

## The Crystal Structure of Isocyanic Acid\*

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The crystal structure of isocyanic acid, HNCO, has been determined by X-ray methods at about  $-125^{\circ}\text{C}$ . The crystals are orthorhombic with  $a = 10.82$ ,  $b = 5.23$ ,  $c = 3.57$  Å. The space group is probably  $Pnma$ , although  $Pn2_1a$  is not excluded. The molecular dimensions are similar to those in the vapor state. The molecules are linked into infinite zigzag chains by  $\text{N-H}\cdots\text{N}$  hydrogen bonds. The anticipated  $\text{N-H}\cdots\text{O}$  hydrogen bonds do not form.

A second crystalline form is stable below about  $-100^{\circ}\text{C}$ ., but the X-ray results apply to the high-temperature form, since it readily supercools. The structure of the low-temperature form has not been determined.

The results obtained are consistent with the infra-red absorption spectra of the two solid modifications.

### Introduction

The structure of the isolated isocyanic acid molecule has been studied in the vapor by electron diffraction (Eyster, Gillette & Brockway, 1940), infra-red absorption (Herzberg & Reid, 1950; Jones, Shooley, Shulman & Yost, 1950), and microwave methods (Jones, *et al.*, 1950). The nitrogen, carbon, and oxygen atoms are collinear and the N-H bond makes an angle of about  $128^{\circ}$  with the N-C-O direction.

The chief interest in studying the crystal was to determine the hydrogen bond pattern in this seemingly simple system.

### Experimental methods

Isocyanic acid was prepared by thermal depolymerization of cyanuric acid, by a modification of the method of Linhard (1938). Samples were vacuum-distilled directly into thin-walled Pyrex capillaries of about 0.5 mm. outside diameter. The capillaries were then sealed off and preserved at Dry Ice temperature to prevent polymerization.

Single crystals were grown by slowly freezing the sample along the length of the capillary (Abrahams, Collin, Lipscomb & Reed, 1950). The samples were cooled by a stream of cold nitrogen from a reservoir of liquid nitrogen. Local melting of the sample was effected by focusing the filament of a 100 W. projection lamp on to the capillary. The melting point of HNCO is  $-80^{\circ}\text{C}$ .

Crystals always grew with the  $c$  axis nearly parallel to the capillary axis. One crystal with  $[102]$  along the capillary axis was obtained by growing a single crystal around the bend in a bent capillary. Three crystals were used to collect the intensity data.

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Powder, rotation, and oscillation photographs were recorded at about  $-125^{\circ}\text{C}$ . with a Unicam camera modified to permit unloading and reloading of the film without interruption of the cooling. Nickel-filtered  $\text{Cu } K\alpha$  radiation was used throughout. Multiple films were prepared for intensity estimation (Robertson, 1943).

The density of solid HNCO was measured approximately by weighing the amount required to fill a glass bulb of known volume when the sample was frozen slowly from the bottom to the top. The value is  $1.40 \text{ g.cm.}^{-3}$  at liquid-nitrogen temperature.

Portions of the infra-red spectra of HNCO samples condensed on rocksalt or silver chloride plates at  $-89^{\circ}$  and at  $-196^{\circ}\text{C}$ . were recorded with a recording double-beam spectrometer (Hornig, Hyde & Adcock, 1950).

### Polymorphism: unit cell and space group

Powder photographs reveal that two crystalline modifications of HNCO exist. The transition temperature seems to be near  $-100^{\circ}\text{C}$ ., but it was not fixed precisely. The low-temperature form was observed only when the supercooled liquid crystallized; the high-temperature form was never observed to convert to the low-temperature form, although samples were cooled to  $-185^{\circ}\text{C}$ . The low-temperature form, however, changed to the high-temperature form on warming.

Interplanar spacings measured from a powder photograph of a partially oriented specimen of the low-temperature form at  $-130^{\circ}\text{C}$ . are recorded in Table 1. The intensities are therefore very approximate. No further X-ray data on the low-temperature form have been obtained.

