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[Contribution from the Stamford Laboratories of the Research Division, American Cyanamid Co.]

The Structure of HCN Tetramer

By Richard L. Webb, S. Frank and W. C. Schneider

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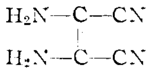
Physical evidence is presented supporting the diaminomaleonitrile structure for HCN tetramer.

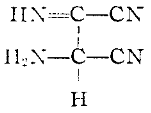
In 1873, Lange[1] obtained a crystalline compound from a black solid resulting from HCN polymerization, which possessed the empirical formula HCN.

Bedel[2] determined the molecular weight of the compound ebullioscopically in methanol and found it to be a tetramer of HCN. Gryszkiewicz-Trochimowski[3] considered it to have the structure of diaminomaleonitrile (I), since on condensation of the tetramer with glyoxal under relatively mild conditions he obtained an 80% yield of 2,3-dicyanopyrazine (m.p. 132.5°).



$$\begin{array}{c} H_2N-C-CN \\ | \\ H_2N-C-CN \end{array}$$

I



$$\begin{array}{c} HN=C-CN \\ | \\ H_2N-C-CN \\ | \\ H \end{array}$$

II

Hinkel[4] and co-workers repeated many of the previous reactions and concluded that the results were in better agreement with the tautomeric structure, aminoiminosuccinonitrile (II). They found that the compound formed a mono- rather than a dihydrochloride in ethereal HCl and concluded that the tetramer could not be a diamine. Further, the reaction of the tetramer with glyoxal was found to proceed through an intermediate with the empirical formula $C_6H_4N_4O$ which did not react with phenylhydrazine. Hinkel interpreted the above reaction and that of the tetramer with nitrous acid as support for structure II.

Hinkel[5] later reported stereochemical evidence in support of structure II which possesses an asymmetric carbon atom not present in I. The *d*-camphorsulfonate of the tetramer was resolved by partial solution in boiling ethyl acetate. It is of interest that on hydrolysis of the resolved salt, the free base obtained was optically inactive.

It was found in these laboratories that the infrared spectrum of the powdered tetramer showed no C–H bond absorption. The crystalline solid, therefore, cannot be aminoiminosuccinonitrile. It was also of interest to study the properties of the tetramer in the dissolved state at ordinary temperatures. Accordingly, the ultraviolet absorption spectra were obtained in ethanol, in distilled water and in 0.1 *N* aqueous HCl and the dipole moment of the molecule was obtained from measurements of the dielectric constants of dilute dioxane solutions. An attempt was made to determine the basic dissociation constant of the tetramer by potentiometric titration of the monohydrochloride in aqueous solution.

Experimental

Materials. HCN Tetramer.—The procedure used for preparation of this compound was similar to that of Linstead, *et al.*[6]

In a typical experiment, 5 ml. of triethylamine was added to 50 ml. of dry, distilled HCN contained in a loosely-stoppered Erlenmeyer flask immersed in a water-bath at 20°. After standing three hours, the mixture was evaporated to give 9–10 g. of dark solid. Extraction of this residue with warm isopropyl alcohol followed by evaporation of the extracts gave 1.0–1.2 g. of red-brown crystals. After several recrystallizations from isopropyl alcohol (Darco) there was obtained an almost colorless product, m.p. 185–186° dec. The hydrochloride of the tetramer was prepared by adding to a solution of 0.9 g. of tetramer in 150 ml. of diethyl ether, 100 ml. of ether saturated with dry HCl. The resulting, nearly colorless, solid was collected and air-dried, m.p. 145° dec.

Fumaronitrile.—This compound was prepared according to the procedure of DeWolfe and van de Straete[7] and recrystallized from ethanol; m.p. 96–97°.

Maleonitrile was prepared from maleamide according to Blomquist and Winslow[8] and recrystallized from ethanol until carbonyl absorption could not be detected in the infrared spectrum, m.p. 32.9–33.1°.

The infrared spectra were obtained on a Perkin-Elmer model 21 spectrophotometer.

The ultraviolet spectra were obtained on a Cary recording spectrophotometer, model 11, using 0.1-, 1- and 10-mm. quartz cells. The data are plotted as log ϵ *vs.* wave number. Since wave numbers are linearly related to energy, this choice of units shows the similarity in form of the curves on an equal energy basis.

