the rates of unimolecular chelate ring opening, which increase with increasing chelate ring size, and the rates of W–S bond breaking in the *cis*-(η^1-DTA)(L)W(CO)$_4$ intermediates produced after chelate ring opening, which increase with increasing steric demands of L.

Acknowledgment. The support of this research by the National Science Foundation under Grant CHE-84-15153 is gratefully acknowledged. Pulsed laser flash photolysis experiments and data analysis were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biomedical Research Technology program of the Division of Research Resources of the National Institutes of Health (Grant RR00886) and by the University of Texas at Austin. The technical assistance of the staff at the CFKR and the experimental assistance of I-Hsiung Wang are much appreciated.

Registry No. (DTD)W(CO)$_4$, 118297-74-8; (DTU)W(CO)$_4$, 118297-75-9; P(O-*i*-Pr)$_3$, 513-02-0; P(OMe)$_3$, 121-45-9; *cis*-(η^1-DTD)(P(O-*i*-Pr)$_3$)W(CO)$_4$, 118297-76-0; *cis*-(η^1-DTU)(P(O-*i*-Pr)$_3$)W(CO)$_4$, 118297-79-3; *cis*-(η^1-DTD)(P(OMe)$_3$)W(CO)$_4$, 118297-77-1; *cis*-(η^1-DTU)(P(OMe)$_3$)W(CO)$_4$, 118297-78-2; (η^1-DTD)W(CO)$_4$, 118297-80-6; (η^1-DTU)W(CO)$_4$, 118297-81-7.

Supplementary Material Available: Listings of values of k_{obsd} for reactions of (DTA)W(CO)$_4$ with L to afford *cis*-(η^1-DTA)(L)W(CO)$_4$ complexes in chlorobenzene at various temperatures (Appendix I), rate constants for chelate ring reclosure in *cis*-[(η^1-DTA)(CB)W(CO)$_4$] intermediates produced via pulsed laser flash photolysis at various temperatures (Appendix II), and values of k_4 for dissociation of DTA from *cis*-(η^1-DTA)(L)W(CO)$_4$ complexes in the presence of L in CB at various temperatures (Appendix III) (8 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Wisconsin—Madison,
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Natural Bond Orbital (NBO) Analysis of Substituent Effects in Borazine Derivatives

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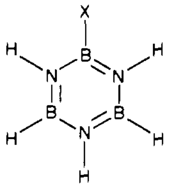
The natural bond orbital (NBO) method of wave function analysis has been applied to characterize electronic substituent effects in B-monosubstituted borazine derivatives. The calculations indicate that the highly polar nature of the ipso B–N π^* antibonds and π bonds allows for enhanced interaction with π donors and limits the interaction with π acceptors relative to benzene. Calculated para π-electron density changes are smaller in magnitude than those in benzene derivatives, indicating decreased but still significant resonance delocalization. Calculated substituent/ring interaction energies and para π-electron density changes for B-monosubstituted borazines give improved Hammett correlations over those for analogous benzene systems.

Introduction

Borazine (Ia) has often been referred to as the "inorganic benzene" because its physical and structural properties are similar to those of benzene.[1]



Ia, X = H
b, X = NH$_2$
c, X = OH
d, X = F
e, X = Cl
f, X = CN
g, X = NO$_2$

Recent interest in borazine derivatives has intensified due to their utility as precursors to high molecular weight polymers and boron–nitrogen ceramics.[2] Electron diffraction studies have shown that the borazine molecule has a planar D_{3h} symmetry with all B–N bond lengths being equivalent (r_{B-N} = 1.44 Å).[3] The B–N bond lengths are shorter than a representative B–N single bond (cf. H$_3$BNH$_3$, r_{B-N} = 1.56 Å) and suggest the B–N bond order in borazine is significantly greater than 1.

