pentanol was isomerized to a mixture which was largely **14** by powdered KOH.[5]

cis- **and** *trans*-**1-Allyl-2-phenyl-1,2-cyclohexanediol.**—Into the Grignard reagent prepared from 30.6 g (0.40 mol) of allyl chloride, 12.1 g (0.50 g-atom) of magnesium, and 700 ml of anhydrous ether was added a solution of 8.7 g (0.05 mol) of ketone, largely 2-hydroxy-2-phenylcyclohexanone, in 125 ml of ether. The reaction was vigorous and a thick paste formed. After standing overnight, the mixture was poured into ice water. No acid or ammonium chloride was added. After layer separation, the thick aqueous layer was extracted twice with ether. The ether portions were combined and distilled. Vacuum distillation gave 7.5 g of highly viscous oil. A portion (2.25 g) was placed on a column of silica,[28] 1 × 25 in., made up with benzene. Elution was with benzene, and 250-ml portions were collected. The residues of bottles 4–8, after several cycles of cooling and rewarming, finally solidified. Large lumps (0.7 g, mp 57–60°) were obtained from cyclohexane.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.83; H, 8.82.

The residues from bottles 9–16 remained liquid. When the flow of 5% ethyl acetate in benzene was started, a second series of bottles (17–21) gave residues which solidified still more slowly than those of bottles 4–8. Seeding was most advantageous. Fractions 17–21, when dissolved in hot cyclohexane, gave fine hairs, mp 82–83°.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.74; H, 8.78.

A larger run (5.8 g) on the same size column gave 2.1 and 1.7 g.

Ozonolysis of Glycol 15.—The glycol, prepared from 2.58 g of cyclic carbonate as described above, was dissolved in 100 ml of ethyl acetate, cooled to −70° in a bath of ethyl acetate and Dry Ice, and treated with oxygen containing 1% ozone until the solution developed a faint blue color. Evaporation of the ethyl acetate under reduced pressure (20 mm) without heating gave a colorless, thick oil. It could be stored at room temperature for several days but gradually became tan, then darker brown. Its ir spectrum showed that hydroxyl, carbonyl, and perhaps lactone groups were present. When, in an earlier run, the liquid was heated, it decomposed abruptly but without detonation. The presence of zinc dust made no difference in this property. The mixture became black. A portion (1.18 g) of the thick oil was, directly after preparation, dissolved in 10 ml of pyridine. Faint heat evolution was noted. When 2 ml of benzenesulfonyl chloride was added with stirring, the pyridine came to a boil rapidly. It was allowed to cool to room temperature and then allowed to stand overnight. A small amount of precipitate formed. The mixture was poured into water and extracted with ether. Evaporation of the ether and traces of residual pyridine gave an extremely viscous liquid, no longer sensitive to heat. Addition of 1 ml of cyclohexane and 1 ml of benzene permitted direct crystallization of 0.384 g (32.5%) of hydroxylactone **8**. Chromatography on silica of the residue from the crystallization gave 2% of unsaturated lactone **7** and an additional 12.7% of **8**. The total yield was thus 47%. The lactones so prepared did not depress the melting points of the lactones produced by rearrangement.

Registry No.—**1,** 3645-89-4; **2,** 34219-59-5; **3,** 34201-78-0; **4,** 34201-79-1; **5,** 34201-80-4; **5** 2,4-DNP, 34219-60-8; **6,** 34219-61-9; **7,** 34219-62-0; **8,** 34201-81-5; **12,** 34219-63-1; **14** tetrahydropyranyl ether, 34219-64-2; **15,** 34219-65-3; **16,** 34216-97-2; **17,** 34216-98-3; **18,** 34201-82-6.

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[28] Size was 70–325 mesh. EM Laboratories, Inc., Elmford, N. Y. 10523.

Structural and Conformational Studies of 2-Phenyl-1,3,2-diaza- and -dioxaboracycloalkanes

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Received November 4, 1971

A series of 1,3,2-diaza- and -dioxaboracyclohexanes have been investigated by means of proton and boron nmr in order to obtain information concerning the conformation of the rings, hybridization and stereochemistry of the nitrogens, and effects of ring substitution on boron chemical shifts. The data suggest that the $N-C_4-C_5-C_6-N$ and the $O-C_4-C_5-C_6-O$ regions adopt normal rapidly inverting chair type conformations. Substituents on nitrogen appear to strongly prefer equatorial orientations presumably because of extensive nitrogen to boron π bonding. The difference in boron chemical shifts observed for five- and six-membered rings in the diazaboracycloalkanes may be explained by assuming pyramidal hybridization of the nitrogens.