High-temperature HNCO is orthorhombic. Reflections  $hk0$  were present only for  $h$  even, and reflections  $0kl$  were present only for  $k+l$  even. These absences

Table 1. *Interplanar spacings in low-temperature HNCO*

Spacing (Å)	Relative intensity	Spacing (Å)	Relative intensity
6.6	<i>s</i>	1.86	<i>w</i>
4.2	<i>m</i>	1.75	<i>vw</i>
3.9	<i>m</i>	1.68	<i>vw</i>
3.6	<i>vs</i>	1.54	<i>vw</i>
3.5	<i>vs</i>	1.51	<i>vw</i>
3.33	<i>m</i>	1.44	<i>s</i>
2.89	<i>ms</i>	1.40	<i>w</i>
2.70	<i>s</i>	1.32	<i>vw</i>
2.61	<i>s</i>	1.29	<i>w</i>
2.46	<i>m</i>	1.23	<i>vw</i>
2.37	<i>m</i>	1.20	<i>m</i>
2.24	<i>w</i>	1.13	<i>vw</i>
2.14	<i>m</i>	1.08	<i>vw</i>

are characteristic of space group  $Pnma$  or  $Pn2_1a$ . The choice of the former as more probable is discussed in subsequent sections.

Preliminary values of axial lengths were obtained from rotation photographs. These values were refined from measurements on a powder photograph having a superposed NaCl powder pattern for calibration. At  $-130 \pm 5^\circ \text{C}$ . the axial lengths are

$$a = 10.82 \pm 0.08, \quad b = 5.23 \pm 0.05, \quad c = 3.57 \pm 0.03 \text{ \AA}$$

The X-ray density, calculated from these dimensions on the assumption of 4 molecules per unit cell, is  $1.412 \text{ g.cm.}^{-3}$ . This is in good agreement with the measured value,  $1.40 \text{ g.cm.}^{-3}$  at liquid-nitrogen temperature.

### Structure factors

Relative intensities were estimated visually by comparison of spots on multiple-film oscillation photographs with a set of standard spots prepared by timed exposures. Of the approximately 250 independent reflections within the range of Cu radiation, 148 were recorded and estimated, 73 were too weak to observe, and 31 occurred in regions of the reciprocal lattice not explored in this work. Intensities of individual reflections were averages of usually four independent estimates from at least two different exposures.

An approximate correction was made for the difference in absorption between equatorial and upper layer lines. The relative intensities were at first placed approximately on an absolute scale by the method of Wilson (1942). Intensities were converted to structure-factor magnitudes in the usual way.

### Determination of the structure

The Patterson projection  $P(u, v)$  was calculated first. This projection exhibited pronounced ridges at  $v=0$  and  $\frac{1}{2}$ , which indicates that the molecules lie at least very nearly in parallel planes separated by  $\frac{1}{2}b$ . There is no symmetry basis for this in space group  $Pn2_1a$ , but it arises automatically in space group  $Pnma$  if the

planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ . It was therefore assumed that  $Pnma$  is correct.

Trial structures were deduced from the details of this Patterson projection and of the projection  $P(u, w)$ . The first trial structure failed to refine but the second refined smoothly.

The final electron-density projections  $\rho(x, y)$  and  $\rho(x, z)$  are shown in Fig. 1(a, b). In both, the atoms are

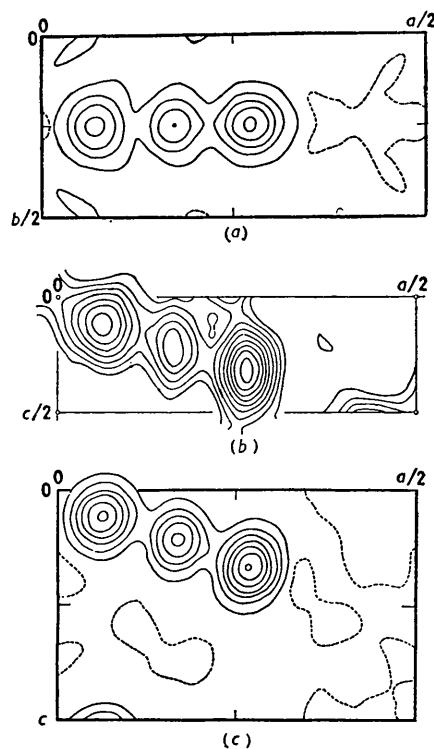


Fig. 1. (a) Electron density projected on (001). Contours are drawn at arbitrary intervals of approximately 0, 1, 2, 4, 6 and  $8 \text{ e.}\text{\AA}^{-2}$ ; the zero contour is broken.

