vibrational frequencies associated with each of the MH_3 moieties, considered as free molecules with C_{3v} symmetry, and three arising as a consequence of the P–B bond; a fourth skeletal frequency, the P–B torsional motion of a_2 symmetry, is inactive. The Raman effect for this model should also display the same 11 fundamentals.

Two possible alternatives for the structure of the solid are: (1) $[PH_4][H_2P(BH_3)_2]$, as originally proposed by Gamble and Gilmont;[1] (2) $[H_2B(PH_3)_2][BH_4]$, analogous to the structure of the "diammoniate of diborane." The infrared and Raman spectra of both of these structures should differ significantly from those of the C_{3v} monomer. If the BH_3 groups in (1) and the PH_3 groups in (2) are considered as point masses and all angles are assumed to be tetrahedral, each molecule contains ions of T_d and C_{2v} symmetry on the basis of which skeletal frequencies can be predicted. The T_d moieties should display two infrared-active motions and four fundamentals in the Raman effect. Likewise, the C_{2v} moieties would be expected to give rise to eight infrared frequencies and nine Raman. Internal motions of the MH_3 groups would increase the complexity of the observed spectrum in the regions of hydrogen frequencies. Thus, it is apparent that, if either (1) or (2) is the correct structure of the solid, the spectrum observed in the infrared should differ significantly from that in the Raman effect. In particular, the spectra should display complexity in areas characteristic of P–B and MH_3 motions.

We have found the infrared and Raman spectra of the solid to be similar, relatively simple and easily related to the C_{3v} model. Accordingly, we believe the evidence strongly indicates that solid "diborane diphosphine" is monomeric as is the liquid. The observed infrared and Raman frequencies are listed in Table I. No evidence for $[PH_4^+]$ or $[BH_4^-]$ is obtained upon comparison of these spectra. Only one P–B motion could be assigned, and the spectra are relatively simple.

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Boron–Nitrogen Compounds. XXV.[1,2] Substituted 1,3,2-Diazaboracycloalkanes

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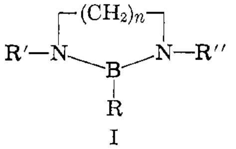
Boron- and nitrogen-substituted 1,3,2-diazaboracycloalkanes have been prepared by a transamination between bis(dimethylamino)boranes and α,ω-diamines. Partial substitution of the nitrogen of the diamine does not appear to inhibit this reaction; five-, six-, and seven-membered heterocyclic systems are readily obtained by the described procedure. However, the low yields of product obtained in those reactions involving an olefinic α,ω-diamine indicate that steric factors may play an important role. The mechanism of the formation of the boron–nitrogen–carbon heterocycles is discussed, and some spectroscopic data are briefly evaluated.

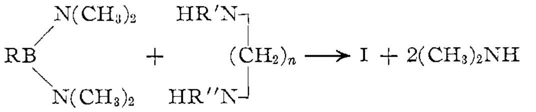
In the decade since the discovery of the 1,3,2-diazaboracycloalkanes system (I) by Goubeau and Zappel[3] several preparative routes have been explored to provide access to this type of compound.[4] However, with the exception of six compounds, only those derivatives of I in which R′ = R″ = H have been described.



I

Moreover, the six cited exceptions[5–8] are all 1,3,2-diazaboracyclopentanes (*i.e.*, I, $n = 2$) in which R′ = R″.

The present study reports on a simple synthesis of a variety of 1,3,2-diazaboracycloalkanes of differing ring size which are substituted at both the boron and the nitrogen sites in the molecule. These compounds are readily produced through a transamination reaction as illustrated in eq 1. Pertinent data are listed in Table I.



$$RB[N(CH_3)_2]_2 + HR'N{-}(CH_2)_n{-}NHR'' \longrightarrow I + 2(CH_3)_2NH \quad (1)$$

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[1] Part XXIV: K. Niedenzu and P. Fritz, *Z. Anorg. Allgem. Chem.*, in press.

[2] Supported by the U. S. Army Research Office, Durham, N. C.

