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NR-017-607

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Technical Report No. 2

THE CRYSTAL STRUCTURE OF CYANOGEN CHLORIDE

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1 November 1955

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ABSTRACT

The crystal structure of cyanogen chloride, ClCN, has been determined at about -30°C by X-ray diffraction techniques. The crystals are orthorhombic with cell dimensions $\underline{a}$ = 5.68, $\underline{b}$ = 3.98, and $\underline{c}$ = 5.74 Å. The space group is Pmmn. The molecules form infinite linear chains parallel to the $\underline{c}$ axis. The chains are packed so as to approximate closest packing of cylinders.

The distance along a chain between adjacent molecules is short, only 3.01 Å. This indicates that strong intermolecular attractions exist along the chains. The results can be explained by assuming resonance between the structures Cl-C ≡ N and $\overset{+}{Cl}$ = C = $\overline{N}$. Thus they do not provide any independent support for the suggestion of others that one important resonance hybrid is the polymer structure -$\overset{+}{Cl}$-$\overline{C}$ = N-.

THE CRYSTAL STRUCTURE OF CYANOGEN CHLORIDE

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 and Dailey (1952) concluded, from the value of the nuclear quadrupole coupling constant of I in solid ICN, that molecules are joined by a bond with about 10% single covalent character. This is consistent with the crystal structure determination of Ketelaar and Zwartsenberg (1939); the I atom of one molecule is only about 2.8 Å distant from the N 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 and Schawlow, 1955). This 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 Dr. D. J. Berets of American Cyanamid Co. Additional material was prepared by the method of Coleman, Leeper and Schulze (1946). The crude product was agitated with mercury, sodium bicarbonate,

and zinc oxide to remove chlorine, HCl, and HCN, the expected impurities. It was then dried over calcium chloride and distilled. Since the compound is gaseous at room temperature, it was sealed into thin-walled Pyrex capillaries for subsequent work.

Rotation, oscillation, and Weissenberg photographs were prepared at -30±5°C with CuKα or MoKα 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 the method of melting and refreezing along the length of the capillary (Abrahams, Collin, Lipscomb and Reed, 1950). The crystals showed a strong tendency to grown 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 by using 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 sin 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). They were corrected for Lorentz and polarization effects

to give observed relative structure factor magnitudes. In addition, an approximate correction was applied to intensities taken with CuKα radiation to adjust for the difference in absorption by the sample, capillary and film for different layer lines. This was neglected for MoKα radiation. Since the determination of the structure began before all the intensity data were at hand, notes on the structure factors entering into each stage of the refinement will be included in the discussion of the refinement.

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 CuKα radiation and were calibrated using a superimposed NaCl powder picture. Measurements on the equatorial layers of these photographs yielded the axial lengths a = 5.68±.06, b = 3.98±.01, and c = 5.74±.02 Å. (All tolerances mentioned in this work indicate standard deviations, all of which were derived from the normal equations in a least squares treatment (Whittaker and Robinson, 1940). The rather large value of the standard deviation in the a axial length is a direct result of this treatment.) The density of the crystal was measured pycnometrically and 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 Pmn and Pmmn. The two molecules must therefore lie in special positions; in Pmn they must lie in the mirror plane, while in Pmmn they must lie on the intersection of two mirror planes.

A Patterson projection, P(uv), was prepared using rough structure factors taken from the preliminary oscillation pictures. (The specimen from which these were prepared consisted of three fragments twinned about the c axis. It was impossible to correct for absorption, so reflections from all three fragments were combined judiciously to give approximate structure factors.) The projection exhibited perfectly circular peaks at (0,0) and (1/2, 1/2), indicating that the molecules are alligned parallel to the c axis. This in turn indicates that the proper space group is Pmmn since this arrangement arises automatically in this group whereas it could come about only by accident in Pmn. Consequently the coordinates of all the atoms in the cell are (1/4,1/4,z), when the origin is taken at the center of symmetry.

The trial structure

It was noticed that reflections (hkl) 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 intra-molecular distances fixed at reasonable values.