Chemically, however, borazine behaves very differently from benzene. Unlike benzene, borazine undergoes addition reactions quite readily. Also, electrophilic substitution is not found in borazine chemistry. Thus, it is generally agreed that the chemical properties of borazine are dictated to a greater extent by the polarity of the B–N σ bonds than by the aromaticity of the π system.[1]

Intriguing, however, are the properties of substituted borazine derivatives. Relative ^{1}H NMR shifts of ortho and para N–H protons of B-monosubstituted borazines are strikingly similar to those of the analogous benzene derivatives.[4-6] This suggests that indeed the borazine ring π system is capable of transmitting substituent effects transannularly. Although experimentally known for quite some time, a mechanistic discussion of substituent effects have been ignored in ab initio theoretical studies of borazine.[7-12] In this contribution, we theoretically characterize the magnitude and nature of the aromaticity in borazine and examine the mechanism of transmission of substituent effects through the borazine π system. Results are interpreted within the natural bond orbital (NBO) framework, which has been successfully applied to both localized and delocalized systems.[13] This represents a

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(1) For a recent review see: Borlin, J.; Gaines, D. F. In *Boron Hydride Chemistry*; Academic Press: New York, 1975.

(2) (a) Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Inorganic and Organometallic Polymers*; Zeldin, M.; Wynne, K. J.; Allcock, H. J., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; p 378. (b) Paciavek, K. J. L.; et al. *Ibid.*; p 392.

(3) Harshbarger, W.; et al. *Inorg. Chem.* **1969**, *8*, 1683.

(4) Porter, R. F.; Yeung, E. S. *Inorg. Chem.* **1968**, *7*, 1306.

(5) Beachley, O. T., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5372.

(6) Dunkin, T. R.; Beachley, O. T., Jr. *Inorg. Chem.* **1974**, *13*, 1768.

(7) Anderson, W. P.; et al. *Chem. Phys. Lett.* **1982**, *88*, 185.

(8) Peyerimhoff, S. D.; Buenker, R. J. *Theor. Chim. Acta* **1970**, *19*, 1.

(9) Doiron, C. E.; et al. *Can. J. Chem.* **1979**, *57*, 1751.

(10) Vasudevan, K.; Grein, F. *Theor. Chim. Acta* **1979**, *52*, 219.

(11) Boyd, R. J.; et al. *Chem. Phys. Lett.* **1984**, *112*, 136.

(12) Haddon, R. C. *Pure Appl. Chem.* **1982**, *54*, 1129.

(13) The NBO method has been recently applied to Fenske-Hall wave functions: (a) Kanis, David, Ph.D. Thesis; University of Wisconsin—Madison, 1988. (b) Glendening, E. D.; Weinhold, F. A. *J. Am. Chem. Soc.*, in press. (c) Reed, A. E.; Weinhold, F. A. *J. Am. Chem. Soc.* **1985**, *107*, 1919. (d) Reed, A. E.; Weinhold, F. A.; Weiss, R.; Macheleid, J. *J. Phys. Chem.* **1985**, *89*, 2688. (e) Reed, A. E.; Weinhold, F. A. *J. Chem. Phys.* **1986**, *84*, 2428–2430. (f) Reed, A. E.; Weinhold, F. A. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

novel application of the NBO method of analysis, as well as an alternative formalism in which to interpret substituent effects. Comparative analyses with benzene systems are offered, and correlations with experimental data are afforded wherever possible.

Computational Method

All calculations were performed on a VAX 8650 computer using the GAUSSIAN 82 system of programs[14] employing the NBO analysis in the population link.

All wave functions were computed at the restricted Hartree–Fock level by using the 3-21G basis set.[15] Full geometry optimizations were completed for all borazine derivatives; single-point calculations were performed for benzene derivatives by using experimental geometries.[16]

The NBO method has been previously described in detail.[17] The method is computationally efficient and quite general and has been applied to a variety of molecular wave functions.[13] Essentially, through a series of operations, a molecular orbital (MO) wave function is transformed to an NBO wave function consisting of (i) highly occupied one-center (lone pair) and two-center (bond) orbitals, and (ii) formally unoccupied one-center diffuse Rydberg and two-center antibond orbitals. The former set corresponds to the localized "natural Lewis structure" and serves as a zeroth-order description of the system. Delocalization effects are depicted by a "charge transfer" from the highly occupied bond orbitals into adjacent unoccupied antibond orbitals. The energy lowering $\Delta E^{(2)}_{D\to A}$ due to this donor/acceptor interaction can be approximated through a second-order perturbative treatment of the Fock matrix in the NBO basis:

$$\Delta E^{(2)}_{D\to A} \sim \frac{\langle \varphi_D|F|\varphi^*_A\rangle^2}{\epsilon_A^* - \epsilon_D}$$

where φ_D represents a donor bond orbital from set i, φ_A represents an acceptor antibond orbital from set ii, and ϵ_D and ϵ_A are diagonal Fock matrix elements of orbitals φ_D and φ_A, respectively.[18]

