this method requires a very accurately cut plate of crystal. Observations on the eye of a magnified interference figure, however, given by the same crystal specimen, were consistent with a *positive* rotation (clockwise as seen by the observer looking towards the light source) of about $9° \pm 5°$ per mm, for the crystal having the morphology of Fig. 1. It is hoped to confirm this result and to measure the magnitude of the rotation reliably in due course.

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The Crystal Structure of p-Iodobenzonitrile

BY ELMER O. SCHLEMPER AND DOYLE BRITTON

Department of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

p-Iodobenzonitrile forms monoclinic crystals in the space group $C2/c$ (C_{2h}^6) with four molecules in a unit cell of dimensions, $a = 10\cdot36$, $b = 10\cdot63$, $c = 9\cdot10$ Å and $\beta = 133\cdot1°$. The molecules lie on twofold axes of the crystal and have C_{2v} symmetry. The cyanide group in one molecule is involved in a weak external bond to the iodine atom in the adjacent molecule. The external bond is similar to, but weaker than, that found in iodine cyanide.

Introduction

Recognizable solid state intermolecular interactions between cyanide groups and heavy non-metal atoms are known in a number of cases. The first known and most studied of these is in iodine cyanide (Ketelaar & Zwartsenberg, 1939; Townes & Dailey, 1952) where the external nitrogen–iodine distance is 0·8–0·9 Å less than the sum of the van der Waals radii. Similarly short distances are found in bromine cyanide (Geller & Schawlow, 1955), chlorine cyanide (Heiart & Carpenter, 1956), selenium selenocyanate (Aksnes & Foss, 1954), dimethyl arsenic cyanide (Camerman & Trotter, 1963), and arsenic tricyanide (Emerson & Britton, 1963). As a part of an examination of the condition necessary for the formation of such bonds we have determined the crystal structure of p-iodobenzonitrile, with the expectation that a similar sort of bond could occur here.

Experimental

p-Iodobenzonitrile was prepared by the dehydration of p-iodobenzamide, which had been prepared from p-iodobenzoic acid. The sample melted at the accepted value of 124–125·5 °C. The melting point of a sample prepared by the substitution of –CN for –NH₂ in p-iodoaniline was identical. Crystals suitable for the X-ray work, short needles, were grown by sublimation.

From density and unit-cell measurements we have determined the molecular volumes of p-chloro- and p-bromo-benzonitrile to be 100·1 and 102·9 Å³, respectively. The assumption of four molecules per unit cell yields a molecular volume of 110·1 Å³ for p-iodobenzonitrile. The calculated density is 2·08 g.cm⁻³.

Weissenberg and precession photographs ($CuK\alpha = 1\cdot5418$, $MoK\alpha = 0\cdot7107$ Å) showed this to be the c axis of a monoclinic cell with dimensions:

$$a = 9\cdot10 \pm 0\cdot05, \quad b = 10\cdot63 \pm 0\cdot05, \quad c = 7\cdot83 \pm 0\cdot05 \text{ Å};$$
$$\beta = 105\cdot0 \pm 0\cdot2°.$$

The systematic extinctions for hkl data ($h + k + l = 2n + 1$) and for $h0l$ data ($h = 2n + 1$, $l = 2n + 1$) indicate the space group to be Ic or $I2/c$. A roughly cylindrical needle 0·3 mm in diameter was chosen for intensity measurements, and multiple film Weissenberg photographs using Mo $K\alpha$ radiation were collected for the zero through 8th layers for rotation around the c axis. Intensity photographs were taken of the $h0l$ and $0kl$ zones on a precession camera to provide data to

correlate the Weissenberg layers. Intensities were measured by comparison with a series of timed exposures of a selected spot.* Lorentz and polarization correction was applied in the usual way. No correction was made for absorption; the linear absorption coefficient is 48·5 cm^{-1}. The collected data included 883 reflections of measurable intensity, and 306 more reflections that fell within the range of the observed but were too weak to measure. These were included in the calculations with a value equal to half the minimum observed intensity.

Determination of the structure

The unit cell was changed to the more conventional Cc or $C2/c$ with the following dimensions:

$$a = 10\cdot36 \pm 0\cdot05, \quad b = 10\cdot63 \pm 0\cdot05, \quad c = 9\cdot10 \pm 0\cdot05 \text{ Å};$$
$$\beta = 133\cdot1 \pm 0\cdot2^\circ.$$

This was used for all of the calculations and is used throughout the rest of this article. The calculations that follow were made on the Control Data 1604 Computer of the Numerical Analysis Center of the University of Minnesota using programs prepared at Princeton University under the direction of Prof. R. A. Jacobson.