Fourier refinement

When a good single crystal was finally obtained, equi-inclination Weissenberg photographs were prepared with the crystal rotating about its c axis. The important reflections (00ℓ) and (10ℓ) were outside the range of these photographs. Consequently calculated values were supplied, at this stage, for the 10 unrecorded reflections. Two successive electron density line syntheses, $\rho(1/4,1/4,z)$, were computed. The second, which produced no further changes of sign, was followed by a "back shift" synthesis (Booth, 1946).

At last a single crystal was grown in an orientation which allowed the unobserved region of the reciprocal lattice to be explored. The photographs prepared with the crystal rotating about the [110] zone axis completed the intensity data. A total of 86 independent reflections was observed.

A new line synthesis, $\rho(1/4,1/4,z)$ was computed with the complete set of 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 and 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".

Table 1. Atomic coordinates and discrepancy factors for ClCN

Quantity	Fourier	L. S. I	L. S. II
z(Cl)/c	0.149	0.1499	0.1499
z(C)/c	0.424	0.4237	0.4239
z(N)/c	0.624	0.6255	0.6258
R (%)	7.8		8.0

An anisotropic temperature factor of the form $\exp(-B_1h^2 - B_2k^2 - B_3\ell^2)$ 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 $\sum|\log(F_c/F_o)|^2$. 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). 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 $\underline{w} = N(hk\ell)/F(hk\ell)_o^2$, where $N(hk\ell)$ is the number of independent measurements of $F(hk\ell)_o$. This amounts to assuming that each individual intensity measurement has 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 "L. S. 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 "L. S. 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 and Robinson, 1940). They are: $\sigma(Cl) = 0.0005$, $\sigma(C) = 0.0029$, and $\sigma(N) = 0.0019$, 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 and Corey, 1950).

The final values of the temperature factor parameters 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. Thus the vibration is nearly isotropic in directions perpendicular to the molecular chains, and of greater amplitude than along these chains.

Observed and final calculated structure factors are compared in Table 2. Reflections are arranged according to similarity of structure factors. Unobserved reflections were

Table 2. Calculated and Observed Structure Factors for ClCN

hkl	Fcalc.	Fobs	hkl	Fcalc	Fobs	hkl	Fcalc	Fobs
310	17.2	17.8	212	13.4	13.1	214	-5.6	5.7
220	14.8	15.4	302	11.1	10.9	304	-4.9	4.7
400	12.7	13.5	122	10.0	8.9	124	-4.4	3.7
130	8.4	8.4	032	5.1	4.2	034	-2.5	3.4
040	3.5	3.8	522	2.6	< 3.3	524	-1.7	< 3.4
530	2.4	< 3.7						
620	2.6	< 3.7	102	-20.9	19.8	104	7.6	7.9
440	1.6	2.0	012	-18.6	17.6	014	7.0	6.2
710	2.0	< 3.8	322	- 6.2	5.7	324	2.9	3.0
			412	- 6.3	5.9	414	3.0	< 2.8
110	-36.5	34.2	232	- 4.1	3.7	234	2.0	< 3.0
200	-33.3	30.8	502	- 4.4	4.1			
020	-20.1	20.7	142	- 1.9	< 3.3	005	2.3	3.4
420	- 7.2	7.6				315	1.3	< 2.5
510	- 6.7	7.0	003	-10.8	13.0			
330	- 4.4	5.7	313	- 5.7	5.7	115	-1.9	< 1.8
240	- 2.8	3.5	223	- 5.0	5.5	205	-1.8	< 1.9
600	- 4.3	4.5	403	- 4.5	4.2			
150	- 1.1	< 3.9	133	- 3.0	3.7	215	-3.2	3.7
			043	- 1.3	< 3.4	305	-2.8	< 2.4
001	0.3	< 0.9				125	-2.5	3.0
311	1.7	< 2.5	113	8.7	9.3	035	-1.4	< 2.9
			203	8.4	8.7			
111	- 1.4	< 1.8	023	6.1	6.2	105	4.2	4.1
201	- 1.6	< 1.9	423	2.7	3.5	015	3.9	3.6
			513	2.5	< 3.1	325	1.7	< 2.8
211	10.3	10.4						
301	8.5	8.1	213	3.2	3.5	006	2.6	3.7
121	7.7	7.5	303	2.8	2.7	316	1.4	< 2.1
031	4.1	3.8	123	2.5	2.8			
521	2.2	< 3.3	033	1.4	1.6	116	-2.1	3.0
431	1.8	3.0	523	0.7	< 3.4	206	-2.1	< 2.7
611	2.0	< 3.5						
			103	- 4.3	4.1	216	-2.8	3.4
101	-17.4	14.1	013	- 3.9	3.9	306	-2.5	< 2.5
011	-14.7	13.2	323	- 1.7	< 2.7			
321	- 4.9	4.8				106	3.7	3.7
411	- 5.0	4.9	004	-11.8	13.0	016	3.4	3.4
231	- 3.3	3.6	314	- 6.1	5.6	326	1.5	< 1.9
501	- 3.6	3.1	224	- 5.4	5.2			
141	- 1.6	< 3.3	404	- 4.8	4.9	007	2.6	3.0
			134	- 3.3	3.7	317	1.4	< 1.9
002	- 3.2	3.0	044	- 1.4	< 3.2			
312	- 1.6	< 2.4				117	-2.1	2.3
			114	9.5	9.2	207	-2.1	1.7
112	2.6	2.7	204	9.2	8.8	027	-1.5	< 1.7
202	2.5	2.7	024	6.6	6.1			
022	1.8	< 2.2	424	2.8	3.4			
			514	2.7	< 3.2			

