aluminum halide was heated gently by means of a free flame whereupon the reaction soon started. For the preparation of boron chloride gentle heating was found desirable as long as the reaction took place. Then, using two burners, both flasks were heated strongly with a stream of boron fluoride still passing through the reaction flasks. After continued heating, the aluminum fluoride fell from the sides of the flask as a light white powder. For the preparation of the boron bromide the aluminum bromide was refluxed gently in a stream of boron fluoride. The contents of the flask soon solidified and again the mass was strongly heated in boron fluoride. The effluent gases were passed into a U-tube cooled with solid carbon dioxide and alcohol, protected by a drying tube. When the reaction was over the U-tube was sealed off and its contents distilled. In the preparation of boron bromide small amounts of bromine were obtained but were readily removed by shaking with mercury. A little metallic aluminum added to the preparation flask decreased the amount of bromine formed. In order completely to remove boron fluoride from boron chloride or bromide, distillation in a good column was desirable. From one-half a mole of aluminum chloride and two moles of boron fluoride 80% yields of boron chloride have been obtained. Using comparable amounts of reactants, 70% yields of boron bromide have been obtained.

Pure aluminum fluoride was not obtained as the by-product of the reaction, appreciable amounts of chloride or bromide being present. Analysis has shown the amount of bromine to be as high as 40% (theoretical for AlF_2Br is 55%); but this was decreased very markedly when the solid product was heated strongly in a stream of boron fluoride.

Reaction with Potassium Fluoborate.—When either aluminum chloride or bromide was heated with potassium fluoborate, some boron chloride or bromide, together with boron fluoride, was formed. An excess of the aluminum halide increases the percentage conversion of the fluoborate.

In an apparatus somewhat similar to that described above, one mole of aluminum chloride and one-half a mole of potassium fluoborate were heated by means of an oil-bath for four hours, with the temperature slowly increasing from 150 to 175°. The product was condensed in liquid nitrogen. The recovery of pure boron chloride was 0.26 mole, a yield of 56%, based on the potassium fluoborate used. Under comparable conditions yields of around 30% of boron bromide have been obtained.

Summary

Boron fluoride and potassium fluoborate have been found to react with aluminum chloride or bromide to produce good yields of boron chloride or bromide. The conditions of the reactions are given and the use of boron fluoride is particularly recommended as a means of preparing boron bromide. No fluorochlorides or fluorobromides of boron have been isolated in this investigation.

CAMBRIDGE, MASSACHUSETTS

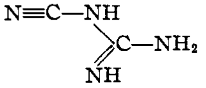
RECEIVED FEBRUARY 19, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 767]

The Crystal Structure of Dicyandiamide

BY E. W. HUGHES

Several different structures have been proposed for the dimer of cyanamide but no absolutely conclusive evidence has ever been given for any one of them. In past years many people have preferred the cyanoguanidine[1] structure I.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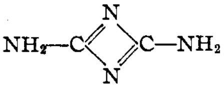
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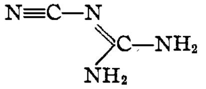
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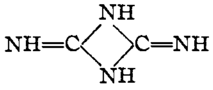
IV

But even fairly recently[2] arguments have been advanced in favor of the cyclic structure II. The closely related alternatives III and IV, which differ from I or II only in the disposition of hydrogens and double bonds, also have been proposed. I have made an X-ray examination of crystalline dicyandiamide for the purpose of resolving this long-standing controversy, with the results reported below.

Several previous crystallographic investigations have been recorded. In 1911 Heydrich[3] reported the crystals as monoclinic holohedral with $a : b : c = 1.1109 : 1 : 1.4213$, $\beta = 115° 20'$. He also found strong positive birefringence and that the acute bisectrix makes an angle of about 11° with c in the acute angle β'. The cleavage on {100} is excellent and that on {001} is good. In 1927 Baier[4] made an independent examination. Although he chose a different axial system, with $\beta = 90° 31'$, his axial ratios, $a : b : c = 1.0021$:

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[1] For a good summary of the arguments, as well as one of the more important original investigations, see Hale and Vibrans, THIS JOURNAL, **40**, 1046 (1918).

[2] Bell, *Sci. Proc. Roy. Dublin Soc.*, **18**, 207 (1926).

[3] Heydrich, *Z. Krist.*, **48**, 278 (1910-1911).

[4] Baier, *ibid.*, **65**, 719 (1927).

1 : 0.4854, are compatible with Heydrich's (within somewhat large experimental error) when recalculated for the older axial system. He confirmed Heydrich's crystal class and birefringence assignments. At the same time a superficial X-ray examination was made by Dehlinger.[5] On the basis of insufficient data, and following the axial system of Baier, he reported a cell with a = 13.8 Å., b = 4.4 Å., c = 6.2 Å. and β = 90°. The space group was said to be C_{2h}^3 (= $I2/m$) with four molecules per cell. No structure was proposed.

The Unit Cell and Space Group

The material used in this examination was kindly supplied by Professor A. W. Browne of Cornell University. Crystals were grown from water solutions by evaporation in a thermostat at about 35°. They were lath-like needles elongated along b. Complete sets of oscillation photographs were made about b and c (Heydrich's axes) using Cu radiation. An additional oscillation picture was made about a to confirm the length assigned to that axis. One 5° oscillation photograph with Mo radiation was made about b to observe the reflection 12,08, which is beyond the range of Cu radiation, but of important intensity.

A preliminary attempt to index the b axis pictures using Dehlinger's unit showed that the latter was incorrect and that the dimensions had to be doubled in both the a and c directions, yielding a cell with sixteen molecules and an inconvenient type of centering. By reverting to Heydrich's axes a much simpler unit was obtained for which was found a = 15.00 Å., b = 4.44 Å., c = 13.12 Å. (all ±0.5%, CuKα, λ = 1.540 Å.) and β = 115° 20′ (Heydrich). This cell contains eight molecules of $H_4N_4C_2$. The calculated and observed (Heydrich) densities are 1.405 g./cc. and 1.404 g./cc., respectively. The only consistent extinctions, hkl when $h + k$ is odd and $h0l$ when l is odd, indicate the space group $C2/c$, thus confirming Heydrich's assignment to the holohedral class.

