

Structures of Molecular Addition Compounds. II. Methyl Cyanide-Boron Trifluoride, $\text{H}_3\text{CCN-BF}_3$

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An X-ray diffraction study of crystals of $\text{H}_3\text{CCN-BF}_3$ leads to an orthorhombic unit of structure with $a = 7.76$, $b = 7.20$, $c = 8.34$ Å., and containing four stoichiometric molecules. All of the X-ray data are consistent with the space group $Pnma$. Approximate positions of the atoms (other than hydrogen) were determined by Patterson and Fourier syntheses. The parameters so obtained were refined by the method of Booth.

Bond distances, $\text{B-F} = 1.32$ Å., $\text{B-N} = 1.64$ Å., and bond angles, $\text{F-B-N} = 103^\circ$, $\text{F-B-F} = 114^\circ$ were observed. It is of interest to compare these results with those of Geller & Hoard for $\text{H}_3\text{CH}_2\text{N-BF}_3$ who found $\text{B-F} = 1.37$ Å., $\text{B-N} = 1.58$ Å., $\angle\text{F-B-N} = 108^\circ$, $\angle\text{F-B-F} = 111^\circ$. $\text{H}_3\text{CCN-BF}_3$ is completely dissociated in the vapor phase at 50°C . whereas monomethylamine-boron trifluoride is stable at this temperature. The weaker bond in the former is characterized by a longer B-N distance and smaller changes in the original planar configuration of BF_3 accompanying the formation of the donor-acceptor bond. We conclude that the nature of this type of bond and the resulting configuration of the addition compound depends on the character of the substituent groups attached to the 'donor' atom and that simple bond theory, which predicts complete hybridization of bond orbitals and the 'equivalent' tetrahedral configuration of bonds about the 'acceptor' atom (i.e. boron), is not adequate.

The C-C distance of 1.44 ± 0.02 Å. agrees well within limits of combined error with that observed in methyl cyanide by Pauling and co-workers.

Introduction

In an attempt to learn more about the bonding between boron in boron trihalides and a 'donor' nitrogen in certain molecules, X-ray diffraction studies of several addition compounds such as $(\text{H}_3\text{C})_3\text{N-BF}_3$, $\text{H}_3\text{CH}_2\text{N-BF}_3$ and $\text{H}_3\text{CCN-BF}_3$ have been carried out in this Laboratory. The purpose of these investigations is not only to determine the distance between the 'donor' and 'acceptor' atoms in the co-ordinated molecule but also to study the effects of this bonding on the component molecules which go to make up the whole.

When a boron trihalide adds to a compound having a donor nitrogen, the simplest bond theory has assumed that complete hybridization of bonds takes place with consequent formation of 'equivalent' tetrahedral bonds about boron. BF_3 itself is a coplanar molecule with 120° bond angles and an observed B-F bond distance of 1.30 ± 0.02 Å. (Levy & Brockway, 1937). The valence structure is formulated in terms of two single bonds and one double bond resonating among the three positions, and the B-F bond also may possess some ionic character (Pauling, 1945). In the formation of the addition product, the F atoms were thought to move away from the donor to assume three of four 'equivalent' tetrahedral positions about boron at a distance of 1.39 Å. as predicted by Bauer & Beach (1941). For the B-N distance in such a tetrahedral configuration, these workers predicted a single covalent bond of 1.50 Å. on the basis of

the Schomaker & Stevenson (1941) formula for the calculation of interatomic distances.

Geller & Hoard (I and III of this series), however, in X-ray diffraction studies of trimethylamine- and monomethylamine-boron trifluorides have found the B-N distance to be considerably longer, the distance in the latter being 1.58 Å. This value happens to agree very well with that obtained by adding the covalent radii for boron and nitrogen as originally listed by Pauling & Huggins (1934). However, the studies thus far completed in this series provide definite evidence that the length of the donor-acceptor bond varies with the character of the substituent groups attached to the donor atom. Further, changes in the configuration and B-F bond distances of the BF_3 molecule accompanying the formation of the donor-acceptor bond also depend upon the relative stability of the resulting addition compound.

The first structural work on $\text{H}_3\text{CCN-BF}_3$ was done prior to the study of the amine compounds, and the parameters obtained at that time were determined from consideration of projections alone. As a result of the more recent investigations mentioned above, it appeared advisable to reconsider the earlier work. Since the cyanide compound is much less stable than $\text{H}_3\text{CH}_2\text{N-BF}_3$ and in fact undergoes complete dissociation in the vapor phase, it seems reasonable that the B-N distance should be longer. The analysis reported here shows indeed that

a bond length of 1.64 Å. exists between boron and nitrogen in methyl cyanide-boron trifluoride. In addition the character of the weaker bond is confirmed by the fact that the F-B-N angles are less than tetrahedral and the B-F distance is 1.32 Å., 0.07 Å. less than that previously predicted, and only 0.02 Å. greater than in BF₃ itself. In H₃CH₂N-BF₃ the B-F distance is 1.37 Å. These results indicate that complete hybridization of bond orbitals around the boron does not take place and that the resulting configuration of the addition compound cannot be predicted by the simplified theory as heretofore employed.

Determination of the structure

The properties of this compound have been reported by Laubengayer & Sears (1945). The density of the solid is 1.59 ± 0.05 g.cm.⁻³. The dipole moment is appreciable, a tentative value of 5.8 debyes being reported. Since the compound is readily hydrolyzed on contact with the moisture in the air, it was prepared and kept under vacuum. At room temperature and the pressures used, it is a solid. At slightly higher temperatures it sublimes readily so that single crystals could be grown by sublimation. The crystals were grown in thin-walled cylindrical capillary tubes with diameters calculated for optimum X-ray absorption. Wall thicknesses varied from 0.0015 to 0.0005 cm. The compound was sublimed from a reservoir in one end of a long tube into the capillary tip. The growth and orientation of the crystal were observed under a polarizing microscope. The tip of the tube was sealed off when a suitable crystal had formed. Thus by a trial-and-error process separate crystals with desired axes parallel to the capillary axis were obtained.

