The Crystal and Molecular Structure of a Novel Boron–Nitrogen Cage Compound

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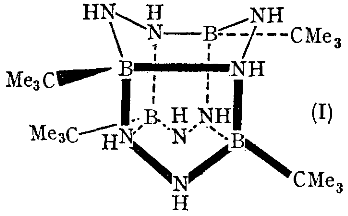
MILLER and JOHNSON[1] have recently prepared a compound $(C_4H_{11}BN_2)_4$, to which they have assigned structure (I) on the basis of infrared, ^1H n.m.r., and mass spectra. We here report the results of a single crystal *X*-ray analysis on this compound to confirm the structure and to provide detailed geometrical information on the novel boron–nitrogen cage.[2]



(I)

Crystal data: $C_{16}H_{44}B_4N_8$, $M = 391 \cdot 8$, m.p. 161—163°, tetragonal, $a = 12 \cdot 17(2)$, $c = 7 \cdot 86(1)$ Å, $D_m = 1 \cdot 11$, $Z = 2$, $D_c = 1 \cdot 13$. Mo-K_α-radiation ($\lambda = 0 \cdot 7107$ Å), precession camera. Systematic absences, *hhl* when $l = 2n + 1$, and *h*00 when $h = 2n + 1$, determine the space group as $P\bar{4}2_1c$ (No. 114). The molecule is required to occupy a position of site symmetry $S_4(\bar{4})$, which imposes various constraints on the position and orientation of the molecule in the unit cell. The structure was determined by a combination of Patterson and trial and error methods and has been refined to an *R*-factor of 0·10 on 517 independent non-zero reflexions obtained from photographic data by the equi-inclination Weissenberg method (Cu-K_α) at 25°.

A drawing of the molecule viewed down the *c*-axis is shown in the Figure. The structure (I) proposed by Miller and Johnson[1] is confirmed by the *X*-ray study. The bond distances and angles, uncorrected for thermal vibrations, are given in the Table.

The cage can be considered as two six-membered rings, joined to each other in four positions and thus forming four five-membered rings on the "sides" of the cage. The six-membered ring is in the "boat" conformation, with N(2) 0·76 Å out of the best plane through B, N(1), B′, and N(1′). The five-membered ring approximates to an envelope conformation, with N(2″) 0·64 Å out of the best plane through B, N(1), B″, and N(1‴). The one boron–trisubstituted nitrogen distance [B–N(2)] is significantly shorter than the two boron–tetrasubstituted nitrogen distances [B–N(1) and B–N(1‴)]. The B–N(1) length of 1·66 Å is longer than any previously reported with the exception of the remarkably long 2·02 Å found in tribenzotalarene.[3,4] Distances varying from 1·415 Å in *BBB*-trichloroborazine[5] to 1·60 Å in $H_3N–BF_3$[6] and in $Me_3N–BMe_3$,[7] and 1·64 Å in $F_3B–N{\equiv}C–CH_3$[8] have been described.[9] There must be considerable doubt as to what constitutes typical B–N single and double bond lengths without consideration of the detailed molecular environment,[9] and the analogy to the carbon system should be drawn with care.[9,10] Two of the valency angles at boron are less than tetrahedral to allow incorporation of the boron atom in the five-membered rings; this effect is accommodated

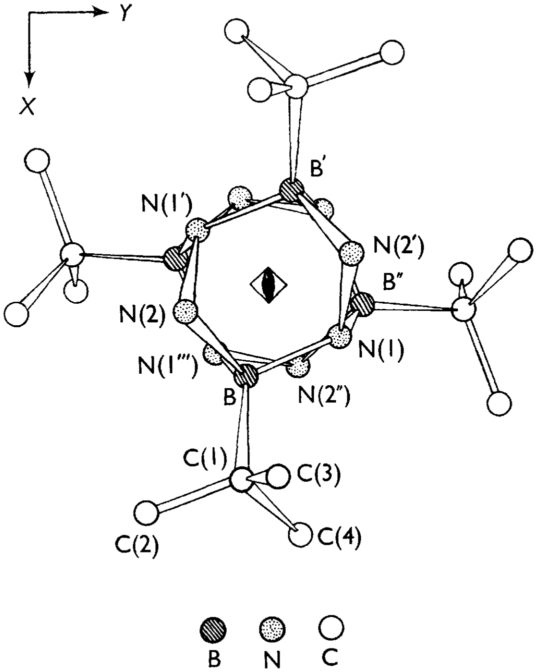


FIGURE. *View of the molecule looking along the* c-*axis. The symmetry-independent atoms are* B, N(1), N(2), C(1), C(2), C(3), *and* C(4).

TABLE

Bond distances (±0·01 Å) *and angles* (±0·8°)

B–N(1)	1·66	N(2)–N(1′)	1·45
B–N(2)	1·49	C(1)–C(2)	1·56
B–N(1‴)	1·60	C(1)–C(3)	1·56
B–C(1)	1·57	C(1)–C(4)	1·52
N(2)–B–N(1)	108·6	B–N(1)–B″	105·5
N(2)–B–N(1‴)	102·8	N(2′)–N(1)–B″	107·4
N(2)–B–C(1)	115·2	B–C(1)–C(2)	113·6
N(1)–B–N(1‴)	98·4	B–C(1)–C(3)	110·8
N(1)–B–C(1)	111·7	B–C(1)–C(4)	111·4
N(1‴)–B–C(1)	118·4	C(2)–C(1)–C(3)	105·2
B–N(2)–N(1)′	104·3	C(2)–C(1)–C(4)	108·2
B–N(1)–N(2′)	109·7	C(3)–C(1)–C(4)	107·3

by significant increases in the bond angles involving the t-butyl group. The B–N(2)–N(1′) angle, although in a six-membered ring, is considerably less than tetrahedral.

We thank Dr. John Miller of Rohm and Haas Company for the sample used in this study.

(*Received, July* 1*st*, 1968; *Com.* 867.)

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[9] A full list of B–N distances in compounds published up to 1963 is given by W. N. Lipscomb and R. Lewin, *Adv. Chem.*, 1964, **42**, 312.

[10] For example, in tetra-*B*-isothiocyanatotetra-*N*-t-butylborazocine which might be considered structurally analogous to cyclo-octatetraene, the alternating B–N distances are 1·40 and 1·46 Å [P. T. Clarke and H. M. Powell, *J. Chem. Soc.* (*B*), 1966, 1172].