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The Crystal Structure of Cyanogen Chloride

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Solid cyanogen chloride, ClCN, at about −30° C. is orthorhombic with $a = 5{\cdot}68$, $b = 3{\cdot}98$, $c = 5{\cdot}74$ Å. The space group is *Pmmn* and there are two molecules per unit cell. The molecules are arranged in infinite linear chains parallel to the c axis. The packing of the chains approximates closest packing of cylinders. The distance along a chain between the ends of adjacent molecules is short, only 3·01 Å. This indicates that strong intermolecular attractions exist along the chains. Cyanogen chloride is isostructural with cyanogen bromide.

Introduction

Before this work was begun it was expected that the ClCN molecules would be arranged in linear chains and that an exceptionally strong attraction would act between the chlorine atom of one molecule and the nitrogen atom of another. Evidence for such an attraction came from studies of cyanogen *iodide*: Townes & Dailey (1952) concluded, from the value of the nuclear quadrupole coupling constant of iodine in solid ICN, that the molecules are joined by a bond with about 10% single covalent character. This is consistent with the crystal structure determination of Ketelaar & Zwartsenberg (1939); the iodine atom of one molecule is only about 2·8 Å distant from the nitrogen atom of the next molecule, which is far less than the sum of the van der Waals radii. A similar condition has very recently been found in a crystal structure and quadrupole coupling study of cyanogen bromide (Geller & Schawlow, 1955). The present study of cyanogen chloride was undertaken with the hope that the smaller halogen in this compound would permit accurate interatomic distances to be determined, which was not possible in the cases of the bromide and iodide.

Experimental methods

One sample of cyanogen chloride was kindly provided by The American Cyanamid Company through Dr D. J. Berets. Additional material was prepared by the method of Coleman, Leeper & Schulze (1946). The crude product was agitated with mercury, sodium bicarbonate, and zinc oxide to remove the expected impurities: chlorine, hydrogen chloride, and hydrogen cyanide. It was then dried over calcium chloride, distilled, and sealed into thin-walled Pyrex capillaries. The melting point is −6° C.

Rotation, oscillation, and Weissenberg X-ray photographs were prepared at −30±5° C. with Cu $K\alpha$ or Mo $K\alpha$ radiation. The samples were kept at the desired temperature by directing a stream of cold nitrogen gas over the capillaries.

Single crystals were obtained by melting and refreezing along the length of the capillary (Abrahams, Collin, Lipscomb & Reed, 1950). The crystals showed a strong tendency to grow with the c axis parallel to the axis of the capillary. Only once did a crystal grow spontaneously in a different orientation and it was very badly twinned. (Twinning of the crystals occurred very readily on the (110) plane.) It was possible, however, to grow a sample with the [110] zone axis parallel to the capillary axis in a capillary with a right angle bend near the end. The crystal was started in the end of the capillary and grown around the bend without change of orientation. These two orientations sufficed to permit all measurable reflections to be surveyed, since the rather rapid decline of intensity with increasing angle prevents missing any reflections at large θ.

All of the intensity measurements were taken from equi-inclination Weissenberg photographs. The intensities were estimated visually by the multiple-film technique (Robertson, 1943). An approximate correction was applied to intensities recorded with Cu $K\alpha$ radiation to adjust for the difference in absorption by the sample, capillary, and film for different layer lines. This was neglected for Mo $K\alpha$ radiation. Relative structure-factor magnitudes were extracted in the usual way. A total of 82 independent reflections were of measurable intensity.

Structure determination

Unit cell and space group

Several preliminary oscillation photographs were indexed on an orthorhombic lattice. This indexing made it possible to index two subsequent rotation pictures with the crystal rotating about c and the [110] zone axis respectively. These rotation pictures were prepared with Cu $K\alpha$ radiation and were calibrated with a superimposed NaCl powder picture. Measurements on the equatorial layers of these photographs yielded the axial lengths

$$a=3\cdot684\pm0\cdot007,\quad b=3\cdot977\pm0\cdot004,\quad c=5\cdot740\pm0\cdot002\ \text{Å}\ .$$

(All tolerances mentioned in this paper represent standard deviations, all of which were derived from the normal equations in a least-squares treatment (Whittaker & Robinson, 1940). The usual 'limit of error' is greater than this, so that the third decimal place in the axial lengths is of doubtful significance.)

