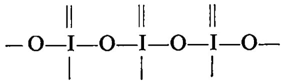
explained from the location of the three iodine orbitals used for the bonding: 5*p*, possibly mixed with some 5*s*. Just as in H_5IO_6 the short lengths of the coordinate bonds indicate, however, a substantial amount of π-bonding due to partial occupation of the iodine 5*d* orbitals by lone pairs of the O^- ions. HIO_3 and I_2O_5 are therefore represented best by the formulae with the double bonds shown before. It should be noted that corresponding bonds in HI_3O_8 and in H_5IO_6 (Table 8) have equal lengths, although different orbitals are assumed to be used for the σ bonds in the iodine(V) and iodine(VII) compounds.

In addition to the covalent character mentioned above, the I–O bonds will have some ionic character, the electronegativities of oxygen and iodine being 3·5 and 2·5 respectively (Pauling, 1960, p.90). The short intermolecular I $\cdots$ O distances have not been explained yet. Contributions of covalent structures like



$$-\mathrm{O}-\overset{\|}{\underset{|}{\mathrm{I}}}-\mathrm{O}-\overset{\|}{\underset{|}{\mathrm{I}}}-\mathrm{O}-\overset{\|}{\underset{|}{\mathrm{I}}}-\mathrm{O}-$$

may play a part, in addition to dipole interaction, polarization effects and London dispersion forces.

We wish to thank Professor E. H. Wiebenga for his valuable suggestions and his interest in the progress of this work. Thanks are due also to the staffs of the computing centers at Leeds, Kjeller and Groningen, where various calculations were performed.

We are grateful to the Royal Dutch Blastfurnaces and Steelworks N.V., Ymuiden, which gave one of us (Y. D. F.) the opportunity to finish the structure determination.

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The Crystal Structure of Methyldicyanoarsine

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(*Received* 7 *June* 1965 *and in revised form* 22 *October* 1965)

Methyldicyanoarsine, $CH_3As(CN)_2$, is monoclinic, space group $P2_1/c$, $a=6{\cdot}28$, $b=8{\cdot}19$, $c=11{\cdot}73$ Å, $\beta=121{\cdot}9°$, with four molecules in the unit cell. The molecules have approximate C_m symmetry with angles: As–C(1)–N(1) 177, As–C(2)–N(2) 173, C(1)–As–C(2) 89·4, C(2)–As–C(3) 93·5, C(3)–As–C(1) 98·3°, and bond lengths: As–C(1) 1·97, As–C(2) 1·99, As–C(3) 2·00, C(1)–N(1) 1·09, C(2)–N(2) 1·15 Å. An intermolecular interaction is apparent in a 2·94 Å As–N distance, which is considerably below the expected van der Waals distance of 3·5 Å. This distance is intermediate between the corresponding short distances observed in $As(CN)_3$, 2·74 Å and $(CH_3)_2AsCN$, 3·18 Å. A further refinement of the structure of $As(CN)_3$ (Emerson & Britton, 1963) is also reported.

In both cacodyl cyanide, $(CH_3)_2AsCN$ (Camerman & Trotter, 1963), and arsenic tricyanide, As $(CN)_3$, (Emerson & Britton, 1963. See also the Appendix to this paper), intermolecular As–N interactions are a recognizable feature of the crystal structure. However, the As–N distance in $As(CN)_3$ is significantly shorter than in $(CH_3)_2AsCN$. We report here the crystal structure of $CH_3As(CN)_2$, which has been determined to see whether the shortening represents a real trend. A comparison of the melting points of $CH_3As(CN)_2$, 126–

127·5 °C, and CH_3AsCl_2, −42·5 °C, supported the expectation that something stronger than the usual van der Waals interactions would be present.

Experimental

Methyldichloroarsine, prepared by the method of Long, Emeleus & Briscoe (1946), was refluxed with silver cyanide in benzene to produce a mixture of silver chloride and methyldicyanoarsine. The benzene was distilled off, and the methyldicyanoarsine was separated by sublimation or by extraction with chloroform. It crystallized from chloroform as flat needles. The infrared spectrum in chloroform solution showed bands in the cyanide–isocyanide region at 2080 and 2170 cm^{-1}. The melting point of a sample in a sealed tube filled with nitrogen was 126–127·5 °C compared with the earlier reported value, 115·5–116·5 °C (Grichkiewitch-Trohimowski, Mateyak & Zablotski, 1927).

The unit-cell dimensions and the space group were determined from Weissenberg, oscillation and precession photographs using Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) and Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. They are given in Table 1 together with the corresponding data given by Daly for methyldicyanophosphine, $CH_3P(CN)_2$ (quoted by Maier, 1963), which appears to be isomorphous with the arsine. No suitable medium was found for the determination of the density. The assumption of four molecules per unit cell led to a molecular volume of 128·1 Å^3 compared with 138·7 Å^3 for $As(CN)_3$ and 129·4 Å^3 for $(CH_3)_2AsCN$.

Multiple film Weissenberg data for the layers $hk0-hk5$ were collected and used in the preliminary structure determination described below. It was eventually found that these data were too limited to give a satisfactory refinement, and a second set of data was collected for the least-squares refinement. For the second set a needle, elongated along c, 0·1 × 0·2 × 4 mm, was mounted inside a glass capillary, which was then filled with nitrogen and sealed. Multiple film Weissenberg photographs of the $hk0-hk9$ layers were collected along with two 20° multiple film oscillation photographs for correlation of the layers. The pictures were taken with Mo $K\alpha$ radiation and the intensities were measured by visual comparison with a series of timed exposures of a selected spot. A total of 479 independent reflections of measurable intensity were observed, 213 additional reflections in the same region of reciprocal space being too faint to observe. The latter were included in the eventual least-squares calculations with intensities equal to one-half the minimum observable intensity. The usual Lorentz and polarization corrections were made. No absorption corrections were made ($\mu = 68{\cdot}3$ cm^{-1} for Mo $K\alpha$ radiation).

Table 1. *Space group and unit cell of methyldicyanoarsine and methyldicyanophosphine*

	$CH_3As(CN)_2$	$CH_3P(CN)_2$* (Daly; Maier, 1963)
a	6·28 ± 0·01 Å	6·18 Å
b	8·19 ± 0·01	7·99
c	11·73 ± 0·02	11·64
β	121·9 ± 0·2°	121·5°
Volume	512·3 Å^3	490·1 Å^3
Z	4	4
D_{calc}	1·842 g.cm^{-3}	—
Space group	$P2_1/c$	$P2_1/c$

* The original report gives a cell with $P2_1/n$ and $\beta = 90{\cdot}6°$. It was necessary for us to use $P2_1/c$ in the computer programs available to us and we have converted the $CH_3P(CN)_2$ cell for comparison.

