

that there is any difference in the size of unit cells of the two polytypes other than the 1:3 ratio of the c axes. A difference of say 0.1% should have been observable.

Solid solution of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$ in $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$

Jones & Roberts concluded that a solid solution between α_1 - (or α_2 -) $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$ and α_1 - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ exists in the aqueous system with a limiting composition corresponding to $2.4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10.2\text{H}_2\text{O}$. They were, however, unable to differentiate between pure α_1 - $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and the solid-solution phase by optical or X-ray examination. Although the X-ray patterns of the two pure compounds are quite distinctive, the unit cell sizes are very similar (the di-calcium aluminate hydrate is larger by 0.45% in the a direction, and 0.91% in the c direction). By comparing the mixtures of the suspected solid solution and the pure components, good agreement was obtained between calculated and estimated values for the a and c axes. However, detailed analysis

of the results from different zones of reflections suggested that the expected differences were of the same order as certain systematic deviations mentioned above in describing the α_2 -phase, and it must be concluded that the X-ray data does not provide adequate proof of the existence of a solid solution series.

I should like to thank my colleague Dr M. H. Roberts for allowing me to use the X-ray films he took for his work on the system of $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. The work described is part of the research programme of the Building Research Board of the Department of Scientific and Industrial Research, and this paper is published by permission of the Director of Building Research. Crown Copyright is reserved.

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The Crystal Structure of Disordered Trimethylamine Triborane

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The crystal structure of the disordered high temperature (transition temperature -64°C .) modification of trimethylamine triborane, $\text{B}_3\text{H}_7\text{N}(\text{CH}_3)_3$, has been determined by single-crystal X-ray diffraction techniques. It has been possible to roughly determine the molecular configuration, and to estimate bond parameters. The nature of the disorder also is indicated.

1. Introduction

Coordination compounds containing the triborane group, B_2H_7 , were first prepared by Edwards, Hough & Ford (1957) in these laboratories. The preparation of trimethylamine triborane, the most stable and most easily purified of the compounds prepared, is typical of the reactions used:



This reaction was postulated to proceed by a 'symmetrical' cleavage of the hydrogen bridge bonds in tetraborane by analogy with the reactions of Lewis bases with diborane (Edwards, Hough & Ford, 1957). Shortly following this work, the compound ammonia triborane, $\text{NH}_3\text{B}_3\text{H}_7$, was prepared in the laboratory of R.W. Parry at the University of Michigan (Kodama, Parry & Carter, 1959).

Thermodynamic studies have shown that trimethylamine triborane and ammonia triborane both undergo low temperature phase transitions of a similar type (Westrum & Levitin, 1959; Levitin & Westrum, 1959). Crystal structure analyses have been reported recently for both the disordered high temperature, and ordered low temperature phases of ammonia triborane (Nordman & Reimann, 1959). The B_3H_7 group was found to have a structure close to the one expected for the 'symmetrical' cleavage fragment of tetraborane. The work reported herein establishes a similar structure for the B_3H_7 radical in trimethylamine triborane and affords further corroboration for the symmetrical cleavage reaction mechanism.

2. Experimental

Several specimens of crude reaction product were supplied by Messrs. W. V. Hough and M. D. Ford of these laboratories. The crude material was purified by

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several recrystallizations from methyl alcohol-water solution. Crystals large enough for single-crystal X-ray diffraction studies were grown from methyl alcohol-water solution by slow evaporation of solvent at 0 °C. The crystals were soft with no sharply defined faces and tended to grow in aggregates. Crystals mounted for X-ray study were sealed into capillary tubes (0.01 mm. wall thickness) to prevent oxidization.

The crystals were found to yield diffuse, streaked single-crystal diffraction patterns, the streaks being tangential to the Debye-Scherrer circles. For the best crystal found, the streaks on a long exposure Weissenberg photograph were as long as 1.5 cm. for very strong reflections. Because of strong thermal damping and/or disorder, only about one-fourth of the reflections available from the copper sphere were observed.