To determine the density, ClCN was distilled into a 1 ml. bulb on a vacuum line, and then slowly frozen. Mercury was added to fill the gap between sample and bulb wall. The bulb was sealed off, the level of mercury in the neck at −30° C. was marked, and the whole was weighed. The bulb was carefully opened and the ClCN was allowed to vaporize. The empty bulb and the mercury were weighed separately. The volume of the bulb at −30° C. was subsequently determined. From these measurements, the density was found to be 1·55 g.cm.$^{-3}$ at −30° C. For two molecules in the unit cell the calculated X-ray density is 1·58 g.cm.$^{-3}$.

The only systematic absences were reflections $hk0$ with $h+k$ odd. The orthorhombic space groups consistent with these extinctions are $Pm2_1n$ and $Pmmn$. The two molecules must therefore lie in special positions; in $Pm2_1n$ they must lie in mirror planes, while in $Pmmn$ they must lie on the intersections of mirror planes.

A Patterson projection, $P(u, v)$, was prepared using rough structure factors taken from the preliminary oscillation pictures. The projection exhibited perfectly circular peaks at (0, 0) and $(\frac{1}{2}, \frac{1}{2})$, indicating that the molecules are aligned parallel to the c axis. This in turn indicates that the proper space group is probably $Pmmn$ since this arrangement arises automatically in this group whereas it could come about only by accident in $Pm2_1n$. This conclusion was confirmed by the success of the refinement. Consequently the coordinates of all the independent atoms in the cell are $(\frac{1}{4}, \frac{1}{4}, z)$, when the origin is taken at a center of symmetry.

The trial structure

It was noticed that reflections $hk1$ and $hk2$ with $h+k$ even were accidentally absent. (Reflections 001 and 002 are observable, but at this stage they had not yet been examined.) Hence, a trial structure was obtained by minimizing these structure factors with respect to the z coordinate of the chlorine atom while keeping the intramolecular distances fixed at reasonable values.

Fourier refinement

The important reflections $00l$ and $10l$ were outside the range of the photographs at hand at this stage. Consequently, calculated values were supplied, at this stage, for the ten unrecorded reflections. Two successive electron-density line syntheses, $\varrho(\frac{1}{4}, \frac{1}{4}, z)$, were computed. The second, which produced no further changes of sign, was followed by a 'back-shift' synthesis (Booth, 1946).

A new line synthesis, $\varrho(\frac{1}{4}, \frac{1}{4}, z)$, was subsequently computed with the complete set of observed structure factors. Two successive back-shifts were applied; the structure factors used in the second back-shift were calculated from the results of the first. The atom centers were located by fitting error curves to the electron density values near each peak (Carpenter & Donohue, 1950). The Fourier refinement appeared to have converged at this point and the resulting atomic coordinates are included in Table 1 under the heading 'Fourier'.

The preceding back-shift corrections were large: 0·002, −0·007, and 0·011 for the z coordinate of the chlorine, carbon, and nitrogen atoms, respectively. Even larger back-shifts were found by Geller &

Table 1. *Atomic coordinates and discrepancy factors for* ClCN

		Least squares	
Quantity	Fourier	I	II
z(Cl)	0·149	0·1499	0·1499
z(C)	0·424	0·4237	0·4239
z(N)	0·624	0·6255	0·6258
R (%)	7·8	—	8·0

Schawlow (1955) in BrCN. It seems not unreasonable that this should be the case when the asymmetric unit contains only one heavy atom and two light atoms, all in special positions. Further justification for the use of these large corrections comes from the closeness of the corrected positions to those obtained in the subsequent least-squares refinement.

