Table II. Rate Data for Solvolysis of *tert*-Butyl Chloride and Norbornyl Chlorides in Aqueous Acetone at 25 °C

% acetone	10^6k_1, s^{-1}, 25 °C: *tert*-butyl chloride[a]	*exo*-norbornyl chloride	*endo*-norbornyl chloride
80	1.97	4.63×10^{-2}	2.09×10^{-4}
70	12.5	0.15	6.75×10^{-4}
60	58.0	0.709	3.12×10^{-3}
50	224	2.02	7.3×10^{-3}
40	887	6.01	1.84×10^{-2}
0	[22000][b]	[72][c]	[0.235][c]

[a] Data taken from Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* 1956, *78*, 2770. [b] Rate calculated from the *Y*-log *k*(*tert*-butyl chloride) plot; $Y_{H_2O} = 3.493$. [c] Calculated rates from log *k*(*tert*-butyl)–log *k*(norbornyl chloride) plots.

to support a proposal of any significant nucleophilic solvent contribution to the rates of solvolysis of *endo*-norbornyl derivatives.

Consequently, the present study of the effect of solvent on the exo/endo rate ratio in the 2-norbornyl chlorides confirms the conclusions reached earlier for the related study of the effect of solvents on the exo/endo rate ratio in the 2-norbornyl tosylates. Moreover, the results appear to be independent of the leaving group and are apparently not distorted significantly by F strain effects.

In conclusion, we now have three independent tests for the significance of nucleophilic solvent contribution to the exo/endo ratio in the solvolysis of the 2-norbornyl tosylates and chlorides. All three studies fail to reveal the solvent influence anticipated for true k_s processes. The results are in better agreement with the exo/endo rate ratio arising either from a k_Δ/k_c or a k_c/k_c solvolytic process.

Fortunately, it now appears possible to provide a reasonable means of deciding between these two possibilities. 2-Methyl-*endo*-norbornyl chloride undergoes solvolysis at a rate that is 53 000 times faster than the rate for *endo*-norbornyl chloride. The solvolyses of both compounds, tertiary and secondary, do not involve significant nucleophilic solvent contributions. That is, they are essentially k_c. Consequently, the factor of 53 000 measures primarily the activating effect of the tertiary methyl group in stabilizing the transition state, one which resembles closely the fully developed cation.[19] A factor of 53 000 is equivalent to 6.5 kcal mol^{-1} in energy.

If *exo*-norbornyl chloride solvolyzes with σ-bridging, the transition state will be stabilized by such σ-bridging. The Goering–Schewene diagram indicates that such nonclassical stabilization will be about 5.5 kcal mol^{-1}.[19] This will be lost in the solvolysis of 2-methyl-*exo*-norbornyl chloride, now accepted to solvolyze by a simple k_c process (see comments of P. v. R. Schleyer in ref 2). Consequently, the activating effect of the tertiary methyl substituent, 6.5 kcal mol^{-1}, will be largely negated by the loss of nonclassical resonance energy, 5.5 kcal mol^{-1}.

But the facts are not in accord with this prediction. The rate ratio for 2-methyl-*exo*-norbornyl chloride to *exo*-norbornyl chloride is 55 000 (≡6.5 kcal/mol^{-1}), essentially identical with that for the endo isomers.

On this basis, we conclude that the solvolysis of *exo*- and *endo*-norbornyl derivatives, both secondary and tertiary, must be the result of processes that are essentially k_c/k_c.

Experimental Section

exo- and *endo*-norbornyl chlorides were prepared according to literature procedures.[17,18]

Kinetic Measurements. *exo*- and *endo*-norbornyl chlorides were solvolyzed in 80, 70, 60, 50, and 40% aqueous acetone and their rates measured. Titrimetric procedure was employed. The rate data and the thermodynamic parameters are listed in Table I.

Registry No. *exo*-norbornyl chloride, 765-91-3; *endo*-norbornyl chloride, 2999-06-6.

