tance of 1.70 Å in this study is almost 0.08 Å shorter than the only other similar distance in the literature[10] (1.78 Å). Of course, no previous value of a P–C distance in a phosphetane ring is known. However, our average value of 1.925 Å is larger than all previously reported P–C distances which range from 1.78 to 1.84 Å.[9–13]

The phosphetane ring presents some interesting features of its own. First, the unique hydrogen on C-2 is *trans* to the phenyl ring. Secondly, the phosphetane ring is decidedly nonplanar with an angle between the planes defined by (C-1–C-2–C-3) and C-1–P–C-3) of 24°. Thirdly, the internal angle at the phosphorus is 82.6° with the adjacent angles averaging to 84.7 ± 0.7° and the internal angle opposite the phosphorus (at C-2) opening up to 103.1°. Finally, the C–C bonds in the phosphetane ring average to 1.614 Å. These do not differ in a statistically significantly manner from their expected values of 1.54 Å. However, these longer distances coupled with the long P–C distances in the phosphetane ring strongly support the chemical evidence which shows that the ring is highly susceptible to ring opening at the 1–2 positions. It further suggests that a study of an unsymmetrically substituted phosphetane ring should be carried out to see whether these distances would still be equivalent, or whether the 1–2 distance would be longer than the 1–4 distance as is suggested by its ring-opening reactions[2] and in analogy to the azetidine ring studies.[14]

Acknowledgments. The authors wish to express their gratitude to the National Institutes of Health (GM-08348-08) for financial assistance in support of this and subsequent studies; to Professor S. E. Cremer, Department of Chemistry, Illinois Institute of Technology; and to the Computer Centers at Louisiana State University at Baton Rouge and Louisiana State University at New Orleans (NSF-GP-2964).

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Barriers to Internal Rotation in Aminoboranes and in Octamethyloxamidinium Bromide[1]

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Abstract: Barriers to rotation about BN bonds have been studied by nmr spectroscopy in *n*-butyl- and phenylbis(dimethylamino)borane, in tris(dimethylamino)borane, in bis(dimethylamino)methylphenylaminoborane, and in tetrakis(dimethylamino)diborane(4), and about CN bonds in octamethyloxadiamidinium dibromide. Activation parameters are reported for those compounds where the barriers were high enough to be measured.

Since aminoboranes are isoelectronic with olefins, the BN bonds in them are expected to have significant π character;[3] rotation about such bonds should be correspondingly hindered, and with suitable substituents, *cis–trans* isomerism should be observed. Isomerism of this kind was first inferred by Niedenzu and Dawson[4] from the long boiling ranges and vapor pressure characteristics of such compounds, and was subsequently confirmed by standard nmr spectroscopic techniques. The first measurement of this kind was reported for (methylphenylamino)dimethylborane (I), leading to a preliminary estimate[5] of 15 ± 3 kcal/mol for the height of the rotational barriers; this was later revised[6] to 10.8 ± 0.7 kcal/mol, while a third estimate[7] puts the barrier at 18.8 ± 0.3 kcal/mol. Barriers to B–N rotation have also been reported for (dimethylamino)phenylchloroborane (II) (18 ± 2 kcal/mol[8]), for two series of aminoboranes III and IV where the barriers varied from 9.9 kcal/mol for IIIe to 26.6 kcal/mol for IVa, the rest lying between 14 and 19 kcal/mol,[7] and for dimethylaminovinylbromoborane (14.0 ± 0.4 kcal/mol[9]).

In compounds I–IV, either nitrogen or boron carries identical substituents, so *cis,trans* isomerism could not be distinguished. Distinguishable isomers have been detected by nmr spectroscopy in the case of methylphenylaminoethoxymethylborane (V),[10] (methylphenyl-

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(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) Israel Mining Industries, Haifa, Israel.

(3) E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

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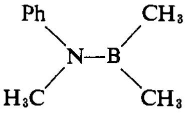
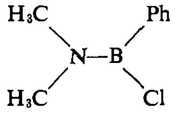
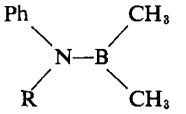
(10) H. T. Baechle and H. J. Becher, *Spectrochim. Acta*, **21**, 579 (1965).