Determination of the structure

A three-dimensional Patterson map was calculated from the first set of data*. The arsenic atom positions were readily deduced, and a three-dimensional Fourier map was prepared, using the arsenic atoms to determine the phases. The methyl carbon and the cyanide group not parallel to the c axis could be recognized, but the other cyanide group was not clearly revealed. After some least-squares and further Fourier refinement it became apparent that the correlation of the layers was poor, and they were recorrelated from a comparison of the observed and calculated structure factors. After the recorrelation another three-dimensional Fourier map revealed the second cyanide group.

Refinement of the structure

After all of the atoms had been located, a least-squares refinement (including individual isotropic temperature factors) converged at an R index† of 0·154 and indicated that the light atoms were poorly defined. At this point the second set of data mentioned above was collected. A slightly smaller crystal was used, and more extensive data were collected. These data were used directly in a full-matrix least-squares refinement starting with the final positions from the previous trial. Final values for R and r for three types of refinement were: isotropic temperature factors for all atoms, $R = 0{\cdot}126$ and $r = 0{\cdot}0314$; anisotropic temperature factors for the arsenic atom, $R = 0{\cdot}115$ and $r = 0{\cdot}0250$; anisotropic temperature factors for all atoms, $R = 0{\cdot}115$ and $r = 0{\cdot}0217$. Since the recorrelation of the layers had had a large effect on the results from the first set of data it was done here also, even though the largest change in the scale factor for an individual layer was 3·2%. The final values for R and r after recorrelation for the same

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* All calculations described from this point on were done on the Control Data 1604 Computer of the Numerical Analysis Center of the University of Minnesota with programs prepared at Princeton University under the direction of Professor R. A. Jacobson.

† $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

$r = \Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4$

It is the numerator of this latter function that is refined in the least-squares procedure. The weighting factor used in the final calculation was $w = 1$ for $F_o < 48$ and $w = (48/F_o)$ for $F_o > 48$.

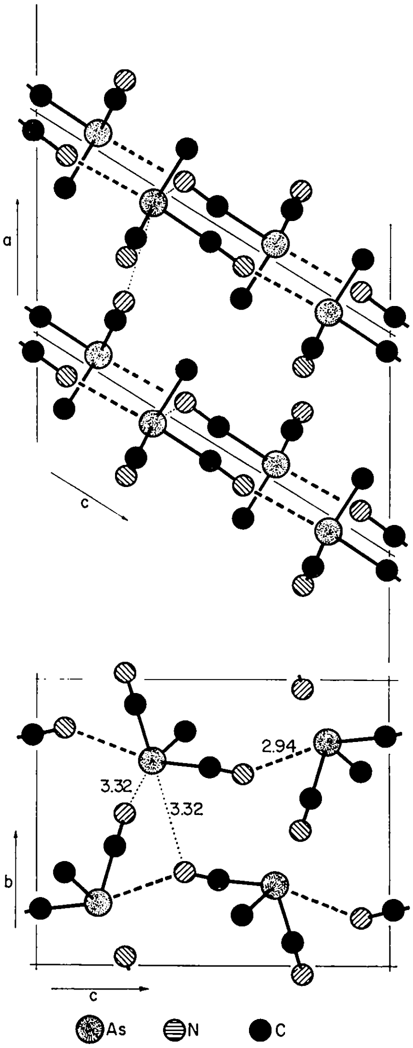

Fig. 1. The crystal structure of $CH_3As(CN)_2$. The short intermolecular distance is shown as a heavy dashed line wherever it occurs. Distances are given in Å.

three types of refinement were: isotropic temperature factors for all atoms, $R=0{\cdot}125$ and $r=0{\cdot}0309$; anisotropic temperature factors for the arsenic atom, $R=0{\cdot}113$ and $r=0{\cdot}0235$; anisotropic temperature factors for all atoms, $R=0{\cdot}111$ and $r=0{\cdot}0204$. The changes in the parameters before and after recorrelation were all less than the standard deviations. If we apply the test described by Hamilton (1965), we find that the recorrelation leads to an improved agreement at better than the 0·995 confidence level, and also that the fit with all atoms anisotropic is better than that with As only anisotropic at better than the 0·995 confidence level. For both of these calculations $r^{\frac{1}{2}}$ values should be and were used for the comparisons. As Hamilton pointed out, these tests assume all the errors are random, and therefore they overestimate the significance of the further refinement in the event there are systematic errors as there are here, where no absorption corrections were made. Still, since the tests do indicate the refinement with all atoms anisotropic to be significantly better, we report the results for this calculation. The final parameters are given in Table 2. The observed and calculated structure factors are given in Table 3; this table was prepared before the paper by Hamilton had appeared and is for As only anisotropic.

Discussion

The crystal structure is shown in Fig. 1. The interatomic distances and angles are given in Table 4 along with corresponding values for related compunds.

The molecule has approximately the C_m symmetry that would be expected, although the two CH_3–As–CN angles are possibly significantly different. The As–C bond lengths are normal and, within experimental error, the same. Comparing the As–C bond lengths in the three compounds $As(CN)_3$, $CH_3As(CN)_2$, and $(CH_3)_2AsCN$ we still cannot see a difference between the As–CN and As–CH_3 bonds. We would expect the covalent radius of C to be smaller in CN than in CH_3, but the As radius might be expected to be larger with

Table 2. *Final parameters for* $CH_3As(CN)_2$

The standard deviations are estimates from a diagonal approximation to the matrix and are optimistic. The anisotropic temperature factors are in the form exp $\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}hl)\}$.

