

The Molecular and Crystal Structure of $(\text{BH}_2)_3[\text{N}(\text{CH}_3)_2]_3$

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Dimethylaminoborane trimer is a chair-shaped six membered ring of alternating BH_2 and $\text{N}(\text{CH}_3)_2$ groups, with $\text{B-N} = 1.59 \pm 0.02$ and $\text{C-N} = 1.49 \pm 0.02$ Å. The crystals are orthorhombic, in the space group $Pnma$ or $Pn2_1a$ with four molecules in a unit cell of dimensions

$$a = 11.20, b = 13.17, c = 8.07 \text{ Å}.$$

Agreement factors assuming the space group $Pnma$, are $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.19$ and $r = \Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4 = 0.13$. The possibility of a transition is discussed.

Our structural results indicate that the chemical formula is $(\text{BH}_2)_3[\text{N}(\text{CH}_3)_2]_3$, rather than $\text{B}_3\text{H}_4[\text{N}(\text{CH}_3)_2]_3$.

Introduction

Two new compounds characterized as $\text{B}_3\text{H}_4[\text{N}(\text{CH}_3)_2]_3$ and $\text{B}_4\text{H}_6[\text{N}(\text{CH}_3)_2]_2$ were prepared by Burg (1957) in a study of the reaction of dimethylamine-borane with B_5H_9 . Formulas were suggested in which B and N were four-coordinated, and hence they were presumed to be ring compounds of a new class with cross-ring bonds.

The present study of the first of these two compounds completes our preliminary report (Trefonas & Lipscomb, 1959) that the compound is really $(\text{BH}_2)_3[\text{N}(\text{CH}_3)_2]_3$. This study also substantiates our agreement with a concurrent and independent study of the B^{11} nuclear magnetic resonance spectrum which contains a 1:2:1 triplet suggesting three equivalent BH_2 groups (Campbell & Johnson, 1959).

Experimental

A crystalline sample almost suitable for X-ray study was located in a capillary containing the material, and precession photographs were taken with the use of $\text{Mo } K\alpha$ radiation of the $h0l$; $h1l$; hkh ; $0kl$; hhl ; $2k, k, l$; $h, l-h, l$; $h, 3l-3h, l$; and $h, k, h+2k$ levels at a precession angle of 25° . Equi-inclination Weissenberg photographs of levels $l=0, 1, 2, 3$ and 4 about $[001]$ were also taken with the use of $\text{Cu } K\alpha$ radiation. Prof. J. Donohue kindly supplied us with excellent, well exposed Weissenberg photographs of the $hk0$, $hk1$ and $hk2$ levels from his preliminary study from which we were able to supplement the data from our relatively poor crystal.

The unit cell is orthorhombic with dimensions

$$a = 11.20 \pm 0.03, b = 13.17 \pm 0.04, c = 8.07 \pm 0.02 \text{ Å}.$$

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From visual estimates of the intensities with the aid of a timed intensity scales from the same crystal, a total of 519 independent reflections was obtained after correlation of the F_{hkl}^2 corrected by the usual Lorentz-polarization factors (Waser, 1951; Tunell, 1939). Systematic extinctions of $0kl$ for $k+l$ odd and of hkl when k is odd lead to either $C_{2v}^9-Pn2_1a$ or $D_{2d}^{10}-Pnma$ as possible space groups. The assumption of four molecules in the unit cell leads to a calculated density of 0.945 g.cm.^{-3} , in reasonable agreement with the observed density of 0.95 g.cm.^{-3} for $(\text{BH}_2)_3[\text{P}(\text{CH}_3)_2]_3$ (Hamilton, 1955), which has a similar structure differing in some aspects of the packing as described below. A statistical study of the intensities by the method of Howells, Phillips & Rogers (1950) did not resolve the space group ambiguity.