Using Cu K α radiation, oscillation photographs were taken to align the respective axes with the rotation axis, using the Hendershot (1937) method, and then complete equi-inclination Weissenberg photographs were obtained. The reflections on the latter were indexed, following the method described by Buerger (1942). The relative intensities of the reflections were estimated visually using an intensity scale with the following ratios of intensities: 1:2:4:8:16:24:32:48:63:125. The triple-film technique was used so that reflections over a wide range of intensity could be suitably recorded for a given exposure time.

The lattice constants determined from the oscillation photographs were

$$a = 7.76, \quad b = 7.20, \quad c = 8.34 \text{ Å.}$$

A correction was applied for the combined error due to film shrinkage and deviation in camera radius from the assumed value of 50 mm. The lattice constant of NaCl was determined using the same camera and type of film. The percent deviation of the experimental value from that given in the *International Critical Tables*, 5.628 Å., was determined and a corresponding correction applied to arrive at the constants above.

The (*hk*0), (*h*0*l*) and (0*kl*) reflections were used to determine the space group, unit cell, and approximate parameters. As will be explained later, the intensities of all observed reflections were used in refining atomic positions to those finally reported herein. The absence of (*hk*0) reflections with *h* odd and of (0*kl*) reflections with *k*+*l* odd makes it very probable that the space group is either *D*_{2h}¹⁶-*Pnma* or *C*_{2v}⁹-*Pna*. The total number of absences is 45 for (*hk*0) and 40 for (0*kl*) reflections. The negative result of a pyroelectric experiment is taken as strong evidence, especially in view of the appreciable dipole moment, that the centrosymmetrical *D*_{2h}¹⁶ group is the more probable.

Assuming four molecules in the unit cell, the calculated density is 1.57 g.cm.⁻³ which compares well with the value obtained by direct determination. The space group *D*_{2h}¹⁶ affords only three sets of positions for four molecules. Of these sets, two, 4 (*a*) and 4 (*b*), consist of special positions corresponding to centers of symmetry. Since the molecule has no center of symmetry, only the set 4 (*c*) need be considered. The positions for 4 (*c*) are: $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z$. In order for this arrangement of the four molecules to conform to the *D*_{2h}¹⁶ space-group requirement of a plane of symmetry at $y = \pm \frac{1}{4}$, the H₃CCN-BF₃ molecule must have a plane of symmetry. The F-B-F angles in another addition compound (H₃C)₂O-BF₃ were found by Bauer (1943) to be approximately tetrahedral and they were assumed at first to be so in our compound. The rest of the molecule was assumed to be at least approximately linear, as for free H₃CCN. This configuration assumed, two of the fluorine atoms must occupy mirror-image positions relative to the plane defined by the remaining atoms. Thus three parameters must be determined for one type of fluorine atom and two parameters for the other atoms of the molecule. No attempt was made to determine directly parameters for the hydrogen atoms. The positions of the latter will be discussed later.

A Patterson projection was made on (010) in order to obtain values for the fluorine parameters. The scattering power of all the atoms of the compound is of the same order of magnitude. However, for this projection two fluorine atoms in 8 (*d*) will behave like one atom in 4 (*c*) with twice the scattering power of fluorine. Since the height of the peak on a Patterson plot is proportional to the product of the scattering powers of the atoms causing it, peaks due to the vectors between equivalent 8 (*d*) fluorines should be from two to four times as high as any one of the other peaks. For the 4 (*c*) positions, the vectors between structurally equivalent atoms are, in component form, as follows: 0, 0; $\pm 2x, \pm 2z$; $\pm (\frac{1}{2} - 2x), \frac{1}{2}$; $\frac{1}{2}, \pm (\frac{1}{2} - 2z)$. Remembering that the coordinates of maxima in *P*(*X*, *Z*) give the components of the vectors along *x* and *z*, there should be a fairly high peak on each of the lines $X = \frac{1}{2}$ and $Z = \frac{1}{2}$ corresponding to vectors between equivalent 8 (*d*) fluorines.

A major peak was found to lie at $X = \frac{1}{2}, Z = 0$. However, a broad unsymmetrical plateau was found on the

line $Z = \frac{1}{2}$ which extended from $X = 0.22$ to 0.34 . The plateau could be accounted for by a juxtaposition of peaks due to the vectors $\pm(\frac{1}{2} - 2x)$, $\frac{1}{2}$ and $\pm 2x$, $\pm 2z$. Values for $\pm(\frac{1}{2} - 2x)$ and $\pm 2x$ both could lie within the range $X = 0.22$ to 0.34 and assignment of the value zero to the vector component $\pm(\frac{1}{2} - 2z)$ would require $\pm 2z$ to be 0.5 . This being the case, the exact value for x could not be obtained directly. Furthermore the greater extension along Z of the plateau near $X = 0.22$ indicated that the peak due to $2x$, $2z$ lay at the end of the plateau and that $\pm 2z$ was not as near to 0.5 as the peak on $X = \frac{1}{2}$ seemed to indicate.

