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°C for 1.5 h and then diluted with 65 mL of ether. The combined organics were washed with 75 mL of a 2:1:1 mixture of water, saturated sodium bicarbonate, and brine. The aqueous phase was back-extracted with an additional 75 mL of ether. The combined organics were dried and concentrated in vacuo to give 515 mg of a pale yellow semisolid. Recrystallization from methylene chloride in hexane gave 260 mg (75%) of 4-iodo-4′-(tetrahydropyran-2-yloxy)-1,1′-bibicyclo[2.2.2]octane, mp 195–196 °C.

The spectral data were the following: IR ($CHCl_3$) 3005, 2950, 2920, 2870, 1460, 1350, 1235, 1220, 1210, 1155, 1130, 1115, 1075, 1030, 1010, 980, 950, 940, 910, 905, 860, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.72 (s, 1 H, acetal), 3.92 (m, 1 H, OC*H*H), 3.42 (m, 1 H, OCH*H*), 2.38 (m, 6 H, CH_2CI), 1.90–1.27 (m, 24 H, CH_2); MS *m/e* ($M - C_5H_9O_2$) 343.0879 (calcd for $C_{16}H_{24}I$ *m/e* 343.0925).

Anal. Calcd for $C_{21}H_{33}IO_2$: C, 57.76; H, 7.48. Found: C, 57.64; H, 7.43.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with the MM2 program of Allinger[8a] for the "[*n*]-rods" and the MMP program of Gejewski[8b] for the "hybrid rods". An approximation of the transition state for interconversion of diasteromers of 4,4′-dihydro-[2]-rod was modeled on the highly symmetric carbon framework obtained from diiodo-[1]-rod and the carbon framework obtained from 1,4-dihydro-[1]-rod. This system was optimized by minimizing the steric energy from varying the central carbon–carbon bond length.

Acknowledgment. Appreciation is expressed to the National Science Foundation for support of and confidence in these efforts and to the NIH (Grant GM07487) for contribution to its inception.

Registry No. **1a**, 143123-40-4; **1b**, 143123-31-3; **2**, 74467-18-8; **3**, 7697-14-5; **4**, 74467-39-3; **5b**, 143123-32-4; **6a**, 143123-33-5; **6b**, 143123-41-5; **6c**, 143123-42-6; **8**, 111-90-0; **9**, 85232-17-3; **10**, 74467-40-6; **11a**, 143123-35-7; **12**, 74467-48-4; **13**, 143123-36-8; **14**, 143123-37-9; **15**, 20534-58-1; **16**, 23062-62-6; **17**, 143123-38-0; **18**, 143123-39-1; **21**, 59880-84-1; **22a**, 10364-05-3; **22b**, 143123-43-7; HO[1]$^+$, 73428-51-0; HO[2]$^+$, 143123-46-0; HO[3]$^+$, 143123-34-6; HO[4]$^+$, 143123-51-7; HO[1]OH$^{\bullet+}$, 143123-50-6; HO[2]OH$^{\bullet+}$, 143123-49-3; HO[3]OH$^{\bullet+}$, 143123-48-2; HO[4]OH$^{\bullet+}$, 143123-47-1; 1,1′-bibicyclo[2.2.2]octane-4,4′-diyl diacetate, 116278-39-8; 1,1′-bibicyclo[2.2.2]octane-4,4′-diol, 116263-79-7; 1,1′-bibicyclo-[2.2.2]oct-4-yl acetate, 143123-44-8; 4′-iodo-1,1′-bibicyclo[2.2.2]-oct-4-yl acetate, 143142-47-6; 4-iodo-4′-[(tetrahydropyran-2-yl)-oxy]-1,1′-bibicyclo[2.2.2]octane, 143123-45-9.

Supplementary Material Available: X-ray crystallographic study of 4 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Azaborines: An ab Initio Study

Michael Kranz and Timothy Clark*

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

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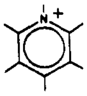
Three different indicators of aromatic electron delocalization have been investigated computationally for 1,2- (**3**), 1,4- (**4**), and 1,3-azaborine (**5**), all of which are experimentally unknown as unsubstituted compounds. MP2/6-31G* optimizations show a varying but considerable degree of electron delocalization. The calculated order of stability (**3** $\gg$ **4** > **5**) resolves the contradictions of former reports. In contrast to the noncorrelated level, consideration of electron correlation significantly lowers the relative energy of the 1,3-isomer, for which not even substituted derivatives are known. Natural bond orbital (NBO) analyses confirm the expected Lewis structures of the 1,2- and 1,4-isomers but offer an interesting description of the intricate π-system of 1,3-azaborine. Isodesmic equations reveal a resonance energy for **4** similar to stable Hückel aromatics and a somewhat smaller effect for **3**, whereas a hyperhomodesmotic equation assigns half the resonance energy of benzene to **4**. Basic differences in the σ framework of the azaborines are considered to be responsible for the stability of **3**. Computational results are supported by comparison of the scarce NMR data with chemical shifts calculated by the individual gauge localized orbitals (IGLO) method.

Introduction

Replacement of a carbon atom in benzene by one of its neighbors in the periodic table yields the charged, isoelectronic 1-borinate anion **1** or the 1-pyridinium cation **2**. Replacing two carbon atoms by one boron and one nitrogen leads to a series of heterocyclic molecules in which the formal charges in **1** and **2** cancel. Three structural isomers can be constructed: 1,2-dihydrido-1,2-azaborine (**3**), 1,4-dihydrido-1,4-azaborine (**4**), and 1,3-dihydrido-1,3-azaborine (**5**).



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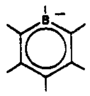
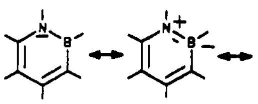


2

Each isomer has six π-electrons, suggesting some degree of aromatic electron delocalization. The differences in electronegativities of nitrogen and boron should, however, reduce the amount of aromatic character. Accurate calculations on the three isomers would provide valuable information about the balance between charge separation and electron delocalization.