(b) Electron density projected on (010). Contours are drawn at equal arbitrary intervals except that the zero and first contours are not shown.

(c) Electron-density section at  $y = \frac{1}{4}$ . Contours are drawn at equal intervals of approximately  $1.6 \text{ e.}\text{\AA}^{-3}$ ; the zero contour is broken.

atoms lie in the 4-fold special positions (c), the mirror reasonably well resolved and the identity of the carbon, nitrogen, and oxygen atoms is apparent from the peak heights.

Atomic positions obtained from these projections were refined further by means of electron-density sections coinciding with a mirror plane. A portion of the final section  $\rho(x, \frac{1}{4}, z)$  is shown in Fig. 1(c).

Table 2. *Final parameters and maximum densities*

Atom	<i>x</i>	<i>z</i>	Maximum electron density
N	0.0648	0.1108	$10.7 \text{ e.}\text{\AA}^{-3}$
C	0.1670	0.2195	9.2
O	0.2705	0.3367	12.0

Table 3. HNCO structure factors

$hkl$	$ F _o(hkl)$	$F_c(hkl)$	$hkl$	$ F _o(hkl)$	$F_c(hkl)$	$hkl$	$ F _o(hkl)$	$F_c(hkl)$
000	—	88.00	1111	2.80	3.08	112	10.39	-10.02
200	15.95	-20.76	1211	2.70	-3.48	212	2.70	2.58
400	13.03	11.67	1311	< 1.43	1.22	312	3.16	2.96
600	10.45	-10.76				412	3.40	-3.42
800	6.22	-4.90	121	10.45	-10.28	512	2.70	-2.56
1000	7.05	-7.03	221	10.82	8.88	612	2.92	-2.84
1200	4.71	4.42	321	< 2.09	1.44	712	7.84	8.00
			421	5.26	5.12	812	6.04	5.18
210	22.24	-21.92	521	< 2.46	-1.16	912	< 3.71	0.76
410	14.58	-14.32	621	< 2.68	-2.60	1012	3.89	-3.76
610	< 2.22	2.56	721	6.87	7.14	1112	2.58	3.12
810	12.19	-11.38	821	8.02	8.36	1212	1.61	1.83
1010	13.03	13.51	921	< 2.92	1.14			
1210	< 2.40	-0.71	1021	8.72	-9.20	022	8.90	8.20
			1121	2.76	2.40	122	2.98	-3.66
020	40.59	-48.48	1221	< 1.95	1.14	222	7.35	-7.28
220	14.16	13.79				322	12.85	12.64
420	7.65	-8.30	031	21.29	21.20	422	< 2.80	0.96
620	7.47	7.82	131	< 2.40	-2.12	522	< 2.92	-1.68
820	5.32	4.37	231	8.48	-8.30	622	< 2.92	2.46
1020	5.92	6.20	331	10.05	10.08	722	5.74	5.38
1220	3.52	-3.99	431	4.07	3.80	822	< 1.84	0.16
			531	< 2.80	0.00	922	3.22	-3.18
230	12.31	9.71	631	< 2.86	-2.46	1022	< 2.16	-1.40
430	6.99	7.52	731	3.59	3.84	1122	2.16	-3.02
630	< 2.80	-1.54	831	3.10	-2.40			
830	7.77	8.22	931	2.98	-2.50	132	6.99	6.50
1030	10.57	-10.63	1031	3.52	-3.84	232	< 2.98	-2.10
1230	< 1.55	0.56	1131	< 1.91	-1.50	332	< 2.92	-2.06
			1231	< 1.01	2.88	432	< 3.41	2.74
040	21.41	20.66				532	< 2.98	1.72
240	6.93	-6.39	141	4.95	4.98	632	< 2.92	2.04
440	4.43	3.58	241	5.32	-5.08	732	6.46	-5.96
640	4.61	-3.85	341	< 2.92	-0.82	832	4.25	-4.08
840	4.71	-3.24	441	2.92	-2.18	932	< 2.70	-0.78
1040	4.43	-4.42	541	< 2.92	0.60	1032	2.98	3.06
			641	< 2.84	1.36			
250	6.47	-5.40	741	5.32	-4.54	042	4.67	-5.12
450	3.77	-3.32	841	5.38	-5.62	142	< 2.76	1.74
650	< 2.46	0.56	941	< 2.16	-0.96	242	3.65	4.44
850	4.86	-5.12	1041	5.08	6.58	342	5.56	-7.62
						442	< 2.92	-0.34
060	9.87	-10.46	051	10.11	10.86	542	< 2.76	0.92
260	2.82	2.98	151	< 2.86	0.74	642	< 2.64	-1.96
460	1.97	-1.48	251	3.89	4.14	742	2.86	-3.70
			351	4.77	-5.18	842	< 2.09	0.00
101	16.25	16.04	451	< 2.70	-1.56	942	—	2.28
201	15.55	-13.96	551	< 2.52	-0.18			
301	< 2.28	-2.02	651	< 2.22	0.98	152	2.80	-2.86
401	7.53	-7.32	751	2.16	-2.32	252	< 2.52	1.48
501	< 2.40	1.56	851	< 1.55	1.74	352	< 2.40	1.20
601	2.46	3.34				452	< 2.22	-1.94
701	7.41	-8.86	161	2.86	-2.70	552	< 1.97	-0.96
801	10.23	-9.82	261	2.70	3.06	652	—	-1.22
901	< 2.03	-1.18	361	< 1.79	0.42	752	—	3.76
1001	9.75	10.48	461	< 1.55	0.90			
1101	2.86	-2.76	561	< 1.31	-0.28	062	—	2.94
1201	< 2.34	-1.30				162	—	-0.72
1301	2.52	3.24	002	11.12	-10.40	262	—	-2.52
			102	3.65	5.00			
011	36.46	-41.76	202	11.48	9.18	103	3.52	-3.66
111	3.34	3.94	302	15.31	-16.02	203	< 1.73	-0.06
211	14.70	15.30	402	< 2.52	-1.40	303	3.40	3.14
311	17.10	-18.14	502	2.76	2.08	403	6.57	-5.86
411	7.05	-7.06	602	3.40	-2.68	503	2.92	-2.74
511	< 2.16	-0.06	702	6.87	-6.30	603	2.64	-1.64
611	4.31	4.56	802	< 2.92	-0.26	703	3.52	3.54
711	5.92	-5.44	902	3.71	3.64	803	2.70	1.92
811	3.77	2.90	1002	2.92	1.56	903	< 2.09	-0.28
911	3.65	3.30	1102	2.46	3.30	1003	—	-0.18
1011	4.07	4.86	1202	—	-2.26			