Unit-cell dimensions were measured from Weissenberg photographs calibrated with superimposed powder patterns of sodium chloride (Christ, 1956). The crystals exhibit $R\bar{3}m$ (rhombohedral) diffraction symmetry with cell dimensions $a=6.04$ Å, $\alpha=104^\circ 14'$. For the hexagonal cell:

$$\begin{aligned} a &= 9.535 \pm 0.020, \quad c = 7.45 \pm 0.05 \text{ \AA} . \\ d_c &= 0.838 \text{ g.cm.}^{-3} \text{ for } Z=3, \\ d_o \text{ (flotation)} &= 0.833 \text{ g.cm.}^{-3}. \end{aligned}$$

The space group was assumed to be $R\bar{3}m$ because of the necessary absence of a center of symmetry in the molecule. This assumption was verified by the subsequent structure analysis.

Low temperature single-crystal and powder diffraction patterns indicate that below the transition temperature, established to be 209.10 °K. by the thermodynamic studies (Levitin & Westrum, 1959), lower symmetry obtains. Nothing was done to establish the unit cell and symmetry of this phase. The patterns obtained below the transition temperature were not improved in quality nor was the range of data extended. Single crystals remained intact in passing through the transition.

Only one crystal was found to be suitable for intensity measurements. This crystal was rod shaped, approximate dimensions 0.4×0.2 mm., with the rod axis colinear with the c axis. Intensities were measured with a standard Weissenberg goniometer modified to accommodate the Norelco Geiger counter attachment (Evans, 1953; Parrish, 1956; Cochran, 1950).

The breadth of the diffraction maxima required about 5° crystal rotation to record the complete peaks from background to background. Since the maximum range of the goniometer crystal rocker was 3° , it was necessary to make two strip chart recordings for each peak, with each record covering slightly more than half of the required range. Composites of the tracings were made from which the intensities were measured by integration with a planimeter. A total of forty-four symmetrically independent intensities with magnitudes significantly greater than zero were measured.

The $000l$ reflections were not accessible to the Geiger counter because of the goniometer geometry. From Debye-Scherrer and precession photographs, the 0003 reflection was observed to be very strong. The 0006 reflection is weak. No others were observed. It was found that photographic intensities estimated with film intensity strips could not be correlated with the Geiger counter data. This was due to the paucity of data, and to the failure, for broad peaks, of the approximation that peak height can be substituted for integrated intensity. Thus it was not possible to include the $000l$ reflections in the structure determination calculations, nor was it possible to establish firmly the relative scales of the layers of data measured with the Geiger counter.

3. Structure determination

An hexagonal unit cell with space group symmetry $R\bar{3}m$ is triply compound with each primitive unit having symmetry C_{3v} . Since there is one molecule of $B_3H_7N(CH_3)_3$ per primitive unit, the molecule must have symmetry C_{3v} if it is to have an ordered arrangement in the crystal. The only possible ordered structures, other than the trivial ones where all atoms of a given species lie on the triad axis, would have the nitrogen atom on the triad axis, the three carbon atoms on one set of mirror planes, and the three boron atoms on either the same, or more probably, on the other set of mirror planes. The arrangement of the heavy atoms for the most probable ordered structure is shown in Fig. 1(a).

Using expected bond lengths and angles for this model, structure factors were calculated yielding a reliability index of $R=0.28$, where

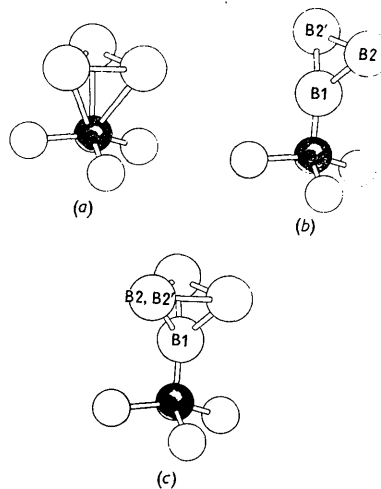


Fig. 1. The small plain spheres are carbon atoms, the shaded sphere is the nitrogen atom, and the large spheres are boron atoms. (a) The most probable heavy atom arrangement for an ordered structure. (b) Heavy atom arrangement assumed for the cylindrically disordered structure. (c) Heavy atom arrangement for the correct disordered structure.