An anisotropic temperature factor of the form $\exp(-B_1h^2-B_2k^2-B_3l^2)$ was next applied, although an isotropic form had been used to obtain the F_c values which were used in the back-shift. The parameters of this expression were evaluated by a least-squares procedure which minimized $\Sigma|\log(F_c/F_o)|^2$. With this temperature factor, the discrepancy value recorded for the Fourier refinement in Table 1 was obtained.

Beevers–Lipson strips (Beevers, 1952) were used for all Fourier syntheses.

Least-squares refinement

Since the limit of the Fourier refinement had been reached, it was decided to continue with a least-squares refinement (Hughes, 1941), wherein not only the atomic coordinates but also the scale and temperature-factor parameters were allowed to vary. The observational equations were weighted by the function $w = N(hkl)/F(hkl)_o^2$, where $N(hkl)$ is the number of independent measurements of $F(hkl)_o$. This amounts to assuming that each individual intensity measurement had a standard deviation equal to a constant fraction of the intensity value. This appears to be reasonable for visual intensity estimation. The results of the first cycle of least-squares refinement are included in Table 1 under the heading 'I'.

Since the changes in the first cycle proved to be appreciable, a second cycle was undertaken. The results are presented in Table 1 under the heading 'II'. Evidently the refinement had converged since the coordinate changes were very small, and the largest change in the other parameters was a 1·5% change in B_2. The increase in the discrepancy value from the Fourier to the final least-squares value is not significant.

The standard deviations of the atomic coordinates were computed from the normal equations (Whittaker & Robinson, 1940). They are: $\sigma(\mathrm{Cl}) = 0{\cdot}0005$, $\sigma(\mathrm{C}) = 0{\cdot}0029$, and $\sigma(\mathrm{N}) = 0{\cdot}0019$, in fractions of the c axial length. These are 'internal estimates of standard errors due to errors in the experimental data and form factors' (Shoemaker, Donohue, Schomaker & Corey, 1950).

The final values of the temperature-factor para-

Table 2. *Calculated and observed structure factors for* ClCN

hkl	F_c	F_o
310	17·2	17·8
220	14·8	15·4
400	12·7	13·5
130	8·4	8·4
040	3·5	3·8
530	2·4	< 3·7
620	2·6	< 3·7
440	1·6	2·0
710	2·0	< 3·8
110	−36·5	34·2
200	−33·3	30·8
020	−20·1	20·7
420	− 7·2	7·6
510	− 6·7	7·0
330	− 4·4	5·7
240	− 2·8	3·5
600	− 4·3	4·5
150	− 1·1	< 3·9
001	0·3	< 0·9
311	1·7	< 2·5
111	− 1·4	< 1·8
201	− 1·6	< 1·9
211	10·3	10·4
301	8·5	8·1
121	7·7	7·5
031	4·1	3·8
521	2·2	< 3·3
431	1·8	3·0
611	2·0	< 3·5
101	−17·4	14·1
011	−14·7	13·2
321	− 4·9	4·8
411	− 5·0	4·9
231	− 3·3	3·6
501	− 3·6	3·1
141	− 1·6	< 3·3
002	− 3·2	3·0
312	− 1·6	< 2·4
112	2·6	2·7
202	2·5	2·7
022	1·8	< 2·2
212	13·4	13·1
302	11·1	10·9
122	10·0	8·9
032	5·1	4·2
522	2·6	< 3·3
102	−20·9	19·8
012	−18·6	17·6
322	− 6·2	5·7
412	− 6·3	5·9
232	− 4·1	3·7
502	− 4·4	4·1
142	− 1·9	< 3·3
003	−10·8	13·0
313	− 5·7	5·7
223	− 5·0	5·5
403	− 4·5	4·2
133	− 3·0	3·7
043	− 1·3	< 3·4
113	8·7	9·3
203	8·4	8·7
023	6·1	6·2
423	2·7	3·5
513	2·5	< 3·1
213	3·2	3·5
303	2·8	2·7
123	2·5	2·8
033	1·4	1·6
523	0·7	< 3·4
103	− 4·3	4·1
013	− 3·9	3·9
323	− 1·7	< 2·7
004	−11·8	13·0
314	− 6·1	5·6
224	− 5·4	5·2
404	− 4·8	4·9
134	− 3·3	3·7
044	− 1·4	< 3·2
114	9·5	9·2
204	9·2	8·8
024	6·6	6·1
424	2·8	3·4
514	2·7	< 3·2
214	− 5·6	5·7
304	− 4·9	4·7
124	− 4·4	3·7
034	− 2·5	3·4
524	− 1·7	< 3·4
104	7·6	7·9
014	7·0	6·2
324	2·9	3·0
414	3·0	< 2·8
234	2·0	< 3·0
005	2·3	3·4
315	1·3	< 2·5
115	− 1·9	< 1·8
205	− 1·8	< 1·9
215	− 3·2	3·7
305	− 2·8	< 2·4
125	− 2·5	3·0
035	− 1·4	< 2·9
105	4·2	4·1
015	3·9	3·6
325	1·7	< 2·8
006	2·6	3·7
316	1·4	< 2·1
116	− 2·1	3·0
206	− 2·1	< 2·7
216	− 2·8	3·4
306	− 2·5	< 2·5
106	3·7	3·7
016	3·4	3·4
326	1·5	< 1·9
007	2·6	3·0
317	1·4	< 1·9
117	− 2·1	2·3
207	− 2·1	1·7
027	− 1·5	< 1·7