During the past five years considerable interest has been directed toward structural and conformational studies of various six-membered ring heterocycle containing more than one heteroatom including dioxa-,[2,3] dithia-,[2,4] and diazacyclohexanes.[2a,5] In contrast, relatively little conformational and structural information is available concerning boron-containing heterocycles. Of particular interest in this area are boron heterocycles containing additional adjacent heteroatoms such as nitrogen or oxygen which have lone electron pairs and thus are capable of π overlap with the vacant p orbital on boron, a topic of considerable interest.[6] In line with our general interest in conformational analysis of heterocyclic compounds[4,5a] and in bonding between boron and other heteroatoms,[6] we have undertaken a proton and ^{11}B nmr spectral study of a series of 2-phenyl-1,3,2-diazabora- and -dioxaboracyclohexanes with the aim of obtaining information concerning the shape of the rings, the stereochemistry about the nitrogens in the diaza derivatives, and the bonding between boron and other heteroatoms.

A considerable amount of evidence has been accumulated which indicates that substantial π bonding occurs between boron and adjacent atoms which bear lone electron pairs.[6,7] In cases where the adjacent atom is

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[1] (a) Senior coauthors to whom correspondence should be addressed. (b) NSF Undergraduate Research Participant, 1969.

[2] Excellent reviews concerning conformational analysis of heterocyclic compounds containing more than one heteroatom are available. See (a) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970), and references cited therein; (b) C. Romers, C. Altona, H. R. Buys, and E. Havinga, "Topics in Stereochemistry," Vol. 4, Wiley, New York, N. Y., 1969, and references cited therein; (c) C. H. Bushweller, "Mechanisms of Reactions of Sulfur Compounds," Vol. 5, Intra-Science Research Foundation, Santa Monica, Calif., 1969, p 75, and references cited therein.

[3] F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970).

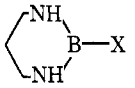
[4] E. L. Eliel and R. O. Hutchins, *ibid.*, **91**, 2703 (1969).

[5] (a) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *ibid.*, **90**, 7174 (1968); (b) P. J. Halls, R. A. Y. Jones, A. R. Katritzky, M. Snarey, and D. L. Trepanier, *J. Chem. Soc. B*, 1320 (1971); (c) H. Booth and R. M. Lemieux, *Can. J. Chem.*, **49**, 779 (1971).

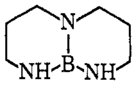
[6] For a review of the pertinent literature see F. A. Davis, I. J. Turchi, and D. N. Greeley, *J. Org. Chem.*, **36**, 1300 (1971).

[7] K. Niedenzu and J. W. Dawson in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 392.

nitrogen, however, there is some question as to the hybridization of the nitrogen atom. Goubeau and Zappel[8] concluded from Raman data that the B–N bond in 2-methyl-1,3,2-diazaboracyclohexane (**1a**) is similar to that in planar borazine, and additional spectroscopic evidence supports a high B–N bond order in this compound.[9] The similarity of the ^{11}B chemical shift of **1a** (−29.9 ppm)[10a] and borazine (−30.4 ppm)[10b] also suggests similar boron to nitrogen bonding. The independence of the nmr spectrum of **1a** (1,3-d_2 derivative) over a temperature range from −70 to 90° was put forth as evidence for planarity of the N–B–N region and thus for essentially sp^2 hybridization of the nitrogen atoms.[11] However, the introduction of sp^2 hybridized boron may reduce the barrier such that the lower temperature (−70°) reached may be insufficient to slow ring inversion.[12]

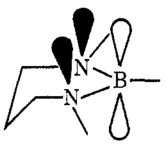


1a, X = CH_3
b, X = C_6H_5
c, X = H

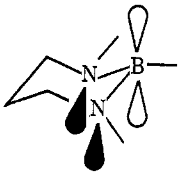


2

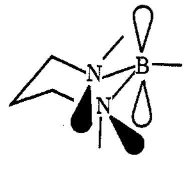
X-Ray crystallographic studies have demonstrated nearly planar nitrogen geometries in various compounds containing B–N bonds including $[(CH_3)_2N\text{–}B{=}CH_2]_3$,[13] $(CH_3)_2N\text{–}B(CH_3)_2$,[14] $(C_6H_4O_2B)_3N$,[15] and 1,8,10,9-triazaboradecaline[16] (**2**).



