably formed."

In the present work, further attempts were made to introduce more than one aldehyde grouping and thereby to establish the possibility of the presence of more than one amino-grouping. As a result of the use of a second, different aldehyde it was shown that not only will aromatic aldehydes replace aliphatic aldehydes, but also one aromatic aldehyde will displace another.

\[
\begin{align*}
\text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 + \text{CHO} & \quad \rightarrow \quad \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 \\
\text{HO} - \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 + \text{CHO} & \quad \rightarrow \quad \text{HO} - \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 \\
\text{HO} - \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3 + \text{CHO} & \quad \rightarrow \quad \text{HO} - \text{CH} = \text{N} - \text{C}_4\text{H}_2\text{N}_3
\end{align*}
\]

It has been found that these reactions are not reversible.
That is, p-nitrobenzaldehyde will replace both the benzylidene and the p-hydroxybenzylidene substituents. Benzaldehyde will only replace a phydroxybenzylidene substituent but p-hydroxybenzaldehyde will replace neither the p-nitrobenzylidene nor the benzylidene substituents.

If the aldehyde derivatives are considered as being derived from aminoiminocetanin, then the change of substituents can only be due to replacement on one amino-group. However in the diaminomaleinitrile formulation VII of the tetrapolymer it is possible that the second molecule may add before the other aldehyde group is released. The replacement of a benzylidene substituent by p-nitrobenzaldehyde may be considered as involving one of the following as an intermediate:

\[
\begin{align*}
\text{NO}_2\text{CH}=\text{N}-\text{C}_4\text{H}_2\text{N}_3 & \quad \text{CH}_2\text{C}_4\text{H}_2\text{N}_3 \\
\text{CH}=\text{N}-\text{C}_4\text{H}_2\text{N}_3 & \quad \text{NO}_2\text{CH}
\end{align*}
\]

That the benzylidene substituent of the benzylidene-acetyl-derivative is not replaced by p-nitrobenzaldehyde is negative evidence for the replacement preceding via the first of these intermediates. The effect of the acetyl substituent may be more than that of merely blocking one amino-group. In addition no trace of any dialdehyde derivative has been found.

The last of the proposed intermediates may be considered to be due to slight hydrolysis,

\[
\begin{align*}
\text{CH}=\text{N}-\text{C}_4\text{H}_2\text{N}_3 & \quad \text{CH}_2\text{C}_4\text{H}_2\text{N}_3 \\
\text{CH}_2\text{C}_4\text{H}_2\text{N}_3 & \quad \text{CH}_3\text{CHO} + \text{NH}_2\text{C}_4\text{H}_2\text{N}_3
\end{align*}
\]

Its presence is supported by the ease with which the benzylidene derivative has been hydrolysed to give free benzaldehyde (this Section page 28). Furthermore, this replacement reaction appears to be acid-catalysed and may
be envisaged as the result of competition for free tetramer.

The nucleophilic amino-group will react most rapidly with the aldehyde in which there is the greatest deficiency of electrons on the carbonyl-carbon atom. Thus a replacement may be expected, in these examples, to be related to the relative dipole moments of the competing species.

**TABLE I**

**DIPOLE MOMENTS OF ALDEHYDES INVOLVED IN REPLACEMENT REACTIONS**

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Electron Displacement</th>
<th>Dipole Moment</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-C=O-CHO</td>
<td>←→</td>
<td>4.19</td>
<td>C₆H₆</td>
<td>46</td>
</tr>
<tr>
<td>CH₃-C=O-CHO</td>
<td>←→</td>
<td>2.75</td>
<td>C₆H₆</td>
<td>61</td>
</tr>
<tr>
<td>CH₃--CH-OH</td>
<td>←→</td>
<td>2.58</td>
<td>C₆H₆</td>
<td>9</td>
</tr>
<tr>
<td>NO₂-C=O-CHO</td>
<td>←→</td>
<td>2.4</td>
<td>C₆H₆</td>
<td>61</td>
</tr>
</tbody>
</table>

The order of decreasing electron density on the carbonyl carbon is paralleled by a decrease in ease of replacement. An exception to this is that benzaldehyde will replace the iso-butylidene substituent. The dipole moments of this pair are however similar and this apparent anomaly may perhaps be explained by resonance stabilization, or by the lower solubility of the benzylidene derivative.

The Benzylidene-Acetyl-Derivative of the Tetrapolymer

Hinkel, Richards and Thomas[26] have found that "Although the benzylidene derivative does not unite with a second molecule of benzaldehyde, yet on vigorous acetylation it
yields an acetyl derivative..." for which they propose
the structure (XVI).

\[
\begin{align*}
\text{CH}_3\text{CO} &= \text{C} - \text{CN} \\
\text{CH} &= \text{N} - \text{C} - \text{CH} \\
\text{H} &= \text{H} - \text{CH} - \text{CH}
\end{align*}
\]

(XVI)

Since an aldehyde can only condense with an amine-group
it is apparent that the acetyl-group must add to the
imino-group present in the amimino-concept of the
bensilidene derivative.

In the present work it has been found that the above
procedure of Minkel, Richards and Thomas may be reversed;
benzaldehyde may be condensed with the monoacetyl
derivative to give the same benzylidene-acetyl-derivative
of the tetrapolymer. Thus their assumption that an amine-
group is acetylated more readily than an imino-group is
invalid, or else the tetrapolymer is behaving here as
diaminomaleinitrile (VII).

i.e. either

\[
\begin{align*}
\text{NH}_2\text{C-CNV} &\xrightarrow{\text{AC}_2\text{O}} \text{NH}_2\text{C-CHCN} \\
\text{NH} &= \text{C} - \text{CN} \\
\text{CH}_3\text{CO} &= \text{C} - \text{CN}
\end{align*}
\]

or

\[
\begin{align*}
\text{NH}_2\text{C-CNV} &\xrightarrow{\text{AC}_2\text{O}} \text{NH}_2\text{C-CNV} \\
\text{NH} &= \text{C} - \text{CN} \\
\text{CH}_3\text{CO} &= \text{C} - \text{CN}
\end{align*}
\]

(XVI)

The possibility that an amine group is acetylated
initially but rearranges under the influence of benz-
aldehyde to produce (XVI) has not been considered.
Acetylation of an imino-group in preference to an amino-
group is to be expected on theoretical grounds as the
former has a potentially greater electron density and the
acetylation reagent is electrophilic.
The addition of an acetyl- group to the tetrapolymer is far easier than its addition to the benzylidene derivative (Richards). That is, the presence of an aldehyde substituent considerably reduces the reactivity of the remaining amino- or imino- group present respectively in the diamino- or aminosimino- formalations of the tetrapolymer. This may account for the fact that a second aldehyde molecule has not been condensed with the tetrapolymer. Similarly it may explain the failure of acetic anhydride to acetylate the p-nitrobenzilidene derivative when using the same procedure as Richards used to acetylate the benzylidene derivative.

An attempt was made to parallel the addition of benzaldehyde to the acetyl- derivative. It was found that using p-nitrobenzaldehyde the acetyl-group was lost and the p-nitrobenzylidene derivative of the tetrapolymer formed, possibly via the apparently unstable p-nitrobenzylidene-acetyl- derivative.

D. EVIDENCE FOR THE PRESENCE OF AN IMINO- GROUP

Hinkel and Watkins have succeeded in obtaining the tetramer in an optically active form. Thus there is no doubt that the tetramer or at least its camphorsulphonate can exist in the asymmetric aminosimino- form. On this basis it might be expected that the tetramer would exhibit reactivity characteristic of the presence of an imino-grouping. Previous workers have brought forward no positive evidence for the existence of this grouping. The evidence which Hinkel, Richards and Thomas present (i.e. condensation of the tetramer with but one aldehyde group, and formation of a monohydrochloride only), is negative and, as was pointed out earlier, is not very significant.

The most marked difference between the behaviour of
amino- and imino- groups is the possibility of hydrolysing only the latter to the corresponding ketone. This provided the basis of the method used in an attempt to establish the presence of an imino- group in the tetramer and its monoacetyl-, benzylidene- and p- hydroxybenzaldehyde derivatives. As the tetramer was known to be completely hydrolysed by both acid and alkali $^{62,35,4,18,26}$ etc. it was necessary to introduce a reagent which would couple with the keto- grouping as soon as it was formed. For this purpose $2:4$- dinitrophenylhydrazine, semicarbazide hydrochloride and hydroxylamine hydrochloride were used under the varied conditions outlined in the experimental section of this section. The intended overall reaction was expected to be,

\[
\begin{align*}
\text{NH}_2\text{CH-CN} & \xrightarrow{H_2O} \text{NH}_2\text{CH-CN} & \xrightarrow{\text{RNHNH}_2} \text{NH}_2\text{CH-CN} \\
\text{NH=CN} & \quad 0 = \text{C-CN} & \text{R.NHN=C-CN}
\end{align*}
\]

but in no case was any such derivative isolated. In several attempts the starting materials were recovered unchanged, while in the case of the benzylidene derivative of the tetramer, some benzylidene $2:4$- dinitro-phenylhydrazone was also isolated. This indicates that the benzylidene group may be hydrolysed from the tetramer.

Failure to isolate the expected derivative of aminoiminosuccinonitrile is extremely doubtful evidence that the imino- group does not exist. The experimental conditions may not have been suitable.

