is not enough to bring the over-all molecular moment up to the value for $CH_3NH_2BH_3$ or H_3NBH_3. In trimethylamine the lone-pair moment of the free base is even lower ($\mu_{\mathrm{e}2} = 0.21$) and the moment of $(CH_3)_3NBH_3$ is lower than that of any of the other three amine boranes.

The effects of the lone pair and the general loosening effect of methyl substitution can be seen by subtracting the value of the lone-pair moment of the free amine from the measured moments of the amine boranes. The values from the middle curve in Figure 2 have been subtracted and the difference plotted in the lower curve of Figure 3. The rising curve indicates that the lone-pair contribution was indeed responsible for the rise and fall of the original curve. The rise of the difference curve reflects the fact that each methyl group tends to loosen the electron cloud so that the polarization of this cloud by the BH_3 group gets larger in the series from NH_3 to $N(CH_3)_3$. The pK data suggest that the most pronounced loosening effect is created by the first methyl group when one goes from NH_3 to NH_2CH_3. This same fact is illustrated by the fact that the difference curve is higher at methylamine than would be expected by a strictly linear relationship.

The foregoing arguments can be summarized as follows. The variation in the moments of amine boranes with alkyl substitution on the nitrogen will be determined by the effects discussed in the section on the methylamines. (1) Replacement of a hydrogen by an alkyl group loosens the electron cloud, particularly of the lone pair. (2) Alkyl groups tend to polarize this cloud toward the alkyl group itself, thus lowering the moment of the free electron pair in the amine or the over-all molecular moments of the amine boranes. A quantitative estimate of the alkyl polarization effect is provided by the variation of the moment of the uncoordinated pair of the free amine shown in Figure 2. (3) Borane groups also tend to polarize the loosened electron cloud; this borane polarization effect tends to increase the moment. A quantitative illustration of this effect is provided by the curve showing the difference between the lone-pair moment and the moments of the amine boranes (lower curve, Figure 3). Such subtraction eliminates the polarization effects due to the alkyl groups (item 2, above) and leaves only borane polarization effects. The significant "loosening effect" or increase in polarizability due to the first alkyl group is clearly apparent in this curve. Smaller effects appear for the succeeding two replacements.

Since the curves in Figure 2 are nearly parallel, the same result would be obtained, regardless of the curve selected from Figure 2. While the absolute scale would shift as one selects different curves in Figure 2, the curve shape and the significant trends would not be affected. The middle curve of Figure 2 was selected for drawing Figure 3 and for determining the size of the lone-pair moments cited since it represents values near the center of the possible range of bond moment values.

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The Structure of Phosphine Borane

BY R. W. RUDOLPH, R. W. PARRY, AND C. F. FARRAN

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On the basis of high-resolution nmr spectra it has been shown that the compound originally reported as $B_2H_6{\cdot}2PH_3$ is the monomer, H_3BPH_3, in the liquid state. Infrared and Raman spectra show that the same structure is maintained in the solid phase.

In 1940 Gamble and Gilmont prepared "diborane diphosphine" by mixing diborane and phosphine at low temperatures.[1] On the basis of rudimentary chemical evidence an analogy was drawn to the diammoniate of diborane and a structure analogous to that accepted at that time for $B_2H_6{\cdot}2NH_3$ was proposed, $[PH_4^+][H_3BPH_2BH_3^-]$. No molecular weight data were available to support the postulated ionic dimer.

Some of the reactions of $[H_3PBH]_n$ can be interpreted best in terms of a single monomeric formulation. For example, trimethylamine displaces PH_3 quantitatively to give $H_3BN(CH_3)_3$,[2] and a kinetic study of the reaction of B_2H_6 and PH_3 by Brumberger and Marcus[3] suggested the monomeric representation.

Since the original structural postulates were presented, a new model for $B_2H_6{\cdot}2NH_3$ has been accepted[4] in place of the earlier ammonium type of solid, $[NH_4^+][H_3BNH_2BH_3^-]$, but neither the new diammoniate

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[1] E. L. Gamble and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 717 (1940).

[2] See footnote 5 of ref 1.

[3] H. Brumberger and R. A. Marcus, *J. Chem. Phys.*, **24**, 741 (1956).

[4] D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958); S. G. Shore and R. W. Parry, *ibid.*, **80**, 12 (1958); R. C. Taylor, D. R. Schultz, and A. R. Emery, *ibid.*, **80**, 27 (1958); C. E. Nordman and C. R. Peters, *ibid.*, **81**, 3551 (1959).

model nor the monomeric model for $[H_3BPH_3]_n$ rationalized the known reaction with ammonia as easily as did the earlier dimeric formulation proposed by Gamble and Gilmont

$$NH_3 + [PH_4^+][H_3BPH_2BH_3^-] \rightarrow [NH_4^+][H_3BPH_2BH_3^-] + PH_3$$

No physical evidence for the structure has been presented.[4a]

In view of the foregoing facts, nmr, infrared, and Raman studies of phosphine borane have been completed; they show that the product obtained from the reaction of B_2H_6 and PH_3 is unequivocally the monomer H_3BPH_3 in the molten state at 37° and that this structure is maintained in the solid.

