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Studies on a Polymerization Product of Hydrogen Cyanide

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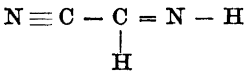
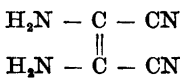
The crystalline compound formed by the polymerization of hydrogen cyanide has been studied by X-ray diffraction methods and infrared absorption measurements. The compound has been found to be a dimer of HCN and not a tetramer as suggested by previous authors. The following structure of the molecule is proposed:



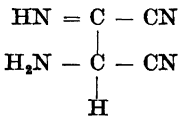
Strong intermolecular hydrogen bonds should be present in the structure.

It has long been well-known that pure hydrogen cyanide or hydrogen cyanide to which a small amount of an alkaline substance has been added polymerizes more or less rapidly depending on the concentration of the alkaline compound and on the temperature. The polymerization of pure hydrogen cyanide is very slow. The product is a dark, almost black, coal-like solid which cannot be reconverted to monomeric hydrogen cyanide. In the dark solid obtained, reddish brown, rodshaped crystals can be found. These crystals can be extracted by means of their solubility in ether. The dark residue, which is X-ray amorphous, is thought to consist of a mixture of several phases.

The structure of the crystalline polymerization compound has been discussed by several authors. From ebullioscopic measurements in methanol, Bedel [1] concluded the compound to be a tetramer of hydrogen cyanide. He suggested the structural formula $CN{\cdot}CH(CN){\cdot}NH_2{\cdot}HCN$. Gryszkiewicz-Trochimowski [2] considered it to have the following structure



while Hinkel and co-workers [3] thought this structure to be wrong and proposed instead the tautomeric structure:



Webb and co-workers [4] studied the compound by means of its ultraviolet absorption spectra, dipole moment measurements and infrared absorption spectra. They considered their data to support the structure proposed by Gryszkiewicz-Trochimowski.

By means of single crystal X-ray data, Sass and Donohue [5] found the unit cell dimensions of the polymer to be

$$a = 6.47 \text{ Å}, \quad b = 18.20 \text{ Å}, \quad c = 5.23 \text{ Å}, \quad \beta = 123°.$$

They did not, however, determine the structure.

EXPERIMENTAL

The polymerization products were obtained from a HCN gas bomb that had been kept for several years. The polymerization in the bomb was complete. From the dark solid, a lot of rod-shaped, reddish brown crystals could be picked out by hand. The crystals were almost colourless when recrystallized from ether. The X-ray patterns obtained from the crystals before and after the purification were identical.

The polymerization product was also prepared according to Linstead and co-workers [6]. The specimen obtained in this way was identical with the above mentioned one.

The purified crystals gave the following analysis:

	C	N (by residue)	H
weight % obs.	44.6	51.6	3.8
weight % calc.	44.4	51.9	3.7

The "melting point" (decomposition temperature) was found to be 180—181°C in good agreement with earlier observations.

The X-ray powder pattern was obtained using a Guinier camera with strictly monocromatized CuKα_1 radiation. The single crystal data were registered by the Weissenberg techniques with CuK radiation.

The infrared absorption spectrum was obtained on a Perkin-Elmer Spectrometer, Model 21. The sample was prepared for the measurements by the potassium bromide technique.

Table 1. The Guinier powder pattern of HCN dimer. Dimensions of the monoclinic unit cell:

$a = 6.511$ Å, $b = 18.31$ Å, $c = 5.208$ Å, $\beta = 121.9°$

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vw	0.00700	020	0.00708
w	0.01941	100	0.01941
st	0.02121	110	0.02118
w	0.02653	120	0.02649
m	0.02836	040	0.02832
m	0.03122	12$\bar{1}$	0.03122
vw	0.03181	011	0.03210
w	0.03540	130	0.03534
w	0.04012	13$\bar{1}$	0.04007
m	0.04612	031	0.04626
m	0.05260	14$\bar{1}$	0.05246
vst	0.05869	041	0.05865

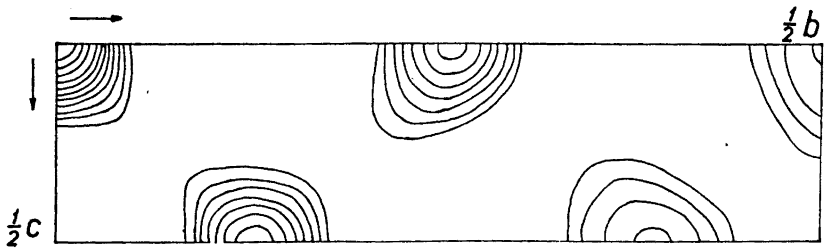


Fig. 1. HCN dimer: Patterson function. Projection along [100].