A three-dimensional Patterson map was calculated with the use of all the data. The iodine positions were readily found; using only the iodine atoms, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0\cdot29$. The iodine atoms were assumed to lie on the twofold axis of $C2/c$ and a three-dimensional electron density map was calculated with the phases determined by the iodine. All of the other atoms, except hydrogen, were readily identified from this map, and their positions confirmed the

* The intensities were actually measured twice, once by E. O. S. and once by Miss Judith Krudener. The values used were averages of these two sets of measurements plus some remeasurements where there were large discrepancies between the two sets. As a test of the value of this additional measurement, the refinement with all atoms isotropic and iodine only anisotropic was carried out on all three sets of data with the results:

Measurement	Averaged data	EOS data	JK data
Isotropic			
R	15·1	19·3	19·3
r	8·2	10·2	10·6
Length of C–C	1·41	1·39	1·40
bonds in ring	1·39	1·46	1·47
	1·42	1·45	1·56
Anisotropic			
R	11·9	17·6	16·6
r	4·7	7·8	6·5
Length of C–C	1·40	1·39	1·42
bonds in ring	1·39	1·47	1·45
	1·41	1·43	1·51

choice of $C2/c$.* Least-squares refinement of the function $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$ with $w = 1$ for $F_o < 20$ and $= (20/F_o)^4$ for $F_o > 20$ was carried out with full matrix calculation. Refinement was carried through three stages, each stage being continued until the parameters ceased to shift. The final refinement parameters in each stage were:

All atoms isotropic	$R = 0\cdot151$	$r = 0\cdot082$
Iodine atom anisotropic	0·119	0·047
All atoms anisotropic	0·117	0·045

Hydrogen atoms were not included in any of the calculations; the positions at which they would be expected fell in regions of positive electron density, but equally positive regions occurred in other parts of the background.

The final positional parameters and their standard deviations, estimated by a diagonal approximation, are given in Table 1. The bond lengths and angles corresponding to these parameters are given in Fig. 1. The molecule is planar within experimental error.
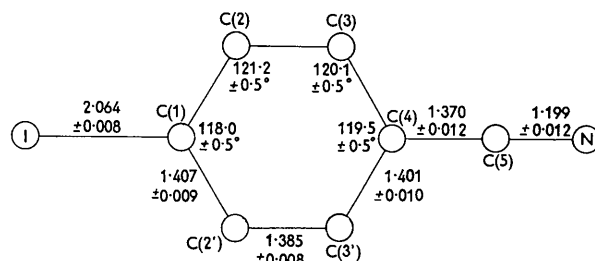

Fig. 1. Bond lengths and bond angles in p-iodobenzonitrile. The standard deviations are based on those in Table 1.

The anisotropic temperature factors are given in Table 2. The magnitudes of the vibration parallel and perpendicular to the molecule are given in Table 3.

Table 1. *Final positional parameters**

Atom	x	y	z
I	0	$1\cdot0265 \pm 0\cdot00004$	$\frac{1}{4}$
C(1)	0	$0\cdot8324 \pm 0\cdot0007$	$\frac{1}{4}$
C(2)	$0\cdot0926 \pm 0\cdot0005$	$0\cdot7642 \pm 0\cdot0006$	$0\cdot2141 \pm 0\cdot0006$
C(3)	$0\cdot0945 \pm 0\cdot0005$	$0\cdot6339 \pm 0\cdot0006$	$0\cdot2162 \pm 0\cdot0006$
C(4)	0	$0\cdot5675 \pm 0\cdot0008$	$\frac{1}{4}$
C(5)	0	$0\cdot4386 \pm 0\cdot0008$	$\frac{1}{4}$
N	0	$0\cdot3258 \pm 0\cdot0008$	$\frac{1}{4}$

* The standard deviations listed were calculated with a diagonal approximation to the matrix. They are probably too small by a factor of about two.

* The iodine atoms alone have $C2/c$ symmetry, so that the Fourier map based on phases calculated from the iodine alone also has $C2/c$ symmetry. However, if Cc were correct, we would expect the light atom peaks to be elongated, or even split, by an amount proportional to the distance from the I atom (if we assume the molecule to have C_{2v} symmetry regardless of space group). No such elongation or splitting was observed. The peak heights varied and the shapes were not always spherical, but neither the variations in height nor those in shape showed any pattern that would suggest Cc rather than $C2/c$ to be the correct space group.

Table 2. *Anisotropic temperature factors**

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}	$B\dagger$
I	0·0201	0·0082	0·0303	0	0	0·0344	4·47
C(1)	0·0107	0·0115	0·0202	0	0	0·0196	3·69
C(2)	0·0182	0·0101	0·0342	−0·0019	−0·0020	0·0385	4·52
C(3)	0·0224	0·0095	0·0340	0·0045	0·0053	0·0419	4·79
C(4)	0·0178	0·0086	0·0249	0	0	0·0291	4·07
C(5)	0·0166	0·0115	0·0188	0	0	0·0208	4·29
N	0·0439	0·0096	0·0389	0	0	0·0614	6·70

* The standard deviations are 0·0004–0·0008 except for N where they are *ca.* 0·0012.
† Value from the last cycle in which the atom was isotropic.

The structure factors calculated in the last cycle of the refinement with only the iodine atom anisotropic are compared with the observed structure factors in Table 4.