These perturbative interactions form a basis for our discussion of substituent effects in aromatic systems. For a rigorous molecular orbital (MO) approach, quantitative interaction energies must be determined via isodesmic bond separation reactions, which involves performing several calculations.[19]

Model compounds chosen for this investigation were the B-monosubstituted borazines. This series of compounds is attractive because of the availability of experimental data needed for correlation with calculations, and because the analogous benzene series is well understood. The various substituents chosen for this study include representative π donors (NH_2, OH, Cl, F) and π-acceptors (CN, NO_2).

Results and Discussion

NBO Description of Borazine. Within NBO framework the "accuracy" of a Lewis structure can be assessed by the percentage of the total SCF electron density (% ρ_{Lewis}) it describes.[20] For the case of borazine, the Kekulē type Lewis structure (Ia) describes 98.6% of the SCF electron density. This indicates that significant resonance delocalization is present in the π system.[21] For benzene % ρ_{Lewis} = 97.1%, indicating greater π delocalization effects.

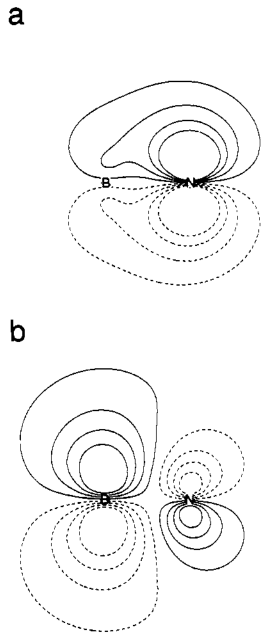
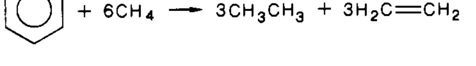


Figure 1. Orbital contour diagram showing (a) the highly polar B–N π bond and (b) the B–N π* antibond of borazine. The π bonds are composed of 90% N 2p and 10% B 2p natural atomic orbitals; the π* antibonds have the opposite polarity.

It is interesting to note that a formal charge analysis of the Kekulē type structure of borazine would suggest each B atom carry a net negative charge and each N atom a net positive charge. Our calculations, in accord with previous experiments,[22] show that indeed the B–N bond polarity is opposite from that implied by the Kekulē structure. Each B atom in fact has a net positive natural charge (q_B = +0.920) and each N atom carries a net negative natural charge (q_N = −1.204).[23] Illustrations of the highly polar B–N π bonds or π* antibonds in borazine are shown in Figure 1. It is important to note that the B–N π bond is highly polarized toward N and the B–N π* antibond is oppositely polarized toward B. This has significant importance in determining substituent interaction with the borazine π system.

Delocalization Energy of Borazine. It is generally accepted that within the ab initio MO framework the delocalization stabilization energy is best estimated by using isodesmic bond separation reactions.[19] Since the various types of computational errors that arise in single-determinant HF theory tend to be bond specific, by conserving the number of types of bonds on each side of the chemical reaction, it is reasonable to assume these errors largely cancel. This procedure has been successfully applied to benzene, using by eq 1;[19] the calculated stabilization energy of +60 kcal/mol (at the 3-21G level) is in excellent agreement with the experimental heat of reaction (+64 kcal/mol). Haddon, in a previous treatment of borazine,[12] has considered two possible forms of isodesmic bond separation reactions shown in eq 2 and 3. He has proposed eq



(1)

$$\Delta E = +64 \text{ kcal/mol}$$

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[14] Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Drishan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. S. "GAUSSIAN 82"; Carnegie Mellon University: Pittsburgh, PA, 1982.

[15] (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

[16] Domenicano, R.; Murray-Rust, P. *Tetrahedron Lett.* **1979**, 2282.

