THE CRYSTAL STRUCTURES OF SOME ORGANIC COMPOUNDS

Thesis by

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Abstract

The crystal structure of acetamide hemihydrochloride has been determined by x-ray diffraction techniques. Three dimensional data were utilized for obtaining the final parameters by least squares and Fourier synthesis refinement techniques with an average positional standard deviation of 0.009 A. The results for the acetamide molecule show bond distances closer to those previously accepted than to those from the investigation of acetamide itself. There is a distance of 2.40 A between two oxygen atoms related by a center of symmetry. This has been interpreted as a hydrogen bond and as such would be the shortest such distance reported.

Potassium dicyanoguanidine crystallizes in an orthorhombic space group, either Pbcm (centrosymmetric) or $Pbc2_1$ (noncentrosymmetric). A structure has been determined conforming to Pbcm using least squares and generalized Fourier projections. The average positional standard deviation is 0.006 A for carbon and nitrogen. One of the C-N distances of the guanidine group is significantly shorter than the others. The two terminal NCN groups are not exactly linear, contrary to what might be expected. Each potassium ion is surrounded by eight nitrogens in a distorted Archimedes antiprism.

A study of the structure of the dimer of phenylisocyanate was initiated but discontinued for reasons which are discussed.

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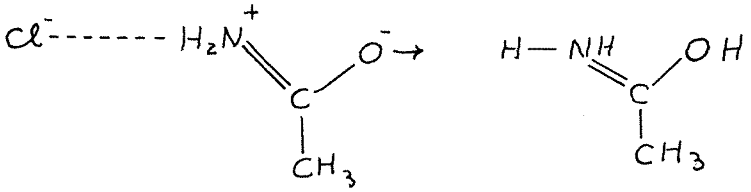
PART I

The Structure of Acetamide Hemihydrochloride

Introduction

Acetamide hemihydrochloride $(CH_3CONH_2)_2HCl$ was first prepared by A. Strecher (1) by passing HCl gas through a solution of acetamide in an ether-alcohol mixture. The analogous HBr and HI compounds were prepared by A. Werner (2) who studied various compounds of organic substances with hydrogen halides. Taylor (3), in his investigation of the hydrolysis of acetamide in acid solution, found that he could explain the results for the more concentrated HCl and HBr solutions only by assuming a complex with acid containing two acetamides which was not hydrolyzed. Many other compounds of acetamide with acids and salts exist with the formula $(CH_3CONH_2)X$, where X is for example HNO_3 (4), CH_3COOH (5), $\frac{1}{2}NaBr$ (6), $\frac{1}{2}CaCl_2$ (7), and HCl (8). Fialkov (9) reported one very unusual compound of this type with X equal to ICl. A very stable compound was prepared from a pyridine solution of ICl and given the formula $(CH_3CONH_2I{-}{-}{-}CH_3CONH_2)Cl$. No structure determination has been reported for any of these compounds, but Kahovic and Knollmuller (10) investigated the Raman spectra of many of them. They proposed the following structure for acetamide hemihydrochloride:



A previous preliminary investigation of the HCl and HBr compounds by Dr. Hughes (11) had indicated that they were isomorphous belonging to space group $P2_1/c$ with two molecules per unit cell. Since the general positions of this space group were four-fold, the two hydrogens (from HCl) might lie in the special positions which were centers of symmetry (instead of being distributed statistically about this position). Since there was one such hydrogen for every two acetamide molecules in the crystal, the possibility existed of a symmetrical hydrogen bond between oxygen atoms. A symmetrical hydrogen is one in which the proton is midway between the atoms rather than being closer (and bonded) to one of them as is usually true. The only established case of this type of bond is in KHF_2 for which thermodynamic and spectroscopic data led to the conclusion that the proton was placed symmetrically between the fluorine atoms (12). There has been much discussion about a symmetrical hydrogen bond between two oxygens. Donohue (13) predicted an interoxygen distance of 2.30 A. This calculation was made using Pauling's rules, assuming that hydrogen is forming two half bonds, and when applied to KHF_2 gives 2.20 A between the fluorines, to be compared to an observed value of 2.26 A. More recently Rundle (14) has claimed 2.45 A to be the interoxygen distance for the symmetrical oxygen case on the basis of a plot of O-H (from neutron diffraction and nuclear magnetic resonance results) versus O-O distances for hydrogen bonded crystals. The usual value found in crystals ranges between 2.6 and 2.8 A. Speakman and associates examined a series of acid salts of organic acids and for potassium hydrogen bisphenylacetate (15), potassium hydrogen di-p-hydrobenzoate hydrate (16), and potassium hydrogen dibenzoate (17) found hydrogen bonds between oxygens related by a center of symmetry. The interoxygen distances were reported to 2.55, 2.65, and 2.51 A respectively with probable errors of approximately 0.05 A. These distances are probably too long to be symmetrical hydrogen bonds and may be a statistical distribution of hydrogens to give the correct symmetry. This was confirmed for the first structure by an infra-red study (18). The shortest distances known at the time this investigation was initiated were 2.44 A for nickel dimethylglyoxime (19) and 2.46 A for maleic acid (20). Later a neutron diffraction study of sodium sesquicarbonate (21) gave some evidence for a symmetrical hydrogen bond with an interoxygen distance of 2.50 A.

The determination of the structure of the acetamide portion of the crystal would in itself be of interest. An X-ray study of acetamide was made by Harker and Senti (22) in 1940. However, because the crystal belonged to a non-centrosymmetric space group and because of the limited computational facilities available, the results were not as accurate as might be wished (probable error 0.05 A). There are large discrepancies between their values and those selected by Pauling and Corey (23) in their discussion of protein structures. These were chosen by examining the results of a number of investigations of various related compounds. Kimura and Aoki (24) made an electron diffraction study of acetamide vapor which gave in general results closer to Pauling and Corey's values though differences still remained. These were attributed to the effect of hydrogen bonding present in crystals but not in the gas phase. The results of these three investigations are given on page 21 along with the results of this study.

Acetamide hemihydrochloride was a favorable crystal to study as it met Lipson and Cochran's (25) criterion for a heavy atom problem, that is, the square of the number of electrons of the heavy atom should be approximately equal to the sum of the squares of the electron numbers of the other atoms. These values are 324 and 370 respectively. If the trial structure proved to be difficult to obtain, the isomorphous hemihydrobromide could be used to obtain rough parameters which would then be refined using the data from the hemihydrochloride. This did not prove to be necessary.

Experimental Work

The crystals were prepared following the procedure used by Dr. Hughes. Stoichiometric amounts of concentrated HCl and acetamide (both reagent grade, Baker and Adamson chemicals) were mixed and, after stirring, the resulting slurry allowed to stand for ten minutes. The crystals were washed with cold acetone, dried with filter paper, and stored in a desiccator, as they are hygroscopic. The crystals prepared for use by recrystallization from hot acetone were slightly flattened needles approximately 0.1 to 0.2 mm in diameter. They could be cleaved along the needle axis but when cleavage was attempted perpendicular to the axis they shattered. They were mounted in lithium borate glass capillaries sealed with Dupont Duco cement for protection from moisture.

Preliminary photographs were in agreement with Dr. Hughes' space group assignment of $P2_1/c$, since the only systematic absences were for $h0\ell$ with ℓ odd and $0k0$ with k odd. A rotation photograph made with a Straumanis type camera and Cu K_α radiation (λ = 1.542 A) was used in determining by least squares the axial lengths of the unit cell. The β angle was obtained from precession photographs. The results were:

$a = 6.33$ A ± 0.01
$b = 8.31 \pm 0.01$
$c = 8.07 \pm 0.01$
$\beta = 111.7^\circ \pm 0.1$

The b axis was perpendicular to the needle axis which was [101].

The zonal reflections used for the first part of this study were obtained from precession ($h0\ell$ and $hk\bar{h}$) and Weissenburg ($hk0$) photographs. For the latter Zr filtered Mo K radiation with standard multiple film, intensity strip techniques were used in conjunction with Lorentz and polarization corrections from Buerger's monograph (26). These methods could not be used for the precession photographs. The use of multiple films would result in only one film being at the correct film to crystal distance, thus giving rise to doubling of reflections on the other films. Also, an intensity strip cannot be made conveniently with a precession camera.

For these reasons carefully timed exposures with a constant tube current were made at each setting and the films developed together to equalize the factor of developer depletion. Zr filtered Mo K_{α} radiation was used with a precession angle of 30 degrees. For the intensity estimation one reflection was chosen as the standard and given the value 100 for the longest exposure and proportionally lower values for the other exposures. Secondary standards were chosen and the photographs measured using these values. These intensities were then corrected for Lorentz and polarization factors by using a template made by C. Nies (27). The intensities used for the final three dimensional refinement were obtained from equi-inclination Weissenburg photographs taken about the needle with Cu K_{α} radiation. The layers were correlated with the previous data and some additional precession data added to give the final set of 518 (62 unobserved) structure factors.

Determination of the Structure

Since there are two chlorines and four acetamides per unit cell, the latter must lie in the general four-fold positions and the chlorines at one of the set of special positions which are centers of symmetry. These may be arbitrarily taken as the set 000 and $0\frac{1}{2}\frac{1}{2}$. Therefore the chlorines make a positive contribution of their full diffracting power to those reflections for which $k + \ell$ is even and none to the $k + \ell$ odd.

This is assuming an isotropic temperature factor but even if this were not the case, their contribution to the $k + \ell$ odd reflections will be small. The $h0\ell$ zone is made up only of reflections with $k + \ell$ even and so would be expected to have the signs of the stronger reflections positive as determined by the chlorines. Since this is not true for any other zone, it seemed that this projection would be the most suitable with which to begin an attack on the problem.

Since the more intense reflections were presumably positive, an $h0\ell$ Fourier projection was calculated using the 21 strongest reflections of the total of 44. An $h0\ell$ Patterson projection was also calculated using all the reflections. Besides the Cl-Cl interaction the main peaks of the latter should be for the interaction of Cl with the acetamide and since the Cl is at the origin it was expected that the Patterson projection would have much the same appearance as the Fourier, which is shown in Figure 1. This proved to be the case.

As can be seen in Figure 1, this first Fourier projection showed two resolved peaks, I and IV, and what appeared to be two overlapping peaks, II and III. Peak II had to be the central carbon atom of the acetamide molecule but there was no basis on which to make further atomic assignments. Signs determined from a structure calculation using James

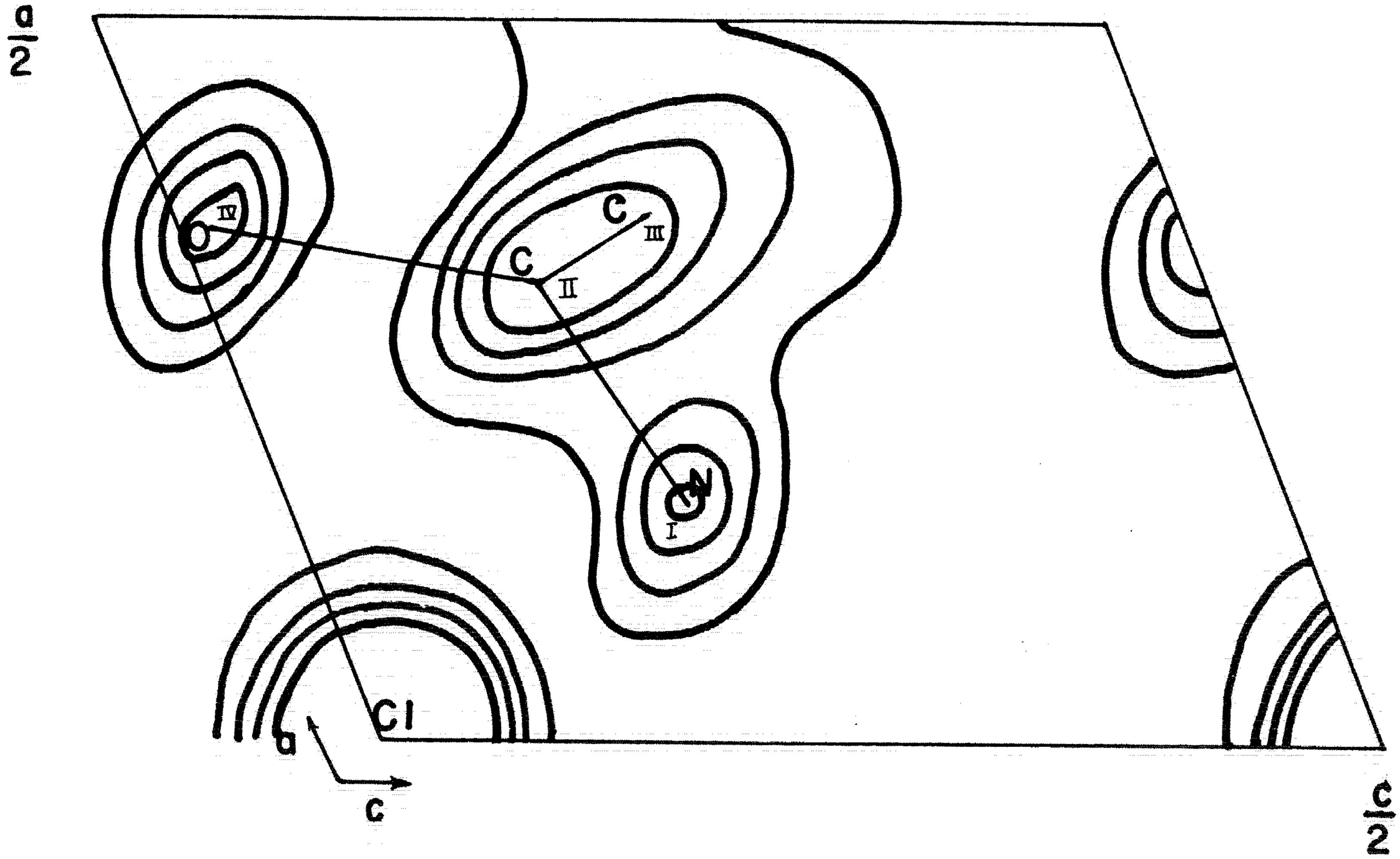


Figure I
HOL Fourier Projection

and Brindley (28) form factors for Cl^-, N^*, and C were used in calculating another Fourier projection. This greatly improved the general appearance of the electron density map but peaks II and III were still badly overlapped. The average peak shift was about 0.1 A. It was evident that more information would be needed for further progress so attention was turned to the $hk\bar{h}$ zone.

The use of this zone was not as simple as that of the $h0\ell$ since 15 of the observed reflections had $k+\ell$ odd and therefore were not determined in sign by the chlorine. However the strong $k+\ell$ even reflections were used for a Fourier projection. *This limitation of the data introduced a false* mirror plane parallel to the b axis, thereby doubling the number of peaks and the problem was to choose a correct set. Although it was evident there was overlapping also, y parameters were assigned with the aid of the previous x and z values. A Fourier projection calculated on the basis of these positions showed that the peaks that were chosen increased in height while the others decreased as expected. Peaks II and III again overlapped somewhat. A series of refinement cycles were made on the $h0\ell$ and $hk\bar{h}$ zones using Fourier, and later, difference Fourier syntheses. During this stage atomic assignments for the peaks were made. This was not done on the basis of relative peak heights on the

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* The form factor of N was used for I, III, and IV.

electron density maps alone but use was made also of the packing distances and environment. Peak II had been assigned previously as the central carbon atom, CI. Peak III was distant from any other atom except CI and showed no signs of hydrogen bonding to other molecules and so was called the *methyl carbon, CII. The IV-IV' distance was so short, 2.25 A* at the time, that it seemed probable that it was a hydrogen bond between two oxygens (there is a center of symmetry between the two atoms so they must be identical). This left peak I as the nitrogen, hydrogen bonded to the chlorine, a not unreasonable environment. These assignments were in agreement with the electron density values. The atomic form factors for carbon, nitrogen, and oxygen were changed to those of Hoerni and Ibers (29) and two isotropic temperature factors were used. The temperature factor constants, obtained by least squares, were 2.95 A^2 for chlorine and 3.25 A^2 for acetamide. At the conclusion of this stage of the investigation, the R factor, defined as $100 \frac{\Sigma |F_o - F_c|}{\Sigma |F_o|}$ was 16 for the $h0\ell$ zone and 12 for the $hk\bar{h}$ zone. For the $k+\ell$ odd reflections present in the latter zone it was 15. The agreement for the $h0\ell$ structure factors was relatively poor because there was greater overlap for this zone so more attention was given the $hk\bar{h}$ zone.

