phosphoric acid; actually the latter, at 20°, hydrolyzes *ca.* $10^3$ as fast as phenyl phosphate.[13] The cyclic mechanism of Westheimer,[11] which postulates a cyclic intermediate of the following nature is particularly attractive as it better accommodates the facts in both the hydrolysis of phosphoric acid esters and amidophosphoric acid. The much faster rates of hydrolysis observed for the monoionic species of amidophosphates as compared to the comparable ionic species of phosphate esters is probably associated with the basicity of nitrogen. The view that the hydrolysis of the monoionic species proceeds primarily by way of an internal hydrogen transfer does not appear as probable as the cyclic intermediate mechanism. If an internal proton transfer were the principal pathway of hydrolysis, then the reactive intermediate would be in fact the zwitterionic form of the monoionic species. It might be anticipated that the reduction in rate of hydrolysis in the dioxane-water mixture would be as pronounced as that observed at the lower *p*H's Actually the rate is lowered but two-fold. The invariance of the rate of hydrolysis of the phosphonamides with substitution (Cl or $OCH_3$) is at least consistent with the cyclic mechanism.

New York, N. Y.

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[Contribution from the Department of Chemistry, University of Canterbury]

# Derivatives of the Hydrogen Cyanide Tetramer: Structure and Chemistry[1]

By P. S. Robertson[2] and J. Vaughan

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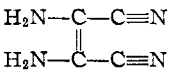
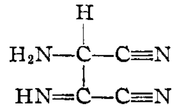
Further physical and some chemical evidence is adduced for the diaminomaleonitrile structure for the hydrogen cyanide tetramer and its acetyl, benzoyl and azomethine derivatives. With the last-named derivatives, it appears that the displacement of one aldehyde by another is related to electron deficiency at the carbonyl carbon atom of the aldehydes concerned.

The structure of the hydrogen cyanide tetramer had been in doubt until the recent work of Webb, *et al.*,[3] and Bredereck, *et al.*,[4] strongly suggested that the tetramer exists as diaminomaleonitrile (I). Such a structure was originally proposed by Grischkevitsch-Trochimovski[5] to account for the relative ease with which derivatives such as 2,3-dicyanopyrazine and 4,5-dicyano-1,2,3-triazole were formed by condensation with glyoxal and nitrous acid, respectively. These cyclic derivatives were analogous with those formed by *o*-phenylenediamine.



$$\begin{array}{c} H_2N—C—C{\equiv}N \\ \| \\ H_2N—C—C{\equiv}N \end{array}$$

I



$$\begin{array}{c} H \\ | \\ H_2N—C—C{\equiv}N \\ | \\ HN{=}C—C{\equiv}N \end{array}$$

II

Hinkel, *et al.*,[6] proposed structure II, aminoiminosuccinonitrile, after reconsideration of the chemistry of the tetramer. The existence of an asymmetric carbon atom in a salt of the tetramer was subsequently established by Hinkel and Watkins.[7] By a process of partial solution they isolated a strongly levorotatory diastereoisomeride, using *d*-camphorsulfonic acid.

Webb[3] demonstrated the absence of a C–H bond in the crystalline tetramer by comparison of its infrared absorption spectrum with that of succinonitrile. From an examination of the ultraviolet absorption spectra they concluded that the tetramer also exists in solution as diaminomaleonitrile (I) and measurement of the dipole moment supported a *cis* configuration for the compound.

Bredereck[4,8] further investigated the chemistry of the tetramer and examined the infrared absorption of the tetramer, and of its mono-, di- and triacetyl derivatives. They confirmed structure I for the solid tetramer and showed that acetyl derivatives also have structures based on the diamino formulation. The infrared absorption due to the C═C bond of the tetramer corresponded to a *cis* formulation.

Thus, the combination of Hinkel's resolution experiments and the later work of the above investigators might be taken to indicate that in solution the tetramer displays tautomerism, with the equilibrium greatly favoring structure I.

In the studies reported here, further details of the chemical behavior of the tetramer are presented and, by measurement of the ultraviolet absorption of a number of derivatives, evidence has been obtained supporting the existence of these compounds in solution as derivatives of structure I.