---

*This is especially true as Hinkel (unpublished work) claims to have obtained

\[
\text{NH}_2\text{CH-CN} \\
(\text{NO}_2)_2 \text{C}_6\text{H}_3\text{NH}-\text{N} = \text{C} - \text{COOH}
\]

from the monoacetyl derivative after prolonged heating with an acid solution of dinitrophenylhydrazine. The present attempt to repeat this was completely unsuccessful.
THE ETHYLENIC DOUBLE BOND OF DIAMINOMALEINITRILE

The greatest difference to be expected in the chemistry of the aminociminoacioconitrile and diamino-
maleinitrile formulations of the tetramer will be due to the existence of an ethylenic double bond in only the
latter.

\[
\begin{align*}
\text{NH}_2 - \text{CH} & \quad \text{NH}_2 - \text{CN} \\
\text{NH} & \quad \text{C} \quad \text{CN} \quad \text{CN} \\
\end{align*}
\]

It is known, however, that this compound would not be expected to exhibit the normal reactivity of such a bond because the unsaturated carbon atoms carry substituents other than hydrogen. Bromination may even be impossible. (See for example, Tarbell and Bartlett\textsuperscript{51}, Korshak and Lisenko\textsuperscript{30}).

Unsaturated compounds in contact with ozone usually form unstable ozonides which, on mild hydrolysis, undergo scission to form ketones, aldehydes, or acids depending on the nature of the other substituents.

The rate at which ozone reacts might be expected to be slow, for Noller and co-workers\textsuperscript{114} have shown that the reaction is slower for compounds in which the double bond is conjugated with a carbonyl linkage. In diamino-
maleinitrile the double bond is conjugated with two cyano groups.

Tetrapolymer.

In practice the treatment of the tetramer (1 mol.) with ozone has been found to yield after hydrolysis, by warming with water, the ammonium salt of oxamic acid (\(\text{NH}_2\text{CO}\text{COONH}_4\)) (0.5 mol.) contaminated with oxamic acid itself, together with an unidentified "oil". As ozone was absorbed by the tetramer it is probable that these products are the result of scission of an ozonide.
The dianimomaleinitrile formulation of the tetramer may form oxamic acid as a result of treatment with ozone, and subsequent hydrolysis of the ozonide thus:

\[
\begin{align*}
\text{NH}_2\text{C-CN} & \quad \text{O}_3 \quad \text{then} \\
\text{NH}_2\text{C-CN} & \quad \text{hydrolysis} \\
\text{NH}_2\text{C-CN} & \quad \text{further} \quad \text{hydrolysis} \quad \text{NH}_2\text{C-COOH} \\
& \quad \text{NH}_2\text{C-CN}
\end{align*}
\]

The main objection to this explanation is that only a quarter of the theoretical yield of ammonium oxaminate was isolated. This may possibly be explained by incomplete hydrolysis, for the "oil" which accompanies the formation of ammonium oxaminate has been found to evolve hydrogen cyanide on standing, while barium hydrolysis evolved ammonia and barium oxalate separated from the solution, which on acidification evolved free hydrogen cyanide.

Alternatively, if it is considered that the tetrapolymer undergoes attack in the aminomino-form then a ketone would be expected to be formed thus:

\[
\begin{align*}
\text{NH}_2\text{CH-CN} & \quad \text{O}_3 \\
\text{NH}_2\text{C-CN} & \quad \text{hydrolysis} \\
\end{align*}
\]

The latter is the first product in the acid or base catalysed hydrolysis of the tetramer, proposed by Richards. His scheme of alkaline hydrolysis proceeds via oxamic acid as an intermediate.

*Although Richards formulates the last step thus,

\[
\begin{align*}
\text{HOO-C-CN} & \quad \text{HOO-C-COOH} + \text{NH}_3
\end{align*}
\]

it may reasonably be assumed that this would proceed via oxamic acid as an intermediate.
Thus it is possible to explain the formation of oxamic acid as a result of ozonolysis of aminocimino-
succinonitrile. As the hydrolysis was performed under
approximately neutral conditions, the isolation of oxamic
acid is not at variance with the normal isolation of
oxalic acid, for oxamic acid is hydrolysed by alkali to
form oxalic acid.

The main evidence against this scheme is that the
formation of an ammonium salt demands that ammonia must
be formed in the reaction. And although it appears that
the reaction did not proceed thus, as aminosacetic acid
was not isolated. Furthermore beryta hydrolysis of the
"oil" (also produced) gave no barium carbonate which
according to Richards' scheme should accompany the forma-
tion of hydrogen cyanide and barium oxalate from

\[
\begin{array}{c}
\text{Diacetyl derivative of the Tetrapolymer} \\
\text{Ozone was apparently not absorbed by a solution of}\n\text{the diacetyl derivative of the tetrapolymer. After the}\n\text{passage of more than twice the theoretical amount of ozone,}\n\text{and hydrolysis with water, the bulk of the diacetyl}\n\text{derivative was recovered unchanged. This difference of}\n\end{array}
\]

*The molecular proportion of ammonium oxalate from
the ozonolysis was at least 0.5 mol. per mol. of tetramer.*
behaviour from that of the tetramer may possibly be attributed to either the presence of larger groups on the ethylene carbon atoms of diacetyl-diaminomaleinitrile or to the resistance to attack of the $\text{N} = \text{C}$ bond of acetil-aminoacetyliminosuccinonitrile which is now conjugated with a carbonyl linkage.

It may be seen that ozonolysis, while pointing somewhat to the diamino-formulation of the tetrapolymer, has not yielded definite evidence for either form. It is however possible that a more intensive investigation may permit a definite conclusion to be reached about which form of the tetrapolymer is attacked.
AN ABBREVIATION OF THE PRESENT CHEMICAL STUDIES OF THE TETRAMER

Prepared by earlier workers.
Prepared in the present studies.
Unsuccessful, attempted reaction.

N.B. In these examples it is not necessarily the aminoform which undergoes reaction.
FIGURE 1.

REDISTILLATION APPARATUS

A. Distilling flask and column
B. Receiver
C. Transfer Vessel
II. EXPERIMENTAL

A. PREPARATION OF THE TETRAPOLYMER

OF HYDROGEN CYANIDE

Purification of Hydrogen Cyanide

Commercial hydrogen cyanide was fractionally distilled from the stabilizer, through an efficient column, the first and last fractions being rejected. The distillate was allowed to stand over phosphorus pentoxide for several days in order to remove traces of moisture. The hydrogen cyanide was then distilled from the drying agent in the apparatus shown in figure 1.

Polymerisation

Several unsuccessful attempts were made to prepare the tetrapolymer by the catalytic method developed by Woodward. A description of these attempts is given in Appendix A.

The failure of the above method necessitated a reversion to the method outlined by Thomas and Richards which produces large quantities of the brown-black "azulmic acid" containing only a small percentage of the tetrapolymer.

Hydrogen cyanide (c.a. 500 cc.) to which had been added a few ml. of either a concentrated sodium hydroxide solution, or 0.880 ammonia, was allowed to stand until the whole solution had polymerised. The brown-black "azulmic acid" so obtained was powdered and exhaustively extracted with ether in a Soxhlet apparatus. The brown solid which separated from the ether was purified by dissolving in boiling water, decolourisation with animal charcoal and rapid cooling. After two similar recrystallisations the tetrapolymer was obtained in colourless plates, m.p. 184°C, with decomposition.
B. THE BASICITY OF THE TETRAMER

A solution of pure crystalline tetrapolymer (380 c.c. of 0.0095M) was dissolved in carbon dioxide-free distilled water, and the pH of the resultant solution measured immediately (pH 6.17) with a calomel-glass-electrode pH meter (Cambridge No. L-238026). The mechanically stirred solution was then rapidly titrated with standard hydrochloric acid (0.1143M) until more than the theoretical volume required to form the dihydrochloride had been added. Accurate results in the range zero to 0.5 c.c. of added hydrochloric acid were obtained by use of a more dilute solution (0.0234M) and a micro-syringe ("Agla" accurate to ±0.00005 c.c.) (Graph 2).

C. THE TETRAPOLYMER WITH ALDEHYDES

The syntheses of the various derivatives referred to in Section I, part C of this Section were based on the methods used by Hinkel, Richards and Thomas for their preparation. The following have not been previously described, although the procedures adopted are similar to that used by Hinkel et. al. for previously known derivatives.

Condensation of the Tetramer with Acrolein

The tetrapolymer (1 g. : 1 mol.) was warmed with freshly distilled acrolein (1.9 c.c. : 3 mol.) until the former had all dissolved. The solution was rapidly cooled. A crystalline compound separated which, after recrystallisation from absolute alcohol, formed bulky, dull yellow crystals (0.8 g.), m.p. 126-126.5°C.

Analysis. Found: N semi-micro Kjeldahl 37.85%. C7H6N4 requires N, 38.35%.
Condensation of the Tetramer with Cinnamaldehyde

The tetrapolymer (0.5 g. : 0.5 mol.) was dissolved in absolute alcohol (5 c.c.) and added to cinnamaldehyde (0.8 c.c. : 0.55 mol.). This solution was refluxed for 45 minutes in which time it became semi-solid. The orange-yellow solid was filtered off and recrystallized, first from acetone, then from absolute alcohol. Orange-yellow plates (0.7 g.) were formed, m.p. 202-203°C with decomposition commencing at 135°C.

