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The Crystal Structures of Hydrogen Cyanide, HCN

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The tetragonal form of hydrogen cyanide has the space group C_{4v}^{9}–$I4mm$. There are two molecules in the unit cell of dimensions $a=4{\cdot}63$, $c=4{\cdot}34$ A. The crystal structure consists of infinite linear chains, all pointing in the same direction, with the molecules along the fourfold axes. The hydrogen-bond distance (C—H...N), based on the microwave C≡N distance of 1·16 A., is 3·18 A. The dielectric constant of the solid just below the melting-point is discussed in terms of a possible re-orientation of occasional molecules. The orthorhombic low-temperature form (below −102·8° C.) has the space group C_{2v}^{20}–Imm. Again there are two molecules in the unit cell of dimensions $a=4{\cdot}13$, $b=4{\cdot}85$, $c=4{\cdot}34$ A. Except for a contraction and expansion of the tetragonal a and b distances respectively, the low-temperature structure is that of the high-temperature modification.

Introduction

The infra-red rotational spectrum shows that the hydrogen cyanide molecule is linear (Herzberg & Spinks, 1934). Linear polymers of variable length have been postulated to explain such physical properties as a high vapor density, and the very high dielectric constant of the liquid which decreases rapidly with increasing temperature (Pauling, 1940, p. 294; Giauque & Ruehrwein, 1939; Coates & Coates, 1944; Smyth & McNeight, 1936). Smyth & McNeight measured the dielectric constant of the solid and concluded from the very low values that there was no molecular rotation in the solid state. The heat-capacity studies of Giauque & Ruehrwein indicate a reversible phase transition at −102·8° C. The present investigation, a determination of the crystal structure of both forms, supplements and agrees with these previous studies.

Experimental

Pure anhydrous hydrogen cyanide was prepared by dropping 18 M-sulfuric acid on solid sodium cyanide and condensing the gas after it had passed through a drying line. It was distilled once through calcium chloride and phosphorus pentoxide and once under vacuum. The material was then distilled into thin-walled pyrex capillary tubes of approximately 0·5 mm. diameter. The hydrogen cyanide was frozen by liquid nitrogen and the tubes were sealed off under vacuum. The Buerger precession and Weissenberg photographs were all taken with Mo $K\alpha$ radiation, using techniques described elsewhere (Abrahams, Collin, Lipscomb & Reed, 1950; Reed & Lipscomb, 1951). The multiple-film method was employed in which the films were interleaved with 0·001 in. brass foil. The higher-temperature photographs were taken at approximately −80° and the low-temperature photographs at approximately −120° C.

Both modifications were tested for piezoelectricity and pyroelectricity. The piezoelectric tests were negative. The high-temperature form gave no indication of pyroelectricity, but on passing through the transition at −102·8° C. the crystals became strongly pyroelectric. In this test a capillary containing HCN was suspended by a thread at approximately $\frac{3}{16}$ in. from the tip of a thermocouple. A Dewar of liquid nitrogen was slowly raised, cooling the capillary as the nitrogen surface approached it. On reaching a temperature of approximately −105° C. the capillary suddenly jumped to the tip of the thermocouple. The temperature was then raised by lowering the Dewar, and at approximately −99° C. the capillary fell away from the tip. The experiment was repeated about six times. Clearly the crystals were strongly pyroelectric in the low-temperature form and reverted to their former state on raising their temperature through the transition point, −102·8° C. Indeed, our diffraction results indicated that a single crystal was again obtained when the temperature of a capillary was raised through the transition point.

Determination of the structures

High-temperature modification

Hydrogen cyanide, which has a molecular weight of 27·026, melts at −13·3° C. (Giauque & Ruehrwein, 1939). The symmetry of the zero- and first-level precession photographs about the [010] and [110] axes was C_{2l}. The symmetry of the zero- and first-level Weissenberg photographs about the [001] axes was C_{4l}. Only those extinctions leading to body centering were observed. The tetragonal cell has the dimensions

$$a=4{\cdot}63\pm0{\cdot}02,\quad c=4{\cdot}34\pm0{\cdot}02\text{ A.},$$

and its volume is 92·9 A.^{3}. The observed density of 0·925 g.cm.$^{-3}$ (Werner, 1929) indicates two molecules in the unit cell; the calculated density is 0·967 g.cm.$^{-3}$.