Up to this point CI and CII overlapped in both projections, causing relatively large errors in their parameters. Normally the method to resolve the positions of these atoms would be a projection perpendicular to the plane of the acetamide molecule. In this case however the chlorine and another molecule would project onto it, making this procedure almost useless. Therefore the hk0 zone in which the oxygen and central carbon slightly overlap but other atoms are resolved was introduced and refinement of all three zones was made with difference Fourier syntheses and least squares methods. Most of these and all later calculations were made on the IBM machines. It became apparent from the difference Fourier projections that an anisotropic temperature factor was necessary for the chlorine. Since the four nitrogen atoms hydrogen bonded to each chlorine form a plane (they are related in pairs by the center of symmetry), it was decided to use a temperature factor of the form (30) $\exp -(A + C \cos^2\delta)\sin^2\theta/\lambda^2$ where δ is the angle between the normal to that plane and the reflection vector $\underline{h}$. The three temperature factor constants (one for acetamide) were determined and refined by least squares. The equations of the vectors and final values of the constants are given in Table 1. Peaks for the three methyl hydrogens and two amide hydrogens were found in the difference syntheses and these hydrogen atoms were introduced into the calculations with McWeeny form factors (31) and a temperature factor constant of 3.0 A^2. The methyl hydrogens were required to have tetrahedral angles and the amide hydrogens to be in the molecular plane with 120° angles. With these restrictions the peaks were fitted as closely as possible. The average distance of the hydrogen

Table 1

Temperature Factor Parameters

Normal to plane through	Cl(000)	$\underline{a} + 0.25\underline{b} + 0.60\underline{c}$
" " " "	Cl($0\frac{1}{2}\frac{1}{2}$)	$\underline{a} - 0.25\underline{b} + 0.60\underline{c}$
Reflection vector $\underline{h}$		$h\underline{a}^* + k\underline{b}^* + \underline{c}^*$
A	2.46 A^2	
C	2.90	
B	3.00	

to the atom involved was 1.0 A. At the conclusion of this phase of the study the R factors were 13, 13, and 12 for the $h0\ell$, $hk\bar{h}$, and hk0 zones respectively. The positional parameters are given in Table 2 and bond lengths and angles in Table 3.

As can be seen in Table 3 the results are normal except for a short C-O distance and the very short hydrogen bond distance. Since the agreement between observed and calculated structure factors was satisfactory, the study might have been concluded at this point. The hydrogen bond distance of interest, while longer than the 2.30 A predicted by Donohue for a symmetrical bond, was shorter than the 2.45 predication of Rundle. However it has a relatively large probable error because it is determined by doubling the distance of the

Table 2

Positional Parameters x 10^3

Atom	x	y	z
O	367	588	029
N	143	639	183
CI	291	550	138
CII	348	385	227
H1(C)	314	303	133
H2(C)	247	367	288
H3(C)	500	371	310
H4(N)	088	732	113
H5(N)	151	630	296

Table 3

Bond Distances and Angles

C-O	1.19 A	∡ C-C-O	120°
C-C	1.53 A	∡ C-C-N	116°
C-N	1.35 A	∡ O-O-N	$123\frac{1}{2}^{\circ}$
O-O'	2.40 A		

oxygen to the center of symmetry. Therefore in order to improve the general reliability of the results it was decided to use three-dimensional data to refine the structure further.

A structure factor calculation of all the available data using the above parameters, but excluding the hydrogens, gave an R factor of 18. The form factors used were changed to those of Bergheis et al. (32) for the chlorine ion, and those of McWeeny (31) for carbon, nitrogen, and oxygen, and later hydrogen. Three least squares cycles reduced the R factor to 15. At this point a three dimensional difference Fourier synthesis was calculated. Peaks were immediately evident for the methyl and two amide hydrogens. Their parameters, chosen with the previous restrictions as to the angles, were used in all further calculations without change with a temperature factor constant B kept at 3.0 A^2. The average shift from the previous hydrogen positions was 0.1 A. The average distance of the hydrogens from the atom involved was 0.95 A. It was also evident in this Fourier synthesis that anisotropic temperature factors would be needed for all the atoms. The parameters of the ellipsoid of vibration were determined from the curvature of the electron density on the difference map in the three ellipsoid axial directions according to the procedure of Leung, Marsh, and Schomaker (33). One ellipsoid direction was taken as the direction perpendicular to the plane of the molecule. No significant deviation from this assumption could be noticed on the difference map and this direction proved to have the largest anisotropy as can be seen in the parameters listed in Table 4. To transform these parameters into a form suitable for calculations, the three directions $\underline{A}_i$ were found in real space and the sum $\sum_i q_i(\underline{A}_i\ \underline{h})$ was evaluated for each atom, q_i being the vibration parameter along $\underline{A}_i$, a unit vector along the ellipse axis, and $\underline{h}$ being the reflection vector in reciprocal space. This gives the temperature factor in the usual form exp-$(\alpha h^2 + \beta k^2 + \gamma \ell^2 + \delta hk + \varepsilon k\ell + \eta h\ell)$. The value for the atom related by the glide plane was obtained by substituting -k for k in the above expression. Three least squares cycles of the positional parameters and two of the temperature factors then gave the final parameters listed in Table 5, with an R factor of 11. The standard deviations were determined following Whittaker and Robinson (34).

$$\sigma_{ij}^2 = \frac{\sum w\Delta^2}{(n-s)}\,\frac{D_{ij}}{D}$$

Where:

σ_{ij} = the square of the standard deviation of the j-th parameter of the i-th atom

D = the determinant of the normal equations

D_{ij} = the minor of the i,j term

n = the number of observations

s = the number of parameters

w = the weighting function

Δ = $F_o - F_c$

Table 4

Temperature Factor Parameters

Atom	q_i	$\underline{A}_i$ Coefficients x 10^3		
		a	b	c
O	4.25 A^2	131	52	97
	3.58	86	-103	20
	3.10	64	32	- 91
N	3.78	131	52	97
	3.29	54	-110	54
	3.06	112	- 14	- 90
CI	3.75	131	52	97
	3.10	89	19	- 99
	2.27	154	-108	54
CII	4.60	131	52	97
	3.74	89	19	- 99
	2.85	54	-108	54
Cl	2.48	102	- 26	103
	2.54	116		- 54
	5.36	25	117	32

Table 5

Positional Parameters
$(\times 10^4)$

Atom	x	y	z	σ
N	1490	6400	1829	007 A
CI	2890	5501	1401	008
CCII	3554	3907	2344	010
O	3649	5891	0239	011
Cl	0	0	0	
H1(C)	3170	3000	1400	
H2(C)	2540	3130	3000	
H3(C)	5120	3850	3140	
H4(N)	0830	7340	1250	
H5(N)	1250	6000	2900	

Discussion of the Structure

Distances and angles involved in the acetamide molecule are shown in Figure 2 and listed in Table 6 compared with the sources mentioned on page 5 and the X-ray determination of the structure of chloroacetamide* by Katayama (35). In general the results of this investigation are closer to those of Pauling and Corey rather than to any of the experimental values. The greatest variation is in the lengths of the C-N bond which range from 1.303 to 1.40 A. A possible explanation for the shortening of this bond in acetamide hemihydrochloride may be seen by examining the resonance structures for this compound, several of which are shown in Figure 3. Structures of type B have a C-N double bond which would shorten this bond. The resulting positive charge on the nitrogen is stabilized by the presence of the negative chloride ion nearby. The resonance structures with a C=C double bond are similar to those used in hyperconjugation, the interaction of a C=C double bond with an adjacent single bond in hydrocarbons. McHugh (37) has found a distance of 1.50 A for the C-C single bond in propylene, isobutene, and cis-2-butene by electron diffraction studies. This type of resonance structure might be expected to make a greater con-

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*The results of Dejace (36) on chloroacetamide were not included as it was felt his final parameters obtained from two zones with R factors of 20 and 23 were not sufficiently accurate for a structure of this type.

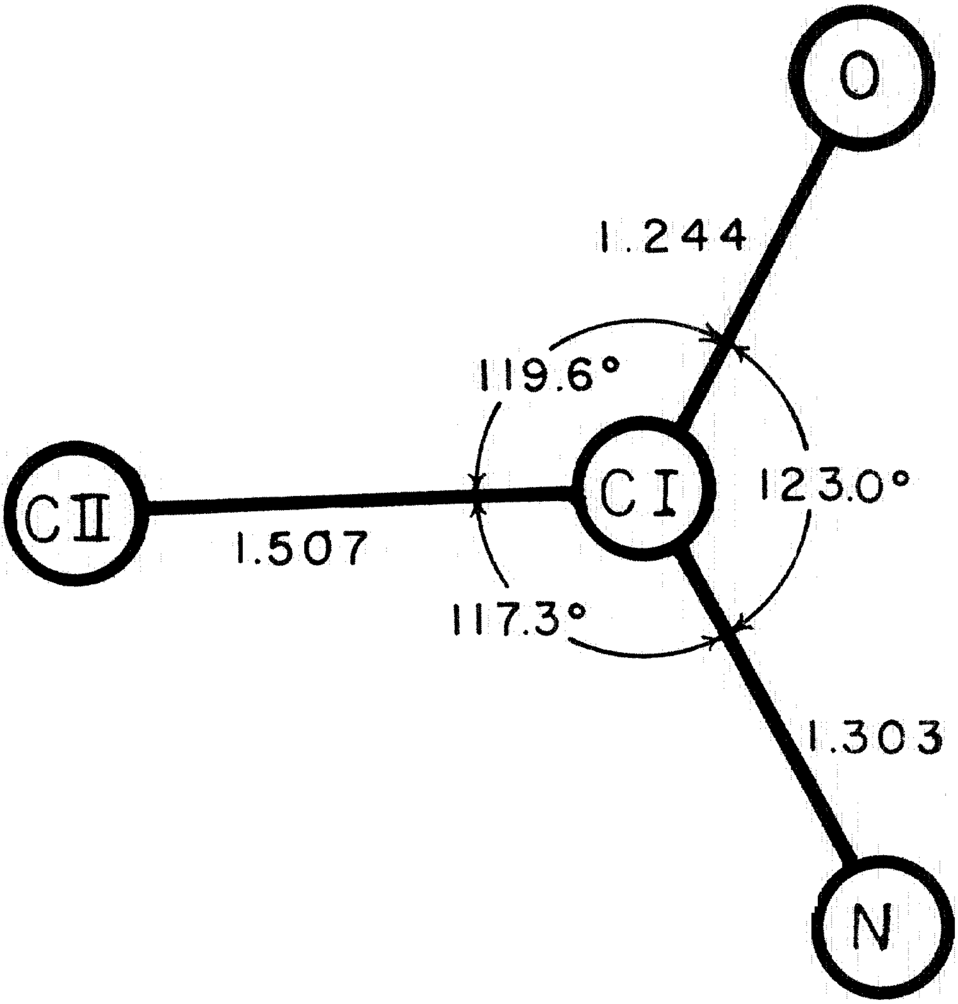

Figure 2

Structure of Acetamide Portion

Table 6

Bond Distances and Angles

	C-O	C-N	C-C	∡ C-C-O	∡ C-C-N	∡ O-C-N	O-O'
Pauling and Corey[22]	1.24 A	1.32 A	1.53 A	121°	114°	125	
Acetamide, X-ray[21]	1.28	1.38	1.51	129	109	122	
Acetamide, E.D.[23]	1.21 ± 0.02	1.36 ± 0.02	1.53 ± 0.03	122 ± 4	113	125 ± 4	
Chloro-acetamide[34]	1.25 ± 0.04	1.40 ± 0.03	1.51 ± 0.03	124	120	116	
Acetamide Hemihydro-chloride	$1.24_4 \pm 0.012$	$1.30_3 \pm 0.013$	$1.50_7 \pm 0.016$	119.6 ± 0.9	117.3 ± 0.9	123 ± 0.9	2.40 ± 0.015

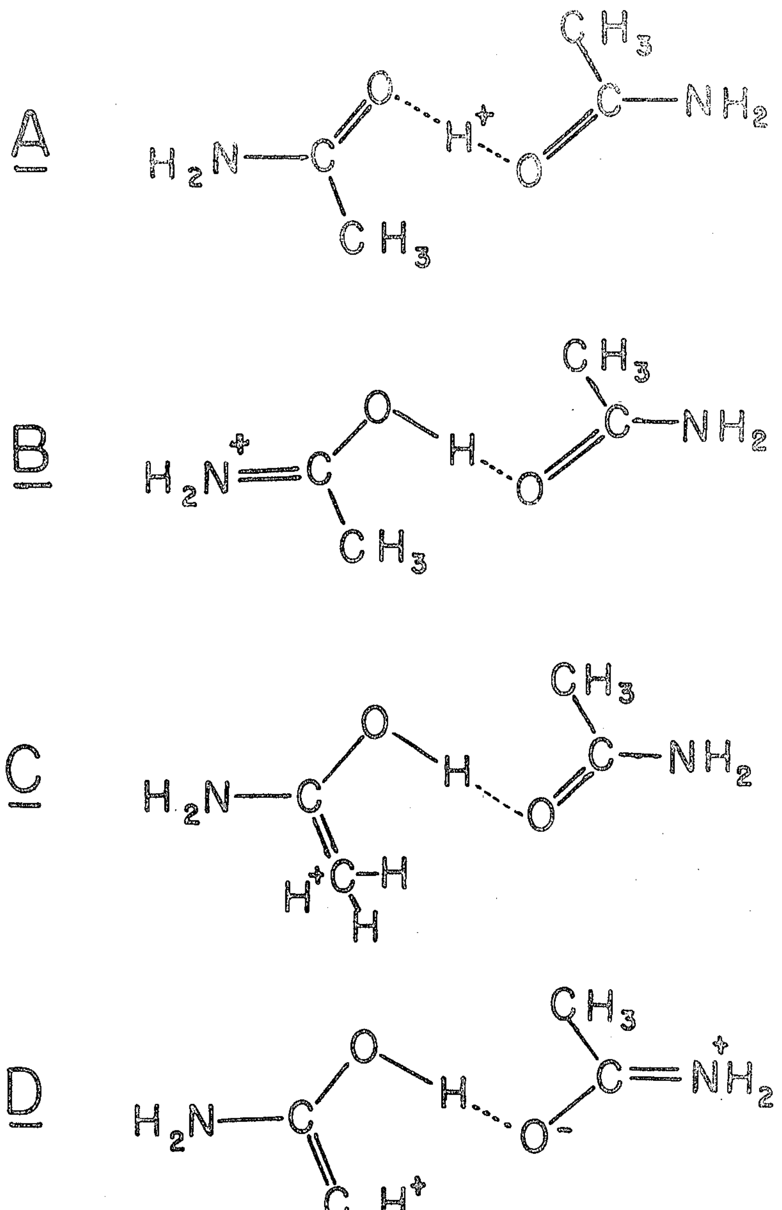

Figure 3

Several Possible Resonance Forms

tribution in this crystal compared to the other compounds in Table 6 because of the stabilizing effect on the partially nonbonded proton due to the proximity of the negative chlorine and oxygen.

The unusual feature of this structure is the value of 2.40 A for the distance between two oxygens. It seems reasonable to assume that this is a hydrogen bond and as such would be the shortest such distance reported up to this time. It lies between the values predicted by Donohue and by Rundle for a symmetrical hydrogen bond and the question arises as to whether this type of bond is present in the crystal. The two oxygen atoms involved are related by a center of symmetry so by this requirement the proton should be on the center, exactly midway between the two oxygens. However, since the diffracting power of the hydrogen is so small, it makes only a small contribution to the diffraction pattern and the symmetry determined by X-rays may not be valid for this atom. This argument does not apply to oxygen so the two oxygen atoms must be at least statistically equivalent. If a symmetrical hydrogen bond is not present two types of structures which satisfy the overall crystal symmetry seem possible.

The first is that there is disorder in the crystal with the proton attached to one oxygen or the other with equal probability. However this does not seem likely in view of the X-ray evidence. The C-O bond would then approach a single bond for half the atoms and a double bond for the rest of the atoms at a given position in the unit cells. Since the two bond lengths differ by about 0.1 A in these types of structures, it would be expected that there would be a smearing of the electron peak on the Fourier syntheses with a lengthening of the bond distance from the expected amount. Such an effect was never detected on either the regular or difference Fourier syntheses or in the temperature factors.

The other possibility, if this is not a symmetrical hydrogen bond, is that the proton is under the influence of a double minimum potential function with a relatively low barrier between the two minima. For this case the proton can move from one minimum to the other with ease, the corresponding picture applied to the crystal being that the proton is vibrating from one oxygen to the other. This is almost the same as a symmetrical hydrogen bond since in the latter the proton would also be vibrating back and forth because of its thermal motion though in a potential function with a single minimum. The average position would be the same and the motion different only in that the proton would spend a little more time in the middle. The difference between the two cases cannot be detected by the present data.

Pimentel and Sederholm (38) have made an extension of Rundle's (14) infrared study of hydrogen bonds. They have examined a large number of hydrogen bonded compounds and found a linear relationship between the shift of the OH frequency and the O-O distance. In view of the results of this X-ray investigation of acetamide hemihydrochloride, a spectroscopic examination of this compound has been initiated by Professor R. Badger and Mr. N. Albert of this department.

The acetamide molecule is planar, fitting the least squares plane $1.001x + 1.035y + 1.023z = 1$ to within 0.005 A for all the atoms. This is almost paralled to the (111) plane. The dihedral angle is 0.8 degrees with the nitrogen slightly closer than the carbons, the average distance from (111) being 0.07 A. The distances are shown in Table 7.