Structure determination

Structure factor calculations made on the assumption that the atomic arrangement could be derived, with modifications of bond radii, from the known $(\text{BH}_2)_3[\text{P}(\text{CH}_3)_2]_3$ structure gave such poor agreement with observed values that we decided to compute the three dimensional sharpened Patterson function. Peak shapes were narrowed and improved by the addition of the gradient function (Jacobson, Wunderlich & Lipscomb, 1959, 1961). Several small, resolved peaks and their symmetry related peaks in Patterson space were chosen for successive three-dimensional point-by-point superpositions, in each of which the minimum function (Buerger, 1951) was used on a high speed digital computer. The structure which emerged, consisting of a non-planar six-membered ring with two additional atoms close to each of three alternate ring atoms, was carefully rechecked in the vectors within 3 Å of the origin of Patterson space. This procedure, however, left the origin of the unit cell ambiguous at

Table 1. *Fractional coordinates and individual temperature factors*

Atom	B ₁	B ₂	N ₁	N ₂	C ₁	C ₂	C ₃	C ₄
<i>x</i>	0.147	0.256	0.079	0.186	0.285	0.093	-0.049	0.068
<i>y</i>	0.152	0.250*	0.250*	0.149	0.067	0.124	0.250*	0.250*
<i>z</i>	0.591	0.342	0.645	0.404	0.382	0.283	0.598	0.822
β_{11}	0.008	0.014	0.007	0.010	0.016	0.014	0.010	0.026
β_{22}	0.008	0.006	0.011	0.004	0.006	0.006	0.012	0.020
β_{33}	0.013	0.031	0.008	0.020	0.040	0.020	0.043	0.007
β_{12}	-0.002	0.0*	0.0*	0.001	0.007	-0.005	0.0*	0.0*
β_{13}	0.000	0.013	0.000	-0.001	0.003	-0.007	0.006	0.005
β_{23}	-0.002	0.0*	0.0*	-0.004	-0.003	0.000	0.0*	0.0*
B, isotropic equivalent (\AA^2)	3.7	7.5	2.8	5.0	9.4	5.5	9.6	5.2

* Parameter fixed by *Pnma* space group symmetry.

0, 0, 0; $\frac{1}{4}$, 0, 0; 0, 0, $\frac{1}{4}$ or $\frac{1}{4}$, 0, $\frac{1}{4}$ because of the extra symmetry in the Patterson function. Rather than carry out additional superpositions, we decided simply to test each of these four choices of origin relative to the molecular coordinates by comparing structure factor agreement $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ after three cycles of least-squares refinement (diagonal terms only, space group *Pn2₁a*). The choice of 0, 0, 0 gave $R = 0.30$, at least 0.15 smaller than any other choice, and was accepted as correct. The molecular structure, which eventually refined, was essentially correct at this stage, and the crystal symmetry was close to *Pnma*. However, small displacements into the lower symmetry of *Pn2₁a* could not be eliminated, and hence some ambiguity remains in the choice of the space group.

In the early stages of refinement by least-squares methods an extinction phenomenon became apparent in a few large intensities. A correction of the form $F_o^2 = F_c^2(1 + \alpha F_c^2)^{-1}$ was then applied, where a single value of α was chosen for the 20 largest reflections. Refinement (on the Remington Rand 1103) with diagonal terms only and isotropic temperature factors, in the space group *Pnma*, finally yielded values of $R = 0.23$ and $r = \sum w ||F_o|^2 - |F_c|^2| / \sum w |F_o|^2 = 0.13$ after addition of the two H atoms on each B, and the addition of six one-half H atoms to represent each presumably disordered H₃ group on CH₃. When all atoms except H were allowed to vary anisotropically, values of $R = 0.20$ and $r = 0.10$ were finally obtained. In these refinements the value of $w = (8F_{\text{min.}}/F_o)^4$ was chosen for all $F_o > 8F_{\text{min.}}$, and $w = 1$ for all $F_o < 8F_{\text{min.}}$.

It is difficult to be sure of the uniqueness of displacement of atoms into the lower symmetry of *Pn2₁a*. However, the displacements would have to be small, in view of the good agreement obtained in *Pnma*, and the molecule would probably have to be rotated or tilted as a whole, in view of the reasonable molecular parameters obtained in *Pnma*. Accordingly, we chose about a 4° rotation of the molecule about an axis through its center and parallel to *z* as the most reasonable displacement. Refinement of this structure on the Remington Rand 1103 reached $R = 0.24$ and $r = 0.20$ when the temperature factors were isotropic, and $R = 0.19$ and $r = 0.10$ when temperature factors

were anisotropic on all atoms except hydrogen, which had been treated as they were in the centrosymmetric refinement. Some further promise of refinement was apparent, even at this stage, but a detailed comparison of structures indicated that, at least, a striking improvement in the agreement would not occur in the space group of lower symmetry.