A consideration of the *c*-axis dimension of 4·34 A., the exaggerated normal decline of the *h*00 and *hh*0 reflections, and the well-known possibility of hydrogen cyanide chains, immediately suggested that the molecules were aligned along the fourfold axes of the cell. Quantitative calculations of structure factors confirmed this atomic arrangement. The X-ray evidence then suggested the space groups C_{4v}^{9}–*I*4*mm* or D_{4h}^{17}–*I*4/*mmm*, but it was felt that D_{4h}^{7}–*P*4/*nmm* was also a possibility, since the HC≡N group is almost symmetrical. The space group D_{4h}^{17} would allow a random orientation of the chains in the *c* direction, while D_{4h}^{7} would require the molecule in the center of the cell to point in the opposite direction.

The argument which we consider most convincing leads to the non-centrosymmetric space group C_{4v}^{9}–*I*4*mm*. It is based on the three observations that: (*a*) the relative intensities of the high- and low-temperature forms are identical; (*b*) the pyroelectric test indicates conclusively that the low-temperature form is non-centrosymmetric; and (*c*) the very small heat effect associated with the reversible transition at −102·8° C. shows, as Giauque & Ruehrwein point out, that the physical process is 'one involving the action of large groups of hydrogen cyanide molecular units'. The interpretation quoted here is in agreement with the reversibility of the transformation as confirmed by our X-ray results, and with the stability of the polymeric chains in the gas phase at higher temperatures. Thus the analysis of the structure of the high-temperature form was made on the basis of the space group C_{4v}^{9}–*I*4*mm*. In addition, however, detailed considerations of the centrosymmetric space groups D_{4h}^{7} and D_{4h}^{17} were also made and are described in later paragraphs.

With the use of a twofold position $(0, 0, z_1)$ for the carbon atom and a twofold position $(0, 0, z_2)$ for the nitrogen atom (ignoring the hydrogen atom), the problem was reduced to the determination of one distance parameter, the C≡N distance, since one of the *z*'s can be chosen arbitrarily. However, the very rapid decrease in *hk*0 intensities, as compared with general *hkl* intensities, required consideration of an anisotropic temperature factor (Helmholz, 1936). This factor,

$$\exp\left[-(A - Bl^2d^2/c^2)\sin^2\theta/\lambda^2\right],$$

may be written

$$\exp\left[-B_1(h^2+k^2) - B_2l^2\right].$$

An attempt was made to refine the *z* parameter (the C≡N bond distance) using all observed *hkl* data in one-dimensional Fourier sections. Because of serious non-convergence, successive changes in the distance parameter were made by comparing peak positions as given by the observed and by the calculated structure factors (Fig. 1). We observed, however, that the parameter was quite sensitive to the values chosen for the scale-factor and temperature-factor constants.

The method of least squares was now applied, since there is no convergence difficulty and since it also gives values for the probable errors (Hughes, 1941). Weighting factors of unity were used and the equations were set up so as to yield corrections to the four parameters: the *z* co-ordinate; λ, the scale factor (which multiplies the F_o); B_1 and B_2, the temperature-factor constants. The approximate parameters, taken from the Fourier refinement, were $z = 1{\cdot}154$ A., $\lambda = 0{\cdot}23$, $B_1 = 0{\cdot}125$, $B_2 = 0{\cdot}04$. This treatment led to final least-squares values and corresponding probable errors of

$$z = 1{\cdot}19 \pm 0{\cdot}15\text{ A.},\quad \lambda = 0{\cdot}238 \pm 0{\cdot}015,$$

$$B_1 = 0{\cdot}113 \pm 0{\cdot}009 \quad\text{and}\quad B_2 = 0{\cdot}05 \pm 0{\cdot}004.$$

The normal equations confirmed that the *z* parameter was sensitive to the other parameters, especially to B_2.