An idea of the position for the 4(c) fluorine was obtained from a third major peak at $X = 0.34$, $Z = 0.25$. Assuming that all the vectors between equivalent 8(d) fluorines were accounted for, the third peak, in view of its height, could be due only to a near coincidence of two or more peaks. Vectors between non-equivalent fluorines will give rise to peaks one half as high as those due to vectors between equivalent 8(d) fluorines. Furthermore, consideration of the possible vectors between non-equivalent fluorines $\pm(x_1 + x_2)$, $\pm(z_1 + z_2)$ and $\pm(\frac{1}{2} - (x_1 - x_2))$, $\pm(\frac{1}{2} - (z_1 + z_2))$, could give rise to peaks at $X = 0.34$ and $Z = 0.25$. Assuming exact superposition of these peaks, a value of $x = 0.25$ would be obtained for the 4(c) fluorine. Its z parameter of about 0.5 (or the equivalent zero) would depend on the value assigned to z for the 8(d) fluorines.

Considerations of packing radii, using plausible dimensions for the molecule, were used to confirm the tentative assignment of the fluorine parameters and to obtain more accurate values for them. Sufficiently good agreement was achieved between calculated and observed amplitudes to make fairly certain the assignment of phase for all but two of the ($h0l$) reflections and for all of the ($hk0$) reflections. This enabled us to make a Fourier projection of relative electron density on (010) and (001).

Because very close overlapping of many of the peaks occurred in both projections, the parameters decided upon at this stage had to be based primarily on the values obtained for the 8(d) fluorine and methyl carbon parameters. The remaining parameters were adjusted, relative to the fixed ones, to make their values consistent with probable bond distances and packing radii. The position of the 8(d) fluorine was practically that previously assigned. A slightly different and quite unambiguous value of 0.395 could be assigned to the x parameter on the basis of the (001) projection. The value for the z parameter was slightly less certain since the peaks due to boron and the 8(d) fluorine overlap on the (010) projection. The approximate position of the very high 8(d) fluorine peak, due to exact superposition of the two atoms, was clearly enough defined to make correction for the overlapping quite feasible. The value for the z parameter was about the same as before. A relatively large change was made in the methyl carbon parameter, the peak due to this atom being far enough

removed from other peaks to make possible quite certain assignment of value. Of the remaining atoms, only for the nitrogen could the parameters be determined with any degree of certainty whatever from the projection. It is of interest to note here that in later work it was the nitrogen that moved most when the methods were refined.

The criterion of probable values for the resulting interatomic distances had to be relied upon almost exclusively in assigning values to the 4(c) fluorine, the cyanide carbon, and the boron parameters. Peaks due to the 4(c) fluorine and the cyanide carbon are almost exactly superimposed in the (010) projection. In the (001) projection the 4(c) fluorine peak lies between the two carbon peaks so that only a single peak is to be observed. That a similar situation would exist for the 4(c) fluorine, the nitrogen, and the cyanide carbon peaks in the (100) projection could be predicted from the 4(c) positions for D_{2h}^{16} and the approximate values for the parameters. Similarly the boron peak on the (001) projection superimposes on the methyl carbon peak. On the (010) projection the boron peak lies too close to the much heavier peak due to exact superposition of the two 8(d) fluorines, and would lie too close to a peak due to almost exact superposition of the 4(c) fluorine and nitrogen peaks on the (100) projection, to make accurate estimation of the boron parameters possible.

Thus parameters were determined to give fairly satisfactory agreement between calculated and observed reflection amplitudes for the ($h0l$), ($hk0$), and ($0kl$) reflections. This was the state of the work when it became evident from the results obtained by Geller & Hoard that further calculations should be carried out, particularly in view of the longer B-N distance obtained by these workers in the monomethylamine-boron trifluoride.

We employed the method of refinement of parameters outlined by Booth (1946), assuming spherical symmetry of electron distribution in the region of maxima. Using intensities of all observed reflections corrected by the Lorentz and polarization and Tunell factors in the case of layer lines other than zero, the first calculation indicated sizeable changes in the parameters for nitrogen, cyanide carbon, and methyl carbon. Corrections to the positions for boron and the fluorines were smaller, but there was definite indication that the assumption of 'equivalent' tetrahedral bonding about the boron was not correct. The large corrections for nitrogen indicated a shift away from the boron while the methyl and cyanide carbons moved in toward each other to shorten the C-C bond. With parameters obtained from this refinement the phases of the amplitudes were recalculated and then a Fourier section in the plane $y = \frac{1}{4}$ was performed, using the Beevers & Lipson (1936) strips to carry out the summations. The section (Fig. 1) indicated that shifts observed in the original Booth calculation had been in the right direction.

To insure the best final determination of parameters a second Booth summation was carried out using positions obtained from the section. This time, corrections to be applied to the positions of atoms in the plane were very much smaller and in no case greater than 0.013 Å. Structure amplitudes were recalculated on the basis of these positions. A small number of phase changes resulted and a final Booth summation was made. Amplitudes from the latter changed phase in the case of the 024 and 652 reflections. However, the small values obtained make it doubtful which phase should be assigned to the observed amplitudes. It was felt that this was of little consequence since a check showed that the changes of sign will not affect bond lengths and also since consideration of original intensity data has set a limit on the accuracy that can be obtained.

A comparison of calculated and observed amplitudes is given in Table 1.

In the calculation of the amplitudes we used an isotropic temperature factor $\exp[-B(\sin\theta/\lambda)^2]$ with a coefficient $B=3 \text{ Å}^2$ determined by a least-squares

method to give best agreement between observed and calculated values. For reflections at low $\sin\theta/\lambda$ discrepancies may be large owing to deviation of the true

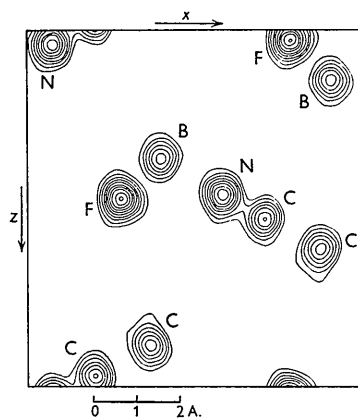


Fig. 1. Fourier section in plane $y=\frac{1}{2}$. Contours start at 50 and are drawn at intervals of 50 in arbitrary relative units of electron density.