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

The nitrogen atom was fixed at the origin, and since the positions of the carbon atoms could be predicted with considerable accuracy, the refinement of this structure was begun by varying the x and z parameters of the boron atoms. The lowest value of R obtained was 0.22. Most of the small decrease in R was due to refinement of the temperature and scale factors.

A section through the three dimensional Patterson function on the plane $Y=0$ of the orthohexagonal cell was calculated on X-RAC. For the ordered structure of Fig. 1(a), a complete set of intramolecular interatomic vectors for the heavy atoms lie in this plane. The Patterson section showed a totally unexpected peak at approximately half the distance between the origin and the expected boron-nitrogen peak. There was considerable diffuseness of the boron-nitrogen peak, and also a large amount of overlap into the plane of the Patterson section of the boron-nitrogen peaks above and below this plane.

At this time, the results of the crystal structure analysis of disordered ammonia triborane by Nordman & Reimann (1959) were made available to the author. In this crystal, which has tetragonal symmetry, the nitrogen atom lies near the c axis, while the B_3H_7 boron triangle is tilted relative to the c axis so that one boron atom may be considered bonded to the nitrogen atom, and the other two are at about the same level further along the c axis. The c axis passes through the boron triangle, and the whole molecule is cylindrically distributed about the c axis.

The complete three dimensional Patterson function for $B_3H_7NCH_3$ was then calculated. This was readily interpreted in terms of a structure, for the B_3H_7 portion of the molecule, similar to that of ammonia triborane; indeed, a toroidal distribution of density with its center on the c axis was observed at the level expected for the two boron atoms furthest from the nitrogen atom.

Using atomic positions taken from the Patterson function, structure factors were calculated assuming cylindrical distribution of the B_3H_7 group about the c axis.* The model shown in Fig. 1(b) was used. Significantly better results were obtained and the discrepancy index dropped to 0.17. This structure was refined by least-squares for the case with B1 on the c axis ($R=12.8\%$) and also with B1 slightly offset from the c axis ($\rho_{B1}=0.4 \text{ \AA}$, $R=10.7\%$). After each cycle of refinement, the scale and temperature factors were determined from plots of $\log F_c/F_o$ versus $(\sin \theta/\lambda)^2$.

At this stage of the work, programs for calculation

* The contribution to the structure factor by the j -th atom distributed cylindrically about the c axis in space group $R\bar{3}m$ is

$$F(hkl)_j = 3f_j J_0((2\pi\varphi_j/\lambda)\xi(h, k)) [\cos 2\pi lz_j + i \sin 2\pi lz_j],$$

where φ_j is the 'radius of rotation' of the j th atom about c , and $\xi(h, k)$ is the perpendicular distance of the reciprocal lattice point hkl from the c^* axis.

of three dimensional electron density were written for the Royal McBee LGP-30 computer. Using the phases calculated from the cylindrically disordered structure, the electron densities in the regions of the atomic positions were calculated. The computed nitrogen and carbon peaks were normal. In the region surrounding B1 a flat diffuse peak with maximum on the c axis was observed. A section normal to c at the level of the B2 atoms is shown in Fig. 2. Clearly these two atoms are not cylindrically distributed as previously assumed, but rather are distributed between the three symmetrically equivalent mirror planes shown by the broken lines in Fig. 2. A model of the disordered structure is shown in Fig. 1(c). This structure was refined by Fourier methods using F_o and F_c syntheses (Booth, 1947). Hydrogen atoms and individual isotropic temperature parameters for the heavy atoms