The centers of symmetry on (111) located at the chlorines and between the oxygens generate parallel molecules alternating slightly above and below this plane. The lattice translations and centers then generate a set of planes parallel to the original one separated by a distance of 3.55 A. Parts of two such planes are shown in Figure 4 with the lower plane drawn with thin lines. These planes may be described as composed of chains of

$$\text{--Cl--}(H_2NAc)\text{--}(AcNH_2)\text{--Cl--}(H_2NAc)\text{--}$$

held together by NH--Cl hydrogen bonds and resulting in layers with large holes between chains. These holes are filled by similar chains nearly parallel to (111) generated by the glide planes. The angle between these two sets of planes is 52 degrees. Part of this inclined plane is shown in Figure 5 enclosed in its parallelogram of four chlorines at the corners. Thus the crystals may be described as formed by two sets of such parallel planes related by glide planes

Table 7

Distance of Atoms from Plane

Atom	Distance from (111)	Distance from L.S. Plane
O	0.079 A.	0.002 A
N	0.061	0.005
CI	0.082	0.004
CII	0.092	0.003
Cl I	0.000	0.123
Cl I	0.000	0.102
(H)$(\frac{1}{2}\frac{1}{2}0)$	0.000	0.063

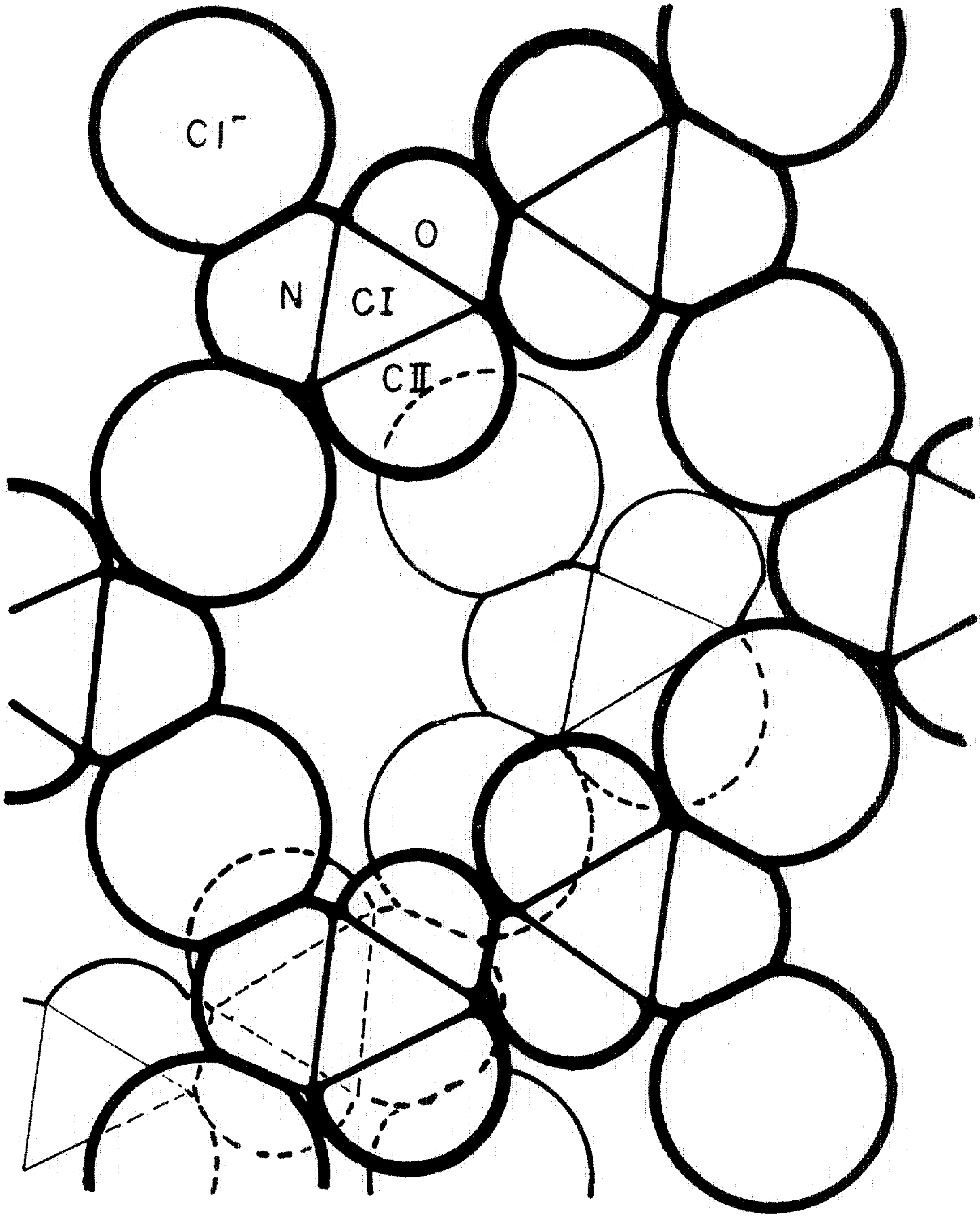

Figure 4

Part of Two Parallel Planes

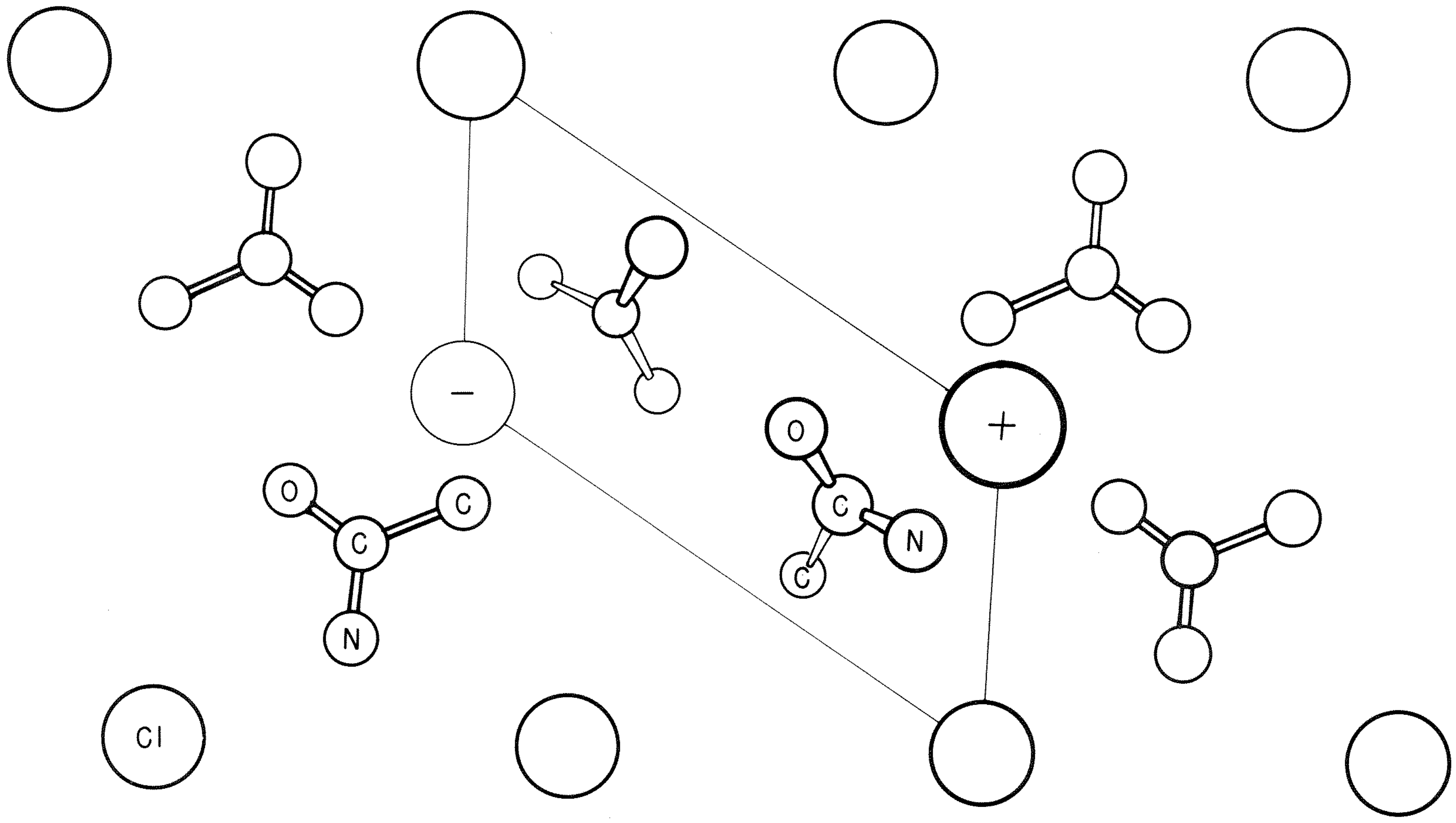

Figure 5. Portion of Two Planes

or screw axes and held together by having their chlorines in common.

This packing explains the ability of the crystals to cleave along the needle axis but not perpendicular to it. The needle axis is [101] which is parallel to the chains in both sets of planes. Therefore, cleaving along the axis breaks only some NH-Cl hydrogen bonds whereas perpendicular to the axis the very strong OHO hydrogen bonds must be broken also.

The Van der Waals distances are listed in Table 8 and shown in Figure 6. The shortest distance of 3.20 A is that between a methyl carbon and the oxygen of another molecule and can be attributed to the strong hydrogen bond between the oxygens. The methyl hydrogens are in such positions that none of them is pointing toward this oxygen. The chlorines are surrounded by four nitrogens at 3.21 and 3.24 A, and four methyl carbons at 3.75 and 4.00 A. There are also four oxygens at 4.07 and 4.09 A. The atoms occur in pairs as the chlorine is at a center of symmetry.

Table 8

Van der Waals Distances

Cl I - O	4.09 A	O - CI_2	3.17
Cl I - CI	4.13	O - CII_2	3.20
Cl I - CII_3	4.00	O_4 - CII_2	3.29
Cl II - O_3	4.07	N - CI_3	3.42
Cl II - CI	3.94	N - CII_3	3.70
Cl II - CII	3.75	N_4 - CII_3	3.95
O - N_3	3.62	CI - CI_3	3.62
O - N_4	3.43	CI - CII_3	4.11
O - CI_3	4.02	CI_4- CII_2	3.53

Hydrogen Bond Distances and Angles

O - O_2	2.40 A	$\measuredangle$ C -OH-O_2	117.2°
Cl I - N	3.31	$\measuredangle$ CI-NH-Cl	120.5
Cl II - N	3.24	$\measuredangle$ Cl-NH-Cl II	115.7
		$\measuredangle$ ($AcNH_2$)-O_2*	3.0

Numbering scheme is shown in Figures 2 and 6.

X_2 Molecule related by center at $\frac{1}{2}\frac{1}{2}0$
X_3 " " " " " $0\frac{1}{2}0$
X_4 " " " c glide at $y = \frac{1}{4}$

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* Angle between plane of acetamide molecule and O-O_2

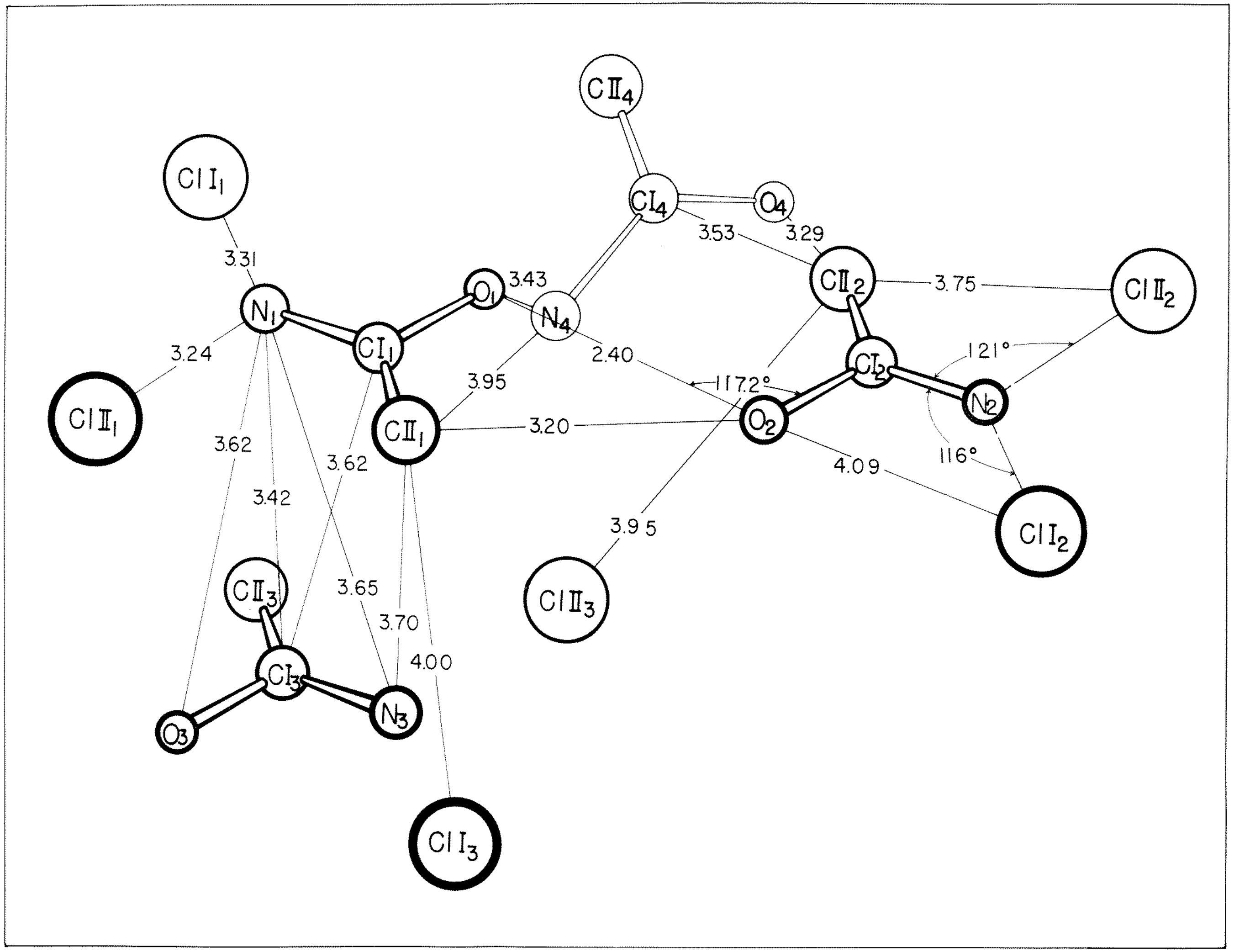

Figure 6. Packing Distances

PART II

THE STRUCTURE OF POTASSIUM DICYANOGUANIDINE

Introduction

The acidity of nitrile substituted guanidines increases with the number of nitrile groups added.* Guanidine itself can add a proton very easily to form the symmetrical guanidinium ion which resonates between three equivalent structures. Its basic strength is comparable to that of KOH. Dicyandiamide (cyanoguanidine) is an amphoteric compound. Dicyanoguanidine is a strong acid with strength comparable to that of HCl. The structures of these compounds are shown in Figure 7. Dicyanoguanidine itself is unstable and polymerizes upon standing, reacting violently if heated. However, its salts are stable, even if heated.

The structures shown in Figure 8 have been proposed for the potassium salt. The first has been favored by the investigators because of "the ultra-violet spectrum which shows a highly conjugated system." The alkali and alkaline earth salts are highly soluble in water and an ionic structure is more probable. This would also allow greater resonance which would stabilize the ion. It was decided to investigate the crystal structure of the potassium salt to determine its structure and attempt to explain its greater stability.

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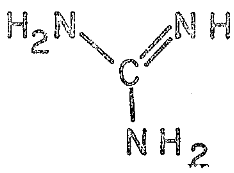
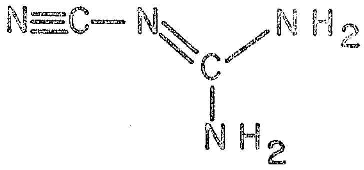
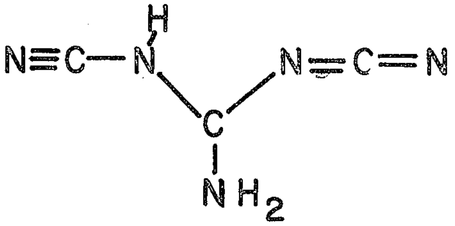
* This discussion is based mainly on Reference 39. As far as is known, all the published investigations of dicyanoguanidine and its salts have been made in the laboratories of the American Cyanamide Company.



Guanidine



Dicyandiamide



Dicyanoguanidine

Figure 7

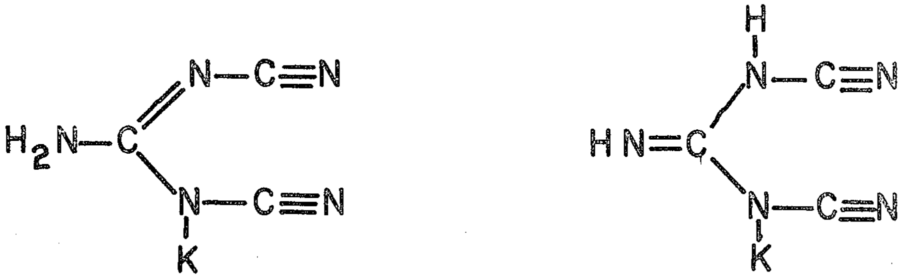


Figure 8

Experimental Work

The sample used was obtained from the American Cyanamid Company. The crystals, prepared by slow evaporation of an isopropyl alcohol water mixture, were rectangular prisms which cleaved parallel to two faces but not the third. They were formed into a roughly cylindrical shape approximately 0.2 mm in diameter by cleavage and by dissolving with moist litmus paper.

