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Structures, Vibrational Frequencies and Polarizabilities of Diazaborinines, Triazadiborinines, Azaboroles, and Oxazaboroles

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Ab initio, second-order, Møller−Plesset perturbation theory calculations of the equilibrium geometries, harmonic vibrational frequencies, relative stabilities, dipole moments, and static dipole polarizabilities are reported for 70 different 6π-electron monocycles containing boron and nitrogen. These include 26 azaborinines isosteric to pyridine, 16 azaboroles, and 28 oxazaboroles. The most stable isomers have the substructure XBHNH, where X = N, NH, or O is the base-ring heteroatom. Planar conformations are stable minima for all but 15 five-membered rings. Lower level calculations are unreliable in predicting which molecules are planar. Good agreement is found with the available electron diffraction and X-ray structures of substituted rings. Additive atom and bond polarizability models which are accurate to within a few percent are constructed for a larger set of 104 planar molecules, including azines, azoles, oxazoles, and azaborinines isosteric to benzene. The presence of boron causes scatter of the polarizabilities of isomers; hence the additive models of polarizability are less accurate than if only heterocycles containing C, N, and O are included.

1. Introduction

Since the first synthesis,[1] in 1957, of a heteroaromatic molecule containing B, N, and C, there has been much interest in making and understanding molecules that bridge the gap between benzene and borazine.[2] Despite great difficulty in making the unsubstituted heteroaromatic monocycles, the interest continues.[3−5] For example, derivatives of one diazaborinine have demonstrated strong antibacterial activity and hence the potential to be useful as drugs.[6,7]

Figures 1−5 show the 70 molecules examined in this paper. They are all five- and six-membered rings that meet the $4n + 2$ π-electron criterion of aromaticity. The nomenclature of heteroaromatic rings follows the extended Hantzsch−Widman system[8] recommended by IUPAC. The full molecule names and relevant Hantzsch−Widman rules for naming such molecules are given in the Supporting Information.

The formula $(CH)_aN_b(NBH_2)_c$, with $a+b+2c=6$, describes all azines ($c = 0$) and azaborinines ($c \neq 0$). We have previously studied[9] the 17 azaborinines with $b = 0$ (the monoazamonobor-, diazadibor-, and triazatriborinines), and use the numbering from that paper[9] for them (**1**−**17**). In this paper, we consider the BN analogues of pyridine: 10 diazaborinines (**18**−**27**) ($b = c = 1$) (Figure 1), and 16 triazadiborinines (**28**−**43**) ($b = 1$, $c = 2$) (Figure 2). Higher values of b yield other azaborinines.

The formula $(CH)_aN_b(NBH_2)_cX$, with $a+b+2c=4$, defines all azoles ($c = 0$) and azaboroles ($c \neq 0$) if X = NH, and describes all oxazoles ($c = 0$) and oxazaboroles ($c \neq 0$) if X = O. We consider all 16 possible azaboroles: 4 diazaboroles (**44**−**47**), 6 triazaboroles (**48**−**53**), 4 tetrazaboroles (**54**−**57**), and 2 triazadiboroles (**58**, **59**) (Figure 3). We also study all 28 possible oxazaboroles: 6 plain oxazaboroles (**60**−**65**), 12 oxadiazaboroles (**66**−**77**) (Figure 4), 6 oxatriazaboroles (**78**−**83**), and 4 oxadiazadiboroles (**84**−**87**) (Figure 5).

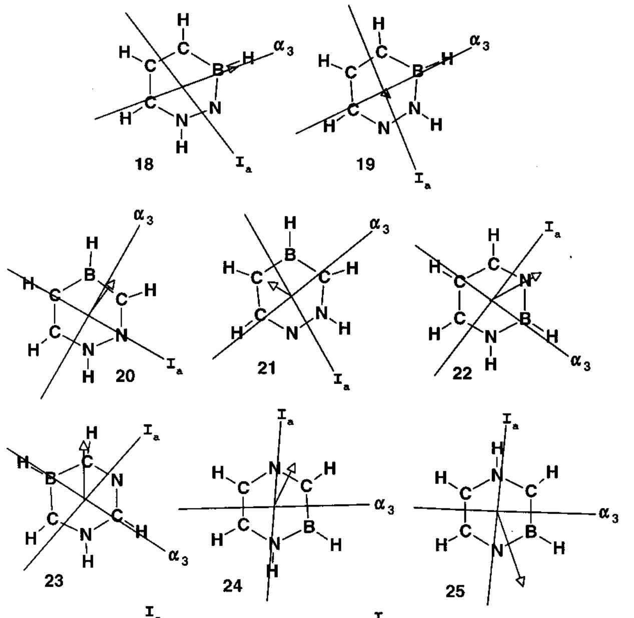

Figure 1. Diazaborinines. All C_s planar. At their MP2/6-31G(d) optimized geometry. Locant numbering is counterclockwise, starting at 6 o'clock. Dipole moments are shown to scale, with origin at center of mass and arrowhead at negative end. The long lines are the principal axis of inertia I_a and the principal axis of highest polarizability α_3.

Although none of the 70 molecules have been synthesized, experimental information is available for substituted forms of 12 of these molecules: four six-membered rings, four five-membered rings without O, and four with O. Ten have been made with ring substituents: **19**,[10] **42**,[5] **46**,[11] **53**,[12] **56**,[13] **59**,[14] **63**,[15] **76**,[16] **85**,[17] **87**,[14] and two others with a fused ring: **22**[16]

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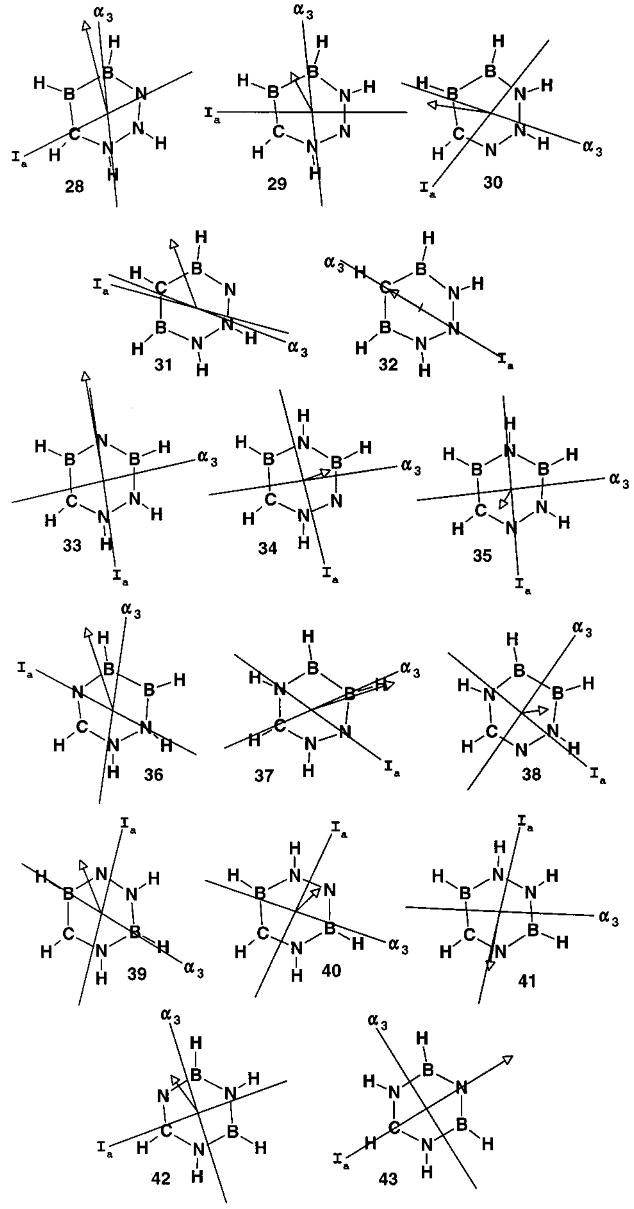

Figure 2. Triazadiborinines. All C_s except **32** and **43** (C_{2v}); all planar. See notes for Figure 1.

and **26**.[18] Experimental X-ray structures are available for five of the 12, **19**,[4,19] **42**,[5] **46**,[3,20,21] **56**,[22] and **76**,[23,24] but there is gas-phase electron diffraction data in only one case, **56**.[25] Detailed vibrational spectral analysis has been performed for derivatives of **56**.[13,26−29] Infrared, and occasionally Raman, data have been reported for **19**,[4,30] **22**,[31−33] **26**,[18] **46**,[3,34] **53**,[12] **59**,[35] **63**,[15] and **76**.[24,31,36] Dipole moments have been measured only for variants of **19**.[37] No experimental polarizabilities are available for these molecules, even in substituted form.

Calculations, largely semiempirical, have been reported for seven of the molecules. A semiempirical geometry and dipole moment were calculated for dimethyl-**56**.[38] Semiempirical geometry[39] and thermochemical and magnetic property[40] calculations were made for **59**. There have been calculations at assumed geometry to determine the molecular orbitals, energy, aromatic stabilization, and spectra of **46**[34] and **56**.[41,42] Semiempirical charge densities and bond orders have been calculated[23] for **76**. Extended Hückel relative stabilities have been reported[43] for three of the diazaborinines, **22**, **24**, and **26**. Neither semiempirical nor ab initio polarizability calculations have been reported for any of these molecules.