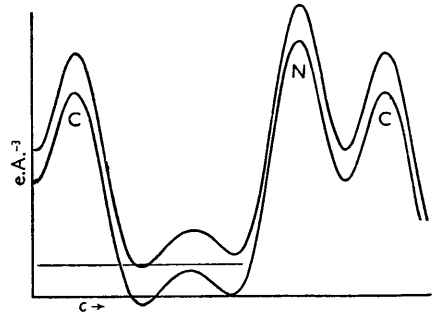

Fig. 1. One-dimensional Fourier analysis of the electron density along the hydrogen cyanide molecule. The origin is displaced as shown for the top curve. The top curve is from observed structure factors, the bottom curve from calculated structure factors. Both curves are based on the least-squares parameters, i.e. $d_{\mathrm{C\equiv N}} = 1{\cdot}19$ A., etc.

The unusually large probable errors are possibly due mainly to the small number of observations. Two sets of structure factors (Table 1) have been calculated, one from the least-squares parameters and one from $z = 1{\cdot}16$ A., with the other parameters determined from the normal equations.

Table 1. *Data for high-temperature modification*

F_c' are for $d_{\mathrm{C\equiv N}} = 1{\cdot}19$ A., $B_1 = 0{\cdot}113$, $B_2 = 0{\cdot}05$, $\lambda = 0{\cdot}238$.
F_c'' are for $d_{\mathrm{C\equiv N}} = 1{\cdot}16$ A., $B_1 = 0{\cdot}116$, $B_2 = 0{\cdot}049$, $\lambda = 0{\cdot}237$.

Reflection	F_c'	α'	F_c''	α''	F_o
110	13·3	0·0°	13·2	0·0°	14·9
130	3·1	0·0	3·0	0·0	3·4
200	8·6	0·0	8·5	0·0	9·2
220	4·2	0·0	4·1	0·0	3·9
330	1·0	0·0	0·9	0·0	0·8
400	1·3	0·0	1·2	0·0	1·1
002	2·4	227·5	2·1	238·5	2·2
004	3·3	178·5	3·4	179·0	3·8
101	9·2	350·0	9·5	350·0	8·7
103	4·4	184·5	4·2	185·0	3·9
202	1·1	222·0	0·9	233·5	0·8
301	2·2	352·0	2·1	353·0	2·1
303	1·5	182·5	1·4	183·0	1·4
112	1·6	226·5	1·4	237·5	1·2
114	2·5	179·0	2·6	179·5	3·1
121	4·2	350·0	4·2	350·0	4·2
123	2·5	183·0	2·4	183·0	2·4
132	0·3	195·5	0·3	203·0	< 1·5
141	0·7	355·5	0·7	355·5	< 1·6
222	0·5	200·5	0·3	240·0	< 0·9
231	1·2	352·5	1·2	353·0	1·4
233	0·9	181·5	0·8	182·0	1·4

The $C{\equiv}N$ and C–H distances, as given by microwave analysis, are 1·157 and 1·061 A. (Simmons, Anderson & Gordy, 1950). The $C{\equiv}N$ vibrational frequency (Hoffman & Hornig, 1949) increases only by 8 cm.$^{-1}$ in the solid state (−180° C.) as compared with the gaseous state, so that the true $C{\equiv}N$ distance in the solid is very probably within $\pm 0{\cdot}005$ A. of 1·16 A. The corresponding C–H vibrational frequency shift is −180 cm.$^{-1}$. This decrease is less than half of that observed for the O–H vibrational frequency in ice, so that the C–H distance is also probably close to the gas-phase value. The O–H distance in ice is estimated to be 0·99 A. (Cross, Burnham & Leighton, 1937), an increase of 0·03 A. over the gas-phase value, so that one may estimate the C–H distance in solid hydrogen cyanide to be $1{\cdot}07 \pm 0{\cdot}02$ A.