Analysis. Found: N, 25.40%. C_{13}H_{10}N_4 requires N, 25.23%.

Condensation of the Tetrapolymer with p-Hydroxybenzaldehyde

The tetrapolymer (1 g. : 1 mol.) and p-hydroxybenzaldehyde (1.1 g. : 1 mol.) were dissolved in absolute alcohol (20 c.c.) and heated under reflux for forty minutes. On cooling, the condensation product separated and was recrystallized from absolute alcohol (3x), which gave pale yellow crystals (1.3 g.), m.p. 222.5 - 223°C.

Analysis. Found: N, 26.45%. C_{11}H_{8}ON_4 requires N, 26.42%.

Condensation of the Tetrapolymer with p-Nitrobenzaldehyde

Alcoholic solutions of the tetrapolymer (2 g. : 2 mol., in 15 c.c.) and p-nitrobenzaldehyde (2.9 g. : 2 mol., in 10 c.c.) were heated under reflux for thirty minutes. The copious precipitate, which began to separate after five minutes, was washed with hot absolute alcohol. The fine, intensely yellow crystals melted at 258 - 258.5°C with decomposition.

Analysis. Found: N, 29.15%. C_{11}H_{8}O_{2}N_5 requires N, 29.02%.

Attempted Condensation of the Tetrapolymer with Phenylacetaldehyde

Phenylacetaldehyde was reacted with the tetrapolymer under the same conditions as for the condensation of
p-nitrobenzaldehyde with the tetramer (Hinkel, Richards and Thomas\textsuperscript{26}). The tetrapolymer was recovered unchanged.

Using the same procedure as above, but with a few drops of acetic acid, and crystals of oxalic acid as catalysts, extensive decomposition was observed without the isolation of a simple derivative.

**Attempted Condensation of the Tetrapolymer with n-butyraldehyde and Acetaldehyde**

As iso-butyraldehyde condenses readily with the tetramer (by a method similar to the condensation of p-nitrobenzaldehyde) an attempt was made to condense n-butyraldehyde with the tetrapolymer by the same method (Richards\textsuperscript{49}). The tetrapolymer was recovered unchanged.

Similar results were obtained with acetaldehyde.

The tetramer was recovered unchanged after it had been boiled under reflux for forty minutes in a large excess of n-butyraldehyde.

**Replacement of One Aldehyde by Another**

It has been found that some of the possible aldehyde substituents of the tetrapolymer may be replaced by other aldehydes.

**p-Nitrobenzaldehyde with the Benzylidene derivative**

To the benzylidene derivative of the tetramer (0.21 g.; 0.1 mol.) dissolved in absolute alcohol (5.5 c.c.) was added p-nitrobenzaldehyde (0.25 g.; 0.17 mol.). The benzylidene derivative was recovered unchanged after the solution had been boiled under reflux for forty five minutes.

This attempted condensation of a second molecule was repeated with the addition of glacial acetic acid (0.25 c.c.), while a reflux period of four hours led to the separation of a yellow solid (0.12 g.) which, after
washing with absolute alcohol, melted at 249.5 - 250°C. A mixed melting point confirmed that the product was the p-nitrobenzylidene derivative of the tetrapolymer. No other derivative was isolated.

Benzaldehyde with the p-Nitrobenzylidene derivative

Freshly distilled benzaldehyde (2 c.c. : 1.7 mol.) was dissolved in absolute alcohol (2 c.c.) and refluxed with the p-nitrobenzylidene derivative (0.5 g. : 0.23 mol.) for four hours with no apparent change. Glacial acetic acid (0.2 c.c.) was then added and refluxing continued for a further eight hours in the oxygen-free system obtained by the passage of nitrogen into the reaction vessel throughout the reaction.

The reverse of the previous condensation does not readily take place as the p-nitrobenzylidene derivative was recovered (0.52 g.) unchanged.

Benzaldehyde with the p-Hydroxybenzylidene derivative

Freshly distilled benzaldehyde (0.25 c.c. : 0.2 mol.) was dissolved in absolute alcohol (3 c.c.) containing the p-hydroxybenzylidene derivative (0.29 g. : 0.14 mol.). After the addition of glacial acetic acid (0.25 c.c.) the solution was boiled under reflux for eight hours. The pale yellow solid which separated on cooling was recrystallized from absolute alcohol and shown by melting point and mixed melting point to be the benzyldene derivative of the tetrapolymer.

p-Hydroxybenzaldehyde with the Benzylidene derivative

This reaction was attempted by the same method as was used in the preceding experiment. The benzylidene derivative was recovered unchanged.
p-Nitrobenzaldehyde with the p-Hydroxybenzylidene derivative

Hot alcoholic solutions of p-nitrobenzaldehyde (0.25 g., 0.17 mol. in 1.4 c.c.) and the p-hydroxybenzylidene derivative (0.33 g., 0.16 mol. in 3.4 c.c.) containing glacial acetic acid (0.15 c.c.) were mixed, and refluxed for four hours. The solid was filtered off (0.1 g.) washed with absolute alcohol, and shown by mixed melting points, with an authentic specimen, to be the p-nitrobenzylidene derivative.

Dilution of the filtrate with water precipitated out a compound (.25 g.) which was shown by mixed melting points, to be unchanged p-hydroxybenzylidene derivative. The replacement is thus not an extremely rapid reaction.

p-Hydroxybenzaldehyde with the p-Nitrobenzylidene derivative

The p-nitrobenzylidene derivative (0.114 g., 0.47 mol.) and p-hydroxybenzaldehyde (0.051 g., 0.42 mol.) were suspended in absolute alcohol (3 c.c.) containing glacial acetic acid (0.15 c.c.). After boiling under reflux for three hours the solution was allowed to stand for fourteen days. The precipitate, after washing with absolute alcohol was shown to be unchanged p-nitrobenzylidene derivative (0.106 g.)

Concentration of the filtrate and washings allowed the recovery of some of the p-hydroxybenzaldehyde.

p-Nitrobenzaldehyde with the Benzylidene-acetyl derivative

The benzylidene-acetyl derivative of the tetrapolymer (0.08 g., 0.03 mol.) and p-nitrobenzaldehyde (0.09 g., 0.06 mol.) were dissolved in a mixture of alcohol (7 c.c.) and acetone (1.5 c.c.) containing acetic acid (0.4 c.c.).
The crystalline precipitate which was filtered off after thirty hours refluxing was shown to be \( p \)-nitrobenzaldehyde.

The filtrate was concentrated by evaporation and a crystalline solid separated out. This was shown by mixed melting points with an authentic specimen to be unchanged benzylidene-acetyl derivative.

THE ALDEHYDE-ACETYL-DERIVATIVES OF THE TETRAPOLYMER

It has already been shown that acetic anhydride may be condensed with the benzylidene derivative of the tetrapolymer (Richards\(^4\)). In the following experiment it may be seen that the reverse procedure is also possible.

Condensation of the Monoacetyl derivative with Benzaldehyde

Freshly distilled benzaldehyde (0.04 c.c. : 0.04 mol.) diluted with absolute alcohol (0.6 c.c.) was heated under reflux with the monoacetyl derivative (0.06 g. : 0.04 mol.) for 35 minutes. Cooling caused a crystalline solid to separate which after recrystallization from absolute alcohol formed colourless, fine crystals (0.055 g.), m.p. 217.5-219°C with darkening and gas evolution. A mixed melting point with an authentic specimen showed this compound to be the benzylidene-acetyl derivative of the tetrapolymer.

Attempted Condensation of the Monoacetyl-derivative with \( p \)-Nitrobenzaldehyde

The monoacetyl derivative (0.26 g. : 0.17 mol.) and \( p \)-nitrobenzaldehyde (0.286 g. : 0.19 mol.) were dissolved in hot absolute alcohol (approximately 1.5 c.c.) containing glacial acetic acid (0.1 c.c.). After heating under reflux for fifty minutes and cooling, a cream crystalline solid separated which was shown to be \( p \)-nitrobenzaldehyde.

A bright yellow solid crystallized out when the
filtrate was concentrated by evaporation. After washing with absolute alcohol these crystals were found (melting point and mixed melting point) to be the p-nitrobenzylidene derivative. As this derivative is normally highly insoluble in alcohol it appears that its isolation from the filtrate indicates that it may be the breakdown product of an unstable, relatively soluble, compound; possibly the p-nitrobenzylidene derivative which was not isolated.

**Attempted Condensation of the p-Nitrobenzylidene derivative with Acetic Anhydride**

The p-nitrobenzylidene derivative of the tetrapolymer (0.34 g.; 0.14 mol.) was heated under reflux for forty five minutes with acetic anhydride (3 c.c.; excess), and filtered hot. Both the precipitate from the cooled filtrate and the undissolved material were shown to be unchanged p-nitrobenzylidene derivative.

**An Attempt to Prepare an Aldehyde - Ketone derivative of the Tetrapolymer**

Diacetyl has been found to condense readily with the tetrapolymer (Richards²⁹) to form a heterocyclic derivative. This suggests that diacetyl might condense with an aldehyde derivative of the tetrapolymer, thereby establishing the presence of a second amino-group.