Table 1. Comparison of calculated with observed reflection amplitudes

F_{hkl}			F_{hkl}			F_{hkl}			F_{hkl}		
hkl	Calc.	Obs.	hkl	Calc.	Obs.	hkl	Calc.	Obs.	hkl	Calc.	Obs.
200	-12.6	12.8	405	-7.7	8.3	211	-11.7	11.6	216	-6.2	5.8
400	-28.0	24.0	505	-5.4	3.4	311	-22.4	21.9	316	-4.6	4.3
600	-22.8	15.9	605	-0.1	3.0	411	+13.1	9.9	416	-1.5	2.2
800	+4.6	1.9	705	-2.8	2.7	511	+7.0	7.4	516	+4.2	2.2
10.0.0	+5.3	2.0	805	-3.9	1.2	611	+13.4	11.6	616	+1.7	0
101	+34.9	20.5	106	+13.5	10.2	711	-8.6	8.5	716	+6.1	3.4
201	+49.5	29.3	206	-8.3	8.4	811	-2.1	0	816	0.0	0
301	-10.7	14.3	306	-8.0	10.8	911	+3.3	4.2	117	-1.5	0
401	+16.0	14.4	406	+10.1	6.5	112	-31.4	19.2	217	+2.3	0
501	+2.5	6.5	506	+4.1	0	212	-36.7	23.4	317	-3.7	1.5
601	-9.8	5.8	606	+1.7	1.6	312	+11.7	13.8	417	-2.4	0
701	-14.8	14.2	706	-3.3	0	412	-17.4	16.3	517	+2.0	2.0
801	-11.4	8.5	806	-1.3	1.1	512	+11.8	10.8	617	+2.7	1.8
901	+4.1	4.3	107	-8.5	2.3	612	+5.2	4.0	717	0.0	1.6
102	+39.0	22.1	207	-3.4	2.3	712	-0.8	0	118	+1.3	0
202	-35.6	26.6	307	+1.7	0	812	+4.1	1.4	218	+8.3	7.7
302	+7.0	6.0	407	-13.6	11.4	912	-2.7	2.0	318	-3.5	2.9
402	+35.5	22.9	507	+7.1	2.0	113	-1.2	2.5	418	+1.9	1.9
502	-6.7	8.3	607	+4.1	1.6	213	+4.1	4.7	518	-0.4	1.2
602	+4.2	0	707	-0.1	1.6	313	-26.6	26.6	618	-2.8	1.8
702	-7.1	6.7	108	+1.2	1.6	413	-16.3	14.7	119	+1.2	0
802	-5.9	4.1	208	-0.6	0	513	+2.0	2.2	219	-0.6	1.9
902	+1.8	2.9	308	-16.2	10.9	613	+3.8	5.3	319	+3.8	1.2
103	-2.6	5.1	408	-5.8	3.7	713	+0.1	0	419	+0.4	1.1
203	-40.8	28.8	508	+1.9	1.6	813	+1.8	0	519	+2.3	0
303	-5.4	8.0	608	-0.7	0	913	+5.9	6.3	1.1.10	-5.5	2.7
403	-21.9	21.3	109	+2.6	0	114	+1.0	2.9	2.1.10	+0.8	0
503	+17.1	15.7	209	+4.5	3.5	214	-3.2	6.7	3.1.10	+1.9	0
603	+13.4	10.8	309	-0.1	0	314	-4.2	7.2	011	-41.3	20.5
703	-5.8	8.3	409	-3.4	0	414	+2.2	2.1	013	+12.1	11.7
803	+2.7	0	509	-3.5	0	514	-3.1	0	015	-22.6	17.7
903	-2.0	0	1.0.10	+9.4	5.4	614	+1.5	3.4	017	-7.3	6.3
104	+1.0	1.1	2.0.10	-0.6	0	714	+3.0	3.6	019	-6.7	5.6
204	-4.7	4.7	3.0.10	+1.8	0	814	-3.7	2.6	220	+24.2	19.2
304	-33.4	20.4	002	+5.2	7.7	914	+1.6	0	420	-8.0	8.2
404	+1.2	5.1	004	+41.4	39.1	115	+12.5	8.8	620	+4.7	6.7
504	+0.6	5.5	006	-5.2	4.2	215	-0.5	2.6	820	+0.2	0
604	-13.0	11.7	008	+9.2	8.0	315	+2.3	0	121	-19.6	16.7
704	+5.6	1.6	0.0.10	-4.3	4.1	415	+0.9	0	221	+15.6	20.0
804	-2.3	4.2	210	+36.5	23.6	515	-1.1	2.9	321	+7.2	7.7
904	+2.8	2.3	410	-0.9	3.1	615	+8.2	7.4	421	+6.2	7.1
105	+21.2	14.4	610	-14.5	12.2	715	-5.1	3.4	521	-6.3	6.9
205	+14.6	12.0	810	-5.0	3.0	815	-1.4	0	621	-4.6	4.4
305	-13.1	16.4	111	+2.0	2.6	116	-6.3	4.0	721	+13.0	12.7

Table 1 (cont.)