[17] (a) Foster, J. P.; Weinhold, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. A. *J. Chem. Phys.* **1983**, *789*, 4066. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. A. *J. Chem. Phys.* **1985**, *83*, 735. For open-shell systems, the corresponding "different hybrids for different spins" NBO analysis permits a similar treatment: (d) Carpenter, J. E.; Weinhold, F. A. *University of Wisconsin Theoretical Chemistry Institute Report*; University of Wisconsin—Madison: Madison, WI, 1985; WIS-TCI-689. (e) Carpenter, J. E.; Weinhold, F. A. *J. Mol. Struct.* (*THEOCHEM*), in press. (f) Blair, J. T.; Weisshaar, J. C.; Carpenter, J. E.; Weinhold, F. A. *J. Chem. Phys.* **1987**, *87*, 392. (g) A version of the natural bond orbital program suitable for general usage is available from the Quantum Chemsitry Program Exchange, Indiana University, Bloomington, IN: Reed, A. E.; Weinhold, F. A. *QCPE Bull.* **1985**, *5*, 141.

[18] For a further discussion, see: Reed, A. E.; Weinhold, F. A. *University of Wisconsin Theoretical Chemistry Institute Report* 1985; WIS-TC-I-697. Glendining, E. D.; Weinhold, F. A. *Ibid.*; 1988; WIS-TCI-733.

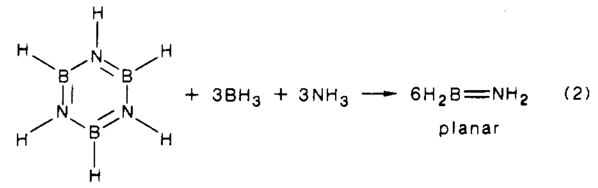
[19] Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab-Initio Molecular Orbital Theory*; Wiley: New York, **1986**, 271.

[20] Carpenter, J. C.; Weinhold, F. A. *J. Am. Chem. Soc.* **1988**, *110*, 368.

[21] For molecules that are well described by a localized Lewis structure such as H_2NBH_2, % ρ_{Lewis} is typically >99.5%.

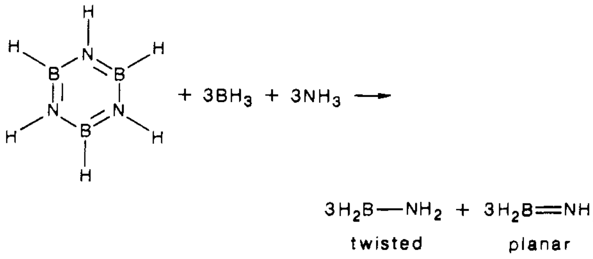
[22] Natural populations have been shown to exhibit improved numerical stability over Mulliken populations. For a further discussion, see ref 15 c.

[23] Lotz, A.; et al. *Chem. Phys.* **1986**, *103*, 317.



$$B_3N_3H_6 + 3BH_3 + 3NH_3 \longrightarrow \underset{\text{planar}}{6H_2B{=}NH_2} \quad (2)$$

$\Delta E = -54.4$ kcal/mol (4-31G)



$$B_3N_3H_6 + 3BH_3 + 3NH_3 \longrightarrow \underset{\text{twisted}}{3H_2B{-}NH_2} + \underset{\text{planar}}{3H_2B{=}NH_2} \quad (3)$$

$\Delta E = +113.1$ kcal/mol (STO-3G)

$\Delta E = +44.6$ kcal/mol (3-21G//3-21G)

$\Delta E = +27$ kcal/mol (experimental)

2 to be the proper form. This reaction is not truly isodesmic, however, because the number of formal B–N single and double bonds is not conserved. As a result, the large negative ΔE would suggest borazine to be destabilized by delocalization effects. We endorse eq 3 as the proper form of the isodesmic bond separation reaction. By inclusion of both the planar and twisted forms of the aminoborane H_2BNH_2, the formal number of B–N single and double bonds are conserved. The calculated ΔE value of +44.6 kcal/mol at the 3-21G//3-21G level is significantly less than the STO-3G value of +113.3 kcal/mol reported by Haddon. This can be attributed to the improved performance realized with the more flexible split-valence basis set employed in the present calculations. The 3-21G//3-21G value is in fair agreement with the experimental value at +27 kcal/mol[24] and suggests that borazine is indeed significantly stabilized by delocalization, albeit to a lesser degree than benzene.