We then decided to finish the refinement in *Pnma*, and, for geographical reasons, these further calculations were carried out on an IBM 704 with the use of the full matrix. Weights were changed to $w = (6F_{\text{min.}}/F_o)^4$ for $F_o > 6F_{\text{min.}}$ in order to agree with our prejudices concerning the measurements of intensities, and the extinction correction was redetermined to give $\alpha = 1.62 \times 10^{-4}$. Our final parameters (Table 1) were obtained after two cycles in which the hydrogen atoms were fixed in position, but entered as described above, and temperature factors on all other atoms were varied anisotropically. Values of atomic parameters are shown in Table 1, and final agreement factors, now $R = 0.19$ and $r = 0.13$, are shown in Table 2. Calculated and observed structure factors are shown in Table 3 for the final centrosymmetric refinement.

Table 2. *R factors for various classes*

Overall $R = \sum F_o - F_c / \sum F_o = 0.193$				
Class	<i>R</i>	sin θ range	<i>R</i>	Number of reflections
0 <i>kl</i>	0.19	0-0.40	0.14	93
<i>h0l</i>	0.17	0.40-0.50	0.18	83
<i>hk0</i>	0.17	0.50-0.60	0.20	112
<i>h = 2n</i>	0.21	0.60-0.65	0.24	54
<i>h = 2n + 1</i>	0.21	0.65-0.70	0.21	59
<i>k = 2n</i>	0.23	0.70-0.75	0.21	51
<i>k = 2n + 1</i>	0.20	0.75-0.80	0.35	31
<i>l = 2n</i>	0.26	0.80-0.85	0.40	24
<i>l = 2n + 1</i>	0.18	0.85-0.90	0.42	8
<i>k + l = 2n</i>	0.25	Above 0.90	0.50	4
<i>k + l = 2n + 1</i>	0.18			
<i>l + h = 2n</i>	0.19			
<i>l + h = 2n + 1</i>	0.23			
<i>h + k = 2n</i>	0.21			
<i>h + k = 2n + 1</i>	0.21			
<i>h + k + l = 2n</i>	0.21			
<i>h + k + l = 2n + 1</i>	0.22			

An electron density map, shown in Fig. 1, indicated no spurious contours as high as $1 \text{ e.}\text{\AA}^{-3}$. Although the two C atoms on the mirror plane of *Pnma* have