Dissolution of the benzylidene derivative (0.228 g.; 0.12 mol.) in diacetyl (0.5 mol.) was accomplished by the addition of absolute alcohol (1.4 c.c.) containing glacial acetic acid (0.15 c.c.). This solution was refluxed for two hours and allowed to stand overnight. The bulk of the benzylidene derivative initially present was recovered unchanged.
D. EVIDENCE FOR THE PRESENCE OF AN IMINO- GROUP

The following is an outline of the attempt to establish the presence of an imino-group, in the tetramer and some of its derivatives, by hydrolysis of this group to a carbonyl group and the subsequent locking of the carbonyl linkage by a suitable reagent.

THE TETRAMER HYDROLYSED BY ACID IN THE PRESENCE OF THE REAGENT

(i) 2 : 4-DINITROPHENYLHYDRAZINE

Approximately 0.2 g. of the tetrapolymer were dissolved in alcohol (3 c.c. of 85%) and added to a saturated solution of 2 : 4 dinitrophenylhydrazine in alcohol (25 c.c. of 85%). The solution was acidified with concentrated hydrochloric acid (0.35 c.c.). As no crystalline hydrazone had separated after three quarters of an hour's standing, the solution was refluxed for twenty four hours, with periodical cooling and scratching to induce crystallization. The solution became brown in colour, but did not yield a crystalline derivative. It appears that the tetramer must have undergone extensive breakdown.

(ii) SEMICARbazIDE HYDROCHLORIDE

The method outlined by Wild (Characterisation of Organic Compounds pp.121) was employed. After twenty hours refluxing two crops of crystals were separated. The less soluble of these was shown by melting point and mixed melting point determinations to be unreacted tetrapolymer. The small yield of more soluble, fawn-coloured, powder charred on heating but did not melt below 410°C.

(iii) HYDROXYLAMINE HYDROCHLORIDE
In order to attain the optimum pH of 4.7 for reaction of hydroxylamine with a ketone (Conant and Bartlett) a buffered solution was used. Half a gram of hydroxylamine hydrochloride, 1 g. of sodium acetate, 0.9 g. of glacial acetic acid and 1.2 g. of the tetrapolymer were dissolved in distilled water (8.5 c.c.). A copious brown precipitate rapidly formed. This was filtered off and was found to have a low solubility in water and alcohol. As oximes are often soluble in alkali, the solid was extracted with a dilute sodium hydroxide solution. Partial neutralization of the alkaline solution by passing carbon dioxide gave a negligible precipitate of "oxime". It is probable that the brown precipitate was a decomposition product of the tetrapolymer.

THE TETRAPOLYMER HYDROLYSED BY ALKALI AND COUPLED WITH HYDROXYLAMINE HYDROCHLORIDE

Hydroxylamine hydrochloride (0.5 g.) sodium carbonate (1.2 g.) and the tetrapolymer (0.20 g.) were dissolved in distilled water (8.5 c.c.) and heated under reflux for ten minutes. The solution became dark brown and a small amount of "azulmin"-like solid separated. Ether extraction gave a trace of yellow solid (unidentified). Crystals separated on standing overnight and were shown to be unreacted tetrapolymer.

THE MONOACETYL DERIVATIVE, ACID-HYDROLYSED AND COUPLED WITH 2:4 DINITROPHENYLHYDRAZINE

The method described for the acid hydrolysis of the tetrapolymer was used for the monoacetyl derivative. The solution had become dark red in colour after twenty four hours refluxing but no crystalline derivative separated on cooling or evaporation.
THE BENZYLIDENE DERIVATIVE, ACID-HYDROLYSED AND COUPLED WITH 2 : 4 -DINITROPHENYLHYDRAZINE

The procedure previously outlined was repeated using the benzylidene derivative instead of the tetrapolymer. After standing for six hours some of the benzylidene derivative initially present crystallized out. More concentrated hydrochloric acid (1 c.c.) was added and after a further three hours an orange solid separated. This solid, after recrystallization, gave a melting point and mixed melting point which showed that benzylidene -2 : 4 - dinitrophenylhydrazone had been formed. Free tetrapolymer was not isolated.

E. TREATMENT OF THE TETRAMER WITH OZONE

An attempt was made to investigate the presence of an ethylenic double bond in the tetramer by the use of ozone. Ozone was generated by a method similar to that described in Organic Synthesis and the actual ozonolysis was based on the method outlined by Vogel. A stream of dry oxygen was passed through the annular space between two concentric glass tubes. The inner tube contained an electrolyte and the outer tube was also immersed in an electrolyte. Application of a potential difference of 7,500 volts caused a silent electric discharge to pass through the oxygen in the annular space. The outgoing oxygen now containing 5-6% of ozone was led, still in an all glass system, through a solution of the tetramer, and finally through an acidified potassium iodide indicator solution before discharge of the now ozone free oxygen in a fume-cupboard.

The tetrapolymer 2.008 g. was dissolved in ethyl acetate (A.R.) (50 ml.) and ozone was passed through the
solution until the boric acid-acidified potassium iodide solution began to show a brown colouration (6 hours). This brown colouration was due to the liberation of free iodine by the ozone no longer absorbed by the solution of the tetramer. An alkali (H₄O₇) trap after the acid trap retained the hydrogen cyanide (0.0199 g.) liberated. The black deposit which has separated from the ozonized solution was unaffected by the mechanical shaking of the ethyl acetate solution with distilled water (200 ml.) (to hydrolyse the cyanide) and was then filtered off. This solid (0.031 g.) had the characteristics of "azulmin". The filtrate (ethyl acetate - water) was evaporated to a small volume (5 ml.) by distillation under reduced pressure (15 m.m. of Hg.). Addition of absolute alcohol (5 ml.) to this concentrate produced a white precipitate (1.0g.), which was filtered off, while the filtrate, after evaporation gave rise to a pale amber oil. It was not found possible to isolate a definite compound from this oil, which was unstable and darkened with hydrogen cyanide evolution.

The white solid was found to be insoluble in the solvents; methanol, ethanol, acetone, ether, carbon tetrachloride and benzene. It was, however, soluble in water and was recrystallized by dissolution in water and fractional reprecipitation by the addition of increasing amounts of absolute alcohol. The resultant fractions were recrystallised further by the same method. Two of these fractions were completely analysed by A.D. Campbell at the University of Otago:
Sample H,% C,% N,% residus,% w.p.,°C.*

A 5.98 23.12 25.1 0.64 221-222
B 4.99 22.65 23.38 0.91 202-204

*Melting accompanied by gas evolution.

The white solid (sample B) was acid to litmus, but evolved no carbon dioxide from a sodium bicarbonate solution. Ammonia was evolved when it was treated with cold sodium hydroxide while with baryta a white precipitate was formed. Quantitative hydrolysis of the white solid (0.1044 g.) with barium hydroxide (1.249 g.) in distilled water (13 ml.) was performed in a Kjeldahl apparatus, the ammonia evolved (0.0299 g.; 23.55%) being steam distilled into a saturated boric acid solution. The precipitate which separated was dried and weighed as a barium salt (0.2355 g.). The barium salt was acidified with 2N. sulphuric acid (40 ml.), the barium sulphate (0.2441 g.) precipitate filtered off. The filtrate was titrated with standard potassium permanganate which established that all the barium salt initially formed was barium oxalate; therefore the white solid is 24.0 % carbon. No hydrogen cyanide or aminoacetic acid was isolated from the filtrate from the barium oxalate.

Consideration of these results and the analytical figures indicated that the white solid isolated from the ozonolysis is a mixture of ammonium oxamate with some free oxamic acid (in sample B the analysis indicates a ratio of 2.50:1 which is closely supported by the ammonia liberated and barium oxalate precipitated, on hydrolysis). This was confirmed by treatment of the mixture with dilute hydrochloric acid, and separation of the undissolved white solid, m.p. 208-209°C. (Oxamic acid, m.p. 210°C.)
When the ozonolysis of the tetramer was carried out at 0°C, no brown-black "azulmin" was formed, nor was any hydrogen cyanide liberated. The oil and the white solid were, however, still formed.

C. TREATMENT OF THE DIACETYL DERIVATIVE

WITH OZONE

The diacetyl derivative of the tetramer (1.278g.) was dissolved in ethyl acetate (A.R.) (200 ml.) and ozone was passed through the solution. No ozone was apparently absorbed as the potassium iodide indicator solution became coloured immediately. Ozone was passed for a period of 45 minutes, before the solution was hydrolysed by shaking for one hour with distilled water (200 ml.). The solution was then concentrated under reduced pressure, and finally evaporated to dryness in a forced draught. White crystals separated (0.36g.) which were shown by melting point and mixed melting point to be unreacted diacetyl derivative.

F. PREPARATION OF THE BENZOLYL-DERIVATIVE

OF THE TETRAPOLYMER

The benzoyl derivative was prepared in order to obtain, for absorption spectra measurement, a derivative in which the benzene system is not conjugated with the tetrapolymer.

The tetrapolymer (1.5 g. : 1.4 mol.) was heated under reflux for one hour with benzoyl chloride (1.7 c.c. : 1.4 mol.) in ether (6 c.c.). Dull yellow crystals were formed which, after washing with water and recrystallization from absolute alcohol, gave white plates (0.9 g.), m.p. 235-236°C. with decomposition.