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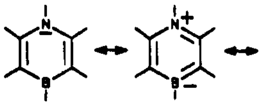

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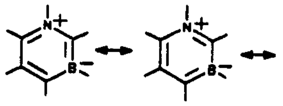

5

None of the three parent heterocycles have been isolated. Unsubstituted **3** was detected in the mass spectrometer[1] by Dewar and co-workers, but could not be isolated because it rapidly polymerizes. The least substituted de-

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rivative isolated was 1-phenyl-1,2-azaborine (6). It exhibits UV and ^{1}H-NMR spectra similar to its pyridine analog,[2] suggesting aromatic character. A comprehensive review summarizes the chemistry of the azaborines.[3]

Substituted derivatives of 3 abound,[4] but only a few compounds with the 1,4-heteroatom arrangement (4) have been reported and we know of no example of 5. Older theoretical calculations at low levels of sophistication[3,5] agree with the experimentally anticipated order of stability 3 > 4 > 5 but disagree on the relative differences in stability. Recently, an MNDO investigation[6] gave the same order of stability and suggested that the least stable isomer 5 is considerably delocalized. The authors' conclusion the azaborines are "more stable than benzene" from the absolute values of the heats of formation is, however, a misinterpretation of these data.[7]

High level ab initio optimizations of azaborines have not yet been performed, especially none including electron correlation.[8] Multiconfiguration SCF calculations for the π-electrons of borazine and benzene have been reported[9] but the σ frameworks of the molecules were confined to experimental geometries. Nonetheless, the authors emphasized the necessity for the inclusion of electron correlation in order to assess the electronic nature of these rings.

Recent theoretical interest in benzene analogs,[8,10] the lack of geometry optimizations at the ab initio level of theory, and the dearth of experimental material triggered the present investigation. Optimized geometries of the three azaborines 3, 4, and 5 at semiempirical and ab initio levels and single-point calculations using a fourth-order Møller–Plesset perturbation correction for electron correlation are discussed below.

A useful tool for investigating the distribution of electrons within a molecular framework is the natural bond orbital (NBO) analysis.[11] It has been applied successfully to six-membered heterocycles,[10c] and a comparison of the results of the hypothetical unsubstituted azaborine systems to NBO data of experimentally verifiable compounds provides useful insight into the bonding in these compounds.

Isodesmic equations are another means of revealing stabilizing or destabilizing effects resulting from cyclic conjugation.[12] However, both the basis set dependency of the data and the many possible definitions of the conjugation energy[13] make this technique less useful than might be expected.

A direct link between calculated data and experimental findings is most desirable. The development of efficient ab initio procedures for the calculation of chemical shifts, such as the individual gauge localized orbitals (IGLO) method,[14] has made combined ab initio/NMR studies for a variety of problems possible.[15] The comparison of the calculated chemical shifts of the three azaborines to the scarce experimental data of their derivatives allows an

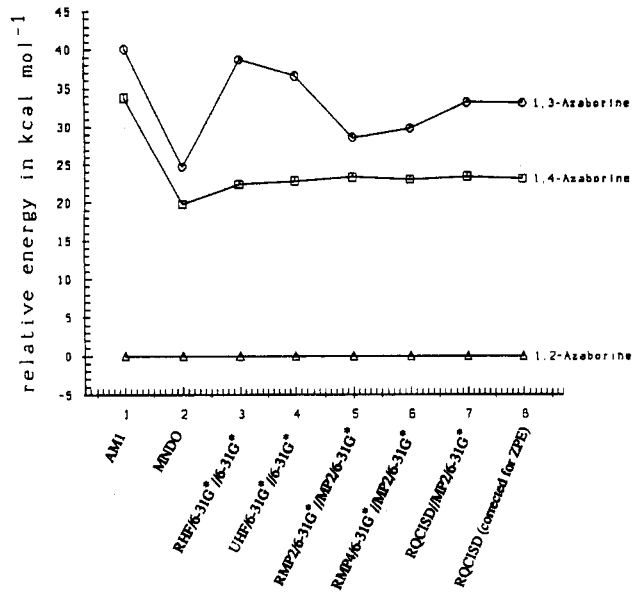

Figure 1. Relative energies of 3–5.

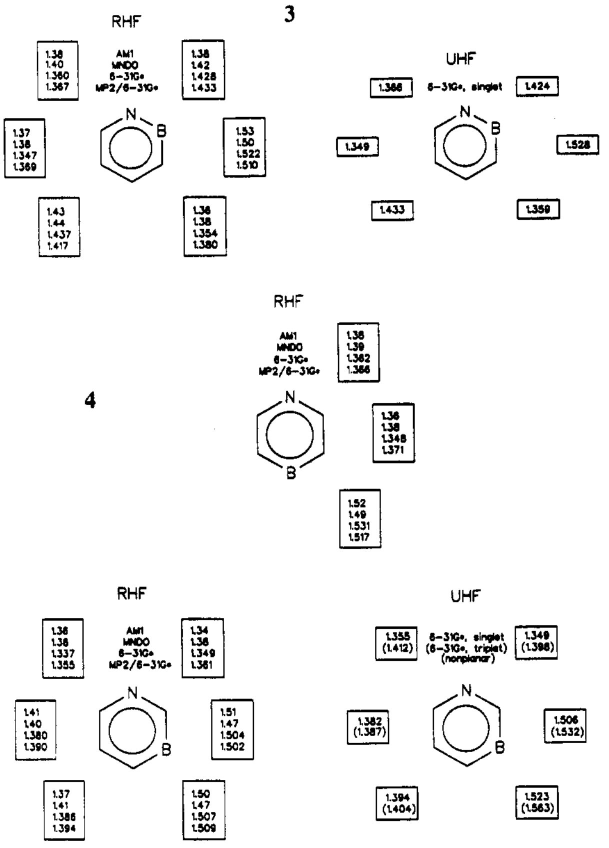

Figure 2. Optimized bond lengths of RHF geometries of azaborines 3–5 and UHF geometries of 3 and 5 (in Å).

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Table I. Relative Energies and Zero Point Energies for 3–5 (in kcal/mol)

	3	4	5	5 (triplet)
AM1 (RHF)	0.0	+33.8	+40.1	+80.6
MNDO (RHF)	0.0[a]	+19.8[a]	+24.8[a]	+65.5
RHF/6-31G*//6-31G*	0.0	+22.5	+38.7	
UHF/6-31*//6-31G*	0.0	+22.9	+36.6	+65.1
RMP2/6-31G*//MP2/6-31G*	0.0	+23.4	+28.7	
RMP4/6-31G*//MP2/6-31G*	0.0	+23.1	+29.9	
RQCISD//MP2/6-31G*	0.0	+23.5	+33.2	
RQCISD (corrected for ZPE)	0.0	+23.2	+33.1	
ZPE (RHF/6-31G*)	+65.62	+65.32	+65.50	

[a] Reference 6.

assessment of the reliability of our calculations.