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 as θ increases within each group. The atom form factors of Viervoll and Ögrim (1949) were employed.

DISCUSSION OF THE STRUCTURE

The interatomic distances in cyanogen chloride are r(Cl-C) = 1.57 Å, r(C-N) = 1.16 Å, and r(N...Cl) = 3.01 Å, all ±0.02 Å.

Cyanogen chloride, bromide (Geller and Schawlow, 1955) and iodide (Ketelaar and 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. Indices beneath each sketch refer to the plane of the projection. In ICN, the indices are referred to hexagonal axes; the axes in BrCN were renamed to correspond to the conventional space group form, Pmmn. The intra-molecular distances in the iodide and bromide sketches are those reported for the gas (Smith, Ring, Smith and 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 "overlap" caused by the short intermolecular distances is depicted by shaded areas.

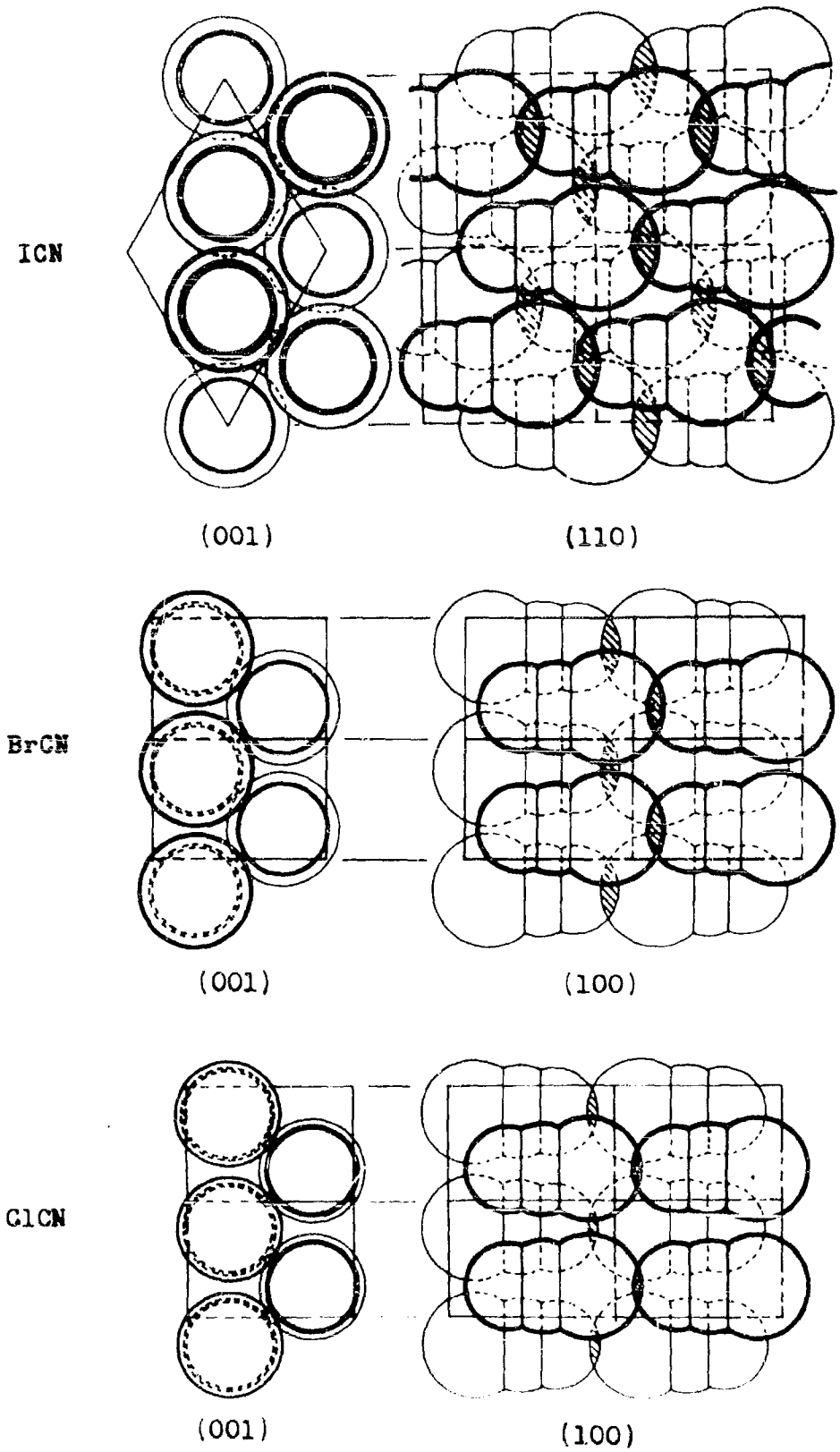

Fig. 1: Cyanogen halide structures

In cyanogen chloride the molecules lie in chains parallel to the c axis (Fig. 1c). 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 3.94 Å, and by two parallel chains at distances of 3.98 Å, so that the structure approximates closest packing of cylinders.

The chains are packed together loosely. The shortest Cl-Cl distance between chains is 3.98 Å, while twice the van der Waals radius of chlorine is 3.60 Å. The next shortest distances, between antiparallel chains, are Cl-Cl, 4.31 Å, and Cl-N, 4.16 