Experimental Section

Materials.—Diborane obtained from Callery Chemical Co., Callery, Pa., was purified before use by fractional condensation in the vacuum line.

Phosphine was prepared by the pyrolysis of phosphorus acid[5] at 200–250°.

All reagents were checked for purity by vapor pressure and infrared spectroscopy.

Procedures.—Standard high-vacuum techniques were used in the manipulation of all reagents. Typically, the nmr sample was prepared *in situ* by condensing 1.91 mmoles of phosphine and 0.98 mmole of diborane into a semimicro nmr tube,[6] sealing the tube under vacuum, and then allowing the reactants to warm slowly to 25°. The white solid melted at 32–33° in the nmr tube without apparent decomposition.

The ^{11}B nmr spectrum was obtained at 37° with a Varian Associates nmr spectrometer operating at 32.1 Mc. Proton spectra were obtained under similar conditions on the Varian A-60. Chemical shifts were obtained by tube interchange and were not corrected for differences in bulk susceptibility.

The infrared spectrum of the solid was observed in transmission through a thin film deposited on the CsI window of a cold cell similar to that described by Wagner and Hornig.[7]

The phosphine borane was prepared in a bulb attached to the cell by maintaining a mixture of liquid phosphine and liquid diborane at −105° until an appreciable amount of white solid had formed. The excess reactants were removed by pumping while the product was maintained at −105°. The solid product was sublimed directly onto the CsI window which was maintained at −180° and the spectrum recorded with a Beckman IR-12 from 200 to 4000 cm^{-1}.

Sample preparation for determination of the Raman effect was similar to that used for the infrared sample; however, the solid was formed in a 5-mm o.d. Pyrex tube which was then sealed under vacuum and transferred to a cold cell designed especially for the determination of the Raman spectrum of a solid at −180°.[8]

The Raman spectra were recorded photographically on Eastman Kodak IIa-0 plates. Exposure times ranged from 16 to 72 hr depending on whether front or back illumination was used. Details of the experimental arrangement are similar to those described by Dahl and Wyma.[8] The monochromator system excluded essentially all of the light generated by two General Electric AH-4 lamps except for 50% of the 4358-A mercury exciting line.

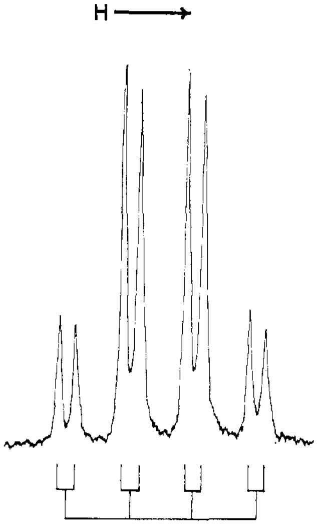

Figure 1.—^{11}B nmr spectrum of $H_3P \cdot BH_3(l)$. J_{PB} = 27 cps; $J_{BH'}$ = 103 cps.

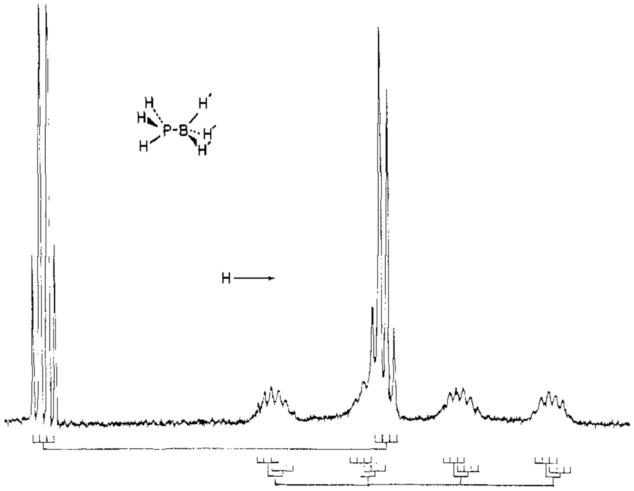

Figure 2.—^1H nmr spectrum of $H_3P \cdot BH_3(l)$. J_{PH} = 372 cps; $J_{BH'}$ = 104 cps; $J_{PH'}$ = 16 cps; and $J_{HH'}$ = 8 cps.