meters correspond to r.m.s. vibration amplitudes (of an average atom) of 0·27, 0·30, and 0·23 Å in the x, y and z directions respectively.

Observed and final calculated structure factors are compared in Table 2. Reflections are arranged according to similarity of structure factors. Unobserved reflections were tabulated only through the first consistent pair in each group since the compatibility of calculated values with the minimum observable values for weak reflections becomes more favorable thereafter. The atom form factors of Viervoll & Ögrim (1949) were employed.

Discussion of the structure

Cyanogen chloride, bromide (Geller & Schawlow, 1955) and iodide (Ketelaar & Zwartsenberg, 1939) all form linear chain structures with shorter-than-normal distances between the molecules along a chain. The chloride and bromide structures are isomorphous, but the iodide has a somewhat different, trigonal, structure. The structures are illustrated for comparison in Fig. 1. All three structures are drawn to the same scale. Intramolecular distances in the iodide and bromide sketches are those reported for the gas (Townes, Holden & Merritt, 1948; Smith, Ring, Smith & Gordy, 1948), since no accurate values could be obtained from the X-ray investigations. The corresponding distances in the chloride sketch are those obtained in the present work. The atoms are drawn with van der Waals radii (Pauling, 1940) and the 'compression' caused by the short intermolecular distances is depicted by shaded areas.

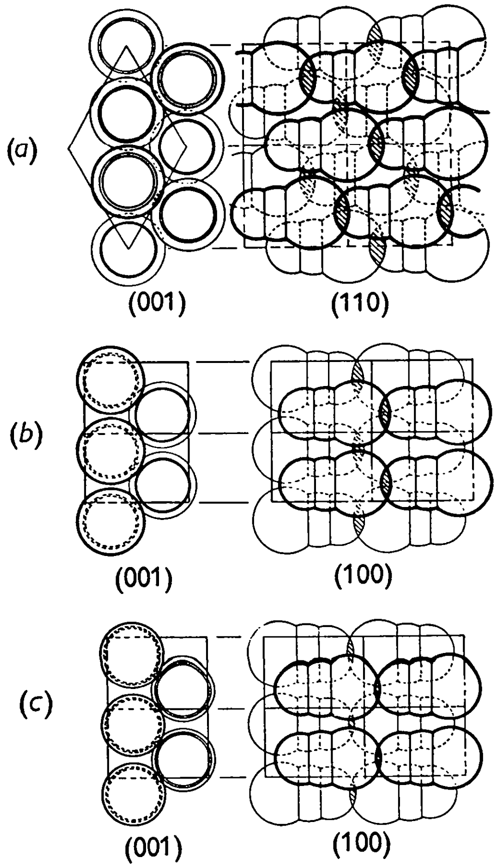

Fig. 1. Cyanogen halide structures: (a) ICN, (b) BrCN, (c) ClCN. Indices give the plane of each projection. In ICN the indices refer to hexagonal axes; in BrCN the axes have been relabelled to correspond to those in ClCN.