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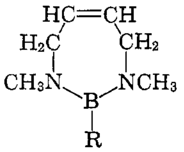
TABLE I

1,3,2-DIAZABORACYCLOALKANES (I)

						Analyses, %							
					Yield,	Boron		Nitrogen		Carbon		Hydrogen	
n	R	R′	R″	Bp, °C (mm)	%	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
2	CH_3	C_2H_5	C_2H_5	33–34 (2)	44	7.73	7.51	20.01	20.00	60.03	59.95	12.24	12.37
2	n-C_4H_9	H	CH_3	33–35 (2)	54	7.73	7.62	20.01	20.23	60.03	60.05	12.24	12.12
2	n-C_4H_9	CH_3	CH_3	31–33 (2)	66	7.02	6.96	18.18	18.26	62.36	62.13	12.43	12.27
2	n-C_4H_9	H	C_2H_5	40–43 (2)	56	7.02	7.17	18.18	18.50	62.36	62.16	12.43	12.00
2	n-C_4H_9	C_2H_5	C_2H_5	45–47 (2)	44	5.99	6.07	15.38	15.35	65.95	66.10	12.73	12.81
2	C_6H_5	H	CH_3	66–68 (2)	64	6.76	6.73	17.51	17.42	67.54	67.50	8.19	8.43
2	C_6H_5	H	C_2H_5	70–72 (2)	62	6.22	5.94	16.10	15.91	69.00	69.11	8.69	8.74
3	CH_3	CH_3	CH_3	30–31 (2)	41	8.59	8.30	22.23	22.41	57.18	57.23	12.00	12.05
3	CH_3	H	C_2H_5	39–41 (1.5)	30	8.59	8.31	22.23	22.09	57.18	57.29	12.00	11.92
3	n-C_4H_9	H	CH_3	44–46 (2)	77	7.02	7.33	18.18	18.41	62.36	62.39	12.43	12.34
3	n-C_4H_9	CH_3	CH_3	48–51 (2)	72	6.44	6.31	16.67	16.88	64.30	64.23	12.59	12.78
3	n-C_4H_9	H	C_2H_5	48–50 (2)	72	6.44	6.49	16.67	16.64	64.30	64.17	12.59	12.77
3	C_6H_5	H	CH_3	74–76 (2)	49	6.22	5.96	16.10	16.25	69.00	69.19	8.69	8.82
3	C_6H_5	CH_3	CH_3	71–74 (2)	68	5.75	5.94	14.90	14.86	70.24	70.04	9.11	9.17
3	C_6H_5	H	C_2H_5	81–83 (2)	66	5.75	5.83	14.90	14.79	70.24	70.09	9.11	9.22
4	CH_3	CH_3	CH_3	34–35 (2)	36	7.73	7.49	20.01	19.96	60.03	59.83	12.24	12.24
4	CH_3	C_2H_5	C_2H_5	43–45 (2)	30	6.44	6.16	16.67	16.79	64.30	64.46	12.59	12.79
4	n-C_4H_9	CH_3	CH_3	52–54 (2)	54	5.94	5.94	15.38	15.30	65.95	66.16	12.73	12.73
4	n-C_4H_9	C_2H_5	C_2H_5	65–68 (2)	53	5.15	5.10	13.33	13.21	68.57	68.26	12.95	13.19
4	C_6H_5	CH_3	CH_3	85–86 (2)	67	5.35	5.19	13.86	14.35	71.37	70.99	9.48	9.58
4	C_6H_5	C_2H_5	C_2H_5	112–114 (3)	55	4.70	4.99	12.17	12.25	73.05	73.24	10.07	10.26

Preliminary experiments have shown that 1,3,2-diazaboracycloalkanes can be dehydrogenated to yield derivatives containing carbon–carbon double bonds. Similar products have also been found to result from a transamination between a bis(amino)borane and an unsaturated α,ω-diamine in analogy to eq 1. For example, utilizing N,N′-dimethyl-1,4-diaminobutene-2 in this reaction, heterocycle II is obtained. However, whereas reaction according to eq 1 produces compounds of type I in good yield, the utilization of the olefinic diamine in an analogous reaction yields intractable material (probably polymeric in nature) as the major product along with small amounts of the desired 1,3,2-diazaboracycloalkene.