F_{hkl}			F_{hkl}			F_{hkl}			F_{hkl}		
hkl	Calc.	Obs.	hkl	Calc.	Obs.	hkl	Calc.	Obs.	hkl	Calc.	Obs.
821	+ 0.6	2.1	431	+18.9	17.9	141	+ 9.2	11.0	280	- 3.4	0
921	- 2.8	2.7	531	- 5.8	5.7	241	-18.5	16.9	480	- 1.9	1.6
122	-19.6	16.2	631	+ 4.5	0	341	- 4.0	2.7	290	- 2.0	2.3
222	+14.5	11.6	731	+ 5.1	6.1	441	- 7.9	5.3	020	-65.8	40.5
322	+ 5.8	6.3	831	- 2.6	0	541	+ 5.4	2.1	040	+23.2	18.5
422	- 3.2	5.8	931	- 3.3	3.0	641	+ 6.2	4.1	060	-38.7	27.6
522	+ 5.6	4.3	132	+ 7.6	8.8	741	- 9.7	9.6	080	+16.0	7.6
622	+10.4	9.6	232	-19.4	16.5	841	+ 1.8	0	151	+ 0.8	5.2
722	+ 2.5	3.4	332	- 4.7	2.6	142	+ 9.8	8.5	251	- 1.9	3.9
822	+ 1.4	2.6	432	- 4.3	5.7	242	- 6.3	0	351	- 9.4	2.9
922	- 2.6	2.1	532	- 2.6	5.6	342	- 5.1	3.0	451	+ 0.6	3.0
123	-15.1	14.7	632	+ 8.2	8.1	442	- 3.3	4.7	551	+ 3.7	0
223	- 5.3	7.5	732	+ 1.8	0	542	- 4.3	3.6	651	+ 4.2	5.5
323	+10.0	12.8	832	+ 5.6	2.7	642	-10.4	7.1	751	- 4.6	3.3
423	+ 4.2	5.6	932	+ 0.4	0	742	- 1.1	2.5	851	- 0.3	0
523	- 5.8	7.4	133	-10.4	6.0	842	- 0.3	1.9	161	- 7.7	8.4
623	- 1.9	3.0	233	+ 8.0	11.5	143	+12.1	10.4	261	-10.8	11.8
723	+ 6.5	5.4	333	+ 5.5	7.2	243	+10.8	11.3	361	+ 3.3	3.0
823	+ 5.5	4.7	433	- 9.3	9.9	343	- 8.0	9.6	461	- 4.5	5.4
923	- 0.6	0	533	- 0.8	4.4	443	+ 0.1	0	561	- 1.4	0
124	-14.0	12.0	633	-15.2	12.8	543	+ 2.3	5.8	661	+ 3.2	3.3
224	+12.6	11.1	733	+ 5.0	2.9	643	- 0.7	0	761	+ 6.8	4.1
324	+12.7	11.7	833	+ 2.0	0	743	- 5.1	3.5	171	- 0.3	4.1
424	-19.0	15.4	933	- 3.9	4.8	843	- 6.2	4.4	271	+ 3.3	2.9
524	+ 0.2	0	134	+15.4	13.5	144	+11.9	9.1	371	+ 3.8	0
624	+ 1.8	2.5	234	+30.8	24.2	244	-10.3	9.6	471	- 5.1	5.0
724	+ 1.0	0	334	- 2.2	3.4	344	- 5.6	7.8	571	- 2.1	0
824	+ 4.9	4.2	434	+ 9.6	10.4	444	+17.7	12.8	671	- 5.6	3.6
924	- 0.9	1.8	534	- 8.4	8.9	544	- 0.4	4.1	181	+ 3.4	2.3
125	- 2.2	3.3	634	- 9.5	6.2	644	+ 0.9	0	281	+ 1.1	0
225	+ 7.8	8.5	734	- 3.2	2.7	744	- 2.1	0	381	- 1.6	0
325	+ 6.1	5.1	834	- 3.6	3.4	844	- 4.8	4.1	481	+ 0.4	0
425	+15.6	14.7	135	+ 2.6	5.5	145	- 1.7	0	191	- 0.8	2.1
525	- 6.2	6.1	235	- 5.1	4.2	245	- 9.8	10.0	051	- 4.5	5.3
625	- 6.3	4.8	335	+13.4	8.9	345	- 3.4	2.5	071	+ 8.4	8.4
725	+ 1.1	2.6	435	+12.0	9.5	445	-13.5	13.7	091	+ 2.8	3.4
825	- 1.5	2.9	535	+ 0.3	0	545	+ 7.2	4.3	152	- 9.5	8.8
126	- 0.8	2.2	635	+ 0.7	0	645	+ 6.2	3.7	252	- 9.8	9.2
226	+ 3.2	2.3	735	- 3.3	0	745	- 0.5	2.5	352	+ 4.8	3.4
326	+21.3	16.6	835	- 1.2	0	146	- 2.0	3.8	452	- 4.2	3.4
426	- 0.1	0	136	- 9.8	6.2	246	- 1.4	0	552	+ 5.3	6.6
526	- 4.5	3.4	236	- 8.5	5.5	346	-19.4	10.9	652	- 0.3	3.1
626	+ 3.7	3.0	336	+ 9.3	9.0	446	- 1.9	0	752	- 1.0	0
726	- 3.2	2.5	436	- 4.8	6.4	546	+ 3.5	3.3	852	+ 0.5	2.6
826	- 0.4	0	536	+ 7.0	3.0	646	- 4.1	2.8	162	- 9.9	6.9
127	- 4.9	4.9	636	+ 3.1	0	746	+ 4.0	2.9	262	+ 9.2	4.9
227	- 5.9	3.4	736	- 3.6	3.5	147	+ 6.4	5.4	362	- 2.5	3.4
327	+ 3.0	2.3	137	- 8.0	4.6	247	+ 6.6	5.3	462	-10.6	6.5
427	+ 8.5	6.8	237	+ 0.8	4.6	347	- 3.2	3.6	562	+ 3.3	3.0
527	+ 2.6	2.1	337	- 9.5	6.3	447	- 5.8	4.6	662	- 1.1	0
627	- 0.8	0	437	- 3.9	2.9	547	- 4.1	2.9	762	+ 3.1	0
727	+ 1.5	1.3	537	- 1.0	0	647	- 0.1	0	172	+ 7.2	4.7
128	- 8.6	4.8	637	- 5.8	5.4	148	+ 8.2	4.8	272	+10.3	9.1
228	+ 2.1	2.3	138	+ 9.0	6.0	248	- 1.9	3.1	372	- 3.6	3.0
328	+ 4.8	4.4	238	- 2.0	2.9	348	- 1.5	3.0	472	+ 4.8	2.7
428	+ 2.0	2.1	338	- 0.6	0	448	- 0.8	0	572	- 4.8	3.3
528	- 1.4	0	438	+ 0.6	0	548	+ 0.8	0	672	- 2.2	0
628	- 1.4	1.3	538	- 7.5	5.1	149	- 6.4	3.9	182	+ 4.8	0
129	+ 5.6	3.0	638	+ 0.6	0	249	+ 0.8	0	282	- 3.7	0
229	- 1.7	2.0	139	+ 4.9	2.5	349	+ 2.8	0	382	+ 0.4	0
329	- 2.7	0	239	- 0.1	0	042	+45.5	30.9	482	+ 2.8	0
429	+ 4.5	4.0	339	+ 4.6	0	044	- 7.2	11.5	022	-61.4	26.3
529	- 2.7	2.0	439	+ 1.2	0	046	+11.7	13.1	062	- 2.9	3.4
1.2.10	- 4.7	3.9	1.3.10	- 1.3	0	048	+ 1.0	0	082	+ 6.4	2.7
2.2.10	+ 0.3	0	2.3.10	- 1.6	0	250	+ 5.3	2.9	153	+ 0.7	8.1
3.2.10	+ 1.5	0	031	-33.9	25.2	450	- 3.4	0	253	- 0.9	4.2
10.2.0	+ 0.9	0	033	+35.1	29.8	650	- 6.2	7.3	353	- 9.1	8.8
230	+27.9	23.9	035	- 6.7	9.9	850	- 0.6	0	453	- 3.7	3.0
430	+19.7	16.1	037	+15.7	15.5	260	+ 3.7	2.3	553	+ 0.6	3.0
630	- 1.4	2.3	039	+ 2.7	2.7	460	+ 9.0	13.1	653	+ 5.0	3.9
830	- 6.1	4.7	240	-18.2	12.2	660	+ 8.4	7.2	753	- 0.9	2.1
131	+ 0.6	11.4	440	+10.5	7.1	270	-10.8	8.8	163	- 1.0	0
231	- 7.6	6.1	640	+ 0.3	1.6	470	- 1.7	2.0	263	+10.3	10.8
331	+20.9	16.8	840	- 1.2	2.0	670	+ 6.9	8.1	363	+ 2.6	0