NBO Description of Substituent Effects in B-Monosubstituted Borazines. Many previous discussions of substituent effects have focused on the perturbative interaction of the frontier orbitals of the substituent with those of the system of interest.[25]

NBO analysis affords a similar approach. Examples illustrating the interactions of π donor and π-acceptor substituents with an aromatic ring π system appear in Figure 2. Estimates of the interaction energies are obtained from a second-order perturbative treatment of the Fock matrix as previously discussed. The advantage to the NBO method is that these donor/acceptor interaction energies can be obtained from a single calculation, whereas by using a strictly MO approach, it would be necessary to construct isodesmic methanolysis or similar bond separation reactions that would require several calculations.[19]

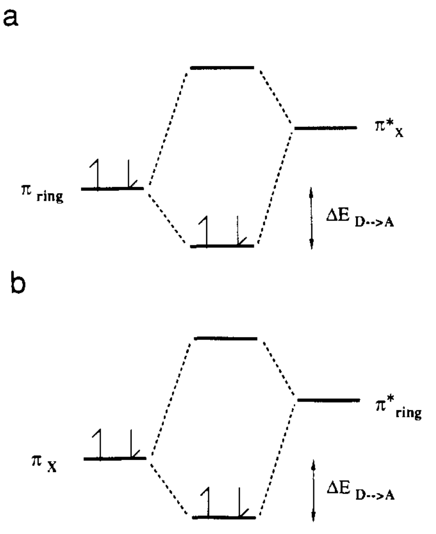


Figure 2. MO diagram illustrating NBO (a) ring π → π*-acceptor and (b) π-donor → ring π* perturbative interactions.

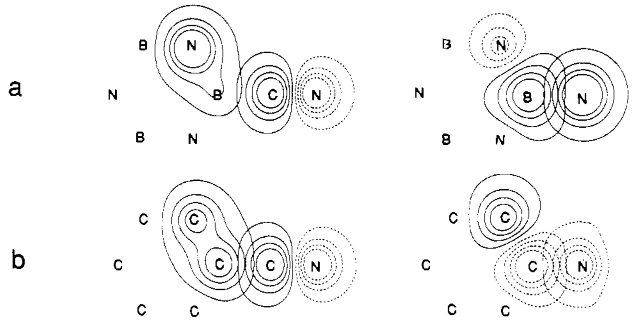


Figure 3. Orbital contour diagrams showing examples of NBO ring π → π*-acceptor (–CN) and π-donor (planar $-NH_2$) → ring π* interactions in (a) borazine and (b) benzene systems.

Table I. NBO Donor–Acceptor Interaction Energies

X	$\Delta E^{(2)}_{D\to A}$,[a] kcal/mol borazine	 benzene
H	0.0	0.0
NH_2	+80.9	+55.6
OH	+67.8	+37.4
F	+52.8	+26.8
Cl	+36.5	+19.5
CN	-2.71	-21.5
NO_2	-2.81	-39.9

[a] These are interaction energies obtained from second-order perturbation theory analysis of Fock matrix in the NBO basis. A + sign indicates charge transfer into the ring; a – sign indicates charge transfer out of ring.

Substituent–Ring Interaction Energies. Ring–substituent interaction energies for benzene and borazine systems are shown in Table I. For interactions involving π donors, the polarity of the ipso ring π* antibond (acting as the acceptor orbital) governs the extent of interaction with the substituent. In borazine, the ipso B–N π* antibond is highly polarized toward B. This results in enhanced interaction with respect to the analogous benzene systems (Figure 3). Experimentally this effect is realized in ^1H NMR data. Beachley has observed that the relative chemical shifts of the ortho protons in π-donor monosubstituted borazines are much larger than in the corresponding benzenes,[26] indicating enhanced interaction at the ipso position. For interactions involving π acceptors, the ring π bond acts as the donor orbital. In borazine the ring B–N π bond is highly polarized away from the substituent and toward the N atom (Figure 1a). This would suggest that the interaction of the borazine ring with a π acceptor is diminished with respect to benzene. Furthermore the borazine system seems to show a "leveling effect" for π-acceptor substituents; the

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(24) This value was calculated from experimental standard enthalpies of formation from the following sources. For BH_3: Wagmon, D. H.; et al. *Selected Values of Thermodynamic Properties*; National Bureau of Standards Technical Note 270-3; U.S. Department of Commerce: Washington, DC, 1968. For NH_3: Kerr, J. A. *Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Astle, M. J., Eds.; Chemical Rubber Co.: Cleveland, OH, 1979. For $H_3B_3N_3H$: Smith, B. C.; Thakur, L. *Nature* **1965**, *208*, 74. For H_2BNH_2 (planar): Kwon, C. T. *U.S. C. F. S. T. I., AD Rep.* **1970**, *AD-711439*. For H_2BNH_2 (twisted), this value was estimated by using the enthalpy of formation of the planar compound and the calculated rotational barrier of 33 kcal/mol) (this work).