A



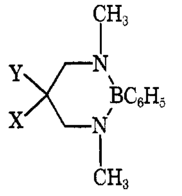
B



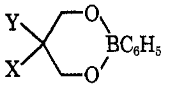
C

On the other hand, Dewar and Rona have argued on theoretical grounds that nitrogen will usually prefer a pyramidal (sp^3) geometry unless the delocalization energy gained by assuming a planar geometry is large.[17] These authors concluded that effective overlap with adjacent unsaturated systems can occur despite sp^3 hybridization of nitrogen. The conclusions are supported by the structure of trisdimethylaminoborane,[18] in which the CNC angle and C–N bond length are nearly identical with those in dimethylamine.[19]

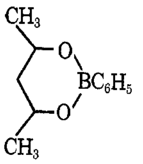
Irrespective of the nitrogen hybridization in 1,3,2-diazaboracyclohexanes, the most effective overlap of the nitrogen lone pairs with the vacant p orbital on boron occurs when the respective orbitals are coplanar, or nearly so, as represented by conformations A or B. However, in these forms the lone pairs are located syn axial to each other. In corresponding 1,3-diazacyclohexane systems this situation leads to unfavorable dipole interactions which force one *N*-methyl group into an axial orientation,[5a,20] as in conformation C. This latter conformation should reduce the nitrogen π overlap. Detection of conformations such as C would provide strong evidence against sp^2 hybridization of the nitrogens. Our approach was to investigate the proton and ^{11}B nmr spectra of 2-phenyl-1,3,2-diazaboracyclohexanes **3** and **4**, in which the N substituents may adopt equatorial or axial positions (as in C), and the spectrum of the corresponding 5,5-dimethyl derivative **5**, in which the *N*-methyl groups are constrained to equatorial sites (as in A or B). Boron chemical shifts are largely dependent upon the electron occupancy of the vacant boron orbital (*i.e.*, an increase in electron density increases the shielding on boron) and are quite sensitive to changes in the conformation of alkylamino groups attached to boron.[6] Consequently, any difference in conformation of the *N*-methyl groups in **3** and **4** should be reflected by a change in the boron chemical shift. In particular, the presence of an appreciable population of conformation C should produce a downfield ^{11}B shift of **5** compared to **3**. In addition, the corresponding 1,3,2-dioxaboracyclohexanes **6–9** were also investigated in order to preclude any boron chemical shift changes caused by ring deformations introduced by 5,5-dimethyl substituents.



3, X = Y = H
4, X = H, Y = CH_3
5, X = Y = CH_3



6, X = Y = H
7, X = H, Y = CH_3
8, X = Y = CH_3



9

Results and Discussion

Compounds **3–5** were prepared from the appropriate *N,N'*-dimethyl-1,3-propanediamines and bis(dimethylamino)phenylboron by transamination. Compounds **6–9** were synthesized from phenylboric acid and 1,3-propanediols by azeotropic removal of water. Identification and characterization were accomplished by elemental analysis and by infrared and proton nmr

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(8) J. Goubeau and A. Zappel, *Z. Anorg. Allg. Chem.*, **279**, 38 (1955).

(9) (a) K. Niedenzu and P. Fritz, *ibid.*, **340**, 329 (1965); (b) J. Goubeau and H. Snedider, *Justus Liebigs Ann. Chem.*, **675**, 1 (1964).

(10) (a) K. Niedenzu, P. Fritz, and S. W. Dawson, *Inorg. Chem.*, **3**, 1077 (1964); (b) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959).

(11) K. Niedenzu, C. D. Miller, and S. L. Smith, *Z. Anorg. Allg. Chem.*, **372**, 337 (1970).

(12) F. R. Jensen and B. H. Beck, *J. Amer. Chem. Soc.*, **90**, 1066 (1968). Introduction of an sp^2 carbon into a six-membered ring lowers the inversion barrier to *ca.* 7.7 kcal/mol (T_{coal} = *ca.* −115°) in methylenecyclohexane and 15.1 kcal/mol (T_{coal} = *ca.* −170°) in cyclohexanone compared to *ca.* 10 kcal/mol for cyclohexane: G. Binsch in "Topics in Stereochemistry," Vol. 3, E. Eliel and N. Allinger, Ed., Wiley, New York, N. Y., 1968, p 97. The effect of an sp^2 boron atom on the ring inversion barrier is unknown but probably should cause a similar decrease.

