The Structure of Tri-(1,3,2-benzodioxaborol-2-yl)amine, $(C_6H_4O_2B)_3N$

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ALTHOUGH aminoboranes (derivatives of $BH_2{\cdot}NH_2$) are common, diborylamines [derivatives of $(BH_2)_2NH$] and triborylamines [derivatives of $(BH_2)_3N$] were unknown until quite recently. Compounds of the last category are of interest in view of the prediction by Buckingham[1] of a planar NB_3 group stabilized by π-bonding similar to that in aminoboranes. We have determined the structure of $(o\text{-}C_6H_4O_2B)_3N$, the first triborylamine to be prepared,[2] and find Buckingham's prediction to be correct.

The structure was determined by X-ray analysis of crystals obtained by sublimation.[2] Tri-(1,3,2-benzodioxaborol-2-yl)amine, $C_{18}H_{12}O_6B_3N$, $M = 370{\cdot}73$, *monoclinic*, $a = 13{\cdot}13$, $b = 5{\cdot}80$, $c = 11{\cdot}14$ Å, $\beta = 100{\cdot}0°$, $U = 835{\cdot}5$ Å^3, $Z = 2$, $D_c = 1{\cdot}48$ g. cm.$^{-3}$, $D_m = 1{\cdot}51$ g. cm.$^{-3}$, space group $P2_1$ (No. 4). The intensities of 2278 X-ray reflexions were measured on a Pailred automatic diffractometer using Mo-K_α radiation. Refinement by least-squares using anisotropic temperature factors has proceeded to $R = 0{\cdot}12$ (reflexions with zero intensity excluded). Hydrogen atoms were placed at positions estimated from the molecular geometry and were included in the calculations.

The bond lengths and angles calculated at this stage of the refinement are given in the Figure. The 28 atoms of the molecule (excluding hydrogens) lie in a plane inclined at 35° to the crystallographic b axis. The greatest deviation of any atom from the mean plane of all 28 atoms is 0·135 Å. The three B–N bonds are very nearly coplanar, the nitrogen atom being only 0·025 Å from the plane through the three boron atoms; in comparison, a pyramidal arrangement of B–N bonds with a $\angle$ BNB = $109\frac{1}{2}°$ would result in the nitrogen atom lying 0·47 Å above the plane of the boron atoms. The nitrogen is therefore sp^2 hybridized and the molecular symmetry is approximately D_{3h} ($\bar{6}2m$).

It might have been thought that in a planar molecule the close approach (2·7 Å) of neighbouring oxygen atoms belonging to different catechol residues would cause the benzodioxaborolyl groups to be twisted slightly about the B–N bonds out of the NB_3 plane. However, this is not the case.

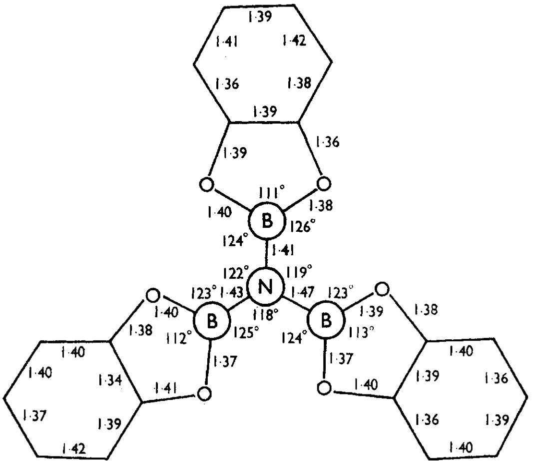

FIGURE. *Bond lengths* (in Å; e.s.d. 0·014 Å) *and bond angles* (e.s.d. 1°).

The average B–N bond length (1·44 Å) is comparable to that in 1,8,10,9-triazaboradecalin,[3] indicating π-bonding by the overlap of $2p$ orbitals on boron and nitrogen. With one lone pair on nitrogen available for π-bonding with three boron atoms, a π-bond order of $\frac{1}{3}$ is expected in addition to each σ bond. It is even possible that one π-system covers the whole molecule including the oxygen atoms.

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[1] A. D. Buckingham, *Proc. Chem. Soc.*, 1962, 351.
[2] M. F. Lappert and G. Srivastava, *Proc. Chem. Soc.*, 1964, 120.
[3] G. J. Bullen and N. H. Clark, *Chem. Comm.*, 1967, 670.

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