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, Holden and Merritt, 1948). The repeat distance in the crystal corresponding to this length is only 5.74 Å. A similar but more drastic "overlap" (cf. Table 4) has been observed in ICN (Ketelaar and Zwartsenberg, 1939) and BrCN (Geller and Schawlow, 1955).

The shortening in ICN and BrCN has been interpreted in terms of three important resonance hybrids for the cyanogen

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	$\overset{+}{X}=C=\overline{N}$	2%	13%	15%	26%
Hybrid III	$-\overset{+}{X}-\overline{C}=N-$	10%	-	9%	-

(*)-Townes and Dailey, 1952 (**)-Geller and Schawlow, 1955

halides (Townes and Dailey, 1952, and Geller and 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 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.

Table 4. Reported bond lengths in the cyanogen halides

Halide	State	r(C-X) (Å)	r(C-N) (Å)	Overlap (Å)*	Method**	Ref.
I	gas	1.995	(1.158)		MW	1
	"	1.995	1.159		MW	2
	solid	-	-	0.8	XRD	3
Br	gas	1.79±.02	1.13±.04		ED	4
	"	1.790	1.158		MW	1
	"	1.789	1.160		MW	2
	solid	-	-	0.6	XRD	5
Cl	gas	1.67±.02	1.13±.03		ED	4
	"	1.629	1.163		MW	1
	"	1.630	1.163		MW	2
	solid	$1.57^{\pm}.01_{8}$	$1.16^{\pm}.02_{0}$	0.4	XRD	6

(*) - Overlap = sum of the bond lengths (Ref. 3 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, Holden and Merritt, 1948. 2. Smith, Ring, Smith and Gordy, 1948. 3. Ketelaar and Zwartsenberg, 1939. 4. Peach and Turkevich, 1939. 5. Geller and Schawlow, 1955. 6. This work.