Table 3. *Temperature factors in molecular directions*

Atom	*B* parallel to the axis of the molecule	*B* perpendicular to the axis of the molecule, parallel to the plane of the molecule	*B* perpendicular to the axis of the molecule, perpendicular to the plane of the molecule
I	3·70 Å²	4·94 Å²	5·10 Å²
C(1)	5·20	3·26	3·42
C(2)	4·56	4·50	5·04
C(3)	4·30	4·85	5·21
C(4)	3·88	4·22	4·18
C(5)	5·20	4·21	3·95
N	4·34	7·46	7·10

The possibility of isocyanide

Inspection of the three-dimensional Fourier map calculated after the isotropic refinement indicated that the compound might be the isonitrile rather than the nitrile. The peak heights for the light atoms were:

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	N
e.Å⁻³	6·8	7·0	7·4	6·6	8·0	5·6

The method of preparation seemed to rule out the possibility, but to be sure, we determined the infrared spectrum of the sample. A sharp peak attributable to the −CN stretch was present at 2230 cm⁻¹. This is clear proof that this was the cyanide and not the isocyanide since the typical frequencies are –CN, 2220–2240; –NC, 2145 cm⁻¹ (Bellamy, 1958).

The least-squares refinement shows the cyanide carbon atom (C(5)) to have a normal temperature factor, but the nitrogen to have very large temperature factors perpendicular to the axis of the molecule, but normal along the axis. If the carbon and nitrogen were incorrectly reversed one would expect the carbon temperature factors to be small, and the nitrogen temperature factors all to be large. Therefore, the explanation for the low peak in the Fourier map must lie in an abnormally large bending of the CN group. This bending is surprising considering the external N–I interaction that is found here, but

is probably real. Much of the detail of the anisotropic thermal motion can be attributed to systematic experimental errors, such as the uncorrected absorption, but the difference between the N and all the other atoms would appear to be real.

To test further the possibility that the space group might be *Cc* rather than *C2/c*, we carried out a least-squares refinement in *Cc* starting with a structure where all of the atoms on the twofold axis had been
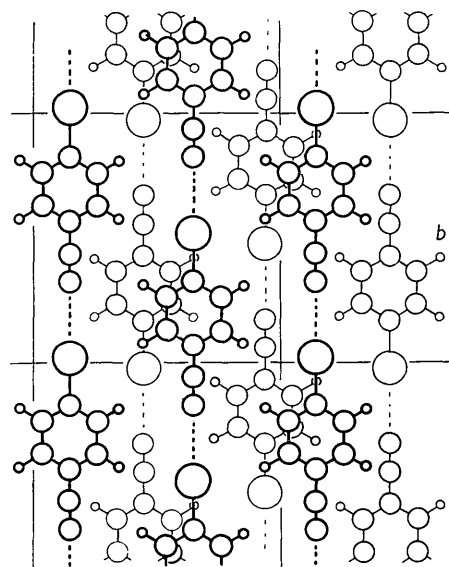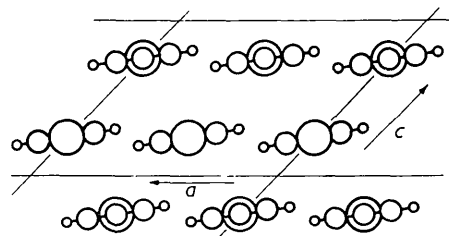
Fig. 2. Packing of *p*-iodobenzonitrile molecules in the crystal. Top view is down the *b* axis. Bottom view is perpendicular to the *C* face, *not* along the *c* axis. Only the two layers of molecules in the complete cell in the top view are shown in the bottom view. Short intermolecular distances are indicated by dotted lines. The hydrogen positions are assumed and not experimental.

displaced randomly from the axis by an amount equal to the standard deviation of the other light atom positions. The iodine was kept fixed, with the anisotropic parameters from the earlier refinement, and the light atoms were isotropic. After three cycles of refinement R had not improved past the corresponding value in $C2/c$, and the positions of the atoms had shifted on the average by another standard deviation, but in no systematic way, so that within experimental error the molecule still lay on the twofold axis in $C2/c$. The instructive feature of this calculation was that the final positions were randomly displaced from the $C2/c$ positions by about twice the calculated standard deviations on the average, indicating clearly that the diagonal approximation used in calculating the standard deviations gives too optimistic results, in this case by about a factor of two for the light atoms.