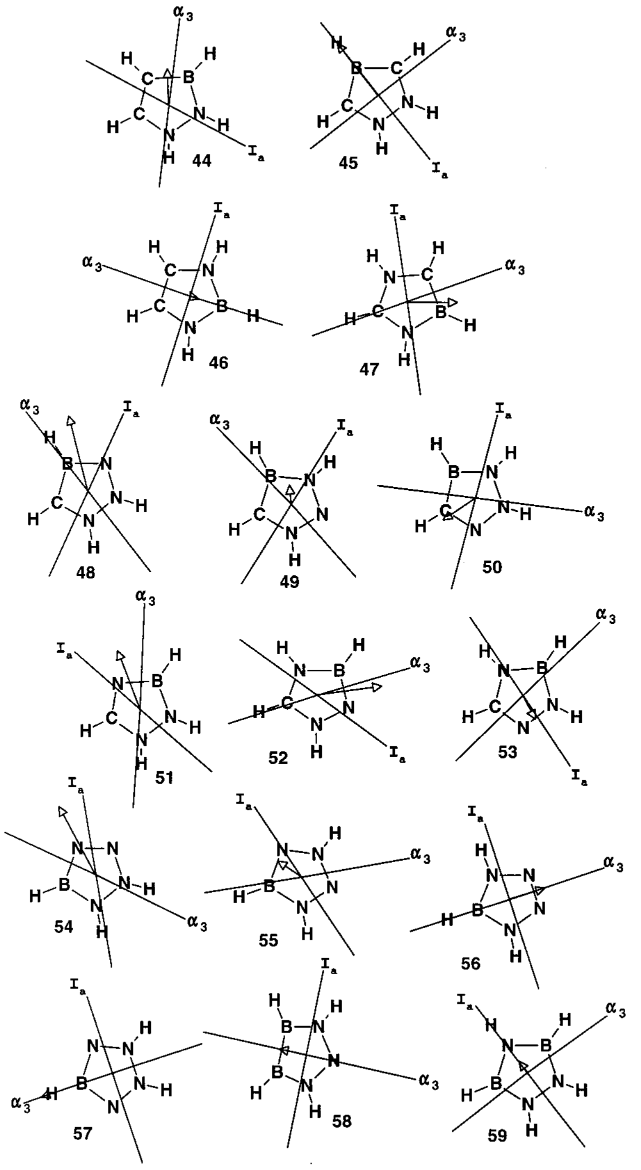

Figure 3. Diazaboroles, triazaboroles, tetrazaboroles, and triazadiboroles. All C_s planar except **44**, **48**, **50**, **51**, and **54** (C_1), **45** and **59** (C_2), **46**, **56**, and **57** (C_{2v}), and **58** (C_s, nonplanar; note the H above the central N). See notes for Figure 1.

We report systematic, electron-correlated, ab initio calculations for all 70 molecules; we consider their geometries, energies and relative stabilities, harmonic vibrational frequencies, dipole moments, and static dipole polarizabilities.

2. Computational Methods

Equilibrium geometries and harmonic vibrational frequencies were computed for all 70 molecules using three different methods. Preliminary calculations were made with the semiempirical modified neglect of differential overlap (MNDO) model.[38,44] Subsequently we calculated ab initio Hartree−Fock (HF) and second-order Møller−Plesset (MP2) perturbation theory[45−47] geometries and harmonic frequencies using the 6-31G(d), and in two cases 6-31G(d,p), split-valence plus polarization basis sets.[48] All calculations were made with GAUSSIAN-90.[49] The harmonic frequencies were used to verify that the calculated geometries are true minima. Dipole moments and polarizabilities were calculated by the finite-field method,[50] using HF and valence MP2 field-dependent energies obtained with a larger [5s3p2d/3s2p] basis set denoted C in our earlier

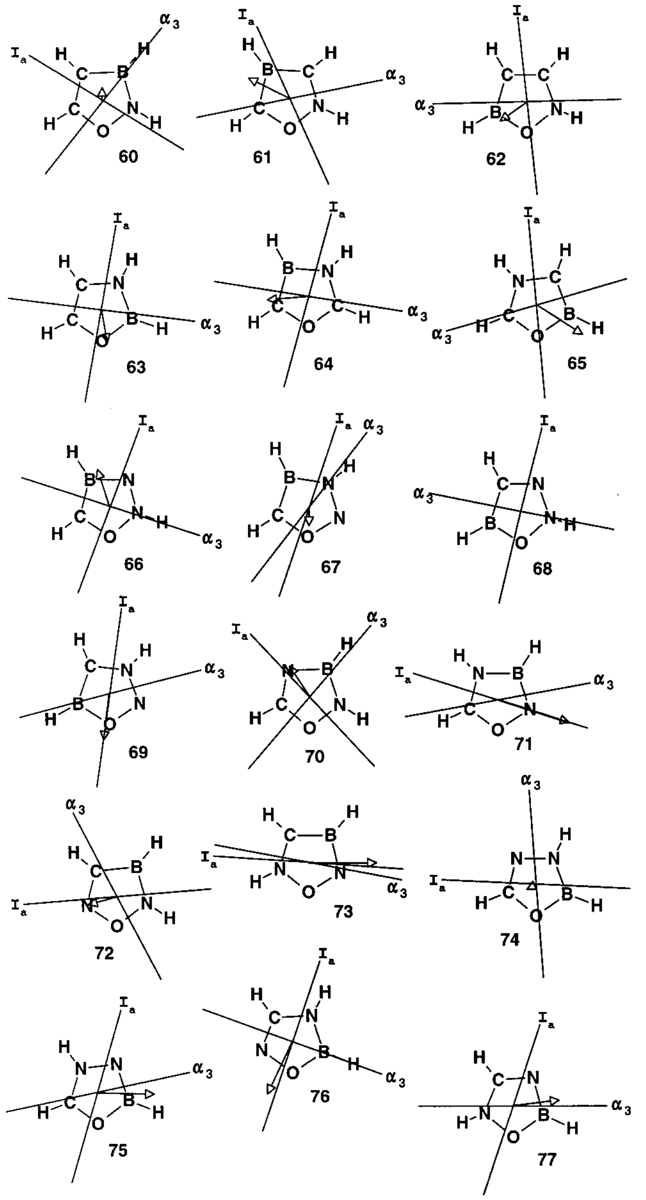

Figure 4. Oxazaboroles and oxadiazaboroles. All C_s planar except **62**, **66**, **68**, and **77** (C_1). See notes for Figure 1.

work.[51] Finite-field HF polarizabilities are equivalent to coupled Hartree–Fock (CHF) ones,[47] so we will refer to them as CHF. We use uncoupled Hartree–Fock (UCHF) polarizabilities[52,53] to estimate the relative contribution of the π-electrons. Further technical details can be found elsewhere.[9,51,54,55]

3. Equilibrium Geometries

3.1. Conformations. The conformational search was restricted to ring isomers. For each molecule, and for each level of calculation, the geometry was first determined under the constraint of planarity. If the planar conformation was a true minimum, then no further search was made. If the planar conformation was not a true minimum structure at a particular level of theory, then that conformation was used as a starting guess to find any nearby minima. All stationary points found at a particular level were used as starting guesses for the next higher level of calculations.

Figure 6 displays the energy gap for those 22 molecules in which planar conformations were higher in energy than nonplanar ones at one or more levels of calculation. It shows that the MNDO and HF models did not reliably predict planarity. Five molecules were nonplanar with MNDO but planar otherwise. Two molecules were planar with MP2 even though both MNDO and HF predicted them to be nonplanar. The HF structure of **66** was planar but the MNDO and MP2 ones were not.

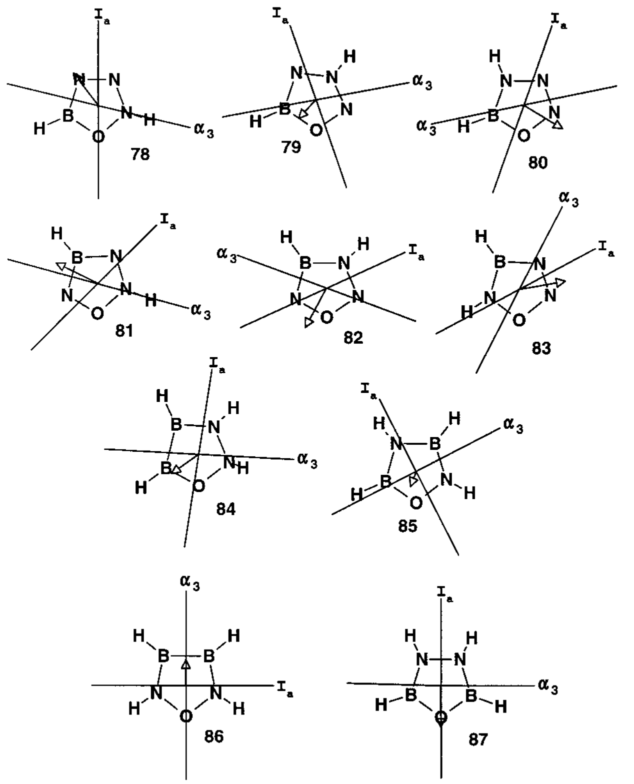

Figure 5. Oxatriazaboroles and oxadiazadiboroles. All C_s planar except **78** and **84** (C_1), **86** (C_{2v}), and **87** (C_2). See notes for Figure 1.