9-(9-Borabicyclo[3.3.1]nonyl)-9-azabicyclo[3.3.1]nonane Radical Cation: A Failure of Bredt's Rule Kinetic Stabilization

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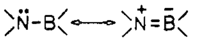
The PE spectrum of 9-(9-azabicyclo[3.3.1]nonyl)-9-borabicyclo[3.3.1]nonane (**5**) shows two low-energy ionizations which differ by only 0.53 eV (IP_v 8.31, 8.84 eV). Cyclic voltammetry shows an irreversible oxidation (CH_3CN, E_p^{ox} 1.75 V vs. SCE), demonstrating that the lifetime of $\mathbf{5}^{+\cdot}$ is short in solution in contrast to other Bredt's rule protected π radical cations, including the isoelectronic olefin radical cation $\mathbf{4}^{+\cdot}$. PE studies of the compounds with each of the bicycloalkyl groups replaced by a pair of methyl groups (9-Me_2N-9-BBN (**7**), 8.73, 9.18 eV; 9-Me_2B-9-ABN (**8**), 8.53, σ onset 9.8 eV) indicate that the HOMO of **5** is indeed the NB π orbital and that the high-lying σ orbital is associated with the 9-BBN group. The σ orbital is assigned to the antisymmetric σ_{CB}-dominated orbital on the basis of MO calculations.

Aminoboranes (I) are isoelectronic with olefins.[1] Tetramethylaminoborane (**1**) has a very low dipole moment,[2] implying that N ← B σ-bond polarization is just compensated by N → B π bonding, as emphasized in resonance structure IB. The double bond order is far lower than in an olefin, as indicated by the observed NB rotational barriers of 10–15 kcal/mol in compounds of proper symmetry for NMR studies.[1] The higher electronegativity of N than B makes the p-orbital coefficient at N much larger than at B in the π orbital. Bock and Fuss[3] emphasized



IA IB

Me_2NBMe_2

1

II

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(1) (a) Niedenzu, K.; Dawson, J. W. "Boron-Nitrogen Compounds"; Springer-Verlag: Berlin, 1965. (b) Steinberg, H.; Brotherton, R. J. "Organoboron Chemistry"; Interscience: New York, 1966; Vol. 2. (c) Noth, H. *Prog. Boron Chem.* 1970, *3*, 211.

(2) Becher, H. J. *Z. Anorg. Allg. Chem.* 1952, *270*, 273.

(3) (a) Bock, H.; Fuss, W. *Chem. Ber.* 1971, *104*, 1687. (b) Fuss, W.; Bock, H. *J. Chem. Phys.* 1974, *61*, 1613.

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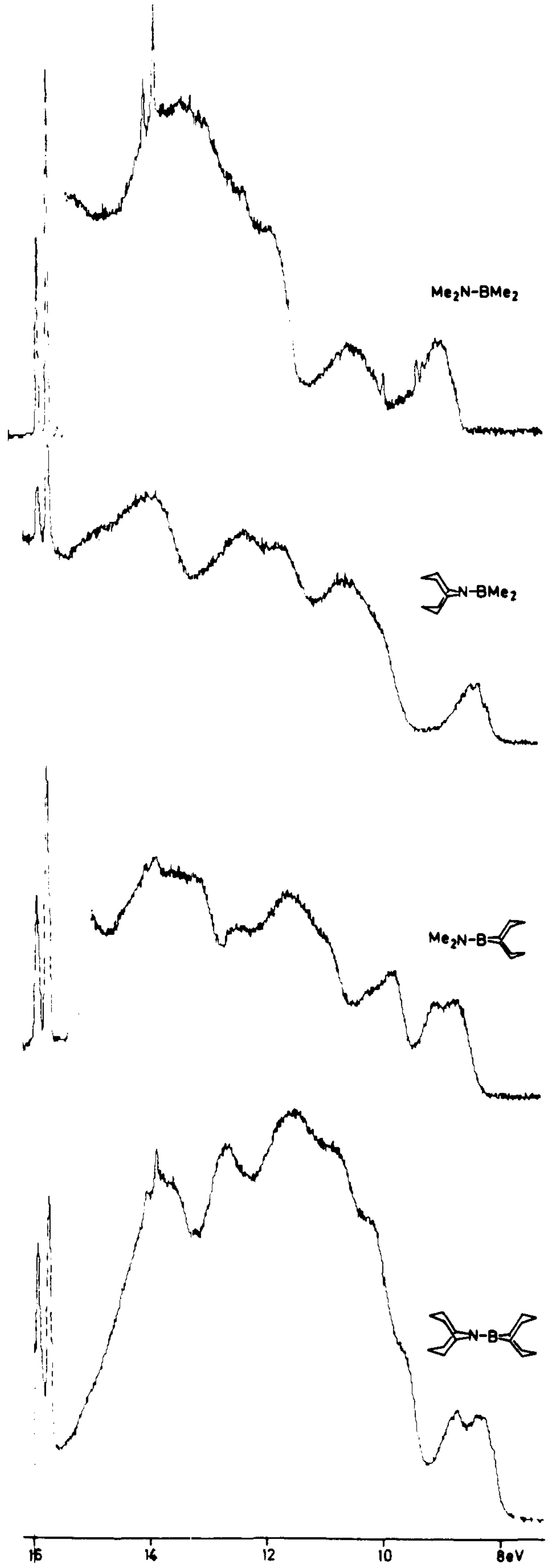
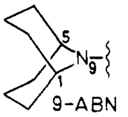


