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Azaborinines: Structures, Vibrational Frequencies, and Polarizabilities

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Ab initio second-order Møller−Plesset (MP2) perturbation theory calculations of the equilibrium geometries, relative stabilities, harmonic vibrational frequencies, dipole moments, and static dipole polarizabilities are reported for all 17 possible azaborinines (commonly called azaborines) of the formula $C_{6-2n}H_6B_nN_n$, $n = 1$, 2, 3. Planar conformations are stable minima for 16 of these molecules; some errors in the literature on this point are corrected. The most stable isomers for $n = 1$, 2, and 3 respectively are 1,2-azaborinine, 1,3,2,4-diazadiborinine, and borazine. Good agreement is found with available X-ray structures of substituted azaborinines. The ratio of MP2 to Hartree−Fock (HF) harmonic frequencies is found to vary around an average of 0.95 for this set of isoelectronic molecules. The polarizabilities of the azaborinines along with our earlier results for the azoles, oxazoles, and azines constitute a uniform quality data set of polarizabilities for 50 heteroaromatic molecules. Simple empirical formulas based upon atom- and bond-additive models correlate the calculated polarizabilities of the 49 planar heteroaromatic rings quite well.

1. Introduction

Borazine has been studied extensively, both experimentally and theoretically, because it is isoelectronic and isostructural with benzene. Borazine, $B_3N_3H_6$, can be obtained conceptually from benzene by replacing each CC group by an isoelectronic BN group. Similarly, one can generate 16 other $C_{6-2n}B_nN_nH_6$ azaborinines from benzene by replacing n pairs of carbon atoms by n nitrogen and n boron atoms. Three monoazamonoborinines, 11 diazadiborinines, and three triazatriborinines are formed when $n = 1$, 2, and 3, respectively. Figure 1 shows all 17 azaborinines.

A note on nomenclature is merited because the azaborinines are often given different names. Sometimes the term borazarobenzenes is used to emphasize that these 17 isoelectronic molecules all have six π-electrons and so are potentially aromatic. Borazine is the common name[1] for 1,3,5,2,4,6-triazatriborinine, but does not follow the IUPAC convention regarding order of prefixes for heteroatoms.[2] The ending "borine" is used frequently,[1] but the correct IUPAC stem for "bora" is "inine".[2] Strict adherence to the IUPAC convention[2] requires the addition of a prefix specifying the location of the hydrogens bonded to atoms other than carbon as in 1,2,3,4-tetrahydro-1,2,3,4-diazadiborinine. We use the more compact "azaborinine" form (e.g., 1,2,3,4-diazadiborinine) since there is a hydrogen bonded to each ring atom in all the molecules studied here.

Of the 17 molecules we consider, only borazine (**17**) has been isolated in unsubstituted form.[3] There have been experiments to determine its geometry,[4,5] its vibrational spectra,[6] its dipole moment,[7] and its polarizability in solution.[8,9] Only indirect experimental work has been done on other azaborinines. There are crystal structures of **6** and **8** with ring substituents[10,11] and of **3** and **1** with fused rings.[12−14] Dewar[15] detected but could not isolate **1**; however, many of its derivatives have been studied.[1] Molecules with fused rings containing an azaborinine unit with the pattern of **10** have been synthesized.[16]

There have been relatively more theoretical calculations on the azaborinines, but most of them focus on borazine. The relative stabilities of all 17 azaborinines were studied at the extended Hückel level by Hoffmann.[17] Semiempirical geometries have been published for 15 azaborinines,[18−20] but electron-correlated, ab initio geometries have been reported for only seven.[21−23] Calculations of other properties are available only for borazine. Ab initio calculations have been reported for the vibrational frequencies[21] and the static dipole polarizability[24−26] of borazine.

We report systematic, electron-correlated, ab initio calculations of the equilibrium geometries, vibrational frequencies, relative stabilities, dipole moments, and static dipole polarizabilities of all 17 azaborinines. Planar conformations are found to be stable minima for 16 of the 17 azaborinines. Additive and other simple models are developed for the dipole polarizability of 49 planar rings including 16 azaborinines and 33 heteroaromatic molecules that we have studied previously.[25,27−29]

2. Computational Methods

Equilibrium geometries and harmonic vibrational frequencies were computed for all 17 azaborinines using three different methods. Preliminary calculations were made with the semiempirical modified neglect of differential overlap (MNDO) model.[30] Subsequently we calculated ab initio Hartree−Fock (HF) and second-order Møller−Plesset (MP2) perturbation theory[31−33] geometries and frequencies using the 6-31G(d) and 6-31G(d,p) split-valence plus polarization basis sets.[34] All these calculations were made with GAUSSIAN-90.[35] The harmonic frequencies were used to verify that all our optimized geometries are true minima.

Dipole moments and static polarizabilities were calculated by the finite-field method,[36] using HF and valence MP2 field-dependent energies. Finite-field HF polarizabilities are equivalent to coupled Hartree−Fock (CHF) ones.[33] The details of the techniques used were the same as in our previous work.[27−29] Hence, only a concise summary is given here. Since the 6-31G(d,p) basis set is inadequate for polarizabilities, we used a [5s3p2d/3s2p] basis set, denoted C in ref 27, of contracted Gaussian-type functions (GTF) for the finite-field calculations. It consists of a double-zeta substrate[37] augmented by diffuse s- and p-type GTF, a set of p- and d-type GTF optimized for