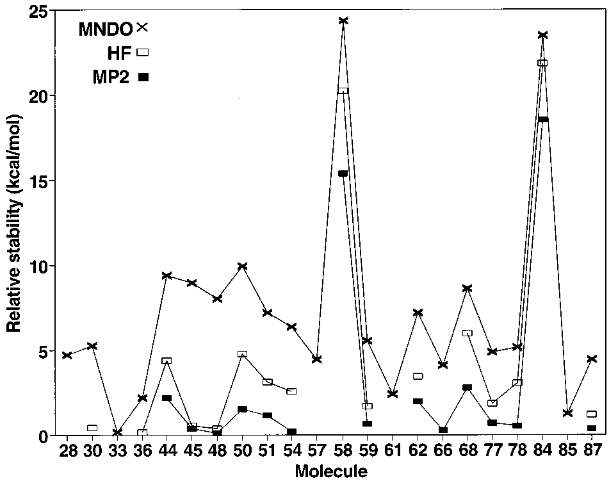

Figure 6. Energy by which the nonplanar conformation is more stable than the planar one. All such cases are shown. Molecule numbering as given in Figures 2–5.

In every case, the energy gap decreases in the order MNDO, HF/6-31G(d), MP2/6-31G(d). A nonplanar form of 1,2,3,4-tetrahydro-1,2,3,4-diazadiborinine (**4**) was previously found[9] to be more stable by 3, 0.6, and 0.0001 kcal/mol at these three levels, but the planar form was more stable with MP2/6-31G(d,p). Hence, we tried increasing basis set size for the two molecules with the smallest MP2/6-31G(d) energy gap: **48** and **54**. At the MP2/6-31G(d,p) level, the gaps shrank to 0.033 and 0.13 kcal/mol for **48** and **54**, respectively; however, the gaps

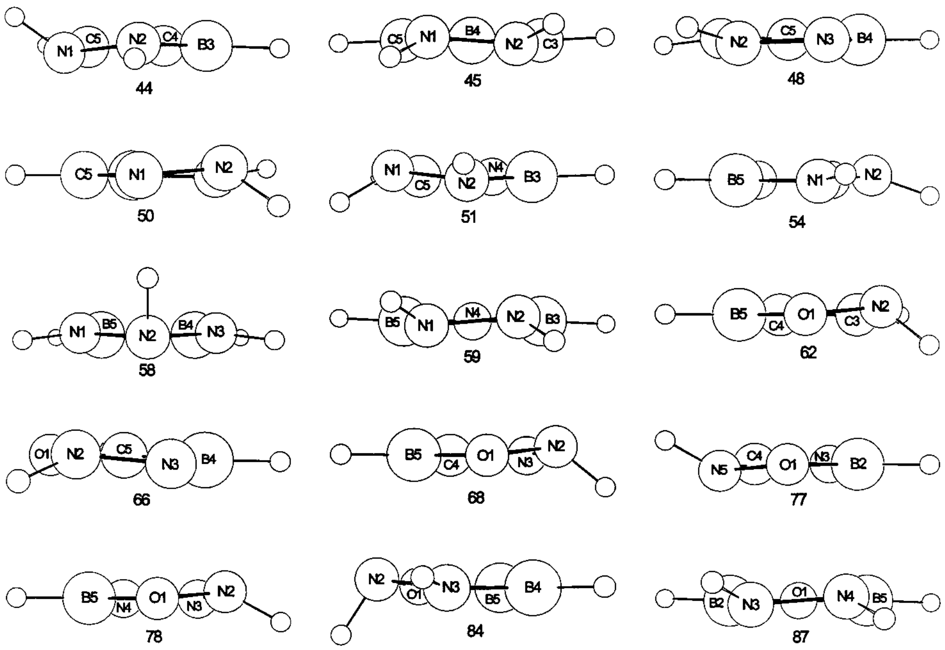

Figure 7. All nonplanar five-membered rings at their MP2/6-31G(d) optimized geometry. Molecule and locant numbering as given in Figures 3−5. Only one of two enantiomers is shown for each molecule.

increased to 0.14 and 0.29 kcal/mol at the MP2/6-311G(d,p) level. So we retain the MP2/6-31G(d) nonplanar structures for **48** and **54**. Future investigations with higher levels of correlation and even larger basis sets may give different results because the difference between planar and nonplanar conformations is very small for some of the molecules.

The minimum structure is nonplanar for 15 of the 70 molecules at the MP2/6-31G(d) level. Their nonplanarity is shown in Figure 7, made with the help of ORTEP-3 for Windows.[56] There are two possible enantiomers for each nonplanar species; one can be obtained from the other by taking the negative of all dihedral angles.

The 15 nonplanar molecules are all five-membered rings. The nonplanar conformation of 11 of these is necessarily of C_1 symmetry. However, **45**, **58**, **59**, and **87** have C_{2v} symmetry in their planar conformations and hence could have either C_s or C_2 nonplanar conformations. In fact, at all three levels of theory, the nonplanar, minimum-energy structure of **45**, **59**, and **87** is C_2 whereas the minimum-energy structure of **58** is C_s but nonplanar. This can be explained by noting the tendency of N to pyramidalize because of its lone pair of electrons, but for B to prefer a trigonal planar structure around it. For **58**, there are three adjacent NH's; for the C_s structure, the central NH bends out-of-plane in one direction while its two neighbors go in the other direction. For **45**, **59**, and **87** there are only two neighboring NH's; one bends up and the other down, yielding the C_2 structure.

Figures 1−5 show the molecules to scale at their MP2/6-31G(d) geometry. The MP2/6-31G(d) geometries for the azaboracycles can be expected[45,46] to be accurate to within 1%. Tables S1−S5 in the Supporting Information list all computed bond lengths and bond angles. Table S6 lists dihedral angles for the nonplanar species.

3.2. Comparison with Previous Work. Calculated geometries have been published previously for only two of these 70 molecules. Maouche et al.'s MNDO geometry[39] of **59** is nearly the same as ours except for an NNB angle that is too large by 1.2°. Our MNDO geometry of **56** differs substantially from an MNDO geometry of the 1,4-dimethyl species.[38]

Table 1 compares the computed and experimental ring bond lengths and angles for every five- or six-membered ring for which there is experimental data. The only gas-phase geometry of a derivative of any of the 70 molecules of this paper is an electron diffraction (ED) geometry by Chang et al.[25] of the **56**-like 1,4-dimethyl-4,5-dihydro-1H-tetrazaborole. They assumed a value for the BH bond length and the NCH angle. Considering all data, they preferred a planar conformation for the molecule, although the evidence was not conclusive. Our ring bond lengths agree within 0.7 pm, which is about the same as the estimated experimental error. Our ring angles differ by 0.6°−2.4°, compared to their estimated errors of 0.6°−1.0°. Interestingly, the ED external ring angles are similar to ours, despite the presence of the methyl groups.

There are relatively more experimental geometries of substituted derivatives obtained by X-ray diffraction. Brett et al.[22] obtained an X-ray geometry of the 1,5-diisopropyl-4-phenyl-derivative of **56**. They found the hetero ring to be planar within 0.2°. The average absolute differences, δ_a, between their ring parameters and the MP2 ones are only 0.9 pm and 0.9° to be compared with experimental errors of 0.4 pm and 0.3°, respectively. However, their N2═N3 bond was only 127.9 pm, noticeably shorter than our 129.6 pm and the 129.1 pm of Chang et al.[25]

Schmid et al.[21] determined the X-ray structure for three versions of **46**, with 1,3-diisopropyl-2-methyl-, with 1,3-diethyl-2-methyl-, and with 1,2,3-trimethyl- substituents. Comparing the three X-ray geometries shows that significant variance occurs just because of different substituents. It is especially valuable that X-ray structures were obtained at two temperatures, −73 and −171 °C, for the trimethyldiazaborole. Two sets of parameters were presented that differ insignificantly in angles but by as much as 2 pm in bond lengths. The lower temperature structure is the one much closer to our unsubstituted MP2 structure; the difference δ_a is only 0.4 pm for ring bond lengths and $\delta_a = 1°$ for angles. This agreement is noteworthy, especially considering that their structures are not C_{2v}, but instead have pairs of parameters that differ by as much as 0.6 pm, presumably because of intermolecular interactions in the crystal.