In cyanogen chloride the molecules lie in chains parallel to the c axis (Fig. 1(c)). The chains are packed side by side in plane layers; the distance between adjacent chains in the same layer is 3·98 Å. These layers are stacked such that the chains in adjacent layers are anti-parallel, and placed so that ridges in one layer fit into valleys in the neighboring layers. Thus each chain is surrounded by four anti-parallel chains at distances of 3·47 Å, and by two parallel chains at distances of 3·98 Å, so that the structure approximates close packing of cylinders.

The chains are packed together loosely. The shortest Cl–Cl distance between chains is 3·87 Å, while twice the van der Waals radius of chlorine is 3·60 Å. The next shortest distances, between chains, are Cl–Cl, 3·98 Å, and Cl–N, 3·70 Å.

Along the chains, however, the molecules are packed together more tightly than might be expected. The length of an isolated ClCN molecule is predicted to be 6·1 Å by adding the van der Waals radii of chlorine (1·8 Å) and nitrogen (1·5 Å) to the Cl--N length (2·79 Å) found in the gas (Townes *et al.*, 1948). The repeat distance in the crystal corresponding to this length is only 5·74 Å. A similar but more drastic 'compression' (cf. Table 4) has been observed in ICN and BrCN.

The shortening in ICN and BrCN has been interpreted in terms of three important resonance hybrids for the cyanogen halides (Townes & Dailey, 1952; Geller & Schawlow, 1955). These are shown in Table 3 together with the estimated contributions of each for the iodide and the bromide in both vapor and crystal. These contributions gave good agreement between the calculated and observed nuclear quadrupole coupling constants. Hybrid III, which contains a covalent intermolecular bond between the nitrogen and halogen atoms, was believed to be the cause of the overall

Table 3. *Estimated contributions of hybrid structures in solid and gaseous cyanogen halides*

		X = I*		X = Br†	
		Solid	Gas	Solid	Gas
Hybrid I	$X-C\equiv N$	88%	87%	76%	74%
Hybrid II	$\overset{+}{X}=C=\overset{-}{N}$	2	13	15	26
Hybrid III	$-\overset{+}{X}-C=\overset{-}{N}-$	10	—	9	—

* Townes & Dailey, 1952.
† Geller & Schawlow, 1955.

Table 4. *Reported bond lengths in the cyanogen halides*

Halide	State	r(C–X) (Å)	r(C–N) (Å)	Compression (Å)*	Method†	Ref.
I	Gas	1·995	(1·158)		MW	1
	Gas	1·995	1·159		MW	2
	Solid	—	—	0·8	XRD	3
Br	Gas	1·79 ± 0·02	1·13 ± 0·04		ED	4
	Gas	1·790	1·158		MW	1
	Gas	1·789	1·160		MW	2
	Solid	—	—	0·6	XRD	5
Cl	Gas	1·67 ± 0·02	1·13 ± 0·03		ED	4
	Gas	1·629	1·163		MW	1
	Gas	1·630	1·163		MW	2
	Solid	$1{\cdot}57 \pm 0{\cdot}01_8$	$1{\cdot}16 \pm 0{\cdot}02_0$	0·4	XRD	6

* Compression = sum of the bond lengths (Ref. 2 for X = I, Br; Ref. 6 for X = Cl) and the van der Waals radii of N and X minus the repeat distance in the crystal corresponding to the length of the molecule.

† MW = microwave spectra; XRD = X-ray diffraction; ED = electron diffraction.