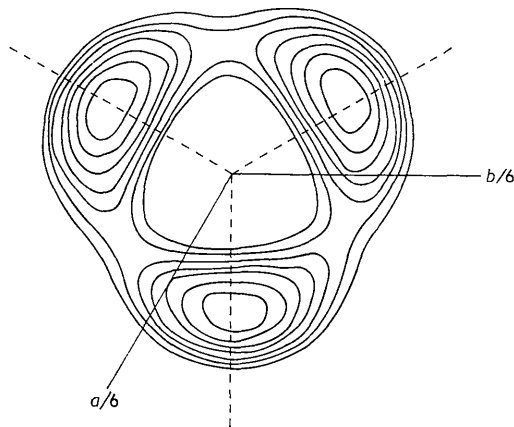


Fig. 2. Three dimensional electron density section containing the centers of the B2 atoms. The electron density was calculated using phases determined for a structure model assuming cylindrical distribution of the B2 atoms about the C axis. The broken lines represent traces of mirror planes. Contours are at intervals of 0.05 e.\AA^{-3} . The lowest contour is at 1.00 e.\AA^{-3} .

were introduced. The temperature parameters were refined from the electron density maps by a method proposed by Atoji (1957). For three-dimensional electron density distributions, the correction, ΔB , to be applied to the temperature parameter is given by

$$\Delta B = 16\pi/3 \cdot \Delta\rho(0)/\rho''(0),$$

where

$$\Delta\rho(r) = \rho_o(r) - \rho_c(r) \quad \text{and} \quad \rho''(r) = \partial^2\rho(r)/\partial r^2.$$

If a Gaussian peak shape is assumed, so that

$$\rho(r) = \rho(0) \exp(-pr^2),$$

then

$$\rho''(0) = -2p\rho(0) \quad \text{and} \quad \Delta B = -8\pi/3 \cdot \Delta\rho(0)/p\rho(0).$$

The constant p is found for a given peak by plotting $\log \rho$ against r^2 . As before, scale factors were determined after each cycle from plots of

$\log F_c/F_o$ versus $(\sin \theta/\lambda)^2$.

A final discrepancy index of 0.085 was obtained for the 44 non-zero reflections of significant intensity magnitude. With non-observed and weak visually

Table 1. Atomic coordinates, temperature parameters and molecular dimensions

(a) Atomic coordinates and temperature parameters

Atom	x/a	$\sigma(x/a)$	z/c	$\sigma(z/c)$	$B \times 10^{16}$
N	—	—	—	—	8.27
C	0.0840	0.0012	0.0710	0.004	10.00
B1	0.0577	(0.0077)	0.819	0.008	8.85
B2	-0.0566	0.0011	0.648	0.011	8.75

(b) Molecular dimensions

Bond	Bond length	Standard deviation
C-N	1.48 Å	0.05 Å
B1-N	1.46	(0.10)
B2-B2	1.62	0.03
C-C	2.40	0.03
C-N-C angle	108°	7°

Table 2. Observed and calculated structure factors

Observed structure factors enclosed in parentheses are derived from visually estimated intensities. These were not used in the structure refinement

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $
1120	62.9	61.6	0333	10.8	11.4
2240	(0.9)	—	0663	(2.8)	1.6
3030	16.4	16.9	1123	11.0	10.3
3360	4.4	5.5	1453	5.8	6.1
4150	6.3	4.4	2243	4.4	3.7
4480	3.6	4.6	2573	(3.9)	2.6
5270	(2.5)	3.4	3033	3.6	6.6
6060	(1.0)	0.3	3363	(3.5)	2.5
7180	(0.9)	2.3	4153	(1.6)	3.7
			4483	(3.3)	2.3
0221	31.3	34.3	5273	0	0.9
0551	13.3	11.7	6063	0	2.0
1011	42.2	40.5			
1341	20.8	21.7	0224	5.6	5.6
1671	2.6	2.8	0554	4.8	6.2
2131	2.3	3.9	1014	8.3	8.0
2461	9.3	8.6	1344	6.5	8.1
3251	4.8	4.3	2134	(1.0)	0.6
3581	4.2	3.9	2464	3.0	3.4
4041	12.8	13.6	3254	2.6	1.5
4371	6.6	6.0	4044	0	1.6
5161	4.5	4.5	4374	(1.1)	1.9
6281	(1.3)	1.4	5164	(1.1)	1.5
7071	0	0.6			
			0115	6.6	9.0
0112	38.3	38.3	0445	3.0	4.0
0442	16.6	15.6	1235	4.7	4.6
0772	0	1.8	2025	4.3	3.6
1232	11.2	11.1	2355	1.7	2.1
1562	4.0	3.5	3145	3.1	3.0
2022	13.4	13.0	5055	(1.4)	3.0
2352	8.9	6.5			
2682	0	0.3	0003	—	31.6
3142	(2.2)	2.5	0006	—	2.1
3472	4.2	3.7			
4262	4.0	4.1			
5052	(1.9)	3.3			
5382	3.3	3.4			
6172	3.9	4.0			