TABLE 1: Comparison of Calculated[a] Ring Bond Lengths[b] and Angles[c] with Experiment[d]

molecule	1−2	2−3	3−4	4−5	5−6	6−1	123	234	345	456	561	612
19	135.2	142.5	151.1	137.7	141.7	132.4	128.2	113.5	117.5	120.5	125.3	115.1
19[e]	137.3	143.2	153.0	140.6	144.5	129.1	125.6	115.2	116.7	118.6	126.8	116.7
19[f]	136.9	143.5	152.8	138.2	144.0	129.5	125.6	113.2	119.3	118.4	125.2	118.2
42	143.4	142.1	143.5	144.7	129.2	137.8	114.7	121.3	119.4	117.5	125.6	121.5
42[g]	145.0	143.2	144.4	141.5	127.2	141.3	119.6	111.4	115.5	120.6	119.4	113.2

molecule	1−2	2−3	3−4	4−5	5−1	123	234	345	451	512
46	142.9	142.9	139.3	136.0	139.3	103.6	109.7	108.5	108.5	109.7
46[h]	143.9	143.4	141.0	132.8	139.4	107.0	105.7	110.5	110.4	106.4
46[h]	144.2	144.2	140.2	133.8	140.2	106.4	106.5	110.3	110.3	106.5
46[i]	143.5	142.5	140.1	140.9	140.4	107.1	108.2	108.2	108.7	107.8
46[i]	143.4	142.5	140.2	141.2	140.1	107.7	107.6	108.8	108.6	107.3
46[j,k]	142.7	143.3	139.8	134.2	140.4	105.0	108.2	109.3	109.3	108.2
46[j,l]	141.0	140.7	140.8	132.7	141.1	105.9	107.9	109.5	108.6	108.2
46[j,m]	144.6	145.0	140.7	136.2	140.9	104.5	108.5	109.3	109.1	108.6
46[j,n]	143.1	143.5	139.2	134.9	139.4	104.6	108.4	109.3	109.2	108.5
56	136.8	129.6	136.8	142.0	142.0	108.5	108.5	111.8	99.4	111.8
56[o]	137.5	127.9	137.6	142.2	141.1	109.2	108.9	110.6	100.5	110.8
56[p]	137.5	129.1	137.5	141.3	141.3	109.6	109.6	110.0	101.8	110.0
76	138.0	142.4	137.5	130.3	142.5	106.2	105.0	114.3	105.0	109.4
76[q]	139.	141.	136.	130.	145.	105.6	107.1	113.6	105.6	108.1
76[r]	138.6	141.9	137.2	129.7	144.1	105.4	106.7	113.4	105.5	109.0

[a] MP2/6-31G(d). [b] In picometers. [c] In degrees. [d] Substituted derivative in all cases; cf. text. [e] X-ray, ref 4. [f] X-ray, ref 19. [g] X-ray, ref 5. [h] X-ray, bis compound, ref 3. [i] X-ray, bis compound, ref 20. [j] X-ray, ref 21. [k] 1,3-diisopropyl-2-methyl-. [l] 1,3-diethyl-2-methyl-. [m] 1,2,3-trimethyl- at −73 °C. [n] 1,2,3-trimethyl-, at −171 °C. [o] X-ray, ref 22. [p] Electron diffraction, ref 25. [q] X-ray, ref 23. [r] X-ray, ref 24.

Weber et al.[3] obtained the X-ray structure of bis(2,3-dihydro-1,3,2-diazaboryl)oxane with *tert*-butyl groups on each N, and Sawitzki et al.[20] determined the X-ray structure of a fused ring molecule containing **46**. As could be expected, these structures differ a little more from our unsubstituted molecule than do the compounds of Schmid et al.,[21] because of substituent effects. However, δ_a is still only 1.3 pm and 2.7° for the Weber et al. compound.[3]

X-ray structures have been reported for 4-methyl-2-phenyl-**76** by Raper[23] and for 2-phenyl-4-(4-methylphenyl)-**76** by Möhrle et al.[24] In each case the heterocycle is nearly planar. Raper[23] reported rather large estimated errors of 1 pm and ≈0.7°. Our geometry differs from his by $\delta_a = 1.3$ pm and 1°. Our MP2 structure agrees more closely with that of Möhrle et al.[24] with $\delta_a = 0.7$ pm and 0.8° for ring parameters. In each case, the largest differences are an O−N bond longer by ≈2 pm and a corresponding ∠234 larger by ≈2° than the unsubstituted MP2 structure.

Klöfkorn et al.[5] made the first triazadiborinine, a derivative of **42**, and obtained its X-ray structure. Their ring bond lengths are similar to our MP2 ones for the unsubstituted ring, with B−N bonds in the range of 141−145 pm, and one long and one short C−N bond. Also, they[5] reported that the sum of three angles at the ring atoms other than N5 was close to 360°. However, the sum of the 6 ring angles is only ≈700°, not the expected 720°, suggesting significant deviation from planarity. Their ring bond angles are quite different from MP2, by as much as 10°. Apart from the usual methodological differences, this could be caused by the nature of the substituents. The two N's have a *tert*-butyl group whereas the two B's have pentafluorobenzyl attached. In the same paper,[5] the structure of a borazine (**17**) derivative was reported with the same substituent pattern. In both structures,[5] the ring angles at N's having the *tert*-butyl substituent are much less than 120°. By contrast, the angles in unsubstituted **17**[57,58] follow the pattern observed for the MP2 geometry of all the azaborinines[9] and the molecules in this paper, with the angle at NH greater than 120°.

Two fused-ring **19**'s have been studied by X-ray diffraction. Comparing Aurivillius and Löfving's 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]pyridine[19] and Groziak et al.'s 1,2-dihydro-1-hydroxy-2,3,1-benzodiazadiborine,[4] the experimental ring bonds are all longer by up to 3 pm, except for the C−N bond which is 3 pm shorter than the MP2 **19** structure. The average difference δ_a between ring bond lengths is 1.3 pm when comparing the two experimental structures, but is 1.7 pm when comparing either to our MP2 structure. Differences occur because of hydrogen bonding in the crystal, the slight nonplanarity of the rings, and the tendency for the fused ring to cause longer bonds in the heteroring.

3.3. Trends in Bond Lengths and Angles. We consider the trends in the MP2 geometrical parameters of all 87 BN rings (**1**−**87**). Bond lengths are within the same range for five- and six-membered rings. Bond angles differ greatly between five- and six-membered rings, obviously because of the different number of angles.

All ring bond lengths, XY, where X and Y are selected from B, C, N, $\underline{\mathrm{N}}$, and O, are shown in Figure 8. It separates those N's that have an H attached (called N) from those that do not (called $\underline{\mathrm{N}}$). Figure 8 shows that bonds between two pyridinic N's ($\underline{\mathrm{N}}-\underline{\mathrm{N}}$) are always shorter than 132 pm, whereas N−N bonds between two pyrrolic N's are always longer than 133 pm. For six-membered rings, the ring angle at $\underline{\mathrm{N}}$ varies between 112.6° and 119.4°, while at N the range is 120.9° to 131.1°. The distinction is not quite as sharp for five-membered rings, but again the angles at N tend to be larger.

Most of the ring bond lengths fall between typical single and double bond lengths because of π-electron delocalization. An extreme case is **43**; it contains both the longest and the shortest of all B−N bond lengths, different by 13 pm. Though they are slightly shorter for five-membered rings, all bond lengths to H lie within 1.2 pm of their average values: 119.2 pm for BH, 108.9 pm for CH, and 101.5 pm for NH. For six-membered rings, the angle at B is at most 120.2°; the range of values is just slightly broader than we found for the 17 azaborinines[9] alone. Angles involving the H's vary greatly. The bond lengths of nonplanar species fit into the range of values found for planar species because the nonplanar conformations are close to being planar.

The dihedral angles are farthest from planar when they include the out-of-plane N−H bond, the most significant nonplanar

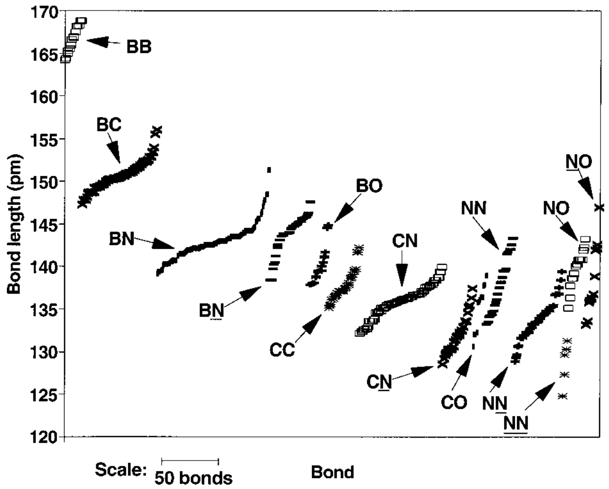

Figure 8. Ring bond lengths in picometers for 87 molecules (**1**−**87**), separated by atom types. N is reserved for pyrrolic nitrogen while N̲ is used to refer to pyridinic nitrogen. At the *best* geometry, whether planar or nonplanar. All MP2/6-31G(d), except for **4** which is MP2/6-31G-(d,p).

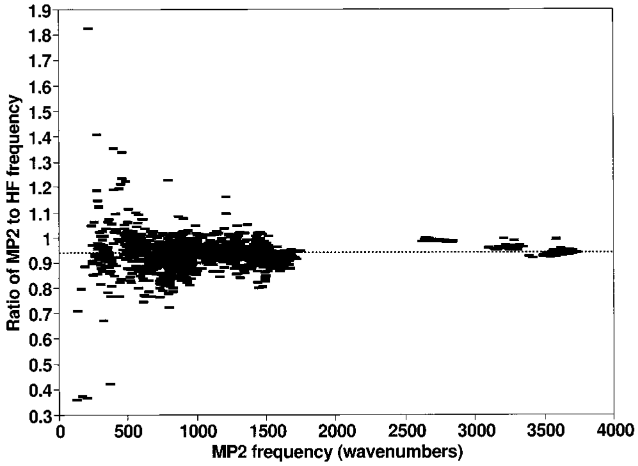

Figure 9. Ratios $r_i = \omega_i(\text{MP2})/\omega_i(\text{HF})$ versus MP2 frequency (in cm^{-1}) for all harmonic vibrational frequencies of 83 molecules (**1**−**87**, except **4**, **30**, **36**, and **66**, for which the HF and MP2 minimum geometries are not of the same symmetry), all with the 6-31G(d) basis. Each molecule's frequencies are paired by order of increasing frequency in each symmetry class. The dotted line shows the average value of r_i, 0.939.

feature. The appropriate HNNH or HNCH dihedral angle is between 26° and 77° for the nonplanar molecules. The 6-31G-(d,p) basis reduces the dihedral angles for **48** and **54**, but 6-311G(d,p) gives almost the same angles as 6-31G(d).