Table 1 (cont.)

<i>hkl</i>	F_{hkl}		<i>hhl</i>	F_{hkl}		<i>hkl</i>	F_{hkl}		<i>kkh</i>	F_{hkl}	
	Calc.	Obs.		Calc.	Obs.		Calc.	Obs.		Calc.	Obs.
463	+ 7.1	5.7	154	- 2.2	0	374	+ 1.9	3.5	755	- 1.6	0
563	- 6.7	5.2	254	- 8.4	8.7	474	- 1.7	3.0	165	- 6.2	7.0
663	- 5.2	3.0	354	- 1.3	3.0	574	+ 1.5	0	265	- 2.9	3.4
763	+ 2.7	2.1	454	- 0.8	0	184	+ 2.0	0	365	+ 5.3	3.4
173	+ 1.8	5.7	554	+ 0.9	2.9	284	- 2.1	0	465	+ 3.2	4.2
273	- 0.9	0	654	+ 2.8	0	384	- 4.5	0	565	+ 1.5	0
373	+ 7.2	3.6	754	+ 1.6	0	024	- 0.5	6.8	665	- 0.5	0
473	+ 5.9	3.4	164	- 1.3	0	064	- 10.6	6.2	175	- 4.0	0
573	- 0.3	0	264	+ 2.2	0	084	+ 1.8	0	275	+ 1.1	2.8
183	+ 1.6	0	364	+ 11.0	8.3	155	+ 3.5	0	375	- 2.0	2.5
283	- 1.9	0	464	- 2.3	0	255	+ 0.4	3.5	475	- 1.3	2.2
383	- 2.1	0	564	0.0	0	355	- 1.6	3.5	185	+ 2.2	4.2
483	- 2.3	0	664	+ 4.9	3.3	455	- 2.0	0	055	- 5.4	0
053	- 2.5	0	174	- 1.5	0	555	- 0.8	0	075	+ 6.7	2.5
073	- 5.6	5.8	274	+ 0.9	0	655	+ 3.0	2.6			

atom form from the assumed spherically symmetrical form, since all the atoms are of a low atomic number and exist not free but combined in a molecule. This may be particularly important for carbon and nitrogen of the cyanide group. It is to be remembered too that extinction probably is present for strong reflections at low scattering angles. In addition we have neglected hydrogen contributions which are generally small and indeed are negligible for values of $\sin \theta / \lambda$ greater than 0.35. Even with the differences that exist, an index of reliability, $R=0.31$ determined from

$$R = \frac{\sum | |F_{\text{obs.}}| - |F_{\text{calc.}}| |}{\sum |F_{\text{obs.}}|}$$

is obtained if we neglect differences when observed amplitudes are zero. It is felt that many of the discrepancies in the table of comparison are due to inadequate cross calibration and comparison of reflections on different films in taking the original intensity data. Unfortunately the crystals used for the original work are no longer available and the photographs obtained at that time do not now permit reading intensities with the precision obtained by Geller & Hoard in their investigation. Even so, we believe that the accuracy of the determination of parameters is rather better than might be implied by the value obtained for R . Evidence supporting this view may be found from consideration of the last two Booth calculations.