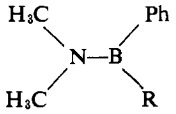
I



II



IIIa, R = Me
b, R = Et
c, R = *i*-Pr
d, R = *i*-Bu
e, R = *t*-Bu



IVa, R = Me
b, R = Et
c, R = *i*-Pr
d, R = *i*-Bu
e, R = *t*-Bu

amino)methylphenylborane (VII),[10-12] and bis(benzylamino)phenylborane (VII).[13]

PhMeNBMeOEt	PhMeNBMePh	$(PhCH_2NH)_2BPh$
V	VI	VII

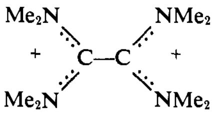
We became interested in this problem in connection with attempts to carry out MO calculations for boron compounds. Recent work in these laboratories has led to the development of two very successful semiempirical SCF–MO treatments of ground states of molecules, one based[14] on the Hückel σ,π approximation, and the other on an approach in which all the valence electrons are taken into account.[15] In order to extend these treatments to compounds containing boron, it is necessary to have suitable thermochemical data in order to determine the various parameters involved. Unfortunately, few reliable heats of formation are available for organoboron compounds, due to their reluctance to undergo complete combustion; the only really satisfactory technique is to measure their heats of combustion in fluorine, and few accurate measurements of this kind have as yet been reported. The barriers to rotation about BN bonds seemed to offer an attractive alternative; for the barrier height should be equal to the difference in energy between the molecule with the BN unit planar, and with it twisted through 90°. These energies can of course be calculated without much difficulty, and it is known[15d] that in the case of ethylene the calculated rotational barrier agrees well with experiment; equating calculated and observed barriers about BN bonds should therefore enable the corresponding MO parameters to be determined.

As indicated above, a number of measurements have been reported for compounds of the type R_2NBR_2 isoelectronic with olefins $R_2C{=}CR_2$; however none as yet seem to have been reported for bis and tris amides of the type $(R_2N)_2BR$ or $(R_2N)_3B$, compounds isoelectronic with amidinium and guanidinium ions, $(R_2N)_2CR^+$ and $(R_2N)_3C^+$. Data for such compounds would of course be especially valuable in the present connection, since the BN bond orders in the mono, bis, and tris amides differ far more than those in different mono amides. We have accordingly studied the barriers to BN rotation in *n*-butyl- (VIIIa) and phenyl- (VIIIb) bis(dimethylamino)boranes, in tetrakis(dimethylamino)diborane(4) (IX), in tris(dimethylamino)borane (X), and in bis(dimethylamino)methylphenylaminoborane (VIIIc). It is of course also useful to have data for the isoelectronic carbon systems for comparison; we have therefore also studied the bisamidinium ion (XI), isoconjugate with IX. The existence of hindered rotation in XI has been established,[16] but no quantitative studies of the barrier height have been reported.

$RB(NMe_2)_2$
VIIIa, R = *n*-Bu
b, R = Ph
c, R = NMePh

$(Me_2N)_2BB(NMe_2)_2$
IX

$(Me_2N)_3B$
X



XI

Experimental Section

Measurements on the aminoboranes were carried out using freshly distilled materials, the purity of which was checked by glpc. Table I lists their physical properties and references to their preparation. Tetrakis(dimethylamino)diborane(4) (IX) was a commercial sample,[17] purified by glpc before use. Octamethyloxadiamidinium dibromide (XI) was prepared according to Wiberg and Buchler,[16] mp 253–254° (lit.[16] 254°).

Table I. Properties of Compounds Used in Nmr Studies of Rotational Barriers

Compd	Ref	Bp, °C (mm)[a]	*n*D (*t*, °C)
VIIIa	*b*	53–55 (5) (37–38 (2))	
VIIIb	*c*	56 (0.5) (59 (3))	1.5155 (25)
VIIIc	*d*	80 (0.5) (68–69 (0.1))	1.5331 (24)
IX	*e*	52–54 (0.5) (55–57 (2.5))	1.4678 (22)
X	*f*	33 (5) (43 (12))	1.4450 (22)

[a] Literature value in parentheses. [b] N. Noth and P. Fritz, *Z. Anorg. Allgem. Chem.*, **322,** 297 (1963). [c] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1,** 738 (1962). [d] R. J. Brotherton and T. Buckman, *ibid.*, **2,** 424 (1963). [e] R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82,** 6242 (1960). [f] H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 4024 (1953).