II

Experimental Section[9, 10]

Starting Materials.—Bis(dimethylamino)phenylborane, $C_6H_5B[N(CH_3)_2]_2$, and bis(dimethylamino)-n-butylborane, n-$C_4H_9B[N(CH_3)_2]_2$, were prepared by the dimethylaminolysis of the corresponding organodichloroboranes. Bis(dimethylamino)chloroborane, $ClB[N(CH_3)_2]_2$, was obtained from a disproportionation between tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, and trichloroborane, and was subsequently allowed to react with methylmagnesium iodide to yield bis(dimethylamino)methylborane, $CH_3B[N(CH_3)_2]_2$. All diamines were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were used without additional purification.

2-*n*-Butyl-1,3-dimethyl-1,3,2-diazaboracyclohexane (Typical Experiment).—A solution of 10.3 g (0.1 mole) of N,N′-dimethyl-1,3-diaminopropane in 50 ml of dry hexane was added to a solution of 15.6 g (0.1 mole) of bis(dimethylamino)-n-butylborane in 100 ml of dry hexane in an inert atmosphere. On refluxing the reaction mixture, dimethylamine was evolved; the reaction was complete within approximately 2 hr. The solvent was stripped off, and the residue was distilled under reduced pressure to yield 12 g (72%) of the desired compound, bp 48–50° (2 mm). The analytical data are compiled in Table I.

In an analogous procedure, the compounds listed in Table I were prepared by the reaction of 0.1-mole portions of variously B-substituted bis(dimethylamino)boranes with the appropriate α,ω-diamine in equimolar quantity. The yields cited represent only one experiment in each case, and no attempt has been made to improve the yields.

2-*n*-Butyl-1,3-dimethyl-1,3,2-diazaboracycloheptene-5.—A solution of 11.4 g (0.1 mole) of N,N′-dimethyl-1,4-diaminobutene-2 in 50 ml of dry hexane was added to a solution of 15.6 g (0.1 mole) of bis(dimethylamino)-n-butylborane in 100 ml of dry hexane in a nitrogen atmosphere. The mixture was refluxed for 2 hr, and the solvent was stripped off. On heating the semiliquid residue under high vacuum in an oil bath at about 200°, a small amount of a slightly yellow distillate was obtained. It was rectified under vacuum to yield 0.5 g (3%) of the desired compound, bp 59–61° (2 mm). *Anal.* Calcd for $C_{10}H_{21}BN_2$: C, 66.68; H, 11.75; B, 6.01; N, 15.56; mol wt, 180.10. Found: C, 67.10; H, 11.94; B, 5.90; N, 15.91; mol wt (cryoscopic in benzene), 186.

In an analogous procedure 1,3,2-trimethyldiazaboracycloheptene-5, bp 43–44° (2 mm), was prepared by the reaction of bis(dimethylamino)methylborane with N,N′-dimethyl-1,4-diaminobutene-2 in 3% yield.

Both of the compounds described above have rather complex infrared spectra, and no attempt has been made to assign specific vibrations. However, the presence of a CC double bond in these heterocycles is clearly indicated by strong absorption near 1650 cm^{-1}.

Discussion

Presumably cyclic derivatives containing the boron–nitrogen linkage are particularly suited as models to use in elucidating the nature of that bond[11] and consequently the vibrational spectra of some 1,3,2-diazaboracycloalkanes where R′ = R″ = H have been

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[9] Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[10] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer using sodium chloride optics.

[11] J. Goubeau and H. Schneider, *Ann. Chem.*, **675**, 1 (1964).

studied in some detail.[1,3,12] However, previous observations on simple monoaminoborane systems, R_2N-BR_2, have shown that the effect of a nitrogen substituent upon the character of the boron–nitrogen bond is more pronounced than that produced by substituting on the boron.[13-15] Accordingly, the newly synthesized materials may be useful for further studies on the nature of the BN bonding in 1,3,2-diazaboracycloalkanes. A qualitative examination of the infrared spectra of the compounds listed in Table I provides the following information.

