

investigators (Andress & Wüst, 1938, 1939; Partridge, Hicks & Smith, 1941; Ingerson & Morey, 1943; Morey & Ingerson, 1941) using thermal, microscopic, X-ray diffraction and molecular-weight-determination methods. The phase diagram (Partridge *et al.* 1941; Morey & Ingerson, 1941) shows that it melts incongruently at 620–622°C. to form a liquid phase and crystalline sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$. Over the range of compositions between 33 and 48% $\text{Na}_4\text{P}_2\text{O}_7$, crystalline $\text{Na}_5\text{P}_3\text{O}_{10}$ separates as the primary phase. It exists in two crystalline forms, as demonstrated by powder diffraction patterns (Partridge *et al.* 1941) and by measurements of the optical properties (Ingerson & Morey, 1943).

In the present investigation small crystals of $\text{Na}_5\text{P}_3\text{O}_{10}$ (I) were obtained by cooling the melt (of composition corresponding to 45% $\text{Na}_4\text{P}_2\text{O}_7$, 55% $\text{Na}_3\text{P}_3\text{O}_9$) from 640 to 565°C. at a rate of 2°C./hr., finally quenching in a bath of dry ice and acetone. If, however, the cooling of the melt was continued to 500°C. before quenching, single crystals of $\text{Na}_5\text{P}_3\text{O}_{10}$ (II) could be isolated from the partially powdered mass. Simulated powder patterns were produced from these single crystals in a manner which did not destroy them for further study by single-crystal methods. The powder patterns so obtained verified the identity of the two forms as previously reported.

X-ray data were obtained by Weissenberg and oscillation methods. $\text{Na}_5\text{P}_3\text{O}_{10}$ (I) is monoclinic with

$$a = 9.73 \pm 0.02, \quad b = 5.41 \pm 0.02, \quad c = 19.97 \pm 0.02 \text{ \AA.}, \\ \beta = 112^\circ 12'.$$

The density determined by the flotation method is 2.52 g.cm.⁻³ (calculated 2.51 g.cm.⁻³), hence the cell contains four molecules. Reflections were systematically absent for (*hkl*) with (*h+k*) odd, (*h0l*) with *h* and *l* odd, (*0k0*) with *k* odd. The space group therefore is either *C2/c* or *Cc*. Samples tested by Dr R. G. Stokes of the Naval Research Laboratory, Washington, D.C., failed to show measurable piezoelectric activity, thus making it impossible to decide with certainty between these two space groups.

$\text{Na}_5\text{P}_3\text{O}_{10}$ (II) is also monoclinic with

$$a = 16.08 \pm 0.02, \quad b = 5.24 \pm 0.02, \quad c = 11.28 \pm 0.02 \text{ \AA.}, \\ \beta = 93^\circ 30'.$$

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Note on the crystalline structures of the methyl cyanide-boron trihalides. By S. GELLER* and O. N. SALMON†, *Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.*

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Crystals of $\text{H}_3\text{CCN-BCl}_3$ and $\text{H}_3\text{CCN-BBr}_3$ grown in glass capillaries as described in the paper on $\text{H}_3\text{CCN-BF}_3$ (Hoard, Owen, Buzzell & Salmon, 1950) were photographed with Cu *K*α radiation. The orthorhombic unit cells all give vanishings characteristic of the space groups

The density, found to be 2.59 g.cm.⁻³ (calculated 2.58 g.cm.⁻³), requires four molecules in the cell. No reflections were observed for (*hkl*) with (*h+k*) odd, (*h0l*) with *h* and *l* odd, and (*0k0*) with *k* odd. The space group could therefore be either *C2/c* or *Cc*, but since no piezoelectric effect could be detected, again, no decision could be made between them.

The space group *C2/c* provides eight general equivalent positions. Since the cells of both forms of $\text{Na}_5\text{P}_3\text{O}_{10}$ contain only four molecules it would be necessary for the $\text{P}_3\text{O}_{10}^{5-}$ ion to possess either a center or a twofold axis of symmetry in order to be compatible with this space group. Although it is impossible for three PO_4 tetrahedra to combine to form an ion with a center of symmetry, several arrangements exhibit twofold symmetry. These ions could lie in the set of special positions (*Internationale Tabellen* (1935), vol. 1, p. 101) at (*e*) which has twofold symmetry.

Preliminary studies indicate that both forms crystallize in *C2/c* and consist of open chains of three PO_4 tetrahedra linked by single oxygen bridges. The ion in each form probably lies at $0, y, \frac{1}{2}$; $0, \bar{y}, \frac{3}{2}$; $\frac{1}{2}, \frac{1}{2} + y, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2} - y, \frac{3}{2}$.

A complete study of these structures is now in progress.

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References

- ANDRESS, K. R. & WÜST, K. (1938). *Z. anorg. Chem.* **237**, 113.
 ANDRESS, K. R. & WÜST, K. (1939). *Z. anorg. Chem.* **241**, 196.
 INGERSON, E. & MOREY, G. W. (1943). *Amer. Min.* **28**, 448.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Bornträger.
 MOREY, G. W. & INGERSON, E. (1941). *Amer. J. Sci.* **242**, 1.
 PARTRIDGE, E. P., HICKS, V. & SMITH, G. W. (1941). *J. Amer. Chem. Soc.* **63**, 454.