4. Harmonic Vibrational Frequencies

MP2/6-31G(d) harmonic vibrational frequencies and qualitative infrared intensity indicators at the best MP2/6-31G(d) geometry for 55 planar and 15 nonplanar molecules are listed in Tables S7-S15 (Supporting Information). Figure 9 plots the ratio $r_i = \omega_i(\text{MP2})/\omega_i(\text{HF})$ (frequencies are matched by symmetry in increasing order) versus MP2 frequency, for 83 of 87 BN-containing molecules that we have studied, including the azaborinines;[9] four molecules are excluded because their HF and MP2 conformations are not of the same symmetry. We find that r_i is consistently 0.99 for B−H stretch (ν) vibrations, 0.96 on average for ν(C−H), and 0.94 for ν(N−H). The ratio r_i is more scattered for the lower frequency vibrations. The overall average is 0.94, close to the ratio of 0.95 found by Scott and Radom[59] for 122 molecules using the same basis set.

Many of the vibrational modes are mixed. Some trends do occur, but often with many exceptions in a set of isomers. The highest fundamental frequencies are X−H stretches occurring around 3650, 3300, and 2800 cm^{-1} for X = N, C, and B, respectively. The next highest frequency is usually ν(C−N), if such a bond is present; the B−H in-plane deformation (δ) is usually quite distinct, between 863 and 987 cm^{-1}; the B−H out-of-plane deformation (γ), at ≈850 cm^{-1}, is usually but not always the highest of the X−H wags. The lowest frequency sometimes involves the whole ring, but other times is γ(N−H). Other types of frequencies vary widely over the series of molecules.

It is difficult to compare harmonic frequencies calculated for isolated molecules with experimental ones that are anharmonic, temperature-dependent, and usually determined in solution. A simple device is to uniformly scale calculated frequencies to improve agreement with experiment. Scott and Radom[59] suggested a scale factor of 0.9427 for MP2/6-31G(d) frequencies. They gave alternate factors that yield maximum agreement for *low* frequencies.

Selected experimental lines have previously been assigned for some BN heterocycles. The results (in cm^{-1}) are ν(N−H), 3240−3450;[4,18,24,30,31,36] ν(C−H), 3045;[30] ν(B−H), 2542−2656;[13,19,26−29] ν(C=N), 1599−1650;[4,31−33,36] ν(B−N), 1340−1400;[12,35] and ν(N−O), 920.[36] The X−H stretch frequencies are about 5% higher than the MP2 values, as expected.

Measured vibrational spectra have been assigned for the 1,4-diphenyl-[13] and 1,4-dimethyl[26] derivatives of **56**. For the latter, liquid and vapor infrared and liquid Raman spectra were obtained,[26] to help assign all lines accurately. The spectra of 1-methyl-4-phenyl-[27] and 1-phenyl-4-chlorophenyl-[29] derivatives of **56** have also been reported. It was straightforward to match seven lines from the 12 or so frequencies of the **56** derivatives that did not explicitly depend on the substituents.[13,26,27,29] The experimental frequencies (from the dimethyl derivative[26] or a range of values from several of the four derivatives previously studied[13,26,27,29]) for ν(B−H), ν(N=N), ring breathing, δ(B−H), γ(B−H), and the two lowest out-of-plane ring folds (γ) of A_2 and of B_2 symmetry are 2648 ± 12, 1363, 1095 ± 4, 1057 ± 12, 814 ± 4, 554, and 522 cm^{-1}, respectively. The corresponding MP2 frequencies are 2825, 1313, 1097, 871, 849, 635, and 525 cm^{-1}, respectively. Agreement is reasonable except for δ(B−H), which however should be strongly affected by substituents at the two neighboring N's.

5. Relative Stabilities

The relative MP2 energies, including zero-point corrections, of the 70 molecules are listed in Table 2, with respect to the lowest energy isomer for each group. All the energies are for the lowest conformation that we found, planar or nonplanar.

The MNDO, HF, and MP2 methods agree on the most stable species of each type. Moreover, the MP2 energy gap between the two lowest energy isomers always exceeds 6 kcal/mol, often by a wide margin. Hence, the identification of the most stable species of each type is likely to be unchanged by higher level calculations. However, the lower levels of calculation do not agree with the MP2 order of some of the higher energy isomers as illustrated in Figure 10 for the six-membered rings. MNDO agrees with MP2 more often than HF does. MNDO tends to underestimate, and HF to overestimate, the MP2 gap between isomers. Beware that higher level calculations may reverse the ordering of pairs of higher energy isomers that are separated by small energy differences, less than 5 kcal/mol.

An −XBHNH− unit is always present in the MP2 lowest energy isomers: X = NH in the four most stable azaboroles, X

TABLE 2: MP2 Relative Stabilities, E_S,[a] Dipole Moments,[b,c] and Polarizabilities[b,d,e]

no.	E_S	μ	$\bar{\alpha}$	$\Delta_1\alpha$	$\Delta_3\alpha$
18	41.1	4.35	66.21	35.25	6.79
19	23.4	0.71	64.06	32.94	5.21
20	48.0	3.27	66.26	34.67	5.42
21	47.5	1.97	66.73	35.07	3.56
22	0.0	4.22	64.48	34.23	3.39
23	40.2	4.37	66.99	36.17	3.90
24	16.0	3.57	65.49	35.29	8.97
25	32.2	5.95	66.99	36.62	8.13
26	6.6	2.12	63.90	32.96	1.48
27	20.1	5.26	64.21	33.09	5.71
28	146.6	7.14	69.17	35.73	5.45
29	114.4	3.36	68.62	35.03	2.73
30	128.0	4.69	70.84	38.73	8.26
31	106.8	5.44	70.22	37.56	2.42
32	80.4	2.12	70.11	37.58	1.95
33	100.7	8.33	68.41	36.44	10.92
34	66.3	2.13	65.88	34.55	12.75
35	34.6	1.75	62.07	30.43	9.58
36	100.0	6.40	66.55	35.49	9.45
37	97.0	6.42	69.98	38.82	6.07
38	69.8	1.94	64.61	33.19	5.95
39	79.4	4.15	67.66	36.91	5.29
40	58.8	2.47	66.95	35.57	6.08
41	80.8	4.50	63.83	32.46	6.07
42	0.0	3.34	60.82	29.37	5.91
43	24.6	7.44	64.45	32.27	8.29
44	44.0	2.74	55.25	22.93	6.13
45	75.0	4.99	59.00	24.64	1.77
46	0.0	0.68	54.05	21.57	4.19
47	30.3	3.53	59.47	25.23	10.17
48	67.8	5.79	52.46	23.41	0.97
49	38.2	1.37	50.75	20.97	1.57
50	49.2	2.94	50.94	22.91	7.67
51	24.5	4.64	49.36	21.95	4.94
52	21.4	4.82	51.81	23.95	7.57
53	0.0	1.92	48.21	20.38	3.46
54	33.6	5.71	46.38	21.78	6.87
55	15.0	2.02	44.93	20.18	3.45
56	0.0	2.75	43.71	18.79	2.22
57	44.6	5.59	45.91	21.11	4.34
58	81.1	3.06	55.07	23.09	9.50
59	0.0	1.02	52.08	19.67	2.81
60	58.9	0.89	48.85	19.93	2.72
61	93.9	3.39	53.16	22.61	7.86
62	53.2	2.56	49.56	21.31	9.12
63	0.0	2.46	47.53	19.09	4.70
64	44.3	2.97	54.74	24.69	13.99
65	34.0	4.05	54.02	24.12	12.94
66	87.3	2.94	46.22	20.60	4.95
67	63.4	1.36	44.40	17.60	0.64
68	58.6	0.91	45.05	20.82	8.85
69	54.0	3.49	45.30	19.08	5.28
70	37.6	2.69	43.25	18.84	1.98
71	48.8	5.60	46.93	21.88	8.10
72	74.9	2.21	44.74	19.89	2.63
73	99.4	5.04	48.38	22.88	7.68
74	0.0	0.75	42.26	17.82	4.84
75	24.2	4.24	46.17	21.73	9.96
76	12.3	4.27	42.48	18.36	4.73
77	33.0	3.50	43.74	19.88	7.74
78	33.3	3.06	40.71	19.24	9.19
79	19.6	1.89	39.71	17.97	7.39
80	0.0	3.44	38.44	16.59	4.28
81	65.9	3.43	41.45	19.39	9.29
82	43.0	3.29	40.40	18.07	4.18
83	42.7	3.47	40.81	18.81	4.36
84	102.1	2.65	49.32	21.05	9.88
85	15.7	1.15	46.12	17.73	4.44
86	119.6	1.95	50.34	21.56	5.26
87	0.0	3.20	46.07	17.49	3.44

[a] MP2/6-31G(d)//MP2/6-31G(d) with respect to lowest energy isomer. In kcal/mol. [b] MP2/C//MP2/6-31G(d). [c] In debyes. [d] In au. [e] The spacing between rows indicates groups of isomers.