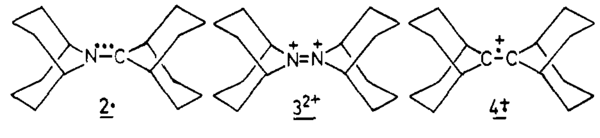
Figure 1. PE spectra of aminoboranes 1, 8, 7, and 5.

the considerable similarity of the electronic structure of olefins and aminoboranes, as revealed by their photoelectron (PE) spectra. For tetramethylethylene, the IP$_v$ values are 8.42 eV (π_{CC}, 2b$_{1u}$ in D_{2h}), 10.95 (σ_{CC}, 3b$_{1g}$), 12.2 ($\sigma_{C=C}$, 4a$_g$), and for 1, 8.92 (π_{BN}, 3b$_1$ in C_{2v}), 10.40 (σ_{CB}, 6b$_2$), 11.8–11.9 (σ_{BN}, 7a$_1$). The π level of the aminoborane is stabilized by 0.5 eV relative to the isoelectronic olefin, while σ_{CB} (the σ_{CB},σ_{CN} combination orbital dominated by σ_{CB}, shown diagramatically in II) is destabilized by 0.6 eV because of larger BC than CC bond contributions.[3]

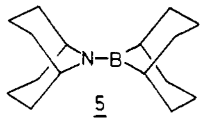
When both the oxidized and reduced forms of an electron-transfer equilibrium have sufficiently long lifetimes in solution (about 10-ms lifetimes are required), measurement of the formal potential for electron transfer, $E^{\circ\prime}$, can be carried out conveniently by using cyclic voltammetry (CV). $E^{\circ\prime}$ measurements provide thermodynamic data since for two electron-transfer couples measured under the same conditions, $\Delta E^{\circ\prime} = \Delta(\Delta G^{\circ})$ for the electron transfer. Unfortunately, rapid cleavage of CH bonds adjacent to the π system precludes making $E^{\circ\prime}$ measurements for couples containing most radicals and radical ions having small π systems. We have found that the Bredt's rule effect of a bicyclic system which holds such CH bonds perpendicular to the π orbitals provides powerful kinetic stabilization.[4] The 9-azabicyclo[3.3.1]nonyl system (abbreviated 9-ABN) is a dialkylamino group which does not react rapidly when there is only one lone-pair electron at nitrogen and provides an electrolytically reversibly oxidized trialkylamine, chloramine, and a pentaalkylhydrazine cation.[4] Bredt's rule stabilization is also responsible for the long lifetimes observed for species 2·,[4] 3^{2+},[5] and 4$^{+\cdot}$,[5] in which a two-center π system shares three, two, and one π electron(s), respectively. Because of these precedents, we expected the protected aminoborane 5 to show reversible one-electron oxidation, providing an interesting thermodynamic comparison with the isoelectronic 4,4$^{+\cdot}$ couple.[6]



9-ABN



2· 3^{2+} 4$^{+\cdot}$



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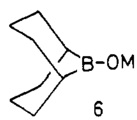
Results and Discussion

Because it is known that treatment of 9-methoxy-9-BBN (6) with alkyllithiums gives 9-alkyl-9-BBN derivatives,[7] we



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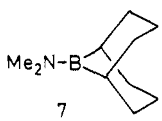

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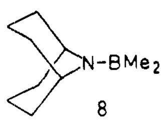

8

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(4) (a) Nelsen, S. F.; Kessel, C. R.; Brien, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 702. (b) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490.