Methods

All of the molecules considered were preoptimized with the AM1 semiempirical procedure[16] using VAMP 4.4[17] on a Convex C-220/256. These geometries were then used as starting points for optimizations at the spin-restricted Hartree–Fock (HF) SCF-level using the 6-31G* basis set[18] implemented in the Cambridge Analytic Derivatives Package (CADPAC)[19] on a Cray YMP-432. The spin-unrestricted Hartree–Fock (UHF) formalism[20] was employed in the case of 5. Analytical frequencies were calculated at the 6-31G* basis set level in order to confirm the nature of the stationary points located. Electron correlation was considered using second-order Møller–Plesset (MP2) theory (including core electrons) for optimizations and fourth order (MP4/SDTQ) keeping the core electrons frozen[21] for single points. The GAUSSIAN 90 series of programs were used.[22] QCISD single points keeping the core electrons frozen were also performed.[23]

Natural bond orbital (NBO) analyses[24] were performed on the Convex C-220 using the GAUSSIAN 88 series of programs.[25] The individual gauge localized orbitals (IGLO) method[14] was employed to calculate the ^{13}C- and ^{11}B-NMR chemical shift parameters using the DZ and II′ basis sets.[26]

Geometries

Table I and Figure 1 show the relative energies of 3–5, Figure 2 and Table III summarize their geometrical parameters and those of some reference compounds. The RHF geometries calculated with MNDO were taken from the literature,[6] and the MNDO-UHF calculations for 5 were added for the sake of completeness.

All three isomers were optimized at the AM1 semiempirical level without symmetry restrictions. However, they deviated from planarity by less than 1°. According to experimental findings[4] and MNDO calculations[6] 1,2-azaborine 3 is distinctly more stable than 1,4-azaborine 4 (by 33.8 kcal/mol) and 1,3-azaborine 5 (by 40.1 kcal/mol). As 1,3-azaborine 5 cannot be represented satisfactorily by a unique Lewis structure, we also calculated the structure for the UHF-triplet state. However, an AM1 multielectron configuration interaction (MECI-) calculation[27] showed that the triplet state is 40.5 kcal/mol higher in energy than the singlet state. The differences in stability between the three isomers is significantly smaller according to MNDO (Table I) than with AM1 but the triplet state is again 40.7 kcal/mol less stable than the singlet.

Table II. Dominant Configurations and Wavefunction Coefficients of QCISD Calculations of 3–5

3	4	5
HOMO → LUMO 0.075	(HOMO-1) → (LUMO+1) 0.074	HOMO → LUMO 0.105
HOMO → (LUMO+1) 0.066	HOMO → (LUMO+1) 0.060	HOMO → (LUMO+1) 0.061
(HOMO-1) → LUMO 0.065	HOMO → LUMO 0.056	(HOMO-1) → LUMO 0.055

Table III. Selected RHF Bond Lengths of Reference Compounds (in Å)[a]

	benzene C–C	ethylene C=C	*cis*-butadiene C–C	*cis*-butadiene C=C	borazine N–B
AM1	1.40	1.33	1.45	1.34	1.40
MNDO	1.41	1.34	1.46	1.35	1.43
6-31G*	1.386	1.317	1.480	1.332	1.426
MP2/6-31G*	1.395	1.335	1.470	1.342	1.430

	NH_2CH_3 N–C	$NHCH_2$ N=C	BH_2CH_3 B–C	$BHCH_2$ B=C
AM1	1.43	1.27	1.53	1.38
MNDO	1.46	1.28	1.53	1.33
6-31G*	1.453	1.250	1.574	1.377
MP2/6-31G*	1.464	1.281	1.561	1.385

[a] As taken from: *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Pittsburgh, PA, 1983 and *The Erlangen Quantum Chemistry Archive System*; Clark, T., Schleyer, P. v. R., Eds.; Erlangen, 1991.

At the ab initio levels the geometries were restricted to be planar (in accord with parallel investigations[8,10b]). Normal vibration calculations at HF/6-31G* confirmed the planar structures to be local minima on the potential-energy surface. Second derivatives were not determined for the MP2/6-31G* structures. At 6-31G* 1,2-azaborine 3 again is the most stable of the three isomers followed by the 1,4-azaborine 4 (+22.3 kcal/mol) and the RHF-geometry of the 1,3-azaborine 5 (+38.6 kcal/mol). The differences in stability between 3 and 4 do not change dramatically on inclusion of electron correlation, either with Møller–Plesset or with configuration interaction (Figure 1). This is not true for the relative stability of 5. The extra stabilization of 5 at the MP4 (energy relative to 3 = +29.8 kcal/mol) and CI levels (+33.1 kcal/mol) indicates that the electronic structure of this isomer is not well described by a single configuration. However, the CI wavefunctions of 3–5 each have the same coefficient (c = 0.93) for the HF configuration. The dominant excited state contributions are pair excitations from the two highest occupied to the two lowest unoccupied orbitals of each isomer (Table II).

Considering the possibility that 5 may have significant diradical character, we also investigated the UHF/6-31G* wavefunction of its singlet state. The resulting total energy is 2.46 kcal/mol lower than the RHF-value ($\langle S^2 \rangle = 0.48$). Pople and Hehre[28] have proposed this energy difference

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between the closed shell (RHF) and the open shell (UHF) singlet wavefunction as an indication of the relative diradical character in their investigation of the electronic nature of the 22- and 24-electron 1,3-dipoles. At the 6-31G* level the energy difference [E(RHF) − E(UHF)] for the latter 1,3-dipoles ranges between 5 and 48 kcal/mol. Pople and Hehre correlated increasing stability of the UHF singlet calculations with the more important diradical participation in the electronic structure of these species.

Applying the 6-31G* UHF (singlet) formalism to 3 and 4 results in an identical wavefunction for the latter isomer. Surprisingly, the UHF-wavefunction of 3 is 0.37 kcal/mol $(\langle S^2 \rangle = 0.10)$ more stable than RHF. However, the minor changes in geometry between the two states (Figure 2) and the small energy difference diminish the importance of this finding.

The 6-31G* UHF triplet-state-optimized geometry of planar 5 displays two degrees of freedom with imaginary frequencies. Releasing the symmetry restrictions yielded a structure with no negative eigenvalues $(\langle S^2 \rangle = 2.22)$ that has a pyramidal nitrogen and a slightly corrugated ring (Figure 2). It is 28.5 kcal/mol higher in energy than the UHF singlet state.