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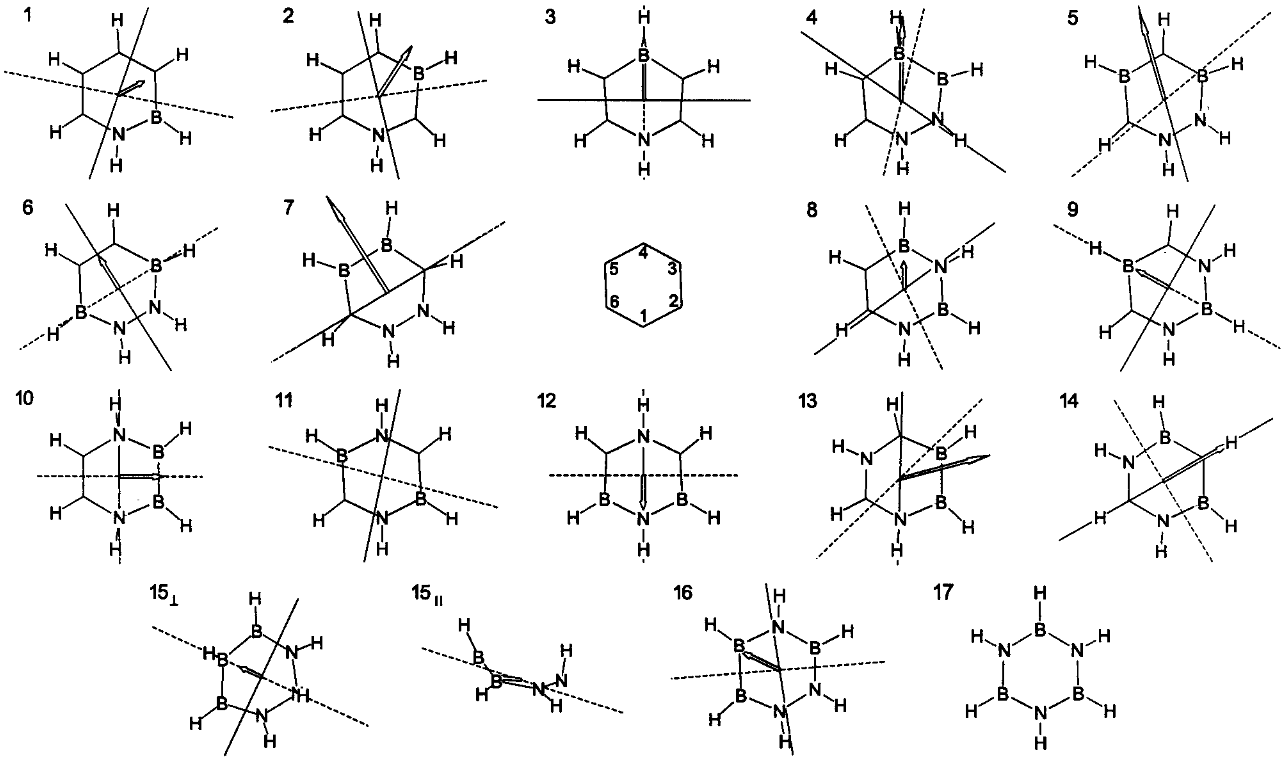

Figure 1. Azaborinines at their MP2/6-31G(d) optimized geometry (except **4** at MP2/6-31G(d,p)) (with C_s symmetry or as listed in parentheses): 1,2-azaborinine (**1**), 1,3-azaborinine (**2**), 1,4-azaborinine (**3**) (C_{2v}), 1,2,3,4-diazadiborinine (**4**), 1,2,3,5-diazadiborinine (**5**), 1,2,3,6-diazadiborinine (**6**) (C_{2v}), 1,2,4,5-diazadiborinine (**7**) (C_{2v}), 1,3,2,4-diazadiborinine (**8**), 1,3,2,5-diazadiborinine (**9**) (C_{2v}), 1,4,2,3-diazadiborinine (**10**) (C_{2v}), 1,4,2,5-diazadiborinine (**11**) (C_{2h}), 1,4,2,6-diazadiborinine (**12**) (C_{2v}), 1,5,2,3-diazadiborinine (**13**), 1,5,2,4-diazadiborinine (**14**) (C_{2v}), 1,2,3,4,5,6-triazatriborinine (**15**) (two views are given of this nonplanar molecule, one perpendicular to the C_s plane and the other parallel), 1,2,4,3,5,6-triazatriborinine (**16**), and borazine, or 1,3,5,2,4,6-triazatriborinine (**17**) (D_{3h}). MP2/C dipole moments are shown to scale, with the arrow head pointing to the negative end. The solid line is the I_a-axis of inertia, and the dotted line is the 3-axis of polarizability (nonunique and therefore not shown for borazine).

polarizabilities,[27] and another set of p- and d-type GTF optimized for electron correlation.[38] Complete details of this basis set can be found in ref 27 except the exponent of the diffuse d-GTF on boron, which was taken to be 0.15. We use uncoupled Hartree−Fock (UCHF) polarizabilities[39,40] to estimate the relative contribution of the π-electrons. Full details are given in ref 27.

3. Equilibrium Geometries

3.1. Results. It is not obvious how many of the 17 azaborinines have planar geometries. At the MNDO level, we found 12 azaborinines to be planar. Five molecules were more stable as nonplanar species: **16** and **5** by about 0.2 kcal/mol, **7** and **4** by 3−4 kcal/mol, and **15** by 23 kcal/mol, each compared to stationary saddle points on the planar potential energy surface. At the HF/6-31G(d) level, **16** is a planar molecule and planar conformers of **7** and **5** are within 0.0001 kcal/mol of the stable nonplanar forms. Only **15** (22 kcal/mol) and **4** (0.6 kcal/mol) are significantly more stable in nonplanar conformations. Next, at the MP2/6-31G(d) level, **15** and **4** were the only remaining nonplanar species, by 13 and 0.0001 kcal/mol, respectively. Finally, at the MP2/6-31G(d,p) level, the planar form of **4** was a true minimum, but **15** was still more stable as a nonplanar C_s molecule by a substantial 12 kcal/mol. It is conceivable but unlikely that **15** would be found to be planar at an even higher level of theory. We adopted the MP2/6-31G(d) geometry for all molecules except **4**, for which we chose the MP2/6-31G-(d,p) planar geometry. Thus we have planar geometries for 16 of the 17 azaborinines.

A few methodological observations are of interest. There are significant differences between our MNDO, HF, and MP2 geometries. Let us compare the methods using the average δ_a and maximum δ_m values of the absolute difference of bond lengths and angles from their MP2/6-31G(d) values for all planar conformations of the azaborinines. We find that MNDO bond lengths and angles respectively deviate from MP2/6-31G(d) values by an average of $\delta_a = 1.8$ pm and $\delta_a = 1.3°$ and a maximum of $\delta_m = 7.6$ pm and $\delta_m = 5.8°$. The HF/6-31G(d) results are better than the MNDO ones; the average deviations of bond lengths and angles are reduced to 1.3 pm and 0.6°, respectively. But the maximum differences from MP2 are still large: the worst case HF bond length, B5C6 in **5**, is too long by 4.9 pm, and the worst bond angle, HBN in **15**, is too large by 2.7°.