## Results and Discussion

**The Tetramer.**–As in the work of Webb, *et al.*,[3] the ultraviolet absorption evidence was considered in the light of the spectra to be expected from structures I and II. The wave lengths of maximum absorption ($\lambda_{max}$) of conjugated diene systems are usually significantly lower than those of conjugated trienes, which usually display a $\lambda_{max}$ in the region of 2600 Å. The observed $\lambda_{max}$ of the tetramer is 2980 Å. (in methanol; see Fig. 1); the presence of two bathochromic amino groups has extended the resonance of the conjugated system and has thus further increased $\lambda_{max}$.

**Acetyl and Benzoyl Derivatives.**—Bredereck,

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(1) From thesis of P. S. Robertson, University of New Zealand, 1953.

(2) The Dairy Research Institute (N.Z.), Massey College P. O., Palmerston North, New Zealand.

(3) R. L. Webb, S. Frank and W. C. Schneider, This Journal, **77**, 3491 (1955).

(4) H. Bredereck, G. Schmötzer and H. J. Becher, *Ann.*, **600**, 87 (1956).

(5) E. Grischkevitsch-Trochimovski, *Roczniki Chem.*, **8**, 165 (1928).

(6) L. E. Hinkel, G. O. Richards and O. Thomas, *J. Chem. Soc.*, 1432 (1937).

(7) L. E. Hinkel and T. I. Watkins, *ibid.*, 1206 (1940).

(8) H. Bredereck and G. Schmötzer, *Ann.*, **600**, 95 (1956).

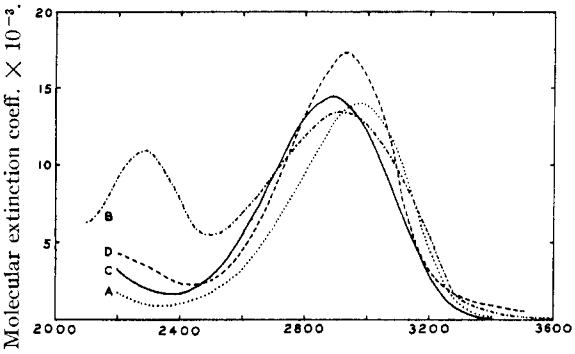
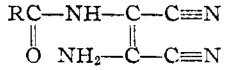


Fig. 1.—Ultraviolet absorption spectra of the tetramer and its acetyl and benzoyl derivatives in methanol: A, ......, tetramer; B, —·—·—·, benzoyl derivative; C, ———, monoacetyl derivative; D, --------, diacetyl derivative.

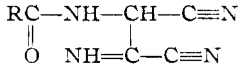
*et al.*,[4] have established, by infrared examination, the structure of acetyl derivatives of the tetramer in the solid state. The following results now establish the structure of these derivatives in solution *via* their ultraviolet absorption spectra.

The monoacetyl derivatives have been considered to have structure III, IV or V.



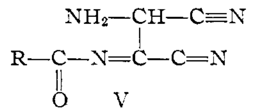
$$\begin{array}{lll}\mathrm{RC{-}NH{-}} & \mathrm{C{-}C{\equiv}N} & \\ \ \| & \ \| & \\ \mathrm{O\ \ NH_2{-}} & \mathrm{C{-}C{\equiv}N} & \end{array}$$

III



$$\begin{array}{ll}\mathrm{RC{-}NH{-}} & \mathrm{CH{-}C{\equiv}N}\\ \ \| & \ | \\ \mathrm{O\ \ NH{=}} & \mathrm{C{-}C{\equiv}N}\end{array}$$

IV



$$\begin{array}{ll} & \mathrm{NH_2{-}CH{-}C{\equiv}N}\\ & \qquad\ \ | \\ \mathrm{R{-}C{-}N{=}} & \mathrm{C{-}C{=}N}\\ \quad \| & \\ \quad \mathrm{O} & \end{array}$$

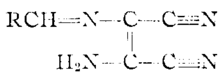
V

In structure III the R–CO– grouping is isolated from the triene system of the maleonitrile formulation and when R is unsaturated the compound would be expected to yield an ultraviolet spectrum which retained the identity of each of the two unsaturated systems. In structure V, the inclusion of the R–CO– grouping leads to a more extensive conjugated system than in the succinonitrile structure for the tetramer. One would therefore expect an increase in $\lambda_{\max}$, especially when R is unsaturated and conjugated with the carbonyl group. The observed spectra of the monoacetyl and monobenzoyl derivatives (Fig. 1) are closely similar to that of the tetramer except that the benzoyl derivative gives rise to a peak expected from an isolated benzoyl group. These derivatives thus appear to adopt structure III.