x (Fractional)	y (Fractional)	z (Fractional)	Peak height (e.Å ⁻³)	Atom	Closest distance (Å)	Remarks
0.02	1.72	2.10	4	23	28	6,10,2
0.04	1.72	2.10	4	23	28	6,10,2
0.10	1.72	2.10	4	23	28	6,10,2
0.16	1.72	2.10	4	23	28	6,10,2
0.22	1.72	2.10	4	23	28	6,10,2
0.28	1.72	2.10	4	23	28	6,10,2
0.34	1.72	2.10	4	23	28	6,10,2
0.40	1.72	2.10	4	23	28	6,10,2
0.46	1.72	2.10	4	23	28	6,10,2
0.52	1.72	2.10	4	23	28	6,10,2
0.58	1.72	2.10	4	23	28	6,10,2
0.64	1.72	2.10	4	23	28	6,10,2
0.70	1.72	2.10	4	23	28	6,10,2
0.76	1.72	2.10	4	23	28	6,10,2
0.82	1.72	2.10	4	23	28	6,10,2
0.88	1.72	2.10	4	23	28	6,10,2
0.94	1.72	2.10	4	23	28	6,10,2
1.00	1.72	2.10	4	23	28	6,10,2
0.02	1.72	2.10	4	23	28	6,10,2
0.04	1.72	2.10	4	23	28	6,10,2
0.06	1.72	2.10	4	23	28	6,10,2
0.08	1.72	2.10	4	23	28	6,10,2
0.10	1.72	2.10	4	23	28	6,10,2
0.12	1.72	2.10	4	23	28	6,10,2
0.14	1.72	2.10	4	23	28	6,10,2
0.16	1.72	2.10	4	23	28	6,10,2
0.18	1.72	2.10	4	23	28	6,10,2
0.20	1.72	2.10	4	23	28	6,10,2
0.22	1.72	2.10	4	23	28	6,10,2
0.24	1.72	2.10	4	23	28	6,10,2
0.26	1.72	2.10	4	23	28	6,10,2
0.28	1.72	2.10	4	23	28	6,10,2
0.30	1.72	2.10	4	23	28	6,10,2
0.32	1.72	2.10	4	23	28	6,10,2
0.34	1.72	2.10	4	23	28	6,10,2
0.36	1.72	2.10	4	23	28	6,10,2
0.38	1.72	2.10	4	23	28	6,10,2
0.40	1.72	2.10	4	23	28	6,10,2
0.42	1.72	2.10	4	23	28	6,10,2
0.44	1.72	2.10	4	23	28	6,10,2
0.46	1.72	2.10	4	23	28	6,10,2
0.48	1.72	2.10	4	23	28	6,10,2
0.50	1.72	2.10	4	23	28	6,10,2
0.52	1.72	2.10	4	23	28	6,10,2
0.54	1.72	2.10	4	23	28	6,10,2
0.56	1.72	2.10	4	23	28	6,10,2
0.58	1.72	2.10	4	23	28	6,10,2
0.60	1.72	2.10	4	23	28	6,10,2
0.62	1.72	2.10	4	23	28	6,10,2
0.64	1.72	2.10	4	23	28	6,10,2
0.66	1.72	2.10	4	23	28	6,10,2
0.68	1.72	2.10	4	23	28	6,10,2
0.70	1.72	2.10	4	23	28	6,10,2
0.72	1.72	2.10	4	23	28	6,10,2
0.74	1.72	2.10	4	23	28	6,10,2
0.76	1.72	2.10	4	23	28	6,10,2
0.78	1.72	2.10	4	23	28	6,10,2
0.80	1.72	2.10	4	23	28	6,10,2
0.82	1.72	2.10	4	23	28	6,10,2
0.84	1.72	2.10	4	23	28	6,10,2
0.86	1.72	2.10	4	23	28	6,10,2
0.88	1.72	2.10	4	23	28	6,10,2
0.90	1.72	2.10	4	23	28	6,10,2
0.92	1.72	2.10	4	23	28	6,10,2
0.94	1.72	2.10	4	23	28	6,10,2
0.96	1.72	2.10	4	23	28	6,10,2
0.98	1.72	2.10	4	23	28	6,10,2
1.00	1.72	2.10	4	23	28	6,10,2

Table 4. Difference Fourier peaks down to 0.2 e.Å⁻³ in height

x (Fractional)	y (Fractional)	z (Fractional)	Peak height (e.Å ⁻³)	Atom	Closest distance (Å)	Remarks
0.12	0.25	0.87	0.73	C ₄	0.7	Possible hydrogen
0.25	0.25	0.67	0.73	B ₂	0.0	On B ₂ position
0.32	0.25	0.25	0.65	B ₂	1.0	Possible hydrogen
0.42	0.18	0.82	0.59	C ₃	1.2	Possible hydrogen
0.24	0.15	0.63	0.58	B ₁	1.1	Possible hydrogen
0.18	0.17	0.40	0.55	N ₂	0.2	Very near N ₂ position
0.08	0.25	0.63	0.52	N ₁	0.0	On N ₂ position
0.28	0.03	0.25	0.47	C ₁	1.2	Possible hydrogen
0.08	0.17	0.13	0.41	B ₂	1.3	Possible hydrogen
0.35	0.25	0.45	0.41	B ₂	1.3	Possible hydrogen
0.08	0.18	0.45	0.36	N ₂	1.3	Spurious peak
0.30	0.21	0.51	0.35	B ₂	1.5	Spurious peak
0.25	0.12	0.27	0.35	C ₁	1.2	Spurious peak
0.20	0.20	0.93	0.35	C ₁	1.9	Spurious peak
0.50	0.25	0.07	0.34	C ₃	1.4	Possible hydrogen
0.48	0.18	0.13	0.34	C ₂	1.6	Possible hydrogen
0.25	0.07	0.42	0.33	C ₁	0.5	Near possible hydrogen
0.22	0.20	0.20	0.32	B ₂	1.4	Spurious peak
0.33	0.25	0.09	0.32	C ₃	1.3	Near possible hydrogen
0.03	0.09	0.05	0.31	C ₂	2.0	Possible peak
0.25	0.00	0.77	0.30	C ₁	1.5	Spurious peak