For three molecules, **4**, **5**, and **15**, we can compare our MP2/6-31G(d) and MP2/6-31G(d,p) geometries. The main difference is that all MP2/6-31G(d,p) XH bonds are predictably shorter by an average of 0.75, 0.58, and 0.54 pm for X = B, N, and C, respectively. This is similar to the results of Boese et al.,[5] who found that MP2/6-31+G(d,p) BH and NH bond lengths in borazine (**17**) differ from their MP2/6-31G(d) counterparts by 0.8 and 0.4 pm, respectively. Ramondo et al.[21] found that at the SCF level bond lengths and angles of borazine changed by no more than 0.3 pm and 0.2° upon enlargement of the 6-31G-(d) basis set.

Figure 1 shows all the azaborinines to scale at our best geometries. Notice that **15** is in a boat conformation; we have drawn it from two perspectives, one showing a plane perpendicular to the C_s plane and the other showing a plane parallel to the C_s plane. Tables S1 and S2 list our best calculated geometries for all the azaborinines except borazine. We do not list our geometry for borazine (**17**) because an identical one can be found in Ramondo et al.'s work.[21] The MP2/6-31G(d) geometries for the azaborinines can be expected[31,32] to be accurate to within 1%.

3.2. Comparison with Previous Calculations. Our MNDO geometries are in reasonable agreement with previous work[18−20] at the same level. However, unlike us, Massey and Zoellner[20] did not find a minimum ring geometry for **7**; their optimizations all ended with a chain conformation. Their incorrect result could be due to their rather inappropriate choice of starting guess geometries such as a regular hexagon with all bond lengths equal to 80 pm.

Our HF/6-31G(d) geometry for borazine is in perfect agreement with Ramondo et al.[21] But our HF/6-31G(d) bond lengths have noticeable discrepancies of 0.3 pm or greater with Kranz and Clark's[22] results for **1**, **2**, and **3**. In particular, their N1C2 bond length[22] for **3** is too long by 0.9 pm. This suggests that their[22] HF geometries were not completely converged. Kar et al.'s HF/6-31G(d) geometry[23] of **8** is in error by 1.4 pm for the BC bond length (and the adjacent angles are also wrong), as can be inferred even by comparing with their own HF/6-31G+(d,p) geometries.

Our MP2/6-31G(d) geometries agree virtually exactly with previously published ones for seven azaborinines:[21−23] **1**, **2**, **3**, **8**, **11**, **14**, and **17**. Our MP2/6-31G(d) geometries for six of these molecules are included in Tables S1 and S2 because Kranz and Clark[22] reported only ring bond lengths for **1**, **2**, and **3**, and Kar et al.[23] reported only ring bond lengths and angles for **1**, **8**, **11**, and **14**.

3.3. Comparison with Experiment. Experimental gas-phase geometries are available only for borazine (**17**). Harshbarger et al.[4] measured the borazine geometry by electron diffraction, but they could not determine whether it was planar D_{3h} or nonplanar C_2. Landolt−Börnstein[41] increased Harshbarger et al.'s error estimates by a factor of 2. The MP2/6-31G(d) geometry is in fairly good agreement with the electron diffraction geometry. The small residual differences, primarily due to vibrational effects, have been analyzed by Ramondo et al.[21] More recently, Boese et al.,[5] using assumed values for the XH bond lengths, obtained a C_2 X-ray crystal structure for borazine with mean values of 142.9 ± 0.1 pm for the BN bond length, 117.1 ± 0.1° for ∠NBN, and 122.9 ± 0.1° for ∠BNB. Remarkably, their crystal structure agrees almost exactly with the D_{3h} MP2/6-31G(d) structure.

There are X-ray crystal structures for substituted derivatives of the planar azaborinines **6** and **8**. Siebert et al.[10] obtained a crystal structure of 4,5-diethyl-3,6-dimethyl-1,2,3,6-diazadiborinine (a derivative of **6**) with a planar ring having N−N, N−B, B−C, and C−C bond lengths of 139.1, 138.7, 156.1, and 137.1 pm, respectively, all with an estimated uncertainty of ±0.4 pm. The largest difference between their bond lengths and our MP2/6-31G(d) values is 2.7 pm for B−C. Our C−C bond length is the same as theirs, but contrary to their result, we find the N−B length to be greater than N−N. Their ring angles, ∠NNB = 123.2°, ∠NBC = 117.2°, and ∠BCC = 119.5°, differ by less than 1° from our values. Schreyer et al.[11] determined the X-ray structure of 1,3,2,4-diazadiborinine (**8**) with six bulky ligands: a *tert*-butyl group on each N, a methyl ester group on each C, and a methyl group on each B. Their ring is a boat shape with B2 and C5 at the two ends, although their bond lengths suggest some cyclic delocalization.[11] Their bond lengths are longer than our calculated ones by an average of 1.6 pm. Their N−B bond lengths differ from ours by more than 2 pm, whereas their bond lengths for the other half of the ring are quite similar to ours. Their two ring angles at N are ≈118° or more than 5° smaller than ours, their prow and stern angles are larger by ≈3°, while the other two ring angles are within 1° of the MP2/6-31G(d) values.

TABLE 1: Trends in MP2/6-31G(d) Geometries of 15 Planar Azaborinines[a]

bond	number	average	maximum	minimum
BH	29	119.7	120.1	119.1
CH	32	108.8	109.1	108.3
NH	29	101.5	102.0	101.1
BB	4	166.3	168.8	164.4
BC	22	150.5	153.4	147.8
BN	28	143.2	148.5	140.2
CC	10	137.8	141.7	135.4
CN	22	136.0	138.6	132.7
NN	4	136.3	139.5	133.4
angle at				
B	29	115.1	118.8	112.7
C	32	120.4	122.1	118.8
N	29	124.4	126.9	122.9

[a] All azaborinines except **4** and **15**. Bond lengths in picometers and bond angles in degrees.