Two pictures were made for each oscillation range, their exposure ratios being always 6:1. From these the $h0l$, $hk0$ and $hk\pm1$ intensities were carefully estimated visually and corrected for the Lorentz-polarization factor. The structure factors derived from them by taking their square roots are recorded in Tables I, II and III. They have been adjusted to approximately absolute scale by comparison with the corresponding values calculated from the final structure and are arranged in order of decreasing spacing. The $hk0$ and $hk\pm1$ intensities are not as reliable as the $h0l$ values because in recording them the needle axis was perpendicular to the oscillation axis. However, the lath-like needle was extremely thin (not over 0.1 mm.) in the direction perpendicular to the {100} faces and about 0.3 mm. perpendicular to the {001} faces so bad absorption need be feared only for a few reflections for which the emergent beams were almost exactly parallel with the needle axis. These have been indicated in Table II.

TABLE I

STRUCTURE FACTORS OF THE ($h0l$) REFLECTIONS

$h0l$	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$	$h0l$	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
200	+ 1	3	2.0,10	+10	< 7
002	+ 62	66	$6,0,\overline{12}$	−37	41
$20\bar{2}$	+ 62	66	806	−45	48
202	− 12	9	$12,0,\overline{10}$	−17	14
$40\bar{2}$	− 19	16	$4,0,\overline{12}$	−16	20
400	−142	126	$14,0,\bar{6}$	+14	< 8
$20\bar{4}$	− 21	24	10,0,4	+ 5	< 8
004	−109	121	$14,0,\bar{4}$	+ 7	< 8
$40\bar{4}$	+ 36	28	608	−10	13
$60\bar{2}$	+ 3	8	$2,0,\overline{12}$	− 1	< 8
402	− 80	88	$10,0,\overline{12}$	+44	56
204	+ 68	78	12,0,2	−11	14
$60\bar{4}$	− 62	62	$14,0,\bar{8}$	−14	10
600	− 5	9	$14,0,\bar{2}$	−14	7
$40\bar{6}$	− 23	25	4.0,10	− 6	< 8
$20\bar{6}$	− 32	28	0,0,12	+ 4	< 8
006	+ 22	21	$14,0,\overline{10}$	−29	29
$60\bar{6}$	− 20	21	$12,0,\overline{12}$	−18	17
$80\bar{4}$	+ 33	28	14,0,0	− 8	< 8
602	− 52	50	10,0,6	0	< 8
404	+ 29	24	$16,0,\bar{8}$	− 4	< 8
$80\bar{2}$	− 3	6	12,0,4	− 8	< 9
206	+ 36	36	$6,0,\overline{14}$	− 2	< 9
$80\bar{6}$	− 23	29	$16,0,\bar{6}$	−14	15
800	− 19	21	$8,0,\overline{14}$	+ 1	< 9
$40\bar{8}$	− 26	22	808	−27	27
$20\bar{8}$	− 1	< 5	2,0,12	+14	11
$60\bar{8}$	+ 33	25	$16,0,\bar{4}$	−23	24
604	− 31	26	$4,0,\overline{14}$	−18	23
$10,0,\bar{4}$	+ 35	38	$10,0,\overline{14}$	− 1	< 9
008	+ 39	34	$14,0,\overline{12}$	−13	9
$10,0,\bar{2}$	+ 1	< 5	6,0,10	− 9	< 9
$80\bar{8}$	− 18	16	14,0,2	+ 6	< 9
802	+ 40	42	$16,0,\bar{2}$	− 7	< 9
406	− 23	25	$16,0,\overline{10}$	− 3	< 9
$10,0,\bar{6}$	+ 13	9	$2,0,\overline{14}$	− 8	< 9
10,0,0	+ 8	9	$12,0,\overline{14}$	+ 3	< 9
208	− 4	< 6	4,0,12	− 2	< 9
$10,0,\bar{8}$	− 19	19	$16,0,\overline{12}$	+ 4	< 9
$4,0,\overline{10}$	− 9	5	16,0,0	+ 7	< 9
$6,0,\overline{10}$	− 10	9	0,0,14	+20	18
804	− 16	12	12,0,6	+24	24
$12,0,\bar{4}$	− 2	6	$14,0,\overline{14}$	− 3	< 9
$2,0,\overline{10}$	− 4	< 6	10,0,8	+10	14
$12,0,\bar{6}$	+ 26	25	$18,0,\bar{6}$	−18	17
$8,0,\overline{10}$	+ 31	32	$18,0,\bar{8}$	+20	19
606	− 8	8	14,0,4	+ 2	< 9
$12,0,\bar{2}$	+ 8	10	$8,0,\overline{16}$	+ 4	< 9
10,0,2	+ 20	19	$18,0,\bar{4}$	−21	17
408	+ 1	< 7	8,0,10	+13	13
0,0,10	− 7	11	$6,0,\overline{16}$	+22	25
$10,0,\overline{10}$	+ 26	26	$10,0,\overline{16}$	−19	18
$12,0,\bar{8}$	+ 21	16	$18,0,\overline{10}$	+17	16
12,0,0	+ 16	10	12,0,8	+23	21
$8,0,\overline{12}$	+ 27	28			

Determination of the Structure

Since there are eight molecules per cell it appears that each of the atoms of the molecule must

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(5) Dehlinger, *Z. Krist.*, **65**, 296 (1927).

TABLE II

STRUCTURE FACTORS OF THE (*hk*0) REFLECTIONS

*hk*0	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$	*hk*0	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
110	+ 55	61	040	+ 1	< 7
310	+118	109	240	− 2	< 7
510	+ 25	30	930[a]	−27	22
020	+ 2	4	440	+ 2	< 7
220	− 48	50	13,1,0	− 9	8
420	+ 8	10	12,2,0	+ 3	< 8
710[a]	+ 39	27	640	+ 2	< 8
620	+ 61	61	11,3,0	+ 9	10
130	+ 12	7	840[a]	− 7	9
910	− 12	10	15,1,0	− 8	< 8
330	− 4	4	14,2,0	+ 5	< 8
820[a]	− 9	8	150	− 4	< 8
530	+ 14	15	350	+ 2	< 8
11,1,0	+ 6	< 6	10,4,0	+ 4	< 8
730	− 12	12	13,3,0	+16	16
10,2,0[a]	+ 18	10	550[a]	+ 2	< 8

[a] Probably subject to absorption.