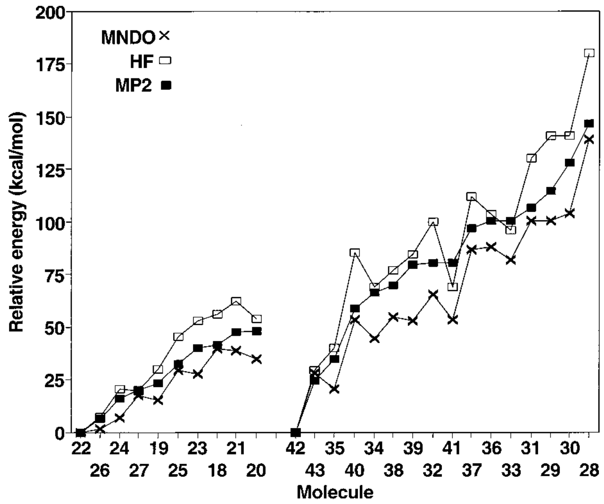

Figure 10. Stabilities of the diazaborinines and triazadiborinines. Each is relative to their most stable ring isomer, and includes zero-point energy corrections. For HF and MP2, the 6-31G(d) basis set was used.

= O in the four lowest energy isomers of the oxazaboroles, and X = N in the most stable isomer, **22**, of the diazaborinines. That is, the most stable MP2 structure always has a boron atom sandwiched between two more electronegative neighbors (N or O). The lowest energy pair of triazadiborinine tautomers has an additional BN pair, i.e., a −NBHNHBHNH− unit. Hoffman[43] calculated the following order of extended Hückel energies for diazaborinines: **22** < **26** < **24**. Those are the three lowest energy isomers in the MP2 order.

Certain features are unsatisfactory predictors of stability. All 12 molecules for which there is experimental data have a −BHNH− unit but this alone is not a guarantee of greater relative stability. Two such units are found in **41**, but it is relatively unstable because of its adjacent NH's. The oxazaboroles **60** and **63** each have a −BHNH− next to O, but **63** is more stable by 59 kcal/mol because of the preferred OBN order. Tautomers can be equally stable (e.g., **20** and **21**, within 0.4 kcal/mol) or separated by as much as 66 kcal/mol (**33** and **35**). Each of the four most stable azaboroles, **46**, **53**, **56**, and **59**, is the isomer with smallest dipole moment, but this trend does not hold for the other types of molecules. The molecules that we found to be nonplanar are sometimes but not always the highest energy isomers.

In the highest energy species, adjacent pairs of BH's or of NH's are found. For example, the two highest energy triazadiborinines, **28** and **30**, have both of these features, whereas **32** is relatively more stable despite having an NNN pattern because the dehydro- position is at the middle N. In molecules without BH or NH pairs, there are other patterns. For the diazaborinines, the common structure for the three least stable isomers is −NNH−. The highest energy oxadiazaboroles and oxatriazaboroles contain −NONH− and/or ONN (with or without one H).

The ease with which a molecule can be synthesized is related to the relative energetic stability of that molecule compared to its isomers. Ten of the 12 molecules that have been made (with substituents) are the lowest energy isomers. The two exceptions are **19**, which is one of three known diazaborinines, but is only the fifth most stable; and **76**, which is only the second most stable oxadiazaborole. We predict derivatives of **74**, the lowest energy isomer of the 12 oxadiazaboroles, and **80**, similar to **56** and the most stable of the hitherto unobserved oxatriazaboroles, to be accessible synthetic targets.

6. Dipole Moments

6.1. Results. Table 2 lists the magnitude of the MP2/C dipole moments. Figures 1−5 show the dipole moments drawn to scale, with the arrowhead at the negative end. Figures 1−5 also show the principal inertial axes I_a calculated using the masses of the most abundant isotopes for each atom. The angle θ_a between the dipole moment vector and I_a suffices to describe the orientation of the dipole moment for the 55 planar molecules because symmetry requires the dipole moment vector to be in the molecular plane. For the nonplanar molecules, the angles θ_b and θ_c between the dipole moment and the inertial axes I_b and I_c are required to complete the specification of the orientation. The three angles are given in Tables S6 and S16 (Supporting Information).

The dipole moments vary in size from 8.33 D in **33** to under a debye in **19**, **46**, **60**, **68**, and **74**; they vary greatly for isomers and tautomers. Figure 7 shows that each C_1 molecule has one N pyramidalized such that it is out of plane and its H is further out on the other side of the plane. The dipole moment is parallel to this N−H with the negative end toward the N. The "in-plane" electron distribution of **68** is so remarkably uniform that μ is almost perpendicular to the "molecular plane"; this is why the dipole moment of **68** is not shown in Figure 4.

6.2. Comparison with Previous Work. The dipole moments of 5-ethyl-2,3-dimethyl and 4-ethyl-2,3-dimethyl derivatives of **19** were measured[37] to be 1.2 and 1.3 D, respectively, in benzene at 25 °C. The contributions made by the substituents to the dipole moment of **19** can be estimated by comparing dipole moments of various methylpyridines and ethylpyridines.[37,60] The methyl groups should counteract each other with a net addition of only ≈0.05 D to the dipole moment of **19**. By analogy with the dipole moment difference between ethylpyridine and pyridine,[60] the ethyl group in the 5- and 4-positions should add ≈0.3 and ≈0.4 D, respectively, to the dipole moment of **19**. Subtracting these substituent contributions from Gronowitz and Maltesson's measurements[37] leads to an estimate of $\mu = 0.85 \pm 0.1$ D for **19** in benzene to be compared with our MP2 value of 0.71 D for isolated **19**. Dewar and Dougherty[30] calculated the MNDO dipole moment of the 1,3-dimethyl derivative of **56** to be 2.3 D. By comparison, our MNDO and MP2 results for **56** are 2.37 and 2.75 D, respectively.

7. Polarizabilities

7.1 Results. It is most useful to report quantities invariant to the choice of coordinates. The invariants that we chose are the mean polarizability:

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

and three measures of anisotropy:

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

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

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

where $\alpha_1 \leq \alpha_2 \leq \alpha_3$ are eigenvalues of the dipole polarizability tensor. We use atomic units for polarizabilities; one atomic unit of polarizability $= 4\pi\epsilon_0 a_0^3 \approx 1.648\,78 \times 10^{-41}$ F m^2 in SI units.

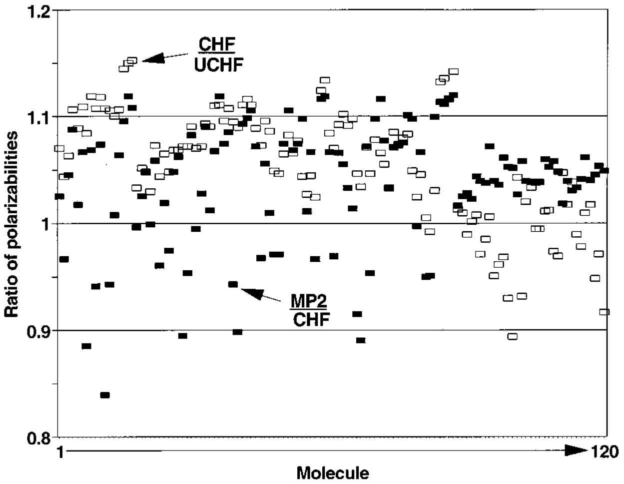

Figure 11. Ratios of CHF/UCHF and MP2/CHF for the mean polarizability. In basis C. The molecules are numbered as in Figures 1−5 and text.

TABLE 3: MP2/C Properties at Nonplanar Equilibrium Geometries and Planar Stationary Points

molecule	μ	$\bar{\alpha}$	$\Delta_1\alpha$	$\Delta_3\alpha$
62 nonplanar	2.56	49.56	21.31	9.12
62 planar	3.06	50.51	21.67	8.61
66 nonplanar	2.94	46.22	20.60	4.95
66 planar	3.16	46.45	20.80	5.77
78 nonplanar	3.06	40.71	19.24	9.19
78 planar	3.69	41.04	19.80	8.97

Table 2 lists MP2/C average and anisotropic $\Delta_1\alpha$ and $\Delta_3\alpha$ polarizabilities for molecules **18**−**89** at their calculated equilibrium geometries. Figures 1−5 show the principal axis of greatest polarizability, α_3, for each molecule. Table S16 lists α_1, α_2, α_3, the Kerr anisotropy ($\Delta_2\alpha$), and the angle ϕ_3 between α_3 and the principal inertial axis I_a. The mean polarizabilities vary by almost a factor of 2, from 38 au for **80** to 72 au for **30**. The most polarizable five-membered rings, **45** and **47**, are almost as polarizable as the least polarizable six-membered ring, **42**.

Table 3 compares MP2/C dipole moments and polarizabilities of three nonplanar molecules with their counterparts at MP2/6-31G(d) planar stationary points. It shows that the dipole moments for the planar conformations are larger by as much as 20%, whereas the $\bar{\alpha}$, $\Delta_1\alpha$, and $\Delta_3\alpha$ values for the two conformations differ by no more than 3%.