There are X-ray crystal structures of polycyclic derivatives of the azaborinines **1** and **3**. Bel'skii et al.[12] determined the crystal structure of 2,7,9-trimethyl-10-phenyl-9-aza-10-boraanthracene, which contains **3** as its central ring. Their molecule has C_1 symmetry, with the phenyl ring rotated 49° with respect to the primary plane. Their six central ring angles differ by an average of only 0.8° from our MP2 values for **3**. Their N−C bonds are longer than ours, and their C−C bonds are 4 pm longer than ours presumably because of the fused rings. Kranz et al.[13] measured the crystal structure of a different substituted heteroanthracene with the azaborinine **3** as the central ring and 1-methyl and 4-mesityl substituents. The central ring was slightly twisted.[13] Their X-ray bond lengths had rather large error estimates of ±1.5 to 1.8 pm. They compared their X-ray structure with their own MP2/6-31G(d) calculation[22] for **3**. The C−C bonds common to two rings are again 4.4 pm longer than the calculated ones for **3**. Harris et al.[14] found the crystal structure of 10-hydroxy-10,9-borazarophenanthrene, which has the azaborinine **1** as the central ring. They gave the geometry for one of two different structures contained in the unit cell, but they did not specify how close the central ring is to planarity. Their CNB angle is the same as our MP2/6-31G(d) value for **1**, but their N−B bond length is 1.9 pm shorter and their NBC angle is 2.3° larger than ours.

The overall agreement of the X-ray crystal structures with our calculated MP2/6-31G(d) ones is as good as could be expected given the differences created by the substituents and by the packing forces in the solid state.

3.4. Geometrical Trends. Table 1 presents overall trends for the MP2/6-31G(d) bond lengths and angles of the 15 azaborinines (all but **4** and **15**) that are planar at that level of calculation. Each type of XH bond is almost constant with a range no greater than 1 pm. Ring bonds are significantly more variable; the range for BN bonds is more than 8 pm. It is remarkable that the ring angle at nitrogen is always greater than the ideal sp^2 value of 120° and the angle at boron is always less than 120°. By contrast, the angle at carbon is close to 120° but can be on either side of it. Compared to the carbons in benzene, a boron will be further out, while a nitrogen will be a slightly smaller distance in toward the center of the molecule.

The scale drawing in Figure 1 shows that the azaborinines differ in size and shape. A measure of size is the area A enclosed by the ring. It ranges from 0.518 to 0.552 nm^2 for the planar azaborinines as compared with 0.506 nm^2 for benzene.

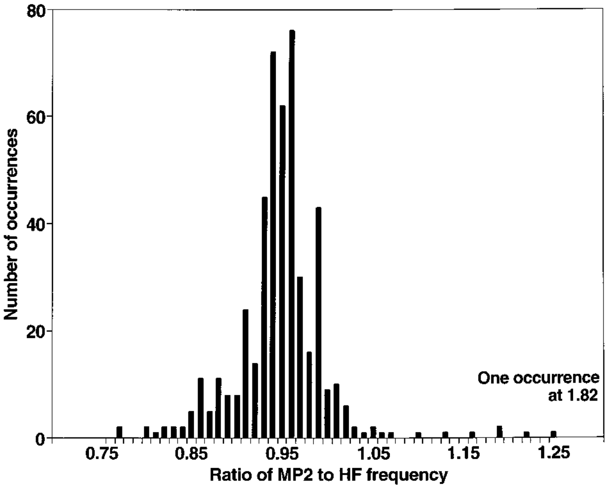

Figure 2. Distribution of ratios $r_i = \omega_i(\mathrm{MP2})/\omega_i(\mathrm{HF})$ for all harmonic vibrational frequencies of the azaborinines (excluding 1,2,3,4-diazadiborinine) with the 6-31G(d) basis. The height of a bar labeled 0.95 is the number of all ratios such that $0.945 < r_i \leq 0.955$. Each molecule's frequencies are paired by order of increasing frequency in each symmetry class.

The $n = 1$ azaborinines with a single N and B have the smallest *A*; next smallest is **8**, noticeably smaller than the other diazadiborinines. The three molecules that have two adjacent B atoms and two adjacent N atoms have the highest *A*; **16** is the largest. Another size measure is the span *L*, the longest distance between a pair of atoms in the molecule. *L* ranges between 505 and 534 pm for the azaborinines as compared with 496 pm for benzene. Because the BH bond length is longer than the CH or NH bond length, *L* can be expected to be, and indeed is, longest for the azaborinines (**6**, **9**, **11**, **16**) with a pair of BH's on opposite sides of the ring. Azaborinines **3**, **17**, and **14**, with N's and B's directly opposite each other, have the smallest *L*.

4. Harmonic Vibrational Frequencies

Tables S3 and S4 list our MP2/6-31G(d) harmonic vibrational frequencies ω_i for the azaborinines at our best geometries; the frequencies are MP2/6-31G(d,p) for **4**. Frequencies for borazine (**17**) are not listed because MP2/6-31G(d) values were reported earlier;[21] Ramondo et al.[21] found that they correspond reasonably well to the gas-phase IR and liquid Raman spectra.[6] Tables S3 and S4 show that the lowest frequency of the planar azaborinines ranges from a minimum of 86 cm^{-1} for **4** through 283 cm^{-1} for borazine to a maximum of 381 cm^{-1} for **3**.

HF harmonic frequencies are sometimes scaled by a factor close to 0.90 to obtain values that are presumed to be more accurate. Figure 2 is a histogram of the ratio $r_i = \omega_i(\mathrm{MP2})/\omega_i(\mathrm{HF})$ in the 6-31G(d) basis for 16 azaborinines; **4** was excluded due to its nonplanarity in the 6-31G(d) basis. Note that r_i varies around an average of 0.95 but can exceed 1. Thus a simple scaling is moderately accurate in an isoelectronic set of molecules like the azaborinines.