The proton nmr spectra were measured using a Varian DP-60 spectrometer probe especially modified for low temperature by Dr. Ben A. Shoulders. Down to −80°, trichlorofluoromethane (Matheson, "Freon-11," 99.9% minimum purity) was used as solvent, and below this dichlorodifluoromethane (Matheson, "Freon-12," 99.0% minimum purity). Tetramethylsilane (TMS) was used as internal standard, the spectra being calibrated with the aid of radiofrequency side bands. Measurements above room temperature were carried out with a Varian A-60 spectrometer with variable-temperature probe. Temperatures were controlled to ±1°.

Results

As would be expected, the methyl signal from X remained single down to the lowest temperatures studied (−145°); the remaining compounds, however, all showed splitting of the NMe_2 methyl peak at low temperatures, due to restricted rotation about the $>BNMe_2$ bond. In the case of VIIIa, the splitting was too small for the methyl signals to be clearly re-

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(11) H. T. Baechle, H. J. Becher, H. Beyer, W. G. Brey, Jr., J. W. Dawson, M. E. Fuller, II, and K. Niedenzu, *Inorg. Chem.*, **2**, 1065 (1963).

(12) H. J. Becher and H. T. Baechle, *Chem. Ber.*, **98,** 2159 (1965).

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(17) We are very grateful to U. S. Borax Research, Anaheim, Calif., for a gift of this material.

Table II. Nmr Parameters for Aminoboranes

Compd	Temp, °C	Chemical shifts[a] NMe	NMe	NMe	Ph	n-Bu
VIIIa	−127	7.4				8.9,[b] 9.0
VIIIb	−82	7.5	7.1		2.8[b]	
VIIIc	−44	7.6	7.3	7.15	3.15[b]	
IX	−80	7.29	7.44			

[a] On τ scale, measured at 60 MHz in 5% w/v solution in Freon-11, except for VIIIa (Freon-12). [b] Center of multiplet.

Table III. Activation Parameters for Aminoboranes and for Octamethyloxadiamidinium Dibromide

Compd	$\Delta\nu_{AB}$[a]	T_c,[b] °C	$\Delta H^{\ddagger}$, kcal/mol	ν_0, sec^{-1}	$\Delta S^{\ddagger}$,[c] eu	$\Delta G_c^{\ddagger}$,[c] kcal/mol	$\Delta G_c^{\ddagger}$,[d] kcal/mol
VIIIb	20.4	−69.7	11.1	7.6×10^{14}	3.7	9.9	10.4
VIIIc	16.0	−13.5	13.7	3.7×10^{14}	1.8	12.7	13.3
IX	8.6	−65.5	12.7	8.5×10^{15}	8.5	10.5	10.8
XI	18.0	119.0	25.0	8.1×10^{16}	11.7	19.6	20.3

[a] $\Delta\nu_{AB}$ is the difference in chemical shift between the resolved N-methyl signals in the absence of exchange, measured at 60 MHz. [b] Coalescence temperature. [c] Calculated from value of k given by eq 1. [d] Calculated from k_c, given by eq 2.

solved; the other amides all gave clearly resolved methyl peaks. Table II lists nmr parameters for these aminoboranes below their coalescence temperatures.