The pK_b for HCN tetramer was found to be too high to measure accurately. Thus, 0.2144 g. of tetramer hydrochloride dissolved in 100 ml. of water and titrated potentiometrically with 0.1007 *N* NaOH gave a *p*H at one-half titration of 2.18 (equivalent weight found: 149.2; theory: 144.5).

The dipole moment of HCN tetramer was determined in dioxane solution employing an apparatus and technique previously described.[9] Measurements were made on freshly prepared solutions and showed no appreciable change with time. Table I lists the experimental values of ϵ, dielectric constant; *d*, density; and *w*, weight fraction for dioxane solutions at 35.0°. The dipole moment was cal-

Table I

Dielectric Constants, Densities and Polarizations in Dioxane at 35.0°

w	ϵ	d
0.00000	2.2178	1.01704
.00080	2.2657	1.01737
.00106	2.2733	1.01765
.00138	2.2958	1.01739
.00201	2.3356	1.01785

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[1] O. Lange, *Ber.*, **6**, 99 (1873).

[2] C. Bedel, *Compt. rend.*, **176**, 168 (1923).

[3] E. Gryszkiewicz-Trochimowski, *Rocz. Chem.*, **8**, 165 (1928); *C. A.*, **22**, 4475 (1928).

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

[5] L. E. Hinkel and T. I. Watkins, *ibid.*, 1206 (1940).

[6] R. P. Linstead, E. G. Noble and J. M. Wright, *ibid.*, 920 (1937).

[7] J. DeWolfe and L. van de Straete, *Bull. sci. acad. roy. Belg.*, **21**, 216 (1935); *C. A.*, **29**, 3985 (1935).

[8] A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

[9] W. Schneider and I. Halverstadt, This Journal, **70**, 2626 (1948).

culated by a modified Hedestrand method identical to that employed by Schneider.[10]

Atomic polarization was neglected and molecular refractions were calculated from the atomic refractions listed in "Landolt–Börnstein Tabellen." The values obtained from these calculations are: α 67.8, β 0.360, ∞P_T 1230, $MR_{D\text{calcd}}$ 30.8, and μ 7.8 D.

Results and Discussion

Infrared Absorption Spectra.—The absence of absorption in the C–H stretching region (near 2900 cm.$^{-1}$) of the infrared spectrum of the crystalline tetramer, Fig. 1, rules out the existence of the tetramer in the solid state as aminoiminosuccinonitrile. The marked C–H absorption in this region for succinonitrile may be seen in Fig. 2.

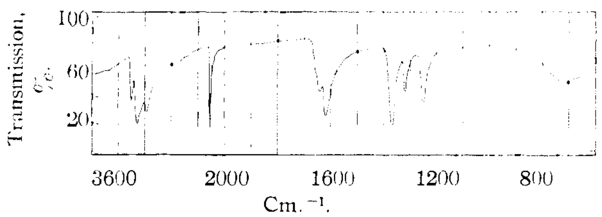

Fig. 1.—Infrared spectra of HCN tetramer: solid line, Nujol mull; dotted line, perfluorolube oil mull.

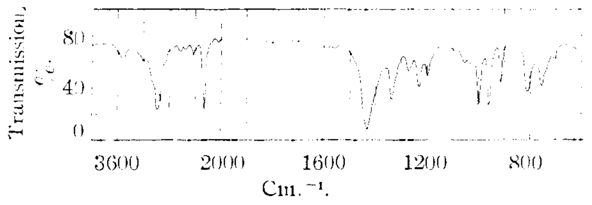

Fig. 2.—Infrared spectra of succinonitrile.

Ultraviolet Spectra and Basicity.—If HCN tetramer possessed the fully-conjugated diaminomaleonitrile structure I, it would be expected to have an ultraviolet absorption maximum (Fig. 3) at a considerably longer wave length than its parent compound maleonitrile (log ϵ 4.14 at 220 mμ or 45,440 cm.$^{-1}$) due to the bathochromic effect of the two amino substituents. The dialkyl amino group, for example, has been shown to shift the maxima of α,β-unsaturated carbonyl compounds 60 to 85 mμ toward the visible, when located on the β-carbon atom.[11] The addition of an amino group to the β-position of an α,β-unsaturated nitrile produces a similar marked shift as evidenced by *cis*- and *trans*-β-aminocrotononitrile which have maxima at 258 and 256 mμ in ethanol, respectively, compared to acrylonitrile at 204 mμ.[12]