5. Relative Stabilities

Figure 3 shows MNDO, HF, and MP2 energies relative to the most stable isomer of a given molecular formula, for planar conformations only. The relative energies include zero-point energy (ZPE) corrections. Table 2 lists our MP2/6-31G(d) relative stabilities. Figure 3 shows that HF differs from MP2 in many places for the relative stability of the 11 $n = 2$ isomers, whereas MNDO only puts **9** out of place. The energy gaps for the $n = 3$ isomers are much larger than for the $n = 1$ isomers. All three methods predict that the most stable $n = 1, 2, 3$ isomers are 1,2-azaborinine (**1**), 1,3,2,4-diazadiborinine (**8**), and borazine (**17**), respectively.

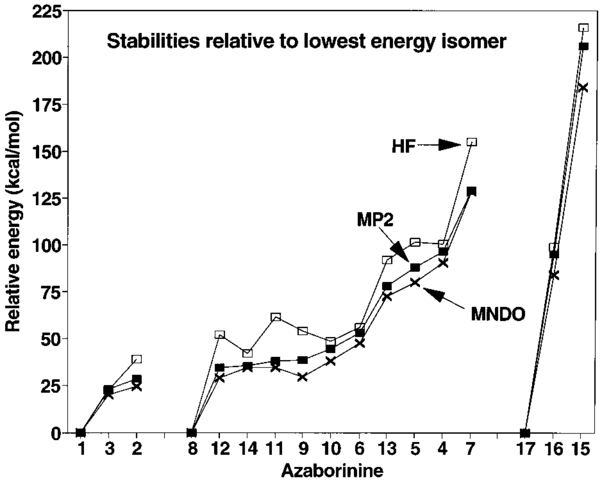

Figure 3. Stabilities of the azaborinines relative to the most stable isomer for each *n*.

Hoffmann reported calculations[17] for all 17 azaborinines using the extended Hückel (EH) model with idealized planar geometries and standard bond lengths. The EH model gets the three most stable isomers correct but not the second most stable diazadiborinine; it is **12**, not **14**. Massey and Zoellner[19,20] compared the MNDO ΔH_f of the $n = 1$ and 2 isomers at their MNDO geometries. We found slightly different energies compared to their results, in addition to their error in the planarity of **7** discussed in section 3.2.

Kar et al.[23] examined the relative stability of various isomers of azabora derivatives of benzene and naphthalene. They assumed that the most stable isomers would be those with consecutive, alternating B and N pairs, so they considered only three diazadiborinines, **8**, **11**, and **14**, and found energies identical to ours. However, **12**, which they left out, is more stable than **11** or **14**. It is conceivable that this omission may render incorrect their conclusions[23] about the most stable azaboranaphthalene isomers as well.

Kranz and Clark[22] also considered relative stabilities of the $n = 1$ isomers. Our MP2/6-31G(d) energies agree with theirs. They gave as their best result QCISD/6-31G(d)//MP2/6-31G(d) energies corrected by the HF/6-31G(d)//HF/6-31G(d) ZPE. All methods show **1** to be the most stable and **2** the least stable; also, **2** remains fairly constantly about 23 kcal/mol above **1**. Adding the MP2/6-31G(d) ZPE correction to our MP2/6-31G(d) energies reduces the gap between **2** and **3** from 5.3 to 5.2 kcal/mol. Kranz and Clark's QCISD calculations[22] led to a considerably larger gap of 9.9 kcal/mol; it is reduced to 9.6 kcal/mol if our MP2 ZPE is used.

6. Dipole Moments

Table 2 lists the magnitude of our MP2/C dipole moments and the angle θ_a between the dipole moment and the principal axis of inertia I_a. The dipole moments are depicted to scale in Figure 1, which also shows the inertial axis I_a. The dipole moments of **11** and **17** vanish by symmetry. In the other azaborinines, the dipole moments range from a modest 1.6 D in **15** to a large 7.6 D in **7**. The dipole moment vectors of the azaborinines with C_{2v} symmetry necessarily coincide with the symmetry axis. The dipole moments of the azaborinines with

TABLE 2: Relative Stabilities[a] E_S, Dipole Moments[b,c] and Angles,[b,d] Polarizabilities[b,e] and Angles,[b,d] π-Fractions[f,g] f, and Reciprocal Hardnesses[e,h,i]

no.	E_S	μ	θ_a	α_1	α_2	α_3	$\bar{\alpha}$	$\Delta_1\alpha$	$\Delta_2\alpha$	$\Delta_3\alpha$	ϕ_3	$f(\perp,\pi)$	$f(\parallel,\pi)$	η^{-1}
1	0	2.03	46.0	46.26	79.29	85.04	70.20	35.90	36.25	4.98	83.9	58.8	52.2	5.92
2	28.4	4.03	45.0	47.41	82.01	88.20	72.54	37.69	38.07	5.37	88.0	60.7	57.6	6.46
3	23.2	4.24	90	47.18	80.45	84.36	70.66	35.22	35.39	3.39	90	58.5	50.4	5.63
4	96.3	5.75	54.7	48.77	81.48	91.62	73.96	37.79	38.79	8.78	66.4	52.2	45.0	6.02
5	87.8	6.06	0.6	49.99	85.23	91.96	75.73	38.60	39.04	5.83	66.7	58.1	52.4	6.50
6	52.9	2.56	0	46.53	76.98	82.97	68.83	33.45	33.85	5.19	90	53.6	44.0	5.27
7	129.2	7.61	0	50.45	88.07	89.41	75.98	38.29	38.30	1.16	90	58.5	57.6	7.31
8	0	1.89	56.4	45.99	74.01	81.44	67.15	31.74	32.38	6.43	78.5	54.2	43.7	5.57
9	38.4	2.52	90	47.57	84.85	89.25	73.89	39.48	39.67	3.82	90	59.5	57.0	6.94
10	44.6	3.03	90	46.85	77.70	89.78	71.44	36.89	38.35	10.46	90	51.7	45.5	6.11
11	37.8	0		47.64	79.89	88.39	71.97	36.49	37.23	7.36	85.0	59.8	61.9	7.08
12	34.4	2.28	0	47.73	77.28	92.31	72.44	37.06	39.28	13.01	90	57.2	56.5	6.57
13	78.1	6.13	73.6	50.24	88.63	96.02	78.29	42.08	42.57	6.40	42.8	56.6	53.8	7.20
14	35.6	5.55	0	49.94	84.33	87.25	73.84	35.85	35.94	2.53	90	58.0	48.6	6.67
15	205.8	1.60	90	52.16	71.82	72.91	65.63	20.21	20.23	0.94	90			4.90
16	94.7	2.85	56.2	46.35	73.20	83.03	67.53	31.77	32.89	8.51	86.5	46.0	34.8	5.33
17	0	0		45.09	71.44	71.44	62.66	26.35	26.35	0		49.4	34.9	4.50

