Ab Initio Study of the Relative Energies and Properties of Fluoroborazines

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In the effort to compute molecular properties more accurately and at a lower cost in terms of computational time, density functional theory has emerged as an alternative to more expensive methods to include correlation corrections. In this paper the optimized geometries, harmonic frequencies, and electronic energies of ab initio calculations performed on borazine and the fluorinated derivatives of borazine at the B3LYP/6-31G** and MP2(FC)/6-31G** levels of theory are presented. We compare the results of the density functional method with second-order perturbation theory and, where possible, compare experimental observations with computed properties. A qualitative assessment of the aromaticity of borazine as a function of fluoro substitution is proposed. The calculations indicate, at both levels of theory, evidence for in-plane π bonding between fluorine and boron and fluorine and nitrogen in the fluorinated deriatives of borazine.

Introduction

Hartree−Fock theory is well established in its ability to predict energetic, structural, vibrational, and electronic properties of many different molecules.[1] However, one major disadvantage to using Hartree−Fock theory is its neglect of instantaneous electron correlation.[2] Moller−Plesset perturbation theory includes the effects of electron correlation, and has been used extensively. Density functional theory (DFT) methods, such as B3LYP,[3] Becke's three parameter hybrid method using Lee, Yang, and Parr's correlation correction, also include electron correlation but do not lead to as severe a scaling problem as the MPn methods.

In this paper we are interested in calculating the electronic energies, molecular geometries, and vibrational frequencies of fluorinated borazines. The assignment of the molecular symmetry of borazine, $B_3N_3H_6$, has been difficult. Gas-phase IR and Raman spectra of borazine have been interpreted using the D_{3h} point group.[4] In an electron diffraction experiment, a decision between a D_{3h} structure, with large amplitude vibrations perpendicular to the ring plane, and a nonplanar C_2 model was not possible.[5] It has been concluded that borazine has crystallographic C_2 symmetry from a single-crystal X-ray diffraction experiment.[6] Our ab initio calculations of the equilibrium geometry indicate the molecular symmetry is D_{3h}; this same conclusion has been reached by others (MP2/6-31G* level of theory).[7] Free borazine most likely possess D_{3h} symmetry with an extremely flat potential energy surface with respect to out-of-plane nuclear motion.

Borazine is isoelectronic with benzene and has six π electrons which are formally on the nitrogen atoms. These π electrons from nitrogen can be donated to the empty p orbitals of boron, thereby forming a N−B π bonding interaction. Consequently, borazine is believed to possess aromatic stabilization.[8] The degree of this stabilization will depend on the ability of nitrogen to donate its π electrons to boron, and since the nitrogens are more electronegative than boron, it may be expected that the amount of electron transfer to boron will be small. A Mulliken analysis of borazine (HF/double-ζ basis) suggests that the boron atoms of borazine are significantly positive as a consequence of the overall B → N charge transfer of 0.46e.[9] However, the Mulliken analysis also indicates that there is an overall N → B π-charge transfer of 0.40e, and this N → B π-charge transfer is an important factor in the aromaticity of borazine. It has been suggested that replacing a hydrogen atom of boron with a more electronegative substituent will draw more electron density from nitrogen onto boron, thereby increasing the aromatic stabilization of the molecule.[10]

We believe that electron correlation will be an important factor in predicting accurate properties of borazine and its fluorinated derivatives. Because of this, and the fact that MP2 calculations using a moderate basis set (6-31G**) on a molecule such as $F_3B_3N_3H_3$ are costly in terms of computational time, we turned to DFT as an alternative to MP2. However, in the interest of comparing the two methods we have included MP2 calculations. Where possible, we compare the calculated properties (bond lengths, angles, and vibrational frequencies) of borazine and its fluorinated isomers with experiment.

Computational Procedure

B3LYP and MP2 geometry optimizations were done using the Gaussian 94 suite of programs[11] on either a Cray JP916 or Y-MP computer. Structures were constructed and visualized[12] using Unichem 3.0. All geometry optimizations (B3LYP/6-31G** and MP2/6-31G**) were followed by frequency calculations, using the same correlation level and basis set, to characterize the stationary point as a true minimum and to obtain the zero point energy (ZPE). The B3LYP/6-311+G(2df,p) energy calculations were performed at the B3LYP/6-31G** optimized geometries. The ZPEs and the frequencies were scaled[13] by 0.9434 (MP2 level) or 0.9613 (B3LYP level).