All compounds exhibit a strong absorption near 1500 ± 15 cm^{-1}, which is assigned to the antisymmetric BN_2 stretching mode. No significant shift of this band is observed when the ring size of I is changed by varying n from 2 to 3 or 4. This observation indicates that the BN bond nature in I apparently is not influenced to any substantial degree by the ring size; this conclusion is in agreement with previous findings.[1] In addition, on changing either one or both of the substituents R′ and R″ from H to CH_3 or C_2H_5, no appreciable shift of $\nu_{as}BN_2$ could be observed. In the case of $R' $ or $R'' = H$, an NH stretching vibration is observed in the 3400-cm^{-1} region. This relatively low value for νNH may be accounted for by assuming a minor association of the molecules. Indeed, molecular weight determinations of I by the cryoscopic method in 0.05 *m* benzene solution indicated the existence of up to 10% association.

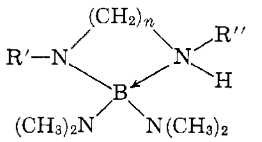
In agreement with previous work,[1] a CC valence vibration which has the character of a ring pulsation is observed for I: $n = 2$ near 870 ± 20 cm^{-1}, for $n = 3$ near 760 cm^{-1}, and in the case of $n = 4$ in the (700 ± 25)-cm^{-1} region. These spectroscopic findings suggest that substitution at either or all of the 1, 2, and 3 ring atoms of compounds of type I by "neutral" organic groups does not exhibit any pronounced influence on the nature of the bonding within the ring.

The preparation of heterocyclic boron–nitrogen compounds as possible carcinostatic agents appears to be a worthwhile undertaking if their hydrolytic instability can be reduced.[16] Qualitative data indicate that 1,3-dimethyl-1,3,2-diazaboracycloalkanes may be more stable to hydrolysis by a factor of about 10 than their unsubstituted or unsymmetrically substituted (*i.e.*, $R' = H$, $R'' = CH_3$) counterparts. Furthermore, it has been demonstrated that 1,3,2-diazaboracycloalkanes are useful precursors for the synthesis of novel types of heterocycles containing boron and nitrogen,[17-19] and thus the synthesis of the N-substituted derivatives as described in this work may offer additional and interesting preparative possibilities.

On considering the present research in conjunction with previous work,[18] it now appears possible to formulate a mechanism for the reaction depicted in eq 1. It is likely that in the first step of the reaction only one dimethylamino group is separated from the bis(dimethylamino) borane as illustrared in eq 2. The

$$RB[N(CH_3)_2]_2 + HR'N-(CH_2)_n-NR''H \longrightarrow \underset{\text{III}}{(CH_3)_2N-BR-NR'-(CH_2)_n-NR''H} + (CH_3)_2NH \quad (2)$$

postulated mechanism is supported by the fact that in general about 60–80% of the dimethylamine expected according to eq 2 can be pumped off after mixing the reactants at room temperature. At this point, spectroscopic investigation of the reaction mixture fails to provide any evidence of the existence of cyclic σ-bonded structures. All attempts to isolate pure compounds of type III, however, have been unsuccessful. It is likely that III exists as a coordinated cyclic structure IV, and attempts to prepare adducts of III have failed.



IV

Isolation of III (or IV, respectively) by distillation could not be achieved, since, in the second step of the over-all reaction depicted in eq 1, the all-σ-bonded system I is formed by intramolecular condensation of III or IV, respectively, at elevated temperatures. The temperature of condensation is, however, much lower than the boiling point anticipated for a material of either type III or IV. It should be noted that aminoboranes of the type $R_2B-NR'-(CH_2)_n-NR''H$ (R, R′, $R'' =$ alkyl) are known and have been reported to exist as coordinated heterocycles.[4]

That the second step of the reaction may be influenced by steric factors is illustrated by the following. An examination of molecular models reveals that in the case of III, $n = 2$, 3, or 4, the NHR″ group may be located contiguous to the $B-N(CH_3)_2$ part of the molecule. This circumstance is not as probable, however, if the carbon chain of III contains a double bond which reduces the free rotation within the molecule. Consequently, in the latter case linear polymerization of III through elimination of dimethylamine may compete strongly with the cyclization and thus account for the low yield of II. Since hydrolysis of the residual material results in almost quantitative recovery of the initial olefinic diamine, polymerization of the CC double bonds is highly improbable.

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