TABLE III

STRUCTURE FACTORS OF THE (*hk*±1) REFLECTIONS

hk±1	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$	*hk*±1	$F_{\text{calcd.}}$	$F_{\text{obsd.}}$
$11\bar{1}$	− 20	20	041	+ 2	< 7
111	− 85	83	$24\bar{1}$	+14	11
$31\bar{1}$	− 90	91	241	+ 3	< 7
311	−104	103	$93\bar{1}$	−20	12
$51\bar{1}$	− 39	40	$44\bar{1}$	−10	< 7
021	+ 28	26	$13,1,\bar{1}$	+ 4	< 7
511	+ 8	18	$12,2,\bar{1}$	− 9	< 7
$22\bar{1}$	− 9	11	441	−16	11
221	+ 2	11	931	−15	20
$42\bar{1}$	− 5	< 6	$64\bar{1}$	− 6	< 8
$71\bar{1}$	+ 34	26	13,1,1	− 4	< 8
421	− 6	< 6	641	+ 2	< 8
711	+ 52	55	12,2,1	− 1	< 8
$62\bar{1}$	+ 38	28	$11,3,\bar{1}$	− 7	< 8
621	+ 24	24	$84\bar{1}$	− 1	< 8
$91\bar{1}$	+ 9	8	11,3,1	− 5	< 8
$13\bar{1}$	+ 14	< 7	$15,1,\bar{1}$	+ 2	< 8
131	+ 20	18	$14,2,\bar{1}$	+ 5	< 8
$33\bar{1}$	+ 15	18	841	+ 9	< 8
$82\bar{1}$	+ 22	12	$15\bar{1}$	+ 2	< 8
331	0	< 7	151	+15	13
911	+ 13	8	$10,4,\bar{1}$	−10	< 8
$53\bar{1}$	− 3	< 7	$13,3,\bar{1}$	+24	19
821	− 7	9	$35\bar{1}$	0	< 8
531	+ 3	9	14,2,1	+14	16
$11,1,\bar{1}$	− 9	< 7	351	0	< 8
$73\bar{1}$	+ 5	< 7	15,1,1	− 3	< 8
$10,2,\bar{1}$	− 26	17	$55\bar{1}$	− 4	< 8
731	+ 6	< 7	10,4,1	+ 4	< 8
11,1,1	− 6	< 7	13,3,1	+10	12
10,2.1	− 27	23	551	−10	< 8

occupy one of the eightfold general positions of $C2/c$: $(000\ ;\ {}^1/_2,{}^1/_2,0) + x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ \bar{x}, y, {}^1/_2 - z;\ x, \bar{y}, {}^1/_2 + z$. There are thus eighteen parameters to be determined, neglecting, as is customary, the hydrogens.

Because of the unusual shortness of the *b* axis, which is only slightly longer than the ordinary van der Waals separation of the atoms involved, it was decided to evaluate first the *x* and *z* coördinates which define distances perpendicular to this short axis. For this purpose, the *h*0*l* intensities were used to prepare a Patterson projection onto (010). The series summed was $P(x, z) = \Sigma_h\ \Sigma_l\ F^2_{h0l}\ \text{Cos}\ 2\ \pi\ (hx + lz)$. The summation was effected by Beevers–Lipson strips[6] at intervals of ${}^1/_{60}\ a$ and ${}^1/_{30}\ c$, and the function is plotted as a contour map in Fig. 1. Since for $C2/c$, *h*0*l* reflections always occur with both *h* and *l* even, only a fourth of the cell, containing only two molecules, need be considered.

This function tends toward maxima at values of *x* and *z* corresponding to the differences between the *x* and *z* coördinates of all the atoms of the cell taken in pairs. Because of the relatively large number of atoms involved, the extremely large number of such maxima possible superimpose and are not resolved individually. Each of the various peaks observed in Fig. 1 is the result of dozens of interatomic interactions falling near together and the interpretation of the result is consequently very difficult and uncertain. In the present instance, however, some simplification is introduced by the shortness of *b*. The smallest distance to be expected between two atoms in different molecules is about 3.0 Å., corresponding to a hydrogen bond $>$N—H. . . N$\lessdot$. Because every atom has others only 4.44 Å. above and below it in the *y* direction, the shortest possible component of this nearest approach parallel to the *xz* plane is easily calculated to be $\sqrt{3^2 - b^2/4}$ = about 2.0 Å. Consequently all interactions between atoms in different molecules are two or more ångströms from the corners of the plot. The area so blocked off is indicated in Fig. 1 by the heavy circles of two ångströms radius about the corners. The details inside these circles must be explained by the interactions arising inside single molecules and thus depend only on the shape and orientation of the molecules but not upon their positions.

The only striking point about this portion of the plot is that the large central peak at (0,0), which comes from the interaction of each atom with itself, is not symmetrical but is considerably elongated along a line making an angle of about 35° to *c* in acute angle β'. This indicates that a

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(6) Lipson and Beevers, *Proc. Phys. Soc.*, **48**, 772 (1936).