Results and Discussion

Table 1 presents the MP2 and B3LYP bond distances and angles of borazine, and lists experimental values where available. The parameters involving only boron and nitrogen atoms agree well with those obtained from both X-ray and electron diffraction experiments. However, the calculated distances for both the B−H and N−H bonds are significantly shorter than those reported from the electron diffraction study. Experimental values yield statistically averaged bond lengths and angles due to molecular vibrations, and consequently may differ significantly from the equilibrium values.[14] This is especially true when the mass of one of the atoms is small relative to the other, as in the B−H and N−H bonds. It is also important to consider

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TABLE 1: Selected ab Initio and Experimental Bond Lengths (Å) and Angles (deg) of Borazine (Experimental Parameters Are for a C_2 Structure)

parameter	MP2/ 6-31G**	B3LYP/ 6-31G**	electron diffraction[5]	X-ray crystal structure[6]
B−H	1.190	1.195	1.258 ± 0.014	
N−H	1.007	1.010	1.050 ± 0.012	
B−N	1.431	1.431	1.4355 ± 0.0021	1.429
N−B−N	117.1	117.1	117.7 ± 1.2	117.1
B−N−B	122.9	122.9	121.1 ± 1.2	122.9
H−B−N	121.5	121.4		
H−N−B	118.5	118.6		

intermolecular forces when interpreting computed parameters. However, in the case of borazine, intermolecular forces are taken to be minor even in the solid phase.[6]

The equilibrium structure of borazine is determined to be D_{3h} at both the MP2 and B3LYP levels. The calculated B−N bond distance, N−B−N angle, and B−N−B angle are the same for the two methods. The methods agree to within 0.1° with respect to the H−B−N and H−N−B angles. There is a 0.005 Å difference in the B−H bond length for the two methods, and a 0.003 Å difference in the N−H bond length. In our opinion, this is an acceptable level of variance. Because the density functional method uses considerably less computer time to optimize a structure, it is the preferred method in this case.

As was stated previously, the MP2 and B3LYP B−H bond lengths are shorter than the electron diffraction bond length by 0.068 and 0.063 Å, respectively. The MP2 and B3LYP N−H bond lengths are also shorter than the experimental bond lengths with differences of 0.043 and 0.40 Å, respectively. This may be attributed to vibrational averaging in the experiment. The MP2 and B3LYP B−N bond lengths are in excellent agreement with one another and fall within the range of the B−N bond length offered by the two experiments. The two ring angle parameters agree remarkably well with the ring angles of the X-ray structure. These parameters are in reasonable agreement with the electron diffraction structure.

Figures 1 and 2 show the numbering schemes and the B3LYP and MP2 geometrical parameters for the B-fluorinated and N-fluorinated derivatives of borazine, respectively. Experimental parameters for B-trifluoroborazine from an electron diffraction study[15] are also presented in Figure 1. The calculational results for B-trifluoroborazine are in good agreement with the experimental results. All calculated bond lengths are shorter than experimental bond lengths. The experimental uncertainty in the ring bond angles is one degree. The calculated ring bond angles are well within this range. As was the case for borazine, the MP2 and B3LYP methods give results which agree remarkably well with one another.

Several trends are apparent upon examining Figure 1. First, upon going from B-monofluoroborazine to B-trifluoroborazine the B−F bond becomes progressively shorter. Also, the B−N bond length becomes shorter on going from borazine (1.431 Å) to B-trifluoroborazine (1.428 Å). Another important phenomenon is the change in ring bond angles on going from borazine to B-trifluoroborazine. In borazine, the N−B−N angle is 117.1° and the B−N−B angle is 122.9°. In B-trifluoroborazine the N−B−N angle is 118.5° and the B−N−B angle is 121.4°. The bond angles in B-trifluoroborazine more closely approach the idealized sp^2 bond angle of 120°. The fact that the B−N bond distance tends to decrease and the ring angle approaches 120° as borazine is fluorinated at boron is suggestive of an increase of the aromatic character of the molecule.