Table S16 includes the UCHF/C parallel and perpendicular π fractions $f(X,\pi) = \alpha(X,\pi)/\alpha(X)$, $X = \parallel, \perp$ for the planar molecules. The π-electron contribution to the mean polarizability varies from 35% to 58% implying that the contribution of the core and valence σ-electrons varies from 42% to 65%. Clearly, a π-electron model cannot satisfactorily account for the polarizabilities of these molecules.

7.2. Observations on Methodology. It is often, but not always, true that the polarizability increases as one improves the theoretical level of description from uncoupled Hartree−Fock (UCHF) to coupled Hartree−Fock (CHF) to finite-field MP2. This is demonstrated in Figure 11 which shows the CHF/UCHF and MP2/CHF ratios for the mean polarizability. Figure 11 includes our current results for molecules **18**−**87**, and also our previous results for azaborinines, **1**−**17**, benzene and 12 azines (**88**−**100**), pyrrole and 9 azoles (**101**−**110**), and furan and 9 oxazoles (**111**−**120**), ordered as in our previous papers.[9,51,54,61] A similar pattern is also observed for α_2, α_3, $\Delta_1\alpha$, and $\Delta_2\alpha$. Figure 12 shows that the out-of-plane component α_1 behaves differently; the UCHF α_1 is usually higher than its CHF

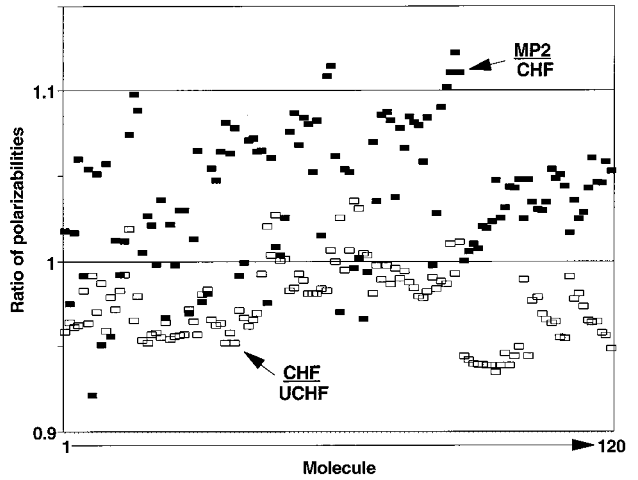

Figure 12. Ratios of CHF/UCHF and MP2/CHF for out-of-plane polarizabilities. See notes for Figure 11.

counterpart. The average absolute differences between the UCHF and CHF values for the boron-containing molecules (**1**−**87**) are 7%, 27%, and 25% for $\bar{\alpha}$, $\Delta_1\alpha$, and $\Delta_2\alpha$ respectively. The average absolute differences between the MP2 and CHF values of $\bar{\alpha}$, $\Delta_1\alpha$, and $\Delta_2\alpha$ are 7%, 11%, and 12%, respectively.

7.3. Trends in the Polarizabilities. In the azines,[61,62] azoles,[51] and oxazoles,[54] we found that isomers are almost equally polarizable. However, this is not true for the azaborinines[9] and the 70 molecules of this work; for example, the mean polarizability of the triazadiborinines **28**−**43** ranges from 61 to 71 au. In the molecules **1**−**87**, the most stable isomer is the least polarizable, isomers with adjacent B's tend to be the most polarizable, and isomers with adjacent C's are the least polarizable.

Azasubstitution, i.e., replacing CH by N, invariably reduces the polarizability, because the polarizability of N is smaller than that of CH. In the 62 cases, among **1**−**87**, where one molecule differs from another by a single azasubstitution, the average effect is a reduction by 4.6, 5.8, and 6.5 au for $\alpha_\perp$, $\bar{\alpha}$, and $\alpha_\|$, respectively. This is a slightly larger azasubstitution effect than found previously for the azoles,[51] oxazoles,[54] and azines,[61] where the corresponding reductions were 3.2, 4.5, and 5.2 au for $\alpha_\perp$, $\bar{\alpha}$, and $\alpha_\|$, respectively. Replacement of NH in an azaborole by the less polarizable O to form an oxazaborole always reduces $\alpha_\perp$, $\bar{\alpha}$, and $\alpha_\|$, by an average of 4.3, 5.6, and 6.3 au, respectively, just as we found previously[56] that replacing NH in an azole to form an oxazole reduces $\bar{\alpha}$ by 5.1 au.

By contrast, the replacement of C_2H_2 by BNH_2 sometimes increases and sometimes decreases the polarizability. The differences between the mean polarizabilities of the diazaborinines and pyridine range from +3.04 to −0.05 au, and the polarizability differences between the triazadiborinines and the corresponding diazaborinines range from +4.2 to −6.9 au. No simple rule holds but a gross trend can be seen. The first BN-for-CC substitution and the second one in the six-membered rings tend to increase the polarizability, whereas the second substitution in the five-membered rings and the third substitution in the six-membered rings generally decrease the polarizability.

7.4. Additive Polarizability Models. Molecular polarizabilities can be modeled as sums of polarizabilities of atoms, or of bonds, or of chemical groups.[63,64] An additive atom model[51] of polarizability applicable to both $\bar{\alpha}$ and $\Delta_1\alpha$ for five- and six-membered rings containing B, C, N, and O atoms is:

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

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.

TABLE 4: Parameters and Errors of Polarizability Model 5 and Fit 5b

	$\bar{\alpha}$		$\Delta_1\alpha$	
	5	5b	5	5b
b_B	15.13	−19.4	16	−9.3
b_C	10.58	−11.7	9.9	−6.2
b_N	6.7	−5.9	3.9	−5.27
b_O	2.6	−1	−2.3	−4.86
b_H	1	8.4	−3.8	1.5
b_A	0	3.97	0	2.87
b_η	0	3.2	0	2.32
δ_a(%)	2.95	1.6	6.01	4.67
δ_m(%)	14.09	6.12	40.04	27.86

TABLE 5: Parameters and Errors of Polarizability Model 6

	$\bar{\alpha}$	$\Delta_1\alpha$
c_{BB}	19	10.8
c_{BC}	16	8
c_{CC}	11.3	5.7
c_{BN}	11.1	5.2
c_{CN}	9	4.8
c_{BO}	9	2.7
c_{NN}	7.1	3.46
c_{CO}	7	2
c_{NO}	5	1.53
δ_a(%)	2.33	6.33
δ_m(%)	9.03	19.15

Linear regression of our MP2/C polarizabilities for all 55 planar molecules from this work and 49 planar azaborinines,[9] azoles,[51] oxazoles,[56] and azines[63] leads to the parameters shown in Table 4. The b_i values are very close to those obtained previously[9,63] for smaller subsets of these molecules. The b_i are smaller than the corresponding free atom polarizabilities,[65] indicating that bonding has lowered the polarizability. The average absolute error δ_a of model 5 is 3% and 6% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively, but the maximum errors δ_m are 14% and 40%.

The additive connections model[51] 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 120 molecules there are 12 distinct n_{ij}, only one (n_{BO}) more than for our previous set of 50 molecules.[9] There are four stoichiometric constraints, and hence the model has nine linearly independent terms which we choose as follows:

$$\alpha \approx c_{BB}\, n_{BB} + c_{BC}\, n_{BC} + c_{CC}\, n_{CC} + c_{BN}\, n_{BN} + c_{CN}\, n_{CN} + c_{BO}\, n_{BO} + c_{NN}\, n_{NN} + c_{CO}\, n_{CO} + c_{NO}\, n_{NO} \qquad (6)$$

The parameters obtained for model 6 by linear regression of our MP2/C polarizabilities for 104 planar molecules are listed in Table 5. The c_{ij} values are close to those obtained previously[9,63] for smaller subsets of these molecules. The average absolute error δ_a of model 6 is 2.3% and 6.3% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively. The small improvement in accuracy of model 6 over model 5 does not seem worth nearly doubling the number of parameters from five to nine.

The connections model can be refined[51] by distinguishing nitrogens bonded to H from those not bonded to H. This refinement requires six more parameters and improves the δ_a to 1.6% and 4% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively. An analogous refinement is impossible for model 5 because of linear dependencies. The errors of the various models increase noticeably if the nonplanar molecules, 1,2,3,4,5,6-triazatriborinine (**15**), 8 azaboroles, and 7 oxazaboroles, are included in the data set.

For models 5 and 6, δ_a increases by 0.2% and 0.1% for $\bar{\alpha}$, and by 0.8% and 1.1% for $\Delta_1\alpha$, respectively.

Less precise models can be constructed using only HOMO and LUMO energies, and molecular areas or volumes. A simple model for $\bar{\alpha}$ based on the ring area A

$$\alpha = \text{constant} + b_A A \tag{7}$$

leads to $\delta_a \approx 8\%$ for the 104 planar molecules. The relationship between polarizability and hardness has been studied often.[66,67] However, replacing the area term in model 7 by either $b_\eta \eta$ or $b_{\eta^{-1}}/\eta$ in which $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$ is a hardness measure leads to a much larger $\delta_a \approx 15\%$ for the 104 planar molecules. Table S16 lists our SCF/C values of η^{-1}.