(13) H. Hess, *Acta Crystallogr., Sect. B*, **25**, 2334 (1969).

(14) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

(15) G. J. Bullen and P. R. Mallinson, *ibid.*, 2213 (1970).

(16) G. J. Bullen and N. H. Clark, *ibid.*, 404 (1969).

(17) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

(18) A. H. Clark and G. A. Anderson, *J. Chem. Soc. D*, 1082 (1969).

(19) B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, **64**, 2561 (1968).

(20) The phenomenon is found in various systems and has been termed the "Rabbit-ear,"[21] "Edward-Lemieux,"[22] or "Generalized Anomeric"[23] effect and attributed to syn-axial lone pair repulsions[21,24] or polar bond repulsions.[22]

(21) E. L. Eliel, *Sv. Kem. Tidskr.*, **81**, 22 (1969); E. L. Eliel, L. D. Kopp, J. E. Dennis, and S. A. Evans, Jr., *Tetrahedron Lett.*, 3409 (1971).

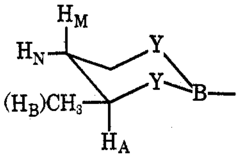
(22) S. Wolfe, A. Rauk, L. Tel, and I. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

(23) H. Booth and R. M. Lemieux, *Can. J. Chem.*, **49**, 779 (1971).

(24) F. P. Chen and R. G. Jesaitis, *J. Chem. Soc. D*, 1573 (1970).

TABLE I

PROTON NMR PARAMETERS FOR 2-PHENYL-1,3,2-DIAZABORACYCLOHEXANES AND 2-PHENYL-1,3,2-DIOXABORACYCLOHEXANES[a]



Compd	δ_A	δ_B	δ_M	δ_N	J_{AB}	J_{MN}	J_{AM}	J_{BM}	J_{AN}	δ_{NCH_3}
3	2.92[b]	2.92[b]	1.92[c]	1.92[c]						2.45
4	2.78[d]	2.78[d]		(0.96)			d	d		2.48
5	2.71[e]	2.71[e]	(1.00)	(1.00)						2.48
6	4.02[f]	4.02[f]	1.84[g]	1.84[g]						
7	3.64	4.06	2.27	(0.83)	11	(7)	10.0	4.4		
8	3.79	3.79	(1.02)	(1.02)						
9	4.18		1.33	1.87		14	11		2.3	

[a] Measured as $CDCl_3$ solutions; chemical shifts in parts per million from TMS internal standard. [b] H_A, H_B appear as a triplet, J = 5.5 Hz. [c] H_M, H_N appear as a pentet, J = 5.5 Hz. [d] H_A, H_B appear as a "deceptively simple" doublet, $J = (J_{AM} + J_{BM})/2 = 7$ Hz. [e] H_A, H_B are isochronous. [f] H_A, H_B appear as a triplet, J = 5.4 Hz. [g] H_M, H_N appear as a pentet, J = 5.4 Hz.

data. The 1,3,2-diazaboracyclohexanes showed strong absorption at 1500 cm^{-1}, attributable to the antisymmetrical BN_2 stretching mode.[25] Compounds **6–9** all showed strong bands in the 1310–1350 cm^{-1} region, indicative of B–O stretching.[26] The nmr spectra of compounds **3–9** were recorded at 60 or 100 MHz and the parameters were extracted by first-order analysis presented in Table I. Compounds **3** and **6** displayed similar patterns for the ring protons consisting of two sets of isochronous absorptions, a two-proton pentet representing the C_5 hydrogens, and a four-proton triplet at higher field for the $C_{4,6}$ protons. Compounds **5** and **8** both showed a singlet for the $C_{4,6}$ protons and a second high-field singlet for the 5,5-dimethyl groups. The spectrum of 5-methyl-1,3,2-dioxaboracyclohexane (**7**) showed a more complex $(AB)_2X$ pattern for the ring protons. The presence of a relatively large vicinal coupling ($J_{AX} \cong$ 10 Hz) was indicative of an H_{axial}–H_{axial} coupling[27] and allowed the assignment of the H_A and H_B chemical shifts. The smaller J_{BX} (4.4 Hz) was indicative of an $H_{4\ equatorial}$–$H_{5\ axial}$ coupling and was consistent with the assignment. The spectrum of the analogous diaza derivative **4** was much less complex. The $C_{4,6}$ region appeared as a "deceptively simple"[28] doublet from which only $(J_{AX} + J_{BX})/2$ could be obtained. The average value (*ca.* 7 Hz) suggested the presence of a large and a small coupling similar to those obtained for **7**. The spectrum of **9** appeared as an $(A)_2MN$ pattern (excluding the $C_{4,6}$ methyl coupling) with $J_{AM} \cong$ 11 and $J_{AN} \cong$ 2.3 Hz, again suggestive of an axial–axial and an axial–equatorial coupling.[29,30]