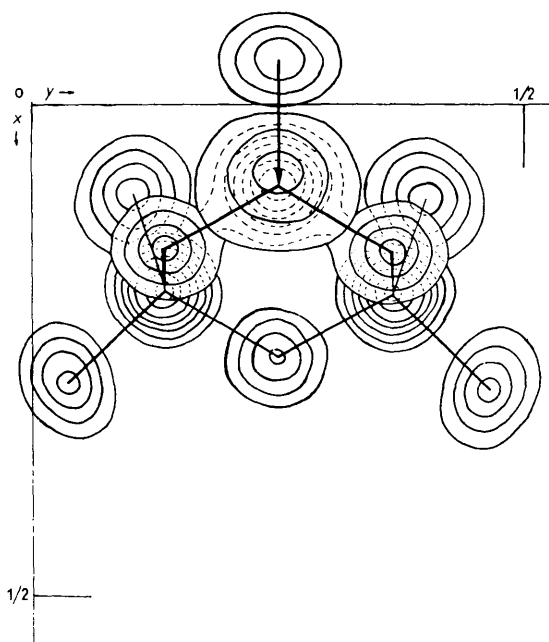


Fig. 1. Composite electron density map projected along the c axis with a skeleton of the molecule superimposed. Contours are at intervals of $1 \text{ e.}\text{\AA}^{-3}$. Lowest contour is at $1 \text{ e.}\text{\AA}^{-3}$. Dashed contours are shown for atoms behind those having solid contours.

lower peak densities than any of the B atoms, the integrated electron density of each C atom is substantially greater than that for B. This effect shows up, at least on an average, in the temperature factors (Table 1).

A difference electron density map, also in the space group $Pnma$, was calculated in three dimensions with B, C and N subtracted out. The results, summarized in Table 4, indicated 12 peaks at or near probable H positions, 3 peaks within 0.2 \AA of B or N, and no negative regions lower than $-0.1 \text{ e.}\text{\AA}^{-3}$. Of the 22 peaks at heights ranging from $0.75 \text{ e.}\text{\AA}^{-3}$ to $0.3 \text{ e.}\text{\AA}^{-3}$, the highest peak not interpreted as H or a residue of B or N is at $0.36 \text{ e.}\text{\AA}^{-3}$.

Results and discussion

Within experimental error a chair shaped molecule of C_{3v} symmetry (Fig. 2) results from the refinement of the crystal structure (Fig. 3) in the centrosymmetric space group, $Pnma$. The standard derivations of bond lengths and angles (Table 5) as calculated from the complete matrix of the least-squares refinement in $Pnma$ are $\pm 0.022 \text{ \AA}$ for B-N, $\pm 0.019 \text{ \AA}$ for C-N and $\pm 1.5^\circ$ for the bond angles. The average C-N distance of 1.49 \AA agrees quite well with the expected value of 1.47 \AA (Pauling, 1960). However, the average B-N distance of 1.59 \AA is in poor agreement with the value of 1.47 \AA calculated from the Schomaker-Stevenson rule (1941) assuming $r_{\text{B}} = 0.81 \text{ \AA}$, $r_{\text{N}} = 0.74 \text{ \AA}$ and 0.08