The rates of isomerization were estimated as a function of temperature by fitting the observed line shapes to the line-shape function of Gutowsky and Holm,[18] *i.e.*, in their notation

$$g(\nu) = \frac{k\tau(\nu_A - \nu_B)^2}{[{}^1\!/_2(\nu_A + \nu_B) - \nu]^2 + 4\pi^2\tau^2(\nu_A - \nu)^2(\nu_B - \nu)^2} \qquad (1)$$

where k is a normalizing constant. The calculations were carried out using the CDC 6600 digital computer at the University of Texas Computation Center. Rate constants (k_c) at the coalescence temperature (T_c°) were also calculated from the expression[18]

$$k_c = \pi\Delta\nu\sqrt{2} \qquad (2)$$

where $\Delta\nu$ is the limiting line splitting (in hertz) at low temperatures. Free energies ($\Delta G^{\ddagger}$), heats ($\Delta H^{\ddagger}$), and entropies ($\Delta S^{\ddagger}$) of activation were calculated from the rate constants using the usual Eyring equations

$$-RT \log k = \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (3)$$

The results are shown in Table III; the last two columns show values ($\Delta G_c^{\ddagger}$) of $\Delta G^{\ddagger}$ at the coalescence temperature (T_c), calculated from values of k given by eq 1 and 2, respectively. The values of $\Delta H^{\ddagger}$ seem to be reliable to ±1 kcal/mol, judging by the internal consistency of the rate constants as indicated by their reproducibility and the linearity of Arrhenius plots. The last two columns of Table III list values of $\Delta G_c^{\ddagger}$ corresponding to the rate constants k_c from eq 1 and 2, respectively.

The nmr spectrum of bis(dimethylamino)phenylborane (VIIIb) showed an unusual effect at low temperatures. Below the coalescence point and down to about −100°, the two N-methyl signals appeared as single sharp peaks, but below −100° the one at low field began to broaden while the one at high field remained sharp (Figure 1). A similar effect was observed in the case of IX though less clearly, due to the smaller separation between the methyl signals. In the case of VIIIa, the methyl signals were not resolved, but at low temperatures the line broadened asymmetrically; analysis with a DuPont 310 Curve Resolver showed that the peak could again be represented as a superposition of a sharp signal at high field and a broad one at low field (Figure 2). Neither VIIIc nor X showed any such effect, the methyl signals all broadening to a comparable extent at low temperatures and the broadening being little more than that shown by TMS (Figure 3). The ^{11}B nmr spectra of several of the aminoboranes were also measured, with the results shown in Table IV.

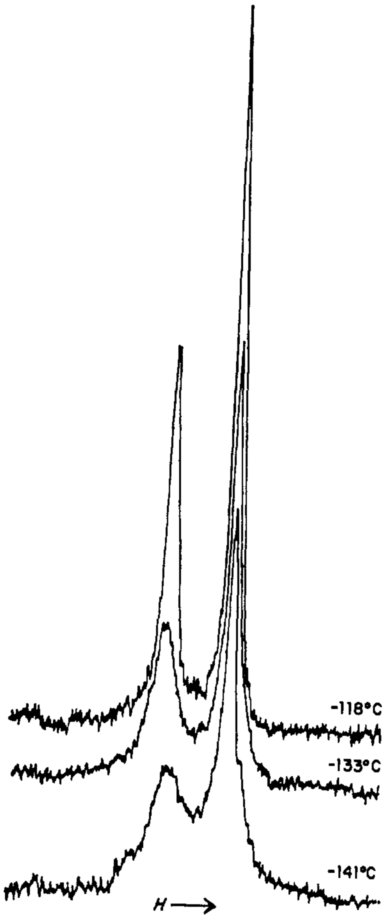

Figure 1. N-Methyl signals in the nmr spectra of VIIIb at low temperatures.

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[18] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965.

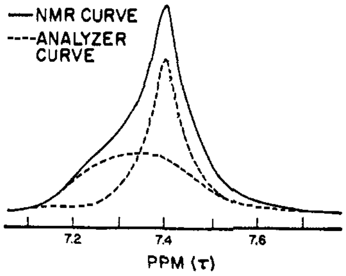

Figure 2. Analysis of the N-methyl nmr signal of VIIIa at −140°.

