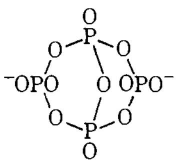
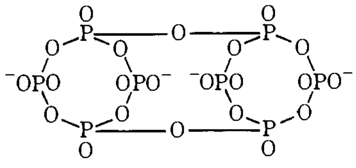
group. The requirement of chemical equivalence supports a rather simple cage structure such as I and II.



I



II

From reaction of P_4O_{10} with diisopropylurea in tetramethylurea (and thus reversing the carbodiimide condensation), it is found that the doubled-triplet nmr pattern discussed above appears with some other nmr signals, while the particles of phosphorus pentoxide are observed to be readily dispersible and not gummy.[14] This finding supports the choice of structure I for the subject compound. Although this particular $M_2P_4O_{10}$ structure (I) has been postulated many times[15,16] with respect to the solvolyses of the P_4O_{10} molecule, this is the first evidence for its existence.

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(14) J. R. Van Wazer and S. Norval, *J. Amer. Chem. Soc.*, **88**, 4415 (1966).

(15) See p 694 of ref 2.

(16) G. Burkhardt, M. P. Klein, and M. Calvin, *J. Amer. Chem. Soc.*, **87**, 591 (1965). (The reader is referred to ref 14 for a reinterpretation of the findings of this paper.)

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Reactions of Hexaborane(10) with Molecular Lewis Bases. Proton Abstraction and Molecular Addition

Sir:

Although strongly basic anions have been shown to deprotonate B_6H_{10} through removal of a bridge proton to form $B_6H_9^-$,[1,2] the effect of molecular bases on hexaborane(10) until the present study has been relatively unexamined with the exception of a previous report of an adduct with triphenylphosphine in a 1:1 molar ratio.[3] We, however, observe the formation of $B_6H_{10}[P(C_6H_5)_3]_2$. Indeed, adducts of composition $B_6H_{10}L_2$, where L = $N(CH_3)_3$, $P(CH_3)_3$, and $P(C_6H_5)_3$, have been isolated in this laboratory and are apparently molecular addition compounds. On the other hand, ammonia reacts with hexaborane(10) according to the following deprotonation reaction

$$B_6H_{10} + NH_3 \longrightarrow NH_4^+B_6H_9^-$$

This result suggests that B_6H_{10} is a significantly stronger Brønsted acid than could be inferred from earlier observations of acidity[1,2] and is further support for an earlier suggestion by Parry and Edwards[4] that the bridge hydrogens of the boron hydrides are sufficiently acidic to interact with ammonia.

Hexaborane(10) in liquid ammonia (−78 to −33°) and 1 NH_3:1 B_6H_{10} mixtures in THF (−78 to −45°) and $(C_2H_5)_2O$ (−78 to −70°) produced boron-11 nmr spectra which revealed the presence of only $B_6H_9^-$ over the temperature ranges indicated. At more elevated temperatures in THF and $(C_2H_5)_2O$ a competing reaction involving bridge cleavage of the B_6 framework predominated. This competing reaction, details of which will be reported at a later date, is believed to be analogous to the reaction of NH_3 with B_5H_9, recently reported by Kodama,[5] in which $BH_2(NH_3)_2^+B_4H_7^-$ was formed. It is of interest to note that Johnson and Shore[6] have recently shown that competing reactions occur between B_4H_{10} and NH_3 in $(C_2H_5)_2O$. Depending upon reaction conditions chosen either $NH_4^+B_4H_9^-$ or $BH_2(NH_3)_2^+B_3H_8^-$ can be made to be the predominant product.

In addition to the nmr data indicating deprotonation of B_6H_{10} by NH_3, further evidence was obtained through the following metathesis reaction in which NH_4Br precipitated and from which $N(n\text{-}C_4H_9)_4B_6H_9$ was isolated from the filtrate.

$$NH_3 + B_6H_{10} + N(n\text{-}C_4H_9)_4Br \xrightarrow[\text{(small amount of THF)}]{CH_2Cl_2} N(n\text{-}C_4H_9)_4B_6H_9 + NH_4Br\downarrow$$