X-RAY STUDIES

A crystal was picked out from the dark solid and rotated around the rod-axis in the Weissenberg-camera. The identity period in this direction was found to be about 6.5 Å. Complete single crystal data were collected with this crystal setting. The crystal was monoclinic. Using the single crystal data, the powder pattern could be indexed as shown in Table 1. The following unit cell dimensions were thus derived:

$$a = 6.511 \text{ Å}, \quad b = 18.31 \text{ Å}, \quad c = 5.208 \text{ Å} \quad \beta = 121.9°.$$

The volume, 527.3 Å^3, gives a calculated density of 1.36 for 16 formula units HCN in the cell in fair agreement with the observed value of 1.31. The density was determined with the flotation method. The deviation from the value 1.41 determined by Sass and Donohue [5] is remarkable.

The reflexions which were systematically absent were $0k0$ with k odd and $h0l$ with l odd. This is in agreement with the space group $P2_1/c$, but the reflexion material may be insufficient (because of the high termal motion of the atoms) to draw definite conclusions.

The Patterson projection $P(vw)$ was calculated (*cf.* Fig. 1). It shows only eight strong, sharp and well resolved maxima. The spacing between the maxima in the projection is never less than 3.1 Å, which greatly exceeds the intramolecular distances of a compound of this kind. The structure must thus contain chain molecules running parallel to the a axis and distributed in the bc plane just like the maxima of Fig. 1. The length of the molecules must therefore correspond to the dimer (HCN_2). Adjacent molecules are probably connected by hydrogen bonds — this may also be inferred from the somewhat distorted appearance of the maxima in $P(vw)$.

Further studies on the crystal structure, which also include low-temperature investigations, are in progress.

DISCUSSION OF THE MOLECULAR STRUCTURE

In addition to the available X-ray data, some physical data concerning this substance are of particular interest. According to Webb and co-workers [4], the compound is a strong dipole and hence the molecule must be asymmetric.

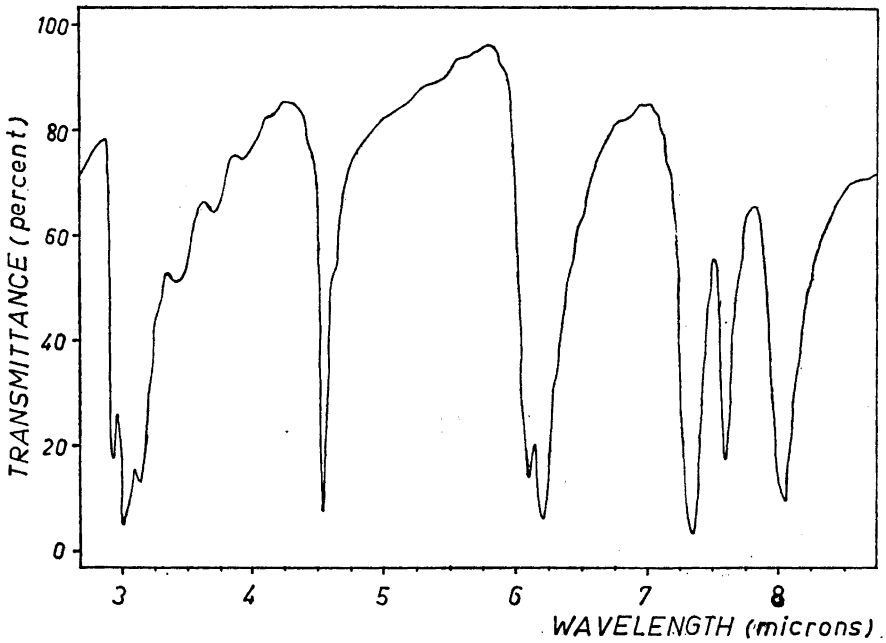


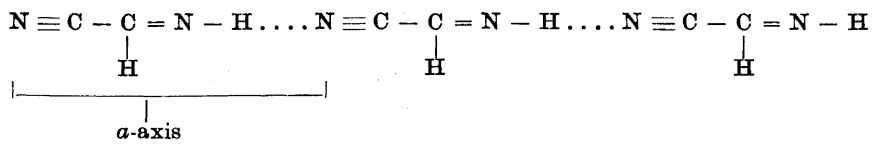
Fig. 2. Infrared spectra of HCN dimer.