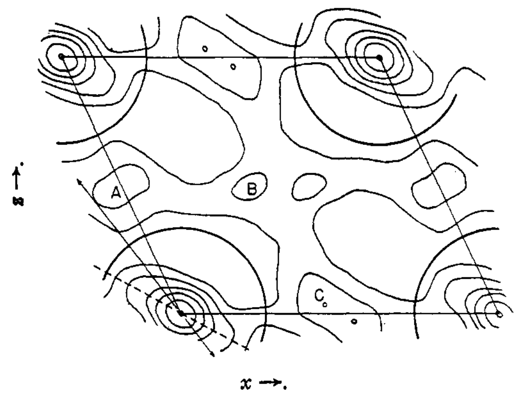

Fig. 1.—$P(x, z)$. The cell outlined is only a quarter of the true cell. P is in arbitrary units and negative contours have been omitted.

number of interatomic distances, probably chemical bonds, are oriented in this direction. The number can be estimated by approximately resolving the peak in the following way. The values of $P(x, z)$ along the ridge of the peak are plotted against distance from the origin and likewise the values of $P(x, z)$ in a direction perpendicular to the ridge, as in Fig. 2. If we assume that there are no important interactions exactly in the direction perpendicular to the direction of the ridge, this latter curve represents approximately the true shape of the central peak. The difference between the two curves (dashed curve) then represents the distorting maximum sought. It is seen to fall at about 1.2 Å. from the origin and is nearly half as high as the central peak, although these values are very uncertain because the base for the curves can only be estimated. Since the central peak corresponds to six atoms per molecule, the distortion must represent two or three atomic interactions and from their distance from the origin they must be the *xz* components of two or three nearly parallel chemical bonds. Now the direction of easiest polarization of the molecule, as given by the position of the acute bisectrix, is only 11° from *c* in acute angle β', as indicated in Fig. 1 by the arrow through the origin. We are thus led to a molecular model which has two or three bonds approximately parallel, but making an angle of about 24° with the direction of easiest polarization of the molecule on one side only of the latter. This eliminates quite clearly both cyclic formulas II and IV since their bonds are symmetrically distributed about the long axis of the molecule. Either I or III is acceptable, however. They differ very little as far as carbons and nitrogens are concerned and do in fact have three parallel or nearly parallel bonds making a suitable angle with the long way of the molecule. Such molecules are expected to be at least approximately coplanar. The orientation of the planes of the molecules was set approximately at plus and minus 45° to *b*, because Heydrich[8] had found the two smaller refractive indices of the crystal to be very nearly equal (α = 1.5212, β = 1.5493, γ = 1.8471, D lines). If the planes of the molecules were all even approximately parallel, one of these smaller indices would be considerably larger than the other

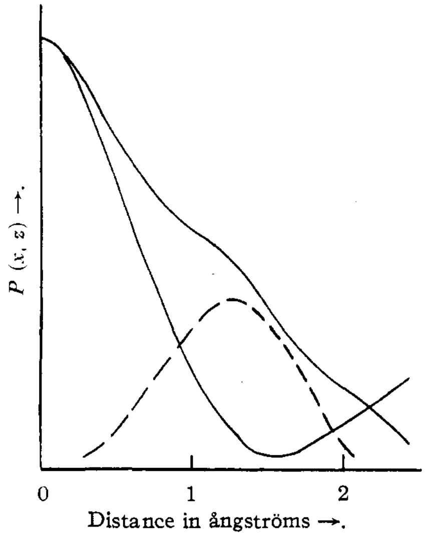

Fig. 2.—Cross section curves resolving the peak at the origin of Fig. 1.

The above arguments completely determine the approximate configuration and orientation of the molecule. The projections of the three parallel bonds are parallel to the long axis of the central peak, that of the long axis of the molecule is parallel to the acute bisectrix and the planes of the molecules make angles of about 45° alternately plus and minus with the *b* axis. All the interactions contributing to $P(x, z)$ which arise from within the same molecule were now marked on the plot as required by this model. Average bond distances and angles were used as no choice had yet been made between I and III. These interactions explained quite well the peak marked A but left the peaks B and C to be explained almost entirely by interactions arising between different molecules. An examination of the problem shows that these latter interactions form a pattern which depends only upon the shape and orientation of the molecules. But the position of the pattern as a whole depends upon the position of the molecule. The pattern suggested by the above model was drawn to proper scale on tracing paper, placed in proper orientation on Fig. 1 and shifted about to obtain the best possible fit with the observed peaks, paying attention of course to the additional interactions produced from the pattern by the action of the symmetry elements of the projection. The possibilities are considerably restricted by the fact that all these interactions must fall outside the 2.0 Å. circles. The x and z coördinates of the atoms were determined from the position giving the best agreement. These parameters were then tested by computing the $h0l$ structure factors. The scattering factors of Pauling and Sherman[7] were used with a temperature factor of $e^{-B\,\mathrm{Sin}^2\theta/\lambda^2}$, where $B = 2.00$. The factors for NH_2 were estimated by adding to those for N the differences between those for O and O″. These differed very little from nitrogen factors except at small scattering angles. In these early calculations model III was used to identify atoms but no significant error could be introduced in this way. The agreement between the observed F's and those calculated from the approximate parameters was unexpectedly good and it was possible to proceed at once to refine the parameters by Fourier syntheses.

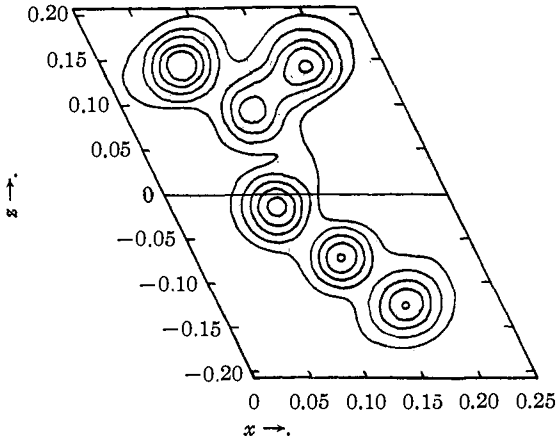

Fig. 3.—Projection of electron density on {010}. Contour intervals are approximately 2 electrons per sq. Å.

The summations of $\rho(x, z) = \Sigma_h\Sigma_l F_{h0l} \cos 2\pi (hx + lz)$ were carried out by Beevers–Lipson strips[5] at intervals of $^1/_{120}\ a$ and $^1/_{120}\ c$. One-eighth of the final projection, which included all observed F's, is shown in Fig. 3. All atoms are satisfactorily resolved. The x and z coördinates were read from this plot to the nearest 0.0005 and are recorded in Table IV. The structure factors calculated from them are included in Table I and are seen to be in satisfactory agreement with the observed values.