Discussion

Simple boron amides of the type R_2BNR_2 are isoelectronic with olefins, $R_2C{=}CR_2$, while bis amides of the type $RB(NR_2)_2$ are isoelectronic with allyl anions, $RC^{-}(CR_2)_2$. Now the total π-bond energy in allyl is less than twice that in an olefin; the energy required to twist through 90° about one of the CC bonds is therefore less than that required to twist the double bond of an olefin through 90°. One would therefore expect the BN rotational barriers in bis amides to be lower than those in mono amides; the results reported here seem to suggest that this is the case. Thus the barriers in bis amides seem to be about 12 kcal/mol (Table II), compared with 18.8 kcal/mol[7] for I (IIIa) and 26.6 kcal/mol[7] for IVa; the other isomers III and IV show somewhat lower barriers, probably due to steric hindrance of coplanarity. Admittedly a lower value (10.8 kcal/mol[6]) has been reported for I; however this value seems improbably low, and furthermore it was quoted only in a review article,[6] without experimental details. Equally, the value reported[7] for IVa seems improbably high.

Table IV. ^{11}B Nmr Spectra of Some Aminoboranes

Compd	Chemical shift[a]	Line width, Hz[b]
VIIIc	−27.9	253
IX	−36.4	126
X	−27.5	49

[a] In parts per million (ppm) relative to boron trifluoride etherate (BTE); spectra measured at 19.3 MHz using neat liquid and BTE as external standard on a Varian DP-60 spectrometer. [b] At half height.

Analogous reasoning would lead one to expect even lower barriers in trisamides, $B(NR_2)_3$; however our value for the $BNMe_2$ barrier in VIIIc was if anything slightly greater than those for VIIIb and IX. This discrepancy can, however, be attributed to steric effects; for examination of models shows that the three amino groups in VIIIc must be far from coplanar. Indeed, the most favorable arrangement seems to be one in which the two dimethylamino groups and the boron atom are approximately coplanar, while the methylphenylamino moiety lies in a plane almost perpendicular to the rest of the molecule; in this case the two NMe_2 groups will be equivalent, and the π MO's will comprise only the $B(NMe_2)_2$ system. The barrier to rotation should then be very similar to that in a typical bis amide such as VIIIb, as indeed it is.

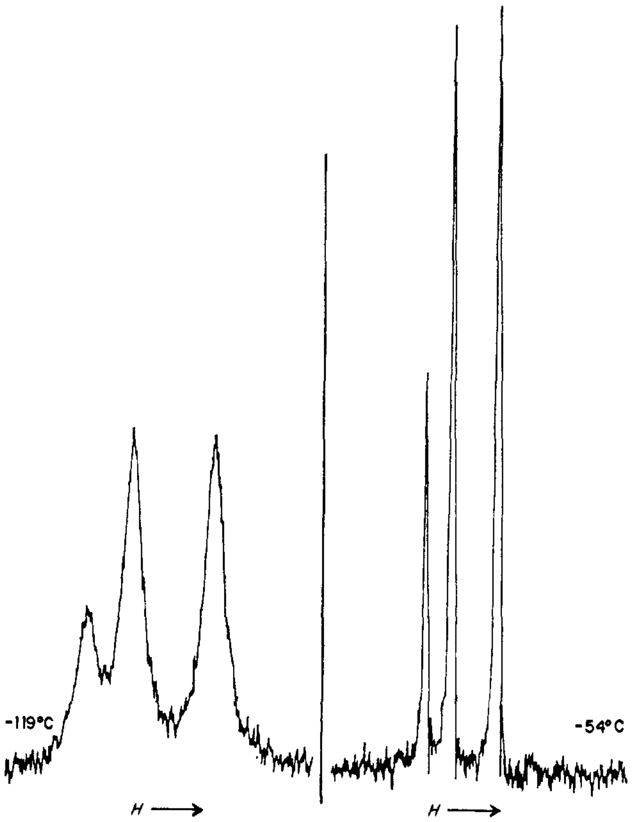

Figure 3. N-Methyl signals in the nmr spectra of VIIIc at low temperatures.

Admittedly the ^{11}B nmr data in Table III seem at first sight to be at variance with this suggestion; for the chemical shifts of VIIIc and X are similar, and both absorb upfield in comparison with IX. However the unshared nitrogen electrons of the -NMePh group could exert a shielding effect on boron, even if there is no direct π interaction between boron and nitrogen; this was pointed out in a recent communication[19] where it was shown that a large "lone pair effect" of this kind has to be postulated to account for the observed chemical shifts in boric esters and boron trihalides, and where a theoretical interpretation was also given.

