# Piperidinium Tetramethoxyborate

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**Abstract.** $C_5H_{12}N^+ . C_4H_{12}BO_4^-$, orthorhombic, *Pnma*, $a = 13.325$ (3), $b = 9.603$ (2), $c = 10.305$ (4) Å, $Z = 4$ (assumed; no density measurement could be made). $F(000) = 488$, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71069$ Å. Data were measured using a Syntex $P2_1$ four-circle diffractometer, and the structure was solved by direct methods. $R = 0.051$ for 494 observed reflections. Discrete cations and anions lying on mirror planes at $b/2$ are linked by hydrogen bonds.

**Introduction.** The rate of exchange of alkoxy groups at B in trialkoxyboranes with alcohols is reported to be increased on addition of amines (Denson & Crowell, 1957). In some cases solid addition compounds are formed, $ROH.B(OR)_3.NR_3$, and these have been postulated to exist as ionic tetraalkylammonium tetraalkoxyborates (Wilson, 1973). We report here the first crystal structure of an adduct of this type, piperidinium tetramethoxyborate (I). It contains discrete cations and anions which are, however, linked loosely by hydrogen bonds.

Very hygroscopic crystals of (I) were obtained by mixing trimethoxyborane, methanol and piperidine in $1:1:1$ mole ratio at room temperature; colourless crystals immediately formed (m.p. 332–334 K). A suitable crystal was mounted (in a dry box) in a capillary to prevent decomposition, using Apiezon grease. It was immediately cooled to 213 K, using the Syntex LT-1 device, both to hold it firm and to prevent decomposition.

Cell constants and standard deviations were determined by a least-squares method from the positions of 15 reflections with the standard programs of a Syntex $P2_1$ four-circle diffractometer. Data were collected with this instrument in the $\theta$–$2\theta$ mode, range $(2\theta)$ $(\alpha_2$–$\alpha_1) \pm 1.05°$, with variable scan rates of $1.2$–$29°$ $min^{-1}$ depending on the intensity of a 2 s prescan; $2\theta_{max}$ was $50°$. Three standards examined every 100 reflections exhibited no significant change during data collection. 1378 reflections were collected and used in the direct-methods solution; 494 were considered observed $[I/\sigma(I) \geq 3.0]$ and used in refinement. Lorentz and polarization corrections were applied but no correction was made for absorption.

The systematic absences $0kl$, $k + l = 2n$ and $hk0$, $h = 2n$ indicated either space group *Pnma* or *Pn2$_1$a*. The former was assumed in the initial structure solution using direct methods [*MULTAN*; Germain, Main & Woolfson (1971, version of 1980)] and shown to be correct by the successful refinement. *MULTAN* 80 revealed all the non-hydrogen atoms with B, O(1), N(1), C(2), C(4) and C(5) in special position 4(c), on the mirror plane. The structure was refined by Fourier and least-squares methods (XRAY 76; Stewart, 1976) to $R = 0.051*$ with anisotropic temperature factors for

**Table 1.** *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$), *with standard deviations in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i U_{ii}.$$

| | $x$ | $y$ | $z$ | $U_{eq}/U$ |
|---|---|---|---|---|
| B(1) | −202 (3) | 2500 | 7636 (4) | 45 |
| C(1) | 7909 (2) | 1198 (4) | 4263 (3) | 68 |
| C(2) | 7783 (3) | 2500 | 3449 (4) | 70 |
| C(3) | 7205 (2) | 1213 (3) | 5410 (2) | 48 |
| C(4) | 898 (3) | 2500 | 5712 (4) | 59 |
| C(5) | −836 (3) | 2500 | 9840 (4) | 56 |
| C(6) | −432 (2) | 11 (3) | 7477 (3) | 65 |
| O(1) | 817 (2) | 2500 | 7078 (2) | 44 |
| O(2) | −804 (1) | 1331 (2) | 7200 (2) | 49 |
| O(3) | 5 (2) | 2500 | 9021 (2) | 44 |
| N(1) | 7332 (2) | 2500 | 6193 (3) | 43 |
| H(1) | 7990 | 2500 | 6567 | 69 |
| H(2) | 6853 | 2500 | 6890 | 69 |
| H(3) | 7321 | 404 | 5945 | 69 |
| H(4) | 6530 | 1158 | 5095 | 69 |
| H(5) | 8590 | 1133 | 4569 | 69 |
| H(6) | 7799 | 371 | 3737 | 69 |
| H(7) | 8254 | 2500 | 2746 | 69 |
| H(8) | 7120 | 2500 | 3088 | 69 |
| H(9) | 557 | 1692 | 5355 | 69 |
| H(10) | 1546 | 2500 | 5296 | 69 |
| H(11) | −1242 | 3308 | 9669 | 69 |
| H(12) | −725 | 2500 | 10766 | 69 |
| H(13) | 221 | −117 | 7075 | 69 |
| H(14) | −354 | −113 | 8404 | 69 |
| H(15) | −810 | −813 | 7204 | 69 |