All of the above nmr data are most consistent with a chairlike X–C_4–C_5–C_6–X region of the molecules for X = O and N. The relatively simple spectra obtained for **3**, **5**, **6**, and **8** point strongly to the presence of rapid ring inversion at ordinary temperatures which renders the $C_{4,6}$ and the C_5 proton sets isochronous. Only slight broadening was observed in the spectrum of compound **3** upon cooling to −80°, indicating that the inversion barrier is probably quite low.

In an attempt to obtain information concerning the nitrogen stereochemistry and hence the shape of the N–B–N region of the rings, the boron chemical shifts were determined and the data are presented in Table II.

TABLE II

BORON-11 CHEMICAL SHIFTS OF 1,3,2-DIAZA- AND DIOXABORACYCLOALKANES

Compd	Ref	Solvent	Chemical shift,[a] ppm	Line width,[b] Hz
1b	c		−27.2[c]	
3	d	Neat	−30.6	359
		Benzene	−29.5	144
4		Neat	−29.0	520
		Benzene	−29.4	136
5		Neat	−28.8	306
		Benzene	−29.0	126
6	e	Neat	−27.0 (−27.7)[f]	407
7		Benzene	−26.6	226
8	e	Benzene	−26.2	157
		Acetonitrile	−26.4	93
9		Acetonitrile	−26.9	135
10	g	Benzene	−31.1	111
11	e	Benzene	−31.2 (−31.9)[f]	100

[a] In parts per million relative to boron trifluoride etherate. Estimated error, ±0.15 ppm for line width <100 Hz, ±0.3 ppm for line width <200 Hz, ±1.0 ppm for wider lines. [b] At Half-height; estimated error ±5%. [c] Reference 10a. [d] Reference 25. [e] Reference 33. [f] Unpublished results reported in W. R. Henderson and E. F. Mooney, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 219 (1969). [g] Reference 32.

Replacing hydrogen by methyl in compound **1** to give **3** produced a downfield shift of 2 ppm, in contrast to the expected inductive shielding effect produced by alkyl groups on boron.[6] The deshielding observed is probably due to nonbonded interactions between the *N*-methyl substituents and the ortho hydrogens of the *B*-phenyl ring. Such interactions apparently twist the phenyl group so that conjugation with boron is less effective. Compounds **3** and **4** should have the same stereochemistry at the nitrogen atoms and thus overlap of the lone pairs with boron should be the same in both.

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(25) W. Weber, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **5**, 726 (1966).

(26) R. L. Werner and K. G. O'Brian, *Aust. J. Chem.*, **8**, 355 (1955); **9**, 137 (1955).

(27) N. Bhacca and D. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 51.

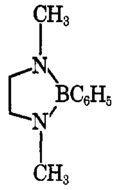
(28) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, New York, N. Y., 1965, p 363. In this case, simplification probably arises as a consequence of $\delta_{AB} \simeq 0$ and $^1/_2\ (J_{AX} - J_{BX})/J_{AB}$ small compared to J_{AB}.

(29) The $C_{4,6}$ region of **9** was very similar to that of other analogous heterocyclic systems including 1,3-dioxacyclohexanes[30] and 1,3-dithiacyclohexanes.[4]

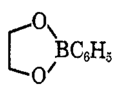
(30) E. L. Eliel and Sr. M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

As expected, the boron chemical shifts of **3** and **4** are essentially the same (Table I). The presumably equatorial 5-methyl substituent in **4** apparently has no measurable effect. The introduction of the second, necessarily axial, methyl group at position 5 should greatly disfavor any population of axial *N*-methyl conformations[31] (as C) and any conformational change should appear as a shielding of the boron in **5** and a shift to higher field. The nearly identical chemical shifts for **3**, **4**, and **5** (*ca.* −29.0 ppm) strongly suggests that all three have similar, diequatorial orientations for the *N*-methyl groups. Any "Rabbit-ear"[20,21] or "Anomeric"[28] effect apparently is overshadowed by stabilization due to π bonding or to sp^2 hybridization of the nitrogens. The corresponding dioxa derivatives **6–9** also exhibited practically identical boron chemical shifts, indicating that ring substitution plays very little role in determining such shifts. A similar result has been observed in a series of trialkyl borates which showed no dependence of the boron chemical shift on the type of alkyl substituent.[6]