Bis(amino)boranes are isoelectronic with amidinium ions; *cf.* IX with XI. However since boron is less electronegative than carbon, the sharing of the π electrons will be less uniform in the aminoboranes; there the nitrogen atoms will take a lion's share of the π electrons, and the π-bond orders of the BN bonds should therefore be less than those of the CN bonds in the isoconjugate amidinium ions. The barrier to rotation should consequently be less in the aminoborane, as indeed it is; thus the barrier in XI is about double that in IX.

In these considerations of steric and resonance effects, a vital factor is of course the geometry of the nitrogen atoms in aminoboranes; there seems as yet no clear agreement concerning this. Indeed, much confusion seems to exist generally in the literature as regards the conditions under which trivalent nitrogen adopts a planar, sp²-hybridized geometry. The following simple

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[19] F. A. Davis, M. J. S. Dewar, and R. Jones, *J. Am. Chem. Soc.*, **90**, 706 (1968).

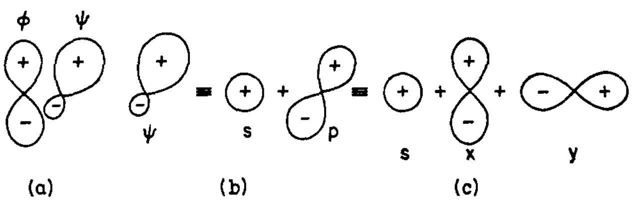

Figure 4. (a) Overlap between sp^3 AO (ψ) of nitrogen and p AO (ϕ) of an adjacent atom; (b) ψ expressed in terms of the 2s AO (s) of nitrogen and a p AO (p) lying along the axis of ψ; (c) ψ expressed in terms of s, and two 2p AO's lying parallel (x) and perpendicular (y) to ϕ.

argument[20] indicates that this is probably much less generally the case than has sometime been supposed.

Consider an sp^3-hybridized nitrogen adjacent to an atom with an empty 2p AO (ϕ), and oriented so that the lone pair AO (ψ) of nitrogen can interact with ϕ to form a π-like bond (Figure 4a). According to simple Hückel theory, the bond energy (E_π) of this bond will be approximately equal to minus twice the corresponding resonance integral, *i.e.*

$$E_\pi = -2\int \phi \mathrm{H} \psi \mathrm{d}\tau \qquad (4)$$

Now as indicated in Figures 4b and 4c, the hybrid AO ψ can be expressed in terms of the 2s AO (s) of nitrogen, and of two 2p AO's x and y (Figure 4c), as

$$\psi = \left(\frac{1}{4}\right)^{1/2}\mathrm{s} + \left(\frac{3}{4}\right)^{1/2}\mathrm{p} = \left(\frac{1}{4}\right)^{1/2} + \left(\frac{3}{4}\right)^{1/2}(x \sin\theta + y\cos\theta) \qquad (5)$$

when θ is the tetrahedral bond angle. Substituting this expression in eq 4

$$E_\pi = -2\int \phi \mathrm{H}\left[\left(\frac{1}{4}\right)^{1/2}s + \left(\frac{3}{4}\right)^{1/2} \times (x\sin\theta + y\cos\theta)\right]\mathrm{d}\tau \qquad (6)$$

$$= -2\left(\frac{3}{4}\right)^{1/2}\sin\theta \int \phi \mathrm{H} x \mathrm{d}\tau \qquad (7)$$

$$= -2\left(\frac{3}{4}\right)^{1/2}\beta\sin\theta = -1.66\beta \qquad (8)$$

where β is the normal π-type resonance integral between parallel p AO's of the two atoms; eq 7 follows from eq 6 since the integrals $\int \phi \mathrm{H} s \mathrm{d}\tau$ and $\int \phi \mathrm{H} y \mathrm{d}\tau$ vanish through symmetry.