(5) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392.

(6) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503. (b) Reference 6a employs adamantylidineadamantane. The behavior of the 4,4$^{+\cdot}$ couple is entirely comparable: Kliewer, W. R., unpublished results.

(7) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

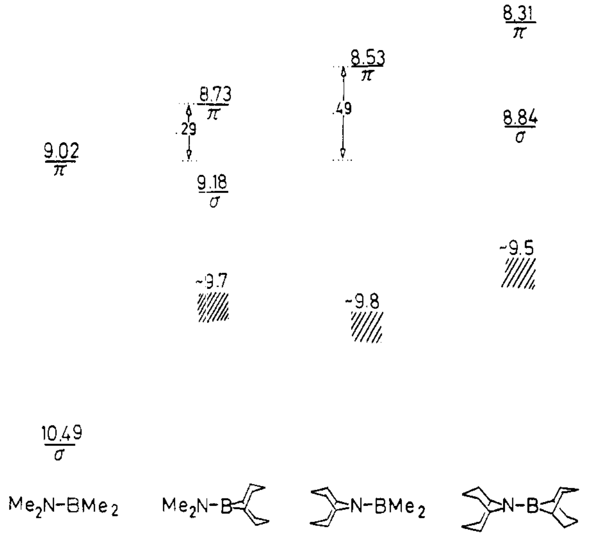

Figure 2. Diagramatic comparison of the lowest vertical IP values for **1**, **7**, **8**, and **5**. The onset of badly overlapping σ orbitals is shown as a broad hatched area.

tried treatment of **6** with 9-lithio-9-ABN and found that this is a convenient way to prepare 9-(dialkylamino)-9-BBN derivatives **5** and **7**. The CV of **5** was found to be totally irreversible in acetonitrile, $E_p^{ox} = 1.75$ V (vs. SCE, 500 mV/s scan rate, Pt electrode), indicating that $5^{+}\cdot$ has a very short lifetime despite Bredt's rule protection of its π cation. The PE spectrum of **5** was also surprising, for it has two low-energy ionization peaks which only differ in IP_v by 0.53 eV and are well separated from the onset of many overlapping σ ionizations for this molecule (see Figure 1). The bicyclic alkyl substituents of **5** must destabilize one of the σ orbitals more strongly than either the π or the many other high-lying σ orbitals. We were particularly intrigued by the possibility that the HOMO of **5** might actually be this σ orbital rather than π_{NB}. This would provide an easy rationalization for the short lifetime of $5^{+}\cdot$, because the σ radical cation would not be Bredt's rule protected and, by analogy with the known electrochemistry of adamantane,[8] would be expected to have an irreversible CV.

MO calculations on H_2NBH_2 give the σ_{BH} and π_{NH} orbitals having very similar energies, with the σ orbital higher than the π orbital for ab initio calculations with larger basis sets.[9] MINDO/3 calculations on **1** gave $-E$ 8.57 eV (σ_{CB}, $6b_2$), 9.27 (π_{BN}, $3b_1$), 9.77 (σ_{BN}, $7a_1$), that is, with π_{BN} and σ_{CB} inverted from the literature assignment for **1**, but the bicyclic alkyl groups of **5** clearly destabilize a σ orbital. To test the hypothesis that **5** might have a σ orbital as its HOMO, we prepared **7** and **8** and compared their PE data with those for **5** and **1** (which we reran to have directly comparable numbers) in Figure 2. These data leave no room for doubt that the HOMO in all four cases is the π_{BN} orbital. For **8** we observed vibrational structure in the first PE band. The IP_1 reported is the third observed maximum (splitting 0.13 eV), which is experimentally equal in intensity to the second. With the assignment of Figure 2, the π level is raised in energy more with bicyclic alkyl than with methyl substitution at N (ΔIP_1 (**1** − **8**) = 0.49 eV, ΔIP_1 (**7** − **5**) = 0.42) than at B (ΔIP_1 (**1** − **7**) = 0.29, ΔIP (**8** − **5**) = 0.22), as expected from the larger p coefficient at N. The presence of an exceptionally high-lying σ orbital is clearly associated with the 9-BBN system; **5** and **7** have IP(σ) − IP(π) of 0.53 and 0.45 eV, respectively, while this difference is 1.47 eV for **1** and about 1.3 for **8**. The highest σ orbital for **1**,[3] and presumably **5** and **7** also, is the antisymmetric σ_{CB}-dominated orbital (see II).