7.5. Polarizability Fits. Models 5 and 6 can yield better fits to the polarizabilities if they are modified by adding terms proportional to A, $A^{3/2}$, or η^{-1}. Unfortunately, strong correlations between the added terms and the original ones lead to drastic changes in the parameters common to the original and extended models. Some of the b_i parameters in the extended model 5 become negative destroying their interpretation as effective atomic polarizabilities. Thus, these extensions should be considered fits rather than models. The most efficient fit (called 5b) is provided by adding $b_A{}^A + b_\eta/\eta$ to model 5. With just the seven parameters listed in Table 4, one finds $\delta_a = 1.6\%$ and 4.7% for $\bar{\alpha}$ and $\Delta_1\alpha$, respectively. Similar extensions of model 6 are possible.[9,55]

Less accurate but more compact fits to the mean polarizability can be obtained by eliminating small terms from model 5. Eliminating the n_H term and refitting, one obtains a fit with $\delta_a = 3.1\%$. Eliminating both the n_H and n_O terms and refitting, one gets a fit with $\delta_a = 3.7\%$.

8. Concluding Remarks

Our MP2 calculations of the equilibrium geometries, harmonic vibrational frequencies, relative stabilities, dipole moments, and polarizabilities have helped paint a broad-brush picture of 70 azaboracycles. The most stable isomers have the substructure XBHNH, where X = N, NH, or O is the base-ring heteroatom. Planar conformations are stable minima for all but 15 five-membered rings. Replacement of CH by N, and of NH by O, reduces the polarizability. Inclusion of B causes scatter of the polarizabilities of isomers, which lowers the accuracy of simple additive models of polarizability.

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Supporting Information Available: Tables S1−S16 contain additional MP2/6-31G(d) geometric parameters, harmonic vibrational frequencies, infrared intensities, dipole moment angles, polarizability components and angles, and reciprocal hardnesses of **18**−**87**. The IUPAC names of the 70 molecules and relevant nomenclature rules are also recorded. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ulmschneider, D.; Goubeau, J. *Chem. Ber.* **1957**, *90*, 2733.

(2) Morris, J. H. Boron in ring systems. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, UK, 1982; Vol. 1, p 311. Housecroft, C. E. Compounds with three- or four-coordinate boron, emphasizing cyclic systems. In *Comprehensive Organometallic Chemistry* II; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, UK, 1995; Vol. 1, p 129.

(3) Weber, L.; Dobbert, E.; Stammler, H.-G.; Neumann, B.; Boese, R.; Bläser, D. *Chem. Ber./Recueil* **1997**, *130*, 705.

(4) Groziak, M. P.; Chen, L.; Yi, L.; Robinson, P. D. *J. Am. Chem. Soc.* **1997**, *119*, 7817.

(5) Klöfkorn, C.; Schmidt, M.; Spaniol, T.; Wagner, T.; Costisor, O.; Paetzold, P. *Chem. Ber.* **1995**, *128*, 1037.

(6) Wendler, F.; Bergler, H.; Prutej, K.; Jungwirth, H.; Zisser, G.; Kuchler, K.; Högenauer, G. *J. Biol. Chem.* **1997**, *272*, 27091.

(7) Baldock, C.; Rafferty, J. B.; Sedelnikova, S. E.; Baker, P. J.; Stuitje, A. R.; Slabas, A. R.; Hawkes, T. R.; Rice, D. W. *Nature* **1996**, *274*, 2107.

(8) Powell, W. H. *Pure Appl. Chem.* **1983**, *55*, 409.

(9) Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem. A* **1998**, *102*, 4679.

(10) Namtvedt, J.; Gronowitz, S. *Acta Chem. Scand.* **1968**, *22*, 1373.

(11) Merriam, J. S.; Niedenzu, K. *J. Organomet. Chem.* **1973**, *51*, C1.

(12) Paetzold, P. I. *Z. Anorg. Allg. Chem.* **1963**, *326*, 64.

(13) Greenwood, N. N.; Morris, J. H. *J. Chem. Soc.* **1965**, 6205.

(14) Nöth, H.; Regnet, W. *Z. Naturforsch., B: Chem. Sci.* **1963**, *18*, 1138.

(15) Letsinger, R. L.; Hamilton, S. B. *J. Org. Chem.* **1960**, *25*, 592.

(16) Yale, H. L.; Bergeim, F. H.; Sowinski, F. A.; Bernstein, J.; Fried, J. *J. Am. Chem. Soc.* **1962**, *84*, 68.

(17) Kroner, J.; Nölle, D.; Nöth, H.; Winterstein, W. *Chem. Ber.* **1975**, *108*, 3807.

(18) Dorokhov, V. A.; Boldyreva, O. G.; Bochkareva, M. N.; Mikhailov, B. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1979**, *28*, 163.

(19) Aurivillius, B.; Löfving, I. *Acta Chem. Scand.* **1974**, *B28*, 989.

(20) Sawitzki, G.; Einholz, W.; Haubold, W. *Z. Naturforsch., B: Chem. Sci.* **1988**, *18*, 1179.

(21) Schmid, G.; Polk, M.; Boese, R. *Inorg. Chem.* **1990**, *29*, 4421.

(22) Brett, W. A.; Rademacher, P.; Boese, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 689.

(23) Raper, E. S. *Acta Crystallogr., Sect. B: Struct. Sci.* **1978**, *34*, 3281.

(24) Möhrle, H.; Bluhme-Hensen, K.; Middlehauve, B.; Mootz, D.; Wunderlich, H. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 1219.

(25) Chang, C. H.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 1677.

(26) Downs, A. J.; Morris, J. H. *Spectrochim. Acta* **1966**, *22*, 957.

(27) Morris, J. H.; Perkins, P. G. *J. Chem. Soc. A* **1966**, 580.

(28) Leach, J. B.; Morris, J. H. *J. Chem. Soc. A* **1967**, 1590.

(29) Leach, J. B.; Morris, J. H.; Perkins, P. G. *J. Chem. Soc. A* **1970**, 1077.

(30) Dewar, M. J. S.; Dougherty, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 433.

(31) Yale, H. L. *J. Heterocycl. Chem.* **1971**, *8*, 205.

(32) Meller, A.; Maringgele, W.; Maresch, G. *Monatsh. Chem.* **1974**, *105*, 637.

(33) Maringgele, W.; Meller, A. *Z. Anorg. Allg. Chem.* **1977**, *433*, 94.

(34) Niedenzu, K.; Merriam, J. S. *Z. Anorg. Allg. Chem.* **1974**, *406*, 251.

(35) Niedenzu, K.; Fritz, P.; Jenne, H. *Angew. Chem.* **1964**, *76*, 535.

(36) Goel, A. B.; Gupta, V. D. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2997.

(37) Gronowitz, S.; Maltesson, A. *Acta Chem. Scand.* **1971**, *25*, 2435.

(38) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

(39) Maouche, B.; Gayoso, J. *Int. J. Quantum Chem.* **1983**, *23*, 891.

(40) Maouche, B.; Gayoso, J.; Ouamerali, O. *Rev. Roum. Chim.* **1984**, *29*, 613.

(41) Morris, J. H.; Perkins, P. G. *J. Chem. Soc. A* **1966**, 576.

(42) Armstrong, D. R.; Perkins, P. G.; Scott, J. M.; Stewart, J. J. P. *Theor. Chim. Acta* **1972**, *26*, 237.

(43) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2474.

(44) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(45) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(46) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(47) Dykstra, C. E. *Ab Initio Calculation of the Structures and Properties of Molecules*; Elsevier: Amsterdam, 1988.

(48) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(49) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*, Revision J.; Gaussian, Inc.: Pittsburgh, PA, 1990.

(50) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34.

(51) El-Bakali Kassimi, N.; Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem.* **1995**, *99*, 12790.

(52) Dalgarno, A. *Adv. Phys.* **1962**, *11*, 281.

(53) Thakkar, A. J.; Doerksen, R. J. *UCHF*, unpublished.

(54) El-Bakali Kassimi, N.; Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem.* **1996**, *100*, 8752.

(55) Doerksen, R. J. Ph.D. Thesis, University of New Brunswick, 1998.

(56) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(57) Harshbarger, W.; Lee, G.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8*, 1683.

(58) Boese, R.; Maulitz, A. H.; Stellberg, P. *Chem. Ber.* **1994**, *127*, 1887.

(59) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(60) McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1989; Vol. 3. Also, cf. Vols. 1 and 2.

(61) Doerksen, R. J.; Thakkar, A. J. *Int. J. Quantum Chem.* **1996**, *60*, 421. In Table 2, some of the entries for 1,2-diazine are incorrect. The correct values are: $\alpha_2 = 67.78$, $\bar{\alpha} = 58.99$, $\Delta_1\alpha = 31.77$, $\Delta_2\alpha = 31.92$, and $\Delta_3\alpha = 3.12$.

(62) Archibong, E. F.; Thakkar, A. J. *Mol. Phys.* **1994**, *81*, 557.

(63) Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.

(64) Stout, J. M.; Dykstra, C. E. *J. Phys. Chem. A.* **1998**, *102*, 1576.

(65) Das, A. K.; Thakkar, A. J. *J. Phys. B* **1998**, *31*, 2215.

(66) Roy, R. K.; Chandra, A. K.; Pal, S. *THEOCHEM* **1995**, *331*, 261.

(67) Simonmanso, Y.; Fuentealba, P. *J. Phys. Chem. A* **1998**, *102*, 2029.