For example, the x parameter for nitrogen from the Fourier section was 0.573. The correction obtained from the refinement was such as to reduce it toward 0.572. The final refinement, in which 0.572 was used in the calculation, corrected the x co-ordinate such as to increase it toward 0.573 again. This behavior was noted for three of the atoms, since over-corrections of 0.001 in the atomic co-ordinates had been made. This indicates that we obtained convergence. Still more evidence lies in the fact that when *calculated* amplitudes were substituted for observed amplitudes as a check calculation in the refinement for methyl carbon we found that we were led to the same correction as the observed values had given within the limits of accuracy claimed. We feel that the probable error in the determination of bond

distances (excluding C-H bonds) does not generally exceed 0.02 Å. Table 2 lists the final values of the parameters.

Table 2. Atomic co-ordinates

	x	y	z
8 (<i>d</i>) F	0.398	0.097	0.273
4 (<i>c</i>) F	0.270	$\frac{1}{4}$	0.471
4 (<i>c</i>) B	0.391	$\frac{1}{4}$	0.359
4 (<i>c</i>) N	0.573	$\frac{1}{4}$	0.460
4 (<i>c</i>) C _{CN}	0.698	$\frac{1}{4}$	0.530
4 (<i>c</i>) C _{CH₃}	0.860	$\frac{1}{4}$	0.615
8 (<i>d</i>) H	0.87	0.13	0.69
4 (<i>c</i>) H	0.96	$\frac{1}{4}$	0.53

Discussion of results

Fig. 2 is a sketch of the unit cell showing how the molecules pack. The hydrogens of the methyl group are not shown. Interatomic distances and bond angles are listed in Table 3. As has been said, with the exception of the 8 (*d*) fluorines and 8 (*d*) hydrogens the molecules lie in the planes $y = \pm \frac{1}{4}$. The molecules are stacked along y end-for-end, the distance of closest approach between molecules in a stack is about 2.7 Å., between 8 (*d*) F and 8 (*d*) H. Any given stack has four nearest neighbors, the four being arranged centro-symmetric with respect to the central stack. The closest contact occurs between the 8 (*d*) H atoms of the projecting methyl groups of one stack and the 8 (*d*) F atoms of another, the distance being about 2.5 Å. For adjacent parallel molecules in the same plane (i.e. unit translation along x) the distance of closest approach is that between 4 (*c*) H and 4 (*c*) F of 2.5 Å. also. The question of whether or not the hydrogens are *cis* or *trans* with respect to the fluorines was considered. Assuming tetrahedral bonds around the methyl carbon and a C-H bond length of 1.07 Å. we have calculated hydrogen positions in the two possible configurations. To decide which is the more probable orientation the intermolecular distances H-H and H-F must be considered. It turns out that for the *cis* orientation the 8 (*d*) H-8 (*d*) H separation between $\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z$ and $\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z$ is 2.6 Å. whereas with a *trans* orientation no such close approach of hydrogens is observed. From considerations of stability, it would

appear that the *trans* orientation with hydrogens linking fluorines is the more likely. We have therefore concluded that the 4 (c) H is *trans* to the 4 (c) F in the molecule.

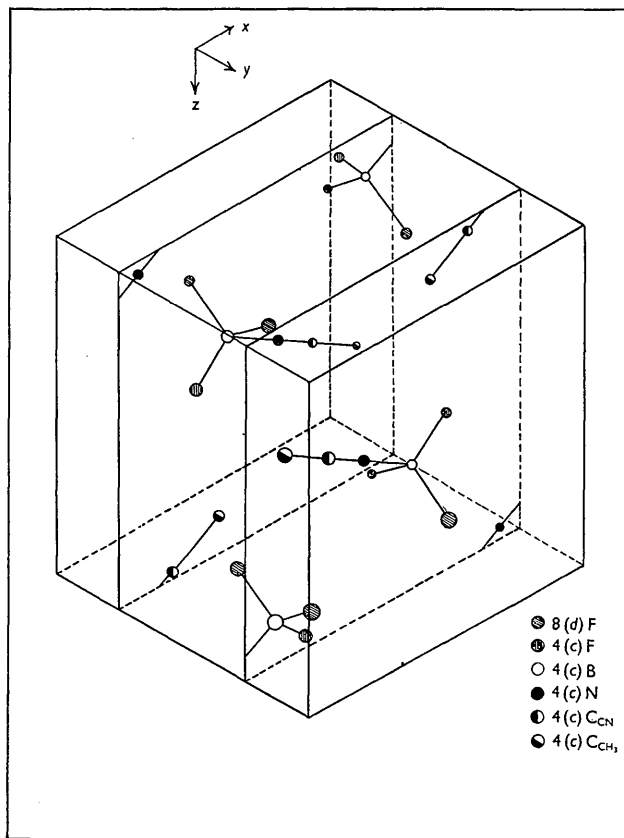


Fig. 2. Isometric sketch of unit cell.

