# The Molecular Structure of Trisdimethylaminoborine

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*Summary* The structure of trisdimethylaminoborine in the vapour phase has been determined by electron diffraction.

TRISDIMETHYLAMINOBORINE, $[(CH_3)_2N]_3B$, has previously been investigated thermochemically[1] and by Raman[2] and i.r.[2,3] spectroscopy. These studies have led to the conclusion that the B–N bonds present contain $\pi$-character, and to the expectation[1] that they are similar in length to the corresponding bonds in borazines (1·41—1·44 Å).[4,5] We have investigated this molecule in the vapour phase by electron diffraction and have determined its structure.

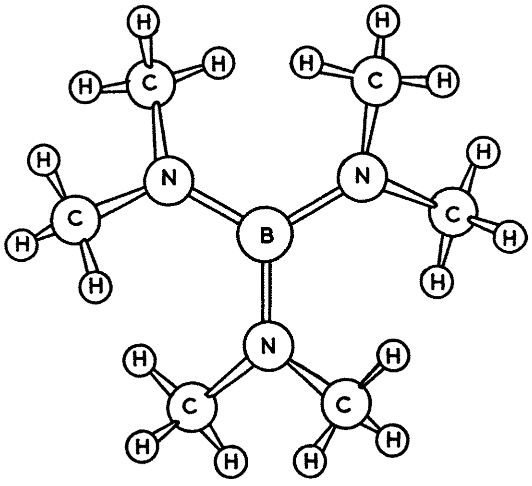
The sample employed in diffraction experiments was prepared by a method modified slightly from that of Skinner and Smith[1] and its purity was established by mass spectrometry. Intensity data were collected at Oslo by means of a Balzers electron-diffraction unit,[6] and extended over the $s$-range, 2·00—30·00 Å$^{-1}$. The nozzle temperature was approximately 40°. The molecular structure of the compound was determined by least-squares refinement assuming a model of $D_3$ symmetry (see Figure). This model assumed that the $BN_3$ and each of the $BNC_2$ atomic configurations are planar, but allowed the three dimethylamino-groups to twist through a variable angle about the B–N bonds. An additional angle of twist allowing the two methyl groups attached to nitrogen to rotate in opposite directions away from an eclipsed configuration relative to the B–N bond was also included as a variable. These two parameters were refined together with the B–N, N–C, and C–H bond lengths, the BNC and NCH valence angles, and the eleven most important vibrational amplitudes. A diagonal weight matrix[7] was employed throughout. A satisfactory fit to the observed intensity data was achieved when the seven geometric parameters had the values listed in the Table. The e.s.d.'s assigned to them were obtained by multiplying the original estimates calculated by the least-squares program by a factor of three to compensate for correlation of the intensity data,[8] and by making a further addition of 1·0 p.p.t. to take into account systematic errors. The structural parameters quoted have not been corrected for shrinkage.

TABLE

*Structural parameters and estimated standard deviations for trisdimethylaminoborine*

| | |
|---|---|
| B–N | 1·431 (12) Å |
| N–C | 1·454 (7) Å |
| C–H | 1·109 (12) Å |
| ∠BNC | 123·9° (1·0°) |
| ∠NCH | 111·1° (1·9°) |
| $-N(CH_3)_2$ twist | 32·8° (2·6°) |
| $-CH_3$ twist | 10·0° (4·1°) |

The B–N bond length obtained confirms the expectations of previous workers[1–3] as it is considerably shorter than the distance found in compounds containing tetrahedrally co-ordinated boron and nitrogen such as $H_3NBH_3$ (1·56 Å),[9] and indicates that, despite the rotation of the dimethylamino-groups out of the $BN_3$ plane, there remains sufficient overlap between the lone pair of electrons on each of the nitrogen atoms and the vacant *p*-orbital on the central boron atom to effect delocalisation and consequent $\pi$-bonding. These conclusions are also confirmed by a recent crystallographic investigation[10] of a similar compound, 1,8,10,9-triazaboradecalin, in which the B–N distance has a mean value of 1·421 Å and has been assigned a $\pi$-bond order of 0·3.



FIGURE

The angle of rotation about the B–N bond observed for each of the three amine groups in trisdimethylaminoborine is evidently required to relieve steric strain produced by non-bonded interaction between neighbouring methyl groups. The dimethylamino-group has a structure similar to that found for dimethylamine by electron diffraction[11] ($\gamma_{CN}$ = 1·455 Å and ∠CNC = 111·8°), although a shortening of the C–N bond and an increase of the CNC valence angle might have been expected for the present compound on account of the $sp^2$-hybridisation appropriate to the nitrogen atoms.

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[1] H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 1953, 4025.
[2] H. J. Becher, *Z. anorg. Chem.*, 1956, **287**, 285.
[3] D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1960, 5239.
[4] K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, 1955, **59**, 193.
[5] W. Harshbarger, G. H. Lee, R. F. Porter, and S. H. Bauer *J. Amer. Chem. Soc.*, 1969, **91**, 351.
[6] L. Wegmann, J. Hasse and W. Zeil, "Proceedings of Sixth International Congress for Electron Microscopy," Maruzen, Tokyo, 1966, p. 257.
[7] B. Andersen, H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, in the press.
[8] H. M. Seip, T. G. Strand, and R. Stølevik, *Acta Chem. Scand.*, in the press.
[9] E. W. Hughes, *J. Amer. Chem. Soc.*, 1956, **78**, 502.
[10] G. J. Bullen and N. H. Clark, *J. Chem. Soc.* (*A*), 1969, 404.
[11] B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, 1968, **64**, 2561.