1,2-Azaborine 3. Benzene and borazine, the organic and inorganic parents of the hybrid azaborine, serve as references for bond length comparisons to 3 (Table III, Figure 2). All the methods employed reveal about the same variations in C–C bond lengths around the calculated benzene value. The strongly decreasing C–C bond length alternation on going from Hartree–Fock to the MP2 level is remarkable. It seems reasonable to compare the carbon backbone of 3 with *cis*-butadiene (Table III). At the noncorrelated level the C–C bond lengths of 3 are almost exactly midway between those of their butadiene equivalents and the benzene value, whereas at the correlated level a distinct shift toward the C–C bond length of benzene can be observed. The semiempirical N–B bond lengths are a little shorter than in borazine but all ab initio values correspond almost exactly to the N–B bond length of borazine. The C–N bond is relatively close to the average bond length of methylamine and methylenimine at each level of theory, while the C–B distance shows a tendency toward the single bond length of methylborane. For both heteroatom–carbon bonds AM1 tends toward the single bond whereas the MP2 level 3 approaches the average of the heteroatom–carbon single and double bond lengths. As a whole, the geometrical data at the MP2 level suggest that 3 delocalizes its π-electrons over the four carbon atoms, nitrogen and boron. The cyclic π-conjugation does, however, appear to be broken by the long B–C bond.

1,4-Azaborine 4. The bonding characteristics of 4 are in good agreement with the above findings for 3. The N–C bond lengths are roughly the average of their single and double bond analogs. The C–C bond distances shift slightly between the benzene and the ethylene values at each level of theory. Furthermore, the B–C bond length is much closer to the carbon–boron distance in methylborane than in methyleneborane. The overall bonding scheme of 4 can be described as an at least partly delocalized 3-azapenta-1,4-diene with a boron atom connecting the two carbon ends but not involved in the electron delocalization.

1,3-Azaborine 5. In accord with MNDO findings[6] both ab initio optimization procedures reproduce the C–C bond length of benzene in 5 (AM1 does not quite agree in this respect). The most striking support for a strongly delocalized electron system in 5 are the altogether much shorter heteroatom–carbon bond lengths in this isomer compared to 3 and 4. This effect is more pronounced for nitrogen. At the MP2 level the somewhat extended B–C bonds slightly spoil the straightforward picture of a fully delocalized π-system.


3 4 (α-spin) 5 (β-spin)

Figure 3. Lewis structures according to NBO analyses for 3, 4, and α- and β-spin orbitals of 5.

Finally, we note that MNDO reproduces the ab initio geometries of 3–5 better than AM1.

Bond Orders

There is more than one way to "allocate the electrons in some fractional manner among the various parts of the molecule".[29] Natural bond orbital (NBO) analysis, which can be "conceived as a chemist's basis set that would correspond closely to the picture of localized bonds and lone pairs as basic units of molecular structure",[30] is generally more consistent than Mulliken population analysis and has been used here.

Localization of bonds in order to define a Lewis structure results in two different resonance structures for 5, both with formal charges on the heteroatoms (vide supra). The NBO analysis of the UHF (singlet) wavefunction for 5 handles this apparent drawback by generating two different sets of electrons for the π-system (Table IV). The two sets of π-electrons produced for 4 are identical and hardly differ from each other in the case of 3. The arrangement of π-electrons for the latter two isomers qualitatively reflect 'chemical intuition'.

The three highest energy occupied orbitals in 3 are the π-bonds between C_3 and C_4, C_5 and C_6, and N and B (see Figure 3). Their electron occupation is lower than the maximum of 2, and the differences can be found in the corresponding π^* orbitals. 1.6% of the total electron density cannot be described by this Lewis structure.[31] This percentage is much lower than the 2.9% of benzene[32] but comparable to the 1.4% of borazine.[33] Natural localized molecular orbital (NLMO) analysis[34] reveals a minor participation of neighboring atoms in the π-bonds.

In 4 the two degenerate C–C π bonds are again the highest energy binding orbitals followed by the lone pair on nitrogen, which is occupied by only 1.66 electrons. The NBO analysis assigns 0.31 electrons to the formally empty p-orbital on boron and 0.17 electrons to the slightly higher C–C π^*-antibonds. A considerable 2.1% of the total electron density must be ascribed to non-Lewis structures. The partially filled p-orbital of boron participates with 7% in both C–C π bonds according to the NLMO analysis.

For the α- and β-spin orbitals of 5 the NBO analysis generates two distinct ways of allocating the six π-electrons. The α-spin electrons populate three π-bonds (N–C_2, B–C_4, C_5–C_6; see Figure 3) to a major degree and the non-Lewis structure makes up for only 1.8% of the total α-spin electron density. As in 3, adjacent atoms are slightly involved in the π-bonds. Just two π bonds (C_2–B, C_4–C_5) are formed by the β-spin electrons along with a lone pair

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(28) Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1987, *109*, 1871.

(29) Reference 12; p 27.

(30) Reference 24; p 899.

(31) Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* 1988, *110*, 368.

(32) Hommes, N. J. R. v. E. Private communication.

(33) The NBO analyses of the RHF/6-31G* geometry, which is identical to the UHF singlet geometry.

(34) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* 1985, *83*, 1736.

Table IV. Summary of NBO Analyses of 3–5, Benzene, and Borazine

	NBO		NLMO
		1,2–azaborine **3**	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+6.81	π^* C_3–C_4	0.13	
+6.47	π^* N–B	0.15	
+5.96	π^* C_5–C_6	0.20	
−8.72	π C_3–C_4	1.82	91% π C_3–C_4; 6% B; 2% C_5; 1% C_6
−9.79	π C_5–C_6	1.85	93% π C_5–C_6; 4% C_4; 1% C_5; 1% B
−10.99	π N–B	1.84	92% π N–B; 5% C_6; 2% C_5
			total non-Lewis: 1.63%
		1,4-azaborine **4**	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+6.12	π^* C_3–C_4/C_5–C_6	0.17	
+4.74	LP* B	0.31	
−9.16	π C_3–C_4/C_5–C_6	1.83	92% π C_3–C_4/C_5–C_6; 7% B; 1% C_6/C_2
−9.90	LP N	1.66	83% LP N; 5% C_2/C_6; 2% B; 2% C_3/C_5
			total non-Lewis: 2.08%
		1,3-azaborine **5**, α-spin orbitals	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+7.44	π^* B–C_4	0.03	
+5.39	π^* N–C_2/C_5–C_6	0.09/0.15	
−6.94	π B–C_4	0.83	83% π B–C_4; 11% C_5; 3% C_2
−10.07	π C_5–C_6	0.93	93% π C_5–C_6; 4% C_2; 2% N
−12.22	π N–C_2	0.96	96% π N–C_2; 2% B
			total non-Lewis 1.77%
		1,3-azaborine **5**, β-spin orbitals	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+7.09/+6.73	π^* C_4–C_5/C_2–B	0.05/0.04	
+1.19	LP* C_6	0.32	
−8.06	π C_2–B	0.91	91% π C_2–B; 5% C_4; 4% C_6
−8.06	π C_4–C_5	0.85	85% π C_4–C_5; 11% C_6; 2% N
−10.11	LP N	0.82	79% LP N; 17% C_6
			total non-Lewis: 2.47%
		benzene	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+4.49	3 π^* C–C	0.33	
−6.86	3 π C–C	1.66	83% π C–C; 6% ortho-C; 3% meta-C
			total non-Lewis: 2.91%
		borazine	
orbital energy (eV)	molecular orbital	electron occupancy	atomic hybrid contribution
+5.61	3 π^* N–B	0.14	
−8.96	3 π N–B	1.86	93% π N–B; 6% ortho-B;
			total non-Lewis: 1.41%