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	B†
As	0·0775 (1)	0·2148 (1)	0·1733 (1)	2·93
C(1)	0·2814 (12)	0·4145 (11)	0·2188 (6)	3·6
N(1)	0·3955 (11)	0·5254 (9)	0·2496 (7)	5·4
C(2)	0·0858 (11)	0·1937 (9)	0·0071 (7)	4·0
N(2)	0·1079 (11)	0·1681 (8)	−0·0824 (6)	4·1
C(3)	−0·2612 (13)	0·3193 (10)	0·0785 (8)	3·8

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{23}(\sigma)$	$\beta_{31}(\sigma)$
As	0·0331 (2)	0·0102 (1)	0·0072 (1)	−0·0030 (5)	−0·0002 (2)	0·0197 (1)
C(1)	0·014 (2)	0·031 (2)	0·0034 (7)	−0·029 (3)	−0·018 (2)	0·009 (2)
N(1)	0·059 (2)	0·026 (1)	0·0100 (7)	−0·038 (3)	−0·009 (2)	0·032 (2)
C(2)	0·049 (2)	0·010 (1)	0·0158 (8)	−0·008 (3)	0·004 (2)	0·045 (2)
N(2)	0·042 (2)	0·022 (2)	0·0075 (6)	−0·008 (3)	−0·004 (1)	0·023 (2)
C(3)	0·036 (2)	0·019 (2)	0·0079 (7)	0·005 (3)	−0·000 (2)	0·021 (2)

† From the last cycle in which the atom was isotropic.

respect to CN than with respect to CH_3 since the CN group is more electronegative. To answer whether these two tendencies cancel each other would require better data, either from smaller crystals or including absorption corrections. The reactivity of these compounds in air makes either of these alternatives difficult.

Together with the effect on bond lengths we would expect the angles to increase in the order NC–As–CN < NC–As–CH_3 < H_3C–As–CH_3, and this is perhaps observed although by no means conclusively.

The CN distances are normal within the large experimental error, and the slight deviation from linearity in the As–C–N bond angles, which may or may not

Table 3. *Observed and calculated structure factors*

An asterisk indicates an unobserved reflection.