Table 3. *Interatomic distances and bond angles*

(Bonded)	8 (d) F-B	1.32 ± 0.02 A.
	4 (c) F-B	1.32 ± 0.02
	B-N	1.64 ± 0.02
	N-C	1.13 ± 0.02
	C-C	1.44 ± 0.02
(Non-bonded)	8 (d) F-8 (d) F	2.21 ± 0.02
	4 (c) F-8 (d) F	2.22 ± 0.02
Bond angles:	8 (d) F-B-8 (d) F	114°
	8 (d) F-B-4 (c) F	114°
	8 (d) F-B-N	103°
	4 (c) F-B-N	103°

It is to be noted that the bonds around boron are not tetrahedral. The F-B-N and F-B-F angles are 103° and 114° respectively. Boron is closer to the plane of the three fluorines, indicating less deformation of the original planar BF_3 molecule than previously expected. As has been said, the B-F bond length in planar BF_3 is 1.30 A. It is reasonable that this length in the coordinated compound would be a little larger owing to deformation and resulting weakening of the bond. However, our value of 1.32 A. is less than the value of 1.39 A. predicted by the Schomaker & Stevenson formula. Geller & Hoard (1950), in studies on monomethylamine-

boron trifluoride, obtained a value of 1.37 A. with F-B-F and F-B-N angles of 111° and 108° respectively. This would indicate that in $\text{H}_3\text{CCN-BF}_3$ the change in character of the original B-F bond in BF_3 is much less than that in monomethylamine-boron trifluoride. If we further consider the B-N distance in the two compounds, we find that in our case it is 1.64 A. whereas the aforementioned workers report 1.58 A.

Now methyl cyanide-boron trifluoride is much less stable (decomposes in vapor phase at $50^\circ\text{C}.$) than the monomethylamine compound which is quite stable at ordinary temperatures. Comparison then leads us to believe that the strength of the donor-acceptor bond and the degree of hybridization of the bond orbitals of boron does depend on the nature of the donor molecule. It is hoped that further study of this bond in other related compounds will add to our knowledge of this relationship.

The $\text{C}\equiv\text{N}$ distance of 1.13 ± 0.02 A. that we find agrees well with that of 1.16 ± 0.02 A. determined in electron-diffraction studies on H_3CCN by Brockway (1936). The short C-C distance of 1.44 ± 0.02 A. is particularly striking. However, Herzberg, Patat & Verleger (1937), in studies of methyl acetylene in the photographic infra-red, report a C-C distance of 1.463 A. Badger & Bauer (1937) discuss reasons for this behavior. Pauling, Springall & Palmer (1939), interested in Herzberg's result, carried out electron-diffraction studies on methyl acetylene, dimethyl acetylene and methyl cyanide and obtained C-C distances of 1.46 ± 0.02 A., 1.47 ± 0.02 A., and 1.49 ± 0.03 A. respectively. To explain the short C-C distance as compared to the 1.54 A. value usually observed, they assume that there is a partial double-bond character in the bond. Thus, within the combined limits of error, there is agreement with the results obtained by these investigators.

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Unit-Cell Dimensions of Graphite

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It is shown that the variation with particle size of the c dimension of the graphite unit cell, often reported for small crystallites, can be followed through the range of relatively well-crystallized specimens. The value of c is found to be a linear function of the reciprocal of the number of carbon layers in the crystallite. The a dimension remains constant over this range, although there are small displacements of the $hki0$ lines, probably on account of admixture of a proportion of turbostratic material.

Introduction

In the course of determinations of the unit-cell dimensions of various types of graphite further data have been obtained concerning the variations of these dimensions with crystallite size. Earlier measurements, such as those of Hofmann & Wilm (1936), have shown the difference between normal graphite and graphites with very small particles. The present measurements show that there is a continuous variation of the c dimension of the unit cell through the range of relatively well-crystallized specimens (both natural and artificial), the value tending to a limit for the best crystallized samples available. Over the same range the a dimension is found to remain constant, although there are apparent changes when measurements are based on $hki0$ lines, due presumably to superposition of a displaced maximum from a proportion of turbostratic material.

Experimental details

The spacing measurements were made by the method described by the writer (1948). Extruded specimens of powdered graphite mixed with a little NaCl were employed, using Cu $K\alpha$ radiation in a 19 cm. camera. All the spacing values were taken as the mean of those found from four or more pairs of films. For determination of the c dimension the 0008 reflexion at $\theta = 67^\circ$ was measured in the case of the samples with fairly large crystallites, but with decrease of crystallite size the 0008 reflexion becomes too diffuse for accurate measurement and in these cases 0006 at 44° was used. Using this relatively low-angle reflexion it was shown that there was no significant error due to orientation by extrusion,

of the type described by Nelson & Riley (1945*a*), this being established by subsidiary experiments in which small cylinders, 0.05 cm. in diameter, were turned in a lathe from a large uniform block of graphite and mounted directly in the camera. Measurement was made of the angular difference between the 1120 and 0006 reflexions. These lines have θ values differing by only 4.8° , and their measured angular separation will be little influenced by absorption corrections. Moreover, the 1120 line will be uninfluenced by orientation and serves therefore as a constant reference position. It was found that the separation measured was the same, to 0.0001 A., as that for the extruded specimens containing NaCl. A similar experiment established the reliability of the 0008 reflexion, when it could be employed, measurement being made of the angular separation between the 0008 and 1230 reflexions.

For the a dimension the main measurements were of the 1230 and 1231 reflexions, which occur at $\theta = 73$ and 74° respectively. Calculation shows that the position of the latter is influenced very little by the precise value chosen for c . The 1120 line at 39° was also measured.

The crystallite sizes of the samples were determined from the X-ray line widths, which were interpreted on the graphite model proposed by Hofmann & Wilm (1936). This model explains the particular characteristic of the graphite photograph, namely $hkil$ lines which become increasingly broad with increase of the l index, except for the $000l$ lines which are sharp. This is explained by assuming that the carbon planes are stacked regularly for an average thickness t , at successive intervals of which there is a random twist about the