If the nitrogen atom were planar, the bond energy (E_π') of the π bond formed by it to the AO ϕ would be 2β in the above notation; hence

$$E_\pi \simeq 0.82E_\pi' \qquad (9)$$

Contrary to the statements in many standard texts, pyramidal nitrogen can therefore conjugate very effectively with an adjacent unsaturated system R, the resonance interactions being about four-fifths those for planar N.

Let us now consider the relative energies of RNH_2 with pyramidal and planar nitrogen respectively, R being a conjugated group. Let us first start with a hypothetical structure with pyramidal nitrogen but no resonance interaction between R and N (A in Figure 5), if we allow a π-like bond to form between R and N (B in Figure 5), the change (δE) in energy will be approximately

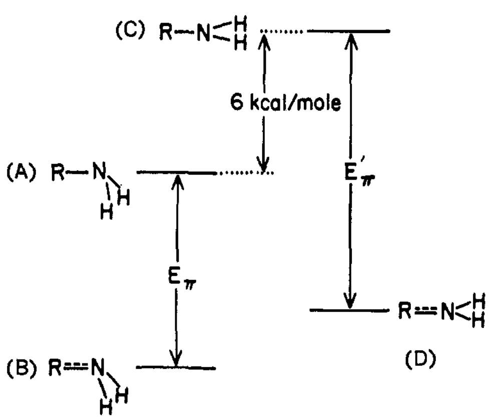

Figure 5. Relative energies of various forms of RNH_2.

$$\delta E \simeq -p_{\mathrm{RN}}E_\pi \qquad (10)$$

when p_{RN} is the bond order of the RN π bond. Next let us flatten out the nitrogen in the original "nonresonating" structure A to give a corresponding structure with planar nitrogen (C in Figure 5); the energy absorbed will be about 6 kcal/mol (the barrier height to inversion in ammonia). If we now allow a π bond to form in C between R and N (D in Figure 2), the change ($\delta E'$) in energy will be given approximately by

$$\delta E' = -pE_\pi' \qquad (11)$$

We can now compare the energies of B and D by relating them to that of A.

$$\begin{array}{ll} A \longrightarrow B & \Delta E = -pE\pi \\ A \longrightarrow D & \Delta E = 6 - pE\pi' \end{array} \qquad (12)$$

Thus from eq 11 and 12, the planar structure D will be more stable than the pyramidal structure B if, and only if

$$6 - pE_\pi' < -pE_\pi \qquad (13)$$

From eq 10 and 14, this will be so only if

$$E_\pi' > 33 \text{ kcal/mol} \qquad (14)$$

In current terminology, $E\pi'$ is the resonance energy of the planar structure D, due to π interactions between the unshared pair 2p electrons of nitrogen and the π system of R. Equation 14 implies that unless this quantity is very large, D will be less stable than the pyramidal structure B. Of course this argument is based on a very crude treatment; nevertheless it does suggest that compounds of this type should always be nonplanar unless there is a very large degree of resonance stabilization, an amount which probably would not easily be attained in any neutral molecule (where such resonance interactions lead to charge separation). Recent structural studies have indeed shown simple amides to be noncoplanar;[21] The same should also be true of aminoboranes, given that the BN rotational barriers in them are not significantly greater than those

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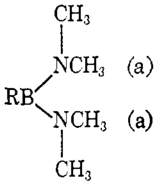
(20) While this argument is very obvious and has been used by one of us in lecture courses for a number of years, it does not seem to be generally familiar or to have appeared in print.

(21) D. R. Lide, *Ann. Rev. Phys. Chem.*, **15**, 245 (1964).

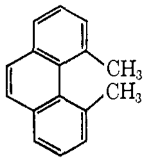
in normal amides (*e.g.*, 18 kcal/mol in formamide,[22] one of the amides where nitrogen has been shown[21] to be pyramidal).

Equally, of course, this argument suggests that observable free carbanions should be planar; for such ions can exist as independent entities only if the corresponding stabilization is very large. Recent studies[23] suggest that the pK_A's of simple paraffins are >70; the carbanion from a hydrocarbon acid as weak as toluene ($pK_A \sim 30$) must therefore have a net resonance stabilization of the order of 50 kcal/mol.