Table 5. Bond distances and bond angles

Individual distances		Average over whole molecule	Average deviation
$\text{N}_1\text{-B}_1$	1.56 \AA	$\overline{\text{B-N}}$ 1.59 \AA	$\pm 0.027 \text{ \AA}$
$\text{B}_1\text{-N}_2$	1.58		
$\text{N}_2\text{-B}_2$	1.63		
$\text{N}_2\text{-C}_1$	1.55	$\overline{\text{N-C}}$ 1.49	± 0.042
$\text{N}_2\text{-C}_2$	1.46		
$\text{N}_1\text{-C}_3$	1.48		
$\text{N}_1\text{-C}_4$	1.43		
$\text{N}_1\text{-N}_2$	2.65	$\overline{\text{N-N}}$ 2.66	± 0.010
$\text{N}_2\text{-N}_2'$	2.67		
$\text{B}_1\text{-B}_2$	2.68	$\overline{\text{B-B}}$ 2.64	± 0.050
$\text{B}_1\text{-B}_1$	2.57		
$\text{C}_2\text{-C}_3$	3.43	$\overline{\text{C-C}}$ 3.39	± 0.053
$\text{C}_2\text{-C}_2'$	3.31		
$\text{C}_1\text{-C}_4$	4.93	$\overline{\text{C-C}}$ 4.89	± 0.050
$\text{C}_1\text{-C}_1'$	4.82		
Individual angles		Average over whole molecule	Average deviation
$\angle \text{B}_1\text{-N}_1\text{-B}_1'$	$111\frac{1}{2}^\circ$	$\angle \overline{\text{B-N-B}}$ 113°	$\pm 1^\circ$
$\angle \text{B}_1\text{-N}_2\text{-B}_2$	$113\frac{1}{2}^\circ$		
$\angle \text{N}_1\text{-B}_1\text{-N}_2$	$115\frac{1}{2}^\circ$	$\angle \overline{\text{N-B-N}}$ 114°	$\pm 2^\circ$
$\angle \text{N}_2\text{-B}_2\text{-N}_2$	$110\frac{1}{2}^\circ$		
$\angle \text{C}_1\text{-N}_2\text{-C}_2$	106°	$\angle \overline{\text{C-N-C}}$ 104°	$\pm 2\frac{1}{2}^\circ$
$\angle \text{C}_3\text{-N}_1\text{-C}_4$	100°		
$\angle \text{C}_1\text{-N}_2\text{-B}_2$	101°	$\angle \overline{\text{C-N-B}}$ $109\frac{1}{2}^\circ$	$\pm 3\frac{1}{2}^\circ$
$\angle \text{C}_2\text{-N}_2\text{-B}_2$	$108\frac{1}{2}^\circ$		
$\angle \text{C}_1\text{-N}_2\text{-B}_1$	109°		
$\angle \text{C}_2\text{-N}_2\text{-B}_1$	$116\frac{1}{2}^\circ$		
$\angle \text{C}_3\text{-N}_1\text{-B}_1$	$113\frac{1}{2}^\circ$		
$\angle \text{C}_4\text{-N}_1\text{-B}_1$	$108\frac{1}{2}^\circ$		

as the constant in the electronegativity equation (Pauling, 1960). The tetrahedral radius of boron (0.88 \AA) would improve the agreement somewhat, but the concept of a particular covalent radius for boron in its covalent compounds is questionable. Nevertheless, our B-N bond distance of 1.59 \AA is in excellent agreement with the distance of 1.58 \AA found in

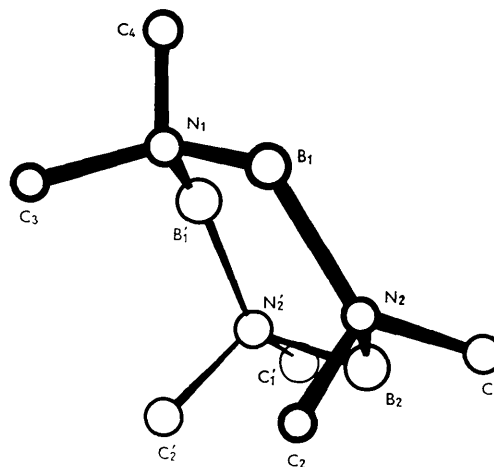


Fig. 2. Perspective view of isolated molecule. Primed atoms are related to unprimed atoms by a mirror plane.