References: 1. Townes *et al.*, 1948. 2. Smith *et al.*, 1948. 3. Ketelaar & Zwartsenberg, 1939. 4. Beach & Turkevich, 1939. 5. Geller & Schawlow, 1955. 6. This work.

shortening of the chains in the crystal. The individual bond lengths in the bromide and iodide crystals unfortunately could not be determined precisely enough to give further confirmation of this explanation.

In cyanogen chloride, however, the individual bond lengths are accurate enough to show that the C–Cl bond is significantly shorter in the crystal than in the gas (cf. Table 4; the gas values of the C–Cl bond length are three standard deviations greater than the crystal value). Nuclear quadrupole coupling constant data are not available. Accordingly, it seems appropriate to carry the analysis of the cyanogen chloride structure as far as possible before considering the conclusions from quadrupole data.

The shortening of the C–Cl bond on passing from the vapor to the crystal would be found if either hybrid II or hybrid III were to become more important in the crystal, as a consequence of the double bond in II or of the charges on the carbon and chlorine atoms in III. Similarly, either II or III would lead to a shortened N · · · Cl distance in the solid because of the charges on the nitrogen and chlorine atoms in II or of the bond between them in III. The fact that the C–N distance is slightly greater than the normal triple bond length does not discriminate between II and III. Thus the crystal structure alone indicates that either II or III or both contributes increasingly in passing from vapor to crystal, but it does not indicate if one is more important than the other.

Consideration of the theoretical shape of hybrid III argues against its importance. Hybrid III would normally be bent because the unshared electron-pairs on the carbon and nitrogen atoms occupy some portion of the solid angle around these atoms. But the Patterson projection, $P(u, v)$, showed that the molecules were linear. Then hybrid III can participate only if the unshared electron-pairs on the carbon and nitrogen atoms are confined to pure $2p$ orbitals. This situation is energetically unfavorable because an unshared pair normally occupies a hybrid orbital comprised of more than its proportionate share of s orbital. Consequently, this line of argument suggests that hybrid II is a more significant contributor than is hybrid III in the cyanogen chloride structure. This in turn indicates that the short intermolecular distance is due to electrostatic attraction between the chlorine atom of one molecule and the nitrogen of the next, and perhaps to changes in the normal van der Waals radii.

Since this argument against structure III is based entirely upon the linearity of the molecules, further investigation of this aspect seemed appropriate. If the molecules were actually bent but were rotating or disordered about the chain axis, they would be nearly

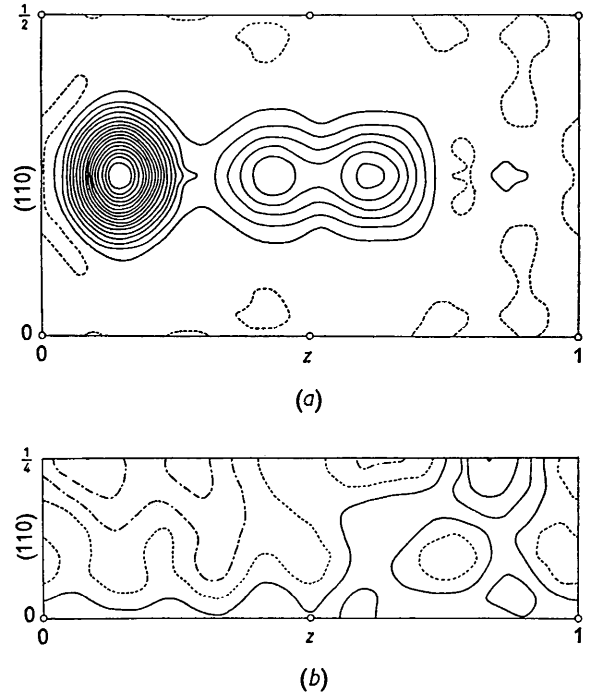

Fig. 2. (*a*) Electron-density section, $\varrho(x, x, z)$. Contours are drawn at intervals of 1·0 e.Å^{-3}, with the zero contour broken.