The $C{\equiv}N$ distance of 1·154 A. obtained by the Fourier method might suggest a preference over the least-squares method in this case. However, the good agreement with the spectroscopic value was obtained through a somewhat fortuitous choice of the other parameters. Good agreement could also have been obtained at 1·10 or 1·20 A. by reasonable adjustment of the other parameters. Since the structure has tetragonal symmetry and some of the structure factors thereby have a multiplicity of sixteen in the Fourier expression, the errors may enter systematically instead of being distributed more or less randomly over as many as possibly eight reflections (assuming Friedel's law). Since the *hkl* reflections may be measured independently more often, the corresponding required accuracy in the intensity measurements appears to be obtainable. However, the intensity measurements in the present study are probably only slightly better than usual, although they appeared to have shown a rather satisfactory precision. The remaining errors are those peculiar to the visual photographic method, and those due to lack of accuracy in the Lorentz factor as determined for certain reflections[*] on the precession photographs (Evans, Tilden & Adams, 1949; Buerger, 1944). Finally, the greatest difficulty may be that reflections could be obtained only out to $\sin\theta/\lambda = 0{\cdot}50$ on zero-level precession photographs because the crystals always grew with their *c* axis along the capillary.

The Fourier sections (Fig. 1), based on both calculated and observed data, have carbon and nitrogen peak heights of 4·0 and 5·0 e.A.$^{-3}$, respectively, which are properly different by about 1 e.A.$^{-3}$, although these peaks are somewhat below the six- and seven-electron heights which may be expected. This lowering is probably due primarily to the large temperature factor, but perhaps also partly to non-convergence.

The structures based on the centrosymmetric space groups D_{4h}^{7} and D_{4h}^{17} may now be considered. The only reasonable positions in D_{4h}^{7}–$P4/nmm$ which satisfy the approximate structure of parallel linear chains are $\frac{1}{4}, \frac{1}{4}, z_N$; $\frac{1}{4}, \frac{1}{4}, z_C$; $\frac{1}{4}, \frac{1}{4}, z_H$, and those related by a center of symmetry at the origin. Assumption of a $C{\equiv}N$ bond distance of 1·16 A. and a C–H bond distance of 1·07 A. reduced the problem to one parameter, which was taken as z_C. Choosing without loss of generality $z_N < z_C$, we then found quantitative disagreement for all possible values of z_C. The value $z_C = 0{\cdot}385$ came closest to satisfying the observations. For $0{\cdot}383 < z_C < 0{\cdot}391$ the reflections (001), (003) and (201) remain just below the observational limit, but for $0{\cdot}370 < z_C < 0{\cdot}400$ the intensity of (102) remained from two to four times the observational limit. In fact, the intensity of the unobserved (102) reflection remains greater than the readily observable (112) and (002) reflections throughout the range $0{\cdot}370 < z_C < 0{\cdot}400$. Values of z_C outside of these ranges produced even more serious inconsistencies with the observations. Proper scale and temperature factors were included in these calculations. These factors were not essentially different from those required for the non-centrosymmetric model. It is felt that these discrepancies unambiguously eliminate the space group D_{4h}^{7}–$P4/nmm$ for the high-temperature modification.

The space group D_{4h}^{17}–$I4/mmm$ was tested by assuming an average of carbon and nitrogen at the positions 0, 0, z; 0, 0, $\bar{z}$, plus the positions related by body centering. The parameter was fixed by assumption of a $C{\equiv}N$ distance of 1·16 A., and structure-factor calculations were made including the proper scale and temperature factors. The structure factors for (002) and (112) are 1·2 and 0·8, respectively, and are regarded as significantly lower than the observed values (Table 1). All of the other structure factors were in satisfactory agreement. Thus, on the basis of these two discrepancies alone, perhaps there is only a slight preference for the non-centrosymmetric space group C_{4v}^{9} over D_{4h}^{17}. We do feel, however, that D_{4h}^{17} is also unreasonable on physical grounds, and that the magnitude of the heat of transition is very strong evidence for the non-centrosymmetric space group for the high-temperature form.[*]

Low-temperature modification (*below* −102·8° C.)