(NH_3) $_2\text{BH}_2\text{Cl}$ (Nordman & Peterson, 1959) and of 1.58 found in (NH_3) $_3\text{B}_3\text{H}_7$ (Nordman & Riemann, 1959). The average C–N–C angle is $104 \pm 3^\circ$, while the B–N–B angles average to $113 \pm 1^\circ$. These angles differ, perhaps only barely significantly, in a relative way which is consistent with a predicted deviation from sp^3 hybridization: a central atom bonded with local C_{2v} symmetry should show a C–N–C angle of 106° if the B–N–B angle is assumed to be 113° and if the bonded atoms lie in the directions of the hybrid orbitals (Coulson, 1948).

Thus the molecular structure is known, although a comparison of results for refinement in $Pnma$ and $Pn2_1a$ does not completely resolve the space group assignment. Perhaps the major reason for this difficulty is that the ratio of observations to unknowns is only 4.8, or 1.9 if four parameters are included for each H atom, in $Pn2_1a$. These ratios are approximately twice as large in $Pnma$. Thus we cannot be sure that slightly lower agreement factors obtainable in $Pn2_1a$ are really significant. In addition our refinements in $Pn2_1a$ have led to average deviations of coordinates 1.8 times larger than those in $Pnma$, and positions of C atoms which differed in these space groups by about $6(\sigma_a + \sigma_c)$, where σ_a and σ_c are standard deviations of atomic positions in the acentric and centric space groups, respectively. Thus it would appear, assuming purely random errors in the observations, that the final atomic positions in the centric and acentric refinements differ significantly. However, the molecular structure itself shows internal inconsistency in $Pn2_1a$. For example, the two B–N distances differing most differ by 0.07 Å in $Pnma$ but by as much as 0.30 Å in $Pn2_1a$. We are reluctant, therefore, to claim that our errors in observational data are completely random, and, perhaps, to favor slightly the choice of $Pnma$ over $Pn2_1a$ merely on the grounds of internal consistency of the molecular parameters.

Although the difference electron density function gave some evidence for all H atoms on B atoms, the H's on CH_3 groups were not found. An attempt to place these latter H's by steric arguments has yielded some interesting conclusions. Actually, no completely satisfactory fixed arrangement of H atoms was found in either $Pnma$ or $Pn2_1a$. The steric interactions were more serious in $Pnma$, where intramolecular H···H distances as low as 1.85 Å occurred when a strictly staggered arrangement of CH_3 was assumed relative to the remainder of the molecule. However, in the lower symmetry of $Pn2_1a$, the shortest intramolecular H···H distance of 2.1 Å was much more satisfactory, and was obtained only by a simultaneous reorientation by 30° of the methyl H's of C_2 , C'_2 and C_3 in the same relative direction, and a 15° reorientation of the methyl H's of C_1 , C'_1 and C_4 (Fig. 2). In addition, H atoms of CH_3 and H atoms of BH_2 showed intramolecular contacts of 2.05 Å, which could be lengthened somewhat by slight reorientation of the BH_2 groups. Fig. 3 exhibits these important short H···H

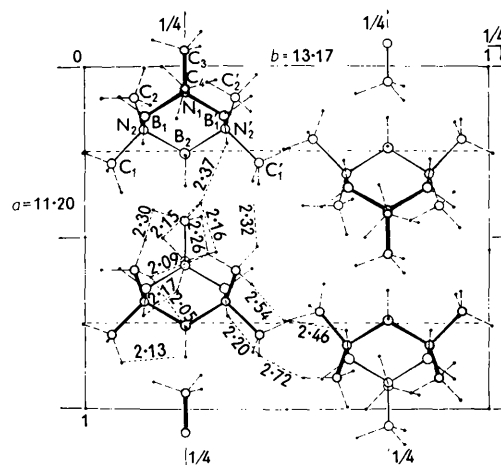


Fig. 3. Projection of the unit cell along the c axis including hydrogen atom positions as calculated from heavy atom positions so as to maximize hydrogen H···H contact distances. The closest H···H distances between groups are shown by dotted lines. Methyl hydrogens follow $Pn2_1a$ symmetry while all other atoms follow $Pnma$ symmetry. Primed atoms are related to unprimed atoms by the mirror planes. $Pnma$ space group symmetry elements are shown except for the mirror planes at $y = \frac{1}{2}, \frac{3}{2}$ and the screw axes parallel to c at $(\frac{1}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{1}{2}), (\frac{3}{2}, \frac{3}{2})$ which interfere with the projected structure.