Preliminary photographs showed Laue symmetry mmm. Measurements of Weissenburg photographs (Cu K_α, λ = 1.542 A.) gave the following cell edges:

a	9.16 A	± .02
b	9.03	± .02
c	7.13	± .02

Four molecules per unit cell gave a density of 1.65 g/cc which was confirmed approximately by immersion in carbon tetrachloride (S.G. 1.6). Intensities were estimated from equi-inclination Weissenburg photographs made about the [001] and [101] axes using Mo K_α and, also in some instances, Cu K_α radiation, with standard multiple film intensity techniques. 529 reflections (with $\ell \leq 3$) were estimated including 49 unobserved reflections. The maximum value of $\sin\theta/\lambda$ was 0.8 A^{-1}, considerably beyond the Cu K_α limit.

Determination of the Structure

$0k\ell$ reflections were absent when k was odd and $h0\ell$ when ℓ was odd but no other systematic absences were observed for the hk0 reflections. These absences are compatible with centrosymmetric space group Pbcm and non-centrosymmetric space group $Pbc2_1$ ($Pca2_1$ with the axes changed to conform with the Tabellen (27)). Pbcm is the same as $Pbc2_1$ with the addition of a mirror plane perpendicular to c which generates two-fold axes and centers of symmetry. A piezoelectric test for a polar axis gave a negative result.* Examination of the reflections showed that the ℓ even reflections were in general much stronger than those with ℓ odd. Further regularities in the distribution of intensities were evident, particularly upon examination of the photographs taken about [101] which had values of ℓ up to 10 or 12. The reflections could be divided into three sets depending on their value of ℓ.

Set I	ℓ congruent to 0(mod 4)
Set II	ℓ congruent to 2(mod 4)
Set III	ℓ congruent to 1 or 3(mod 4), i.e. ℓ odd.

Within each set, for each value of h,k, all the reflections had

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* This test was made through the courtesy of Dr. W. Sly of this Laboratory with a modified Giebe and Scheibe apparatus with an oscillation range of 0.4 to 7.5 megacycles/sec.

the same intensity if allowance was made for the gradual change in the temperature and form factors with ℓ. This strongly suggested a layer structure parallel to (001) and separated by c/4. Since this is an indication of the presence of a mirror plane, it was decided to attempt to solve the structure using space group Pbcm.

The general positions of Pbcm are eight-fold so the potassium ion and the dicyanoguanidide anion (DCG^-) must lie in some of the special positions which are:

m	mirror planes	$z = \frac{1}{4}$
2	two-fold axes	$y = \frac{1}{4},\ z = 0$
i	centers of symmetry	$\frac{1}{2},0,0$
i	" " "	$0,0,0$

The probable configurations for DCG^- are shown in Figure 9. None of these models has a center of symmetry so these positions are possible only for the potassium. The 00ℓ reflections which were observed to ℓ equal to 12 were examined. If the potassium and DCG^- had the same z parameters, i.e. on the center and the two-fold axis or both on the mirror plane, the two would always diffract in phase so far as the 00ℓ reflections are concerned and these structure factors would show normal decline. This is not the case. The other possibility is that one ion is at z equal to zero and the other at z equal to $\frac{1}{4}$. For this case they would diffract exactly in

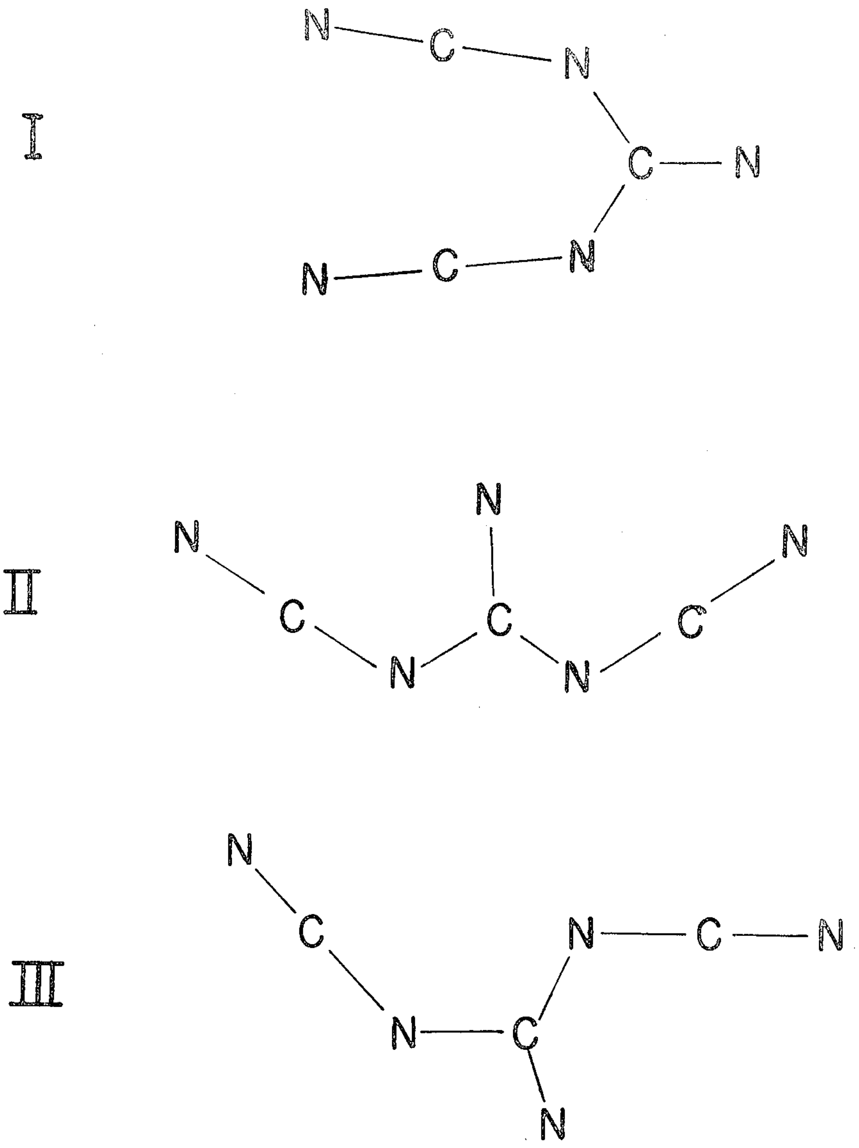

Figure 9

Possible Configurations

phase for $\ell \equiv 0 (\mathrm{mod} 4)$ and 180 degrees out of phase for the $\ell \equiv 2(\mathrm{mod} 4)$ reflections.* Very good agreement between calculated and observed structure factors is obtained with this assumption, as is shown in Table 9.

Table 9

Reflection	$F_o/4$	$F_c/4$
002	23.6	23.2
004	28.8	28.5
006	3.4	4.9
008	9.9	9.1
00,10	1.1	1.4
00,12	3.2	2.8

The temperature factor constant was taken as 1.2 A^2 and an arbitrary scale factor was used. This excellent agreement was partially fortuitous as the first two reflections are extremely strong with correspondingly large reading and extinction errors.

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* If the DCG^- is on the two fold axis it still must be approximately parallel to the mirror planes since otherwise the symmetry related ion would be too close. Therefore the calculated structure factors and the later statement as to the location of peaks in Patterson space are still approximately true.

Before further progress in the assignment of a trial structure could be made, more information was needed. In addition to an hk0 Patterson projection, a generalized Patterson projection was calculated. Beside the interaction between potassiums, the peaks needed are for the interaction of potassium with DCG^-. With the assumption of the z parameters from above, the locations of peaks in Patterson space are as follows:*

$w = 0$ Between two K and between two DCG^- in the same plane

$w = \frac{1}{4}$ Between K and DCG^-

$w = \frac{1}{2}$ Between two K and between two DCG^- in different planes.

The function calculated was:

$$P(u,v) = \sum_h \sum_k [F^2(hk0) - F^2(hk2)] \cos 2\pi hu \cos 2\pi kv$$

The weighting function for the peaks is thus $\cos 2\pi lw$. For the hk0 reflections this gives unit weight to all the peaks and for hk2 +1, -1, and +1 for those at w equal to 0, $\frac{1}{4}$, and $\frac{1}{2}$ respectively. Therefore the above function would be expected to show the K-DCG^- peaks located at $\frac{1}{4}$ with a weight of two with the other peaks removed. The resulting generalized Patterson projection with the addition of the location of the K-K peak from the regular projection is shown in Figure 10. The generalized Patterson projection showed no

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* See footnote on page 39.

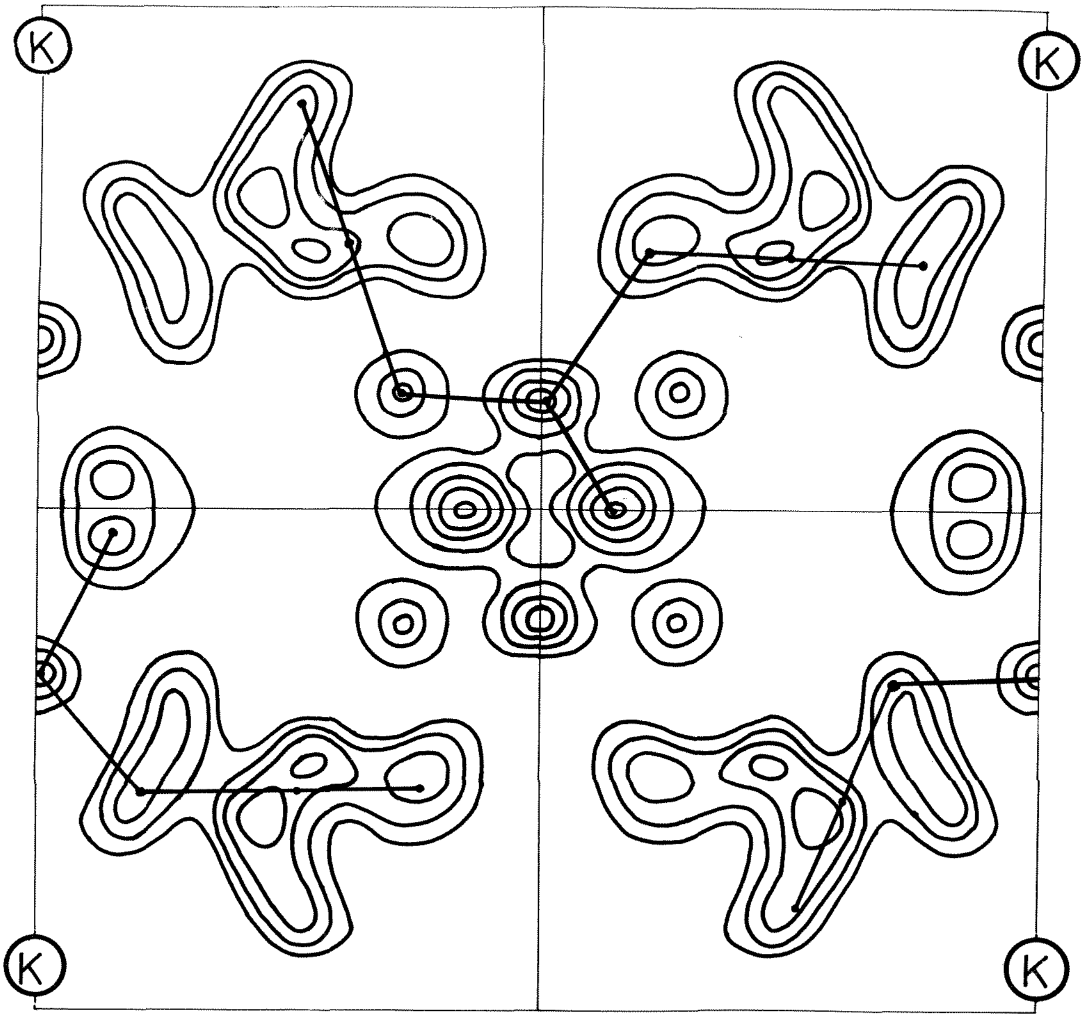

Figure 10. Generalized Patterson Projection

evidence of any K-K interaction but otherwise had the same general appearance as the regular projection although the peaks were sharper.

A trial structure was assigned on the basis of the Patterson projections and the previous considerations. The expected position of the K-K interaction on the projection depends on the location of the potassium ions in the crystal as follows:

Center of symmetry	One double peak at 0, $\frac{1}{2}$
Mirror plane	Two peaks; one at 0, v and one at u, v.
	If it is exactly over a center one double peak at 0, $\frac{1}{2}$
	If it is exactly over the two-fold axis one double peak at u, $\frac{1}{2}$
Two-fold axis	One double peak at u, $\frac{1}{2}$

Since the actual peak is at 0.050, $\frac{1}{2}$, the potassium can be either on the two-fold axis or on the mirror plane with a y parameter of $\frac{1}{4}$. When an attempt was made to fit the peaks of the DCG$^-$, it was possible to fit only configuration III. Since this configuration does not have a two fold axis, the DCG$^-$ was placed in the mirror plane thereby placing the potassium on the two-fold axis. The positions assigned are shown in Figure 10. Two other arrangements are possible both of them attaching the nitrile groups to different nitrogens but keeping the same basic guanidine location. Both of these other structures are of configuration III. These other possibilities were rejected because the symmetry related ion gave an unreasonable Van der Waals distance for one and did not fit the Patterson projection as well for the other.

A structure factor calculation of the hk0 and hkl reflections was made using McWeeny form factors (31) for carbon and nitrogen and those of Bergheis _et al_. (30) for the potassium, with a temperature factor constant of 1.2 A^2. The results were disappointing as the R factors were 40 and 62 respectively. A generalized Fourier projection was calculated with low order terms (about $\frac{1}{2}$ of the total) using the following expression:

$$\rho\ (x,y) = \sum_h \sum_k [F(hk0) - F(hkl)] \quad \cos 2\pi\, \underline{h} \cdot \underline{r}$$

As the mirror planes are perpendicular to the c axis an [001] projection is a logical choice for a Fourier projection. However in this structure such a synthesis would be very difficult to interpret. The DCG^- is almost bisected by the projection of the two-fold axis resulting in very bad overlap with the ion related by this symmetry element. Nevertheless the situation is ideal for a generalized Fourier projection. With the above expression the hk0 reflections give a unit weighting factor to the projected peaks and the hkl reflections give weights of 0, 1, 0, and -1 for z equal to 0, $\frac{1}{4}$, $\frac{1}{2}$. and 3/4 respectively. The net weights are therefore 1, 2, 1, and 0 respectively so the DCG^- should be resolved. The potassium ions have a projected weight of two since the two ions related by a mirror plane have the same x and z parameters.

The resulting generalized Fourier projection showed a clear indication of all atoms (although with wrong relative peak heights) except C 1 which had only a small peak. A false peak was present on the extension of the C2-N3 bond. One possibility was that a wrong structure had been assigned and C 1 should be removed with the "new atom" replacing it. However since C 1 is the central guanidine carbon such a structure could not be devised. Since the false peak can be related by symmetry with N3 it seemed likely that this effect was due to poor sign assignments, particularly for the hkl reflections. Considerable shifts were indicated and a new structure factor calculation gave R factors of 39 and 48 for the hk0 and hkl reflections which represents considerable improvement for the latter. The resulting generalized Fourier projection was also greatly improved. However two more refinement cycles only reduced the R factors to 31 and 44.

Since the refinement was so slow another trial structure was considered in which the cyanide group C2-N3 was moved to N 1. However the structure factor agreement was poor and the generalized projections showed a very poor peak for C 2' while showing a peak in its original position. (The nitrogen position was approximately the same in the two structures.) Despite refinement procedures this situation continued so this trial structure was discarded. The original structure was refined using both least squares and generalized Fourier projections (at first regular projections, and later difference projections) and making shifts only when the indicated changes were the same in the two methods. These procedures eventually succeeded in reducing the R factors to 16 and 18.

At this stage the hk2 and hk3 structure factors were calculated and yielded R factors of 17 and 21 respectively. After one least squares the calculations were transferred to the Datatron computor using the program of Pasternak, Nathan, and Marsh for space group $P2_1/a$. The structure factor expressions are the same for the two space groups if the atoms are kept arbitrarily in their special positions and the x and z parameters are interchanged. After several refinement cycles the ℓ even layers (containing potassium contributions) had a larger R factor than the ℓ odd layers. This was explained by the fact that the even layers had very strong reflections which were calculating much larger than the observed values. Their effect on the least squares was small as they had a small weighting factor. Since this was probably due to extinction, a correction was made by plotting I_c/I_o versus I_c and applying the extinction coefficient, taken from the slope of the curve, to the strong reflections (40). An anisotropic term, unique in the c direction, was also introduced in the temperature factor for the DCG^-. This was evaluated by comparison of the hk1 and hk3 reflections. These structure factors depend only on DCG^- and the trignometric portion has the same magnitude for a given value of h,k. Therefore the only differences were due to the form factors and temperature factor in the c direction. The temperature factor constants were:

B (K)	1.85 A^2
$B_{\perp c}$(DCG)	0.90
$B_{\parallel c}$(DCG)	3.84

After several refinement cycles the indicated shifts were 0.001 to 0.002 A. The final parameters are given in Table 10 with the corresponding R factors. The standard deviations were obtained as described on page 16. The observed and calculated structure factors are given in Appendix II.