Table 3 (cont.)

<i>h k l</i>	$ F _o(hkl)$	$F_c(hkl)$	<i>h k l</i>	$ F _o(hkl)$	$F_c(hkl)$	<i>h k l</i>	$ F _o(hkl)$	$F_c(hkl)$
0 1 3	—	— 0.96	1 3 3	< 2.92	1.86	3 0 4	2.10	1.06
1 1 3	< 3.04	— 2.76	2 3 3	2.92	2.80	4 0 4	2.22	— 1.68
2 1 3	4.43	— 3.58	3 3 3	4.25	— 4.74	5 0 4	2.28	— 3.04
3 1 3	6.22	6.34	4 3 3	< 2.64	1.14	6 0 4	3.46	3.28
4 1 3	< 2.80	— 1.40	5 3 3	< 2.52	2.50	7 0 4	—	1.72
5 1 3	2.80	— 3.30	6 3 3	4.55	— 3.84			
6 1 3	5.80	4.70	7 3 3	2.46	— 3.06			
7 1 3	3.95	3.84	8 3 3	< 1.49	— 0.92			
8 1 3	< 2.28	1.12				1 1 4	—	0.26
9 1 3	1.85	— 1.72	1 4 3	< 2.46	— 2.22	2 1 4	—	0.12
10 1 3	—	0.34	2 4 3	< 2.52	0.16	3 1 4	2.40	— 2.24
			3 4 3	< 2.09	1.92	4 1 4	3.77	3.56
			4 4 3	2.46	— 3.78	5 1 4	2.16	1.92
1 2 3	3.65	3.18	5 4 3	—	— 1.64	6 1 4	—	0.24
2 2 3	< 2.92	0.08	6 4 3	—	— 1.06			
3 2 3	2.98	— 2.74				0 2 4	—	1.82
4 2 3	5.14	5.22	0 5 3	—	— 0.32	1 2 4	—	1.00
5 2 3	2.76	2.36	1 5 3	—	— 1.02	2 2 4	—	0.66
6 2 3	< 2.70	1.46	2 5 3	—	— 1.88	3 2 4	< 2.70	— 1.00
7 2 3	2.92	— 3.06				4 2 4	—	1.50
8 2 3	< 2.09	— 1.76				5 2 4	—	2.76
9 2 3	< 1.61	0.24	0 0 4	—	— 2.04			
			1 0 4	—	— 1.16	1 3 4	—	— 0.20
0 3 3	—	0.62	2 0 4	—	— 0.72	2 3 4	—	0.12
						3 3 4	—	1.84