Analysis. Found: N, 26.25%. C_{11}H_{10}N_{4} requires N, 26.42%.

A melting point of 220°C. was quoted by Grischkevitsh-Trochimowski for the brown plates of benzoyl derivative which he prepared by a similar method.
SECTION IV

ULTRAVIOLET ABSORPTION OF THE

TETRACENE AND DERIVATIVES

I. THEORY, RESULTS AND DISCUSSION

A. THEORETICAL DISCUSSION

When light is passed through any compound the difference between the intensity of the incident light ($I_0$) and the intensity of the emergent light ($I$) is due to interaction of light energy with the molecules present. When this interaction is in the ultraviolet to visible region there is a transition of the molecule from its ground state to an ionic, electronically excited state. The difference in energy of these states determines the frequency of the light absorbed

$$E_t - E_0 = h
\nu = \frac{hc}{\lambda}$$

where $c$ is the velocity (cm/sec.) of light and $\lambda$ the wavelength in Ångstroms ($10^{-8}$ cm).

Resonance is an important factor. It is the difference rather than the magnitude of resonance-stabilisation which determines the wavelength of absorption. As the number of double bonds in a conjugated system increases the number of possible excited states becomes proportionately greater than the number of ground state structures and the absorption shifts to progressively longer wavelengths. The longest wavelength band is the most important as it corresponds to the transition of least energy. Intensity (magnitude of extinction coefficient) of an absorption band is determined by the probability of interaction of the molecule with light energy. The polarity
of the excited state is involved and strong absorption results when large electric moments are present in the transition to the excited state.

The first postulation of the quantitative relationship governing the absorption of light is generally attributed to Lambert. This law states that the optical density, $d$, is a linear function of the thickness, $l$, of the absorbing medium when homogeneous. Optical density is defined as $\log_{10} \frac{I_0}{I}$. This law was extended by Beer to include a linear relation between optical density and concentration, $c$, (moles/litre), of a solute in a pure solvent.

$$d = \log_{10} \frac{I_0}{I} = \varepsilon cl$$

where $\varepsilon$ is a constant known as the extinction coefficient. In the present work it is assumed that Beer's law is obeyed, and consequently that plots of extinction coefficient against wavelength are independent of concentration for the dilute solutions used.

B. ULTRAVIOLET LIGHT ABSORPTION OF:

The Tetrramer

The two possible structures for the tetrramer

\[
\begin{align*}
\text{V} & : \text{NH}_2 - \text{C} - \text{C} = \text{N} \\
\text{VI} & : \text{HN} - \text{C} - \text{C} = \text{N}
\end{align*}
\]

\[
\begin{align*}
\text{VII} & : \text{NH}_2 - \text{C} - \text{C} = \text{N} \\
\text{VIII} & : \text{HN} - \text{C} - \text{C} = \text{N}
\end{align*}
\]

contain the conjugated systems $\text{N} = \text{C} - \text{C} = \text{N}$ (XVIII) and $\text{N} = \text{C} - \text{C} - \text{C} = \text{N}$ (XX) respectively.
Table II

Systems containing two conjugated chromophores (Braude)

<table>
<thead>
<tr>
<th>System</th>
<th>Example</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \varepsilon_{\text{max}} )</th>
<th>Solvent*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C-C=C</td>
<td>Butadiene</td>
<td>2170</td>
<td>20,900</td>
<td>H</td>
</tr>
<tr>
<td>C=C-C=N</td>
<td>N-p-Butylcrotonaldehyde</td>
<td>2190</td>
<td>25,000</td>
<td>H</td>
</tr>
<tr>
<td>C=C-CN</td>
<td>Propylene cyanide</td>
<td>2500</td>
<td>3</td>
<td>H</td>
</tr>
<tr>
<td>N=C-C=N</td>
<td>Dimethyl glyoxime</td>
<td>2260</td>
<td>17,000</td>
<td>A</td>
</tr>
<tr>
<td>N=C-CN</td>
<td>Cyanogen</td>
<td>2200</td>
<td>2</td>
<td>V</td>
</tr>
</tbody>
</table>

*H = Hexane, W = aqueous solution, V = vapour, A = alcohol.

The replacement of C=C in butadiene by C=N results in a negligible shift in the wavelength of maximum absorption, \( \lambda_{\text{max}} \) (see Table II) and it may reasonably be assumed that the two groups are similar in type. On this basis, replacement of the C=C in propylene cyanide by N=C would be unlikely to increase \( \lambda_{\text{max}} \) appreciably above 2500 \( \text{Å} \). That is, the only conjugated system, N=C-C=N, present in the aminimino form of the tetrimer would be expected to absorb in the vicinity of 2500 \( \text{Å} \). Furthermore the substituent group, NH\(_2\) - C = C\equiv N, present in this system will have a negligible bathochromic influence since its unsaturated centres are isolated from the chromophoric system by a carbon-carbon single bond. The observed absorption maximum for the tetrimer is, however, at 2380 \( \text{Å} \) which makes the aminiminosuccinimitrile structure somewhat unlikely.
GRAPH 3
Plot of log Extinction Coeff. against wavelength for the TETRAPOLYMER

GRAPH 3a.
Independant determinations of the spectrum of the TETRAPOLYMER
- Beckmann (D.P.L.)
- Uvispec.
### Table III

*Systems containing three conjugated chromophores*

<table>
<thead>
<tr>
<th>System</th>
<th>Example</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Solv.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C-C=C-C=C</td>
<td>Hexatriene</td>
<td>2600</td>
<td>-</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>C=C-C=C-C=C</td>
<td>Octatetriene</td>
<td>2670</td>
<td>53000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>C=C-C=C-C=C</td>
<td>Octa-3,5-dien-7-yne-ol</td>
<td>2600</td>
<td>34,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>C=C-C=C-C=C</td>
<td>Sorbaldehyde</td>
<td>2630</td>
<td>27,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>N=C-C=C-C=N</td>
<td>Maleinitrile</td>
<td>2800</td>
<td>700</td>
<td>M</td>
<td>50</td>
</tr>
<tr>
<td>N=C-C=C-C=N</td>
<td>Tetramer</td>
<td>2980</td>
<td>14,000</td>
<td>M</td>
<td></td>
</tr>
</tbody>
</table>

*Legend: A = ethyl alcohol; M = methyl alcohol*

The wavelength of maximum absorption of systems containing three conjugated chromophores is considerably higher than that of systems with only two conjugated chromophores as may be seen by a comparison of Tables II and III. Replacement of the terminal $C=O$ groups of hexatriene by $C≡N$ groups to give maleinitrile results in a $\lambda_{\text{max}}$ of 2800 Å, which is relatively close to that of tetramer.

In the conjugated system XX, representing one structure of the tetramer, there are present two bathochromic amino-groups directly coupled to the conjugated system. The presence of these groups would be expected to produce an increase in both $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$. As the results in Table IV indicate the shift in a three chromophore system might easily be sufficient to account for the observed absorption spectra of the tetrapolymer.
Table IV
Effect of Aurochromes on Ethylenic Chromophores

<table>
<thead>
<tr>
<th>Example</th>
<th>$\lambda_{\text{max}}$ ($\bar{\alpha}$)</th>
<th>$\epsilon_{\text{max}}$</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et-CH = CH-Bu</td>
<td>1850</td>
<td>80</td>
<td>H</td>
<td>127</td>
</tr>
<tr>
<td>Et-CH = CH-NC$<em>6$H$</em>{11}$</td>
<td>2280</td>
<td>100</td>
<td>H</td>
<td>128</td>
</tr>
<tr>
<td>CH$_2$=CH-CH = CH$_2$</td>
<td>2170</td>
<td>20800</td>
<td>H</td>
<td>111</td>
</tr>
<tr>
<td>CH$_2$=CH-CH=CH-NEt$_2$</td>
<td>2810</td>
<td>23500</td>
<td>H</td>
<td>127</td>
</tr>
<tr>
<td>CH$_5$=CH=CH-COO-Et</td>
<td>2500$^a$</td>
<td>100-</td>
<td>H</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>1980</td>
<td>19900</td>
<td>}</td>
<td></td>
</tr>
<tr>
<td>NH$_2$-CMe=CH-COOEt</td>
<td>2650</td>
<td>15800</td>
<td>H</td>
<td>129</td>
</tr>
<tr>
<td>Me$_2$-CMe=CH-COOEt</td>
<td>2750</td>
<td>20000</td>
<td>H</td>
<td>129</td>
</tr>
</tbody>
</table>

$^a$Inflection

From this evidence the structure of the tetramer appears to be diaminomaleinitrile,

\[
\begin{align*}
\text{NH}_2 - &\quad \text{C} - \text{C} = \text{N} \\
\text{NH}_2 - &\quad \text{C} - \text{C} = \text{N}
\end{align*}
\]

which contains a three conjugated system.

Acyl Derivatives

If it was assumed that the tetramer has the aminosuccinonitrile structure then as has been shown earlier the acetyl group would probably be attached to the imino- and not the amino- group suggested by Hinkel and co-workers$^{26}$.

\[
\begin{align*}
\text{NH}_2 - \text{CH-CN} &\quad \text{CH}_3 - \text{CO-NH-CH-CN} &\quad \text{CH}_3 - \text{CO-NH-C-CN} \\
\text{CH}_3 - \text{CO-N} = \text{C-CN} &\quad \text{NH} = \text{C-CN} &\quad \text{NH}_2 - \text{C-CN} \\
\text{XX} &\quad \text{XXI} &\quad \text{XXII}
\end{align*}
\]

The structure XX contains the system O=C-N=C-C=\text{N} which would be expected to have a markedly different absorption spectra from that of the structure N=C-C=\text{N}.
from which it was derived.