estimated reflections included, $R=0.107$. Atomic coordinates and temperature factors are listed in Table 1(a). Structure factors are listed in Table 2. The standard deviations of atomic coordinates in Table 1(a) were calculated from the equations (Cruickshank, 1949, 1954)

$$\sigma(X) = \sigma(\partial \rho(X, 0, Z)/\partial X) / \partial^2 \rho(X, 0, Z)/\partial X^2,$$

$$\sigma(Z) = \sigma(\partial \rho(X, 0, Z)/\partial Z) / \partial^2 \rho(X, 0, Z)/\partial Z^2,$$

where X and Z are the orthohexagonal coordinates (i.e. $X=x-y$, $Z=z$) and

$$\sigma(\partial \rho(X, 0, Z)/\partial X) = \frac{\partial}{\partial X} (\rho_o(X, 0, Z) - \rho_c(X, 0, Z))$$

$$\sigma(\partial \rho(X, 0, Z)/\partial Z) = \frac{\partial}{\partial Z} (\rho_o(X, 0, Z) - \rho_c(X, 0, Z)).$$

The calculations were done on the LGP-30 computer. The standard deviation for x/a of atom B1 has dubious significance, and accordingly is enclosed in parentheses.

During the course of the refinement, frequent attempts were made to establish definitely the distribution of B1 about the c axis. Little success was attained although it is felt that the radial distance of B1 from the c axis is accurate to about ± 0.2 Å. Throughout the final stages of refinement, B1 was taken to lie on the x axis (a general sixfold position) at $x=0.55$ Å. After the final cycle was completed, structure factors were calculated with the following dispositions of atom B1:

- cylindrically distributed about the c axis at $\rho=0.55$ Å, $R=0.135$,
- $x=y=0$, $R=0.112$,
- $x=-y$, i.e., on a set of mirror planes, $R=0.094$.

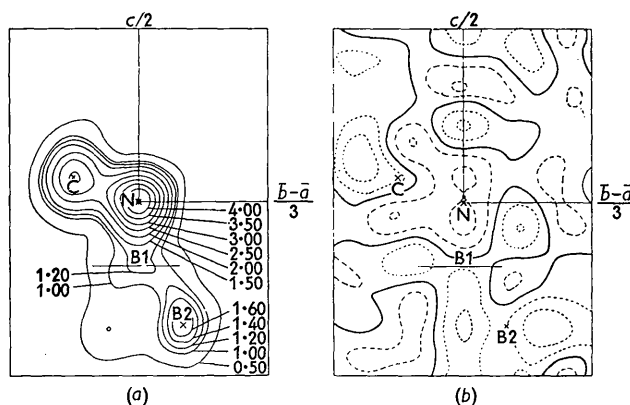


Fig. 3. (a) Final three dimensional electron density section at the plane $Y=0$ in the orthohexagonal cell. The C, N, and B2 atom positions are marked with X. The B1 atom position is designated by a line which indicates the uncertainty of its position. The contour levels shown are in units of $e.\text{Å}^{-3}$. (b) Final three dimensional difference electron density section at the plane $Y=0$ in the orthohexagonal cell. The atomic positions are labeled as in (a). Contours are drawn at intervals of $0.05 e.\text{Å}^{-3}$. The solid contours are at the zero level. The long dash contours are positive. The short dash contours are negative.