Table IV

	C_1	C_2	N_3	N_4	N_5	N_6
x	0.1285	0.1145	0.1635	0.0920	0.1795	0.0705
y	.103	.171	−.037	.251	−.061	.334
z	−.0725	.0935	−.1265	−.0150	.1430	.1450

No assumption has been made so far with regard to the nature of the symmetry element at the origin of the Fourier plot. It may be a symmetry center at $y = 0$, one at $y = {}^1/_4$ (lying between the c glide planes), a twofold axis or a twofold screw axis. A molecular model of average expected dimensions, adjusted in orientation to project exactly onto the Fourier peaks, was now moved along the y direction, assuming in succession each of the possible symmetry elements, and the interatomic distances to atoms in surrounding molecules produced by the symmetry elements were calculated as a function of the y coördinate of one of the atoms. It was found that satisfactory packing could not be obtained using symmetry axes at the origin. Nor did the center of symmetry between the glide planes give acceptable distances. Only when the origin was taken at a symmetry center in a glide plane did a structure with reasonable atomic separations result. In this way approximate y coördinates were obtained.

It was obvious at once from this approximate structure that there was no possible Fourier projection which would resolve any atom in such a way as to fix its y parameter. The six y coördinates had to be refined by the arduous trial and error procedure, using $hk0$ and $hk\pm1$ intensities. It seemed highly improbable that the four atoms of the guanidine group could be non-coplanar, or that the cyanimino group could be non-linear. The projection of the latter was in fact linear in the Fourier synthesis to the accuracy with which the plot could be prepared and read. Consequently, in refining the y parameters the trial adjustments were always made in such a way as to maintain the stated configurations. A survey of the final results indicates that even without these constraints the two groups would not have deviated from the expected shapes by more than the experimental errors.

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(7) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

In comparing the calculated and observed structure factors no weight was given to those spectra believed to be influenced by absorption. The final accepted values are recorded in Table IV and the structure factors calculated from them (and the previously fixed x and z parameters) for $hk0$ and $hk\pm1$ are in Tables II and III. The agreement with observed values, while not as good as for the $h0l$ spectra, is satisfactory if one allows for the reduced reliability of the data.

Discussion

The resulting molecule is shown, as viewed parallel to and perpendicular to the plane of the guanidine group, in Fig. 4(a) and (b). The interatomic distances and bond angles are recorded on the figure (see also Table V). The underscored numbers give the heights of the atoms above the plane of the drawing in ångströms. The exact planarity of the guanidine group and the linearity of the cyanimino group have been imposed as described above, but the calculations indicate that unadjusted results would differ from these configurations by displacements not greater than the experimental errors. The probable error in the position of an atom is estimated to be about ±0.015 Å. and the probable error of a bond length consequently about ±0.02 Å. It is not very likely that any bond length is in error by more than ±0.04 Å.

TABLE V

INTERATOMIC DISTANCES

Chemical bonds		Hydrogen bonds	
1—3	1.22 Å.	6—4A, 4—6A	2.94 Å.
1—4	1.28	6—3C, 3—6D	3.02
2—4	1.36	5—3B′, 3—5B′	3.04
2—5	1.37	5—3C, 3—5D	3.16
2—6	1.34	5—6′, 6—5′	3.15

Van der Waals Contacts

$NH_2\cdots NH_2$		$NH_2\cdots C$	
5—5E	3.49 Å.	1—6A′	3.34 Å.
6—5E	3.62	2—5′	3.53
6—6A′	3.76	1—6A	3.68
		2—6A	3.85
$NH_2\cdots N$		2—6′	3.87
		2—6A′	3.88
6—4A′	3.47	6—1C	3.94
4—5′	3.61	1—5B	3.95
5—3B	3.62		
3—6A′	3.65	$N\cdots C$	
5—4A′	3.77		
		2—4A′	3.39
$N\cdots N$		2—3C	3.47
		2—3B	3.56
4—3B	3.56	2—4A	3.81
4—4A	3.69	1—3′	3.86
4—4A′	3.70	1—4′	3.94
3—3B′	3.73		
$C\cdots C$			
1—1B	3.56		

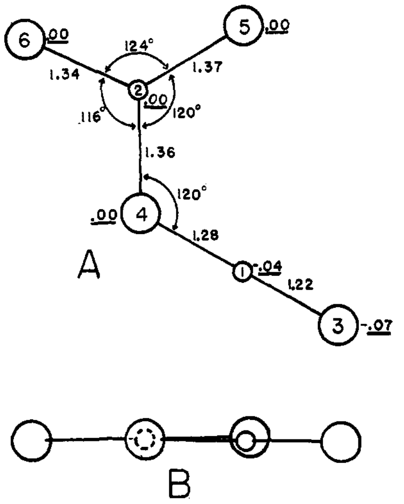

Fig. 4.—(a) View of the molecule perpendicular to plane of guanidine group. Underscored numbers are heights in ångströms of atoms above plane. (b) View of molecule parallel to same plane.

In a recent discussion[8] of double bond lengths it has been suggested that some of the double bond radii in common use recently have been too long. The present work supports this view. The previously accepted value for N═C was 1.28 Å. On this basis the 1.28 Å. bond of the cyanimino group would be a pure double bond and the corresponding structure $\dot{:}N{=}C{=}\dot{N}\diagdown$. This would require in turn that the other bond also be 1.28 Å. (or longer if one allows for the formal charge effect), whereas the observed value is 1.22 Å. If we accept the new constant for estimating double bond lengths, the theoretical C═N bond becomes 1.47 − 0.21 = 1.26 Å. and this value permits a satisfactory interpretation of both bond distances. If the cyanimino group resonates between the structures $:N{\equiv}C{-}\ddot{N}\diagdown$ (25%) and $\dot{:}N{=}C{=}\dot{N}\diagdown$ (75%) the calculated bond lengths[9] become 1.22 Å. and 1.28 Å. in agreement with the observed values. These values differ from those previously predicted[10] for the cyanimino group, 1.20 Å. and 1.32 Å., respectively, partly because

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(8) Stevenson, Burnham and Schomaker, THIS JOURNAL, **61**, 2922 (1939).