If on the other hand the monoacetyl tetramer had the structure XXII arising from the diaminomaleimide form of the tetramer, then as there was no change in the conjugated system itself this derivative would be expected to have a spectrum similar to that of the tetramer. Introduction of an electron-withdrawing acetyl group might however be expected to result in a decrease, in the bathochromic effect, of one amino group and hence in \( \lambda_{\text{max}} \). The absorption curve actually found for the acetyl derivative is very similar to that of the tetramer but its \( \lambda_{\text{max}} \) is slightly less. (Graph 4).

\[
\begin{align*}
\text{CH}_3\text{CO-NH-CH-C=N} & \quad \text{CH}_3\text{CO-NH-C=CH} \\
\text{CH}_3\text{CO-N = C - N=N} & \quad \text{CH}_3\text{CO-NH-C = CH}
\end{align*}
\]

XXIII  

XXIV

The absorption spectra of the diacetyl derivative of the tetramer will also be seen (Graph 4) to have \( \lambda_{\text{max}} \) close to that of the tetramer and consequently may be assumed to have a similar conjugated system. This provides a further basis for rejection of monoacetyl structures XX and XXI, for both will form the same diacetyl derivative XXIII. For the reasons outlined previously structure XXIII would be expected to have an absorption markedly different from that of the aminomaleimide form of the tetramer V whereas that of structure XXIV would be expected to be similar to the diaminomaleimide form of the tetramer VII.

A possibility which must not be overlooked is that diaminomaleinitrile could by a tautomeric change give rise to derivatives of the types XX and XXIII, the absorption of which might be similar to that of the tetramer. Compounds containing the system \( \text{O-C - N = C - C=N} \) would by
GRAPH 4

TETRAPOLYMER and ACYL DERIVATIVES

EXTINCTION COEFFICIENT $\times 10^3$

WAVELENGTH - ANGSTROMS

TETRAPOLYMER
BENZOYL derivative
ACETYL derivative
DIACETYL derivative
analogy with the results in Table V be expected to have a wavelength of maximum absorption significantly greater than that of the system \( O=\text{C}-\text{N}=\text{C}-\text{C}=\text{N} \). But \( \lambda_{\text{max}} \) of the benzoyl derivative is also similar to that of the tetracer. This is strong evidence that the mono- and di-acyl derivatives are of structural types,

\[
\begin{align*}
R-\text{O}\!&\!\text{-NH-}\!\text{-C-}\!\text{-C}=\!\text{N} && \text{and} && R-\text{O}\!\text{-NH-}\!\text{-C-}\!\text{-C}=\!\text{N} \\
\bigg\| && \bigg\| && \bigg\| && \bigg\|
\end{align*}
\]

\( \text{O} \!\text{-NH}\!\text{-C-}\!\text{-C}=\!\text{N} \) \hspace{1cm} \text{and} \hspace{1cm} R-\text{O}\!\text{-NH-}\!\text{-C-}\!\text{-C}=\!\text{N} \\

and that the tetracer is diaminomaleonitrile.

\begin{table}[h]
\centering
\caption{Related Linear and "Cross" conjugated systems}
\begin{tabular}{lcccc}
\hline
Example & \( \lambda_{\text{max}} \) & \( \varepsilon_{\text{max}} \) & Solvent & Ref. \\
\hline
\( \text{CH}_2=\text{CH-CH} \) & 2170 & 15,500 & A & 5 \\
\( \text{CH}_2=\text{CH-CH} \) & 2360 & 9,500 & A & 5 \\
\( \text{CH}_2=\text{CH-CH} \) & 2600 & - & 31 & \\
\hline
\( \text{CH}_2=\text{CH-CH}_3 \) & 2100 & 6,500 & A & 5 \\
\( \text{CH}_2=\text{CH-C-} \) & 2475 & 10,500 & A & 5 \\
\( \text{CH}_2=\text{CH-CH=CH-} \) & 2800 & 28,000 & A & 6 \\
\hline
\( \text{CH}_2=\text{CH-CH}_3 \) & 2850 & 23,000 & A & 6 \\
\( \text{CH}_2=\text{CH-C-} \) & 3490 & 65,000 & A & 6 \\
\( \text{CH}_2=\text{CH-CH=CH-} \) & 328 & 41,000 & A & 6 \\
\hline
\end{tabular}
\end{table}
Table V (continued)

<table>
<thead>
<tr>
<th>Example</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}^\equiv\text{O}^\equiv\text{C}^\equiv\text{H}_3$</td>
<td>2400</td>
<td>13,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{O}^\equiv\text{C}$</td>
<td>2780</td>
<td>11,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{C}$</td>
<td>2520</td>
<td>20,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>3300</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{CH}^=\text{CH}$ (trans)</td>
<td>2950</td>
<td>27,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{CH}^=\text{CH}^=\text{CH}^=\text{C}$</td>
<td>3400</td>
<td>32,000</td>
<td>A</td>
<td>6</td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{CH}^=\text{CH}^=\text{CH}^=\text{CH}^=\text{C}$</td>
<td>3490</td>
<td>65,000</td>
<td>A</td>
<td>6</td>
</tr>
</tbody>
</table>

The presence, in the spectrum of the benzoyl derivative of a secondary peak similar in position and size to that of an isolated benzamide group is further confirmation that this group is in fact isolated.

Table VI

Isolated benzoyl group

<table>
<thead>
<tr>
<th>Example</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}^\equiv\text{NH}^\equiv\text{C}^\equiv\text{C}=\text{N}$</td>
<td>2290</td>
<td>10,900</td>
<td>M</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{C}^\equiv\text{C}=\text{N}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}^\equiv\text{CH}_3$</td>
<td>2400</td>
<td>13,000</td>
<td>A</td>
<td>111</td>
</tr>
</tbody>
</table>

The Aldehyde Derivatives of the Tetrapolymer

Aldehydes condense with the tetramer to form derivatives of the type $\text{R}^\equiv\text{C}^\equiv\text{N}^\equiv\text{C}_4^\equiv\text{H}_2\text{N}_3^\equiv$ for which the
structures XX and XXI have been proposed. These arise from the aminoimino- and diamino- formulations of the tetramer respectively.

\[
\begin{align*}
\text{NH}_2\text{-CH-CN} & \quad \text{R-CH=N-CH-CN} \\
\text{NH}=\text{C-CN} & \quad \text{NH}^\equiv\text{C-CN} \\
\text{V} & \quad \text{XX}^* \\
\end{align*}
\]

That the tetramer only forms a mono aldehyde derivative has been suggested as evidence for (XX). However, the observed spectra of these derivatives, while supporting structure (XXI) appear to refute the suggestion of structure (XX). With the exception of iso-butyraldehyde (which will be neglected from consideration at present) all the aldehydes are such that "R" is a chromophore conjugated to the group -CN=N- in (XX) and (XXI). Structure (XX) has thus two conjugated systems. Now it is known (Braude\textsuperscript{6}) that when such isolated systems are present in the same molecule the resultant spectrum is the sum of their individual spectra. Derivatives of type (XX) would therefore be expected to have spectra with peaks corresponding in wavelength and intensity to those of both the tetramer and the group R-CH=N.
Graph 5
Aldehyde Derivatives
Of Varying Unsaturation

Extinction coefficient x10⁻³

- iso-Butylidene Deriv.
- Allylidene Deriv.
- Benzylidene Deriv.
- Cinnamylidene Deriv.

Wavelength (Ångstroms)
Graph 6

The Tetramer and Aryl Aldehyde Derivatives

- Tetramer
- Benzylidene Derivative
- Acetylbenzylidene Deriv.
- p-Hydroxybenzylidene Deriv.
- p-Nitro Benzylidene Deriv.

Wavelength (Angstroms) — Extinction Coefficient x10^3
Table VII
Absorption maxima of the tetramer and its aldehyde derivatives

<table>
<thead>
<tr>
<th>Name</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\epsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracer</td>
<td>2070</td>
<td>5300</td>
<td>2980</td>
<td>14000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>isobutylidene-tetramer</td>
<td>2100</td>
<td>4500</td>
<td>3150</td>
<td>15400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>allylidene-tetramer</td>
<td>2330</td>
<td>9700</td>
<td>3430</td>
<td>22500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzylidene-tetramer</td>
<td>2080</td>
<td>11400</td>
<td>2560</td>
<td>14000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cinnamylidene-tetramer</td>
<td>2070</td>
<td>11900</td>
<td>2800</td>
<td>14000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-hydroxybenzylidene-tetramer</td>
<td>2080</td>
<td>9200</td>
<td>2740</td>
<td>12200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-nitrobenzylidene-tetramer</td>
<td>2180</td>
<td>9200</td>
<td>2640</td>
<td>12750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzylidene-acetyl-tetramer</td>
<td>2090</td>
<td>10500</td>
<td>2610</td>
<td>12900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-benzylidene-methylanine</td>
<td></td>
<td></td>
<td></td>
<td>2470</td>
<td>17000</td>
<td></td>
</tr>
</tbody>
</table>

From the results in Table VII or, more clearly from the graphs 5 and 6, it may be seen that in none of the derivatives is there an absorption maximum related to that of the tetramer. This rules out the possibility that V gives rise to XX. There remains, however, the possibility that the tetramer exists:

(a) as VII and the derivative in the form XX

(b) as V and the derivative in the form XXI

(c) as VII and the derivative in the form XXI

The first of these possibilities may be discarded since it is impossible on this basis to account for the presence of a peak in the spectra of the benzylidene derivative at 3600 Ångstroms; both the isolated groups $\cong\text{CH}=\text{N}$ and $\cong\text{NH}=\text{C}=\text{C}=\text{N}$ absorb in the region of 2500 Ångstroms (Table VII and page 50). A similar argument applies to the other aldehyde derivatives.