[a] MP2/6-31G(d)//MP2/6-31G(d) with respect to lowest energy isomer. In kcal/mol. [b] MP2/C. [c] In debyes. [d] In degrees. [e] In atomic units. [f] Of UCHF polarizabilities. [g] In percent. [h] In C basis. [i] All except stabilities at the geometries of Figure 1.

C_s symmetry lie in the symmetry plane, which is the molecular plane for all but **15**. I_a is perpendicular to the symmetry plane for **15**, and thus θ_a is 90°; for a complete specification of the dipole moment orientation in **15**, it is necessary to add that the angle between the dipole moment and I_b is 8.7°. We did not find any previous calculations or measurements of these dipole moments other than a confirmation[7] that $\mu = 0$ for borazine.

Molecular dipole moments can be interpreted as vector sums of bond dipoles. This allows us to draw some conclusions from Figure 1. The BH group is more negative than the CH (cf. **10** and **12**) and NH groups (cf. **3**, **7**, **14**, **15**, and **16**). Similarly CH is more negative than NH (cf. **6** and **9**). The molecule **7** with the largest dipole moment has two B's on one side and two N's on the other. The azaborinines with the next three largest dipole moments (**13**, **5**, and **4**) all differ from **7** by a single exchange of a pair of atoms that leads to a slightly more balanced distribution of charge. The C−B bond dipole ≈ 1.1 D from **12**, and the N−C bond dipole ≈ 1.3 D from **9**. Structure **1** suggests that the N−B bond dipole is about 2 D, whereas molecule **14** suggests about 2.8 D. Thus a bond dipole model would not be quantitative. Roughly speaking, $\mu_{N-C} + \mu_{C-B} \approx \mu_{N-B}$.

7. Polarizabilities

7.1. Results. Polarizabilities are important because they determine long-range intermolecular induction and dispersion forces, various cross sections, and phenomena such as collision-induced spectral line shifts.[42,43] It is most useful to report quantities that are invariant to the choice of coordinate system. Familiar polarizability invariants can be constructed from the eigenvalues of the polarizability tensor $\alpha_1 \leq \alpha_2 \leq \alpha_3$. The most common invariant is the mean polarizability:

$$\bar{\alpha} = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \tag{1}$$

The difference between the mean in-plane and out-of-plane components is an invariant:

$$\Delta_1\alpha = \alpha_{\parallel} - \alpha_{\perp} = \frac{1}{2}(\alpha_2 + \alpha_3) - \alpha_1 \tag{2}$$

The plane is the molecular plane except for **15**, in which it is the symmetry plane. An invariant related to the Kerr effect is

$$\Delta_2\alpha = \left[\frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{2}\right]^{1/2} \tag{3}$$

The in-plane (defined as above) anisotropy is a more intuitive invariant:

$$\Delta_3\alpha = [(\Delta_2\alpha)^2 - (\Delta_1\alpha)^2]^{1/2} = \frac{\sqrt{3}}{2}(\alpha_3 - \alpha_2) \tag{4}$$

In this work we use atomic units for polarizabilities; one atomic unit of polarizability $= 4\pi\epsilon_0 a_0^3 \approx 1.64878 \times 10^{-41}$ F m^2 in SI units.

Table 2 lists our MP2/C polarizability eigenvalues and invariants for the azaborinines. The orientation of the principal 3-axis of greatest polarizability is shown in Figure 1 and specified in Table 2 by the angle ϕ_3 between the 3-axis and the inertial axis I_a. For **15**, the 3-axis is in the symmetry plane but I_a is not; the angle between the 3-axis and I_b is 2.4° (I_b runs between α_3 and μ, if they all are considered to pass through one point). Borazine is a symmetric top, and its 3-axis can be placed anywhere in the molecular plane.

7.2. Comparison with Previous Work. Experimental and previously calculated polarizabilities are available only for borazine. The average polarizability was determined from molar refraction data[8] to be 59.7, which is about 5% below our MP2/C result. Dennis and Ritchie[9] obtained the magnitude of the polarizability anisotropy $\Delta_2\alpha$ from the molar Kerr constant of a dilute solution of borazine in cyclohexane measured at 632.8 nm. They[9] made the assumption that the static anisotropy is approximately the same as that at optical frequencies. Not unexpectedly, their result of 17.6 ± 1.0 is lower than our free molecule value by 33%. Their planned gas-phase experiments[9] should give much closer agreement with our anisotropy, as was the case for benzene (for which our calculated value[29] was 6% low).

Our CHF/C polarizability components for borazine differ only slightly from the CHF values computed at the HF/6-31G geometry[44] by Lazzeretti et al.[24] with the Sadlej (S) basis set.[45] Archibong and Thakkar's best hybrid values[25] for borazine, at a planar geometry taken from Harshbarger et al.,[4] differ from our MP2/C results by only 0.96% and 1.4% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively. Recently, Fowler and Steiner[26] published CHF/

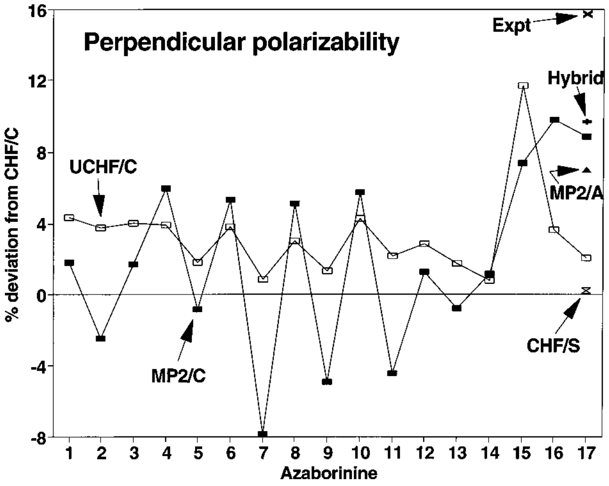

Figure 4. Percent differences between the smallest principal component of the polarizability computed by a given method and its counterpart calculated at the CHF level in basis C. The molecules are numbered as in Figure 1. MP2/A is a small basis set calculation from ref 25.