The change in ring angle can also be explained by Bent's rule,[16] which states that the more electronegative atom prefers hybrid orbitals with more s character. In borazine, the more electronegative nitrogens prefer hybrid orbitals with more s character while the less electronegative borons will have hybrid orbitals with less s character, hence, the alternating bond angles in borazine. In B-trifluoroborazine, the B−H bond has been replaced by a B−F bond, and the fluorine acts as a σ-electron withdrawing substituent. The effect of fluoro substitution is that the boron in B-trifluoroborazine appears to be more electronegative relative to the nitrogens, altering the hybridization about boron. The result is to place more s character on the borons thereby increasing the N−B−N angle and decreasing the B−N−B angle. The molecule approaches the idealized sp^2 angle of 120°.

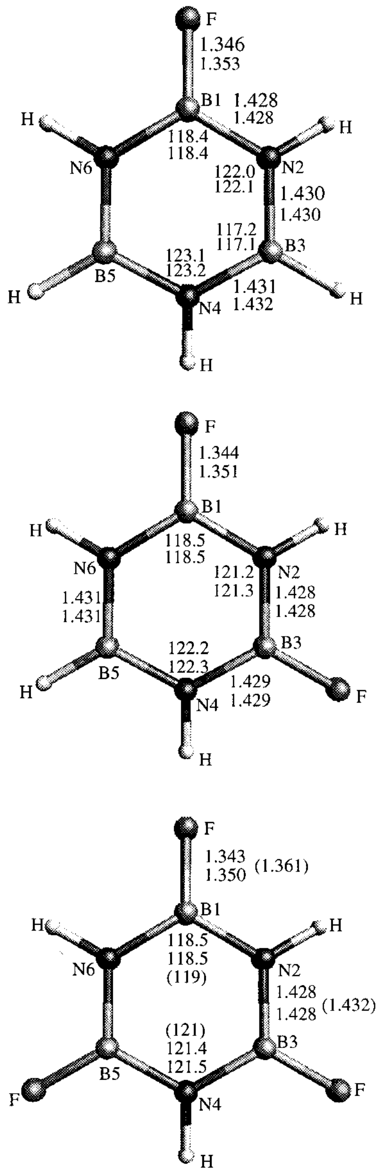

Figure 1. Selected bond lengths (angstroms) and angles (degrees) of the B-fluorinated borazine derivatives. B3LYP values are in the upper position, while MP2 values are in the lower position. (B3LYP, MP2) B1...N4 distances are 2.842, 2.842 Å; 2.850, 2.850 Å; and 2.858, 2.857 Å for B− mono, di, and trifluoroborazine, respectively. Experimental values[15] of B-trifluoroborazine are indicated in parentheses.

Although N-trifluoroborazine is known,[17] there is no experimental data available regarding its structure. Figure 2 shows the calculated equilibrium geometries of the N-fluorinated borazines. The calculations show that the N−F and B−N bond distances tend to decrease with increasing N-fluorine substitution. The B−N−B and N−B−N ring angles of N-trifluoroborazine deviate greatly from the idealized sp^2 hybridization,

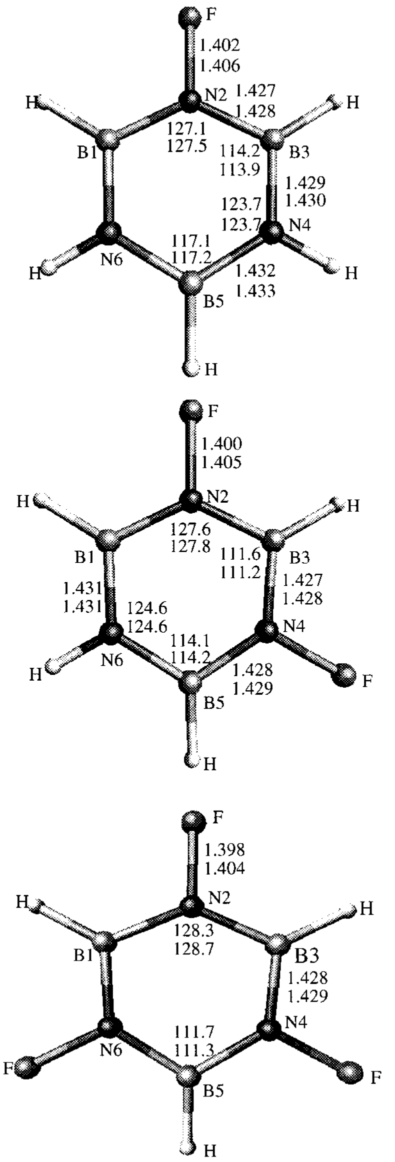

Figure 2. Selected bond lengths (angstroms) and angles (degrees) of the N-fluorinated borazine derivatives. B3LYP values are in the upper position, MP2 values are in the lower position. (B3LYP, MP2) N2...B5 distances are 2.811, 2.807 Å; 2.832, 2.831 Å; and 2.848, 2.849 Å for N-mono, di, and trifluoroborazine, respectively.