on nitrogen (see Figure 3). The p orbital on C_6, the lowest nonbonding orbital energetically, is occupied by 0.32 electrons, leading to a 17% participation of this p-orbital in the lone pair on nitrogen according to the NLMO analysis. This β-spin electron distribution has 2.5% non-Lewis character, which is fairly close to the benzene value of 2.9%. The average of both non-Lewis contributions of **5** (2.12%) is close to the value of **4** (2.08%). Thus, the NBO analyses suggest a similar delocalization effect in these two azaborine isomers.

Thermochemical Stabilities

Interactions between the various bonds of a conjugated system have to be eliminated in order to estimate the amount of electron delocalization in a molecule. This can be achieved by splitting the molecule into smaller subunits. Hydrogens are placed at the unconnected ends to complete the fragment structures. The numbers and kinds of bonds as well as the number of lone pairs remain the same on each side of the equation. By comparing the energy of the fragments to that of the whole, a reasonable estimate for resonance energy can be expected.[35] There are two disadvantages to these isodesmic reactions. Firstly, a well-defined valence bond description of the molecule is necessary. This turns out to be an ambiguous task in the case of the 1,3-azaborine **5**. Secondly, by breaking the ring into its acyclic parts all of the other effects such as ring strain, hyperconjugation, etc. are discarded. Nevertheless, there has been good agreement between the energy differences for isodesmic reactions and experimental findings.[12]

Homodesmotic[36] and hyperhomodesmotic[37] reactions, which maintain greater similarity of bond types on both sides of the reaction, are known to be superior to isodesmic equations in assessing the gain in energy through cyclic conjugation.[13] Unlike the case for hydrocarbons and purely

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(35) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(36) George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121.

(37) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

heteroatomic cycles, there is no straightforward way of constructing satisfactory fragments for the homo- or hyperhomodesmotic reactions of azaborines. The lack of even electron, uncharged fragments of **5** prohibits a thermochemical investigation of this isomer entirely. The RHF/6-31G* energies have not been corrected for zero-point vibrational energies (ZPE) because those corrections are known to increase the bond separation values by a nearly constant 0.1–1.1 kcal/mol only,[38] but the trends remain the same. The results are summarized in Table V together with some well-known examples of delocalized structures.

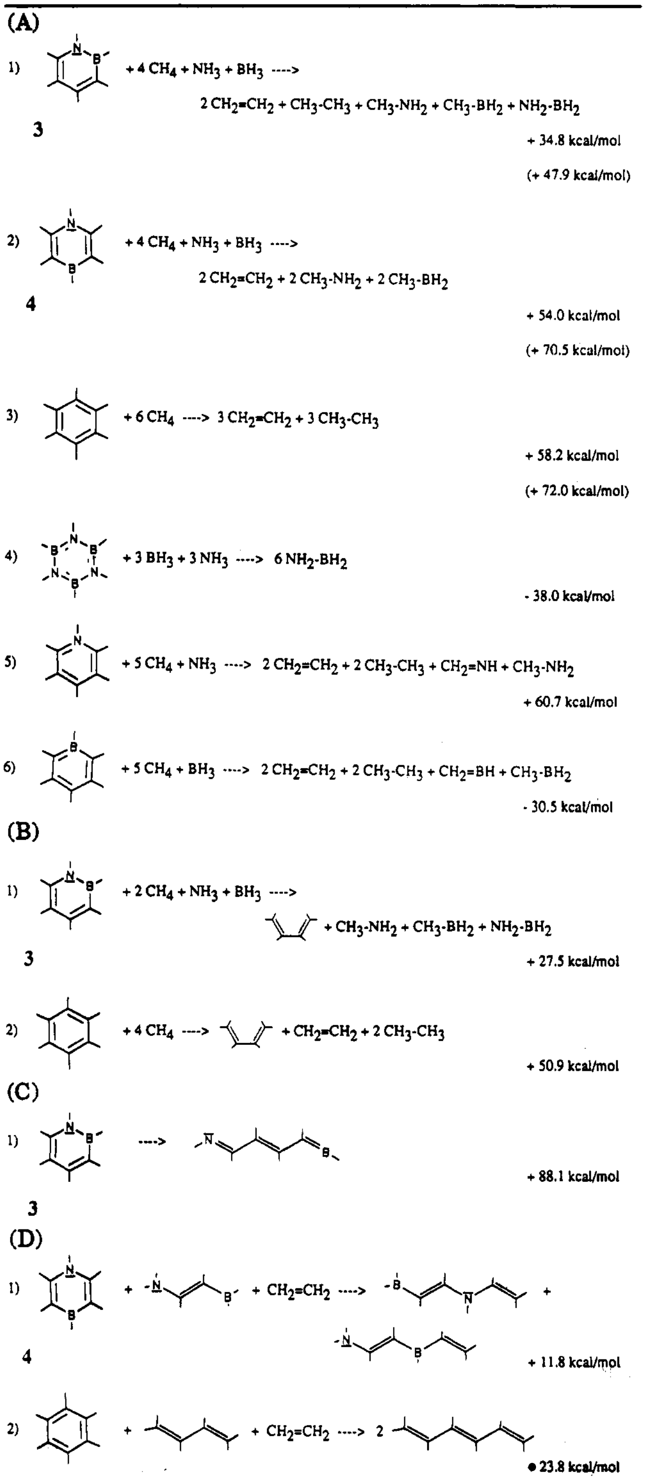
The delocalization effect is more pronounced in the 1,4-azaborine **4** than in the 1,2-isomer **3** and this does not change on inclusion of electron correlation. A decrease in electron delocalization with increasing electronegativity differences has been described in a computational survey of heteropolar analogs of benzene.[10b] Homodesmotic reactions confirm that a rising bond polarity in the order B–P < B–N < Al–N leads to a localization of electronic charge. For the azaborines the difference in electronegativity is highest between N and B. This is the most obvious reason for the lower resonance energy of **3** compared to **4**. The value for **4** is actually close to the data found for some very stable 'aromatics' (A 3 and 5 in Table V). The much lower value for **3** can be accounted for by the interruption of electronic delocalization in the carbon backbone by the heteroatoms. Introducing cisoid butadiene instead of ethylene and ethane into the isodesmic equation for **3** (B 1) diminishes the delocalization energy by about 10 kcal/mol only. Thus, the aminoborane moiety still contributes a considerable amount of delocalization energy (27.5 kcal/mol) to the 1,2-azaborine molecule **3**. However, introducing cisoid butadiene into the isodesmic equation of benzene reduces the delocalization energy by 7.3 to 50.9 kcal/mol (B 2). This means that bridging a cisoid butadiene with aminoborane yields roughly half as much resonance energy as with ethylene. The large stabilization exerted by the heteroatoms in **3** on each other is reflected by the amount of cyclization energy of linear 1-imino-2-butenylen-4-borane of 88 kcal/mol (C 1).