(*b*) Electron-density difference section, $\varrho_o(x, x, z) - \varrho_c(x, x, z)$. Contours are drawn at intervals of 0·1 e.Å^{-3}. Solid contours represent positive regions, chain contours negative regions, while the zero contour is broken.

indistinguishable from a fixed linear molecule in the Patterson projection, $P(u, v)$. But an electron-density section through the centers of the atoms should reveal these conditions. Therefore, a three-dimensional electron-density section, $\varrho(x, x, z)$, was prepared to determine whether the atoms departed significantly from circular cross-section in this plane passing through the chain axes. The final observed structure factors were used in this synthesis, which is shown in Fig. 2(*a*). The carbon and nitrogen atoms appear normal. The chlorine atom, on the other hand, appears to be elongated. However, a difference synthesis, $\varrho_o - \varrho_c$, (Booth, 1948), shows that this distortion is merely a result of series termination (cf. Fig. 2(*b*)). Hence, as far as can be determined from this study, the molecules are truly linear.

If, now, the interpretation that hybrid II is the more important contributor in the cyanogen chloride crystal is carried over to cyanogen bromide and iodide, it should become even more prominent because the less electronegative halogens are less reluctant to assume a positive charge, as hybrid II requires. This prediction is consistent with what is known of the structure of BrCN and ICN: the 'compression' in Fig. 1 and Table 4 increases from the chloride to the bromide to the iodide. (The magnitudes of the compressions are somewhat uncertain for BrCN and ICN because of the lack of knowledge of the bond distances in the crystals, but the overall shortening of the chains from what would be expected from the vapor molecule is real.)

Townes & Dailey (1952) have reported, however, that the charge distribution of the hybrid II is electrostatically unstable in the ICN lattice relative to the isolated molecules. A repetition of this calculation leads to the opposite conclusion. Since no details were given by the former workers, it is not possible to locate the source of disagreement. In the present work, the electrostatic lattice energy was calculated by essentially the method of Ewald (1921). Fractional point charges were located on the iodine and nitrogen atoms in the crystal, with the intramolecular $I \cdots N$ distance calculated from the length of the molecule in the vapor (Smith *et al.*, 1948). The result is that the total electrostatic energy of this charge distribution corresponding to hybrid II is $-166x^2$ kcal./mole, where x is the fraction of the electronic charge on either atom. Of this amount, $-105x^2$ kcal./mole is contributed by the electrostatic energy within separate molecules, so that the difference, $-61x^2$ kcal./mole, indicates the stabilization of hybrid II in the crystal relative to the vapor.* (The numerical value is correct only if other contributions to the energy difference between crystal and vapor are independent of x.) A similar calculation for hybrid II in cyanogen chloride shows that it is stabilized in the crystal by $40x^2$ kcal./mole. It seems reasonable to assume that this hybrid is also favored in the bromide crystal, although the calculation for this case was not carried out.

Thus far, the observations on all three compounds can be explained by an increasing contribution from hybrid II in the crystal. This explanation conflicts, however, with the interpretation of the nuclear quadrupole coupling data for BrCN and ICN. These data appear to require that hybrid III be important in the crystal. The purely structural data cannot decide whether hybrid III is a necessary ingredient. Quadrupole coupling measurements on cyanogen chloride are highly desirable to complete the picture.

One further feature of the structure determination which deserves some comment is the peak in the electron density at $(\frac{1}{4}, \frac{1}{4}, \frac{52}{60})$ (cf. Fig. 2(*a*)). This peak has a maximum density of 1·3 e.Å^{-3}, which amounts to 20% of the adjacent nitrogen peak height, but the difference synthesis (Fig. 2(*b*)) shows a peak of only +0·4 e.Å^{-3} at this point. This would still seem to be substantial. However, this peak is located very near the mirror image of the chlorine atom position; consequently the Fourier terms in the electron density are large at this peak so that the density there is a small difference of large numbers. Hence small errors in F easily give rise to a false peak at this point.