giving B3LYP values of 128.3 and 111.7°, respectively. According to Bent's rule the nitrogen atoms have been rehybridized to include more s character and the borons have been rehybridized to include more p character. This is opposite of the rehybridization of the orbitals in B-trifluoroborazine. Because the ring angles are diverging from 120°, it is reasonable to expect a decrease in the overlap of the pπ orbitals of the molecule. Less effective pπ overlap should lead to a decrease in the aromatic character of the molecule.

Table 2 lists the relative energies of selected fluorinated borazines at the B3LYP/6-31G**, B3LYP/6-311G+(2df,p), and MP2/6-31G** levels of theory. The B-fluorinated isomers are always more stable than the corresponding N-fluorinated isomers in a given set. The energy difference for B-monofluoroborazine vs N-monofluoroborazine is 110.2 kcal/mol at the B3LYP/6-311G+(2df,p) level. Furthermore, the energy difference seems to be nearly additive. For example, N-trifluoroborazine is 295.1 kcal/mol higher in energy than B-trifluoroborazine. The result is that each N−F bond of N-trifluoroborazine destabilizes the molecule by approximately 98 kcal/mol relative to the corresponding B-fluoroborazine.

We believe the added stability of the B-fluorinated systems is due to at least 3 different effects: (1) There is lone-pair/lone-pair electron repulsion in the N−F bond. This effect is absent in the B−F bond. (2) The degree of polarization of the B−F bond is greater than the N−F bond. For example, in B-trifluoroborazine (MP2/6-31G** level) the charges on B and F are +0.596e and −0.276e respectively, where e equals 1.602192×10^{-19}C. In N-trifluoroborazine (MP2/6-31G** level), the charges on N and F are −0.081e and −0.237e, respectively. Effects one and two are due to the difference in B−F and N−F bond energies. (3) The third effect concerns the aromaticity of borazine. We predict that the B-fluorinated isomers will be more aromatic than the N-fluorinated isomers. Our basis for this prediction lies in π electron delocalization. In borazine the B−N bond is polar due to the differences in electronegativity of boron and nitrogen. At the MP2/6-31G** level the partial charges on boron and nitrogen are 0.364e and −0.547e, respectively. This leads to a dipole along the B−N bond of 6.26 Debyes, while the overall dipole moment of the molecule is zero. In the B-fluorinated isomers, the fluorine acts to polarize the B−N bond to favor π electron donation from nitrogen to boron. For example, in B-trifluoroborazine, the partial charges on boron and nitrogen are 0.596e and −0.609e, leading to a dipole of 8.26 Debyes along the B−N bond. In the N-fluoro isomers, the dipole along the B−N bond is 2.91 Debyes and the partial charges on B and N are 0.343e and −0.081e.

Vibrational Analysis. One of the goals of this paper is to examine the effect that substitution has on the aromaticity of borazine. Aromaticity is not a property which is easily quantifiable, but should be linked to the bond order of the B−N bond. It has been postulated that ring vibrations of aromatic molecules may be directly related to the aromaticity of a molecule.[10] In the case of borazine, the result of fluoro substitution at boron should be to increase the bond order between B and N. This can be understood in terms of a reorganization of electron density in the molecule as borazine is fluorinated. Fluorine acts as a strong σ electron withdrawing substituent and a weak π donor. As σ electrons are drawn away from boron, nitrogen reacts by donating lone pair electron density to boron. The result is to increase the bond order of the B−N bond. Consequently the force constant of the bond will be increased, increasing the vibrational frequency of the B−N bond. The overall effect is to delocalize the lone pair nitrogen electrons into the π system of the molecule.