To a reaction vessel fitted with a glass frit, 2.03 mmol of B_6H_{10} and 4.12 mmol of NH_3 were distilled into a solution of 2.07 mmol of $N(n\text{-}C_4H_9)_4Br$ in 25 ml of CH_2Cl_2 and 5 ml of THF. A white precipitate formed which was always maintained between −78 and −45°. Filtration on the vacuum line allowed isolation (98% theory) and identification of the precipitate which was shown to be NH_4Br from its X-ray powder diffraction pattern. Volatiles were distilled from the filtrate and separated. A 2.06-mmol quantity of NH_3 was recovered, thereby indicating a reaction ratio of 1.00 NH_3:1.00 B_6H_{10}. The solid which remained upon removal of volatiles from the filtrate was shown to be $N(n\text{-}C_4H_9)_4B_6H_9$ from its X-ray powder pattern compared with that of an authentic sample of this salt.[7] This metathesis reaction is the simplest method available for preparing $N(n\text{-}C_4H_9)_4B_6H_9$.

Attempts to prepare $N(n\text{-}C_4H_9)_4B_5H_8$ through an equivalent metathesis reaction involving equimolar mixtures of B_5H_9, NH_3, and $N(n\text{-}C_4H_9)_4Br$ in methylene chloride in the presence of THF failed, presumably because of the weaker Brønsted acidity of B_5H_9 than B_6H_{10}. On the other hand, B_5H_9 can apparently be deprotonated by NH_3 in liquid NH_3.[8]

The bis-$N(CH_3)_3$ and bis-$P(CH_3)_3$ adducts of B_6H_{10} were best prepared in hydrocarbon solvents such as

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(1) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

(2) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 9, 908 (1970).

(3) R. E. Williams and F. J. Gerhart, *J. Amer. Chem. Soc.*, **87**, 3513 (1965).

(4) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).

(5) G. Kodama, *ibid.*, **92**, 3482 (1970).

(6) H. D. Johnson, II, and S. G. Shore, *ibid.*, in press.

(7) Authentic samples of $N(n\text{-}C_4H_9)B_6H_9$ were prepared through the following metathesis reaction which was developed by Mr. Vincent Brice of this laboratory

$$N(n\text{-}C_4H_9)_4I + KB_6H_9 \xrightarrow{CH_2Cl_2} N(n\text{-}C_4H_9)_4B_6H_9 + KI\downarrow$$

(8) G. Kodama and R. W. Parry, private communication.

methylcyclohexane or *n*-heptane, while the bis-$P(C_6H_5)_3$ adduct was prepared in $(C_2H_5)_2O$. Tensiometric titrations at 0° established stoichiometries of reactions involving the volatile ligands. Elemental analyses established compositions of all of the adducts. Thermal stabilities are in the following order of ligands

$$P(C_6H_5)_3 > P(CH_3)_3 \gg N(CH_3)_3$$

The phosphine adducts are stable at 100°, while the amine adduct decomposes noticeably at room temperature under vacuum after a period of about 1 day. With the exception of the bis-$P(C_6H_5)_3$ adduct, which is significantly more stable than its counterpart with B_5H_9, thermal stabilities parallel those of the $B_5H_9L_2$ analogs.[9] The boron-11 nmr spectrum of B_6H_{10}-$[P(CH_3)_3]_2$ at 32 MHz consists of three peaks in the area ratio 2:2:2 (a doublet at 2.5 ppm, J_{BH} = 114 Hz; a singlet at 19.4 ppm; and a triplet at 50.2 ppm, J_{BH} = 105 Hz). The boron-11 nmr spectrum of B_6H_{10}-$[N(CH_3)_3]_2$ consists of two peaks in an area ratio of 4:2 (an asymmetric singlet at +21.6 ppm and a doublet at −2.1 ppm, J_{BH} = 96 Hz). All chemical shifts are given with respect to $BF_3 \cdot O(C_2H_5)_2$.

Attempts to produce a 1:1 adduct involving $N(CH_3)_3$ and B_6H_{10} always showed that the apparent reaction is in a 2:1 ratio of amine to B_6H_{10}. Thus, when equivalent amounts of $N(CH_3)_3$ and B_6H_{10} were placed in THF solution, the boron-11 nmr spectrum at −60° revealed the presence of $B_6H_{10}[N(CH_3)_3]_2$ and unreacted B_6H_{10} in apparently equal amounts. Addition of excess KH to the system at −78° produced 0.5 equiv of H_2 which came from the unreacted B_6H_{10}, since $B_6H_{10}[N(CH_3)_3]_2$ in THF does not react with KH in the temperature range −78 to −45°.