Like Webb and co-workers, we have also studied the infrared absorption spectrum of the compound. However, our interpretation of the spectrum is not in agreement with theirs. As is seen in Fig. 2, the diffuse, weak absorption maxima at 3.42 μ (2 924 cm^{-1}), 3.70 μ (2 703 cm^{-1}) and 3.92 μ (2 551 cm^{-1}) clearly demonstrate the presence of strong hydrogen bonds. Furthermore, there is a characteristic maximum at 4.54 μ (2 203 cm^{-1}) corresponding to a carbon-nitrogen triple bond. The maxima at 6.08 μ (1 645 cm^{-1}) may correspond to a carbon-nitrogen double bond. The maxima at 2.93 μ (3 413 cm^{-1}), 3.01 μ (3 322 cm^{-1}) and 6.20 μ (1 613 cm^{-1}) correspond to nitrogen-hydrogen bonds. The maxima at 3.15 μ (3 175 cm^{-1}) and 7.35 μ (1 361 cm^{-1}) and possibly also at 7.60 μ (1 316 cm^{-1}) can probably be assigned to carbon-hydrogen bonds. The cause of the maxima at 8.05 μ (1 242 cm^{-1}) is uncertain.

A molecule satisfying the above mentioned physical data can thus be written:

$$N \equiv C - \underset{\displaystyle H}{\overset{\displaystyle |}{C}} = N - H$$

A suitable name for the compund seems to be iminoacetonitrile. The sum of the three bond lengths N $\equiv$ C, C—C and C = N is about 3.8 Å, if conventional bond distances are used. The chains are arranged along the *a*-axis as follows:



The bond distance N—H....N will thus be quite short, indicating strong hydrogen bonds in agreement with the infrared data. (The result obtained by Bedel in his molecular weight determination may be due to these hydrogen bonds.)

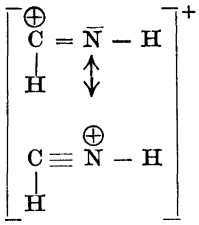
The high "melting" point, 181°C, for such a small molecule supports this suggestion concerning the presence of strong hydrogen bonds.

PROPOSED MECHANISM FOR THE POLYMERIZATION

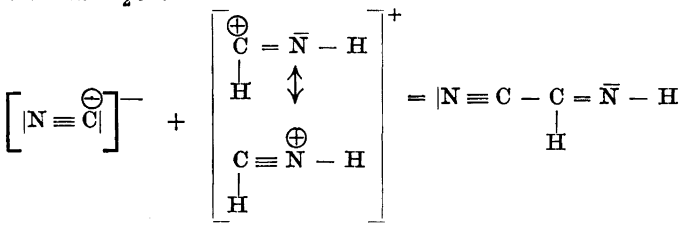
Pure hydrogen cyanide exhibits autoprotolyse according to the scheme

$$HCN + HCN = H_2CN^+ + CN^-$$

The ion H_2CN^+ can be written in two resonance forms:



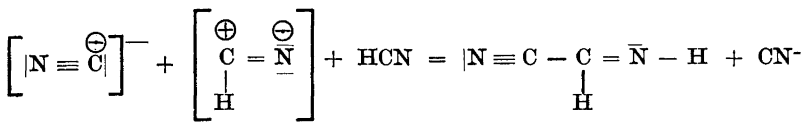
The dimer may thus be formed by the combination of the CN^--ion and the upper resonance form of H_2CN^+



In the presence of hydroxyl ions, the protolysis of hydrogen cyanide follows the scheme

$$HCN + OH^- = CN^- + H_2O$$

The cyanide ion may react with another molecule of hydrogen cyanide according to



The process evidently regenerates the cyanide ion and the polymerisation may thus be caused by a very small quantity of an alkaline substance.

It is interesting to note that no real melting occurs when the dimer is heated at temperatures above its "melting point". Some decomposition occurs and a black, X-ray amorphous residue is left which is stable up to several hundred degrees. The black residue resembles the dark solid formed originally during the polymerization of hydrogen cyanide. Further studies on this subject are in progress.

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