Table 3 presents the B3LYP/6-31G** and MP2/6-31G** calculated vibrational frequencies of the highest frequency in-plane B−N asymmetric stretching mode of fluorinated borazines. This mode corresponds to an E′ species in borazine; the experimentally observed vibrational frequency[4] is 1465 cm^{-1} . The calculated, scaled values for this mode of borazine are 1433 cm^{-1} (B3LYP) and 1438 cm^{-1} (MP2). The frequency of this vibrational mode decreases from a maximum in B-trifluoroborazine to a minimum in N-trifluoroborazine. The conclusion that may be drawn from this trend is that fluoro substitution of borazine at boron increases the aromatic stabilization of the molecule, while fluoro substitution at nitrogen decreases the aromaticity of borazine. Consequently, the theoretical results indicate a decrease in the aromaticity in the order B-trifluoroborazine > B-difluoroborazine > B-monofluoroborazine > 1,2-difluoroborazine ≈ 1,4-difluoroborazine ≈ borazine > N-monofluoroborazine > N-difluoroborazine > N-trifluoroborazine. We have included the mixed difluoro isomers, 1,2-difluoroborazine and 1,4 difluoroborazine, for comparison. A similar comparison for the other ring stretching modes was not

TABLE 2: Relative Energies of the Various Isomers of the Fluorinated Borazines (*E* = electronic energy, ZPE = zero-point energy)

empirical formula	isomer	E+ZPE B3LYP[a] (hartrees)	relative energy[a] (kcal/mol)	E+ZPE B3LYP[b] (hartrees)	relative energy[b] (kcal/mol)	E+ZPE MP2[b] (hartrees)	relative energy[b] (kcal/mol)
$B_3N_3H_6$	borazine	−242.672698	NA	−242.594600	NA	−241.817777	NA
$B_3N_3H_5F$	B-monofluoro	−342.049191	0	−341.907357	0	−340.914997	0
	N-monofluoro	−341.873633	110.2	−341.755175	95.5	−340.751163	102.8
$B_3N_3H_4F_2$	B-difluoro	−441.383217	0	−441.219938	0	−440.012175	0
	1,4-difluoro	−441.228013	97.4	−441.067110	95.9	−439.847618	103.3
	1,2-difluoro	−441.224169	99.8	−441.063696	98.0	−439.844246	105.4
	N-difluoro	−441.071993	195.3	−440.913392	192.4	−439.682111	207.1
$B_3N_3H_3F_3$	B-trifluoro	−540.738021	0	−540.532254	0	−539.109188	0
	N-trifluoro	−540.267767	295.1	−540.069142	290.6	−538.610525	312.9

[a] 6-311+G(2df,p) basis. [b] 6-31G(d,p) basis.

TABLE 3: Highest Frequency In-Plane, Asymmetric B−N Ring Stretching Vibrations (cm^{-1}) Calculated at the B3LYP and MP2 Levels Using the 6-31G(d,p) Basis

borazine molecule	B3LYP	MP2
B-trifluoro	1489	1486
B-difluoro	1462, 1486	1462, 1483
B-monofluoro	1436, 1474	1442, 1472
1,2-difluoro	1423, 1477	1428, 1475
1,4-difluoro	1423, 1474	1429, 1471
borazine	1433	1438
N-monofluoro	1420	1426
N-difluoro	1403, 1408	1414, 1417
N-trifluoro	1393	1406

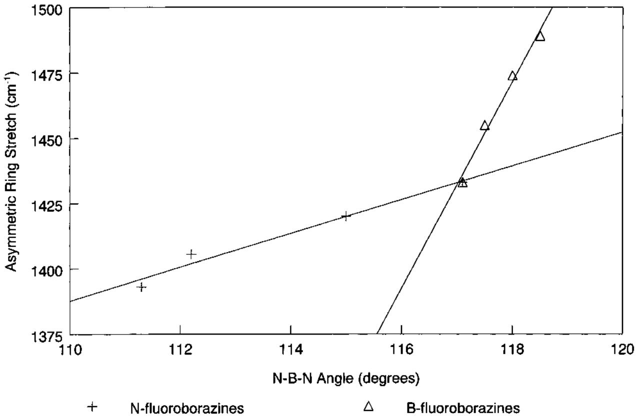

Figure 3. Plot of the highest asymmetric ring stretching frequency vs average N−B−N angle (MP2/6-31G**) in fluorinated borazines.