The $B_6H_9^-$ ion does not react with $N(CH_3)_3$ at low temperature in solution.

Acknowledgment. We wish to acknowledge, gratefully, support of this research through Grants No. GP-7557X and GP-8321 by the National Science Foundation.

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[9] M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

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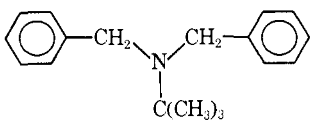
Nonequivalent Methylene Protons in Neopentylamines and Benzylamines[1]

Sir:

Two groups of workers have recently reported that separate proton-resonance lines are observed from the two methylene protons on each benzyl of dibenzylmethylamine at low temperatures.[2,3] In both cases the results were interpreted in terms of a slow nitrogen inversion, although Bushweller and O'Neil[2] point out that their observations could also be explained by a hindered rotation about the carbon–nitrogen bond. However, this explanation was rejected because the barrier to rotation for trimethylamine had been reported to be 4.4 kcal/mol[4] which was significantly smaller than the 6.0 ± 0.5 kcal/mol[5] estimated from the coalescence temperature for dibenzylmethylamine. Actually the two barriers are not comparable since the former is $\Delta H^{\ddagger}$ and the latter $\Delta G^{\ddagger}_{127}$. We wish to present some results from a continuing study of benzyl- and neopentylamines which suggest that it may be hindered rotation rather than slow inversion which gives rise to the proton nonequivalence.

Proton resonance spectra were obtained on a Varian Associates HA 100D spectrometer. At very low temperatures where concentrations were limited by solubility, spectra were sometimes obtained by the Fourier transform technique.[6] Exchange rates were determined by comparison with theoretical spectra which were calculated as previously described.[7] From these results it was possible to calculate enthalpies and entropies of activation for the process producing equivalence of the methylene protons. All errors listed are standard deviations.



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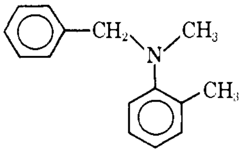

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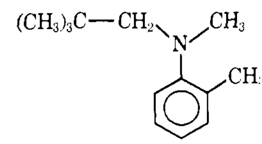

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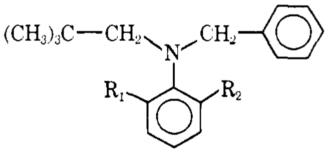

4a, $R_1 = H$; $R_2 = CH_3$
4b, $R_1 = R_2 = H$
4c, $R_1 = R_2 = CH_3$

Broadening and separation of the methylene signal for **1** dissolved in CF_2Cl_2 was observed in the temperature range 163–123°K (δ_{AB} = 0.56 ppm, $\Delta H^{\ddagger}_{298}$ = 3.7 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −19 ± 18 eu). Similar results were found for **2** (δ_{AB} = 0.60 ppm, $\Delta H^{\ddagger}_{298}$ = 3.7 ± 0.2 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −21 ± 7 eu). The coalescence temperature of **1** is 130°K with $\Delta G^{\ddagger}_{127}$ = 6.1 kcal/mol; for **2**, 133°K with $\Delta G^{\ddagger}_{127}$ = 6.2 kcal/mol; compared with 127°K and $\Delta G^{\ddagger}_{127}$ = 6.0 kcal/mol[2] and 136°K and $\Delta G^{\ddagger}$ = 6.5 kcal/mol[3] for dibenzylmethylamine. The lines from the neopentyl methylene protons of solutions of **3** and **4a** dissolved in CS_2 broadened and split in the temperature range 200–160°K. For **3**, δ_{AB} = 0.69 ppm with $\Delta H^{\ddagger}_{298}$ = 8.5 ± 0.2 kcal/mol, $\Delta S^{\ddagger}_{298}$ = 1 ± 5 eu. For **4a**, δ_{AB} = 0.59 ppm with $\Delta H^{\ddagger}_{298}$ = 7.7 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −5 ± 9 eu. At low temperatures separate signals were observed for each of the methylene protons of the

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[1] Issued as NRCC No. 11700.

[2] C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970).

[3] M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

[4] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).

[5] Dewar and Jennings[3] give 6.5 kcal/mol.

[6] R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

[7] S. Brownstein, E. C. Horswill, and K. U. Ingold, *Can. J. Chem.*, **47**, 3243 (1969).