(25) For a comprehensive treatment of benzoid systems see: Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1.

(26) (a) Beachley, O. T., Jr. *J. Am. Chem. Soc.* **1970**, 5372. (b) Beachley, O. T., Jr. *Inorg. Chem.* **1973**, *12*, 2503.

Table II. Relative π-Electron Populations[a] on Ring Atoms for B-Monosubstituted Borazines

X	$\Delta q_\pi{}^b$ ortho	$\Delta q_\pi{}^b$ para	$\Delta q_\pi{}^b$ meta	para $\delta(^1H)$, ppm
NH_2	+0.076	+0.014	+0.008	+0.65 $(-N(CH_3)_2)^c$
OH	+0.030	+0.010	0	+0.35 $(-OCH_3)^c$
F	+0.026	+0.005	-0.004	$+0.24^c$
Cl	+0.009	0	-0.009	$+0.12^c$
CN	-0.004	-0.005	-0.009	-0.55^d
NO_2	-0.011	-0.006	-0.015	

[a] Relative to $H_3B_3N_3H_3$. [b] Calculated by using natural population analyses. [c] From ref 26. [d] Beachley, O. T., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 5066.

Table III. Relative π-Electron Populations[a] on Ring Atoms for Monosubstituted Benzenes

X	$\Delta q_\pi{}^b$ ortho	$\Delta q_\pi{}^b$ meta	$\Delta q_\pi{}^b$ para
NH_2	+0.105	-0.044	-0.074
OH	+0.079	-0.031	+0.051
F	+0.051	-0.028	+0.029
Cl	-0.005	-0.006	-0.007
CN	-0.040	+0.001	-0.035
NO_2	-0.073	+0.015	-0.070

[a] Calculated by using natural population analyses. [b] Relative to benzene.

Table IV. Relative ^{11}B and ^1H NMR Chemical Shifts[a] for B-Monosubstituted Borazines

X	borazine: ipso ^{11}B NMR shift, ppm	borazine: para ^1H NMR shift, ppm	benzene para ^1H NMR shift, ppm
NH_2	+4.7	+0.65 $(-N(CH_3)_2)$	0.65
OH	+3.5	+0.35 $(-OCH_3)$	0.45
F	+2.5	+0.24	0.19
Cl	+1.8	+0.12	0.09
CN	-6.7	-1.1	-0.28
NO_2			-0.38

[a] From ref 26.

$\Delta E^{(2)}{}_{D\to A}$ values for $-NO_2$ and $-CN$ are essentially the same.

Transmission of Substituent Effects. The extent of substituent effect transmission through the ring π system must be determined by examining the positions meta or para to the substituent. Field and inductive effects are likely to be negligible since they decrease rapidly with distance from substituent. Any electronic changes at the para position, thus, are purely a resonance effect. Tables II and III contain relative π-electron densities in ring atoms (calculated from natural population analyses) for borazine and benzene, respectively.

