Novel Cyclic Boron–Nitrogen Compounds

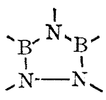
By IRING GEISLER and HEINRICH NÖTH*
(*Institut fur Anorganische Chemie, Philipps-Universität,* 355 *Marburgh/Lahn, Germany*)

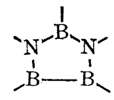
HETEROCYCLIC compounds containing only boron and nitrogen atoms in a five-membered ring have only recently[1] received attention. While alkyl and aryl derivatives of 1,3,4-triaza-2,5-diborines (1) are stable, such derivatives are unstable in the case of 2,5-diaza-1,3,4-diborines (2) because of electron deficiency in the system. It was expected on the basis of electron delocalization that replacement of the two boron atoms in the 3- and 4-positions of (2) by two silicon atoms would lead to enhanced stability in the system (3), reminiscent of the diazaborolidines (4).[2] Similarly, derivatives of (5) should show properties intermediate between those of (3) and (4).

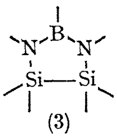
Chemical shift data of 1,3-*diaza*-2-*bora*-4,5-*disilacyclopentane and of* 1,3-*diaza*-2-*bora*-4-*silacyclopentane* (p.p.m.)

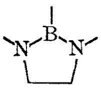
Compound	(10)[a]	(7)	(6)	(11)[b]	(9)	(8)
$\delta^{11}B$[c]	−31·5[5]	−34·6	−38·2	−22·1[6]	−23·7	−24·0
δCH_3B[d]	−0·21[4]	−0·29	−0·37	—	—	—
δCH_3N[d]	−2·40[4]	−2·55 −2·71	−2·59	—	—	—
δCH_2[d]	—	−2·24	—	—	−2·35	—
$\delta Si(CH_3)_2$[d]	—	−0·10	−0·16	—	−0·15	−0·21

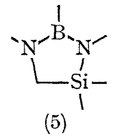
[a] (10 = $CH_3B(NHCH_3)_2$.
[b] (11) = 1,8,10,9-Triazaboradecalin.
[c] External standard $BF_3{\cdot}OR_2$.
[d] Internal standard Me_4Si.


(1)

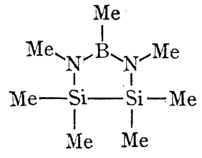

(2)

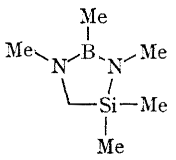

(3)

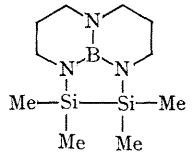

(4)

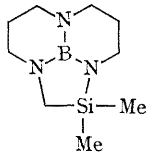

(5)

Syntheses of the ring systems (3) and (5) were achieved *via* the very versatile *N*-lithio-derivatives of bis(methylamino)-methyl borane and 1,8,10,9-triazaboradecalin.[3] Temperatures below −30° are required to achieve smooth metallation of the aminoboranes in diethyl ether or tetrahydrofuran. Reaction of the *N*-lithio-derivatives with *sym*-dichlorotetramethyldisilane and chloromethyldimethylchlorosilane affords the derivatives (6)—(9) in 36—70% yield.


(6) b.p. 74·5°/10 mm.


(7) b.p. 151°/760 mm.


(8) b.p. 70°/0·8 mm.
m.p. 58°


(9) b.p. 96–97°/8 mm.

The colourless liquids and solids are all monomeric and relatively resistant to oxidation and thermal decomposition. Spectroscopic data suggest planarity of the five-membered rings. ^{11}B n.m.r. data are in agreement with substantial B–N π-bonding, which is more strongly reduced in (6) and (8) as compared with (7) and (9), as indicated by the deshielding of the boron nuclei. This reduction is possibly due to competitive Si–N back-bonding, as the effect is less pronounced in (8) and (9) where the third amino-nitrogen atom helps to balance the electronic environment of the boron atom. This trend is also reflected in a deshielding of the protons in the CH_3N and CH_3B groups (see Table), and this has also been observed in many aminoboranes.[4]

(*Received, May* 19*th*, 1969; *Com.* 705.)

---

[1] For a review, see A. Finch, J. B. Leach, and J. H. Morris, *Organometallic Chem. Rev.*, 1969, *A*, **4**, 1.
[2] K. Niedenzu, *J. allg. prakt. Chem.*, 1966, **17**, 596.
[3] P. Fritz, K. Niedenzu, and J. W. Dawson, *Inorg. Chem.*, 1965, **4**, 886.
[4] H. Nöth and H. Vehrenkamp, *J. Organometallic Chem.*, 1968, **12**, 23.
[5] H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **99**, 1049.
[6] K. Niedenzu, P. Fritz, and J. W. Dawson, *Inorg. Chem.*, 1964, **3**, 1077.

Printed by W Heffer & Sons Ltd Cambridge England