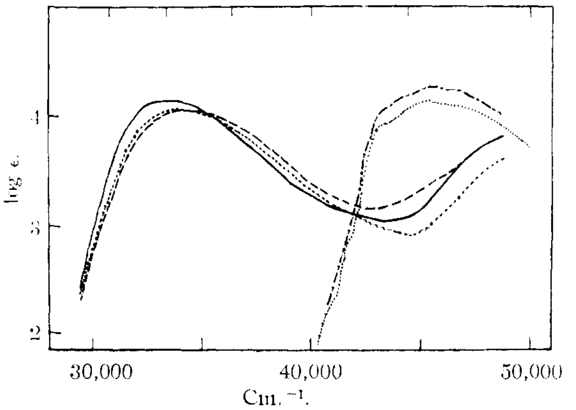

Fig. 3.—Ultraviolet absorption spectra: —, tetramer in ethanol; ---, tetramer in water; — — —, tetramer in 0.1 N HCl; . . . . ., maleonitrile in ethanol; -·-·-, fumaronitrile in ethanol.

If, on the other hand, the tetramer possessed the shorter conjugated system of structure II, one would expect to find the absorption maximum at a wave length the same as, or shorter than, that for acrylonitrile (204 mμ or 49,020 cm.$^{-1}$),[13] since Barany, *et al.*,[14] have shown that conjugated azomethine compounds consistently absorb at shorter wave lengths than the corresponding methylene compounds.

HCN tetramer possesses an absorption maximum in water at 295 mμ (33,890 cm.$^{-1}$, log ϵ 4.08) and in ethanol at 300 mμ (33,330 cm.$^{-1}$, log ϵ 4.15) which is consistent with structure I.

The spectrum of the tetramer is scarcely changed, in either position or intensity, with a shift of solvent from water (295 mμ, log ϵ 4.08) to 0.1 N HCl (290 mμ, log ϵ 4.06). Since salt formation would be expected to alter the spectrum, it appears that no appreciable salt formation has occurred in the acid medium and that the amino groups possess a very low basicity. This low basicity was demonstrated further by potentiometric titration of the monohydrochloride in aqueous solution. It was found that the pK_b of the tetramer was greater than 11.5 and thus too high to be measured by the technique employed.

Dipole Moment.—The foregoing spectral evidence has demonstrated that the tetramer cannot be structure II. The data can be explained in terms of structure I or its geometrical isomer diaminofumaronitrile. In order to provide physical evidence for a decision between these isomers, the dipole moment of the tetramer was determined.

The dipole moment values expected for the two isomers have been estimated. The values 0, 0.4, 0.5, 1.3 and 3.0 Debye units were taken, respectively, for the C–C, C–N, H–N and C≡N bond moments. A bond angle of 180° was taken for the C—C≡N angle; 109° for the C–C–C, H–N–H and H–N–C angles; and 120° for the C=C—C angle. Since each isomer possesses amino groups potentially free to rotate about the adjacent C–C bond, a maximum and minimum value is given for each structure in Table II.

TABLE II

ESTIMATED DIPOLE MOMENTS (DEBYE UNITS)

Compound	Maximum	Minimum
Diaminomaleonitrile	5.2	4.2
Diaminofumaronitrile	2.2	0
Observed value	7.8	

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[10] W. Schneider, THIS JOURNAL, **72**, 761 (1950).

[11] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

[12] J. J. Conn and A. Taurins, *Can. J. Chem.*, **31**, 1211 (1953).

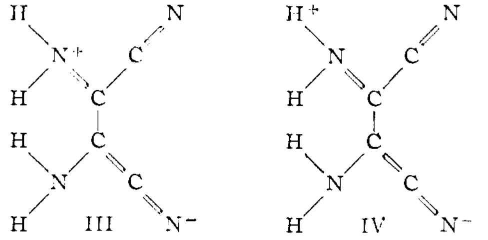
[13] H. Brieger, F. Rieders and W. A. Hodes, *Arch. Ind. Hyg. Occupational Med.*, **6**, 128 (1952).

[14] H. C. Barany, E. A. Braude and M. Pianka, *J. Chem. Soc.*, 1898 (1949).

An extreme configuration of the amino groups in the *trans* derivative (where the cyano dipoles cancel) leads to an estimated moment of 2.2 *D* while a centro-symmetric configuration leads to zero moment.

In the *cis* derivative, the powerful cyano dipoles no longer cancel and an estimated moment of 4.2 or 5.2 *D* results (depending on the rotation of the amino groups).