Table 4. *Comparison of observed and calculated structure factors*

HH	KK	LL	F(OBS)	F(CALC)
0	0	6	56.0	-55.3
0	0	8	22.1	15.7
0	2	2	134.1	-119.1
0	2	3	33.1	34.2
0	2	4	84.4	75.5
0	2	5	11.8	-16.1
0	2	6	35.0	-36.8
0	2	7	6.4	5.5
0	2	8	18.0	14.5
0	4	0	116.5	107.5
0	4	1	121.1	-116.8
0	4	2	94.0	-89.1
0	4	3	93.9	77.1
0	4	4	56.9	53.8
0	4	5	33.1	-35.7
0	4	6	23.8	-24.6
0	4	7	15.1	15.8
0	4	8	10.2	8.7
0	6	0	62.0	56.1
0	6	1	60.1	-67.6
0	6	2	49.0	-49.3
0	6	3	56.1	51.9
0	6	4	34.8	30.8
0	6	5	29.1	-30.3
0	6	6	15.0	-15.0
0	6	7	14.8	13.9
0	6	8	7.9	5.8
0	8	0	16.0	17.3
0	8	1	75.6	-75.5
0	8	2	13.2	-13.7
0	8	3	52.5	54.0
0	8	4	6.4	6.5
0	8	5	29.7	-28.3
0	8	6	2.9*	-1.3
0	8	7	13.5	11.0
0	8	8	6.6*	-.5
0	10	0	13.0	-15.3
0	10	1	56.0	-53.7
0	10	2	11.2	12.8
0	10	3	47.6	40.0
0	10	4	3.4*	-7.8
0	10	5	24.0	-22.6
0	10	6	3.2*	3.5
0	10	7	12.9	9.9
0	12	0	8.7	-11.3
0	12	1	25.8	-28.5
0	12	2	7.6	9.6
0	12	3	23.6	21.2
0	12	4	3.8*	-6.0
0	12	5	13.6	-11.9
0	12	6	3.5*	2.8
0	14	0	11.0	-12.1
0	14	1	6.3	-10.1
0	14	2	9.6	10.5
0	14	3	8.3	7.9
0	14	4	5.5	-7.0
0	14	5	4.3	-4.8
0	16	0	6.3	-7.9
0	16	1	5.9	-7.0
0	16	2	6.6	6.9
0	16	3	6.4	5.2
-1	1	3	8.0	11.4
1	1	4	54.2	57.0
-1	1	4	97.6	89.2
1	1	5	1.7*	2.8
1	1	6	23.7	-24.5
-1	1	6	41.8	-45.5
1	1	7	6.0	-.6
-1	1	7	2.3*	8.5
-1	1	8	18.3	17.9
-1	1	9	5.7*	-3.7
1	3	0	153.0	150.6
1	3	1	79.4	-78.3
1	3	2	113.3	-109.4
1	3	3	47.3	48.1
-1	3	3	66.2	60.4
1	3	4	51.5	57.5
-1	3	4	95.2	80.4
1	3	5	18.6	-22.6
-1	3	5	41.1	-31.6
1	3	6	22.6	-23.3
-1	3	6	36.6	-36.7
1	3	7	9.1	8.3
-1	3	7	12.1	12.9
-1	3	8	15.0	12.8
-1	3	9	7.6	-4.0
1	5	0	119.7	106.7
1	5	1	97.9	-86.4
-1	5	1	104.9	-96.0
1	5	2	99.9	-81.5
-1	5	2	102.5	-93.6
1	5	3	58.3	56.3
-1	5	3	80.3	75.4
1	5	4	41.5	45.6
-1	5	4	62.0	57.7
1	5	5	29.3	-28.3
-1	5	5	44.0	-44.0
1	5	6	19.8	-20.0
-1	5	6	26.9	-27.6
1	5	7	14.1	11.4
-1	5	7	19.2	20.1
-1	5	8	13.9	10.5
-1	5	9	8.1	-7.3
1	7	0	34.2	34.7
1	7	1	102.8	-89.2
-1	7	1	104.2	-95.6
1	7	2	28.0	-25.2
-1	7	2	33.0	-37.2
1	7	3	68.7	58.9
-1	7	3	80.7	71.2
1	7	4	12.7	15.0
-1	7	4	33.9	29.8
1	7	5	30.1	-28.9
-1	7	5	43.3	-38.6
1	7	6	9.7	-7.6
-1	7	6	16.7	-18.2
1	7	7	13.6	10.6
-1	7	7	16.3	15.7
-1	7	8	10.7	8.8
-1	7	9	8.7	-4.8
1	9	0	11.1	11.9
1	9	1	50.4	-49.5
-1	9	1	57.3	-56.5
1	9	2	12.2	-9.6
-1	9	2	9.8	-10.1
1	9	3	38.7	33.1
-1	9	3	50.4	48.6
1	9	4	5.6	5.6
-1	9	4	6.3	5.9
1	9	5	19.4	-17.3
-1	9	5	36.6	-31.6
1	9	6	4.8*	-2.3
-1	9	6	2.6*	-2.4
1	9	7	12.2	7.3
-1	9	7	16.9	15.9
-1	9	8	5.2*	.6
1	11	0	11.9	-8.5
1	11	1	35.3	-38.7
-1	11	1	40.2	-41.7
1	11	2	9.8	6.6
-1	11	2	9.0	8.0
1	11	3	29.8	27.0
-1	11	3	33.0	33.6
1	11	4	3.6	-3.7
-1	11	4	7.1	-5.3
1	11	5	14.3	-14.4
-1	11	5	20.5	-20.4
1	11	6	5.3*	1.4
-1	11	6	2.9*	2.6