In the refinement by means of this section, atoms were located by an analytic method (Carpenter & Donohue, 1950). 'Back-shift' corrections (Booth, 1946) were applied to reduce finite-series errors. Scale- and temperature-factor parameters were readjusted at each stage of the refinement by a least-squares procedure which minimizes  $\Sigma(|F|_o - |F|_c)^2$ . An anisotropic temperature factor of the form  $\exp[-(b_1h^2 + b_2k^2 + b_3l^2)]$  was used. The final values of the temperature-factor parameters correspond to r.m.s. displacements (of an average atom) of 0.16, 0.16, and 0.21 Å in the *a*, *b*, and *c* directions, respectively. The refinement was terminated when no further sign changes occurred and no atom moved more than 0.01 Å between successive structures.

All Fourier syntheses were performed with Bevers-Lipson strips (Bevers, 1952).

The final *x* and *z* parameters and maximum electron densities are shown in Table 2. (The *y* parameters are all  $\frac{1}{4}$ .)

Observed and calculated structure factors are presented in Table 3. The atom form factors of Viervoll & Ögrim (1949) were employed. Hydrogen contributions are omitted.

The conventional discrepancy factor is 9.9% for observed reflections only. Reflections (020) and (011) seem to be considerably in error because of extinction; if they are omitted, the discrepancy factor is reduced to 9.3%.

Standard deviations in atomic positions, calculated from the formula given by Cruickshank (1949) and by Shoemaker, Donohue, Schomaker & Corey (1950), amount to about 0.005 Å for each atom in each direction. The average error in atomic position, by the graphical method of Luzzati (1952), lies between 0.03 and 0.04 Å.

### Description and discussion of the structure

A view down the *b* axis of the high-temperature crystal structure is shown in Fig. 2. Atoms are drawn with van der Waals radii (Pauling, 1945).

Intramolecular distances are given in Table 4 for the crystal and for the vapor. The differences between the molecule in the crystal and in the vapor are not significant. The X-ray results locate the carbon atom 0.011 Å from the line joining the nitrogen and oxygen

Table 4. Intramolecular distances in HNCO

Dis- tance	Vapor		Crystal X-r.d.‡
	E.d.*	Sp.†	
N-C	1.19 ± 0.03 Å	1.207 ± 0.01 Å	1.183 ± 0.02 Å
C-O	1.19 ± 0.03	1.171 ± 0.01	1.184 ± 0.02
N-O	2.38 ± 0.03	—	2.367 ± 0.02
N-H	1.01 (est.)	0.987 ± 0.01	—

\* Electron diffraction (Eyster *et al.*, 1940).

† Spectroscopic (Jones *et al.*, 1950).

‡ X-ray diffraction (this work).