Except for the 00*l* reflections (which had the same relative intensities and spacings), each reflection observed on the *h*0*l* zone of the high-temperature precession photograph, became two distinct reflections. Therefore there were at least two different reciprocal-lattice planes on this photograph. Both were aligned approximately, but only a rough estimate could be made of how far each plane was tilted from the position of perfect alignment. An identical pair of zones was obtained upon reorientation by 90° about *c*. The *hhl* zone, except for a reciprocal-lattice expansion per-

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[*] These reflections include those near the outer boundary of zero-level photographs, and those near the center or outer boundary of *n*-level photographs.

[*] Other possible positions in the space groups considered in the text and in D_{2d}^{9} and D_{2d}^{11} for the high-temperature form (D_2^{8} and D_2^{9} for the low-temperature form) led to models which were of the higher symmetries already considered, or to completely unacceptable structures.

pendicular to the *c* axis, was the same as the high-temperature form; except for (110), no splitting was visible. (The very strong (110) reflection, which remained well confined to the area of the high-temperature (110) reflection, showed a splitting which was barely visible. This phenomenon was not observed on any other *hhl* reflection and was not thought to be due to a distortion of the structure in this zone.)

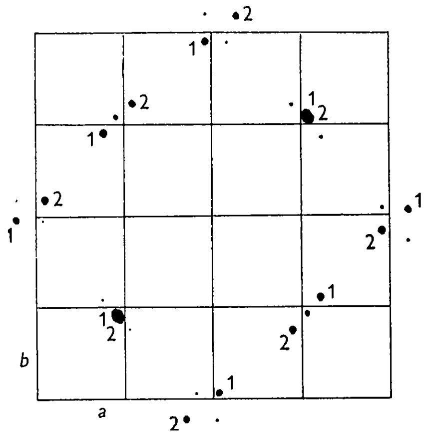

Fig. 2. Plot of a portion of the *hk*0 Weissenberg data in an undistorted reciprocal plane. The square net represents the high-temperature form. The low-temperature reflections have areas which are roughly proportional to their intensities. The sets of reflections '1' and '2' constitute two orthorhombic *hk*0 zones oriented at approximately 90° from one another. Similarly, the weak reflections may be numbered to give the same interpretation.

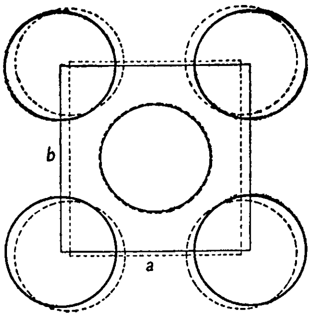

Fig. 3. The nature of the two unit cells. Full lines represent the high-temperature form; broken lines the low-temperature form.

In order to ensure a proper interpretation of these observations, the *hk*0 and *hk*1 reflections (from Weissenberg photographs of the same crystal at −80 and −120° C.), were plotted in the same reciprocal space. Fig. 2 shows a plot of the most pertinent portion of the *hk*0 data. Although four fragments are indicated, there are two main ones of approximately equal size. Confining our attention to the more intense reflections, we see that the sets marked '1' and '2' constitute two orthorhombic *hk*0 zones oriented at approximately 90° from one another. The same comment applies to the weak reflections. This observation shows that both *h*0*l* and 0*kl* reflections would occur on the same precession photograph, and, of course, the occurrence of unsplit *hhl* reflections agrees with this interpretation. The most probable space group consistent with the body-centering extinctions and the pyroelectric test is C_{2v}^{20}–*Imm*. The cell parameters are

$$a = 4{\cdot}13 \pm 0{\cdot}02, \quad b = 4{\cdot}85 \pm 0{\cdot}02, \quad c = 4{\cdot}34 \pm 0{\cdot}02\ \text{A.},$$

and the volume of the unit cell is 86·8 A.^{3}. Fig. 3 shows the simple contraction and expansion of the tetragonal *a* and *b* parameters. It was evident that the temperature factor was very similar to, although slightly less than, that of the high-temperature crystal. All the relative intensities were those of the high-temperature crystal, so that no table of observed and calculated factors is presented for the low-temperature form.