-1	11	7	10.2	9.5
1	13	0	11.9	-12.6
1	13	1	20.7	-18.7
-1	13	1	21.1	-20.0
1	13	2	12.2	9.8
-1	13	2	10.9	12.5
1	13	3	15.5	13.0
-1	13	3	15.8	15.9
1	13	4	5.7	-5.9
-1	13	4	11.3	-9.5
1	13	5	4.7	-6.7
-1	13	5	11.9	-9.4
-1	13	6	4.2	5.6
1	15	0	13.1	-14.9
1	15	1	9.3	-7.6
-1	15	1	7.7	-8.1
1	15	2	13.6	12.4
-1	15	2	13.3	13.4
1	15	3	4.4*	5.3
-1	15	3	6.3	6.7
1	15	4	8.9	-7.8
-1	15	4	10.7	-9.2
-2	0	2	260.5	-256.2
2	0	4	83.4	85.2
-2	0	4	154.3	146.0
2	0	6	34.5	-35.0
-2	0	6	74.4	-67.4
-2	0	8	28.3	26.3
-2	0	10	13.8	-8.6
-2	2	2	231.6	-162.9
2	2	3	18.9	23.4
2	2	4	38.5	44.3
-2	2	4	138.6	120.4
2	2	5	9.0	-11.2
-2	2	5	9.5	-11.8
2	2	6	20.6	-17.6
-2	2	6	67.8	-65.5
-2	2	7	4.1	4.9
-2	2	8	32.0	28.2
-2	2	9	4.3*	-1.3
-2	2	10	14.0	-9.6
2	4	0	89.5	95.2
2	4	1	101.3	-88.1
2	4	2	61.4	-66.1
-2	4	2	99.9	-97.6
2	4	3	46.6	50.5
-2	4	3	99.7	91.8
2	4	4	32.3	34.1
-2	4	4	75.9	70.6
2	4	5	23.6	-23.0
-2	4	5	59.5	-53.9
2	4	6	13.9	-13.6
-2	4	6	42.2	-37.8
-2	4	7	24.8	25.0
-2	4	8	14.8	15.6
-2	4	9	9.9	-9.4
-2	4	10	8.4	-5.0
2	6	0	53.9	55.1
2	6	1	65.1	-62.1
-2	6	1	92.1	-82.4
2	6	2	33.4	-36.4
-2	6	2	62.2	-59.7
2	6	3	33.7	35.2
-2	6	3	85.9	78.7
2	6	4	18.2	18.3
-2	6	4	47.5	45.4
2	6	5	16.5	-15.5
-2	6	5	61.3	-53.6
2	6	6	9.9	-7.2
-2	6	6	26.3	-25.5
-2	6	7	27.2	27.4
-2	6	8	10.4	11.0
-2	6	9	12.6	-10.8
-2	6	10	6.8*	-3.7
2	8	0	7.8	8.0
2	8	1	64.7	-59.0
-2	8	1	66.8	-66.9
2	8	2	8.9	-8.8
-2	8	2	4.0*	-2.9
2	8	3	39.4	38.0
-2	8	3	50.8	55.1
2	8	4	3.5	5.7
-2	8	4	4.4	-2.0
2	8	5	19.0	-13.3
-2	8	5	38.0	-33.4
2	8	6	6.1*	-2.3
-2	8	6	3.3*	3.6
-2	8	7	16.4	15.2
-2	8	8	3.1*	-2.8
-2	8	9	6.7	-5.3
2	10	0	9.4	-10.6
2	10	1	51.8	-44.4
-2	10	1	53.9	-52.8
2	10	2	8.1	9.3
-2	10	2	7.2	8.6
2	10	3	30.1	28.0
-2	10	3	46.6	46.7
2	10	4	3.9	-6.0
-2	10	4	3.8*	-5.0
2	10	5	17.0	-13.6
-2	10	5	36.3	-30.9
2	10	6	6.8*	2.9
-2	10	6	3.6*	2.2
-2	10	7	16.0	15.7
-2	10	8	3.4*	-.8
2	12	0	8.6	-9.7
2	12	1	24.9	-23.5
-2	12	1	25.8	-27.3
2	12	2	7.8	7.2
-2	12	2	7.4	9.6
2	12	3	15.3	15.3
-2	12	3	20.5	23.7
2	12	4	3.4*	-3.9
-2	12	4	4.2*	-7.0
2	12	5	7.1	-7.5
-2	12	5	16.4	-15.5
-2	12	6	4.0*	3.8
-2	12	7	5.8	7.7
2	14	0	9.6	-11.3
2	14	1	10.0	-9.3
-2	14	1	10.7	-11.9
2	14	2	9.4	8.2
-2	14	2	11.2	11.6
2	14	3	5.9	5.5
-2	14	3	8.7	11.6
-2	14	4	6.1	-9.3
-2	14	5	10.4	-8.4
-2	14	6	4.4*	5.5
-2	14	7	6.3*	4.6
2	16	0	6.5	-7.5
2	16	1	6.3	-5.5
-2	16	1	4.5*	-5.8
-2	16	2	8.9	7.9
-2	16	3	4.6*	4.6
-3	1	2	189.8	-144.0
-3	1	3	72.2	62.7
3	1	4	30.6	33.6
-3	1	4	124.9	115.8
3	1	5	3.4*	1.6
-3	1	5	40.3	-40.6
-3	1	6	75.4	-67.1
-3	1	7	16.7	18.4
-3	1	8	29.5	29.4
-3	1	9	3.9*	-6.2
-3	1	10	13.4	-10.0
-3	1	11	8.6*	1.2
3	3	0	103.7	101.0
3	3	1	44.7	-48.6
3	3	2	55.6	-64.5
3	3	3	25.2	27.7
-3	3	3	60.2	55.9