H	K	L	OBS	CALC
0	0	6	43.1	47.4
0	0	8	29.9	-35.4
0	1	4	82.2	86.5
0	1	5	6.7	5.4
0	1	6	21.5	-23.0
0	1	7	9.3	8.8
0	1	8	30.9	-31.3
0	2	0	109.7	-110.3
0	2	1	21.0	-19.2
0	2	2	4.8	7.1
0	2	3	24.7	23.0
0	2	4	41.6	39.8
0	2	5	33.7	31.6
0	2	6	53.7	-60.9
0	2	7	27.9	-26.8
0	2	8	36.6	35.5
0	2	9*	5.4	-1.4
0	3	1	45.1	-41.7
0	3	2	60.2	58.1
0	3	3	47.2	44.3
0	3	4	47.9	-48.4
0	3	5	36.0	-31.5
0	3	6	13.5	8.1
0	3	7	11.2	-9.7
0	3	8	27.2	25.6
0	3	9	21.6	17.4
0	4	0	53.3	51.3
0	4	1	51.5	48.2
0	4	2	35.2	-33.9
0	4	3	19.0	-21.8
0	4	4	6.5	-8.3
0	4	5	43.6	-40.5
0	4	6	36.6	34.1
0	4	7	43.7	39.6
0	4	8	16.6	-14.7
0	4	9*	6.0	-4.8
0	5	1	36.1	35.3
0	5	2	28.6	-28.3
0	5	3	55.5	-53.1
0	5	4	23.8	24.1
0	5	5	42.8	38.3
0	5	6*	6.8	-6.1
0	5	7*	7.5	8.7
0	5	8*	7.5	-7.6
0	5	9	22.6	-18.9
0	6	0*	6.9	-4.1
0	6	1	51.3	-52.5
0	6	2	15.9	17.0
0	6	3	10.1	11.8
0	6	4*	5.6	1.2
0	6	5	28.9	28.5
0	6	6	17.9	-13.6
0	6	7	31.8	-30.7
0	6	9*	7.0	5.7
0	7	1	23.4	-21.1
0	7	2*	6.6	1.6
0	7	3	34.1	37.8
0	7	4*	6.2	-3.1
0	7	5	24.4	-24.5
0	7	6*	8.0	.7
0	7	7	10.6	-9.9
0	7	9	19.2	18.1
0	8	0*	8.3	-14.4
0	8	1	28.1	28.5
0	8	3*	6.9	2.8
0	8	5	22.4	-21.1
0	8	7	21.4	21.2
0	9	1	13.0	11.3
0	9	3	19.9	-22.8
0	9	5	14.7	13.5
0	9	7*	7.2	3.8
0	10	1*	9.9	-18.2
0	10	3*	8.1	1.3
0	10	5	11.4	7.4
1	0	0	91.7	117.1
1	0	2	33.8	-37.6
1	0	4	24.6	23.4
1	0	6	34.6	40.2
1	0	8	36.6	-39.2
1	1	0	59.2	-63.5
1	1	1	36.4	38.3
1	1	2	29.8	-32.9
1	1	3	31.8	-29.9
1	1	5	22.8	20.2
1	1	6	35.1	-39.5
1	1	7*	4.6	-7.7
-1	1	7	13.7	13.2
1	1	8	13.7	-13.7
-1	1	8	54.2	-56.0
1	1	9*	6.0	-2.3
-1	1	9	7.9	-10.2
1	2	0	113.9	-116.5
1	2	1	62.5	-54.6
-1	2	1	10.8	5.2
1	2	2	64.7	61.0
-1	2	2	32.9	29.2
1	2	3	20.5	16.8
1	2	4	19.5	-21.7
-1	2	4	53.2	51.9
1	2	5	22.1	20.4
-1	2	5	25.6	24.2
1	2	6	31.0	-34.1
-1	2	6	53.2	-56.1
1	2	7	22.5	-20.0
-1	2	7	27.4	-26.6
1	2	8	32.4	32.6
-1	2	8*	4.8	6.4
1	2	9	11.5	9.7
-1	2	9	8.9	-8.0
1	3	0	30.6	26.4
1	3	1	7.4	-9.5
-1	3	1	80.4	-77.0
1	3	2	36.1	36.6
-1	3	2	70.1	65.6
1	3	3	31.9	27.6
-1	3	3	46.6	46.7
1	3	4	53.5	-51.0
-1	3	4	47.3	-44.6
1	3	5	33.4	-26.5
-1	3	5	16.0	-16.1
1	3	6	27.3	28.8
-1	3	6	16.9	-13.3
1	3	7*	5.1	6.0
-1	3	7	22.6	-21.4
1	3	8*	7.3	7.6
-1	3	8	37.9	34.6
1	3	9	9.1	10.0
-1	3	9	24.0	23.1
1	4	0	40.5	37.0
1	4	1	80.5	75.7
-1	4	1	20.4	16.2
1	4	2	38.3	-37.7
-1	4	2*	4.8	.4
1	4	3	34.4	-34.0
-1	4	3	11.8	11.3
1	4	4*	5.0	-.9
-1	4	4	32.7	-29.2
1	4	5	13.9	-12.5
-1	4	5	48.9	-46.9
1	4	6	25.7	25.2
-1	4	6	41.7	41.2
1	4	7	26.4	21.9
-1	4	7	39.9	39.5
1	4	8	20.4	-18.8
-1	4	8	8.8	-11.0
1	4	9	11.4	-9.6
-1	4	9*	5.4	5.2
1	5	0*	6.3	-12.1
1	5	1*	6.6	3.4
-1	5	1	61.8	62.8
1	5	2	15.1	-16.8
-1	5	2	35.0	-34.5
1	5	3	38.4	-36.1
-1	5	3	46.0	-47.6
1	5	4	22.5	19.3
-1	5	4	13.2	14.0
1	5	5	39.1	34.2
-1	5	5	16.4	15.7
1	5	6	16.2	-11.2
-1	5	6*	6.4	5.9
1	5	7*	5.8	-6.6
-1	5	7	30.9	29.2
-1	5	8	11.7	-16.0
1	5	9*	7.1	-10.0
-1	5	9	31.3	-30.1
1	6	0*	7.0	-7.2
1	6	1	49.3	-52.4
-1	6	1	26.7	-23.0
1	6	2	21.4	21.6
-1	6	2*	6.0	-.7
1	6	3	18.9	20.9
-1	6	3	20.0	-20.1
1	6	4*	5.9	.5
-1	6	4*	5.5	4.8
1	6	5	12.6	12.5
-1	6	5	47.5	46.1
1	6	6*	7.9	-3.7
-1	6	6	15.6	-14.4
1	6	7	29.5	-25.5
-1	6	7	31.0	-30.8
-1	6	8*	7.6	8.0
-1	6	9*	6.6	-2.1
1	7	0*	7.7	3.9
1	7	1*	7.9	-2.0
-1	7	1	35.9	-36.4
1	7	2*	6.8	-.6
-1	7	2*	6.6	7.4
1	7	3	33.3	31.6
-1	7	3	32.8	35.7
1	7	4*	6.4	1.9
-1	7	4*	6.0	-.4
1	7	5	28.1	-29.6
-1	7	5	12.3	-12.3
-1	7	6*	7.8	3.1
1	7	7*	6.6	4.4
-1	7	7	19.7	-21.8
-1	7	9	19.6	21.7
1	8	1	29.5	33.9
-1	8	1	22.0	25.0
1	8	3	13.4	-14.8
-1	8	3*	6.9	9.8
1	8	5*	5.5	-5.9
-1	8	5	26.7	-26.6
1	8	7	18.8	17.8
-1	8	7	12.2	13.8
1	9	1*	9.3	-.9
-1	9	1	22.3	18.8
1	9	3	14.5	-16.9
-1	9	3	21.2	-22.6
1	9	5	14.8	16.7
-1	9	5*	5.6	6.4
-1	9	7	14.4	12.3
1	10	1*	10.0	-13.4
-1	10	1	18.6	-10.9
1	10	5*	6.3	2.4
-1	10	5	15.5	16.2
2	0	0	35.8	41.3
2	0	2	61.0	-60.7
-2	0	2	29.8	31.5
2	0	4	39.3	36.6
2	0	6	18.0	19.0
2	0	8	27.4	-26.7
2	1	0	93.8	-98.9
2	1	1	7.5	-12.9
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2	1	2*	4.8	-2.4
-2	1	2	53.8	-54.6
2	1	3*	4.8	6.0
-2	1	3	45.5	-45.8
2	1	4	47.6	46.9
2	1	5	9.7	7.9
2	1	6	33.3	-33.1
2	1	7*	5.5	-6.8
2	1	8*	7.8	2.5
2	1	9*	6.9	-1.6
-2	1	9*	2.8	.8
2	2	0	48.2	-44.8
2	2	1	52.6	-53.0
-2	2	1*	5.0	-.2
2	2	2	67.8	62.2
-2	2	2	30.1	-25.0
2	2	3	23.6	22.8
-2	2	3	22.9	-22.9
2	2	4	34.2	-33.5
-2	2	4	75.6	76.8
2	2	5*	4.1	-7.3
-2	2	5	26.2	25.2
2	2	6	14.4	-12.8
-2	2	6	64.3	-62.6