The large moment found for the tetramer thus is incompatible with the *trans* configuration. While the estimated moments for the *cis* compound fall short of the observed moment, a favorable situation exists for participation by a number of highly polar resonance forms, III (2 forms), and IV (4 forms) which would increase the estimated moment.


III IV

Heretofore the structure of the tetramer has been argued on the basis of its chemical reaction products. However, these reactions can be explained on the basis of either structure I or II since the possibility always exists that either structure may be converted to the other under the influence of any of the chemical reagents employed. It is important therefore to decide such a question by physical methods which would not be likely to alter the structure of the molecule. It is believed that the foregoing physical evidence supports the view that HCN tetramer exists as diaminomaleonitrile, both in the crystalline state and in dilute solutions in neutral solvents at ordinary temperature.

The assistance of the following members of the Stamford Laboratories is gratefully acknowledged: Dr. R. C. Hirt and Mr. F. T. King in the preparation and interpretation of the ultraviolet spectra; Dr. R. C. Gore, Mr. N. B. Colthup and Dr. J. E. Lancaster in the preparation and interpretation of the infrared spectra; Mr. R. McFarlane, Jr., in the determination of the dipole moment.

STAMFORD, CONNECTICUT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Amination of Chloromethylsiloxanes

BY P. D. GEORGE AND J. R. ELLIOTT

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The amination of chloromethylpentamethyldisiloxane was studied in detail in order to develop a general procedure for aminating chloromethylsiloxanes without siloxane rearrangement. Application of the method to chloromethylheptamethylcyclotetrasiloxane gave the corresponding amines in 35–60% yields. Several (trimethylsilylmethyl)-amines also were synthesized. The alkylamine-substituted dimethylsiloxanes exhibited an extraordinary order of siloxane bond lability inasmuch as they polymerized on standing at room temperature and depolymerized on standing in solution. The physical properties and infrared spectra of the aminomethylsilicon compounds were determined and are discussed.

Previous publications on aminoalkyl silicon compounds have dealt principally with aminoalkylsilanes[1,2] and with aminoalkylsiloxanes[1,3] derived from them by hydrolysis or by sulfuric acid cleavage of methyl groups. Few aminomethylsiloxanes have been prepared by the amination of the corresponding chloromethylsiloxanes,[4,5] and no amine-substituted dimethylsiloxanes have been obtained in this way. We wish to describe the reaction of chloromethylpentamethyldisiloxane (MM'Cl)[6] and chloromethylheptamethylcyclotetrasiloxane ($D_3D'Cl$) with ammonia and amines, and we wish to report the properties of a number of novel compositions, particularly the amine-substituted dimethylsiloxanes, obtained in this way.

Studies aimed at developing a general procedure for amination of chloromethylsiloxanes were based on MM'Cl as a model compound because its structural features would permit ready detection of any siloxane rearrangement or silicon–carbon cleavage which might occur. The following was found to be a satisfactory procedure. Anhydrous liquid ammonia and MM'Cl in a 50:1 mole ratio were stirred for ten hours at 70° in a glass-lined autoclave. The ammonia was evaporated and the product slurry was filtered. Fractional distillation of the filtrate gave a 55% yield of pure aminomethylpentamethyldisiloxane ($MM'NH_2$). Important process vari-

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(1) (a) J. E. Noll, J. L. Spier and B. F. Daubert, THIS JOURNAL, **73**, 3867 (1951); (b) J. E. Noll, B. F. Daubert and J. L. Speier, *ibid.*, **73**, 3871 (1951).

(2) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

(3) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

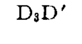
(4) J. L. Speier, U. S. Patent 2,567,131, September 4, 1951.

(5) Dow Corning Ltd., British Patent 697,684, September 30, 1953.

(6) For the sake of conciseness and clarity the carbon-functional siloxanes are designated by a short-hand system which is an extension of a system frequently used in the past. M signifies the $Me_3SiO_{0.5}$ group and D designates the $-SiMe_2O-$ group. The application of a prime to these symbols serves to indicate the presence of a substituent other than a methyl group; for example D' and D'' have served to designate $-SiMePhO-$ and $SiPh_2O-$, respectively. In the present case the prime indicates the presence of a methylene group thus:

$Me_3SiOSiMe_2CH_2-$

MM'



$$\underbrace{OSiMe_2OSiMe_2OSiMe_2OSiMeCH_2-}$$

D_3D'