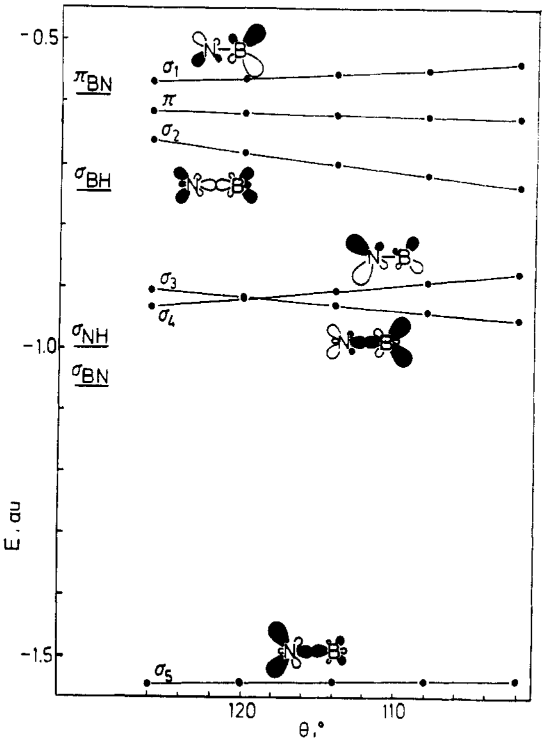

Figure 3. INDO-SCF-MO orbital energies of aminoborane plotted as a function of HBH and HNH bond angles (taken to be equal). Calculations were carried out on an idealized planar C_{2v} geometry, with $R_{NH} = 1.025$, $R_{BN} = 1.370$, and $R_{BH} = 1.190$ Å. The LCBO composition of each labeled σ MO is approximately

$$\sigma_1\text{:}\quad 0.61(\sigma_{BH} - \sigma'_{BH}) + 0.35(\sigma_{NH} - \sigma'_{NH})$$

$$\sigma_2\text{:}\quad 0.66\sigma_{BN} - 0.43(\sigma_{BH} + \sigma'_{BH}) - 0.31(\sigma_{NH} + \sigma'_{NH})$$

$$\sigma_3\text{:}\quad 0.55(\sigma_{BH} + \sigma'_{BH}) - 0.36(\sigma_{NH} + \sigma'_{NH} - \sigma_{BN})$$

$$\sigma_4\text{:}\quad 0.36(\sigma_{BH} - \sigma'_{BH}) - 0.61(\sigma_{NH} - \sigma'_{NH})$$

$$\sigma_5\text{:}\quad 0.64\sigma_{BN} + 0.52(\sigma_{NH} + \sigma'_{NH}) + 0.13(\sigma_{BH} + \sigma'_{BH})$$

The orbital energy of each contributing bond orbital is shown at the left of the figure.

The origin of the high-lying σ orbital for the 9-BBN systems **5** and **7** can be qualitatively understood in terms of a linear-combination-of-bond-orbitals (LCBO) analysis,[10] carried out here at the INDO-SCF-MO level[11] on H_2NBH_2. The orbital energies of the relevant σ_{BN}, σ_{NH}, σ_{BH} and π_{BN} bond orbitals are shown at the left of Figure 3. The π_{BN} orbital (which has the approximate composition $0.8p_N + 0.6p_B$) is symmetry forbidden from interacting with the σ BO's and remains essentially unaffected by distortions of the planar σ skeleton. σ_{BH} at −0.74 au is conspicuous for its high orbital energy, far above the usual INDO values for σ_{CH} (ca. −0.94 au) and σ_{NH} (ca. −0.93 au), and will thus come to dominate the highest occupied σ MO. Such a high-lying orbital is expected to mix strongly, by the overlap phase effect,[12] with any orbital of "odd" overlap and as shown in Table I the trans NH bond ($\sigma_{NH(t)}$) bears such a phase relationship to each σ_{BH} bond. Finally, the two high energy $\sigma_{BH} + \lambda\sigma_{NH(t)}$ combinations will interact

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[8] (a) Miller, L. L.; Koch, V. R.; Koenig, T.; Tettle, M. *J. Am. Chem. Soc.* **1973**, *95*, 5075. (b) Koch, V. R.; Miller, L. L. *Ibid.* **1973**, *95*, 8631.