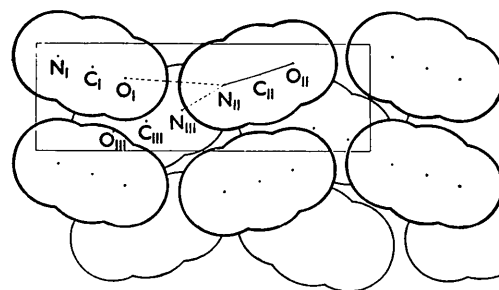


Fig. 2. The structure of the high-temperature form of HNCO, viewed down the *b* axis. Atoms are drawn with van der Waals radii. The heavily-outlined molecules lie at  $y = \frac{1}{4}$ , the lightly-outlined molecules at  $y = -\frac{1}{4}$ .

atoms; these atoms are thus collinear to within the limits of the present work. The shape of the molecule and the shortness of the N-C and C-O bonds can be accounted for by resonance involving structures with triple bonds.

Table 5 presents the intermolecular distances of less

Table 5. *Intermolecular dimensions in high-temperature HNCO*

Within one mirror plane		Between adjacent mirror planes	
O...N	3.18 <sub>9</sub> Å	N...N	3.07 <sub>1</sub> Å
C-N...O	157.3°	C-N...N	120.6°
C-O...N	162.9°	N <sub>III</sub> ...O <sub>I</sub>	3.17 <sub>0</sub> Å
N...N	3.57 Å	C <sub>III</sub> ...O <sub>I</sub>	3.02 <sub>7</sub> Å
N...C	3.37 <sub>3</sub> Å	C <sub>I</sub> ...O <sub>III</sub>	3.48 <sub>5</sub> Å
C...C	3.57 Å	C <sub>I</sub> ...C <sub>III</sub>	3.63 <sub>9</sub> Å
C...O	3.34 <sub>3</sub> Å	O <sub>I</sub> ...O <sub>III</sub>	3.19 <sub>7</sub> Å
O...O	3.57 Å		

than 4 Å and the most significant angles. The most interesting problem for which these distances provide information is the location of the hydrogen atoms. The observed N...O distance of 3.19 Å, and the angles 157° and 163° which this direction forms with adjacent bonds, make the existence of the expected N-H...O hydrogen bond here quite implausible.

The possibilities of O-H...N or O-H...O hydrogen bonds, corresponding to the possible cyanic acid tautomer, HOCN, are similarly ruled out by long distances and awkward angles.

The shortest distance not involving a carbon atom is the N...N distance, 3.07 Å. This suggests that N-H...N hydrogen bonds exist in the crystal. The angles formed by the N...N direction, C-N...N = N...N-C = 120.6°, are quite reasonable for hydrogen-bond formation.

The crystal must then be described as composed of zigzag chains of HNCO molecules, joined by N-H...N hydrogen bonds, running along the *b* axis. All distances between atoms in adjacent chains exceed, at least slightly, the sum of the van der Waals radii.

### Further consideration of the hydrogen positions

Location of the hydrogen atoms on the N...N lines brings the space group into question again. If *Pnma* is indeed correct, then either each hydrogen atom is located at a center of symmetry midway between two nitrogen atoms, or else the hydrogen atoms are disordered, with one-half hydrogen, on the average, on both sides of this center of symmetry. The former possibility is extremely unlikely in view of the length of the N...N distance, and will not be considered further. If, however, the space group *Pn2<sub>1</sub>a* is correct after all, then the hydrogen atoms are not disordered and lie nearer to one nitrogen atom than to the other. In this case, the heavy atoms in the structure would lie in parallel planes only by accident.

In order to distinguish between the reasonable

possibilities, several tests were performed. First, it was assumed that the correct space group is *Pn2<sub>1</sub>a*, and an approximate calculation was performed to see how far the N-C-O portion of the molecule could be twisted out of the mirror plane without seriously increasing the discrepancy factor. This calculation showed that a displacement of the nitrogen and oxygen atoms of more than 0.02 Å on opposite sides of this plane would not be consistent with the observed intensities. Thus, to within experimental error, the space group *Pnma* is correct for the heavy atoms, and so probably for the hydrogen atoms as well. This conclusion was confirmed qualitatively by examination of the structure factors with fixed *h* and *l* and increasing *k*; the magnitudes decrease with the average atom form factor for even values of *k*, and separately for odd values of *k*. This can be the case only if the *y* coordinates of the heavy atoms are very near  $\frac{1}{4}$  or  $\frac{3}{4}$ .