To obtain a more definitive answer concerning the hybridization of the nitrogen atoms in compounds **3–5**, we measured the boron chemical shifts of the diaza- and dioxaboracyclopentane derivatives **10**[32] and **11**.[33] The chemical shift of **10** (−31.1 ppm) is deshielded by 2 ppm compared with that of **3–5**. If nitrogen in compounds **10** and **3–5** were sp,^{2} then the chemical shifts of these compounds should be nearly identical. However, if the nitrogen atoms in **3–5** and **10** are sp,^{3} then Drieding models show that in the cyclopentane derivative **10** the lone pairs on nitrogen and the vacant orbital on boron cannot be coplanar without severely deforming the ring. The models further suggest that in **3–5** coplanarity of the orbitals on boron and nitrogen are much better. This downfield shift can then be attributed to lower π bonding in the five- than in the six-membered ring compounds.



10



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A similar argument can be used to explain the large downfield shift (−5 ppm) observed between the five- and six-membered ring 1,3,2-dioxaboracycloalkanes (**11** and **6–9**). In these compounds oxygen will be sp^3 hybridized. The much larger difference in chemical shift observed between the 1,3,2-dioxaboracycloalkanes and the 1,3,2-diazaboracycloalkanes may be attributed to the greater electronegativity of oxygen over nitrogen.

The above argument, therefore, suggests that the nitrogens in the 1,3,2-diazaboracycloalkanes are sp^3 hybridized provided that the boron chemical shifts in these compounds are primarily determined by the degree of π electron density on boron and not to some additional parameters.[34]

Experimental Section

^{11}B nmr chemical shifts were measured with a Varian HR-100 at 32.1 MHz referenced against a capillary containing boron trifluoride etherate. Proton nmr spectra were measured on Varian A-60A and HR-100 instruments, and infrared spectra were measured on a Perkin-Elmer 457 spectrometer.

General Procedure for Preparation of the 2-Phenyl-1,3,2-diazaboracyclohexanes.—The 1,3,2-diazaboracyclohexanes were prepared by transamination between bis(dimethylamino)phenylboron[25] and the appropriate *N*,*N'*-dimethyl-1,3-propanediamine in benzene.

2-Phenyl-1,3,5-trimethyl-1,3,2-diazaboracyclohexane (4).—Bis(dimethylamino)phenylboron (0.71 g, 0.0041 mol) and *N*,*N'*-2-trimethyl-1,3-propanediamine (Ames Laboratories) (0.47 g, 0.0041 mol) gave 0.61 g (73%) of **4**, bp 75° (1 mm).

Anal. Calcd for $C_{12}H_{19}BN_2$: C, 71.31; H, 9.48. Found: C, 71.16; H, 9.35.

Compound **4** has the following properties: infrared (thin film) 3080–2800 (s), 1950 (w), 1870 (w), 1810 (w), 1690 (m), 1510 (s), 1440 (s), 1410 (s), 1370 (s), 1280 (s), 1210 (s), 1190 (s), 1140 (m), 1120 (w), 1090 (s), 1060 (s), 1030 (s), 970 (m–w), 930 (m), 890 (w), 870 (w), 750 (s), 705 (s), 650 (m–s), and 618 cm^{-1} (m).

2-Phenyl-1,3,5,5-tetramethyl-1,3,2-diazaboracyclohexane (5).—Bis(dimethylamino)phenylboron (0.90 g, 0.005 mol) and *N*,*N'*-2,2-tetramethyl-1,3-propanediamine (see below) (0.64 g, 0.005 mol) gave 0.97 g (90%) of **5**, bp 108–111° (2 mm).

Anal. Calcd for $C_{13}H_{21}BN_2$: C, 72.24; H, 9.79. Found: C, 72.06; H, 9.91.

Compound **5** had the following properties: infrared (thin film) 3200 (w), 2980–2795 (s), 1595 (w), 1500 (s), 1440 (s), 1405 (s), 1380 (s), 1355 (s), 1290 (s), 1235 (s), 1190 (s), 1125 (w), 1090 (w), 1065 (s), 1035 (m), 955 (w), 940 (w), 910 (w), 750 (s), 700 (s), and 645 cm^{-1} (m).