If the spectra of the acyl derivatives (Section IV) have established that the tetramer does not normally
exist in the aminoimino- form (V), the second possibility would then be rejected.

The third possibility is, however, supported by the observed spectra. The isobutylidene, allylidene, benzylidene, cinnamylidene derivatives form a series in which the length of the conjugated system, and consequently \( \lambda_{\text{max}} \) is increasing. Their spectra are related to those of systems containing from three to four more double bonds than the ethylenic homologues of the systems \( R-\text{CH}=\text{N} \) (\( R \) is saturated or unsaturated) (see Table VII).

This is readily explained by the substituted diaminostructure (XXI) in which the chromophoric system \( R-\text{CH}=\text{N} \) is coupled directly to a diene system with a bathochromic amino substituent, and "cross" conjugated with a nitrile group.

### Table VIII

\( \lambda_{\text{max}} \) of the aldehyde derivatives and ethylenic chromophores (Braude\(^6\)) of similar \( \lambda_{\text{max}} \).

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda_{\text{max}} )(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C} = \text{C} -)_4)</td>
<td>2990</td>
</tr>
<tr>
<td>(\text{CH}=\text{N}-\text{C}_4\text{H}_2\text{N}_3)</td>
<td>3150</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_5)</td>
<td>3280</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_6)</td>
<td>3600</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_3)</td>
<td>3490</td>
</tr>
<tr>
<td>(\text{C}=\text{N}-\text{C}_4\text{H}_2\text{N}_3)</td>
<td>3600</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_4)</td>
<td>2470</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_5)</td>
<td>3750</td>
</tr>
<tr>
<td>((\text{C} = \text{C} -)_6)</td>
<td>3720</td>
</tr>
</tbody>
</table>
"Cross" conjugated systems have an absorption maximum at a wavelength greater than that of either of the individual chromophoric systems but usually less than that of the corresponding "straight"-chain systems (see Table V).

The electromeric effects of the hydroxy- and nitro-groups in the p-hydroxybenzylidene and p-nitrobenzylidene derivatives of the tetramer are in opposite directions. The spectra of both these derivatives, however, show peaks at wavelengths greater than those of the benzylidene derivative itself (Graph 6). This is to be expected, for the presence of these groups will increase the ease of separation of charges and will thereby reduce the energy difference between the ground and excited states.

The spectrum of the benzylideneacetyl derivative supports the structure,

\[
\begin{align*}
\text{NH}_2 - C - CN \\
\text{CH} = N - C - CN
\end{align*}
\]

for the benzylidene derivative. Acetylation of the amino-group leads to a decrease in wavelength of the main maxima, presumably owing to a reduction in its bathochromic properties. If the benzylidene derivative had the structure

\[
\begin{align*}
\text{NH} = C - CH - CN \\
\text{CH} = N - CH - CN
\end{align*}
\]

there should have been for reasons outlined earlier an increase in \( \lambda_{\text{max}} \).

The significance of the second bond in the ranges 2550 to 2800 Å in the spectra of most of the aldehyde derivatives is uncertain and may possibly be due to a
partially localised system, or to excitation of the molecule to a higher energy level.

C. STABILITY OF THE TETRAMER AND ITS DERIVATIVES IN METHANOL

In all cases where solutions of the tetramer and its derivatives have been allowed to stand for long periods there have been considerable changes in the measured absorption spectra. Although the rate of change varies from compound to compound the direction of change is the same in every case. $\epsilon_{\text{max}}$ decreases.

From the figures in Table IX it is apparent that quite large changes in $\epsilon_{\text{max}}$ occur while the change in the wavelength of maximum absorption is negligibly small.

Table IX

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decrease in $\epsilon_{\text{max}}$, from time of first measurement</th>
<th>Change in $\lambda_{\text{max}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramer</td>
<td>15 days, 2.5%; 61 days 7.5%</td>
<td>10</td>
</tr>
<tr>
<td>Tetramer U.V. Irradiated</td>
<td>10 min., 28%; 23 min., 35%; 37 min., 41%</td>
<td>25</td>
</tr>
<tr>
<td>Benzyldiene derivative</td>
<td>5 days, 3.2%</td>
<td>0</td>
</tr>
<tr>
<td>Benzyldiene-acetyl derivative</td>
<td>2 days, 3%; 3 days 4%</td>
<td>5</td>
</tr>
<tr>
<td>Allyldiene derivative</td>
<td>2 days, 8%; 7 days, 18%</td>
<td>0</td>
</tr>
<tr>
<td>Diacetetyl derivative</td>
<td>9 days, 22%; 16 days, 22%; 30 days, 22%</td>
<td>30</td>
</tr>
</tbody>
</table>

There are two possible explanations for this decrease in $\epsilon_{\text{max}}$. Either the derivatives are decomposing, hydrolysing, etc., or else the derivatives, all of which
GRAPH 7

FRESH SOLUTION

AFTER 16 DAYS

DIACETYL DERIV.

WAVELENGTH - ÅNGSTROMS

EXCITATION COEFFICIENT x 10^3
contain a double bond, are undergoing geometric isomerism. It is known (Brade) that cis and trans forms often have markedly different $\varepsilon_{\text{max}}$. This may be accompanied by a small difference in the wavelength of maximum absorption.

The first possibility appears unlikely. In the examples where the whole curve has been redetermined after a decrease in $\varepsilon_{\text{max}}$, there is found to be no change in the overall shape of the curve (see graph 7). This is incompatible with the presence of decomposition products, some of which might be expected to absorb above 2050\AA. The overall curve can scarcely be attributed to a decomposition product as it is so closely similar to that of the starting material.

Cis-trans isomerization may explain the observed changes in the spectrum of the diacetyl derivative of the tetramer. $\varepsilon_{\text{max}}$ for this compound undergoes a rapid decrease to a value twenty two per cent smaller than that of a fresh solution, after which there is no further change. The decreasing rate of change which is also observed in the other derivatives may also be explained by approach to an equilibrium between the cis- and trans- forms.

Irradiation of a solution of the tetramer with intense ultraviolet light, which is known to promote such isomerism, led to an initially rapid decrease in $\varepsilon_{\text{max}}$ followed by a slower, steady decrease (Table IX) (Appendix B, Table X). The latter may possibly be attributed to photodecomposition whereas the initially rapid decrease may be accounted for by cis-trans isomerism.

These results of irradiation are to be considered as tentative only as a more detailed investigation is required.

---

*Grischkevitsch-Trochimovski has indicated that since the tetramer condenses with glyoxal and nitrous acid to give heterocyclic derivatives, its reactive groups must be cis to one another.
II. EXPERIMENTAL

A. PURIFICATION OF REAGENTS

Solutes

The tetropolymer and its various derivative, of which the ultraviolet absorption has been measured, were purified by repeated recrystallisation, and thoroughly dried. The tables in Appendix B of the extinction coefficients observed also record the melting points of the samples used.

Solvent

Methanol was used for all measurements of absorption spectra. Commercial methanol, initially of 99% purity, was purified by standing for at least one month over solid silver nitrate, boiling under reflux for eight hours and distilling the methanol (now free from reducing agents) through an efficient fractionating column. The middle fraction was then dried by boiling under reflux with magnesium, following a method devised by Bjerrum and outlined by Weisberger and Froskauer.

E. MEASUREMENT OF ABSORPTION SPECTRA

The Uvispek

A Hilger Uvispek (H. 700.302/51373) was used for the determination of the spectra of the tetrramer and its various derivatives. This instrument may be used to record absorption from 2000Å to 10,000Å by the use of a hydrogen lamp as source from 2000Å to about 4000 Å and a filament lamp above this range. Two photocells with different ranges of sensitivity are used for intensity measurement.

The principle of this instrument is that a beam of
light from a stabilised source is dispersed by a quartz prism. As a result, monochromatic light is passed through a quartz cell containing the solvent used. The emergent beam activates a photocell, the amplified output of which is counterbalanced by adjusting a variable resistance until there is no deflection of the detector galvanometer. Having allowed for the absorption due to the solvent, the "blank" cell is replaced by a cell containing the solution to be measured and the galvanometer deflection is counterbalanced by another rheostat calibrated in both "per cent transmission" and "density" (d). By this means the absorption of the solute alone may be determined. Movement of the quartz prism, by rotation of a drum calibrated in Ångstrom units, varies the wavelengths of the monochromatic beam, while the intensity of light falling on the absorbing cell is regulated by means of two slits.