At all stages of the refinement procedure the terminal NCN groups were not linear. Whenever an attempt was made to straighten these groups, the atoms moved so as to restore the original non-linearity. Two generalized difference syntheses were calculated using $F_o - F_c$ from the final parameters, one with the hk0 and hk1 data and the other with the hk2 and hk3. Neither indicated any shifts which would tend to straighten these groups. They do indicate that both hydrogen atoms are on N 1. The combination of these syntheses is shown in Figure 11.

The question arises as to the validity of using space group Pbcm for this structure. In view of the excellent agreement between calculated and observed structure factors, there does not seem to be much doubt that the structure is close to the special positions assumed. Small deviations

Table 10

Positional Parameters
(x 10^4)

Atom	x	y	z
K	0247	7500	0000
N 1	4909	3222	2500
N2	2321	3418	2500
N3	2404	6151	2500
N4	3520	1127	2500
N5	1093	-0098	2500
C 1	3588	2638	2500
C2	2424	4871	2500
C3	2230	0531	2500

Standard Deviations

K	0.0018 A
N	0.0059
C	0.0066

R factors

hk0	9.5
hk1	10.3
hk2	9.3
hk3	11.0
Overall	9.7

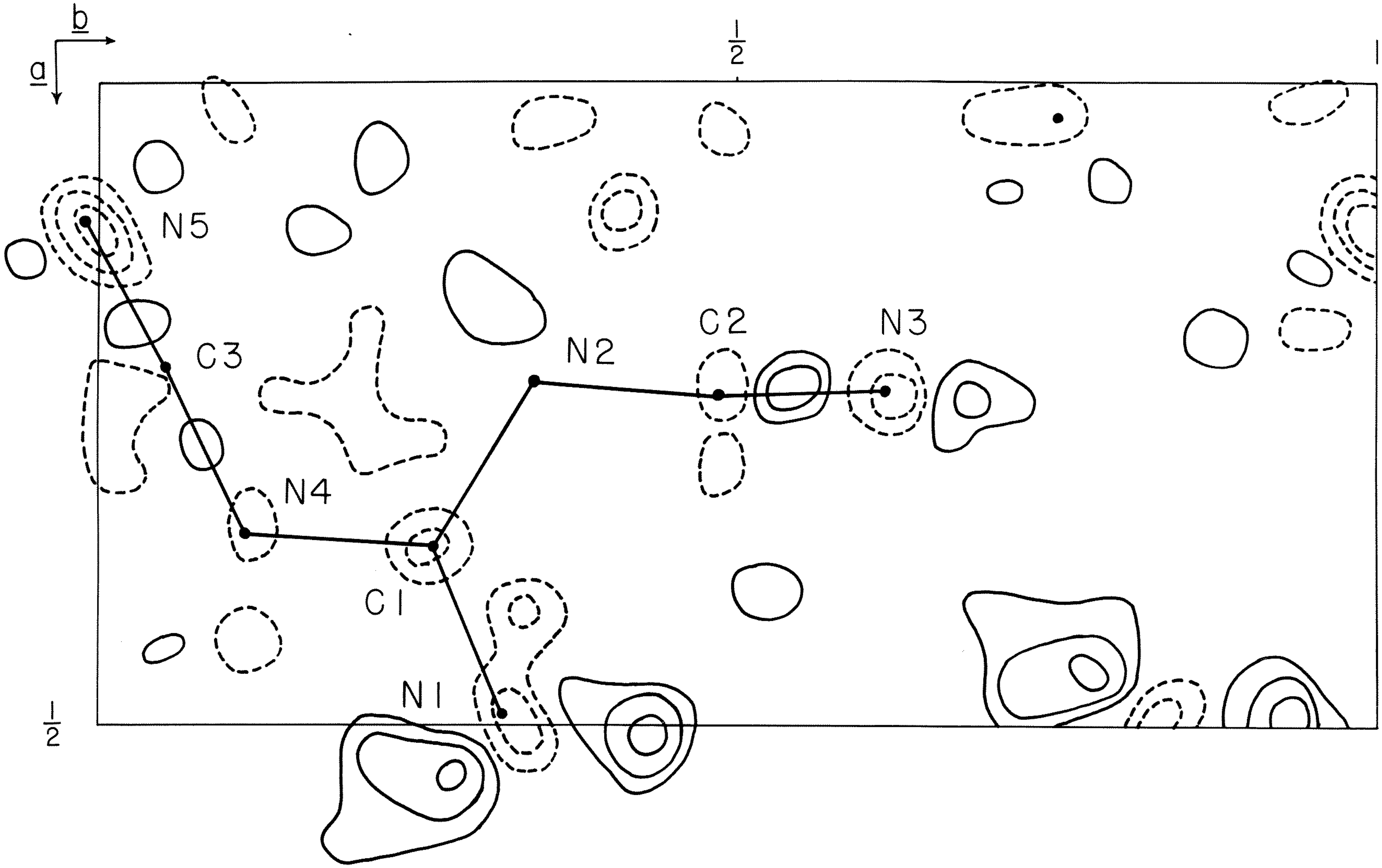

Figure 11. Combined Generalized Difference Fourier Projections

Contour - $\frac{1}{4}$ electron

of the DCG^- from the mirror plane would have very small effects on the bond lengths inside a layer. A displacement of 0.1 A would increase a bond length of 1.30 A by 0.004 A. The effect of random deviations from this plane on the structure factors would be compensated by the anisotropic temperature factor.

Discussion of the Structure

The intramolecular distances and angles are shown in Figure 12 and are given in Table 11 compared with results from other related investigations.* Several of the possible resonance forms for DCG^- are shown in Figure 13. The two hydrogen atoms have been placed on N1 as indicated by the difference syntheses. The only other reasonable possibility is one hydrogen on N1 and one on N4. Placing a hydrogen on any of the other nitrogens would tend to give them a positive charge which is unlikely in view of the proximity of the potassium ions. Both of the possible structures have a large number of resonance forms and are in agreement with the hydrogen bonding scheme discussed below. However since only the first agrees with the peaks on the difference synthesis, it was chosen.

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* A carefully refined investigation of the distances in the guanidinium ion has not yet been made. Studies of guanidinium iodide (44) and guanidinium bromate (45) gave 1.18 A and 1.34 A respectively for the C-N distances. Trisodium tricyanomelamine trihydrate (the sodium salt of cyanuric tricyanide) has also been studied but not carefully refined (46).

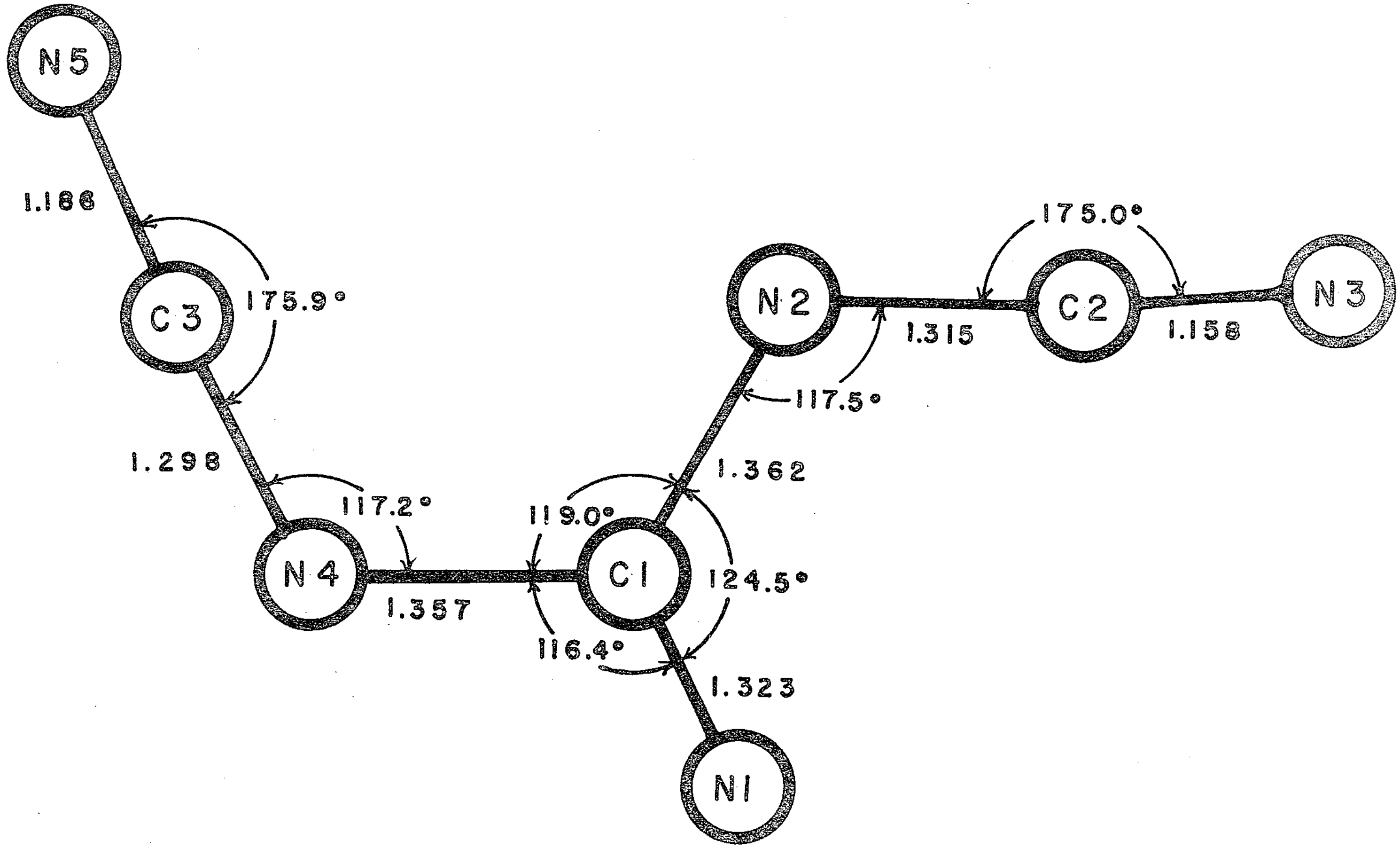

Figure 12

Molecular Dimensions

Table 11

Bond Distances and Angles

	I	II	III	IV
C 1-N1	1.315 A	1.34 A	1.33 A	1.34 A
C 1-N2	1.362	1.37	1.32	1.34
C 1-N4	1.357	1.36	1.33	1.35
N2-C2	1.315	1.28		
N4-C3	1.294			
C2-N3	1.158	1.22		
C3-N5	1.186			
∡N1-C 1-N2	124.5°	116°	117.5°	129°
∡N2-C 1-N4	119.0	120	122	112
∡N1-C 1-N4	116.5	124	120.5	118
∡C 1-N2-C2	117.5			
∡C 1-N4-C3	117.2			
∡N2-C2-N3	5.1			
∡N4-C3-N5	4.0			
σ (C-N)	0.009 A	0.02 A*	0.007 A	0.015 A
σ (angle)	0.6°		0.5°	

I	Potassium Dicyanoguanidine
II	Dicyandiamide (41)
III	Methyl Guanidinium Nitrate (42)
IV	Nitroguanidine (43)

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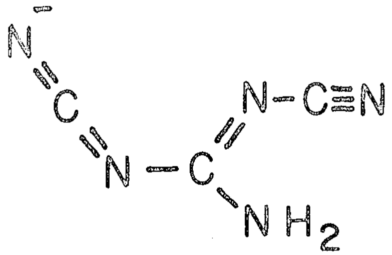
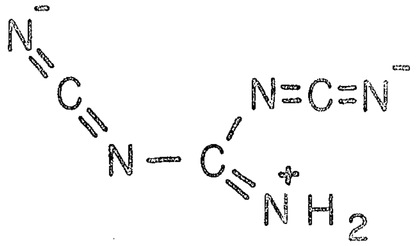
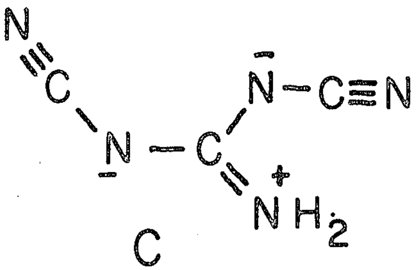
* Estimated probable error



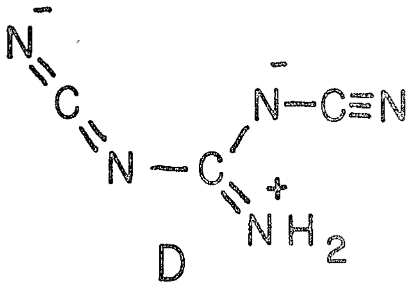
A



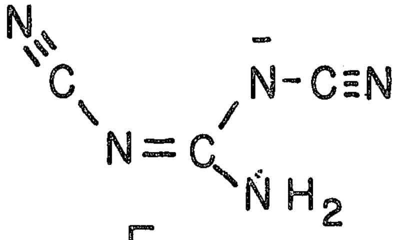
B



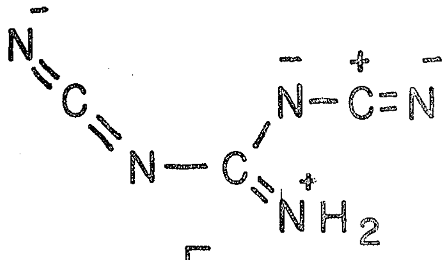
C



D



E



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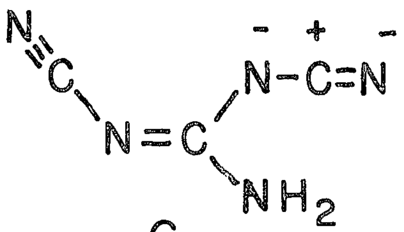
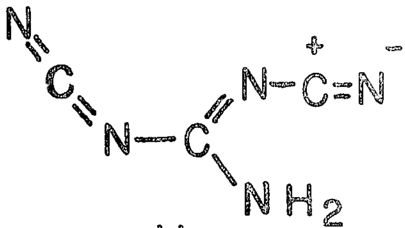


G



H

Figure 13

Resonance Structures

There is a significant[*] difference between the guanidine C-N distances which does not occur in the other compounds. This indicates that the resonance structures having C 1-N1 double bonds predominate. This is reasonable as these structures place greater negative formal charge on the nitrogens which are stabilized by the potassium ions nearby. The differences in the angles is possibly due to the effects of hydrogen bonding as discussed below.

In the crystal the two terminal NCN groups are not equivalent as they have different environments. In particular N2 is near a potassium while N4 is involved in hydrogen bonding. C2-N3 appears to have more triple bond character and C2-N2 less double bond character than the corresponding bonds on the other portion of the ion and this is possibly significant. Since N5 is near four potassium ions while N3 is near only two it might have a greater tendancy to acquire a negative charge, meaning a greater contribution of the resonance forms with a C3-N5 double bond. Application of the electrostatic valence rule (48) indicates that N5 has a charge of $-\frac{1}{2}$ and N2 and N3 each has a charge of $-\frac{1}{4}$.

In view of the uncertainty of the equivalence of the two sides of the ion and the many possible resonance forms, there does not seem to be much point in making a detailed valence bond correlation of the bond lengths and derived bond numbers with distribution of resonance forms. The C-N double

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[*] Significance terminology used is that of Cruickshank and Robertson (47).

bond character is approximately 30, 30, and 40% in the guanidine group and 50% for the adjacent C-N bonds. Since the total number of bonds about N2 and about N4 is approximately 2.8, this indicates a 20% contribution of resonance forms such as E which have only two bonds to the nitrogen, giving it a negative formal charge.

One disturbing result of this investigation is the possible non-linearity of the NCN groups. Application of the significance tests indicates that these deviations are highly significant. If so, this effect might arise as a result of the packing in the crystal. Figure 14 shows that N5(IV) is pushing on C2, 3.21 A away. Since N2 and N3 tend to be held in place by the attraction of the potassium ions, this would result in C2 moving in the observed direction. Also this might cause N5 to bend back. This effect would be facilitated by the contribution of resonance forms such as G related to the resonance structure used to explain the large dipole moment of HCN (Ref. 48, page 198). For making an estimate of the energy required to bend the bonds by these amounts, the bending force constants (49) for either N_2O or HCN might be chosen to approximate that of the NCN group. The former gives 720 and 460 cal/mole and the latter 272 and 174 cal/mole for the two groups. The value for DCG^- may lie between these values. To straighten the 5 degree bend by moving the nitrogens would mean a loss of approximately 2 kcal/mole of electrostatic energy if one-fourth of an electronic charge is assumed to be on each nitrogen. This value is higher than the overall one as the repulsive forces have not been included. The loss of energy due to a straightening by moving the carbon atom is difficult to estimate because of uncertainty in the quantities involved.

The intermolecular distances and angles are shown in Figure 14 and given in Table 12. The potassium ions are spaced by 3.56 A in the c direction. Each potassium is surrounded by eight nitrogens each of which has a partial negative charge. They are arranged to form a distorted Archimedes antiprism.