We have also constructed a chemical equation for **4** that satisfies the requirements for a hyperhomodesmotic reaction[37] (D 1). Although the number of fragments on the right-hand side of the equation and their size on the left-hand side do not coincide with those initially suggested for hydrocarbons,[37] the value calculated in the same manner for benzene (D 2: +23.8 kcal/mol) agrees well with that found by means of the conventional description[37] (+23.4 kcal/mol). According to this equation (D 1) **4** acquires half as much energy through cyclic conjugation as benzene does. This value can be taken as a guide for the delocalization effect in **4**, since homodesmotic reactions are designed for cyclic delocalization effects.[13]

The apparent discrepancy between the more stable **3** and the more highly delocalized **4** and **5** is hidden in the two orthogonal electron systems of the heterocycles. The crucial factors determining the relative stability of **3** on one hand and **4** and **5** on the other are the qualities of the σ bonds. Their net differences are one C–C and one N–B bond for **3** against one N–C and one B–C bond for **4** and **5** each (Table VI). This classification is then reflected in the relative energies: **4** and **5** are much closer in energy to each other than **3** is to either of them (Figure 1).

The resonance energy depends on the amount of perturbation of the π-systems caused by the heteroatoms. In **3** the N–B donor–acceptor pair of atoms show little tendency to delocalize their π-electrons into the remaining butadiene moiety. In **4** (and **5**) the heteroatoms are separated by carbon atoms, thus restricting the perturbation of the π-system to two isolated positions in the ring. This obviously is a smaller obstacle to delocalization than the cumulated B–N arrangement. In accord with NBO analyses, isodesmic equations show a pronounced delocalization effect for **4**. Unfortunately, this cannot be verified by isodesmic equations in the case of **5**, but the arguments for a strong delocalization in **4** also apply to **5**. Thus, the reasons that lead to a stabilization of the σ frame in the azaborines are also those that prevent effective

Table V. Thermochemical Reactions and Energies at RHF/6-31G* (and MP2/6-31G*) for 3, 4, and Reference Compounds



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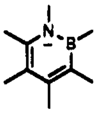
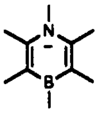
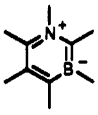
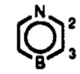
(38) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* 1988, *110*, 4204.

Table VI. Summary of Calculational Results

	structural differences		relative energies	delocalization effects derived from		
	σ-frame	π-system	QCISD + ZPE (kcal/mol)	geometries	NBO analyses	isodesmic eqs
 **3**	C–C, N–B	$^+N{=}B^-$	0.0	weak[a]	weak	weak
 **4**	N–C, B–C	N···B	+23.2	weak[a]	good	modest
 **5**	N–C, B–C	N···B	+33.1	good[a]	good	modest

[a] Across five ring atoms.

Table VII. Calculated (IGLO) and Experimental ^{11}B- and ^{13}C-Chemical Shifts for 3, 4, and Reference Compounds (in ppm)[a]

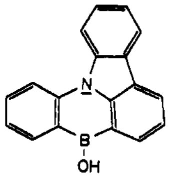
		DZ	II′	II′-avg[b]	expl
1,2-azaborine **3**					
	B	30.3	34.4		36.5–39.0[c]
	C_3	129.9	126.2	106.2	
	C_4	148.4	150.3	145.3	
	C_5	110.4	103.6	115.0	
	C_6	140.0	135.4	152.3	
1,4-azaborine **4**					
	B	39.1	44.8		35.0[d]
	C_2	144.3	141.0	152.3	144.6/143.6
	C_3	119.7	115.8	106.2	124.9/118.3
benzene					
	C	128.3[e]	127.2		128.1–129.5[f]
pyridine					
	C_o	156.7[e]	148.6		149.2–150.4[f]
	C_m	121.8	119.4		123.0–124.2
	C_p	137.9	138.1		134.9–136.2
borabenzene					
	B	85.6	93.4		
	C_o	96.4	88.8		
	C_m	149.3	147.9		
	C_p	110.6	106.4		

[a] Relative to $BF_3{\cdot}OEt_2$ and TMS, respectively. [b] See text. [c] Various solvents: Davies, F. A.; Dewar, M. J. S.; Jones, R. *J. Am. Chem. Soc.* **1968**, *90*, 706. [d] In DMSO-d_6: Kranz, M. Unpublished results. [e] Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360. [f] Depending on solvent: *Carbon-13 NMR Spectra Data*, 4th ed.; Bremser, W., Ernst, L., Fachinger, W., Gerhards, R., Hardt, A., Lewis, M. E. P., Eds.; Verlag Chemie: Weinheim, 1987.

delocalization of the π-electrons.

IGLO Calculations

Nuclear magnetic resonance (NMR) is one of the most powerful tools available for elucidating the structures of organic molecules. Ab initio calculation of chemical shifts with the IGLO method[14] connects theoretical work directly to experiment. Unfortunately, there are no ^{13}C-NMR data available for the numerous derivatives of **3**. Thus, comparisons have to be restricted to ^{11}B shifts for **3** and to ^{11}B and ^{13}C shifts for an unpublished derivative of **4** (**7**).



7

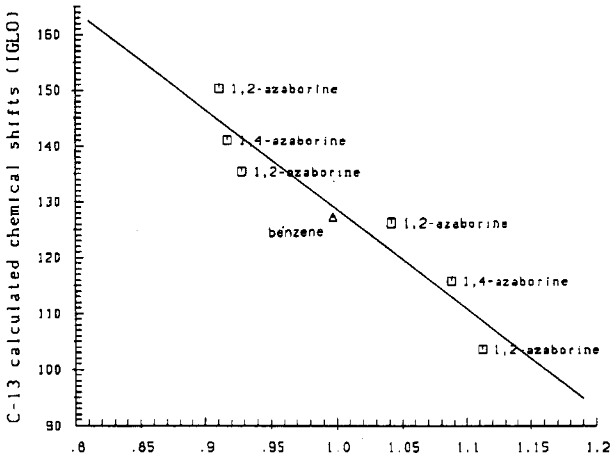


Figure 4. ^{13}C IGLO calculated chemical shifts (II′) plotted against p_z-orbital electron occupany from NBO analyses for **3**, **4**, and benzene (benzene not included in regression line).