2	2	7	14.5	-7.4
-2	2	7	13.8	-12.5
2	2	8	23.6	21.3
2	2	9*	7.1	7.6
-2	2	9	11.9	-7.8
2	3	0	56.9	52.9
2	3	1*	6.0	-2.9
-2	3	1	56.2	-48.3
2	3	2*	5.3	5.3
-2	3	2	56.4	56.4
2	3	3	10.9	11.0
-2	3	3	30.1	31.0
2	3	4	39.1	-34.7
-2	3	4	24.7	-24.5
2	3	5	27.4	-27.7
-2	3	5	26.7	27.5
2	3	6	31.2	30.3
-2	3	6	35.9	-34.3
2	3	7	15.4	17.7
-2	3	7	40.5	-41.1
-2	3	8	45.1	41.0
2	3	9*	7.3	3.5
-2	3	9	19.7	20.6
2	4	0	34.9	30.3
2	4	1	58.3	48.3
-2	4	1*	6.2	-10.0
2	4	2	42.1	-41.7
-2	4	2	13.8	15.5
2	4	3	28.1	-22.7
-2	4	3	42.7	46.2
2	4	4	15.7	16.5
-2	4	4	33.6	-35.8
2	4	5*	4.5	3.9
-2	4	5	49.2	-48.0
2	4	6*	7.6	5.7
-2	4	6	33.3	29.5
2	4	7	18.0	15.8
-2	4	7	14.7	14.9
-2	4	8*	5.9	1.4
-2	4	9	18.3	16.1
2	5	0	17.2	-17.4
2	5	1	20.6	-17.1
-2	5	1	60.5	59.4
2	5	2*	6.2	2.1
-2	5	2	36.6	-36.4
2	5	3	12.5	-10.2
-2	5	3	33.2	-35.6
2	5	4*	6.0	8.2
-2	5	4*	5.0	7.7
2	5	5	25.9	25.2
-2	5	5	15.2	-16.0
-2	5	6	18.7	17.4
2	5	7	9.0	-13.4
-2	5	7	43.6	41.7
-2	5	8	14.7	-15.2
-2	5	9	23.4	-24.7
2	6	0*	7.4	-4.9
2	6	1	39.7	-41.7
-2	6	1*	7.4	-3.8
2	6	2*	6.7	8.3
-2	6	2	8.7	-10.6
2	6	3	27.4	27.6
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2	6	4*	6.4	1.7
-2	6	4	16.2	12.0
2	6	5*	5.1	-6.3
-2	6	5	43.5	44.6
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2	7	1	12.7	16.6
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2	7	2*	7.2	2.4
-2	7	2*	6.8	4.7
2	7	3	14.4	14.9
-2	7	3	23.6	25.7
-2	7	4*	6.1	5.8
2	7	5	24.5	-23.2
-2	7	5*	4.7	5.2
2	7	7	15.7	11.4
-2	7	7	31.7	-29.8
-2	7	9	18.4	20.2
2	8	1	25.4	25.6
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2	8	3	16.6	-21.6
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2	8	5*	5.8	4.4
-2	8	5	28.4	-31.2
-2	8	7*	6.4	8.5
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2	9	1*	9.6	-11.3
-2	9	1	19.3	21.8
2	9	3*	8.0	-9.3
-2	9	3	10.7	-13.8
2	9	5	13.6	12.9
-2	9	5*	5.6	-2.1
-2	9	7	18.5	17.5
-2	10	5	15.6	15.0
3	0	0	15.4	14.1
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3	0	6*	7.8	-4.2
3	0	8	12.6	-14.0
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3	1	2*	5.7	7.9
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3	1	3*	5.7	4.4
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3	1	4	19.7	17.4
-3	1	4	26.0	-25.7
3	1	5*	4.6	7.3
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3	1	6	24.7	-25.1
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3	1	7*	6.3	-4.6
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3	2	0*	6.2	-.8
3	2	1	17.6	-17.5
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3	2	2	40.2	39.0
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3	2	3	16.3	16.0
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3	2	4	28.8	-27.9
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3	2	5	12.9	-10.7
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3	2	7*	6.4	-2.1
-3	2	8	29.1	-28.0
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3	3	2	21.8	-20.2
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3	3	3	11.4	-10.3
-3	3	3	29.5	29.5
3	3	4	10.2	-6.9
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3	3	5	18.4	-16.1
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3	3	6	18.2	16.2
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3	3	7	11.0	10.9
-3	3	7	38.1	-41.1
-3	3	8	37.1	35.3
-3	3	9*	4.3	1.7
3	4	0*	7.0	5.8
3	4	1	20.4	24.5
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3	4	2	23.0	-25.4
-3	4	2	29.3	30.4
3	4	3	26.2	-23.9
-3	4	3	42.2	38.9
3	4	4	15.3	17.2
-3	4	4	36.6	-37.6
3	4	5	13.5	12.8
-3	4	5	32.8	-34.6
-3	4	6	16.1	14.7
3	4	7*	6.8	6.8
-3	4	7	11.2	-12.8
-3	4	8	12.3	14.5
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3	5	0*	7.4	-9.7
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3	5	2	13.9	7.6
-3	5	2	14.8	-14.2
-3	5	3	8.1	-11.9
3	5	4	12.4	8.3
-3	5	4*	5.4	-2.9
3	5	5	18.2	20.2
-3	5	5	33.7	-33.8
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3	5	7	13.2	-14.5
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-3	5	8	18.3	-16.4
-3	5	9	8.7	-10.0
3	6	1	21.6	-20.4
-3	6	1	17.6	14.7
3	6	2	10.2	7.1
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3	6	3	24.4	24.9
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-3	6	4	14.0	8.2
3	6	5	10.5	-12.9
-3	6	5	29.8	33.6
-3	6	6*	7.2	-.9
-3	6	7	10.3	8.9
-3	6	9	27.2	-26.1
3	7	1	23.0	25.6
-3	7	1	33.2	-33.6