The spectrum of the diacetyl derivative (Fig. 1) displays $\lambda_{\max}$ at almost the same wave length as that of the tetramer. For reasons outlined above, this exludes the possibility that this derivative arises from structure IV or V. The work of Bredereck, *et al.*,[4] indicates that it is derived from structure III with one acetyl group on each amino group. The observed ultraviolet absorption is in agreement with this, but does not preclude the possibility that both acetyl groups are situated on one amino group.

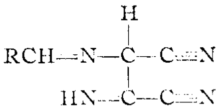
**Azomethine Derivatives.**—We condensed a number of aldehydes with the tetramer and new monoaldehyde derivatives were obtained using acrolein, *p*-hydroxybenzaldehyde, *p*-nitrobenzaldehyde and cinnamaldehyde. Under the experimental conditions a second molecule of aldehyde could not be introduced, and no derivative at all could be obtained with phenylacetaldehyde, *n*-butaldehyde or acetaldehyde. It is of interest that those aldehydes which reacted were those in which the carbonyl group was conjugated with further unsaturated centers in the aldehyde; those which failed in the reaction possessed an isolated carbonyl group. Attempts to condense a second, different aldehyde with a monoaldehyde derivative led to further interesting results. The attempts were unsuccessful, but it was found that in some cases the second aldehyde would displace the aldehyde residue of the original derivative. The results indicated that displacement would occur when the second aldehyde possessed a carbonyl carbon atom of greater electron deficiency than in the original aldehyde. Thus *p*-nitrobenzaldehyde displaced benzaldehyde and *p*-hydroxybenzaldehyde, while benzaldehyde replaced *p*-hydroxybenzaldehyde. Under our conditions it was not possible to reverse these displacements, which are in accord with the order of dipole moment values for the aldehydes. Richards[9] had shown earlier that benzaldehyde will displace isobutyraldehyde. In this case the dipole moments are comparable in magnitude and the preference of the tetramer for benzaldehyde might be linked with the more extensive resonance of the benzylidene derivative. It may be assumed that it is the reversibility of the aldehyde condensation reaction which allows all these displacements to occur.

Aldehyde derivatives of the tetramer are likely to possess either structure VI or VII



$$\begin{array}{ll}\mathrm{RCH{=}N{-}} & \mathrm{C{-}C{\equiv}N}\\ & \ \| \\ \quad \mathrm{H_2N{-}} & \mathrm{C{-}C{\equiv}N}\end{array}$$

VI



$$\begin{array}{ll} & \ \mathrm{H}\\ & \ | \\ \mathrm{RCH{=}N{-}} & \mathrm{C{-}C{\equiv}N}\\ & \ | \\ \quad \mathrm{HN{-}} & \mathrm{C{-}C{\equiv}N}\end{array}$$

VII

Ultraviolet absorption spectra have now been obtained for a number of these derivatives. From Fig. 2 it may be seen that the isobutylidene, allylidene, benzylidene and cinnamylidene compounds

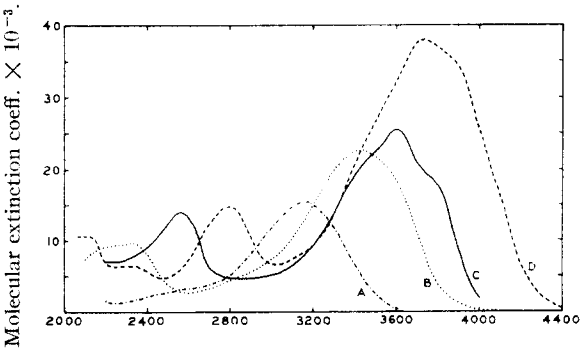


Fig. 2.—Ultraviolet absorption spectra of some aldehyde derivatives of the tetramer of increasing unsaturation: A, —·—·—·, isobutylidene derivative; B, ......, allylidene derivative; C, ———, benzylidene derivative; D, --------, cinnamylidene derivative.