3	3	4	28.7	30.7
-3	3	4	98.6	86.0
3	3	5	12.8	-12.3
-3	3	5	37.0	-36.9
-3	3	6	56.7	-48.4
-3	3	7	18.5	18.5
-3	3	8	20.9	20.6
-3	3	9	7.0	-7.4
-3	3	10	10.7	-6.7
-3	3	11	6.8*	2.4
3	5	0	71.4	69.9
3	5	1	64.8	-62.0
-3	5	1	90.4	-83.3
3	5	2	42.8	-48.2
-3	5	2	73.1	-73.6
3	5	3	34.8	34.7
-3	5	3	74.0	80.0
3	5	4	25.7	25.5
-3	5	4	58.1	56.6
3	5	5	16.4	-15.2
-3	5	5	55.4	-55.3
-3	5	6	36.6	-33.3
-3	5	7	29.3	29.1
-3	5	8	16.5	15.7
-3	5	9	10.7	-12.0
-3	5	10	6.5	-6.1
-3	5	11	7.1*	3.9
3	7	0	42.9	40.8
3	7	1	63.2	-57.2
-3	7	1	81.0	-71.3
3	7	2	21.5	-23.5
-3	7	2	52.8	-51.7
3	7	3	37.3	34.0
-3	7	3	62.4	64.5
3	7	4	11.6	10.5
-3	7	4	43.6	45.7
3	7	5	19.0	-15.4
-3	7	5	43.6	-42.9
-3	7	6	32.2	-29.2
-3	7	7	24.5	21.7
-3	7	8	13.4	14.2
-3	7	9	9.3	-8.6
-3	7	10	5.3*	-5.3
3	9	0	4.3	6.8
3	9	1	50.5	-43.5
-3	9	1	62.8	-60.0
3	9	2	3.1	-5.2
-3	9	2	7.0	-6.4
3	9	3	23.8	23.6
-3	9	3	58.4	60.6
3	9	4	4.5*	3.0
-3	9	4	3.2*	4.4
3	9	5	14.1	-9.8
-3	9	5	43.2	-44.8
-3	9	6	3.7*	-2.3
-3	9	7	26.5	24.7
-3	9	8	2.9*	1.0
-3	9	9	10.6	-10.2
3	11	0	6.9	-7.2
3	11	1	26.3	-28.6
-3	11	1	33.7	-35.9
3	11	2	5.5	4.6
-3	11	2	9.1	8.0
3	11	3	15.6	17.3
-3	11	3	34.1	34.0
3	11	4	5.1*	-2.2
-3	11	4	4.7	-6.5
3	11	5	9.1	-9.1
-3	11	5	26.9	-24.4
-3	11	6	4.1*	3.5
-3	11	7	14.6	13.4
-3	11	8	3.1*	-1.6
3	13	0	9.5	-12.2
3	13	1	16.2	-13.3
-3	13	1	16.1	-16.6
3	13	2	8.0	7.8
-3	13	2	13.5	14.3
3	13	3	7.5	8.0
-3	13	3	16.1	15.6
-3	13	4	11.8	-12.5
-3	13	5	11.3	-11.0
-3	13	6	10.2	8.1
-3	13	7	7.9	5.9
-3	13	8	3.4*	-4.0
3	15	0	8.6	-10.6
3	15	1	5.7	-5.7
-3	15	1	6.3	-7.2
3	15	2	8.3	8.0
-3	15	2	9.8	10.8
-3	15	3	6.6	6.9
-3	15	4	5.7	-8.6
-3	15	6	4.9*	5.4
-4	0	2	156.6	-151.9
-4	0	4	155.5	130.1
-4	0	6	91.0	-83.6
-4	0	8	45.0	42.7
-4	0	10	20.1	-18.3
-4	0	12	7.1*	6.5
-4	2	1	4.7	-11.4
-4	2	2	166.4	-153.5
-4	2	3	4.4	7.9
4	2	4	23.6	26.5
-4	2	4	160.6	135.3
-4	2	5	7.1	-9.5
-4	2	6	85.3	-82.2
-4	2	7	6.5	7.6
-4	2	8	41.0	38.1
-4	2	9	3.4	-3.8
-4	2	10	13.3	-13.7
-4	2	11	5.0*	1.4
-4	2	12	7.1*	3.8
4	4	0	60.5	67.4
4	4	1	44.4	-52.7
-4	4	1	94.5	-78.6
4	4	2	38.5	-39.9
-4	4	2	98.2	-83.6
4	4	3	26.7	27.3
-4	4	3	103.5	83.3
4	4	4	17.7	18.1
-4	4	4	76.6	74.0
-4	4	5	65.6	-61.4
-4	4	6	46.4	-47.4
-4	4	7	39.4	33.8
-4	4	8	26.9	23.1
-4	4	9	13.6	-14.9
-4	4	10	9.6	-8.7
-4	4	11	5.2*	5.3
-4	4	12	7.3*	2.5
4	6	0	41.9	43.0
4	6	1	48.1	-51.6
-4	6	1	99.9	-78.6
4	6	2	21.9	-24.4
-4	6	2	58.5	-55.2
4	6	3	25.9	25.1
-4	6	3	94.6	85.0
4	6	4	12.8	10.5
-4	6	4	44.8	49.4
-4	6	5	63.9	-64.1
-4	6	6	30.3	-31.5
-4	6	7	41.0	35.2
-4	6	8	15.0	15.0
-4	6	9	14.6	-14.4
-4	6	10	4.2	-5.4
-4	6	11	5.4*	4.4
4	8	0	2.9*	-3.3
4	8	1	34.2	-34.1
-4	8	1	54.9	-46.2
4	8	2	2.6*	.4
-4	8	2	8.6	6.5
4	8	3	18.9	19.1
-4	8	3	47.7	47.2