A second test consisted of attempts to locate the hydrogen atoms directly by means of appropriate part-cell projections, sections, and differential syntheses. In no case were unequivocal indications of the hydrogen atoms found. The failure to find the hydrogen atoms in this way provides some support for the disordered model, since at least some trace of a whole hydrogen atom might be expected.

A third test consisted of computing hydrogen contributions to the structure factors for various models. These calculations supported the conclusion that the hydrogen atoms cannot be located along the N...O lines, because this assumption increased the discrepancy factor from 7.9 to 9.2%, for those reflections with  $\sin \theta < 0.5$ . On the other hand, insertion of the hydrogen atoms along the N...N lines decreased the discrepancy slightly, from 7.9 to 7.3%, for the same reflections. However, there was no appreciable difference between the discrepancy for the disordered model with two half-hydrogens and the ordered model with one off-center hydrogen atom.

Thus the X-ray data are unable to distinguish between the ordered- and the disordered-hydrogen models, but definitely locate the hydrogen atoms in N-H...N hydrogen bonds. But in view of the accuracy with which the heavy atoms lie in the special positions required by *Pnma*, the disordered-hydrogen model must be regarded as the more probable.

### Infra-red absorption spectrum

The infra-red spectra of the two solid modifications of isocyanic acid provide additional information. Herzberg & Reid (1950) reported a large shift of the N-H stretching frequency in passing from the vapor to the solid (see Table 6). This they interpreted as evidence of a very strong hydrogen bond in the crystal, comparable in strength to that in ice. Their infra-red specimens were prepared by condensing the vapor on to rocksalt plates cooled to the temperature of liquid

Table 6. N-H stretching frequencies in HNCO

Vapor	Liquid	Solid (-89° C.)	Solid (-196° C.)	Reference
3531	3410		3133	Herzberg & Reid, 1950
3538	3320			Jones <i>et al.</i> , 1950 Goubeau, 1935
		3400	3205 } 3365* }	This work

\* This is a shoulder on the 3205 cm.<sup>-1</sup> absorption.

All frequencies are in cm.<sup>-1</sup>. The values for the liquid are from Raman spectra, those for the vapor and solid are from infra-red absorption.

nitrogen, so their results presumably apply to the low-temperature modification.

Examination of a similar solid sample was repeated in the present investigation, and the large frequency shift was confirmed, although the results differ in details (see Table 6). The earlier work made use of a rather thick film of sample (Herzberg, 1953), which prevented accurate location of the center of the main peak and observation of the shoulder. On the other hand, the details of the spectrum obtained in the present work are somewhat uncertain because it was discovered, subsequent to the experiments, that the spectrometer had been exhibiting periodic noise at various times. However, the position given for the N-H stretching frequency cannot be significantly in error from this cause.

The spectrum of a sample condensed and held at about -89° C. was next obtained, and was found to differ significantly from that recorded at liquid-nitrogen temperature (see Table 6). In particular, the N-H stretching frequency lies between the frequency in the vapor and that in the low-temperature solid. Comparison with the corresponding frequency in the liquid, from Raman spectra (see Table 6), shows that it is conceivable that the spectrum reported here as that of the high-temperature solid at -89° C. is, in reality, that of the liquid. The sample could not be observed directly in the low-temperature cell to see if it was really solid, but it is regarded as extremely unlikely that it was liquid, in view of the manner of preparation of the sample.

The spectrum of the high-temperature solid indicates a weaker hydrogen bond than that present in the low-temperature modification, since the stretching frequency is nearer to that in the vapor. This conclusion is consistent with the X-ray conclusion that N-H...N hydrogen bonds are present in the high-temperature solid; these cannot be extremely strong. Furthermore, the magnitude of the frequency shift of the main band, about 130 cm.<sup>-1</sup>, is similar to that for the vapor-solid transition in ammonia, 118 cm.<sup>-1</sup> (Reding & Hornig, 1951).

The apparently stronger hydrogen bond in the low-temperature solid may possibly be the N-H...O hydrogen bond originally expected to exist in isocyanic acid.

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