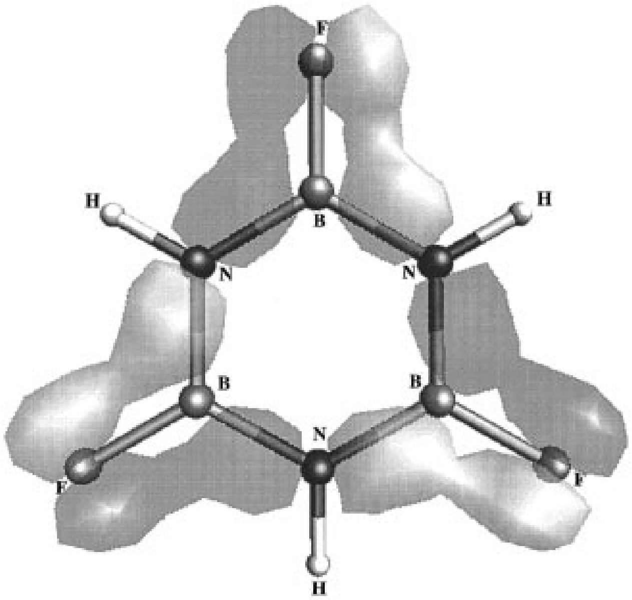

Figure 4. $1a_2'$ orbital of B-trifluoroborazine.

feasible due to mixing between the ring stretching and B−F or N−F stretches.

In Figure 3 we have plotted the asymmetric ring vibration as a function of N−B−N angle for each of the N-fluoro and B-fluoro derivatives of borazine at the MP2 level of theory. Borazine itself has been included as a data point on each line, and it occurs at the intersection of the two lines. The symmetry of B-trifluoroborazine, N-trifluoroborazine, and borazine is D_{3h} so there is only one value of the doubly degenerate ring vibration and one value of the N−B−N angle. The symmetry of a monofluoro or difluoro derivative is C_{2v}, consequently the degeneracy of the ring vibration is broken (except in the case of N-monofluoroborazine) and there is more than one value of the N−B−N angle. We have accounted for this by averaging the values of the nondegenerate ring vibrations and, in cases where there is more than one N−B−N angle, we have averaged those as well.

The graph shows a linear relationship between the highest frequency in-plane ring vibration and N−B−N angle. For the line corresponding to the N-fluoro isomers, the slope is 6.467 cm^{-1}/degree and the intercept is 676.3 cm^{-1}. The correlation coefficient for this line is 0.975. The slope of the line corresponding to the B-fluoro isomers is 39.53 cm^{-1}/degree and the intercept is −3192.4 cm^{-1}. The correlation coefficient of this line is 0.983.

Both parameters graphed in Figure 3 can be indirect measures of aromaticity. The fact that there is a good linear correlation between these parameters shows how fluorine as a substituent can affect the aromaticiy of borazine by methods discussed above. The graph also supports the above prediction of the ordering of the isomers with respect to aromatic character.

Molecular Orbitals. In this section we present selected molecular orbitals of B-trifluoroborazine and N-trifluoroborazine calculated at the MP2/6-31G** level. The results indicate a possibility of an unusual in-plane π type interaction between boron and fluorine in B-trifluoroborazine, and between nitrogen and fluorine in N-trifluoroborazine. In fact, this in-plane π interaction can be seen in any fluorinated borazine.

Figure 4 depicts the $1a_2'$ orbital of B-trifluoroborazine. The orbital has a calculated energy of −19.58 eV and lies 7.90 eV below the HOMO and is characterized by a π type interaction between the fluorine lone pair p electrons which lie in the plane of the ring and the N−B−N σ bonding framework of the ring. Lloyd and Lynaugh[18] have determined from photoelectron spectroscopy that the energy of this orbital is −17.73 eV.

Figure 5 depicts the $1a_2'$ orbital of N-trifluoroborazine. The orbital has a calculated energy of −20.68 eV and lies 8.64 eV below the HOMO. This orbital is characterized by a π type interaction between the fluorine lone pair p electrons which lie in the plane of the ring and the B−N−B σ bonding framework of the ring.