The DCG^- ions are held together in chains parallel to the b direction by hydrogen bonds between N1 and N4(II) and N1(II) and N3(III). The C-NH--N angles are 142 and 119 degrees and it may be that in an effort to approach 120 degrees the N2-C 1-N1 angle has increased to the observed value. The chains are held together in planes by the potassium ions above and below the plane. The planes are separated by 3.56 A. The DCG^- in the other planes have not been shown in Figure 14 but are generated by two-fold axes through the potassiums.

It seems probable that dicyanoguanidine has a structure with a hydrogen atom attached to either N2 or N4 of the dicyanoguanidide anion. Therefore the removal of this hydrogen would result in approximate equivalence of various resonance forms. By analogy with guanidine (or methyl guanidine which is also a very strong base), this would then be a strong acid. The negative charge resulting from the

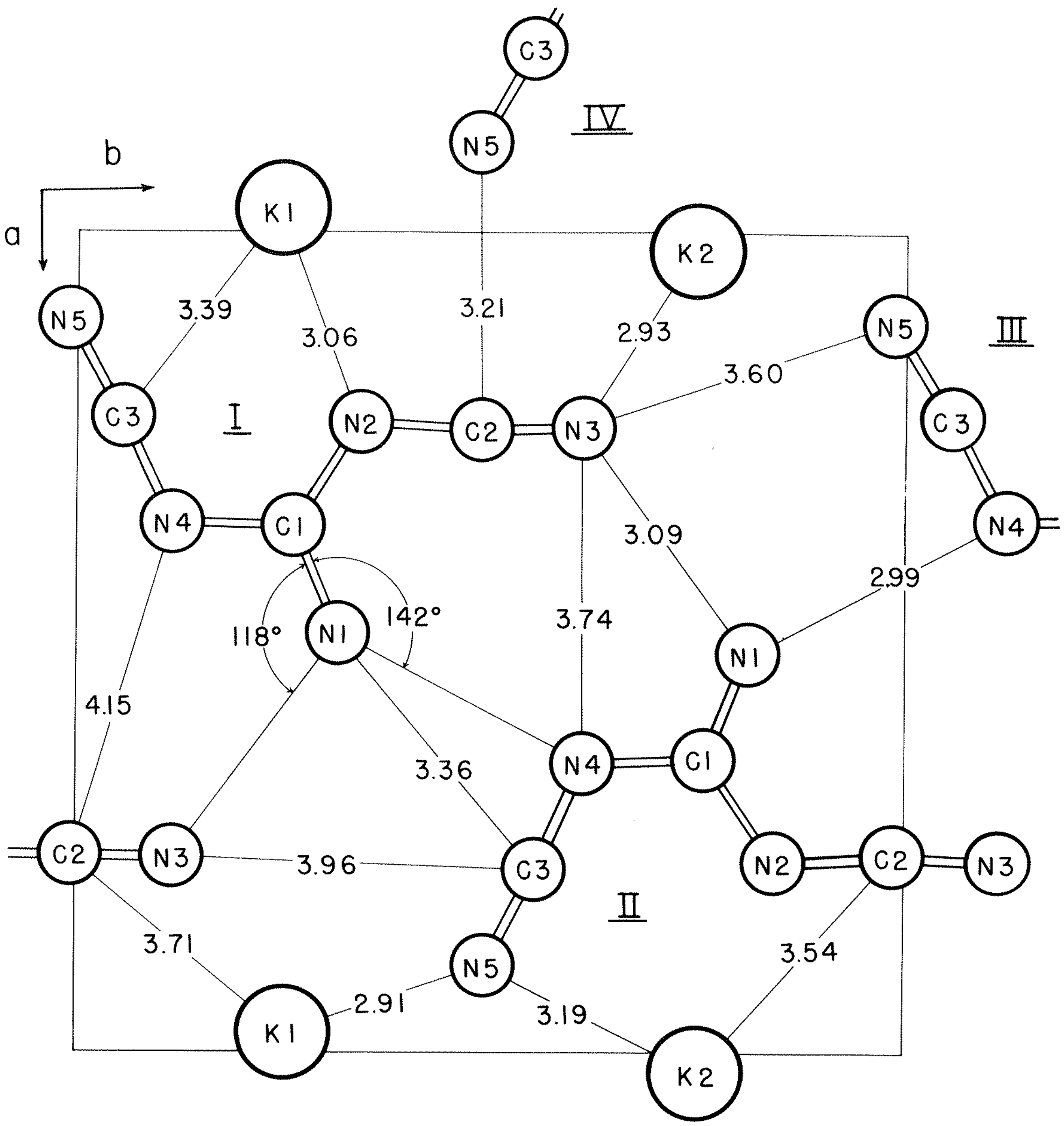


Figure 14. Packing Distances

Table 12

Packing Distances and Angles

K 1-N2	3.07 A
K2-N3	2.93
K 1-N5	3.19
K 1-$N5_{IV}$	2.91
K2-C2	3.57
K 1-C2	3.71
K 1-C3	3.39
N 1-$N3_{V}$	3.09
N 1-$N4_{II}$	2.99
N 1-$C3_{II}$	3.36
N3-$N4_{II}$	3.74
N3-$N5_{III}$	3.60
N3-$C3_{III}$	3.96
C2-$N5_{IV}$	3.21
N2-C3'	3.72
N4-C 1'	3.73
C 1-C 1'	3.57
C2-C3'	3.58
∡C 1-N 1-$N3_{V}$	119°
∡C 1-N 1-$N4_{II}$	142°

See Figure 14 for numbering scheme

X' is an atom in the molecule related by a two-fold axis.

ionization of the acid is distributed to all the nitrogens instead of being localized on one. An equivalence could also be attained by addition of a hydrogen to dicyanoguanidine so that both N2 and N4 would have a hydrogen and the dicyanoguanidine would be acting as a base. However the nitrile groups are electronegative and therefore stabilize the negative ion but not the positive one.

The stability of the ion toward polymerization is probably due to the electrostatic energy present in the salt in addition to the extra resonance energy. The packing is such that apparently this electrostatic energy is the primary consideration in determining the arrangement of the ions.

PART III

THE STRUCTURE OF PHENYL ISOCYANATE DIMER

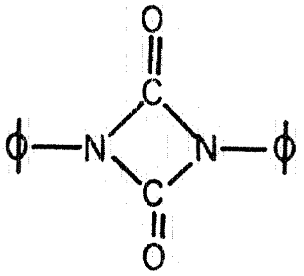
Introduction

Hoffman (50) prepared a dimer of phenyl isocyanate by treating the latter with triethyl phosphine. There are several possible configurations for the dimer as shown in Figure 15. Reasonable five and six membered rings formed from the isocyanate groups cannot be formulated unless a rearrangement of the phenyl groups to the carbon is assumed. Structure I, given by Staudinger (51), was the one generally accepted though it had not been definitely established as the correct one. Therefore an X-ray investigation of the structure of this dimer was undertaken to establish its configuration and to determine its dimensions as no structure containing any of the possible rings had been studied.

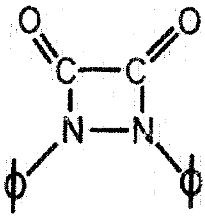
The phenyl isocyanate dimer was obtained from Dr. J. D. Roberts of this department. The crystals used for this study were needles, approximately 0.1 mm in diameter, prepared by slow recrystallization from an alcohol-water mixture by Dr. Hughes. Precession (Mo K_α, $\lambda = 0.7107$ A) and Weissenburg (Cu K_α, $\lambda = 1.542$ A) photographs showed Laue symmetry mmm and an orthorhombic unit cell with:

$$a = 9.13 \pm 0.02 \text{ A}$$
$$b = 11.83 \pm 0.02$$
$$c = 10.62 \pm 0.02$$

The intensity absences were for $0k\ell$ when $k + \ell$ was odd and for $hk0$ when h was odd. This indicates either space group Pnma or $Pn2_1a$, the latter being non-centrosymmetric.



I



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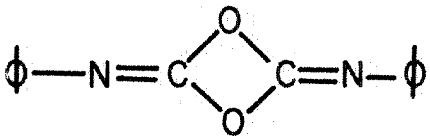

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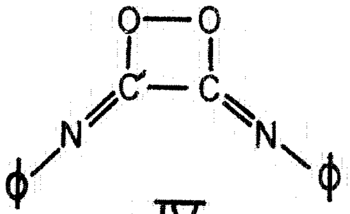
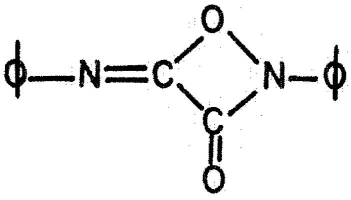
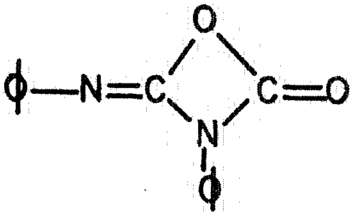


IV



V



VI

Figure 15

Possible Configurations

A piezoelectric test for a polar axis gave a negative result.* It was decided to attempt to determine a structure based on the centrosymmetric space group Pnma. Intensity photographs were made with the precession camera with the same estimation techniques as used for acetamide hemihydrochloride (page 7).

At this stage of the investigation, the structure of the dimer was published by C. J. Brown (52). His X-ray results confirming Staudinger's configuration were obtained from three dimensional data with a final R factor of 21. His crystals were of an entirely different form, being monoclinic with:

a = 12.77 A	c = 8.09	Space Group $P2_1/c$
b = 5.50	β = 92°	Z = 2

The two lattices could not be reconciled though the orthorhombic unit cell had almost twice the volume of the monoclinic cell, the volumes being 1147 and 1134/2 A^3 respectively. This results in almost the same density if four molecules are assumed to be in the orthorhombic cell. Brown's crystals were flat plates obtained by recrystallization from benzene. They were also prepared by Dr. Hughes but were discarded in favor of the needles which were more suitable for X-ray studies.

The results of Dr. Brown's study are shown in Figure 16 taken from his paper. The standard deviation of a bond length is given as 0.014 A. Several of the distances seem quite unusual. One strange result is the large difference of the two C-N bonds in the ring, 1.42 and 1.49 A. Another follows

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* See footnote on page 36.

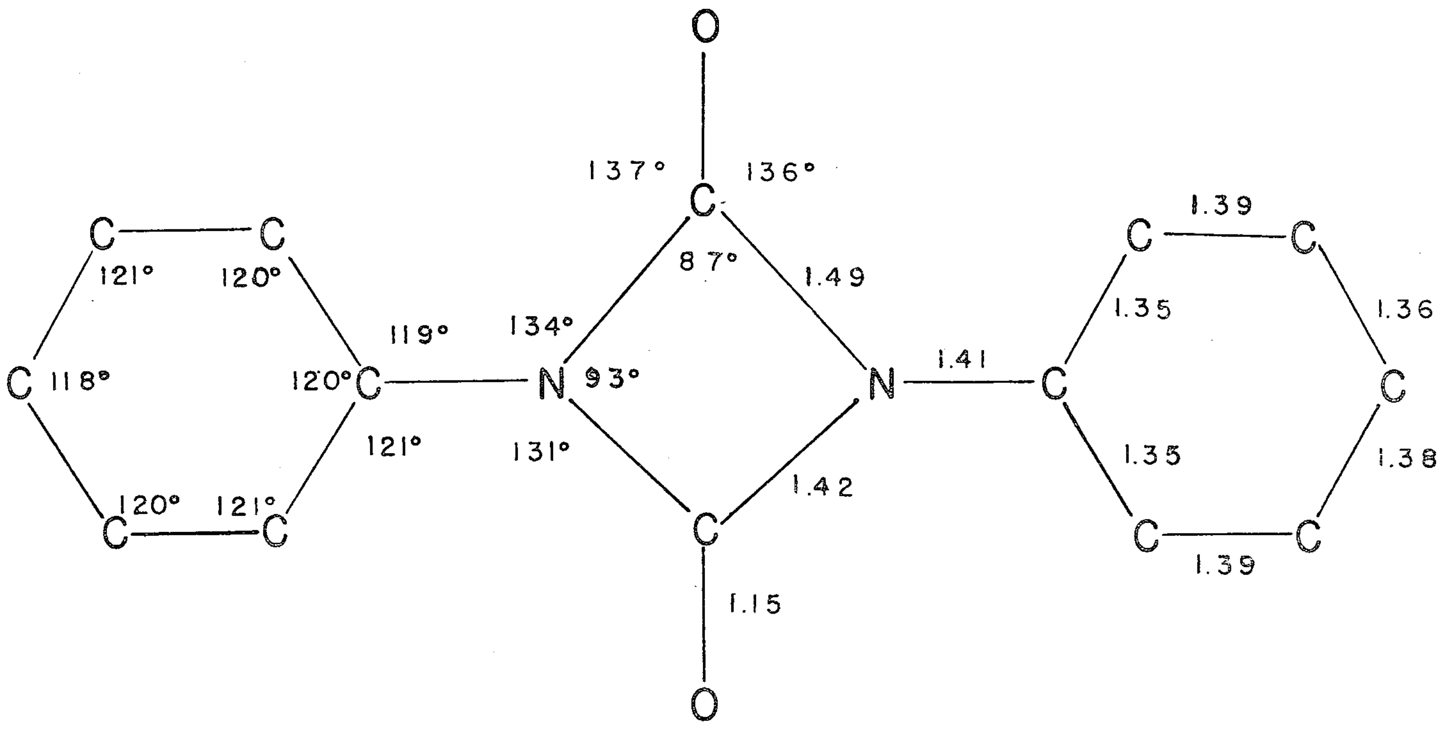
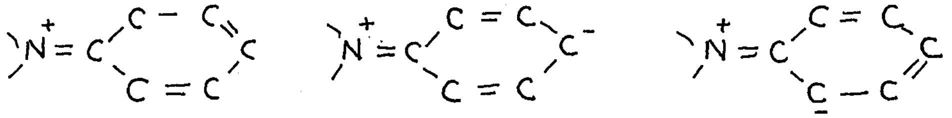


Figure 16

Phenyl Isocyanate Dimer

C.J. Brown, J. Chem. Soc. (1955) 2935

from the fact that the N-C(phenyl) distance of 1.41 A is shortened considerably from the normal C-N single bond distance of 1.47 A indicating contributions of the resonance forms:



This would tend to make the two adjacent C-C bonds of the phenyl group longer than the other four bonds yet the opposite results are obtained. The entire molecule is non-planar.

In view of the above considerations, this investigation was continued. Since the general positions of Pnma are eight-fold, the four molecules must lie in special positions, either on mirror planes or at centers of symmetry. The former were considered first since the molecules must lie either in the mirror plane or perpendicular to it. The y parameters are therefore fixed (assuming reasonable parameters in the second case) and calculation of the 0k0 structure was made for various orientations. The agreement was poor for both cases and this hypothesis was abandoned. The centers were then considered. The possible y parameters were limited in range, being constrained not to approach the mirror planes too closely in order to avoid short intermolecular distances. When a suitable trial structure could not be obtained, it was feared that the true space group was $Pn2_1a$ which had neither mirror planes nor centers of symmetry. Therefore it was decided to make a Wilson intensity distribution test, the principle of which is that a centrosymmetric crystal has a distribution of intensities different from a non-centrosymmetric one (53). The results of this test, using 287 reflections, are shown in Figure 17 compared with the results to be expected for ideal centrosymmetric and non-centrosymmetric structures. N(z) is the fraction of the reflections which have an intensity equal to or less than the fraction z of the average intensity. The N(z) values are averages of values obtained by dividing the reflections into several ranges of sinθ. The curve follows the centrosymmetric line for larger intensities but deviates from it at small intensities. The two ideal curves are calculated assuming a structure with similar atoms distributed in the unit cell with no linear integral relationships between the coordinates (no hypersymmetry). The first condition is satisfied for the phenyl isocyanate dimer but the second is not. Even if the entire molecule does not have elements of symmetry, it contains fragments (the three rings) which do. Therefore it would be expected that the intensity distribution curve would be above that for the ideal case (54). Since the actual curve lies above the non-centrosymmetric one it seems probable that this structure is non-centrosymmetric. The intensity distribution is almost identical with that of di-p-anisyl nitric oxide discussed by Lipson and Woolfson (54). In this case the systematic absences indicated two space groups, one centrosymmetric. However the centrosymmetric space group would require the molecule to have 2/m symmetry which is impossible. Therefore they concluded that the apparently centrosymmetric intensity distribution was a result of the hypersymmetry due