Previous work has shown that a linear relationship exists between the relative ^{11}B NMR shift of the ipso B atom (which indicates the degree of substituent–ring interaction) and the relative ^1H NMR shift of the para N–H proton (which provides a measure of the transmission of substituent effects through the π system).[26] The experimental data are contained in Table IV. Computationally, $\Delta E^{(2)}{}_{D\to A}$ energies provide a measure of substituent–ring interactions and should correlate with the ^{11}B NMR data,[27] whereas ^1H NMR data may likely correlate with relative changes in π-electron density at the para N atom ($\Delta q^\pi{}_{para}$). Figures 4 and 5a reveal excellent correlations in both cases for π-donor substituents. Analogous correlations with benzene systems are provided for comparison. On the basis of the electronic effects produced by π-acceptor substituents on the benzene π system, it would be reasonable to expect similar effects in borazines. This evidently is not the case. The modest values of $\Delta E^{(2)}{}_{D\to A}$ and $\Delta q^\pi{}_{para}$ calculated for $-CN$ and $-NO_2$, suggest only a small downfield shift for both the relative ipso ^{11}B NMR and the para N–H ^1H NMR resonances (Figures 4 and 5a). The experimental NMR data for $H_2(CN)B_3N_3H_3$ (none are available for NO_2) appear to contradict this assertion; both resonances are shifted quite far downfield. It is important to note that both the ^{11}B and ^1H NMR spectra were performed on samples in CH_3CN, a highly polar and nucleophilic solvent. Recent studies have shown that CH_3CN can produce substantial downfield shifts of both ^1H and ^{11}B NMR resonances.[28] It is quite possible that the large downfield shifts in the ^{11}B NMR and ^1H NMR are solvent-induced. It is not surprising that these data do not support our correlations in Figures 4 and 5a, since our calculations characterize only intramolecular interactions. Additional experimental studies of π-acceptor B-monosubstituted borazines are needed to properly characterize their effect.

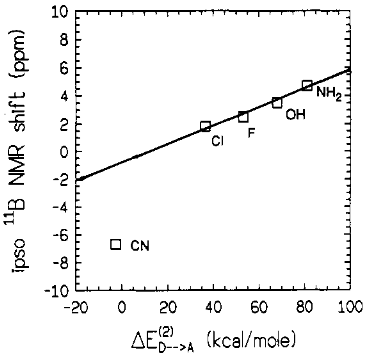

Figure 4. Plot of relative ipso ^{11}B NMR shift vs calculated $\Delta E^{(2)}{}_{D\to A}$ interaction energy for borazine derivatives.

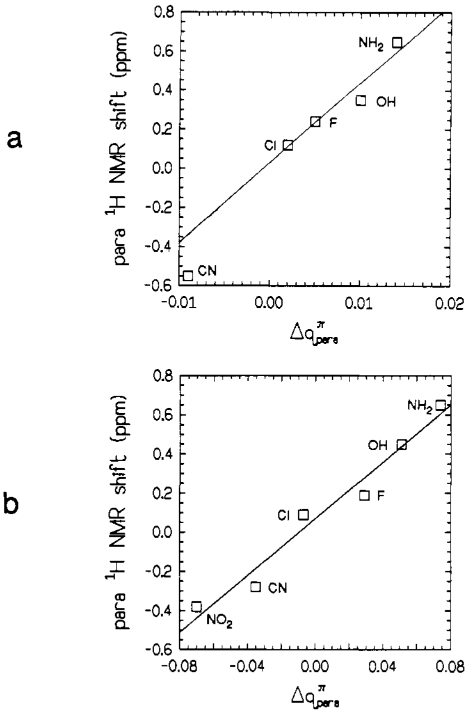

Figure 5. Plot of relative para ^1H NMR shift vs relative para π-electron population ($\Delta q^\pi{}_{para}$) for (a) borazine and (b) benzene derivatives.

Unfortunately synthetic difficulties have hindered attempts at preparing an analogous series of N-monosubstituted borazines. The present calculations indicate a reversal in the relative magnitude of the ring–substituent interactions; π acceptors should show enhanced interaction, whereas that of π donors would be lessened. Predicted effects at the para position seem uncertain. NBO analysis of N-monosubstituted borazines is currently in progress

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(27) Although it has been argued that ^{11}B NMR shifts are governed by changes in π-electron density, it must be emphasized that this assertion has no firm theoretical foundation.[1]

(28) Gaines, D. F.; et al. *Inorg. Chem.* **1984**, *23*, 3252.