Discussion

The ^{11}B Nmr Spectrum (32.1 Mc).—The ^{11}B nmr spectrum of molten H_3BPH_3 at 37° consists of a 1:3:3:1 quartet of doublets centered 60.8 ppm upfield from $B(OCH_3)_3$. The three magnetically equivalent protons split the boron signal into a quartet (J_{B-H} = 103 cps); then each member of the quartet is split into a doublet by coupling with the phosphorus ($I = ^1/_2$) (J_{B-P} = 27 cps). While the 1:3:3:1 quartet of doublets would be expected for both models, H_3BPH_3 and $PH_4[H_3BPH_2BH_3]$, the coupling constant, J_{B-H} = 103 cps, compares well with the values (J_{B-H} = 100 cps) obtained by Gilje[9] for $CH_3PH_2BH_3$ and the values (J_{B-H} = 96 cps, σ = 55.6 upfield from $B(OCH_3)_3$) obtained by Phillips, Miller, and Muetterties[10] for $HP(CH_3)_2BH_3$.

The Proton Nmr Spectrum (60 Mc).—The ^1H nmr

[4a] Note Added in Proof.—After completion of this study a dissertation by Edward L. McGandy, completed in the laboratory of Professor Klaas Eriks [*Dissertation Abstr.*, **22**, 754 (1961)] was kindly brought to our attention by Dr. Robert L. Kuczkowski. The work of McGandy and Eriks provides the first unequivocal evidence for the structure of H_3BPH_3 and gives a structure identical with that arrived at here by spectroscopy. Our conclusions are applicable to the material in both liquid and solid forms.

(5) D. Gokhole and William L. Jolly, *Inorg. Syn.*, to be published.

(6) NMR Specialties Inc., New Kensington, Pa.

(7) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

(8) R. C. Taylor, A. J. Dahl, R. J. Wyma, and C. F. Farran, to be published; A. J. Dahl, Ph.D. Dissertation, University of Michigan, 1963; R. J. Wyma, Ph.D. Dissertation, University of Michigan, 1964.

(9) J. W. Gilje and R. W. Parry, to be published; J. Gilje, Ph.D. Dissertation, The University of Michigan, Ann Arbor, Mich., 1965.

(10) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

TABLE I

VIBRATIONAL SPECTRA OF $H_3BPH_3(s)$

Infrared				Raman[a]	
Frequency, cm^{-1}	Intensity[b]	Remarks	Assignment and symmetry	Frequency, cm^{-1}	Intensity[b]
447.1	w		ν_{12}, PH_3 rock, e	451	w
563.7	w	^{11}B	ν_4, P–B str, a_1	572	m
576.6		^{10}B			
829.5, 825.9, 822.5	w	Split in crystal, overlap of ^{11}B and ^{10}B motions	ν_{10}, BH_3 rock, e	*c*	
968.7	vs	^{11}B	ν_8, HBH def, e	*c*	
988.2		^{10}B			
1068.9	m	^{11}B	ν_2, HBH def, a_1	*c*	
1077.5		^{10}B			
1103.1, 1100.8	w	Split in crystal	ν_{11}, HPH def, e	1102	m
1141.1	m		ν_5, HPH def, a_1	1144	w
2263.8	w		Combination	*c*	s
2272.8	w		$2\nu_5$		
2361.5	s		ν_3, PH str, a_1	2363	s
2392.0	vs		ν_1, BH str, a_1	2401	vs
2399.1	vs		ν_7, BH str, e		
2426.0, 2421.7	s	Split in crystal	ν_9, PH str, e	2416	w, sh

[a] Both ^{10}B and ^{11}B motions could not be resolved in the Raman effect; the Raman spectrum of liquid H_3BPH_3 agreed closely with that of the solid, providing additional evidence for the proposed structure. [b] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [c] Very weak band observed; however, determination of position difficult.

spectrum of $H_3PBH_3(l)$ at 37° shows only two clear groups of hydrogen signals indicating the presence of two hydrogen atom environments in the molecule. A 1:1:1:1 quartet is found centered 0.53 ppm downfield from TMS while a doublet is displayed 4.31 ppm downfield from TMS. The quartet at 0.53 ppm is attributed to the borane hydrogen atoms split into a 1:1:1:1 quartet by ^{11}B ($I = {}^3/_2$). The value of J_{B-H} (104 cps) is in good agreement with the value reported from the ^{11}B spectrum (103 cps) and with that found in $H_2CH_3PBH_3$ (100 cps). The doublet at 4.31 ppm due to coupling of phosphorus with hydrogen shows a J_{P-H} coupling constant of 372 cps which checks well with the value of 370 cps reported by Gilje for $H_2CH_3PBH_3$. Careful examination of each component of the phosphine doublet reveals a 1:3:3:1 quartet (J_{HP-BH} = 8 cps) which would be expected from coupling of the three borane hydrogens with the hydrogens attached to phosphines. Coupling with the borane hydrogens rather than with the boron ($I = {}^3/_2$) is indicated by the 1:3:3:1 line intensities in the quartet. Boron coupling would give 1:1:1:1 line intensities. Such H–P–B–H coupling was also observed by Shoolery[11] in an earlier nmr study of $(CH_3)_2HPBH_3$, where the coupling constant J_{HP-BH} was listed as 6 cps.