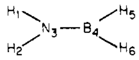
[9] Armstrong, D. R.; Duke, B. J.; Perkins, P. G. *J. Chem. Soc. A* **1969**, 2566.

[10] Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1976**, *98*, 4392.

[11] Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

[12] Weinhold, F.; Brunck, T. K. *J. Am. Chem. Soc.* **1976**, *98*, 3745.

Table I. Fock Matrix Elements (au) $F_{\mu\nu} = \langle\sigma_\mu|\mathbf{F}|\sigma_\nu\rangle$ for Aminoborane in the Bond-Orbital Representation



	$\sigma_{N_3H_1}$	$\sigma_{N_3H_2}$	$\sigma_{N_3B_4}$	$\sigma_{B_4H_5}$	$\sigma_{B_4H_6}$
$\sigma_{N_3H_1}$	−0.999	−0.192	−0.256	−0.091	+0.067
$\sigma_{N_3H_2}$	−0.192	−0.999	−0.256	+0.067	−0.091
$\sigma_{N_3B_4}$	−0.256	−0.256	−1.063	−0.122	−0.122
$\sigma_{B_4H_5}$	−0.091	+0.067	−0.122	−0.745	−0.100
$\sigma_{B_4H_6}$	+0.067	−0.091	−0.122	−0.100	−0.745

out-of-phase to give the σ HOMO (shown diagramatically as II) of the general structure

$$\phi_{\sigma\text{-HOMO}} = [\sigma_{BH} + \lambda\sigma_{NH(t)}] - [\sigma'_{BH} + \lambda\sigma'_{NH(t)}]$$

Since this may be rewritten as

$$\phi_{\sigma\text{-HOMO}} = [\sigma_{BH} - \sigma'_{BH}] + \lambda[\sigma_{NH} - \sigma'_{NH}]$$

involving out-of-phase (destabilizing) mixing of both BH and NH bonds, it is evident that closing the HBH and HNH angles, leading to more destabilizing σ_{BH}–σ'_{BH} or σ_{NH}–σ'_{NH} interactions, will further raise the energy of this orbital. The HBH angle effect would dominate because of the higher σ_{BH} coefficient. The INDO calculations displayed in Figure 3 illustrate this effect nicely. The energies of each occupied MO are plotted as a function of $\theta = \angle HBH = \angle HNH$. The highest σ MO, which has the composition at $\theta = 120°$

$$\phi_{\sigma\text{-HOMO}} = (0.61\sigma_{BH} + 0.35\sigma_{NH}) - (0.61\sigma'_{BH} + 0.35\sigma'_{NH}) + \text{small antibond contributions } (\leq 0.07)$$

is significantly raised as θ is compressed. Thus INDO calculations suggest that closing the CBC angle in the 9-BBN substituted systems **5** and **7** relative to the BMe_2 systems **1** and **8** may well be responsible for the very high-lying σ orbital revealed by the PE spectra of **5** and **7**. The substitution change from methyl to secondary carbons attached to boron is a contributing factor.

Conclusion

The PE work establishes that the postulated σ,π crossing does not quite occur for **5**, yet the CV data demonstrate that $5^{+\cdot}$ does not have the long solution lifetime expected for the π species. The PE spectrum of **5** reveals a small (12 kcal/mol) vertical energy difference between the ground-state π radical cation and the lowest excited-state σ radical cation in the vapor phase. We suggest that this Bredt's rule unprotected and presumably very short-lived σ species is most likely responsible for the rapid decomposition. The ordering of the two radical cation states might be reversed in solution due to geometry relaxation and solution effects. Even if the π species remains the ground state, rapid thermal population of the σ species would occur unless their adiabatic energy separation were substantially greater than their vertical separation in the vapor phase.

Experimental Section

(Dimethylamino)dimethylborane (**1**) was prepared by the literature method:[13] 1.37 g (20%); bp 63–65 °C (atmospheric pressure); ^{1}H NMR ($CDCl_3$) δ 2.74 (s, 6 H), 0.24 (s, 6 H).