***N*,*N'*-2,2-Tetramethyl-1,3-propanediamine.**—The parent diamine was prepared in 45–49% yield by reduction of 2,2-dimethyl-1,3-dinitropropane[35] with iron filings and hydrochloric acid,[36] bp 72–75° (37 mm), $n^{25}\text{D}$ 1.4532 [lit.[37] bp 151–153° (737 mm), $n^{20}\text{D}$ 1.4536]. This material was treated with ethyl chloroformate according to standard procedures[39] to give the dicarbamate in 89–90% yield, mp 68–69° (lit.[40] mp 62–64°). Reduction of the dicarbamate with lithium aluminum hydride in ether gave *N*,*N'*,2,2-tetramethyl-1,3-propanediamine in 51–54% yield, bp 82–84° (68 mm), $n^{22}\text{D}$ 1.4388. Analysis was performed on a derivative of this compound, *N*,*N'*,5,5-tetramethyl-2-phenyl-1,3-diazacyclohexane, which was prepared by treating the diamine with benzaldehyde.

Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16. Found: C, 77.12; H, 10.13.

The final product had the following properties: infrared (thin

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[31] The syn-axial methyl–methyl interaction in these systems is unknown but should be close to the value of 3.7 kcal/mol found in cyclohexyl derivatives.

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[34] The major parameters affecting the ^{31}P chemical shift in symmetrically substituted phosphorus compounds have been suggested as being the bond angles and the degree of π bonding to phosphorous. See J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966), and V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **32**, 1187 (1967). Since boron has a vacant orbital, π bonding to boron in trivalent organoboron compounds would be expected to be the dominant parameter affecting the boron chemical shift. Experimental evidence bears this out.[6]

[35] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

[36] M. Senkus, *Ind. Eng. Chem.*, **40**, 506 (1948). This transformation may be carried out *via* catalytic hydrogenation.[37] An attempt to reduce the dinitro compound with $LiAlH_4$ in ether afforded a mixture (30–40% yield), *ca.* 35% of which proved to be a cyclized product, 4,4-dimethyl-2-pyrazoline,[38] isolated as the 1-carboethoxy derivative: bp 68–71° (0.35 mm); $n^{25}\text{D}$ 1.4700; ir (neat) olefinic 3050 (w), C=O 1705 (vs), C=N 1592 cm^{-1} (m); pmr (CCl_4) δ 1.20 (s, 6, *gem*-Me), 1.30 (t, 3, Me, $J = 7$ Hz), 3.50 (s, 2, ring methylene), 4.17 (q, 2, methylene), 6.65 (s, 1, olefinic H); mass spectrum *m/e* (rel intensity) 170 (parent, 21), 111 (28), 83 (87), 42 (22), 32 (32), 30 (23), 29 (42), 28 (100). *Anal.* Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29. Found: C, 56.55; H, 8.28.

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[39] W. W. Hartman and M. R. Brethen, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1944, p 279.

[40] G. S. Skinner, R. H. Hall, and P. V. Susi, *ibid.*, **79**, 3786 (1957).

film) 3320 (m), 2960–2790 (s), 1470 (s), 1390 (m–s), 1365 (m), 1310 (w), 1270 (w–m), 1245 (m), 1150 (s), 1110 (s), 1030 (w), 965 (w), 940 (w), 910 (m), 880 (w), 800 (m–s), 850 (s), and 640 cm^{-1} (w); nmr (C_6D_6) δ 0.9 (s, 6 H), 0.95 (s, 2 H), and 2.4 (d, 10 H).

General Procedure for Preparation of the 2-Phenyl-1,3,2-dioxaboracyclohexanes.—The dioxaboracyclohexanes were prepared from the appropriate 1,3-propanediol and phenylboric acid in benzene by azeotropic removal of water.

2-Phenyl-5-methyl-1,3,2-dioxaboracyclohexane (7).—Phenylboric acid (2.6 g, 0.021 mol) and 2-methyl-1,3-propanediol[30] (1.9 g, 0.021 mol) gave 3.5 g (95%) of **7**, bp 103–105° (3 mm), mp 30–31°.

Anal. Calcd. for $C_{10}H_{13}BO_2$: C, 68.22; H, 7.45. Found: C, 68.28; H, 7.58.

Compound **7** had the following properties: infrared (thin film) 3060 (w), 2960 (m), 2900 (m), 1600 (m–s), 1480 (s), 1445 (s), 1415 (s), 1380 (w), 1350 (s), 1320 (s), 1300 (s), 1255 (s), 1220 (w), 1170 (s), 1140 (s), 1080 (m), 1030 (m), 950 (w), 880 (w), 765 (m), 730 (m–s), 700 (s), 670 (m), and 650 cm^{-1} (s).