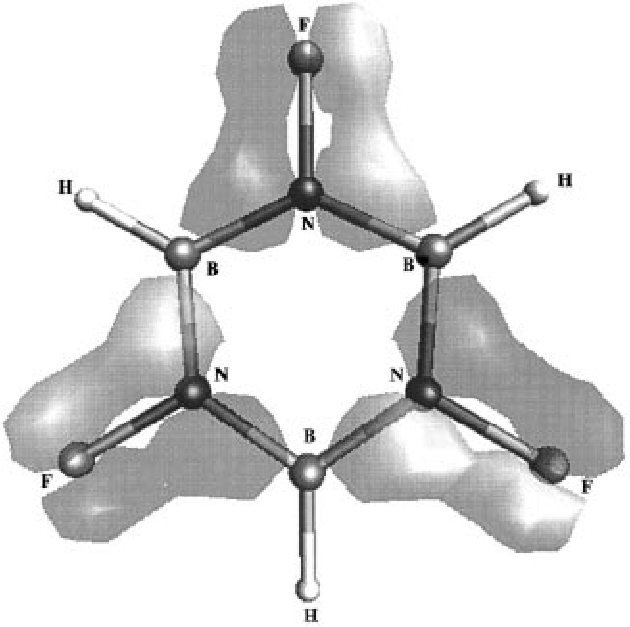

Figure 5. $1a_2'$ orbital of N-trifluoroborazine.

Conclusion

The results of the ab initio calculations on the fluorinated borazines show that B3LYP calculated geometrical parameters are very similar to MP2 parameters using the same basis set. Both methods give results which compare favorably with experiment. We find that the N−B−N and B−N−B bond angles in B-trifluoroborazine deviate only slightly from the idealized sp^2 bond angle of 120°. N-trifluoroborazine has ring angles which deviate significantly from the 120° bond angle. Bent's rule has been used to explain these parameters.

B-fluorinated borazines are always lower in energy than their corresponding N-fluorinated isomers. The reasons for this increased stabilization are: the B−F bond energy is about 2.2 times greater than the N−F bond energy and the B-fluorinated borazines have increased aromatic stabilization relative to the N-fluorinated borazines.

We have applied the concept of ring vibrations being directly related to the aromaticity of the fluorinated borazines. The B-fluorinated borazines have a higher in-plane asymmetric ring stretch than the N-fluorinated borazines. This indicates a larger force constant for the B−N bond of B-fluoroborazines than the B−N bond of N-fluoroborazines, supporting the increased aromatic stabilization of B-fluoroborazines over the N-fluorinated borazines. For the series considered, the aromaticity decreases in the order B-trifluoroborazine > B-difluoroborazine > B-monofluoro-borazine ≈ 1,2-difluoroborazine ≈ 1,4-difluoroborazine > borazine > N-monofluoroborazine > N-difluoroborazine > N-trifluoroborazine.

The three-dimensional plots of the molecular orbitals of borazine indicate an unusual in-plane π interaction between boron and fluorine in the B-fluorinated borazines as well as an in-plane π interaction between nitrogen and fluorine in the N-fluorinated borazines.

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References and Notes

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

(2) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; Dover: New York, 1989.

(3) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(4) Niedenzu, K.; Sawodny, W.; Watanabe, H.; Dawson, J. W.; Totani, T.; Weber, W. *Inorg. Chem.* **1967**, *6*, 1453.

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

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

(7) Ramondo, F.; Portalone, G.; Bencivenni, L. *Journal of Molecular Structure (THEOCHEM)* **1991**, *236*, 29.

(8) Bowser, J. R. *Inorganic Chemistry*; Brooks/Cole Publishing Co.: Belmont, CA, 1993; p 410.

(9) Guest, M. F.; Hillier, I. H.; Shenton, I. C. *Tetrahedron* **1975**, *31*, 1943.

(10) Beyer, H.; Hynes, J. B.; Jenne, H.; Niedenzu, K. *Boron−Nitrogen Chemistry: Advances in Chemistry Series* 42; R. F. Gould, Ed.; American Chemical Society: Washington, D. C.; 1964; p 266.

(11) *Gaussian 94*, Revision D.4; M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc.: Pittsburgh PA, 1995.

(12) Oxford Molecular Group, Burnsville, MN, 55337.

(13) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(14) Davis, Michael I. *Electron Diffraction in Gases*; Marcel Dekker, Inc.: New York, 1971.

(15) Bauer, S. H.; Katada, K.; Kimura, K. *Structural Chemistry and Molecular Biology*: A. Rich and N. Davidson, Eds., W. H. Freeman and Co.: Calif., 1968; p 653.

(16) Bent, H. A.; *J. Chem. Educ*. **1960**, 37, 616.

(17) Margrave, J. L.; Lagow, R. J. Paper presented at Summer Symposium on Fluorine Chemistry, Marquette University: Milwaukee, WI, June 1970.

(18) Lloyd, D. R.; Lynaugh, N. *Philos. Trans. R. Soc. London* **1970**, *268A*, 97.