9-(9-Azabicyclo[3.3.1]nonyl)-9-borabicyclo[3.3.1]nonane (5). A solution of 9-lithio-9-azabicyclo[3.3.1]nonane was prepared by adding 1.35 mL of 1.43 M *n*-butyllithium in hexane (1.93 mmol) to 0.242 g (1.94 mmol) of freshly sublimed anhydrous 9-ABN in 10 mL of dry THF. The yellow solution was stirred for 15 min and then 0.29 g (1.9 mmol) of 9-methoxy-9-BBN[7] (**6**) was added via syringe. After being stirred for 2 h, the colorless, cloudy mixture was concentrated under reduced pressure, stirred for 18 h with 10 mL of hexane, and filtered through a Celite plug. After the solution was dried over sodium sulfate, removal of solvent gave a solid residue which yielded 0.126 g (27%) of **8** as white needles, mp 131.5–132° C (under vacuum), 111–120 °C (under air), after two recrystallizations from acetone:[14,15] ^{1}H NMR ($CDCl_3$) δ 3.94 (br s, 2 H), 1.2–2.3 (m, 26 H); ^{13}C NMR ($CDCl_3$) δ 47.8 (d), 33.7 (t), 32.4 (t), 23.7 (t), 21.0 (t);[16] ^{11}B NMR ($CDCl_3/BF_3\cdot Et_2O$) 44.6 ppm downfield from internal $BF_3\cdot Et_2O$; IR (CCl_4) 1480 cm^{-1} (NB stretch).

9-(Dimethylamino)-9-borabicyclo[3.3.1]nonane (7). The same method was used as for **5**, starting with 0.45 g (10 mmol) of anhydrous dimethylamine and employing 1.52 g (10 mmol) of **6**. The residue after hexane removal was distilled through a short-path column, giving **7** as an oil: bp 88 °C (2 mm); 1.24 g (76%);[15] ^{1}H NMR ($CDCl_3$) δ 2.74 (s, 6 H), 1.3–2.0 (m, 14 H); IR (CCl_4) 1465, 1450, 1410, 1350 cm^{-1}.

9-(9-Azabicyclo[3.3.1]nonyl)dimethylborane (8). After addition of 3.74 mL (45.6 mmol) of BCl_3 to 80 mL of anhydrous benzene being stirred in a 250-mL 3-necked flask, 5.70 g (45.6 mmol) of 9-ABN in 50 mL of benzene was added dropwise over 1 h, while cooling in an ice bath. Triethylamine (freshly distilled, 6.4 g, 45.6 mmol) was then added dropwise, and the mixture was stirred for 15 h. After filtration of the triethylamine hydrochloride and concentration at 35 °C (90 mm), 91.2 mmol of methyl Grignard solution in ether was added. The solvent was removed under reduced pressure, and the residue Kugelrohr distilled to give a clear liquid. Short-path distillation gave **8** as a clear oil: bp 62–63 °C (2 mm); 1.26 g (17%);[15] ^{1}H NMR ($CDCl_3$) δ 3.88 (br s, 2 H), 2.3–1.5 (m, 14 H), 0.24 (s, 6 H); IR (CCl_4) 1465, 1450, 1375 cm^{-1}.

The PE spectra and CV data were obtained as previously described.[4a]

Acknowledgment. We thank the National Science Foundation for partial support of this work through Grants CHE77-24627 and the major instrument program. We are indebted to M. Chen for obtaining the ^{11}B NMR spectrum.

Registry No. 1, 1113-30-0; 5, 73308-98-2; 5 radical cation, 73308-99-3; 6, 38050-71-4; 7, 63366-67-6; 8, 73309-00-9; 9-lithio-9-azabicyclo[3.3.1]nonane, 73309-01-0; 9-ABN, 280-97-7.

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[13] (a) Brown, J. F., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 1219. (b) Erickson, C. E.; Gunderloy, C. E., Jr. *J. Org. Chem.* **1959**, *24*, 1161.

[14] Anal. (Spang Microanalytical Laboratories, Eagle Harbor, MI) Calcd for $C_{16}H_{28}NB$: C, 78.37; H, 11.51; N, 5.71. Found: C, 78.38; H, 11.57; N, 5.78.

[15] Empirical formula established by high-resolution mass spectroscopy (AEI MS 902).

[16] The carbons α to boron are not observed because of the short ^{11}B relaxation time: Noth, H.; Wrackmeyer, B. "Nuclear Magnetic Resonance of Boron Compounds"; Springer-Verlag: New York, 1978, p 103.