3	7	3*	7.5	-1.4
-3	7	3*	6.7	8.7
3	7	5	12.0	-10.7
-3	7	5	23.8	21.9
-3	7	7	29.6	-31.2
-3	7	9	11.7	13.1
3	8	1*	9.5	10.9
-3	8	1*	9.1	-11.1
3	8	3	16.4	-16.4
-3	8	3	26.9	27.7
-3	8	5	24.8	-24.7
-3	8	7*	6.5	-1.5
-3	8	9	21.8	16.6
-3	9	1	16.5	19.3
-3	9	3*	7.8	-2.7
-3	9	5	13.8	-11.8
-3	9	7	18.7	16.3
-3	10	5*	6.1	8.7
4	0	0	20.1	-21.6
4	0	2	21.5	-20.4
-4	0	2	49.8	53.0
4	0	4	29.1	26.9
4	0	6	12.6	-11.7
-4	0	8	41.9	44.6
4	1	0	51.4	-49.9
4	1	1*	7.5	-12.2
4	1	2	24.7	22.4
-4	1	2	16.2	-20.1
4	1	3*	6.6	3.2
-4	1	3*	5.1	4.0
4	1	4*	6.6	-5.4
-4	1	4	44.7	-42.3
4	1	5*	5.3	2.1
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4	1	6	12.7	-14.2
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4	1	7*	7.1	-1.4
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-4	1	8	13.0	-13.4
-4	1	9*	3.9	1.5
4	2	0	14.2	13.7
4	2	1*	7.6	-1.8
-4	2	1	25.9	25.5
4	2	2	18.3	18.5
-4	2	2	42.7	-40.1
4	2	3*	6.7	6.0
-4	2	3	23.6	-23.8
4	2	4	25.1	-21.9
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4	2	5*	5.3	-5.0
-4	2	5	9.8	8.4
-4	2	6	15.3	12.8
4	2	7*	7.2	.1
-4	2	7	14.1	16.2
-4	2	8	50.5	-47.6
-4	2	9	19.3	-20.1
4	3	0	31.5	28.4
4	3	1	23.4	28.3
-4	3	1*	7.3	-6.3
4	3	2	18.4	-17.0
-4	3	2*	6.0	3.6
4	3	3*	6.9	-6.5
-4	3	3*	5.6	-7.6
4	3	4*	6.8	.7
-4	3	4	32.3	32.9
4	3	5*	5.5	-6.6
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4	3	7*	7.3	6.1
-4	3	7	36.7	-35.3
-4	3	8	20.8	19.5
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4	4	0*	7.8	-10.2
4	4	1*	8.2	9.7
-4	4	1	24.5	-26.4
4	4	2	10.2	-8.6
-4	4	2	30.7	31.7
4	4	3	18.5	-17.7
-4	4	3	25.4	28.1
4	4	4	10.0	9.8
-4	4	4	25.4	-26.3
4	4	5	16.4	13.1
-4	4	5	12.2	-12.5
-4	4	6*	6.6	-2.0
-4	4	7	23.2	-22.1
-4	4	8	23.0	21.9
-4	4	9	28.2	27.8
4	5	1	25.5	-31.5
-4	5	1	18.0	18.4
-4	5	2*	6.7	-4.9
4	5	3*	7.4	8.7
-4	5	3*	6.3	3.8
-4	5	4*	5.9	-4.1
4	5	5*	5.8	5.8
-4	5	5	25.5	-28.6
-4	5	6	19.3	17.2
-4	5	7	28.8	29.2
-4	5	8*	7.1	-10.7
-4	5	9*	5.9	2.8
4	6	1*	9.1	-2.5
-4	6	1	27.0	26.2
4	6	3	11.9	14.1
-4	6	3	26.9	-30.1
-4	6	5	15.7	16.0
-4	6	7	15.7	18.6
-4	6	9	20.2	-26.6
4	7	1	14.6	18.9
-4	7	1	17.2	-14.4
-4	7	3*	7.2	-8.8
-4	7	5	25.9	29.9
-4	7	7	23.6	-23.4
-4	7	9*	7.1	1.5
-4	8	3	14.4	19.1
-4	8	5*	5.5	-8.6
-4	8	7	12.7	-14.4
-4	8	9	15.8	20.6
-4	9	5	14.3	-16.6
5	0	0	30.3	-31.0
5	0	2*	7.5	-4.8
5	0	4	18.1	14.6
-5	0	8	47.1	50.2
5	1	0	22.3	-18.8
5	1	1*	6.5	-6.4
-5	1	1*	7.9	-.1
5	1	2	26.8	22.4
-5	1	2*	6.5	6.5
5	1	3*	7.5	.6
-5	1	3*	6.0	6.4
5	1	4	13.5	-9.4
5	1	5*	5.9	.3
-5	1	6	47.3	46.1
-5	1	8*	6.1	5.2
-5	1	9*	4.9	5.6
5	2	0	23.6	24.9
5	2	1*	8.7	-1.0
5	2	2*	7.6	3.0
-5	2	2	26.9	-28.5
5	2	3*	7.5	2.6
-5	2	3	8.7	-10.8
5	2	4	15.0	-11.1
-5	2	4	19.4	17.9
5	2	5*	6.0	-5.5
-5	2	5	10.3	-10.3
-5	2	6	23.8	20.1
-5	2	7	20.4	22.2
-5	2	8	37.1	-38.3
-5	2	9	12.6	-12.1
5	3	0*	8.4	12.8
5	3	1	15.0	16.8
-5	3	1*	8.3	-.8
5	3	2	11.0	-13.9
-5	3	2*	6.8	-7.2
5	3	3*	7.7	-5.4
-5	3	3	15.6	-17.8
5	3	4*	7.6	3.5
-5	3	4	29.3	26.5
-5	3	5	21.4	22.7
-5	3	6	36.1	-27.6
-5	3	7	7.3	-10.1
-5	3	8*	6.8	-3.1
-5	3	9*	5.5	-7.0
5	4	1*	9.2	-5.4
-5	4	1	17.7	-25.4
-5	4	2	14.5	16.5
-5	4	3	23.0	24.5
-5	4	4*	6.1	-6.5
-5	4	5*	4.6	2.5
-5	4	6	17.8	-17.5
-5	4	7	20.5	-23.9
-5	4	8	25.6	23.8
-5	4	9	14.5	16.4
5	5	1	17.9	-18.8
-5	5	1*	9.0	3.9
-5	5	3	15.3	17.9
-5	5	5	26.5	-28.7
-5	5	6	11.1	11.4
-5	5	7	11.9	12.4
-5	5	9*	6.4	8.0
-5	6	1	19.3	19.6
-5	6	3	15.0	-15.7
-5	6	5*	5.2	-4.6
-5	6	7	22.3	25.0
-5	6	9	18.9	-24.8
-5	7	5	20.6	22.6
-5	7	7*	6.6	-7.9
-5	7	9*	7.5	-10.0
-5	8	5*	5.9	1.0
-5	8	7	12.0	-15.4
-5	9	5	15.1	-13.6
6	0	0	25.1	-24.6
6	0	2*	8.4	2.5
6	0	4*	8.0	2.3
-6	0	8	28.7	29.2
6	1	0*	9.1	-2.4
6	1	1*	9.6	-3.1
-6	1	1*	9.0	-1.1
6	1	2	11.9	11.7
-6	1	3*	6.9	4.7
6	1	4*	6.5	-6.1
-6	1	8	14.9	15.3
-6	1	9*	5.9	3.6
6	2	0	19.0	17.6
6	2	1*	9.8	5.1
-6	2	1*	9.1	5.4
-6	2	2	10.6	-13.7
-6	2	3*	7.0	-7.3
-6	2	6	26.8	24.7
-6	2	7	14.3	15.4
-6	2	8	22.0	-24.4
-6	2	9*	6.1	-.4
-6	3	1*	9.4	3.4
-6	3	3	14.3	-12.1
-6	3	4	13.6	17.3
-6	3	5	14.2	14.1
-6	3	6*	7.9	-9.2
-6	3	7*	5.8	5.0
-6	3	9	10.7	-13.4
-6	4	5	10.6	13.1
-6	4	6	15.4	-14.0
-6	4	7	23.6	-26.9
-6	5	5	17.8	-19.9
-6	5	7*	6.4	-1.6
-6	5	9	15.1	14.6
-6	6	5	10.6	-10.0
-6	6	7	18.0	19.7
-6	7	5	15.8	12.9
-6	7	7*	7.1	1.7
-7	1	3*	7.7	2.9
-7	1	8	20.3	20.0
-7	3	7*	6.6	6.1
-7	4	5	11.5	10.1
-7	4	7	15.0	-14.1
-7	5	5*	6.0	-4.7
-7	5	7*	7.1	-9.3
-7	6	7	10.5	11.6
-8	3	7*	7.3	7.6