2-Phenyl-4,6-dimethyl-1,3,2-dioxaboracyclohexane (9).—Phenylboric acid (1.2 g, 0.01 mol) and *meso*-2,4-pentanediol[41] (1.0 g, 0.01 mol) in toluene gave 1.5 g (88%) of **8**, mp 45°, purified by sublimation at 60° (0.5 mm).

Anal. Calcd for $C_{11}H_{15}BO_2$: C, 69.47; H, 7.89. Found: C, 69.64; H, 7.94.

Compound **9** had the following properties: infrared (KBr) 3050 (w), 2990 (m), 2930 (m–w), 1605 (m), 1450 (s), 1410 (s), 1385 (m), 1370 (m), 1360 (m), 1310 (s), 1270 (m–s), 1180 (m), 1155 (s), 1140 (s), 1070 (w), 1030 (m), 900 (w), 830 (w), 780 (m), 715 (s), 660 (m–w), and 650 cm^{-1} (s).

Registry No.—**3**, 6063-69-0; **4**, 29173-11-3; **5**, 34288-22-7; **6**, 4406-77-3; **7**, 34288-24-9; **8**, 5123-13-7; **9**, 7317-42-2; 1-carboethoxy-4,4-dimethyl-2-pyrazoline, 34288-27-2; *N,N'*-2,2-tetramethyl-1,3-propanediamine, 31892-15-6; *N,N'*-5,5-tetramethyl-2-phenyl-1,3-diazacyclohexane, 34288-29-4.

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Azimines. I. Reinvestigation of Some Alleged Azimines

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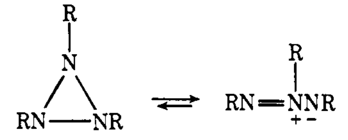
Azimines are the 1,3-dipolar isomers of the unknown triaziridines. Some previously proposed azimine structures are reassigned, based on new spectroscopic evidence. The product formed by bromination and dehydrobromination of *o*-nitrobenzaldehyde phenylhydrazone is assigned structure **5b**; reduction with stannous chloride gives **6b**, *anhydro*-2-(*p*-bromophenyl)-3*H*-benzo-1,2,3-triazinium-4-one hydroxide. Reaction of *o*-aminobenzamide with *N,N*-dimethyl-4-nitrosoaniline gives 4,4'-azoxy-*N,N*-dimethylaniline, not the previously proposed **6c**. Condensation of indazolinone with *N,N*-dimethyl-4-nitrosoaniline does give **6c**, presumably *via* an intermediate triaziridine.

1,3 dipoles have been of substantial interest, originally as intermediates in the synthesis of five-membered heterocycles,[1] and more recently as valence isomers of three-membered heterocycles.[2,3] The three-nitrogen valence isomer pair comprising the cyclic triaziridines and the open dipolar azimines remains, however, almost unexplored. The literature reveals no extant reports of triaziridines,[4] and only scattered examples of azimines (see below). Expecting the latter to be more stable, we here report the establishment of structure of some cyclic azimines. An accompanying paper[5] reports on the reactions of nitrenes with azo compounds, a potential synthetic route to azimines.[6] Other synthetic routes are also being investigated, and will be reported subsequently.[7]



Products from *o*-Nitrobenzaldehyde Phenylhydrazone.—In a series of papers in 1925–1931, Chattaway[8–11] reported that halogenation of *o*-nitrobenzaldehyde phenylhydrazone, followed by treatment with base, gave a series of compounds A, to which he assigned structure **1**[9] (Scheme I). Reduction of compounds A with stannous chloride gave a series of compounds B, assigned triaziridine structures **2**. This work was subsequently reinvestigated by Gibson,[12] who proposed the new structures **3a** and **4a** for materials A and B (Ar = 2,4-dibromophenyl), respectively. The anthranil *N*-oxide structure **3a** was apparently based on mechanistic considerations and ultraviolet and infrared spectra, especially bands at 1248 and 1570 cm^{-1} in the latter, assigned as $>\overset{+}{\mathrm{N}}\overset{-}{\mathrm{O}}$ and -N=N- stretching frequencies, respectively. Compound B was assigned the azimine structure **4a**, since the possibility of B being the straightforward reduction product of **3a**, the

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