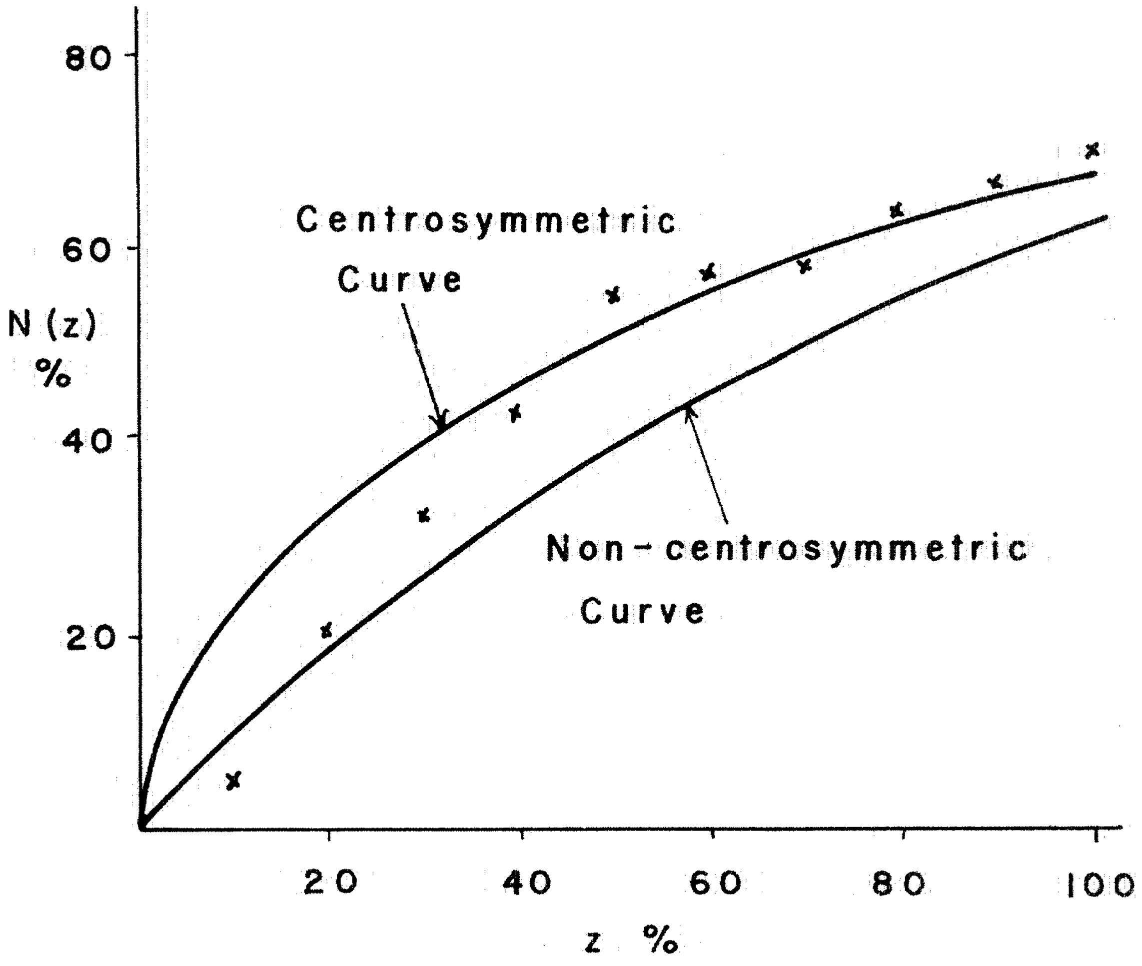


Figure 17

Intensity Distribution

Curves

to the two phenyl groups.

For space group $Pn2_1a$ the constraints of not being too near a center or a mirror plane are removed so a trial structure probably could be obtained. However the computational work has been greatly increased by being a non-centrosymmetric space group and thus introducing a general phase angle in every reflection. In view of the fact that there is another crystalline modification which is known to be centrosymmetric, it did not seem practical to continue the work on the orthorhombic form.

Appendix I

Structure Factor Table for

Acetamide Hemihydrochloride

(electrons x 10)

h	k	ℓ	F_o	F_c
0	0	2	113	94
0	0	4	195	245
0	0	6	177	170
0	0	8	72	64
0	1	1	147	-124
0	1	2	202	-205
0	1	3	273	258
0	1	4	36	40
0	1	5	30	35
0	1	6	< 15	3
0	1	9	76	38
0	2	0	480	508
0	2	1	118	79
0	2	2	312	291
0	2	3	161	152
0	2	5	52	-55
0	2	6	102	106
0	3	1	316	260
0	3	2	180	-181
0	3	3	110	114
0	3	4	15	-13
0	3	5	178	168
0	3	6	< 15	-7
0	4	0	117	-124
0	4	1	26	25
0	4	2	234	230
0	4	3	107	103
0	4	4	24	17
0	4	5	< 20	-18
0	4	6	48	56
0	5	1	260	258
0	5	2	31	-26
0	5	3	151	167
0	5	4	24	-41
0	5	5	138	130
0	5	6	37	30
0	6	0	30	14
0	6	1	32	33
0	6	2	45	44
0	6	3	< 22	-7
0	6	4	34	38
0	6	5	< 20	-2
0	6	6	57	58
0	7	1	144	133
0	7	2	< 25	-19
0	7	3	69	124
0	7	4	42	29
0	7	5	32	41
0	7	6	23	15
0	7	7	84	58
0	8	0	90	82
0	8	1	65	48
0	8	2	26	33
0	8	4	71	78
0	8	5	19	-22
0	9	1	53	64
0	9	4	34	29
0	10	0	34	38

Appendix I (Continued)

h	k	ℓ	F_o	F_c
1	0	0	73	93
1	0	2	204	-205
1	0	4	114	109
1	0	6	63	66
1	0	-2	465	557
1	0	-4	52	-36
1	0	-6	152	168
1	0	-8	67	61
1	0	-10	76	60
1	1	0	203	200
1	1	1	597	772
1	1	2	108	112
1	1	3	275	250
1	1	4	88	-79
1	1	5	84	101
1	1	6	54	51
1	1	7	72	78
1	1	-1	39	9
1	1	-2	34	30
1	1	-3	392	341
1	1	-4	75	66
1	1	-5	166	165
1	1	-6	79	67
1	1	-7	72	72
1	1	-9	72	38
1	2	0	100	100
1	2	1	395	-427
1	2	2	106	95
1	2	3	141	136
1	2	4	91	93
1	2	5	36	-29
1	2	-1	71	-64
1	2	-9	314	302
1	2	-3	134	-127
1	2	-4	145	160
1	2	-5	93	-99
1	2	-6	65	76
1	3	0	232	231
1	3	1	120	103
1	3	2	85	85
1	3	3	146	137
1	3	4	79	-74

h	k	ℓ	F_o	F_c
1	3	5	64	81
1	3	6	47	56
1	3	-1	380	362
1	3	-2	213	193
1	3	-3	29	17
1	3	-4	52	35
1	3	-5	151	161
1	3	-6	94	85
1	3	-7	103	106
1	4	0	234	225
1	4	1	120	-98
1	4	2	242	224
1	4	3	< 26	-15
1	4	4	94	113
1	4	6	71	80
1	4	-1	194	-168
1	4	-2	181	161
1	4	-3	82	-87
1	4	-4	218	219
1	4	-5	< 15	10
1	4	-7	66	-69
1	5	0	56	58
1	5	1	< 20	-7
1	5	2	32	-10
1	5	3	76	72
1	5	4	< 23	11
1	5	6	< 20	-13
1	5	-1	171	149
1	5	-2	107	89
1	5	-3	39	46
1	5	-4	43	-52
1	5	-5	112	113
1	5	-7	68	71
1	6	0	213	201
1	6	1	52	50
1	6	2	123	121
1	6	3	25	-10
1	6	4	95	123
1	6	6	43	52
1	6	-1	73	-71
1	6	-2	102	112
1	6	-3	49	48

Appendix I (Continued)

h	k	ℓ	F_o	F_c
1	6	-4	55	92
1	6	-5	39	33
1	7	0	24	25
1	7	1	70	59
1	7	2	71	-55
1	7	3	42	45
1	7	-1	37	37
1	7	-2	42	-53
1	7	-3	102	126
1	7	-4	18	-41
1	7	-5	42	48
1	8	0	98	89
1	8	1	< 20	7
1	8	2	65	77
1	8	3	31	35
1	8	-1	< 26	4
1	8	-2	42	64
1	8	-3	73	71
1	9	0	< 20	6
1	9	1	47	52
1	9	2	38	-17
1	9	-1	49	64
1	9	-2	32	-51
1	9	-3	66	81
2	0	0	27	-31
2	0	2	206	219
2	0	4	199	181
2	0	-2	260	270
2	0	-4	61	75
2	0	-8	26	48
2	1	0	105	123
2	1	0	135	123
2	1	1	219	230
2	1	2	223	-212
2	1	3	21	36
2	1	4	< 26	6
2	1	5	29	31
2	1	-1	437	434
2	1	-2	266	-247
2	1	-3	151	143

h	k	ℓ	F_o	F_c
2	1	-4	62	-49
2	1	-5	245	258
2	1	-6	< 36	-12
2	1	-7	119	109
2	1	-9	129	107
2	1	-11	43	26
2	2	0	143	105
2	2	1	144	143
2	2	2	205	196
2	2	3	161	163
2	2	4	113	108
2	2	5	42	-49
2	2	-1	62	62
2	2	-2	97	99
2	2	-3	269	213
2	2	-4	227	209
2	2	-5	< 21	18
2	2	-6	76	77
2	3	0	66	-64
2	3	1	112	102
2	3	2	244	-240
2	3	3	91	94
2	3	4	< 26	12
2	3	5	54	82
2	3	-7	118	148
2	3	-1	279	272
2	3	-2	215	-186
2	3	-3	169	162
2	3	-4	33	-26
2	3	-5	75	28
2	3	-6	96	-81
2	4	0	177	166
2	4	1	156	153
2	4	2	122	111
2	4	3	24	31
2	4	4	42	47
2	4	-1	94	92
2	4	-2	94	95
2	4	-3	28	-29
2	4	-4	235	231
2	4	-6	139	113

Appendix I (Continued)

h	k	ℓ	F_o	F_c
2	5	0	165	-137
2	5	1	123	131
2	5	2	< 20	-6
2	5	3	65	70
2	5	4	< 26	-1
2	5	-1	79	69
2	5	-2	59	69
2	5	-3	116	113
2	5	-4	< 15	-7
2	5	-6	66	-73
2	6	0	115	105
2	6	1	44	42
2	6	2	60	50
2	6	3	59	-46
2	6	4	48	57
2	6	-1	29	-17
2	6	-2	159	165
2	6	-3	94	-93
2	6	-4	85	88
2	6	-6	121	104
2	7	0	40	-21
2	7	1	105	102
2	7	2	< 20	26
2	7	3	65	60
2	7	-1	32	18
2	7	-2	83	99
2	7	-3	52	68
2	7	-4	15	-7
2	8	0	73	80
2	8	1	< 27	-13
2	8	2	30	35
2	8	3	21	-13
2	8	-1	67	-63
2	8	-2	80	103
2	9	0	39	36
2	9	1	< 27	23
2	9	3	53	62
2	9	-1	45	45

h	k	ℓ	F_o	F_c
2	10	0	56	58
2	10	1	21	-20
2	10	-1	17	-20
3	0	0	295	297
3	0	2	167	166
3	0	4	83	94
3	0	-2	325	305
3	0	-4	273	274
3	0	-6	177	174
3	0	-8	157	160
3	1	0	42	57
3	1	1	38	38
3	1	2	< 27	-8
3	1	3	25	32
3	1	4	52	50
3	1	5	70	75
3	1	-1	28	21
3	1	-2	99	92
3	1	-3	118	122
3	1	-4	112	-101
3	1	-5	< 36	24
3	1	-6	39	56
3	1	-7	42	40
3	1	-8	39	-40
3	2	0	264	250
3	2	0	275	250
3	2	1	56	56
3	2	2	132	137
3	2	3	107	-105
3	2	4	44	49
3	2	5	< 26	-13
3	2	-1	234	-192
3	2	-2	120	116
3	2	-3	77	78
3	2	-4	183	189
3	2	-8	49	52
3	3	0	< 15	8
3	3	1	31	35

Appendix I (Continued)

h	k	ℓ	F_o	F_c
3	3	2	53	61
3	3	3	111	109
3	3	4	44	52
3	3	5	34	42
3	3	-1	170	159
3	3	-2	36	42
3	3	-3	276	225
3	3	-4	36	-21
3	3	-5	84	70
3	3	-9	98	84
3	4	0	110	96
3	4	1	51	-45
3	4	2	79	84
3	4	3	77	-69
3	4	-1	42	42
3	4	-2	15	22
3	4	-3	35	-29
3	4	-4	39	47
3	4	-5	60	-55
3	5	0	62	-47
3	5	1	84	91
3	5	2	71	76
3	5	3	90	81
3	5	-1	195	190
3	5	-2	64	-62
3	5	-3	156	147
3	5	-4	83	91
3	5	-5	199	149
3	6	0	< 23	-11
3	6	1	56	-40
3	6	2	50	56
3	6	3	< 20	-3
3	6	-1	102	106
3	6	-2	75	76
3	6	-3	59	-58
3	6	-5	< 54	-24
3	7	0	50	-39
3	7	1	99	107
3	7	3	23	27
3	7	-1	102	103
3	7	-2	47	-43
3	7	-3	46	50
3	7	-5	139	114
3	8	0	28	24
3	8	1	< 26	16
3	8	-2	57	76
3	8	-3	< 15	-12
3	9	0	15	-12
3	9	1	54	59
3	9	2	32	-26
3	9	-3	39	29
3	10	0	57	45
4	0	0	50	-55
4	0	2	46	51
4	0	4	< 20	-10
4	0	-2	154	166
4	0	-4	< 36	-5
4	0	-6	51	41
4	0	-8	111	101
4	0	-10	59	71
4	1	0	29	-25
4	1	1	148	166
4	1	2	< 26	12
4	1	3	77	76
4	1	4	< 20	-7
4	1	5	38	51
4	1	-1	134	144
4	1	-2	99	86
4	1	-3	143	150
4	1	-4	24	-16
4	1	-5	215	221
4	1	-6	39	32
4	1	-7	91	87
4	1	-8	63	47
4	2	0	93	88
4	2	1	20	-5
4	2	2	< 26	20
4	2	3	< 27	4
4	2	4	20	24

Appendix I (Continued)

h	k	ℓ	F_o	F_c
4	2	-1	43	-39
4	2	-2	116	121
4	2	-3	97	-88
4	2	-4	< 36	26
4	3	0	< 20	18
4	3	1	67	63
4	3	2	< 26	19
4	3	3	82	86
4	3	4	23	-28
4	3	-1	< 20	19
4	3	-2	39	43
4	3	-3	140	159
4	3	-4	< 36	5
4	3	-5	112	111
4	4	0	188	182
4	4	1	74	-69
4	4	2	< 26	17
4	4	3	26	30
4	4	4	47	56
4	4	-2	104	96
4	4	-3	< 33	4
4	4	-4	108	112
4	5	0	60	67
4	5	1	< 23	5
4	5	2	< 26	8
4	5	3	32	40
4	5	4	32	-28
4	5	-1	30	32
4	5	-2	75	-69
4	5	-3	46	56
4	6	0	85	89
4	6	1	54	-44
4	6	2	54	71
4	6	4	32	35
4	6	-2	66	69
4	6	-3	51	60
4	6	-4	128	128
4	7	1	17	17
4	7	2	< 17	3
4	7	-1	64	71
4	7	-2	44	-43

h	k	ℓ	F_o	F_c
4	8	2	54	58
4	8	-2	39	46
4	8	-4	55	60
4	9	-4	35	-29
5	0	0	33	41
5	0	2	75	81
5	0	4	29	33
5	0	-2	68	69
5	0	-4	197	204
5	0	-6	< 36	-27
5	1	0	39	-29
5	1	1	20	21
5	1	2	22	-18
5	1	4	< 18	7
5	1	-1	118	134
5	1	-2	< 33	-14
5	1	-3	< 36	-4
5	1	-4	< 36	-20
5	1	-5	144	110
5	1	-6	72	-78
5	1	-7	122	135
5	1	-9	67	56
5	2	0	31	41
5	2	1	42	48
5	2	2	29	37
5	2	4	32	44
5	2	-1	19	23
5	2	-2	90	106
5	2	-5	78	83
5	3	0	26	-21
5	3	1	90	103
5	3	2	47	-49
5	3	-1	23	25
5	3	-2	46	-31
5	3	-5	78	90
5	3	-7	84	65
5	4	0	34	32
5	4	1	27	32
5	4	2	< 23	2

Appendix I (Concluded)

h	k	ℓ	F_o	F_c
5	4	-1	27	-21
5	4	-2	90	101
5	4	-5	35	43
5	4	-6	109	99
5	5	0	23	17
5	5	1	60	76
5	5	2	40	-36
5	5	-1	23	24
5	5	-2	< 33	2
5	6	0	37	37
5	6	2	25	22
5	6	-1	44	-38
5	6	-2	25	37
5	6	-4	74	52
5	7	-1	46	48
5	8	0	35	39
5	9	-5	35	39
5	10	0	46	32
6	0	0	67	81
6	0	2	36	33
6	0	-4	167	144
6	0	-6	145	131
6	0	-8	36	33
6	1	0	23	-21
6	1	2	22	26
6	1	-1	43	49
6	1	-2	< 42	30
6	1	-3	72	82
6	1	-4	< 42	26
6	1	-5	58	-49
6	1	-7	67	68
6	2	0	39	36
6	2	2	29	40
6	2	3	22	-30
6	2	-1	< 33	-1
6	2	-6	88	90

h	k	ℓ	F_o	F_c
6	3	0	31	60
6	3	1	21	30
6	3	-1	46	59
6	6	0	27	20
6	7	0	22	-12
6	8	0	32	22
7	0	0	36	31
7	0	-4	46	-44
7	0	-6	77	77
7	0	-8	< 42	15
7	1	-3	91	87
7	1	-4	43	25
7	1	-5	76	69
7	2	0	27	27
7	4	0	35	28
7	6	0	29	26
8	0	0	22	21
8	0	-2	46	39
9	0	-4	46	23