be real, is not a new feature, having been unmistakably observed in $P(CN)_3$ (Emerson & Britton, 1964). Hirshfeld (1964) has offered a possible explanation for this bending.

The most striking trend among the three compounds is the change in the intermolecular As–N distance. It is shortest in $As(CN)_3$ and increases by about 0·2 Å for each CH_3 substituted for a CN. Since the strength of As as an electron acceptor would be decreased by the substitution of a less electronegative CH_3 group for a more electronegative CN group, this trend is qualitatively what would be expected.

One other feature is worthy of comment. In $P(CN)_3$ all three CN groups appeared to be involved in intermolecular interactions. In both the As compounds with more than one CN group only one CN is involved in an obvious intermolecular interaction, although in $CH_3As(CN)_2$ the second CN points directly toward a neighboring As (As–N distance 3·32 Å), and there appears to be no steric reason for a lack of interaction. However, it may be significant that the non-interacting CN points toward the As atom on the side opposite to the CH_3 group, while all of the interacting CN groups point toward the As approximately opposite another interacting CN group, *i.e.* the interactions lead to approximately linear chains. It is also interesting that in the isomorphous and apparently isostructural $CH_3P(CN)_2$ the *c* axis, which is nearly parallel to the line of the intermolecular interaction, is shorter by 0·05 Å per molecule than in the As compound, but the *a* and *b* axes are shorter by 0·10 Å and 0·20 Å respectively. This may indicate that the normal contact

Table 4. *Interatomic distances and angles*

Compound	Distance or angle	Value	Reference
$CH_3As(CN)_2$	As–C(1)(CN)	1·97±0·03 Å	*a*
	As–C(2)(CN)	1·99±0·03	*a*
	As–C(3)(CH_3)	2·00±0·04	*a*
$As(CN)_3$	As–C(1)(CN)	1·89±0·05	*b*
	As–C(2)(CN)	1·98±0·05	*b*
	As–C(3)(CN)	1·92±0·05	*b*
$(CH_3)_2AsCN$	As–C(CN)	2·01±0·03	*c*
	As–C(CH_3)	1·93±0·03	*c*
	As–C(CH_3)	1·93±0·03	*c*
$(CH_3–As)_5$	As–C	1·95±0·05	*d*
$(C_6H_5–As)_6$	As–C	1·97±0·03	*e*
$CH_3As(CN)_2$	C(1)–As–C(2)	89·4 ±2·0°	*a*
	C(1)–As–C(3)	98·3 ±2·0	*a*
	C(2)–As–C(3)	93·5 ±2·0	*a*
$As(CN)_3$	C(1)–As–C(2)	88·8 ±3·5	*b*
	C(2)–As–C(3)	92·0 ±3·5	*b*
	C(3)–As–C(1)	90·8 ±3·5	*b*
$(CH_3)_2AsCN$	CH_3–As–CN	89 ±2°	*c*
	CH_3–As–CH_3	91 ±2	*c*
	CH_3–As–CH_3	105 ±2	*c*
$CH_3As(CN)_2$	C(1)–N(1)	1·09±0·04	*a*
	C(2)–N(2)	1·15±0·04	*a*
$As(CN)_3$	C(1)–N(1)	1·12±0·07	*b*
	C(2)–N(2)	1·08±0·07	*b*
	C(3)–N(3)	1·14±0·07	*b*
$(CH_3)_2AsCN$	C–N	1·16±0·07	*c*
$CH_3As(CN)_2$	As–C(1)–N(1)	177 ±4°	*a*
	As–C(2)–N(2)	173 ±4°	*a*
$As(CN)_3$	As–C(1)–N(1)	174 ±8	*b*
	As–C(2)–N(2)	174 ±8	*b*
	As–C(3)–N(3)	177 ±8	*b*
$As(CN)_3$	As · · · N(3)	2·74±0·05	*b*
$CH_3As(CN)_2$	As · · · N(2)	2·94±0·03	*a*
$(CH_3)_2AsCN$	As · · · N	3·18±0·05	*c*

* The uncertainties quoted for the $CH_3As(CN)_2$ distances and angles are twice those calculated from the standard deviations in Table 2. This approximately corrects for the optimistic values obtained from the diagonal error matrix.

a. Present work.
b. Emerson & Britton (1963). See Appendix also.
c. Camerman & Trotter (1963).
d. Burns & Waser (1957).
e. Hedberg, Hughes & Waser (1961).

opposite the CH_3 group in $CH_3As(CN)_2$ becomes a measurably strong interaction in $CH_3P(CN)_2$. The complete structure of the latter compound would be of interest for this reason.

APPENDIX

The improvement effected by recorrelating the Weissenberg layers internally from the data in the course of the $CH_3As(CN)_2$ refinement suggested that the data of Emerson & Britton (1963) on $As(CN)_3$ be treated this same way, since there had been an anomalous set of anisotropic thermal parameters for the As atom in this earlier work.

The structure of $As(CN)_3$ was determined from *h*0*l*–*h*3*l* Weissenberg data (Cu *Kα* radiation), which had been correlated from four sets of precession data (Mo *Kα* radiation). The average values of F_o/F_c were calculated from the published structure factors; the values were 0·935, 0·969, 1·050 and 1·073 for *h*0*l* through *h*3*l* respectively. After the data were corrected on this basis, least-squares refinement, beginning with the previous parameters, and using the previously reported weighting scheme was carried out. The agreement factors were

	Before recorrelation		After recorrelation	
	R	*r*	*R*	*r*
All atoms isotropic	0·104	0·052	0·082	0·038
Arsenic atom anisotropic	—	—	0·078	0·036
All atoms anisotropic	0·097	0·036	0·073	0·031

The final positional parameters and isotropic temperature factors are compared with those before recorrelation in Table 5, which also gives a similar comparison of the anisotropic temperature factors for As. The bond distances and angles are compared in Table 6.