(9) L. Pauling, "The Nature of the Chemical Bond," revised edition, Cornell University Press, Ithaca, N. Y., 1940, p. 171. The revised radii are listed on p. 164.

(10) Pauling and Sturdivant, *Proc. Nat. Acad. Sci.*, **23**, 615 (1937).

of the revision in the C=N value but chiefly because in the earlier calculation it was assumed that the two resonating structures contribute about equally to the normal state. There is a special reason for the larger contribution of $\vdots\overset{\cdot\cdot}{N}{=}C{=}\overset{\cdot}{N}\diagdown$ in the present structure. As we shall see below, the terminal nitrogen atom has three hydrogen bonds directed toward it. The structure $:N{\equiv}C{—}\overset{\cdot}{N}\diagdown$ has only one unshared electron pair to divide among these bonds which would therefore be weak, as in ammonia where a similar situation prevails.[11] But the alternative structure provides two unshared pairs and would permit much stronger hydrogen bonds. It consequently makes a larger contribution to the normal state, the final result being that the loss in resonance energy is more than made up by the gain in energy of the three hydrogen bonds. The structure $\overset{-2}{\vdots N}{—}C{\equiv}N{—}$ which would provide even more electron pairs is probably of little importance because of the unfavorable bond angle, C—N—C = 120°. But the structure $\overset{-2}{\vdots N}{—}\overset{+}{C}{=}\underset{\diagdown}{N}$ may make a small contribution.

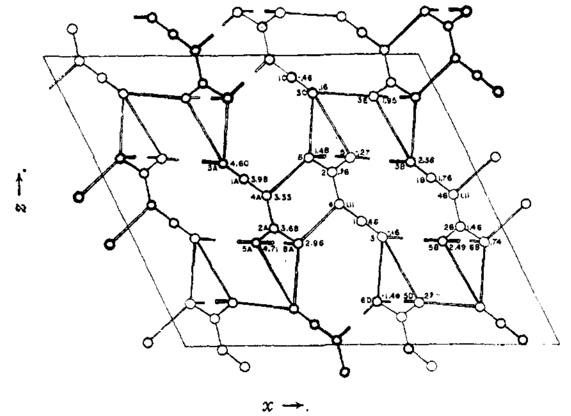
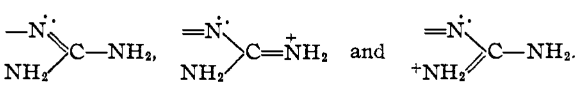


Fig. 5.—View of unit cell projected parallel to *b*. Numbers to right of atoms give heights in ångströms above {010}. Origin is at center of figure. Tubes represent hydrogen bonds.

In the guanidine group the double bond resonates to a certain extent into all possible positions.



$$\begin{matrix}-\overset{\cdot\cdot}{N}\diagdown\\ \mathrm{NH_2}\diagup\end{matrix}\!C{—}\mathrm{NH_2},\quad \begin{matrix}=\overset{\cdot\cdot}{N}\diagdown\\ \mathrm{NH_2}\diagup\end{matrix}\!C{=}\overset{+}{\mathrm{N}}\mathrm{H_2}\quad\text{and}\quad \begin{matrix}=\overset{\cdot\cdot}{N}\diagdown\\ {}^{+}\mathrm{NH_2}\diagup\end{matrix}\!C{—}\mathrm{NH_2}.$$

The observed bond lengths 1.37, 1.36 and 1.34 Å. correspond to 23, 27, and 35% of double bond character, respectively, and the sum of these, 85%, comes fairly close to 100%. Moreover, the structure $\begin{matrix}=\overset{\cdot\cdot}{N}\diagdown\\ \mathrm{NH_2}\diagup\end{matrix}\!C^{+}{—}\mathrm{NH_2}$ which involves no double bond is probably of some importance. Ordinarily we should expect the two amino groups to be equivalent and in fact the difference between their C–N bond lengths is of the order of the experimental error and may be without significance. This, however, will be discussed further in connection with the hydrogen bonds. The bond angles, which have a probable error of about ± 2½°, are compatible with the structures proposed. The deviation of the cyanimino group from the plane of the guanidine group, although probably exceeding experimental error, is quite small, corresponding to a rotation about the $\diagup\!\!\!\diagup N{—}C\langle$ bond of only 2°.

The arrangement of the molecules in the unit cell is shown in Fig. 5. Here the atoms have been projected along the *b* axis, which is normal to the diagram, onto the {010} plane which is in the plane of the diagram. Numbers to the right of an atom give its height in ångströms above {010} while numbers and letters to the left identify the atoms. Numbers 1 to 6 indicate the atoms corresponding to the coördinates of Table IV, the origin being at the center of the figure. The suffix A, B, C, D or E indicates a molecule derived from the first by one of the symmetry operations of the space group. Primes, which occur in Table V, indicate atoms $b(= 4.44$ Å.) above or below corresponding unprimed atoms.

If one singles out sections of crystal parallel to (001) and one molecule thick all the molecules in alternate sections are approximately parallel to (310) while those in the interleaving sections are approximately parallel to $(3\bar{1}0)$. These related planes make angles of about ± 45° with the horizontal and thus about 90° with each other. Within a section the molecules form strips, the atoms of the molecules of a strip all lying within ± 0.15 Å. of a plane parallel to (310) or $(3\bar{1}0)$, depending upon what section the strip is in.

The arrangement about a single molecule is further shown in Fig. 6. Here the crystal has been projected onto the plane parallel to (310) which passes through symmetry centers at 0, ½, 0; ¼, $\bar{1}/4$, 0; etc. Three of the molecules shown, which form part of a strip, lie almost in this plane, as indicated by underscored numbers

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[11] Mark and Pohland, *Z. Krist.*, **61**, 532 (1925); de Smedt, *Bull. Acad. Roy. de Belgique*, **10**, 655 (1925).

which are the heights of the atoms above the plane in question. Portions of molecules in adjacent sections which are parallel to $(3\bar{1}0)$ are seen here edgewise at the top and bottom of the figure. Also are shown one molecule from each of the strips parallel to (310) but one layer above and below the plane of the drawing. The separation of these layers is 3.16 Å. Most of the interatomic distances between different molecules are 3.34 Å. or greater as shown in Table V, and correspond satisfactorily to expected van der Waals distances.[12] Five pairs of distances however are much shorter than van der Waals radii sums and these are indicated by dotted lines on Fig. 6 for the central molecule of the group. The lengths are also recorded there and in Table V. These are interpreted as hydrogen bonds and are represented in Fig. 5 by double lines or "tubes." Where one of these tubes ends before reaching a second atom it is generally directed at an atom *b* (= 4.44 Å.) above or below the atom at which it is directed but in some instances 2*b* (= 8.88 Å.) above or below.