contacts based upon $Pn2_1a$ for the H atoms, and indicates that the shortest intermolecular H···H distances are 2.3 Å, only a bit shorter than the expected van der Waals contact of 2.4 Å.

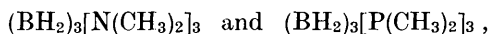
The heavier atoms, on the other hand, were given the symmetry of $Pnma$ in this model, and hence we suggest that cooperative reorientation of H atoms occurs with, possibly, very short range order, but with long range disorder. On the basis of the problems presented by the H···H contacts we suspect that a transition to a lower symmetry than $Pnma$ might be found at lower temperatures.

There is a striking similarity between the structures of $(\text{BH}_2)_3[\text{N}(\text{CH}_3)_2]_3$ and $(\text{BH}_2)_3[\text{P}(\text{CH}_3)_2]_3$, which has symmetry $Pnma$ and lattice parameters,

$$a = 11.16, b = 13.16, c = 10.53 \text{ \AA}$$

(Hamilton, 1955). However, if the fractional coordinates of the phosphorus compound are substituted into the unit cell of the nitrogen compound, and small corrections for differences in covalent radii are made the atomic positions differ by an average of 0.6 Å, a maximum of 0.9 Å and a minimum of 0.3 Å from the final coordinates. Thus there is enough difference in the orientation of molecules in their corresponding unit cells to have given poor agreement when this substitution of parameters was made very early in our study, and hence this method of attack on the structure was unfortunately abandoned; it is, nevertheless, possible that Fourier refinement might have yielded the correct structure but it was not attempted.

The compounds



as well as $(\text{BH}_2)_3[\text{As}(\text{CH}_3)_2]_3$ (Stone & Burg, 1954), form the unique analogues of $\text{C}_6(\text{CH}_3)_{12}$. The pairs BH_3NH_3 and C_2H_6 , and $\text{B}_3\text{N}_3\text{H}_6$ and C_6H_6 extend this analogy. Finally, it is probably safe to assume that $(\text{CH}_3\text{NH})_3(\text{BH}_2)_3$ (Bissott & Parry, 1955) will also be shown to be based on the six-membered saturated inorganic analogue of the cyclohexane ring.

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La Structure des Colloïdes d'Association. III. Description des Phases Mésomorphes des Savons de Sodium Purs, Rencontrées au-Dessus de 100 °C.

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An X-ray diffraction study has been carried out on the colloidal phases of pure sodium soaps at high temperatures. The structures of the various phases have been determined and the parameters of the structural elements are discussed. A mechanism for the stepwise melting of sodium soaps is proposed.

Introduction

Dans les deux premiers mémoires de cette série (Luzzati *et al.*, 1960; Husson *et al.*, 1960) que l'on désignera dans la suite par I et II respectivement, on a décrit la structure des phases mésomorphes que l'on rencontre dans les systèmes binaires amphiphile-eau et on a mis en rapport les phénomènes singuliers que l'on observe dans ces systèmes avec la structure chimique des molécules.

Or on sait que la présence d'eau n'est pas indispensable pour l'existence de phases mésomorphes: de

telles structures ont été observées dans des systèmes binaires savon-solvant non polaire et même dans des savons purs, à haute température.

En particulier les savons de sodium purs passent, lorsqu'on élève la température, par toute une série de phases colloïdales distinctes, comprises entre la phase cristalline rencontrée à température ordinaire et la phase liquide observée au-dessus de 300 °C. De nombreux chercheurs ont étudié ce phénomène par diverses techniques: observation au microscope polarisant (Vold & Vold, 1939), analyse thermique (Vold, 1941a), dilatométrie (Benton *et al.*, 1955). Les températures