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. 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(uv), used to determine the space group, showed that the molecules were linear. With this the case, 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 end chlorine atom of one molecule and the end nitrogen of the next, and perhaps to the changes in van der Waals radii resulting from the charges.

Since this argument against structure III is based entirely upon the linearity of the molecule, further investigation of this aspect seemed appropriate. If the molecules were actually bent

but were rotating about the chain axis, or if they were bent and stationary but disordered with respect to their angular orientation about the chain axis, they would be nearly indistinguishable from a fixed linear molecule in the Patterson projection, P(uv). But an electron density section through the centers of the atoms would reveal these conditions. If the molecules were bent and disordered or rotating, we would expect the atoms to appear elongated in the direction perpendicular to the chains. Therefore, a three dimensional electron density section, ρ(xxz), 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. 2a. Here contours were drawn at intervals of ~~0.1~~ 1.0 electron $Å^{-3}$ with the zero contour dotted. The carbon and nitrogen atoms appear normal. The chlorine atom on the other hand appears to be elongated. However, a difference synthesis, ($\rho_{obs} - \rho_{calc}$)(Booth, 1948), shows that this distortion is merely a result of series termination (cf. Fig. 2b. Here contours were drawn at intervals of 0.1 electron $Å^{-3}$. Solid contours represent positive regions, broken ones negative regions, while the zero contour is dotted.) 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