M.H. Pankhurst (C.U.G. Chemistry Department) had previously checked the calibration of the wavelength drum and density scale by plotting the absorption spectrum of a standard potassium nitrate solution and comparing the resultant curve with the standard curve. The constant value of $\varepsilon_{\text{max}}$ obtained when the absorption spectrum of the tetramer was determined independently with a "Hilger" Medium Quartz spectrograph in this Department, and with a Beckmann spectrophotometer at the Dominion Physical Laboratory is confirmation of the accuracy of the wavelength measurement.

Closely similar curves were obtained on the three instruments, which indicates that the tetramer exhibits negligible fluorescence. (If this had been present the curve from the Hilger Medium Quartz spectrograph would
have been markedly different since it disperses after absorption (Braude, Fowcett and Timmons\textsuperscript{126}).

Use of the Ĭvispek

The measurement of density, \(d\), is most sensitive over the range 0.2 to 0.8 (Martin\textsuperscript{127}) and the majority of measurements of \(d\) in this thesis lie between these limits. Below this range errors arise from the difficulty of matching cells exactly whereas at high densities the accuracy of measurement becomes increasingly more difficult owing to the increased importance of stray radiation and variations in the intensity of the source. The latter is especially noticeable where the intensity of the source is low, as it is for a hydrogen lamp below 2200 Å. In fact the reality, and meaning, of the peak shown by the tetramor and most derivatives in the vicinity of 2100 Å is uncertain.

Although the use of 0.5 cm. cells allowed relatively high concentrations of solute, it had the disadvantage that the measured density, \(d\), at any particular wavelength, changed with time. This change was probably due to different rates of evaporation and water absorption by the two cells. The use of 1 cm. cells made frequent changes of the two solutions unnecessary.

Sensitivity.

The accuracy of density measurement has been shown by Martin\textsuperscript{128} to be normally of the order of five per cent (5%). Furthermore the probable error of weighing the small quantities of solute used is of the order of \(\pm 1\%\).

\textsuperscript{a}Although this discussion is mainly related to infra-red measurements, the results are, as he states, applicable to general spectral measurement.
Volumetric errors are negligible. On this basis the difference of five per cent (5%) in independent determinations of \( \epsilon_{\text{max}} \) for the tetramer (Graph 3a) is within the expected overall accuracy of \( \pm 6\% \).

The accuracy of measurement of wavelength is considerably higher, being of the order of \( \pm 5\% \) which is borne out by the independently determined wavelengths of maximum absorption for the tetramer which agreed to within 0.2\%.
At the commencement of this thesis there appeared to remain unsettled the question of whether the tetramer exists as diaminomaleinitrile or aminoisominosuccinonitrile. Had the theoretically possible tautomeric relationship between the two proposed structures been proved to be absent, then the optical activity demonstrated by Hinkel and Watkins\textsuperscript{27} would have been final; the tetrapolymer could only have been aminoisominosuccinonitrile.

While the chemistry of the tetramer had been investigated in some detail, there was no definite evidence for the existence of some of the bond types and substituents which must be present in one or other of the proposed formulations. The presence of such a relatively large number of reactive groups in a compound of such low molecular weight led inevitably to complications.

Attempts were made to investigate the presence of structural features such as:

- an imino- group, by its hydrolysis to a ketone and subsequent coupling of this ketone with substituted hydrazines;
- a labile hydrogen atom, by its replacement with a sodium atom or a methyl group;
- a carbon-carbon double bond, by its rupture after treatment with ozone.

These attempts led to no conclusive results although the results of ozonolysis did point to the existence of a carbon-carbon double bond and hence to diaminomaleinitrile. It has, however, been established that the basicity of
of the amino-group, present in both formulations of the tetramer, is abnormally low. This supports the suggestion (Griskevitsch-Trochimovski\textsuperscript{19}) that the presence of the cyano group(s) will reduce the basicity of the amino-group.

The non-reversible replacement of an aldehyde substituent of the tetramer by another aldehyde appears to be due to partial dissociation of the derivative into free aldehyde and the tetramer.

It has been found that the benzylidene-acetyl derivative may be prepared by condensation of benzaldehyde with the monoacetyl derivative, as well as by acetylation of the benzylidene derivative. This establishes that the tetramer must either be a diamino-compound, or that the imino-group is always acetylated in preference to an amino-group. Furthermore, since Richards\textsuperscript{49} has found acetylation of the benzylidene derivative more difficult than acetylation of the tetramer, it may be concluded that the presence of an aldehyde substituent reduces the reactivity of the remaining amino- (or imino-)group.

Measurement of the ultra-violet absorption spectra of the tetramer and its derivatives, dissolved in methanol, has proved useful in elucidating the structure of these compounds. The absorption spectrum of the tetramer is similar to that which would be expected for a system containing three conjugated chromophores. Acyl derivatives of the tetramer have absorption spectra closely related to that of the tetramer while the spectra of the aldehyde derivatives are different, and correspond to conjugated systems longer than in the aldehyde substituent itself. These observations lead to the conclusion that the chromophoric system $\text{N}≡\text{C}−\text{C}≡\text{C}$
is present in the tetramer and its acyl derivatives, and that the "cross" conjugated system \[ R-CH=N-C=O=G=N=O \]

is present in the aldehyde derivatives. Both these conclusions support the diamino-maleinitrile structure.

Although Hinkel and Watkins have brought forward definite proof for the existence of amino-iminosuccinonitrile, it may be concluded from the evidence of the absorption spectra, that the tetramer and the derivatives examined exist predominantly in the diamino-maleinitrile form. Thus the existence of a tautomeric relationship between amino-iminosuccinonitrile and diamino-maleinitrile would seem to be established.
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[The references enclosed in the square brackets are the sources actually consulted.]
APPENDICIES
APPENDIX A

AN UNSUCCESSFUL ATTEMPT TO PREPARE

THE TETRAMER IN HIGH YIELD

An attempt was made to obtain high yields of the tetramer by following the procedure here outlined, based on the method of Woodward. In principle the method consists of passing liquid hydrogen cyanide continuously through an insoluble basic catalyst, and subsequently recycling the non-polymerised hydrogen cyanide. The tetramer crystallises out.

Reagents:

**Hydrogen Cyanide.** Pure, re-distilled, anhydrous hydrogen cyanide was prepared as outlined in Section III (Experimental).

**Basic Silica Gel.** Drying grade silica gel was thoroughly washed and then stirred for ten minutes with three times its weight of a 1% NaOH solution. The treated silica was then washed five times with distilled water and finally dried under vacuum at 100°C. for 24 hours.

**Basic Aluminium Oxide.** The proportions of reagents recommended in the patent could not possibly give rise to the stated amount of aluminium oxide. Consequently the following modified procedure was employed. Aluminium sulphate octodecasulphate (1050 g.) in water (1600 ml.) was added very slowly to a hot solution of sodium hydroxide (400 g.) and sodium carbonate (212 g.) in distilled water (2000 ml.). The solution, from which aluminium hydroxide had separated, was digested for two hours in a steam jacketed beaker. After filtering and washing four times with hot distilled water, the aluminium hydroxide was dried first for a few hours at 120°C., then
FIGURE 2.
POLYMERIZATION APPARATUS

A. Bolthead flask
B. Receiver
C. Crystallization chamber
D. Catalyst bed
E. Distilling path
F. Spiral condenser

g. Ball condenser
h. Rubber connection
i. Screened discs
j. To soda-lime tube
k. Water jacket
finally under vacuum at 180-190°C. The resultant aluminium oxide (Al₂O₃) formed with water a paste of pH 9.5-10.

Procedure

Hydrogen cyanide (300 ml.) was transferred to the bolthead flask, A, of the polymerising unit shown in Figure 2. The rate of heating of this bolthead was adjusted so that the silica gel catalyst bed (D) was completely covered with condensed hydrogen cyanide when the rate of flow from the base of the column was 2-2½ drops per second. At hourly intervals one drop of syrupy phosphoric acid was added to stabilize the solution, in the bolthead, which gradually became yellow in colour. Periodically a portion of the yellow solution was drawn through the refrigerated (0°C.) spiral condenser (F) and through the crystallisation chamber (C) into the receiver, B by a vacuum applied first to G, then to H. No crystals of tetramer separated on cooling.

The process was continued in all for twenty hours, after which time the now orange solution was transferred to a distilling apparatus and the solution concentrated. No tetramer was recovered by alcohol extraction of the black layer formed on the sides of the distilling flask.

Similar negative results were obtained in two further attempts to polymerise hydrogen cyanide using a basic aluminium oxide catalyst.

A possible explanation for the failure to obtain detectable quantities of tetramer, when a rate of formation of several grams per hour is claimed, is that the temperature of the catalyst bed was not sufficiently high. The temperature range recommended in the patent was 20 to 70°C. In practice it was not possible to have the
catalyst bed above 20-26°C, without having the system under pressure, the boiling point of hydrogen cyanide being 27°C, at atmospheric pressure.
# APPENDIX B

## TABLE X

**VALUES OF WAVELENGTH AND CORRESPONDING VALUES OF THE EXTINCTION COEFFICIENT, MEASURED FOR THE TETRAPOLYMER AND ITS DERIVATIVES**

(These values are presented graphically in Chapter IV)

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† Diacetyl derivative after standing for sixteen days.
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