Extending the investigation to related heterocycles, the NMR data of pyridine[39] and borabenzene have been calculated and the additivity of chemical shifts was examined by superimposing these two molecules in the appropriate way and calculating the mean value of the two ^{13}C shifts in order to approximate the ^{13}C shifts in the corresponding azaborine isomer. Note that shifts are calculated for isolated molecules, and as differences between gas and liquid phases are generally larger than the discrepancy between theory and experiment[40] an exact coincidence with experimental values must be regarded as fortuitous. The calculated shifts are shown in Table VII.

The ^{13}C shifts of benzene and pyridine calculated with the II′ basis[26] deviate by less than 4 ppm from solution values and are closer than those calculated for the experimental gas-phase geometries of both molecules.[41] The borabenzene ring is only found charged and substituted or coordinated to transition metals. A comparison to the calculated NMR shifts is thus not meaningful. The most

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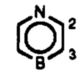
(39) Only IGLO data for the experimental geometry of pyridine are available: Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360.

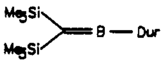
(40) Kutzelnigg, W. *THEOCHEM* **1989**, *202*, 11.

(41) Schindler, M. *Magn. Res. Chem.* **1988**, *26*, 394.

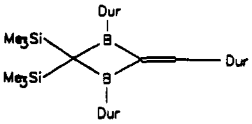
Table VIII. ^{13}C IGLO Calculated Chemical Shifts (II′), p_z-Orbital Electron Occupancy, and Charges from NBO Analyses for 3, 4, and Benzene

		^{13}C-shifts II′ [ppm]	p_z-orbital occupancy	natural charges
1,2-azaborine 3	C_3	126.2	1.042	−0.58
	C_4	150.3	0.911	−0.15
	C_5	103.6	1.112	−0.35
	C_6	135.4	0.928	+0.08
1,4-azaborine 4	C_2	141.0	0.917	+0.09
	C_3	115.8	1.088	−0.64
benzene	C	127.2	0.997	−0.23

similar neighborhood of boron is found in 8[42] and 9[43] with ^{11}B-NMR shifts of 63 and 71 ppm, respectively.



8



9

Dur = 2,3,4,5,-Me_4C_6H

On each level of theory ^{11}B shifts of 3 are a little lower than found experimentally. The averaged II′ values generated from the superposition of pyridine and borabenzene diverge by 10–20 ppm in either direction compared to the directly calculated II′ shifts of 3.

Considering the high degree of substitution of the experimental reference 7, the agreement between the experimental ^{13}C shifts and those calculated at both levels of sophistication is remarkable. The experimental highfield shift of boron can be attributed to the π-back-bonding of oxygen. Again, the II′ averaged values deviate more from experimental ^{13}C data than the shifts calculated directly. One highly substituted reference compound does not warrant an extensive discussion and more experimental results are needed before these tentative conclusions can be generalized.

Finally, we have attempted to relate the molecular property of chemical shifts to the local feature of electron density on the corresponding carbon atoms. Originally proposed by Spiesecke and Schneider,[44] the dependence of ^{1}H and ^{13}C chemical shifts on π-electron density has been demonstrated for many classes of compounds[45] with a variety of methods for determining the electron distribution in the molecules investigated. It has been stressed that the choice of the wavefunction is critical to the quality of the results.[46] The RHF/6-31G* wavefunctions of 3 and 4 localized by the natural population analysis method supply the p_z-orbital electron occupancy needed. ^{13}C shifts do not correlate simply with the charges on the corresponding atoms (Table VIII) but rather with the electron density in the respective p_z-orbitals (Figure 4, correlation coefficient: 0.95). The value for benzene is added for comparison. The slope of the regression line of both azaborines (−194.1 ppm/π-electron) is in the range of those found for other heterocycles.[45]

Conclusion

Molecular geometries of the three azaborine isomers were determined at ab initio RHF/6-31G* and correlated levels (MP2) of theory. Single-point calculations were extended to the MP4 and QCISD levels.

In accord with the latest semiempirical results[6] the order of stability of the azaborines persists at all ab initio levels of sophistication. Electron correlation does not change the relative stability of 3 and 4 but lowers the energy of 5 significantly. Our best estimates of the energies of 4 and 5 relative to 3 are +23.2 and +33.1 kcal/mol, respectively ($3 \gg 4 > 5$). 5 is better described by a UHF (singlet) than the RHF wavefunction, as is 3, although to a minor extent. However, the coefficients of the reference wavefunctions in the CI calculations of all three isomers suggest a comparable participation of other than the ground-state electron configurations in the wavefunctions of these compounds.

Bond lengths within the three heterocycles vary between almost pure single bonds and the average of a single and a double bond between respective atoms. According to the MP2/6-31G* geometry, bond distances in 3 and 4 tend on average toward their single-bond equivalents. Except for the B–C bond, bond distances in 5 are very close to the average between the respective single and double bond lengths.

The NBO analysis of 3 and 4 conform to the intuitively expected arrangements of non-σ electron pairs within the heterocycles, although there is a considerable degree of electron delocalization in 4 according to the total non-Lewis electron density. Two different sets of α- and β-spin orbitals are created for 5 by the NBO analysis. The unconventional electron distribution in the β-spin case leads to a value of 2.5% non-Lewis character of the wavefunction, close to the amount in benzene (2.9%).

The resonance energy of 4 derived from thermochemical equations at 6-31G* is smaller than those for benzene and pyridine, although the exact value depends on the way of fragmentation. Delocalization is less pronounced in 3 on account of charge localization by the aminoborane moiety. The lack of uncharged and even electron fragments for the isodesmic equation of 5 prevents determination of a resonance energy for this isomer. Nevertheless, the arguments supporting a moderate delocalization effect for 4 also apply to 5. The key to the solution of the apparent discrepancy of a most stable 3 with a less delocalized π-system lies in the sigma frameworks of the azaborines. The differences in quality of the sigma bonds favors 3 compared to 4 and 5, while at the same time preventing effective π-electron delocalization.

The agreement of the few experimental NMR shifts of substituted derivatives of 3 and 4 to their theoretical equivalents as calculated by the IGLO method suggests that these heterocycles are described reliably by the methods used.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Volkswagenstiftung, and the Convex Computer Corp. We are grateful to A. Alex, N. v. E. Hommes, and P. v. R. Schleyer for valuable discussions.