[8s6p2d/6s2p]//HF/6-31G(d,p) polarizabilities for borazine. Their results are 2.6% and 3.6% lower than our CHF/C values for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively, because of small differences in the geometry used and deficiencies in their marginally bigger basis set. Presumably using the UCHF method, they found borazine's π-polarizability to be more isotropic than we did; they found $\Delta_1^\pi\alpha = -0.77$, to be compared with our UCHF/C value of -2.58.

7.3. Trends. Table 2 reveals that the mean polarizability ranges from 62.7 for borazine (**17**) to 78.3 for **13**, as compared with 69.3 for benzene.[29] Unlike the azoles, oxazoles, and azines, the azaborinines do not show a systematic trend in the mean polarizability with the number of heteroatoms. The mean polarizabilities of the $n = 2$ azaborinines range from 67.1 to 78.3. Generally, the $n = 3$ azaborinines have a lower mean polarizability than the others. The three azaborinines with the highest mean polarizability, **13**, **7**, and **5**, also have the largest dipole moments. Note that for each fixed n, the molecules with the smallest mean polarizability are the most stable isomers: **1**, **8**, and **17** for $n = 1$, 2, and 3, respectively. The polarizability anisotropies $\Delta_1\alpha$ and $\Delta_2\alpha$ range from 42 and 43 in **13** to 20 in nonplanar **15**, to be compared with 36 for benzene.[29]

Figure 1 shows the principal 3-axis of greatest polarizability in the azaborinines. It tends to pass close to as many of the borons as possible because they are more polarizable than the carbon and nitrogen atoms. The inertial I_a axis tries to pass through as many of the heaviest atoms as possible. Thus the I_a and 3-axis are often nearly perpendicular to each other. Deviations from this overall trend are due to more subtle factors.

Although UCHF polarizabilities are not very accurate, they have interpretative value because they can be partitioned uniquely into contributions from each of the occupied molecular orbitals (MOs). Table 2 includes the UCHF/C parallel and perpendicular π-fractions $f(X,\pi) = \alpha(X,\pi)/\alpha(X)$, $X = \parallel, \perp$ for the planar azaborinines. The π-electron contribution to the mean polarizability varies from 61% to 38%. The contribution of the highest occupied MO (HOMO) (a π-MO for all the planar azaborinines) to the UCHF mean polarizability varies from a large 47% to 16%.

7.4. Observations on Methodology. Figure 4 shows percent differences $\delta\alpha_1(X) = (\alpha_1(X) - \alpha_1(\mathrm{CHF/C})) \times 100/(\alpha_1(\mathrm{CHF/C}))$ between out-of-plane polarizabilities obtained by various methods and their CHF/C counterparts; Figure 5 shows these differences for the mean polarizability.

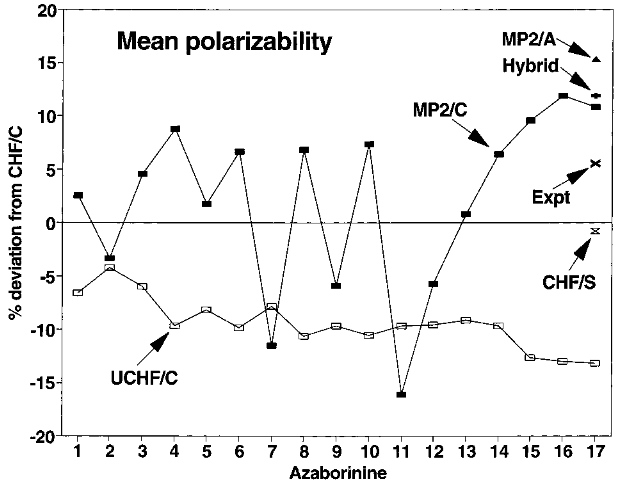

Figure 5. Percent differences between the mean polarizability computed by a given method and its counterpart calculated at the CHF level in basis C. The molecules are numbered as in Figure 1. MP2/A is a small basis set calculation from ref 25.

Electron correlation increases the polarizability of second-period atoms from the right-hand side of the periodic table but decreases the polarizability of second-period atoms from the left-hand side.[46] Thus in our previous work on azoles, oxazoles, and azines, we have usually observed $\alpha_{\mathrm{MP2}} > \alpha_{\mathrm{CHF}}$. However, the presence of the borons in the azaborinines leads to MP2 polarizabilities that are sometimes higher and sometimes lower than the CHF ones; see Figures 4 and 5. The absolute differences between MP2/C and CHF/C average to 7, 13, and 15% for $\bar{\alpha}$, $\Delta_1\alpha$, and $\Delta_2\alpha$, respectively. Correlation effects are largest for molecule **11**: 16, 32, and 43% for $\bar{\alpha}$, $\Delta_1\alpha$, and $\Delta_2\alpha$, respectively.

The correlation effects on the polarizabilities do not have a simple trend with n. However, close examination of the CHF and MP2 polarizabilities reveals that electron correlation irons out some of the extremes of the CHF level, so that the MP2 polarizabilities of the azaborinines vary over a narrower range than do the CHF ones.

The difference between CHF and UCHF polarizabilities can be interpreted[47] as an inductive contribution that in turn is made up of a positive self-interaction term and a negative back-polarization term. The UCHF/C values of $\bar{\alpha}$, α_2, α_3, $\Delta_1\alpha$, and $\Delta_2\alpha$ are always lower than their CHF counterparts by an average of 9, 13, 13, 34, and 34%, respectively, whereas the UCHF/C α_1 is higher than its CHF/C value by an average of 3%. Thus, unlike the cases of the azoles, oxazoles, and azines, there is a uniformly positive inductive contribution dominated by the self-interaction term for all the azaborinines. UCHF is most different from CHF for the azaborinines with no carbons.