These hydrogen bond distances are comparable with those found in ammonium azide,[13] 2.94 Å. and 2.99 Å.

Although the positions of the hydrogens cannot be found by X-ray diffraction effects, we may infer their positions from the arrangement of these short bonds. A hydrogen atom is to be placed, in accord with accepted stereochemical principles, on an atom at one end or the other of each short distance in such a way that there are four hydrogens per molecule. But in this case we have five pairs of bonds and only four hydrogens so we must assume that we have here another example of the so-called "bifurcated hydrogen bond" first reported in glycine.[14] In such a bond a hydrogen is attached to one atom with bond angles so arranged that it is directed equally well toward two other "acceptor" atoms on adjacent molecules. Because of this division of attraction the bonds are expected to be longer and in fact in glycine the two bonds of this type are on the average about 0.20 Å. longer than the other N-H...O bonds, but still definitely shorter than van der Waals approaches. This suggests that in dicyandiamide the two longest pairs of length 3.15 Å. and 3.16 Å. are the split bond and since they converge on atom 5 we place one hydrogen on it with the NH bond bisecting the angle between the two short distances. It was then found possible to distribute the three remaining hydrogens among the three remaining pairs of short distances in only one way without bringing hydrogen atoms on different molecules too close to one another. This way corresponds to the formation of two amino groups from atoms 5 and 6. The proposed positions thus found for the hydrogens are indicated (for the central molecule only) on Fig. 6 by small circles.

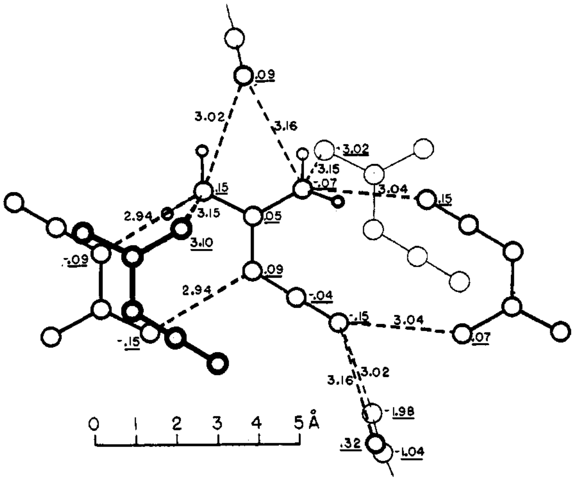

Fig. 6.—A normal projection of a portion of the structure onto (310). Small circles show probable positions of hydrogens. Underscored numbers are heights of atoms in ångströms above plane of diagram. Dotted lines indicate hydrogen bonds.

The N—H bonds were made to make angles of 120° with the C—N bonds (trigonal hybridization). The NH_2 group 6 is coplanar with the guanidine group and directs one of its hydrogens very nearly along (10°) the shortest hydrogen bond (2.94 Å.) while the other makes an angle of about 20° with the medium bond (3.02 Å.). The plane of NH_2 group 5 makes an angle of about 30° with the plane of the guanidine group. One of its hydrogens forms the bifurcated bonds (of lengths 3.15 Å. and 3.16 Å.) while the other makes an angle of about 25° with the second medium bond (3.04 Å.). The rotation of this NH_2 group out of the plane of the guanidine group would tend to force the resonating double bond somewhat out of this $\rangle C—NH_2$ bond and consequently more into the other. The observed $C—NH_2$ distances differ in the right direction for this

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(12) Reference 9, p. 187.

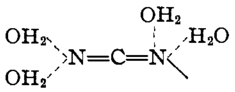
(13) Hughes, Thesis, Cornell University, 1935; Frevel, *Z. Krist.*, **94**, 197 (1936).

(14) Albrecht and Corey, THIS JOURNAL, **61**, 1087 (1939). See also discussion in reference 9, footnote p. 286.

effect and this small difference may therefore well be real. The loss in resonance energy would be compensated for by the energy of forming the second half of the split hydrogen bond. The excess in length of the medium bonds (3.02 and 3.04 Å.) over the short ones (2.94 Å.) is to be accounted for partly by the fact that the hydrogen is more exactly directed along the short bond but probably the chief source of weakness in the medium bonds is the fact that they both converge, along with one half of the split bond, upon a single nitrogen atom which, as already noted, does not have enough unshared electron pairs to provide one pair per hydrogen bond. This is not the case for the short bond. The 3.15 Å. component of the split bond is directed at the p_z orbital of an amino group 6′ of another molecule. This electron pair is involved in double bond formation only to the extent of 35% as indicated above. It thus provides about as good a terminus for a hydrogen bond as the end nitrogen of the cyanimino group.

The proposed structure satisfactorily accounts for the cleavages. The crystal may be cleaved parallel to {100} by breaking only four hydrogen bonds per cell (see Fig. 5), or 0.069 per (Å.^{2}). For the poorer cleavage on {001} the corresponding figures are eight per cell and 0.120 per (Å.^{2}). Any other cleavage will break even more bonds per unit area.

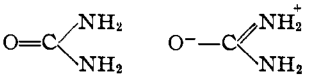
In water solutions the water molecules can form hydrogen bonds in equal numbers to both ends of the cyanimino group



Consequently, unlike in the crystal, the two contributing structures are probably of nearly equal energy and the resonance stabilization large. The addition of a proton at either end to form a cation would disturb this equality and so inhibit the resonance and decrease the stability. Moreover, the addition of a proton to an amino group would completely exclude the resonating double bond of the guanidine group from that atom and so would also cause a considerable decrease in stability. Consequently it is not surprising that the substance shows no basic properties whatever.