Table 6. *Bond distances and angles*

Distance or angle	Value after recorrelation	Value before recorrelation
As —C(1)	1·89 Å	1·85 Å
As —C(2)	1·98	1·82
As —C(3)	1·92	1·96
As —N(1)	3·00	3·03
As —N(2)	3·05	2·95
As —N(3)	3·06	3·09
C(1)–N(1)	1·12	1·19
C(2)–N(2)	1·08	1·13
C(3)–N(3)	1·14	1·14
C(2)–As —C(3)	92·0°	91·5°
C(1)–As —C(3)	90·8	87·6
C(1)–As —C(2)	88·8	91·5
N(2)–As —N(3)	93·1	92·8
N(1)–As —N(3)	93·6	94·9
N(1)–As —N(2)	91·9	91·8
As —C(1)–N(1)	174	171
As —C(2)–N(2)	174	175
As —C(3)–N(3)	177	168
As · · · · · · N	2·74	2·85

The present refinement resulted in an improvement of the agreement factors in every stage of the refinement. It also resulted in what appear to be slightly more reasonable bond distances and angles, and in more reasonable isotropic temperature factors for the light atoms. The most striking improvement, however, is in the ellipsoid of vibration of the arsenic atom. Whereas it had one imaginary amplitude before the recorrela-

Table 5. *Final parameters for* $As(CN_3)$

The first line for each atom contains the values from our refinement based on the recorrelated data (see text); the second line contains the values reported by Emerson & Britton (1963). In both cases the standard deviations (in parentheses) were obtained from the elements of diagonal least-squares matrices.

	x(*σ*)	*y*(*σ*)	*z*(*σ*)	*B*(*σ*)
As	0·2912 (1)	0·0000	0·2616 (1)	2·52 (1)
	0·2904 (4)	0·0000	0·2616 (4)	2·63 (5)
C(1)	0·220 (1)	0·208 (2)	0·366 (2)	3·8 (3)
	0·229 (4)	0·210 (7)	0·362 (5)	4·9 (9)
N(1)	0·188 (1)	0·326 (2)	0·438 (1)	5·4 (2)
	0·188 (4)	0·327 (7)	0·443 (5)	7·1 (11)
C(2)	0·100 (2)	−0·133 (2)	0·254 (1)	2·9 (3)
	0·113 (4)	−0·123 (8)	0·255 (5)	5·7 (11)
N(2)	0·000 (1)	−0·219 (2)	0·245 (1)	5·1 (3)
	0·008 (4)	−0·213 (7)	0·245 (4)	7·0 (10)
C(3)	0·221 (1)	0·125 (2)	0·069 (1)	3·8 (3)
	0·213 (4)	0·135 (7)	0·070 (4)	6·0 (10)
N(3)	0·186 (1)	0·197 (2)	−0·048 (1)	5·2 (3)
	0·183 (3)	0·196 (6)	−0·051 (4)	5·4 (8)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
As	0·0081 (1)	0·0129 (2)	0·0080 (1)	0·0005 (11)	−0·0073 (8)	0·0024 (8)
	0·0098 (3)	0·0124 (3)	0·0082 (5)	−0·0197 (24)	−0·0130 (34)	0·0024 (4)

tion, it now has all real amplitudes. The B values, amplitudes, and direction cosines of the principal axes are (in the order B, amplitude, φ, ψ, ω):

$$3{\cdot}42\ \text{Å}^2,\ 0{\cdot}208\ \text{Å},\ -0{\cdot}316,\ -0{\cdot}685,\ 0{\cdot}706;$$
$$2{\cdot}62\ \text{Å}^2,\ 0{\cdot}182\ \text{Å},\ 0{\cdot}945,\ -0{\cdot}165,\ 0{\cdot}094;$$
$$1{\cdot}55\ \text{Å}^2,\ 0{\cdot}140\ \text{Å},\ -0{\cdot}085,\ 0{\cdot}711,\ 0{\cdot}702.$$

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The Crystal Structure of Imidazole at −150 °C

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(*Received* 2 *September* 1965)

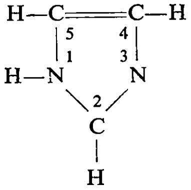
Imidazole, $C_3N_2H_4$, crystallizes in the space group $P2_1/c$. There are four molecules in the cell, the dimensions of which are, at −150 °C: $a = 7{\cdot}582$, $b = 5{\cdot}371$, $c = 9{\cdot}790$ Å; $\beta = 61°\,1'$. The five-membered ring is planar. All bond lengths in the ring indicate considerable double-bond character. NH ··· N bonds with the exceptionally short length of 2·86 Å form chains of molecules along the c axis.

Introduction

The study of the crystal structure of imidazole was started in the Instituto de Fisica Alonso de Santa Cruz (García Blanco & Martinez-Carrera, 1958). A tentative projection of the structure was given, but the X-ray data, taken at room temperature, were insufficient for refinement. Low-temperature data were collected and the structure solved in 1958/59 in this laboratory, while the author held a Netherlands–Spain exchange fellowship. The structure was further refined in 1963 in the Laboratory of Crystallography of the University of Pittsburgh by courtesy of Prof. G. A. Jeffrey. In the meantime Will (1963), apparently unaware of our former work, published a rough trial structure of imidazole at room temperature. Since our experimental low-temperature data are far more complete, they permit an accurate determination of the molecular geometry and of the packing in the crystal.

Experimental

Imidazole, with molecular formula



crystallizes in the monoclinic system, class $2/m$. Single crystals elongated along the b axis were obtained from ethanol solution. The cell constants were determined by least squares, both at room temperature and at −150°C, from $\sin^2\theta$ values of $hk0$ and $h0l$ reflexions. These were obtained from Weissenberg diagrams calibrated with aluminum powder lines. The values found were:

	a	σ_a	b	σ_b	c	σ_c
20°C	7·732	0·002	5·453	0·002	9·766	0·002 Å
−150°C	7·582	0·002	5·371	0·002	9·790	0·003 Å

	β*	σ_β
20°C	62°47′	1′
−150°C	61° 1′	1′

The room temperature values of Will are in somewhat better agreement with those given above than those of García Blanco & Martinez-Carrera.

By comparison of the films it was clear that the structure is basically the same at −150°C and at room temperature. The space group is $P2_1/c$. With four formula units per unit cell the calculated density is 1·297 g.cm^{-3} at −150°C.

The crystals were mounted in thin-walled glass capillaries and the X-ray intensities were obtained on a Weissenberg camera. Cooling of the crystal to −150°C was achieved by a gas stream passed through liquid air (Kreuger, 1955).

The X-ray diffraction intensities were recorded by a multiple-film technique with Cu K radiation. Five

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* β is taken acute, conforming with the original setting of Greenwood (1926).