A disproportionately large UCHF HOMO polarizability is an indicator that the correlation correction will be relatively large. This can be rationalized by noting that a small HOMO–LUMO gap can lead to both these features. Interestingly, those azaborinines with a high (low) UCHF π-fraction have negative (positive) correlation corrections to the polarizability.

7.5. Additive Atom Polarizability Models. The polarizabilities of Table 2, together with those for the azoles,[27] oxazoles,[28] and azines,[29] constitute a set of uniformly good quality polarizabilities for 50 heteroaromatic molecules. This data set will be used to examine the utility and limits of simple

TABLE 3: Parameters[a] and Errors of Additive Atom Models[b] of Polarizability

	$\bar{\alpha}$			$\Delta_1\alpha$
	5	5a	5b	5
b_B	16	19	−22.2	14
b_C	10.8	11.7	−11.1	9.19
b_N	6.75	4.44	−2.7	3.7
b_O	2.5	−2.8	4.6	−1.9
b_H	0.85	−3.84	11.08	−3.034
b_η	0	3.93	3.18	0
b_A	0	0	0.69	0
δ_a(%)	2.4	1.8	1.2	5.1
δ_m(%)	17	6.3	3.5	32

[a] In atomic units. [b] Model numbers refer to the text.

TABLE 4: Parameters[a] and Errors of Additive Connection Models[b] of Polarizability

	$\bar{\alpha}$		$\Delta_1\alpha$	
	6	6a	6	6a
c_1	20.36	17.7	11	13
c_2	16.13	13.9	8.5	10
c_3	11.43	10.1	5.77	6.6
c_4	10.48	9.3	4.58	5
c_5	9.15	7.8	4.76	5.59
c_6	7	5.9	3.32	4
c_7	6.7	4.96	1.86	3
c_8	5.01	3.85	1.9	2.6
c_9	0	1.53	0	−0.94
δ_a(%)	1.4	0.95	4.7	3.9
δ_m(%)	5.0	3.8	17	12

[a] In atomic units. [b] Model numbers refer to the text.

models for these polarizabilities. An additive atom model of polarizability applicable to the azaborinines, azoles, oxazoles, and azines is

$$\alpha \approx b_B n_B + b_C n_C + b_N n_N + b_O n_O + b_H n_H \qquad (5)$$

in which n_i is the number of atoms of type i in a molecule, and b_i can be regarded as the polarizability of an atom of type i in a planar heteroaromatic molecule. Linear regression of our MP2/C polarizabilities for the 16 planar azaborinines and 33 azoles,[27] oxazoles,[28] and azines[29] leads to the b_i parameters shown in Table 3. Notice that the b_i are smaller than the corresponding free atom polarizabilities,[46] indicating that bonding has lowered the polarizability. The values of b_H, b_C, b_N, and b_O are very close to those obtained previously[29] for the 33 azoles, oxazoles, and azines. Table 3 shows that the average absolute error δ_a of Model 5 is 2.4%, but the maximum error is $\delta_m = 17\%$. By contrast, if the azaborinines are excluded, then the additive atom model[29] has an average error of only 1%. This is so because structural isomers of azaborinines have significantly more varied polarizabilities than do the structural isomers of azines, azoles, and oxazoles. The error in Model 5 can be considered a measure of nonadditive effects.

As in our earlier work,[28,29] one- and two-parameter improvements to Model 5 are obtained by adding b_η/η (Model 5a) and $b_\eta/\eta + b_A A^{3/2}$ (Model 5b), respectively, where $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$ is an approximation to the molecular hardness, and A is the ring area, so that $A^{3/2}$ is an approximate molecular volume. Table 3 shows that these terms improve the fit but destroy the physical interpretation of the atomic terms.

Model 5 can be applied to the anisotropies $\Delta_1\alpha$ and $\Delta_2\alpha$ with approximately half the accuracy (see Table 3) obtained for $\bar{\alpha}$. Models 5a and 5b do not significantly improve upon Model 5 for the polarizability anisotropies. Using Model 5 for $\Delta_1\alpha$ is tantamount to using different in- and out-of-plane "atomic polarizabilities" b_i. It works for $\Delta_2\alpha$ as well because $\Delta_2\alpha \approx \Delta_1\alpha$ in these molecules.

7.6. Additive Bond Polarizability Models. The additive connections model[27] (ACM) expresses the polarizability as a linear combination of n_{ij}, the number of connections (i.e., bonds without regard to bond order) between atoms of type i and j. For our 49 molecules there are 11 distinct n_{ij}. However, they are not linearly independent because there are four stoichiometric constraints. Thus the ACM for the 49 azoles, oxazoles, azines, and planar azaborinines has eight terms which we choose as follows:

$$\alpha \approx c_1 n_{BB} + c_2 n_{BC} + c_3 n_{CC} + c_4 n_{BN} + c_5 n_{CN} + c_6 n_{NN} + c_7 n_{CO} + c_8 n_{NO} \qquad (6)$$

The parameters obtained by linear regression for Model 6 and Model 6a (which includes a hardness term) are listed in Table 4. The eight-parameter Model 6 is not as efficient as the seven-parameter Model 5b for the mean polarizability. The nine-parameter Model 6a is our most accurate model, with average errors of 0.95% and 3.9% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively.

The models presented above all exclude nonplanar 1,2,3,4,5,6-triazatriborinine (**15**); the errors of all our models increase perceptibly if molecule **15** is included in the data set. For example, the errors for Model 6 applied to $\Delta_1\alpha$ increase from $\delta_a = 4.7\%$ to 6.5% and from $\delta_m = 17\%$ to 47%. We are continuing attempts to develop simple polarizability models that are more accurate, particularly for anisotropies, and applicable to a larger set of heteroaromatic molecules.

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Supporting Information Available: Tables S1−S4 contain MP2/6-31G(d) geometries and harmonic vibrational frequencies of the azaborinines excluding borazine; the results are MP2/6-31G(d,p) for **4** (4 pages). Ordering information is given on any current masthead page.

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