The spin–spin splitting pattern of hydrogens attached to phosphorus is consistent with the H_3BPH_3 model but is not consistent with the formula $[PH_4^+][H_3BPH_2BH_3^-]$. In the latter representation each member of the P–H doublet should be split into a septet of intensities 1:6:15:20:15:6:1. Even if the outer member of the septet were obscured by low signal intensity, the pattern would be clearly different from the 1:3:3:1 pattern observed.

Under higher resolution each member of the *borane quartet* was seen to consist of a 1:3:4:4:3:1 six-line multiplet as would be expected for two overlapping 1:3:3:1 quartets. One can identify a doublet arising from spin–spin coupling between the borane hydrogens and the phosphorus nucleus of H_3BPH_3 (J_{PBH} = 16 cps) with each member of the doublet split into overlapping 1:3:3:1 quartets by the three phosphine hydrogens (J_{HPBH} = 8 cps).

This spin–spin splitting pattern is completely consistent with the formula H_3BPH_3. It is not consistent with the formula $[PH_4^+][H_3BPH_2BH_3^-]$ where each component of the P–B–H doublet would be split into a 1:2:1 triplet instead of the quartet by two hydrogens (rather than three) attached to the phosphorus.

Finally, peak intensities in the proton spectra are in good agreement with predictions of the formula H_3BPH_3. Boron in the sample is about 80% ^{11}B and 20% ^{10}B. The ^{11}B with a nuclear spin of ${}^3/_2$ gives rise to the quartets observed above. The ^{10}B with a nuclear spin of 3 gives rise to a septet which is not detectable above the background and which is not included in the ^{11}B quartet intensities. Phosphorus with only a single magnetic nucleus does not split the P–H signal beyond the doublet. Thus, the compound H_3BPH_3 should show a ratio of $H_{boron-11}$ to $H_{phosphorus}$ of 0.8 to 1.0 or 0.80. The observed ratio in the spectrum is 0.8 to 1.

The foregoing spectra indicate conclusively that molten $[H_3BPH_3]_n$ is the simple acid–base monomer, H_3BPH_3, not the compound $[PH_4^+][H_3BPH_2BH_3^-]$.

The Infrared and Raman Spectra of $PH_3 \cdot BH_3(s)$

Although the nmr spectra of $H_3P \cdot BH_3(l)$ are consistent with the monomeric structure, on the basis of these data alone one cannot be assured that this structure is maintained upon transition to the solid state. However, we believe the infrared and Raman spectra of $H_3P \cdot BH_3(s)$ are indicative of the monomeric structure for the solid, too. The monomer should display an ethane-type configuration with C_{3v} symmetry for which 11 infrared-active motions would be expected—four

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(11) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

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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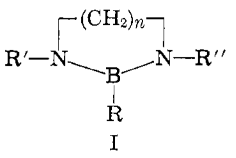
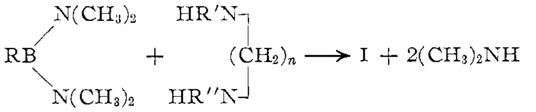
Boron- and nitrogen-substituted 1,3,2-diazaboracycloalkanes have been prepared by a transamination between bis(dimethylamino)boranes and α,ω-diamines. Partial substitution of the nitrogen of the diamine does not appear to inhibit this reaction; five-, six-, and seven-membered heterocyclic systems are 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. Moreover, the six cited exceptions[5–8] are all 1,3,2-diazaboracyclopentanes (*i.e.*, I, $n = 2$) in which $R' = R''$.



I

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.



$$RB\left<\begin{matrix}N(CH_3)_2\\N(CH_3)_2\end{matrix}\right. + \left.\begin{matrix}HR'N\\HR''N\end{matrix}\right>(CH_2)_n \longrightarrow I + 2(CH_3)_2NH \qquad (1)$$

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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.

[3] J. Goubeau and A. Zappel, *Z. Anorg. Allgem. Chem.*, **279**, 38 (1955).

[4] K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Springer-Verlag, New York, N. Y., 1965.

[5] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

[6] P. Fritz, K. Niedenzu, and J. W. Dawson, *ibid.*, **3**, 626 (1964).

[7] E. W. Abel and R. P. Bush, *J. Organometal. Chem.* (Amsterdam), **3**, 245 (1965).

[8] G. Hesse and A. Haag, *Tetrahedron Letters*, **16**, 1123 (1965).