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The Complete Incoherent Scattering Function for Carbon†

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The frequent use of organic substances to put X-ray intensities on an absolute basis gives special importance to the calculation of the incoherent scattering from carbon. Calculations by Berghuis *et al.* for the coherent scattering showed appreciable divergences from older work, and we were motivated to extend the calculations to the incoherent scattering.

The wave functions of Jucys computed by the Hartree–Fock method with exchange were used in computing the complete incoherent scattering function for the configuration $1s^2 2s 2p^3$ and term value ^5S. The calculations show that the incoherent scattering at small and intermediate values of $(\sin\theta)/\lambda$ is appreciably less than previously predicted and more in agreement with the values found experimentally by Laval.

The frequent use of organic substances to put X-ray intensities on an absolute basis gives special importance to the calculation of the incoherent scattering from carbon. Berghuis *et al.* (1955) have recently calculated the atomic scattering factor for carbon, using the wave functions of Jucys (1947), which had been computed by the Hartree–Fock method with exchange. These calculations for the coherent scattering showed appreciable divergences from the older data, and we were thus motivated to extend the calculations to the incoherent scattering. Jucys' wave functions, which appear to be the best now available for carbon, were used.

The incoherent scattering in electron units can be written as $B^{-3}[Z-\mathscr{F}]$ (James, 1948, chap. 9).‡ B is the Breit–Dirac recoil correction factor, Z is the atomic number of the atom, and $\mathscr{F}$, the incoherent scattering function, is given by

$$\mathscr{F} = \sum_{j,k=1}^{Z} |f_{jk}|^2 \tag{1}$$

(James, 1948, chap. 3).

Here

$$f_{jk} = \int \psi_j^*(\mathbf{r})\alpha_j^* e^{i\mathbf{k}\cdot\mathbf{r}}\psi_k(\mathbf{r})\alpha_k dv\,, \tag{2}$$

where $\psi_j(\mathbf{r})$ is the spatial part of the jth one-electron wave function, α_j is the corresponding spin function, and $\mathbf{k}$ is the difference between incoming and outgoing wave vectors ($k = (4\pi\sin\theta)/\lambda$). We have calculated $\mathscr{F}$ for the configuration $1s^2 2s 2p^3$, and term value ^5S. Because the wave functions of this configuration transform orthogonally on axis rotation, $\mathscr{F}$ is independent of the orientation of $\mathbf{k}$. Furthermore, the hybridized atomic orbitals leading to tetrahedral bonding, as in diamond and the saturated hydrocarbons, are also formed by an orthogonal transformation on this configuration (Eyring, Walter & Kimball, 1944). Thus $\mathscr{F}$ is also a correct zero-order approximation for carbon in these covalent compounds.

For this configuration and term, $\mathscr{F}$ reduces to the form

$$\mathscr{F} = 2f_{1s}^2+f_{2s}^2+3f_{2p}^2+2f_{1s2s}^2+6f_{1s2p}^2+6f_{2s2p}^2+6f_{2p2p}^2\,, \tag{3}$$

where

$$\left.\begin{aligned}
f_{1s} &= \int_0^\infty R_{1s}(r)j_0(kr)R_{1s}(r)r^2dr\,,\\
f_{2s} &= \int_0^\infty R_{2s}(r)j_0(kr)R_{2s}(r)r^2dr\,,\\
f_{2p} &= \int_0^\infty R_{2p}(r)j_0(kr)R_{2p}(r)r^2dr\,,\\
f_{1s2s} &= \int_0^\infty R_{1s}(r)j_0(kr)R_{2s}(r)r^2dr\,,\\
f_{1s2p} &= \int_0^\infty R_{1s}(r)j_1(kr)R_{2p}(r)r^2dr\,,\\
f_{2s2p} &= \int_0^\infty R_{2s}(r)j_1(kr)R_{2p}(r)r^2dr\,,\\
f_{2p2p} &= \int_0^\infty R_{2p}(r)j_2(kr)R_{2p}(r)r^2dr\,.
\end{aligned}\right\} \tag{4}$$

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‡ The inverse second power would appear if numbers of quanta were being counted.