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(9) G. O. Richards, Thesis, University of Wales.

form a series in which the length of the conjugated system, and consequently $\lambda_{max}$, is increasing. The spectra of these derivatives are related to those of systems containing from three to four more double bonds than the system R—C=N— alone. This result is explained on the basis of structure VI, in which the chromophoric system R—C=N— is conjugated with a diene system —C=C—C≡N which has a bathochromic amino substituent and is cross-conjugated with a nitrile group. If the aldehyde derivative has structure VII, the absorption maxima should have corresponded in wave length and intensity to those of the isolated systems —N=C—C≡N and R—C=N—. Furthermore, although the —OH and —$NO_2$ substituents of the $p$-hydroxybenzylidene and $p$-nitrobenzylidene derivatives exert resonance effects in opposite directions, both increase the ease of separation of charges and thus reduce the energy difference between ground and excited states. Thus it could reasonably be expected that the spectrum of each compound would display a $\lambda_{max}$ (Fig. 3) at a wave length greater than that of the benzylidene derivative. Finally, acetylation of the benzylidene derivative to give the benzylidene-acetyl compound results in a $\lambda_{max}$ slightly less than that of the benzylidene derivative (Fig. 3). This is considered to be caused by a reduction of the bathochromic influence of the amino group on acetylation, and appears to lend support to structure VI for the products of the aldehyde–tetramer reactions. For, if the aldehyde derivative had structure VII, then the carbonyl group introduced on acetylation would lead to an increase in length of the conjugated system, from —N=C—C≡N to O=C—N=C—C≡N; this should be accompanied by a marked increase in $\lambda_{max}$.

## Experimental

**HCN Tetramer.**—The tetramer (colorless plates, m.p. 184°, dec.) was obtained by a procedure similar to that of Hinkel, *et al.*[6]

**Derivatives Previously Described.**—The monoacetyl, diacetyl, benzylidene, benzylidene-acetyl and isobutylidene derivatives were prepared by methods similar to those of Hinkel, *et al*[6].

The benzoyl derivative was prepared by the method of Grischkevitsch-Trochimovski[5] whose product was brown and melted at 220°. Our product was obtained as white plates, m.p. 235–236° dec.

*Anal.* Calcd. for $C_{11}H_8ON_4$: N, 26.42. Found: N, 26.25.

**Derivatives and Preparations Not Previously Described. Allylidene Derivative.**—The tetramer (1 g., 1 mol.) was warmed with freshly distilled acrolein (1.9 ml., 3 mols.) until dissolved, then rapidly cooled. The crystalline compound which separated was recrystallized from ethanol to give bulky, dull yellow crystals (0.8 g.), m.p. 126–126.5°.

*Anal.* Calcd. for $C_7H_6N_4$: N, 38.35. Found: N, 37.85.

**Cinnamylidene Derivative.**—The tetramer (0.5 g., 0.5 mol.) was dissolved in ethanol (5 ml.) and refluxed with cinnamaldehyde (0.8 ml., 0.55 mol.) for 45 min. An orange-yellow solid was filtered off and recrystallized first from acetone, then from ethanol. Orange-yellow plates (0.7 g.) were obtained, m.p. 202–203° dec.

*Anal.* Calcd. for $C_{13}H_{10}N_4$: N, 25.23. Found: N, 25.40.

**$p$-Hydroxybenzylidene Derivative.**—A solution in ethanol (20 ml.) of the tetramer (1 g., 1 mol.) and $p$-hydroxy-crystalline condensation product separated on cooling and was recrystallized three times from ethanol, giving yellow crystals (1.3 g.), m.p. 222.5–223°.

*Anal.* Calcd. for $C_{11}H_8ON_4$: N, 26.42. Found: N, 26.45.

**$p$-Nitrobenzylidene Derivative. (a) From the Tetramer.**—Alcoholic solutions of the tetramer (2 g. in 15 ml.) and $p$-nitrobenzaldehyde (2.9 g. in 10 ml.) were mixed and refluxed for 30 min. The reaction product, which began to separate after 5 min., was washed with hot ethanol. Fine bright yellow crystals were obtained, m.p. 258–258.5° dec.