D_{2h}^{16} -*Pnma* and C_{2v}^9 -*Pna*. The lattice constants obtained are:

	<i>a</i> (Å.)	<i>b</i> (Å.)	<i>c</i> (Å.)
$\text{H}_3\text{CCN-BF}_3$	7.76	7.20	8.34
$\text{H}_3\text{CCN-BCl}_3$	8.72	7.30	10.20
$\text{H}_3\text{CCN-BBr}_3$	8.91	7.51	10.94

The pycnometric densities of $\text{H}_3\text{CCN-BF}_3$ and $\text{H}_3\text{CCN}_3\text{-BCl}_3$ are very nearly the same (Laubengayer & Sears, 1945), and there are four molecules in each of the unit cells. As far as can be ascertained $\text{H}_3\text{CCN-BBr}_3$ has not been reported elsewhere in the literature and the

* Present address: E. I. duPont de Nemours and Co., Rayon Department, Acetate Research, Waynesboro, Virginia, U.S.A.

† Present address: General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

pycnometric density has not been determined. Since the sizes of the chlorine and bromine atoms do not differ very much, it may be concluded from an examination of the lattice constants that there are four molecules in the $H_3CCN-BBr_3$ unit cell, giving for the X-ray density 2.65 g.cm.^{-3} .

It is strongly indicated that these methyl cyanide-boron trihalides are isomorphous (space group $Pnma$). However, we have decided not to continue the investigations of the structures of the chlorine and bromine compounds since we feel that the heavy atoms bonded to the

boron atom would not permit a highly accurate determination of the boron position.

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References

- HOARD, J. L., OWEN, T. B., BUZZELL, A. & SALMON, O. N. (1950). *Acta Cryst.* **3**, 130.
LAUBENGAYER, A. W. & SEARS, D. S. (1945). *J. Amer. Chem. Soc.* **67**, 164.

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Note on the crystalline structure of trimethylamine-borine, $(H_3C)_3N-BH_3$. By S. GELLER,* R. E. HUGHES and J. L. HOARD, *Baker Laboratory of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.*

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Prof. G. W. Schaeffer, of St Louis University, kindly supplied us with the trimethylamine-borine used in our structural study. The vapor pressure of $(H_3C)_3N-BH_3$ is high enough to permit growing of crystals in thin-walled glass capillaries by the technique employed for $H_3CCN-BF_3$ (Hoard, Owen, Buzzell & Salmon, 1950) and $(H_3C)_3N-BF_3$ (Geller & Hoard, 1951), but we have been unable to grow specimens sufficiently large and well crystallized to provide adequate diffraction data for an accurate determination of structure. Data of rather poor quality, obtained with Cu $K\alpha$ radiation from one crystal, have led to the following results.

The symmetry of the X-ray patterns corresponds to $D_{3d}-\bar{3}m$. The hexagonal unit of structure has

$$a = 9.33 \pm 0.05, \quad c = 5.90 \pm 0.05 \text{ \AA.},$$

and contains three molecules (X-ray density, 0.82 g.cm.^{-3}). However, the data are also consistent with a one-molecule rhombohedral unit having

$$a = 5.74 \text{ \AA.}, \quad \alpha = 109^\circ.$$

With no special vanishings and lattice constants very similar to those of trimethylamine-boron trifluoride, isomorphism of $(H_3C)_3N-BH_3$ and $(H_3C)_3N-BF_3$ is strongly indicated. This conclusion is supported further by a comparison between observed and calculated amplitudes for $(HK.0)$ reflections. Nitrogen and boron atoms lie on the threefold axis and carbon atoms lie in the vertical symmetry planes of $C_{3v}-R3m$. The x parameter of the carbon atom is approximately the same as in the $(H_3C)_3N-BF_3$ structure, namely, -0.090 . The comparison between calculated and observed amplitudes (B taken equal to 2.5 \AA.^2 as in $(H_3C)_3N-BF_3$) for $(HK.0)$ reflections is shown in Table 1.

Table 1. *Calculated and observed reflection amplitudes*

$(HK.0)$	$ F_c $	$ F_o $
03.0	22	18
06.0	5	11
09.0	4	<2
11.0	39	34
14.0	13	21
17.0	7	7
22.0	8	8
25.0	13	15
28.0	2	<2
33.0	19	20
36.0	8	8
44.0	17	16
47.0	4	1
55.0	5	6
66.0	2	<1

It is possible that other methods of obtaining crystals and the use of low-temperature equipment (not at present available in this Laboratory) would yield X-ray data of better quality.

An electron-diffraction investigation of the structure of $(H_3C)_3N-BH_3$ was made by Bauer (1937), in which the B-N distance was found to be $1.62 \pm 0.15 \text{ \AA.}$ The following considerations imply that the value obtained by Bauer is correct within much narrower limits than he indicated. The B-N distance covering the range of most probable values in the compounds $H_3CH_2N-BF_3$ (Geller & Hoard, 1950), $(H_3C)_3N-BF_3$, H_3N-BF_3 (Hoard, Geller & Cashin, 1951) is $1.585 \pm 0.015 \text{ \AA.}$ These compounds are comparable in stability with $(H_3C)_3N-BH_3$.

References

- BAUER, S. H. (1937). *J. Amer. Chem. Soc.* **59**, 1804.
GELLER, S. & HOARD, J. L. (1950). *Acta Cryst.* **3**, 121.
GELLER, S. & HOARD, J. L. (1951). *Acta Cryst.* **4**, 399.
HOARD, J. L., GELLER, S. & CASHIN, W. M. (1951). *Acta Cryst.* **4**, 396.
HOARD, J. L., OWEN, T. B., BUZZELL, A. & SALMON, O. N. (1950). *Acta Cryst.* **3**, 130.

* duPont Post-Doctoral Fellow, 1949-50. Present address: E. I. duPont de Nemours and Co., Rayon Department, Acetate Research, Waynesboro, Virginia, U.S.A.