Table 2. *Bond lengths* (Å), *bond angles* (°) *and* O—H
*contact distances* (<2·5 Å), *with e.s.d.'s in parentheses*

| B—O(1) | 1·475 (4) | N(1)—C(3) | 1·486 (3) |
|---|---|---|---|
| B—O(2) | 1·451 (3) | C(3)—C(1) | 1·509 (4) |
| B—O(3) | 1·454 (5) | C(1)—C(2) | 1·515 (4) |
| O(1)—C(4) | 1·412 (4) | | |
| O(2)—C(6) | 1·391 (4) | | |
| O(3)—C(5) | 1·402 (4) | | |
| | | | |
| O(1)—B—O(2) | 112·9 (2) | C(3)—N—C(3') | 112·5 (2) |
| O(1)—B—O(3) | 102·0 (3) | N—C(3)—C(1) | 111·3 (2) |
| O(2)—B—O(3) | 114·1 (2) | C(3)—C(1)—C(2) | 110·9 (3) |
| O(2)—B—O(2') | 101·4 (3) | C(1)—C(2)—C(1') | 111·2 (3) |
| B—O(1)—C(4) | 117·3 (3) | | |
| B—O(2)—C(6) | 116·4 (2) | | |
| B—O(3)—C(5) | 116·1 (3) | | |
| | | | |
| O(1)···H(2) | 1·74 | O(2)···H(1) | 2·061 |
| O(1)···N | 2·692 (4) | O(1)···N | 2·692 (4) |
| N—H(2)···O(1) | 169 | N—H(1)···O(2) | 147 |
| C(4)—O(1)···H(2) | 123 | C(6)—O(2)···H(1) | 146 |
| B—O(1)···H(2) | 119 | B—O(2)···H(1) | 96 |

all non-H atoms and calculated positions for H atoms
which were given fixed temperature factors and not
refined.

Final atomic parameters are given in Table 1, bond
lengths and angles in Table 2. Computing was on a
Burroughs B6700 computer; scattering factors were
taken from *International Tables for X-ray
Crystallography* (1974) in the analytical form.

**Discussion.** The structure (Fig. 1) consists of alternate
layers, perpendicular to **b**, of cations and anions (Fig.
2), both lying on the mirror planes at $b/2$. The layers
are loosely linked by hydrogen bonds. The primary
hydrogen-bonding interaction is O(1)···H(2), 1·74 Å,
from a piperidinium proton to a methoxy oxygen. As a
result, B—O(1) [1·475 (4) Å] is significantly longer
than the other B—O bonds [1·451 (3), 1·454 (5) Å].
The other piperidinium proton H(1) lies in the $b/2$
mirror plane and is directed between O(2) and the
mirror-related O(2'); the distance O(2)···H(1) of
2·06 Å and the lack of any noticeable lengthening of
B—O(2) suggest that these are weaker interactions,
though they probably contribute to the packing forces.

The existence of this ionic hydrogen-bonded com-
pound in the solid state supports the evidence that the
amine-catalysed exchange of alkoxy groups on boron,
between alcohols and alkoxyboranes, proceeds through
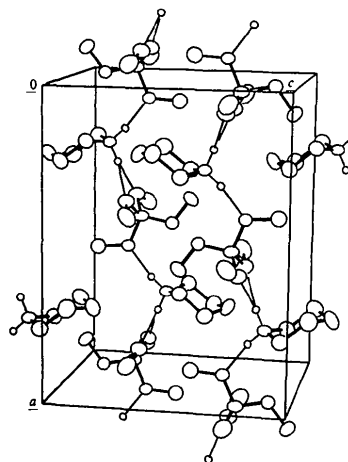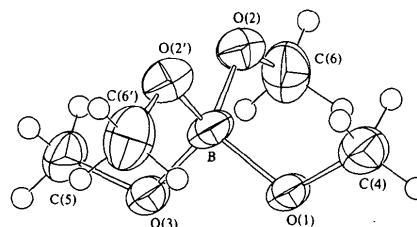an ionic hydrogen-bonded intermediate.



Fig. 1. Packing viewed approximately down **b**.



Fig. 2. The tetramethoxyborate anion showing the atomic
numbering.

**References**

DENSON, C. L. & CROWELL, T. I. (1957). *J. Am. Chem. Soc.*
**79**, 5656–5658.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta
Cryst.* A**27**, 368–376.
*International Tables for X-ray Crystallography* (1974). Vol.
IV. Birmingham: Kynoch Press.
STEWART, J. M. (1976). The XRAY 76 System. Tech. Rep.
TR-446. Computer Science Center, Univ. of Maryland,
College Park, Maryland.
WILSON, J. W. (1973). *J. Chem. Soc. Dalton Trans.* pp.
1628–1630.