Appendix II

Structure Factor Table for
Potassium Dicyanoguanidine
(electrons x 10)

h	k	ℓ	F_o	F_c
0	2	0	440	-412
0	4	0	445	444
0	6	0	197	-160
0	8	0	321	389
0	10	0	150	-140
0	12	0	154	170
0	14	0	97	-140
0	16	0	79	103
1	0	0	348	404
1	1	0	293	-344
1	2	0	176	-161
1	3	0	136	-113
1	4	0	683	633
1	5	0	< 20	-7
1	6	0	256	-268
1	7	0	137	-131
1	8	0	266	272
1	9	0	< 29	-40
1	10	0	166	-149
1	11	0	58	58
1	12	0	104	112
2	0	0	45	-89
2	1	0	427	515
2	2	0	876	-845
2	3	0	125	-148
2	4	0	521	545
2	5	0	168	163
2	6	0	270	-261
2	7	0	213	-203
2	8	0	115	90
2	9	0	113	119
2	10	0	112	-114
2	12	0	132	144
2	13	0	93	86
2	14	0	64	-84
3	0	0	278	334
3	1	0	221	197
3	2	0	589	-588
3	3	0	179	-155
3	4	0	305	320
3	5	0	240	233
3	6	0	489	-498
3	7	0	122	129
3	8	0	318	323
3	9	0	152	148
3	10	0	134	-135
3	11	0	109	-106
3	12	0	82	59
3	13	0	61	61
3	14	0	75	-81
4	0	0	752	691
4	1	0	274	266
4	2	0	337	-361
4	3	0	223	-214
4	4	0	113	98
4	5	0	199	197
4	6	0	60	-59
4	7	0	< 26	17
4	8	0	< 36	30
4	9	0	112	105
4	10	0	158	-160
4	11	0	116	-112
4	12	0	90	85
5	0	0	275	274
5	1	0	435	382
5	2	0	266	-278
5	3	0	252	-225
5	4	0	163	137
5	5	0	204	192
5	6	0	271	-297

Appendix II (Continued)

h	k	ℓ	F_o	F_c
5	7	0	432	-436
5	8	0	138	133
5	9	0	105	107
5	10	0	176	-183
5	13	0	51	47
5	14	0	54	- 43
5	15	0	104	-117
6	0	0	87	65
6	1	0	142	130
6	2	0	402	-425
6	3	0	303	-295
6	4	0	117	124
6	5	0	118	109
6	6	0	201	-221
6	7	0	173	-166
6	8	0	38	32
6	9	0	65	36
6	10	0	70	-81
6	11	0	76	-71
7	0	0	276	-276
7	1	0	239	218
7	2	0	85	-69
7	3	0	279	-261
7	4	0	163	171
7	5	0	207	221
7	6	0	95	-90
7	7	0	101	-78
7	8	0	54	51
7	9	0	137	140
7	10	0	< 33	-17
7	11	0	139	-155
8	0	0	420	441
8	1	0	390	381
8	2	0	55	-45
8	3	0	176	-176
8	4	0	70	74
8	5	0	184	188
8	6	0	< 24	34
8	7	0	125	-123
8	8	0	113	126
8	9	0	143	136

h	k	ℓ	F_o	F_c
8	10	0	< 36	3
8	11	0	139	-134
8	12	0	< 41	67
8	13	0	86	61
9	0	0	201	242
9	1	0	97	86
9	2	0	93	102
9	3	0	151	-150
9	4	0	43	47
9	5	0	145	135
9	6	0	< 33	-8
9	7	0	133	-156
9	8	0	86	101
9	9	0	71	57
10	0	0	104	-105
10	1	0	176	186
10	2	0	< 26	13
10	3	0	186	-202
10	4	0	< 23	57
10	5	0	132	128
10	6	0	87	76
10	7	0	165	-185
10	8	0	113	-107
10	9	0	94	78
11	0	0	109	-105
11	1	0	148	145
11	2	0	76	-15
11	3	0	125	-136
11	5	0	113	149
11	6	0	59	-71
11	7	0	98	-96
11	8	0	80	65
11	9	0	116	130
12	0	0	65	31
12	1	0	103	107
12	2	0	< 35	32
12	3	0	94	-88
12	4	0	48	-77
12	5	0	59	90
12	6	0	79	75

Appendix II (Continued)

h	k	ℓ	F_o	F_c
12	7	0	51	-80
12	8	0	65	-6
12	9	0	66	67
13	0	0	34	-45
13	1	0	120	126
13	2	0	60	70
13	3	0	50	-59
13	4	0	50	-72
13	5	0	109	114
13	6	0	< 39	40
13	7	0	113	-133
14	0	0	< 39	-22
14	1	0	81	74
14	2	0	51	-34
14	3	0	52	-61
14	4	0	92	-73
15	0	0	148	-196
16	0	0	42	-42
16	1	0	88	97
0	2	1	77	-90
0	4	1	442	-440
0	6	1	220	236
0	8	1	159	183
0	10	1	50	-46
0	14	1	143	177
1	1	1	36	44
1	2	1	69	-47
1	3	1	306	-301
1	4	1	188	199
1	5	1	81	65
1	6	1	103	-98
1	7	1	95	98
1	8	1	< 26	-2
1	9	1	34	39
1	10	1	67	69
1	13	1	77	59
2	1	1	76	-73
2	2	1	290	298
2	3	1	260	-266
2	4	1	110	91
2	5	1	238	-247
2	6	1	< 23	-16
2	7	1	< 24	18
2	8	1	80	-75
2	9	1	< 29	-5
2	10	1	< 44	-17
2	13	1	77	-75
2	14	1	95	-107
3	1	1	433	-458
3	2	1	284	-272
3	3	1	43	27
3	4	1	122	118
3	5	1	50	-41
3	6	1	72	73
3	7	1	221	-246
3	8	1	55	-58
3	9	1	120	-138
3	10	1	27	35
3	11	1	76	-85
3	12	1	86	-99
4	1	1	148	-154
4	2	1	170	143
4	3	1	111	90
4	4	1	200	-214
4	5	1	< 29	0
4	6	1	50	-47
4	7	1	104	-111
4	8	1	85	97
4	9	1	54	-51
4	10	1	95	-88
4	11	1	70	-58
4	12	1	58	59
5	1	1	324	309
5	2	1	130	-119
5	3	1	127	-135

Appendix II (Continued)

h	k	ℓ	F_o	F_c
5	4	1	50	-34
5	5	1	< 54	-50
5	6	1	71	-68
5	7	1	167	194
5	8	1	< 35	-29
5	9	1	80	89
5	11	1	64	86
6	1	1	50	44
6	2	1	< 32	33
6	3	1	39	33
6	4	1	40	-36
6	5	1	101	110
6	6	1	33	32
6	7	1	82	88
6	8	1	49	-64
6	9	1	59	72
7	1	1	68	-45
7	3	1	81	102
7	4	1	172	193
7	5	1	68	84
7	6	1	64	-69
7	7	1	57	-48
7	8	1	58	-50
7	9	1	42	-42
7	10	1	46	49
8	1	1	56	61
8	3	1	119	129
8	4	1	83	-99
8	5	1	47	-52
8	6	1	103	108
8	7	1	27	-20
8	8	1	97	91
9	1	1	87	87
9	2	1	69	-73
9	5	1	89	87
9	7	1	49	37
9	8	1	32	46
10	1	1	< 29	-12
10	2	1	82	91
10	3	1	58	-60
10	6	1	83	-73
10	7	1	46	66
11	1	1	79	-90
11	2	1	30	-42
11	3	1	61	-85
11	4	1	54	81
12	1	1	90	-105
12	3	1	57	50
13	1	1	59	71
0	0	2	986	-984
0	2	2	675	-706
0	4	2	476	457
0	6	2	456	-458
0	8	2	110	79
0	10	2	169	-180
0	12	2	82	64
1	0	2	785	779
1	1	2	392	418
1	2	2	791	-869
1	3	2	59	-53
1	4	2	290	269
1	5	2	125	115
1	6	2	376	-350
1	7	2	39	37
1	8	2	184	177
1	9	2	89	94
1	10	2	158	-166
1	11	2	125	-95
1	12	2	122	113
1	14	2	135	-144
2	0	2	1180	1041
2	1	2	60	-87

Appendix II (Continued)

h	k	ℓ	F_o	F_c
2	2	2	249	-241
2	3	2	175	-149
2	4	2	185	269
2	5	2	72	61
2	6	2	280	-311
2	7	2	41	38
2	8	2	300	316
2	9	2	27	1
2	10	2	176	-182
2	11	2	91	-98
2	12	2	90	70
2	14	2	82	-61
3	0	2	681	571
3	1	2	253	255
3	2	2	293	-302
3	3	2	234	-222
3	4	2	352	349
3	5	2	87	76
3	6	2	68	-41
3	7	2	310	-335
3	8	2	77	61
3	9	2	36	18
3	10	2	144	-134
3	12	2	123	128
4	0	2	118	107
4	1	2	293	250
4	2	2	337	-314
4	3	2	265	-229
4	4	2	437	432
4	5	2	168	155
4	6	2	368	-545
4	7	2	271	-269
4	8	2	275	276
4	9	2	98	89
4	10	2	89	-76
4	12	2	85	79
5	0	2	278	266
5	1	2	176	161
5	2	2	257	-233
5	3	2	238	-239
5	4	2	273	280
5	5	2	185	181

h	k	ℓ	F_o	F_c
5	6	2	79	-49
5	7	2	107	119
5	8	2	117	123
5	9	2	122	111
5	10	2	< 33	-14
5	11	2	137	-141
5	12	2	103	113
6	0	2	329	304
6	1	2	391	369
6	2	2	< 50	30
6	3	2	196	-174
6	4	2	189	178
6	5	2	301	264
6	6	2	37	-38
6	7	2	144	-137
6	8	2	151	155
6	9	2	200	189
6	10	2	710	-66
6	11	2	92	-95
7	0	2	557	473
7	1	2	295	252
7	2	2	157	-164
7	3	2	189	-172
7	4	2	51	46
7	5	2	160	153
7	6	2	96	-85
7	7	2	197	-209
7	8	2	94	85
7	9	2	101	92
7	10	2	104	-83
8	0	2	266	-261
8	1	2	95	66
8	2	2	95	-95
8	3	2	238	-224
8	4	2	47	52
8	5	2	167	156
8	6	2	119	-130
8	7	2	164	-156
8	8	2	50	-36
8	9	2	36	84

Appendix II (Continued)

h	k	ℓ	F_o	F_c
9	0	2	140	-157
9	1	2	293	291
9	2	2	120	-154
9	3	2	189	-204
9	4	2	< 30	10
9	5	2	157	173
9	6	2	< 32	-40
9	7	2	100	-103
9	9	2	131	139
10	0	2	95	100
10	1	2	410	143
10	2	2	< 26	-16
10	3	2	108	-108
10	4	2	< 35	-49
10	5	2	155	145
10	6	2	61	-74
10	7	2	52	-44
10	8	2	95	103
10	9	2	88	100
11	0	2	56	59
11	1	2	178	133
11	2	2	73	53
11	3	2	121	-126
11	4	2	50	-66
11	5	2	63	83
11	6	2	65	95
11	7	2	77	-95
11	8	2	89	-84
12	0	2	88	-97
12	1	2	109	117
12	2	2	< 35	35
12	3	2	117	-121
12	5	2	102	97
12	7	2	180	-228
0	2	3	49	54
0	4	3	303	288
0	6	3	178	-173
0	8	3	130	-148
0	10	3	23	38
0	14	3	122	-152
1	1	3	32	-26
1	2	3	36	29
1	3	3	197	195
1	4	3	126	-132
1	5	3	66	-50
1	6	3	72	72
1	7	3	86	-80
1	8	3	< 20	1
1	9	3	35	-35
1	10	3	57	-59
1	13	3	56	-51
2	1	3	41	44
2	2	3	176	-188
2	3	3	173	169
2	4	3	86	-63
2	5	3	176	182
2	6	3	< 15	11
2	7	3	< 17	-16
2	8	3	71	60
2	9	3	< 18	5
2	10	3	23	15
2	13	3	56	65
2	14	3	83	92
3	1	3	295	292
3	2	3	170	173
3	3	3	32	-18
3	4	3	82	-87
3	5	3	46	31

Appendix II (Concluded)

h	k	ℓ	F_o	F_c
3	6	3	61	-58
3	7	3	181	203
3	8	3	48	48
3	9	3	104	113
3	10	3	35	-30
3	11	3	68	73
3	12	3	82	86
4	1	3	113	102
4	2	3	117	-97
4	3	3	79	-66
4	4	3	150	156
4	5	3	18	0
4	6	3	47	39
4	7	3	86	91
4	8	3	65	-80
4	9	3	50	43
4	10	3	65	75
4	11	3	51	50
4	12	3	55	-51
4	14	3	34	-32
5	1	3	220	-228
5	2	3	92	89
5	3	3	93	98
5	4	3	50	26
5	5	3	41	39
5	6	3	55	56
5	7	3	154	-160
5	8	3	< 21	24
5	9	3	65	-77
5	10	3	16	-12
5	11	3	71	-74
6	1	3	39	-31
6	2	3	< 30	-24
6	3	3	< 17	-24
6	4	3	21	29
6	5	3	69	-90
6	6	3	71	-26
6	7	3	63	-72
6	8	3	65	54
6	9	3	55	-62
6	10	3	67	36

h	k	ℓ	F_o	F_c
7	1	3	51	37
7	2	3	14	-19
7	3	3	70	-82
7	4	3	158	-158
7	5	3	48	-67
7	6	3	44	55
7	7	3	41	40
7	8	3	45	43
7	9	3	41	36
8	1	3	48	-50
8	2	3	16	-11
8	3	3	102	-105
8	4	3	65	80
8	5	3	44	43
8	6	3	86	-91
8	7	3	26	18
8	8	3	68	-77
9	1	3	73	-71
9	2	3	57	60
9	3	3	< 24	15
9	4	3	25	27
9	5	3	72	-74
10	1	3	< 20	11
10	2	3	71	-77
10	3	3	53	51
10	6	3	59	63
11	1	3	75	77
11	2	3	29	35
11	3	3	58	72
11	4	3	55	-69
11	5	3	42	46
12	1	3	83	90
13	1	3	50	-61

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Propositions

1. Taking the suggestions of Motzfeldt (1) and Porter (2), the accommodation coefficient, which can affect vapor pressure measurements, could be evaluated by the Knudson effusion-mass spectrometer technique. This could be done conveniently if an effusion cell were to be used with, besides the primary orifice, one (or more) holes which could be closed. This type of cell could also be used in regular vapor pressure measurements to confirm that equilibrium has been attained.
2. Taylor (3) has studied the gas phase of trifluoroacetic acid and deuterated trifluoroacetic acid and suggests that the dissociation energy of the dimer is less in the latter compound than in the former. He attributes this to the "larger volume" of the deuterium bond resulting in "a smaller charge density." It is proposed that these systems should be reinvestigated.
3. The results of the study of acetamide hemihydrochloride suggest that various other compounds be studied.
    a. The structure of acetamide itself should be refined by modern techniques.
    b. The structure of various complexes of acetamide listed on page 1 of this thesis would be of interest, particularly the ICl compound, which has been assigned a structure similar to that of the hemichloride.

   c. If acetamide hemihydrofluoride could be prepared its structure might prove to be very interesting.

   d. A neutron diffraction investigation of acetamide hemihydrochloride could contribute to our knowledge of hydrogen bonds.

4. Contrary to the proposition of Peterson (4), it is proposed that at least one of the SCN groups in Mercury tetrathiocyanate-Copper Diethylenediamine (5) is not linear. While this would not be the result of resonance, it could arise from the packing in this crystal.

5. The crystal structure of m-dinitrobenzene (6,7,8) has had a history of misadventures. It is proposed that the most recent determination (8) is still incorrect in its details.

6. The usual procedure in evaluating an anisotropic temperature factor is to determine the axial directions in reciprocal space and then evaluate the usual coefficients for $h_i h_j$. If the axial directions are determined in real space the computational labor is greatly reduced.

7. A reduction could be made in the duplication of structure determinations if an annual compilation of compounds under study could be made. Conditions are proposed which would make such a list more useful.

8. Glasstone (9) derives the partial molal volume of the i th component in an ideal gas mixture as RT/P_i. This is in-

correct and should be RT/P. The latter leads to the same value of the chemical potential as given in the following paragraph of the text.

9. The existence of the (II) state of Americium has not been established (10). It is proposed that it may be prepared, perhaps in a manner analogous to that of Europium (II) by reduction of the plus 3 state.

10. It has periodically ($\omega = 6\text{x}10^5$ sec) occurred to this observer that slides at seminars should be eliminated. This suggestion is based on observations of many (possibly an unprecedented number for a graduate student) seminars which have firmly established the many advantages to be gained.