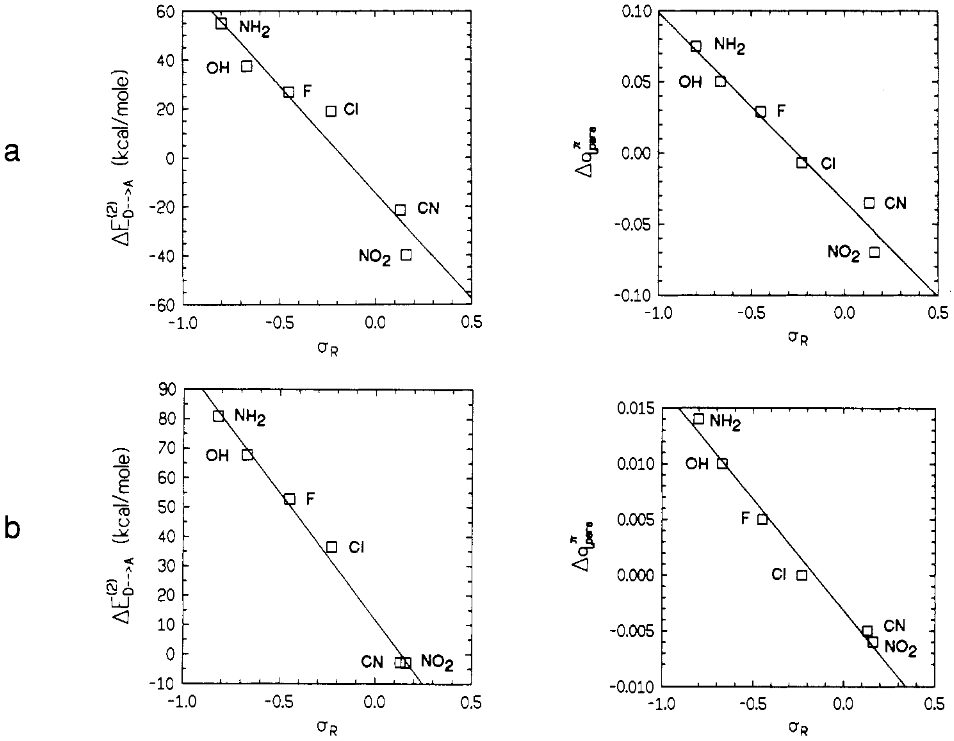

Figure 6. Hammett correlations for (a) benzene and (b) borazine systems. The σ_R substituent constants were taken from ref 24.

Table V. Linear Least-Squares Hammett Correlations for Benzene and Borazine Systems

	Δq^{π}_{para}[a]			$\Delta E^{(2)}_{D\to A}$[b]		
	m	*b*	*r*[c]	*m*	*b*	*r*[c]
borazine	-0.022	-0.003	-0.993	-87.7	11.7	-0.996
benzene	-0.132	-0.003	-0.981	-87.4	-14.3	-0.970

[a] Data were fit to the equation $\Delta q^{\pi}_{para} = m\sigma_R + b$. [b] Data were fit to the equation $\Delta E^{(2)}_{D\to A} = m\sigma_R + b$. [c] *r* represents the least-squares correlation coefficient.

in our laboratory and shall be discussed in a future contribution.

Hammett Correlations. Previous studies have shown that calculated electronic parameters in benzene systems correlate with experimentally derived substituent constants.[25] Figure 6 reveals that $\Delta E^{(2)}_{D\to A}$ and Δq^{π}_{para} data sets for both benzene and borazine derivatives give very good correlations with the σ_R substituent constants. These correlations were obtained via linear least squares fit. The results appear in Table V. Surprisingly, in both cases the borazine system gives a better fit.

Conclusion

Through an NBO analysis of borazine our calculations indicate that, although the π system is highly polarized, it is significantly resonance stabilized. The calculated stabilization energy of +44.6 kcal/mol is in fair agreement with the experimental value of +27 kcal/mol. From a second-order perturbative treatment of the Fock matrix in the NBO basis, energies for substituent-ring interactions have been calculated for a series of B-monosubstituted borazines. The results indicate an enhanced interaction (relative to benzene) for π donors owing to the polar B–N π^* antibond at the ipso position. This trend is in excellent agreement with experimental NMR data. The oppositely polarized ipso B–N π bond limits substituent-ring interaction. This result is in conflict with ^{11}B NMR data. The discrepancy though, is possibly due to a solvent-induced downfield shift of the ^{11}B NMR signal. Transmission of electronic substituent effects were estimated by analysis of para π-electron density changes. These correlate well with ^{1}H NMR data for π-donor moieties. The discrepancy with the CN substituent again is possibly a result of a solvent-induced downfield shift of the para ^{1}H resonance. Both $\Delta E^{(2)}_{D\to A}$ and Δq^{π}_{para} data sets for borazine show better correlation with the σ_R substituent constants than do those for the analogous benzene series.

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