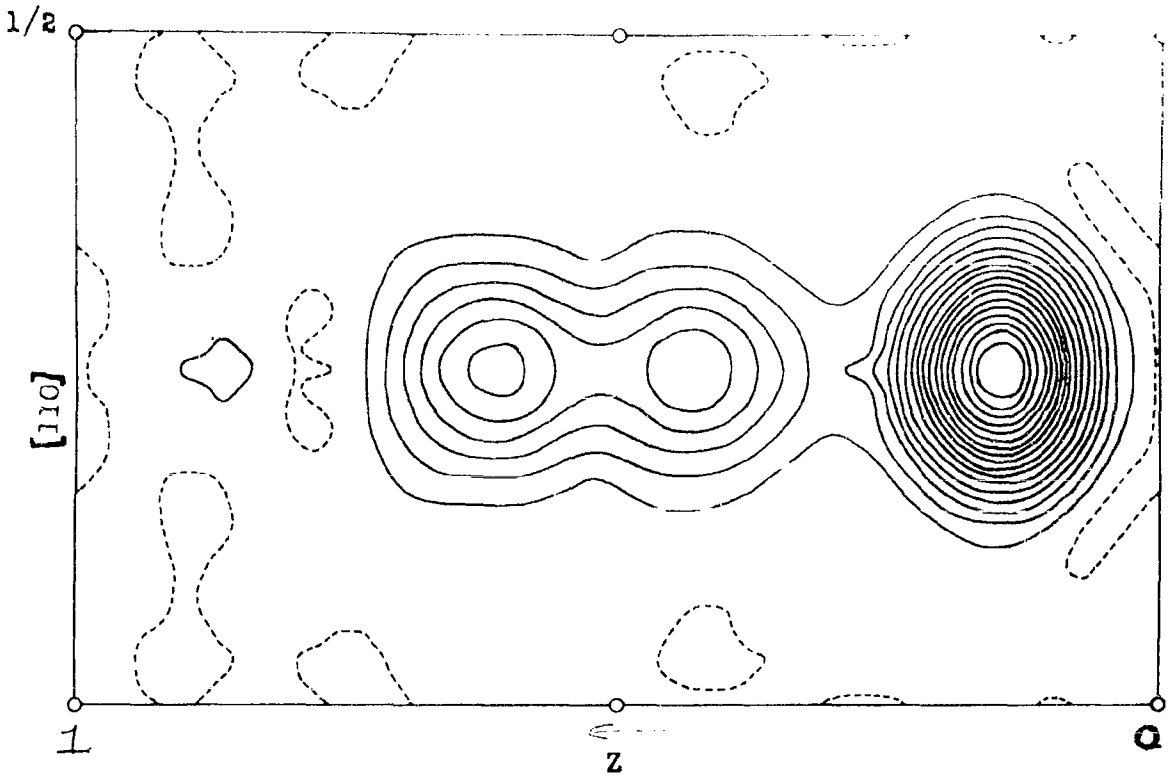

Fig. 2a: Electron density section, $\rho(xxz)$

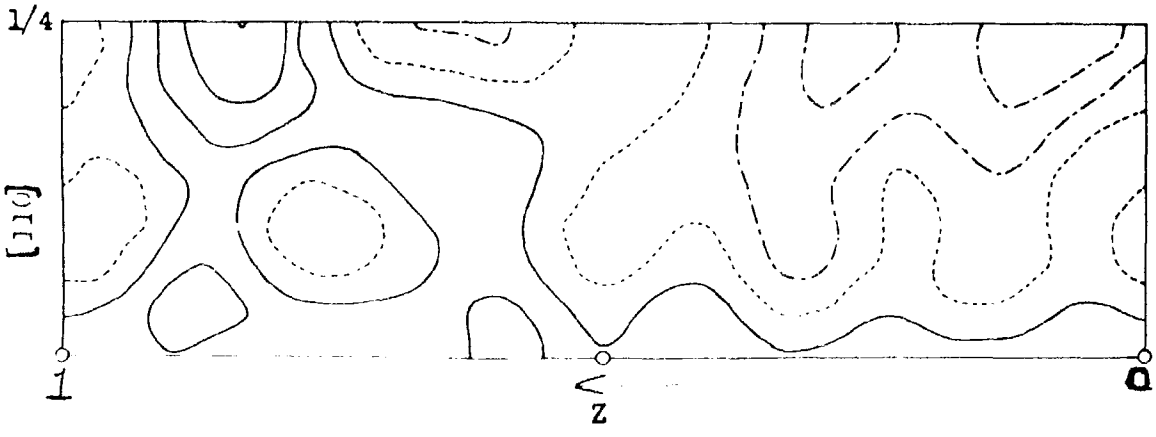

Fig. 2b: Electron density difference section, $(\rho_{obs}-\rho_{calc})_{xxz}$

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 "overlap" in Fig. 1 and Table 4 increases from the chloride to the bromide to the iodide. (The magnitudes of the overlaps 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 and Dailey (1952) have reported, however, that the charge distribution of the hybrid II is energetically unstable in the ICN lattice. 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 electronic point charges were located on the iodine and nitrogen atoms in the crystal, with the I...N distance calculated from the length of the molecule in the vapor (Smith *et al.*, 1948). The result is that the charge distribution of hybrid II in solid ICN is stabilized by $166x^2$ kcal./mole, where x is the fraction of the electronic charge on either atom. A similar calculation for hybrid II in the cyanogen chloride structure shows that it is stabilized by $161x^2$ kcal./mole. It seems reasonable to assume that this hybrid is also favored in the bromide, although the calculation for this case was not carried out.

Thus far, all 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 (1/4, 1/4, 52/60)(Cf. Fig. 2a). This peak has a maximum density of 1.3 electrons $\mathring{A}^{-3}$. This amounts to 20% of the adjacent nitrogen peak height. The difference synthesis, Fig. 2b, shows a peak of +0.4 electrons $\mathring{A}^{-3}$ at this point. Hence about 70% of this extra peak can be attributed to series termination effects. Nonetheless, there remains a "real" peak of height 0.4 electrons $\mathring{A}^{-3}$ to be explained. Table 2 shows that there are several large discrepancies between $\underline{F}_{obs}$ and $\underline{F}_{calc}$. It was thought that these might be due to errors in the estimated intensities and that these errors might account for the spurious peak. Complete elimination of the discrepancies for reflections (110), (200), (101), (011), (003), (004), (005), and (006), however, reduced the spurious peak by only 0.08 electrons $\mathring{A}^{-3}$, leaving a "real" peak of 0.3 electrons $\mathring{A}^{-3}$. This would still seem substantial. The discussion above might suggest that the peak

here is due to the negative charge on the nitrogen atom in hybrid II or even to the bonding electrons between the nitrogen and chlorine atoms in hybrid III.

The authors are indebted to Drs. Geller and Schawlow who furnished the results of their investigations of cyanogen bromide prior to their publication.

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