*Anal.* Calcd. for $C_{11}H_7O_2N_5$: N, 29.02. Found: N, 29.15.

**(b) From the Benzylidene Derivative.**—To the benzylidene derivatives of the tetramer (0.21 g., 0.1 mol.) dissolved in ethanol (5.5 ml.) was added $p$-nitrobenzaldehyde (0.25 g., 0.17 mol.) and glacial acetic acid (0.25 ml.). The mixture was refluxed 4 hr. The yellow solid which separated (0.12 g.) was shown by m.p. and mixed m.p. to be the $p$-nitrobenzylidene derivative.

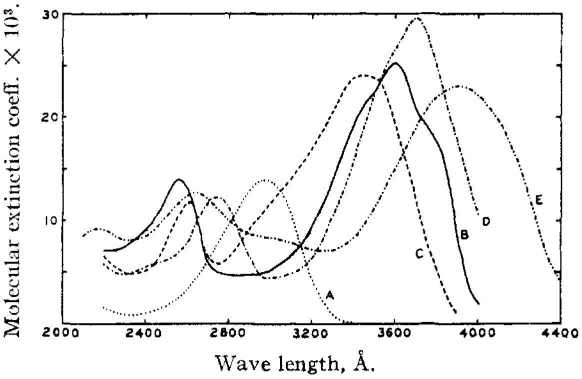

Fig. 3.—Ultraviolet absorption spectra of the tetramer and its aryl aldehyde derivatives: A, ......, tetramer; B, ———, benzylidene derivative; C, --------, benzylidene-acetyl derivative; D, —·—·—, $p$-hydroxybenzylidene derivative; E, —··—··, $p$-nitrobenzylidene derivative.

**(c) From the $p$-Hydroxybenzylidene Derivative.**—Hot alcoholic solutions of the $p$-hydroxybenzylidene derivative (0.33 g., 0.16 mol. in 3.4 ml.) and $p$-nitrobenzaldehyde (0.25 g., 0.17 mol. in 1.4 ml.) were mixed, glacial acetic acid (0.15 ml.) was added and the whole refluxed for 4 hr. The yellow $p$-nitrobenzylidene compound (0.1 g.) separated out.

**(d) From Monoacetyl Derivative.**—The monoacetyl derivative (0.26 g., 0.17 mol.) and $p$-nitrobenzaldehyde (0.29 g., 0.19 mol.) were dissolved in hot ethanol (1.5 ml.) containing a little glacial acetic acid (0.1 ml.). After 50 min. refluxing, the cooled solution deposited some unchanged nitrobenzaldehyde, but after concentration of the filtrate by boiling off some ethanol the $p$-nitrobenzylidene derivative of the tetramer crystallized out. This derivative has very low solubility in ethanol and the above isolation procedure might be taken to indicate that its isolation was *via* the breakdown of a relatively soluble, unstable compound, possibly the acetyl-$p$-nitrobenzylidene compound.

**Benzylidene Derivative from the $p$-Hydroxybenzylidene Derivative.**—The $p$-hydroxybenzylidene derivative (0.29 g., 0.14 mol.) was dissolved in ethanol (3 ml.), freshly distilled benzaldehyde (0.25 ml.) and glacial acetic acid (0.25 ml.) were added and the mixture was refluxed for 8 hr. The pale yellow compound which separated on cooking was recrystallized from ethanol and shown (m.p. and mixed m.p.) to be the benzylidene derivative.

**Benzylidene-acetyl Derivative.**—The monoacetyl derivative of the tetramer (0.06 g., 0.04 mol.) was dissolved in ethanol (0.6 ml.) and refluxed with freshly distilled benzaldehyde (0.04 ml., 0.04 mol.) for 35 min. A crystalline solid separated on cooling and was recrystallized from ethanol. This was the benzylidene-acetyl derivative.

**Ultraviolet Spectra.**—Ultraviolet absorption spectra were obtained on a Hilger Uvispec instrument using 1-cm. quartz cells and pure, dry methanol as solvent. The majority of optical density measurements were confined to the range 0.2–0.8. The absence of appreciable fluorescence by the tetramer was demonstrated by the close similarity of the Uvispec absorption curves and those obtained with a Hilger medium quartz spectrograph which disperses after instead of before absorption.

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