On the other hand, the removal of a proton from one of the amino groups to form an anion would destroy the equivalence of these two groups and although the effect would not be as drastic as that caused by adding a proton, the molecule would be destabilized to some extent by loss of resonance energy. It has been found that the acid properties are almost negligible. K_A is of the order[15] of 10^{-13} and the sodium salt, prepared in alcohol from sodium ethylate, is 95% hydrolyzed in 0.1 M solution in water. In liquid ammonia solution the conductivity of dicyandiamide reported[16] is exceedingly small so it would seem that even here there is very little dissociation despite the fact that some salts of dicyandiamide can be prepared in this solvent by reactions with metals or metal amides.

One may consider dicyandiamide to be an internal salt or zwitter ion in the same sense that urea may be so regarded. In urea the resonance of the double bond from oxygen to the amino groups transfers charges in such a way as to produce a high dipole moment:



etc.

In dicyandiamide the cyanimino group behaves like the oxygen of urea. In the crystal the hydrogen bonds from positive to negative groups tend to neutralize the charges and in fact the formal charge correction[17] has been ignored in calculating interatomic distances above. But in solution the substance would be expected to behave physically much like urea, producing an increase in the dielectric constant of the solution. This salt-like nature and the hydrogen bonds explain the high melting point (205°), low solubility in non-polar solvents, and high temperature coefficient of solubility in water and alcohol.

Crystals from alcohol were too poorly formed for goniometry but yielded a powder picture identical with that from crystals from water.

The dimensions found for the guanidine group are in good agreement with the C—NH_2 distance of 1.37 Å. found[18] in the closely related urea. But they do not agree with the corresponding distances reported[19] for the guanidinium ion, 1.20 Å. in guanidinium bromide and 1.18 Å. in the iodide.

[15] Grube and Krüger, *Z. physik. Chem.*, **86**, 85 (1914); Kameyama, *J. Chem. Ind. Japan*, **24**, 1263 (1921).

[16] Smith, This Journal, **49**, 2162 (1927).

[17] Reference 9, page 164.

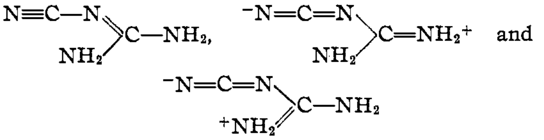
[18] Wyckoff and Corey, *Z. Krist.*, **89**, 462 (1934).

[19] Theilacker, *ibid.*, **90**, 51 and 256 (1935).

The author is indebted to Mr. P. A. Shaffer, Jr., who grew and mounted most of the crystals and assisted with the preparation and indexing of some of the photographs. Thanks are also due to Professor Pauling for encouragement and advice.

Summary

The crystal structure of dicyandiamide has been investigated. The monoclinic unit cell has a = 15.00 Å., b = 4.44 Å., c = 13.12 Å. and β = 115° 20′. The space group is $C2/c$ and there are eight molecules of $C_2N_4H_4$ per cell. The positions of the atoms have been found and correspond to a molecule which is a resonance hybrid, chiefly between structures



The packing of the molecules was found to be dominated by hydrogen bonds, one of which is of the rare bifurcated type. The properties of the compound have been discussed briefly in relation to the structure.

PASADENA, CALIF. RECEIVED MARCH 5, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 768]

An Electron Diffraction Investigation of the Molecular Structure of Tellurium Tetrachloride

BY D. P. STEVENSON AND VERNER SCHOMAKER

Introduction

It has been remarked by Pauling[1] that it is not known whether or not the unshared electron pair in molecules and complexes such as $SeCl_4$, TeC$_4$l, and $[AsCl_4]^-$ is stereochemically inert as it is in the compounds M_2SeBr_6, or stereochemically active as in ammonia-like compounds. From a discussion of the properties of the solid and dielectric constant measurements on dilute benzene solutions, Smyth, Grossman and Ginsburg[2] conclude that $TeCl_4$ has a large dipole moment. But this conclusion is insufficient to fix the structure of the molecule or to determine the steric effect of the unshared electron pair. Through the kindness of Professor J. H. Hildebrand, a pure sample of $TeCl_4$ which had been used for heat capacity determinations[3] was made available to us for the study of the structure of the molecule in the gas phase. The results of our study are reported in this paper.

Experimental

The apparatus used in this investigation has been described by Brockway.[4] The wave length of the electrons determined in the usual manner from transmission photographs of gold foil (a_0 = 4.070 Å.) was 0.0618 Å. The photographs were taken with a camera distance of 10.86 cm.

The low volatility of the compound (b. p. 390°) necessitated the use of the high-temperature nozzle[5] in order to obtain sufficient gas pressure. The photographs were taken with the sample in the boiler at 250–350°. We believe that the material actually present in the diffracting jet of gas was monomolecular tellurium tetrachloride. Simons[6] has shown that tellurium tetrachloride vapor is not appreciably dissociated (into tellurium dichloride and chlorine) up to 500° and that below this temperature the vapor is unassociated. There is the possibility that some of the tellurium tetrachloride reacted with the various metallic parts of the boiler. The only probable volatile product of such reactions is tellurium dichloride. Moderate amounts of tellurium dichloride would have little effect on our determination inasmuch as the tellurium–chlorine distance[7] (2.36 ± 0.03 Å.) in tellurium dichloride is nearly the same as the value found here for tellurium tetrachloride, while the chlorine–chlorine scattering is small compared to the chlorine–chlorine scattering of tellurium tetrachloride.

The photographs show seven rings, two of which are asymmetric. Curve D of Fig. 1, to be dis-

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[1] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 172.

[2] C. P. Smyth, A. J. Grossman and S. A. Ginsburg, THIS JOURNAL, **62**, 192 (1940).

[3] K. J. Frederick and J. H. Hildebrand, *ibid.*, **60**, 2522 (1938).

[4] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[5] L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

[6] J. H. Simons, *ibid.*, **52**, 3488 (1930).

[7] W. Grether, *Ann. Physik*, **26**, 1 (1936).