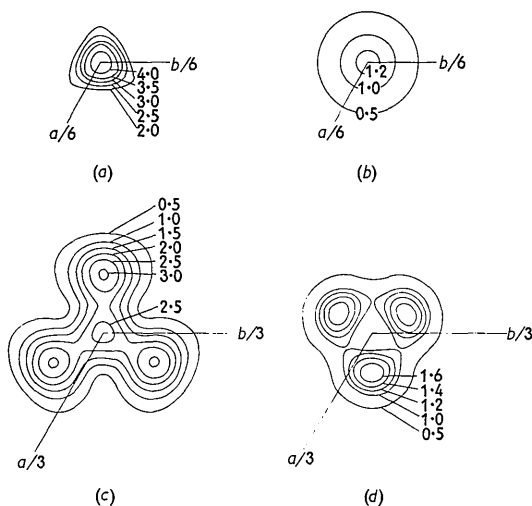


Fig. 4. Final three dimensional electron density sections perpendicular to c and passing through the atomic centers. (a) Nitrogen. (b) Boron B1. (c) Carbon. (d) Boron B2. The contour levels shown are in units of $e.\text{\AA}^{-3}$.

Structure factors also were calculated with B1 omitted, $R=0.178$, and a difference map was calculated in the region of B1. The usual flat diffuse peak with maximum on the c axis was obtained.

Figs. 3(a) and 3(b) are respectively the final three-dimensional electron density and difference sections on $X, 0, Z$. Figs. 4(a), (b), (c), (d) are electron density sections normal to c through the atomic centers.

4. Discussion

In general, the structure appears to be quite consistent with the more accurate results of Nordman & Reimann on ammonia triborane, and of Hoard, Geller & Owen (1951) on trimethylamine adducts of boron compounds. The molecular dimensions and their uncertainties are listed in Table 1(b). The carbon-nitrogen bond parameters would be expected to be the most accurately determined. Accordingly, the bond length of 1.48 \AA agrees quite well with the expected value of 1.48 \AA to 1.50 \AA (Hoard, Geller & Owen, 1951; Sutton, 1958), and the C-N-C angle of 108° is not significantly different from the expected value of 114° . Whereas the quite short B2-B2' distance appears to be significantly smaller, but just barely so, than the distance of 1.74 \AA reported for the comparable bond in ammonia triborane, the B1-N length of 1.46 \AA does not differ significantly from the value of 1.58 \AA found consistently for this type of bond by other

workers (Hoard, Geller & Owen, 1951; Nordman & Reimann, 1959).

Unfortunately, little reliable information is obtainable about the boron-boron bonds involving atom B1. Assuming that B1 lies on the hexagonal x axis at $x=0.55 \text{ \AA}$, the B1-B2 bond lengths are 1.92 \AA and 1.67 \AA . In ammonia triborane these bond lengths are 1.82 \AA and 1.80 \AA . A shift of B1 toward a mirror plane would tend to bring both lengths closer to more reasonable values. Since such a shift is also indicated by the results of the trial and error calculations on the position of atom B1 mentioned above, it would appear reasonable to assume that the B1 atoms lie at intermediate positions between the mirror planes and the x axis on six-fold general positions.

Since atom B1, and hence the molecule as a whole, is distributed between six-fold positions, it is required that both molecular enantiomorphs be statistically distributed among the unit cells with each enantiomorph distributed between the three crystallographically equivalent positions. This would be expected in any case since the enantiomorphs should be synthesized in equivalent amounts. The symmetrical but diffuse electron distributions about the atomic centers, and the consequent apparently high thermal motion now become easily understandable. The elongation of the B2 peak in the plane $Y=0$ may be assumed to be due to differences in the coordinates of atoms B2 and B2'.

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