Note Added in Proof. Since this work was submitted, we have been able to obtain the crystal structure of a highly substituted 1,4-azaborine derivative.[47] The geom-

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(42) Pilz, M.; Stadler, M.; Hunold, R.; Allwohn, F.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 761.

(43) Hunold, R.; Pilz, M.; Allwohn, J.; Stadler, M.; Massa, W.; Schleyer, P. v. R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 759.

(44) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

(45) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Thieme-Verlag: Stuttgart, 1984, pp 88.

(46) Tokuhiro, T.; Fraenkel, G. *J. Am. Chem. Soc.* **1969**, *91*, 5005.

(47) Kranz, M.; Clark, T. *J. Chem. Soc., Chem. Commun.*, in press.

etry of the azaborine ring found experimentally agrees well with the description of the bonding presented here.

Registry No. 3, 6680-69-9; 4, 4438-39-5; 5, 135059-08-4.

Supplementary Material Available: Structures and energies of the calculated molecules in the form of archive entries (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

A Semitheoretical Multiparameter Approach To Correlate Solvent Effects on Reactions and Equilibria

Joseph J. Gajewski

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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A solvent rate effect equation which uses four physical properties of the solvent for parameters has been applied with good success to solvolysis reactions, solvent E_t values, Claisen Rearrangements, Diels–Alder reactions, endo–exo ratios in Diels–Alder reactions, azo-Cope rearrangements, and enol–ketone equilibria of the dimedone and pyridone variety. The coefficients of the parameters, which are the Kirkwood–Onsager function, the solvent cohesive energy density, the specific solvation of chloride ion, and the specific solvation of potassium ion, lead to differences in dipole moments, in volumes between initial and final states, and in the extent of specific solvation of anionic and cationic sites relative to the solvation of chloride ion and potassium ion, respectively.

Concern for solvent effects on chemical reactions has led to more than a few theoretical constructs and empirical correlations to provide not only rationalization but prediction of equilibrium and rate data.[1] For instance, in solvolysis reactions, Winstein–Grunwald solvent Y values[2] have proven remarkably useful not only for correlation purposes, but to assess the sensitivity of the reaction to solvent relative to the standard. The sensitivity of the reaction to Y might appear to be a measure of change in ionic character from ground state to transition state. However, Abraham has provided quantitative data on the stability of *tert*-butyl chloride in various solvents relative to that in DMF and found significant destabilization in the more polar, hydroxylic media.[3b] Indeed, ground-state destabilization is an important contributor to the S_N1 rate differences in polar media as was suggested by Winstein[2] and demonstrated by Arnett.[4] In addition, Abraham found that the solvent cohesive energy density, ced, as defined by Hildebrand, $(\Delta H_{vap} - RT)/V_m$,[5] is the major correlator of the stability of *tert*-butyl chloride in a wide range of solvents. Further, by subtraction Abraham could determine the relative stability of the *tert*-butyl chloride solvolysis transition state in different solvents relative to that in DMF and found behavior which correlated with the Taft solvatochromic π^* parameter.[3a] However, some solvents stabilize the transition state by what has been recognized as a specific hydrogen bonding effect; these solvents include trifluoroethanol, hexafluoroisopropanol, and formic acid. Thus, the coefficient of the hydrogen bonding term, α, in the Taft multiparameter correlation of the *tert*-butyl chloride solvolysis reaction is not insignificant compared to the coefficient of the π^* parameter (eq 1; note that Taft uses δ^2 for the ced term).[3c]

$$\ln k = 5.10\pi^* + 4.17\alpha + 0.73\beta + 0.0048\delta^2 - 14.60 \qquad (1)$$

Interestingly, the ced term appears to be insignificant in the Taft correlation of the solvolysis data despite its importance in correlating the ground-state destabilization. Abraham argues that there is destabilization of the transition state by the ced term so that only the π^* and α terms are important overall. However, there should be concern over the extent to which the ced term is also included in the π^* term as admitted by Taft.[3a] Interestingly, increases in the ced have also been argued to be responsible for increased apolar binding of pyrene with cryptans.[6] References are scattered throughout the literature to the potential interchangeability of rate responses to ced and external pressure studies,[7] although le Nobel's recent review argues vigorously against this.[8]

A particularly relevant approach to solvent effects on enol–ketone tautomeric equilibria was provided by Beak[9] who used the Kirkwood–Onsager function, $[(\epsilon - 1)/(2\epsilon + 1)]$,[10] and Taft's α and β parameters of early 1980's vintage. Remarkable correlations were found for cyclohexane-1,3-dione systems and related rigid systems. This equation with the addition of a ced term and the inclusion of the

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[1] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

[2] Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. See also: Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618.

[3] (a) For the most recent review of parameter values with extensive comments, see: Abraham, M. H.; Grellier, P. L.; Abboud, J.-L. M.; Doherty, R. M.; Taft, R. W. *Can. J. Chem.* **1988**, *66*, 2673. (b) Abraham, M. H.; Grellier, P. L.; Nasehzadeh, A.; Walker, R. A. C. *J. Chem. Soc.* **1988**, 1717. (c) Multiparameter correlation approaches to solvent effects were pioneered by Koppel and Palm.[1]

[4] Arnett, E. N.; Bentrude, W. G.; Burke, J. J.; Duggleby, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 1541 and references contained therein.

[5] (a) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand-Reinhold: Princeton, 1970. Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice-Hall: Englewood Cliffs, NJ, 1962. Hildebrand also called the ced an internal solvent pressure, and many use both terms interchangeably. More recently the internal solvent pressure has been defined as $(dU/dV)_T$. Measured values for this are distinctly different from the ced (see ref 1). (b) For a correlation with the square root of the solvent cohesive energy density, see also; Herbrandson, H. F.; Neufeld, F. R. *J. Org. Chem.* **1966**, *31*, 1140.

[6] Smithrud, D. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 339.

[7] Ouellette, R. J.; Williams, S. H. *J. Am. Chem. Soc.* **1971**, *93*, 466. Dack, M. R. J. *J. Chem. Educ.* **1974**, *51*, 233. Snyder, J. P.; Harpp, D. N. *J. Am. Chem. Soc.* **1976**, *98*, 7821.

[8] le Nobel, W. J. *Chem. Rev.* **1989**, *89*, 549.

[9] (a) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216. (b) Beak, P.; Covington, J. B.; White, J. M. *J. Org. Chem.* **1980**, *45*, 1347.

[10] Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351. Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. For applications of this solvent property see ref 1, Chapter 5.

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