4	8	4	5.7*	.5
-4	8	4	6.8	-6.7
-4	8	5	35.1	-36.3
-4	8	6	3.7*	4.3
-4	8	7	23.7	21.3
-4	8	8	3.6*	-1.9
-4	8	9	10.7	-9.7
-4	8	10	3.5*	.5
4	10	0	3.3*	-3.8
4	10	1	31.5	-30.3
-4	10	1	50.2	-42.4
4	10	2	3.0*	3.4
-4	10	2	3.7*	3.5
4	10	3	17.6	16.4
-4	10	3	44.3	44.4
4	10	4	6.6*	-2.3
-4	10	4	2.4*	-2.9
-4	10	5	28.5	-34.7
-4	10	6	4.1*	2.4
-4	10	7	24.3	20.4
-4	10	8	3.9*	-1.8
-4	10	9	10.8	-9.3
4	12	0	3.7	-6.5
4	12	1	13.6	-15.6
-4	12	1	21.6	-21.4
4	12	2	3.4*	4.1
-4	12	2	5.4	7.8
4	12	3	10.8	8.8
-4	12	3	20.4	22.1
4	12	4	7.3*	-1.9
-4	12	4	2.6*	-7.0
-4	12	5	12.5	-17.3
-4	12	6	4.5*	4.6
-4	12	7	12.9	10.3
-4	12	8	4.3*	-2.3
-4	12	9	3.4*	-4.7
4	14	0	5.9	-9.0
4	14	1	7.2	-8.1
-4	14	1	10.1	-11.8
4	14	2	4.8	5.6
-4	14	2	8.6	10.9
-4	14	3	12.2	12.6
-4	14	4	9.0	-9.9
-4	14	5	7.9	-9.0
-4	14	6	4.9*	6.7
-4	14	7	4.8*	5.7
-4	16	1	4.9*	-3.6
-4	16	2	6.6	7.3
-5	1	1	33.9	-41.8
-5	1	2	122.8	-109.8
-5	1	3	52.4	49.2
-5	1	4	112.4	105.7
-5	1	5	30.2	-31.8
-5	1	6	74.2	-71.9
-5	1	7	10.6	11.9
-5	1	8	45.2	36.2
-5	1	9	3.2*	-1.8
-5	1	10	13.6	-13.9
-5	1	11	3.2*	-.9
-5	1	12	5.3*	4.0
-5	1	13	7.5*	.8
5	3	0	42.6	58.4
5	3	1	24.1	-25.2
-5	3	1	31.7	-39.3
5	3	2	32.7	-31.4
-5	3	2	83.8	-80.8
5	3	3	11.7	12.5
-5	3	3	51.7	45.9
-5	3	4	95.4	80.4
-5	3	5	34.9	-39.5
-5	3	6	61.2	-57.3
-5	3	7	24.1	25.1
-5	3	8	40.0	30.1
-5	3	9	11.2	-12.3
-5	3	10	11.6	-12.0
-5	3	11	6.0	4.7
-5	3	12	5.4*	3.6
-5	3	13	7.6*	-1.4
5	5	0	38.1	39.7
5	5	1	36.2	-37.6
-5	5	1	54.9	-58.5
5	5	2	20.5	-23.1
-5	5	2	62.1	-53.0
5	5	3	19.0	18.5
-5	5	3	85.1	67.5
-5	5	4	61.7	53.8
-5	5	5	50.6	-56.2
-5	5	6	39.6	-41.0
-5	5	7	33.7	34.7
-5	5	8	29.9	24.0
-5	5	9	16.1	-16.5
-5	5	10	10.9	-11.1
-5	5	11	7.6	6.1
5	7	0	32.3	32.8
5	7	1	27.1	-29.6
-5	7	1	45.4	-45.7
5	7	2	16.7	-15.4
-5	7	2	49.5	-43.4
5	7	3	19.3	14.8
-5	7	3	58.2	-53.4
-5	7	4	40.9	40.8
-5	7	5	41.1	-46.5
-5	7	6	24.5	-27.4
-5	7	7	31.7	30.3
-5	7	8	13.9	13.7
-5	7	9	16.5	-15.1
-5	7	10	3.1	-5.2
-5	7	11	4.6	5.8
5	9	0	2.4*	2.8
5	9	1	31.3	-31.1
-5	9	1	51.3	-47.3
5	9	2	4.5*	-1.7
-5	9	2	3.4*	-3.9
5	9	3	15.8	15.3
-5	9	3	60.3	53.0
-5	9	4	3.3*	4.3
-5	9	5	39.9	-43.3
-5	9	6	3.5*	-3.7
-5	9	7	24.8	26.0
-5	9	8	4.1*	2.4
-5	9	9	12.6	-11.7
-5	9	10	3.1*	-1.3
5	11	0	3.5	-4.6
5	11	1	19.6	-17.4
-5	11	1	29.9	-25.8
5	11	2	5.1*	2.5
-5	11	2	5.5	6.2
5	11	3	8.9	9.1
-5	11	3	31.7	29.3
-5	11	4	3.7*	-6.0
-5	11	5	24.1	-25.2
-5	11	6	3.9*	4.2
-5	11	7	14.1	16.6
-5	11	8	4.4*	-2.2
-5	11	9	10.5	-8.5
-5	11	10	3.4*	.8
5	13	0	5.6	-9.3
5	13	1	8.0	-7.8
-5	13	1	10.4	-11.7
-5	13	2	9.7	12.0
5	13	3	7.6*	4.0
-5	13	3	13.9	13.4
-5	13	4	11.9	-11.5
-5	13	5	9.6	-11.5
-5	13	6	5.5	8.2
-5	13	7	6.3	7.5
-5	13	8	4.8*	-4.4
5	15	0	4.4	-6.4
-5	15	1	4.4*	-5.3