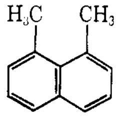
One point of interest in this connection is the curious line broadening shown by certain of our aminoboranes, as described at the end of the preceding section. This seems to imply that in compounds of the type $RB(NMe_2)_2$, the hydrogen atoms of one pair of methyl groups tend to become nonequivalent at very low temperatures. The only explanation that occurs to us is hindered rotation about the corresponding NCH_3 bonds. If the nitrogen atoms in aminoboranes are indeed pyramidal, as the arguments given above imply strongly, then there may be a conformational barrier to rotation of each methyl group of the order of 3 kcal/mol.[24] Furthermore, in the favored near-planar structure XII, the *cis*-methyls (a) will be pressed close together; mechanical interference between them will tend to make them rotate like a pair of meshed gear wheels, further increasing the effective barrier to rotation about the NCH_3 bonds. The two effects together could well be enough to bring about the observed broadening, this being assigned to the signal due to the hindered *cis*-methyls; for even at −145° the lines in question had merely broadened and not split. The barrier to nonequivalence of the methyl protons must therefore be very low, of the order of 5 kcal/mol.



XII



XIII



XIV

On the off chance that the barriers might be predominantly mechanical, rather than conformational, we examined the nmr spectra of two hydrocarbons, XIII and XIV, in which analogous interference exists. However in both cases the methyl signals remained sharp down to the lowest temperatures studied (−145°). It is, of course, well known that there is virtually no conformational barrier to rotation of methyl in methyl derivatives of aromatic hydrocarbons (*e.g.*, toluene); if the observed broadening in VIIIa, VIII, and IX is due to hindered NCH_3 rotation, a large part of the barrier must therefore be conformational in origin.

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(22) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

(23) A. Streitwieser, W. C. Langworthy, and J. J. Braumann, *J. Am. Chem. Soc.*, 85, 1761 (1963).

(24) D. R. Lide, *Ann. Rev. Phys. Chem.*, **15**, 233 (1964).

The Photoreduction of Fluorenone

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Abstract: The photoreduction of fluorenone has been investigated by kinetic methods supplemented by flash photolysis. We have confirmed the previously noted lack of photoreactivity of fluorenone with isopropyl alcohol and found negligible reactivity with toluene and methylcyclohexane. Fluorenone is photochemically reduced in the presence of tri-*n*-butylstannane to give fluorenone pinacol. The reaction proceeds, at least for the most part, from the triplet state of fluorenone. Primary, secondary, and tertiary amines which possess α-hydrogens all photoreduce the fluorenone triplet state in both benzene and acetonitrile solvents. The fluorescence of fluorenone is quenched by the amines with an efficiency which is inversely proportional to their ionization potentials, and the efficiency of quenching is greater in acetonitrile than in benzene. These data support an electron-transfer mechanism for fluorescence quenching, although flash irradiation failed to provide conclusive evidence for this mechanism. The quantum yield of the reaction is also decreased at high amine concentration by those amines which are effective at quenching fluorescence. In at least the reaction of fluorenone with triethylamine in benzene, kinetic evidence is presented for the possibility of some singlet reaction. Flash photolysis has been employed to determine the character and lifetimes of some of the transients produced upon irradiation of fluorenone in solution.

The photochemistry of fluorenone has received relatively little attention. Yang[1] has found only very slow photocycloaddition to trimethylethylene and that the photoreduction of fluorenone by alcohols does not proceed at a measurable rate.[2] By contrast, Singer and Davis[3,4] have found that the fluorenone triplet undergoes very facile photochemical addition to ketenimines with rate constants to the order of 10^8 l. mol^{-1} sec^{-1}. Kinetic evidence for a reactive singlet state has been found in the photocycloaddition of

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(1) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

(2) (a) N. C. Yang, private communication. (b) Note: A study of the photoreduction of fluorenone by triethylamine has been published shortly after completion of this manuscript and has been brought to our attention by a referee: S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 5353 (1968).

(3) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967).

(4) L. A. Singer and G. A. Davis, *ibid.*, **89**, 941 (1967).