Discussion

Fig. 4 represents the high-temperature structure. A hydrogen-bond distance of 3·18 A. indicates a bond of considerable strength. Inasmuch as this is the first time that this distance has been reported, there are no other C–H...N distances available for comparison. The hydrogen-bond distances in ice, solid ammonia and hydrazine are 2·76, 3·38 and 3·19 A., respectively. In the high-temperature form of HCN the closest intermolecular distances are C–H...N, 3·18; H...N, 3·28; C...N, 3·43 A. The low-temperature form has the corresponding distances, 3·18, 3·19 and 3·35 A.

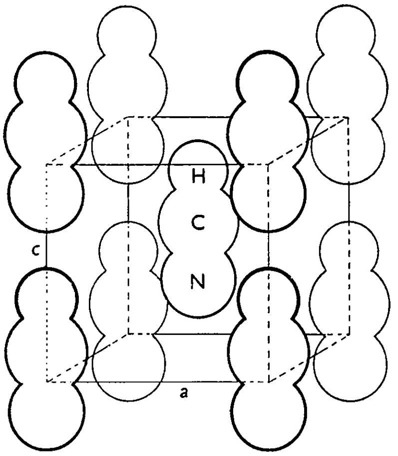

Fig. 4. The structure of hydrogen cyanide, high-temperature form.

The unidirectional alignment of the hydrogen cyanide molecules, and the 3·18 A. hydrogen-bond distance certainly suggest that there would be no molecular rotation in the solid.

The temperature-factor constant, A, is $8\pi\overline{u_c^2}$, where $\sqrt{(\overline{u_c^2})}$ is the r.m.s. amplitude of vibration perpendicular to the *c* axis. The value $B_1 = 0{\cdot}113$ corresponds to $A = 9{\cdot}68 \times 10^{-16}$, so that $\sqrt{(\overline{u_c^2})} = 0{\cdot}35$ A. at −80° C. Since $\sqrt{(\overline{u_c^2})}$ is approximately proportional to the absolute temperature, we find that at −25° C. $\sqrt{(\overline{u_c^2})} \doteqdot 0{\cdot}40$ A.

Rotation of a single molecule in a (100) plane would make the closest H...N approach distance 2·59 A. Reasonable van der Waals radii of 1·2 A. for nitrogen and 1·5 A. for carbon atoms have a sum of only 2·7 A. Therefore, sterically, there is room for molecular rotation if one will allow a small degree of molecular cooperation. Turning in the (100) plane implies a breaking of two hydrogen bonds. However, the hydrogen end of the molecule would be attracted by two electro-negative nitrogen atoms in the adjacent body-center positions. Similarly, the nitrogen end of the molecule would be attracted by two hydrogen atoms in body-center positions. Thus there might conceivably be a position of potential minimum for a molecule lying approximately along the [101] direction. Molecular reorientations of this or a similar type under the influence of an electrostatic field would produce a marked increase in the dielectric constant of the solid.

On the other hand, Smyth & McNeight point out that there is no transition near the melting-point, and suggest that the marked increase in the dielectric constant may be due to the presence of a small amount of impurities and to inaccuracy contributed by the increase in conductivity of the solid in this temperature region. They reasoned that the great polar character of the hydrogen cyanide molecule would result in a potential barrier sufficient to prevent rotation, and also that with a long molecule and parallel packing, neighboring molecules would block rotation. However, in view of the structure, we feel that the dielectric-constant measurements of the solid close to the melting-point may be more indicative of molecular reorientation than these authors would allow.

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