Table 4 (cont.)

HH	KK	LL	F(OBS)	F(CALC)

* indicates unobserved reflection.   Value given corresponds to one half minimum observable intensity.

Discussion

The packing of the molecules in the crystal is shown in Fig. 2. The external N–I distance is 3·18 Å. This is appreciably shorter than the van der Waals distance of 3·65 Å, but is not so short as the distance in ICN (Ketelaar & Zwartsenberg, 1939; Townes & Dailey, 1952) of 2·80 Å. This latter distance was obtained by subtracting the sum of the gas phase I–C and C–N distances from the I–I distance in the crystal and

may be wrong by, at most, 0·1–0·2 Å. The external bond, therefore, is weaker in p-iodobenzonitrile than in iodine cyanide.

Of the distances in the molecule only the C(4)–C(5) and C–N distances may be different from the expected value. For a C–C single bond between sp^2 and sp hybridized atoms one would expect 1·42 Å (Bent, 1962) compared with the 1·37 we find, and for the C–N one would expect 1·16 compared with the 1·20 we find. Both of these differences are slightly larger than

twice the estimated standard deviations, but, as discussed above, the diagonal approximation used to estimate the standard deviation in the positional parameter gives optimistic estimates. If one ignores the normal I–C distance and takes the shortest C–C distance in the ring as significantly shorter, then all of the distances between light atoms suggest that the resonance forms
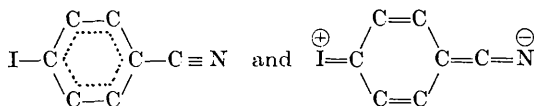
are both important. The second form could contribute to the intermolecular interaction.

It is not apparent why the external bond in ICN should be so much stronger than in this molecule. Except for the N–I there are no unusually short distances between the molecules. In particular the hydrogen atoms on one chain of molecules do not appear to be interfering with the formation of N–I bonds on the next chain. One possibility for the decrease in strength is that the σ bonds in ICN are affected, that the external interaction involves a d orbital which then contributes to the I–C σ bond and causes some rehybridization of the C and N σ orbitals, and that all this rehybridization is necessary for the formation of the external bond. This would not be possible with the benzene ring in between, and the bond would be weakened.

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The Crystal Structure of Silver Cyanate

BY DOYLE BRITTON* AND J. D. DUNITZ

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, Zürich, Switzerland

Silver cyanate is monoclinic, $a = 5\cdot473$, $b = 6\cdot372$, $c = 3\cdot416$ Å, $\beta = 91° 0'$, $Z = 2$, space group $P2_1/m$. The structure has been determined, and refined by full-matrix least-squares analysis of three-dimensional counter data. The silver atoms occupy positions $2(a)$ $(0, 0, 0, etc.)$, the other atoms positions $2(e)$ $(x, \frac{1}{4}, z, etc.)$ with $x_N = 0\cdot786$, $z_N = 0\cdot221$; $x_C = 0\cdot579$, $z_C = 0\cdot326$; $x_O = 0\cdot377$, $z_O = 0\cdot441$. Each silver atom has two linearly coordinated nitrogen atoms at $2\cdot115$ Å; distances within the linear cyanate group are, $N–C = 1\cdot195 \pm 0\cdot011$, $C–O = 1\cdot180 \pm 0\cdot011$ Å.

Introduction

Silver cyanate and silver fulminate provided the first example of isomerism (Liebig & Gay-Lussac, 1824).

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* Present address: Department of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.

† A reinvestigation of potassium cyanate in this laboratory confirms that the crystals are tetragonal, $a = 6\cdot096$, $c = 7\cdot056$ Å, space group $I4/mcm$, in agreement with the early work of Hendricks & Pauling (1925).

In spite of the simplicity of these compounds, the crystal structure of neither appears to have been established. As the first part of an investigation of the structural relationships between these compounds in the solid state, we describe here the crystal structure of silver cyanate. The structures of two polymorphic forms of silver fulminate will be reported later.

Two determinations of unit-cell dimensions and