A Semiempirical Molecular Orbital Calculation of Borazine and Some B-Trifluoroborazines

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A charge self-consistent semiempirical calculation has been performed on borazine and four fluoroborazines in which all the valence electrons of the molecules studied have been included. The results of the Mulliken population analyses are discussed in terms of the effect of fluorine bonded to boron and/or nitrogen. The correspondence between experiment and calculation for the orbital energies is also discussed.

An Hand der Resultate ladungskonsistenter semi-empirischer Rechnungen für Borazin und vier Fluoroborazine unter Einbeziehung aller Valenzelektronen wird mittels Populationsanalyse die Frage diskutiert, wie sich die Bindung von Fluor an Bor und/oder Stickstoff auswirkt. Außerdem wird auf die Korrespondenz zwischen experimentellen Daten und Orbitalenergien eingegangen.

Un calcul semi-empirique avec autocohérence des charges a été effectué sur le borazole et quatre fluoroborazoles avec introduction de tous les électrons de valence. Discussion des résultats de l'analyse de population de Mulliken en termes d'effet du fluor lié au bore et (ou) à l'azote. Discussion de la correspondance entre expérience et théorie pour les énergies orbitales.

1. Introduction

Substituted borazines have aroused considerable interest experimentally for the past decade and theoretically in recent years. B-fluoro substitution has been known since the synthesis of B-trifluoroborazine by Niedenzu [1] in 1962, but only recently has N-fluoro substitution been reported [2].

Theoretical considerations have been limited by the size of the systems to approximative procedures. Lloyd and Lynaugh [3] have carried out all valence electron calculations of B-trifluoroborazine. We report here a semiempirical all valence electron study of the series: borazine, B-trifluoroborazine, N-trifluoroborazine, B-trifluoro-N-methylborazine and hexafluoroborazine [4].

2. Method of Calculation

The semiempirical Mulliken-Wolfsberg-Helmholz (MWH) technique is used to calculate the molecular orbitals. These calculations are similar to those of Carroll *et el.* [5]. All valence electrons are included. Solution of the secular equation $|H_{ij} - ES_{ij}| = 0$ results in eigenvalues of an effective one-electron Hamiltonian. The H_{ii} matrix elements are approximated as the negative of the

atomic valence state ionization potentials (VSIP's). The VSIP's are calculated as functions of atomic charge and orbital population [6], thereby taking into account the changes in the atomic environment within a molecule. The resonance integrals are calculated using the Cusachs approximation

$$H_{ij} = (2 - |S_{ij}|)(H_{ii} + H_{jj}) S_{ij}/2 .$$

This approximation is chosen because it contains no external veriable parameters [7]. Clementi double-zeta functions were used as an atomic orbital basis. Each calculation was processed to charge self-consistency, using a damped iterative procedure [5].

The following atomic orbital basis sets were used in the calculations reported here: H–1s; B, C, N, F–2s, $2p_x$, $2p_y$, $2p_z$. Borazine bond angles were taken as 120° with the following bond lengths: B–N, 1.44 Å; B–H, 1.20 Å; N–H, 1.02 Å; B–F, 1.32 Å; N–C, 1.48 Å; C–H, 1.102 Å.

3. Discussion of Results

The results we obtained with the above method are presented in the Table and Fig. 1. The respective charges on the various atoms are the algebraic sum of σ- and π-charges. We would now like to discuss the five compounds studied as to their charge distribution, ring populations and orbital energies.

The results of the Mulliken population analysis show the borazine ring to consist of a σ-electron drift from boron to nitrogen. Superimposed on this is a π-electron transfer from nitrogen to boron. In borazine, the amount of charge taken out of the ring by the hydrogen on boron is almost counterbalanced by the charge fed into the ring by the hydrogen on nitrogen. In B-trifluoroborazine, the negative charge at fluorine is due to the electronegativity difference between boron and fluorine minus some π-bonding from fluorine to boron. The more electronegative fluorine causes a σ-electron shift toward fluorine in the F–B–N–H bond system, resulting in a positive increase in the σ-charge for B, N and H as compared to borazine. The substitution of the electron releasing methyl group at nitrogen in B-trifluoro-N-methylborazine enhances the net negative charge at N_3; whereas, the charges on the other atoms, as compared to B-trifluoroborazine, are almost unaltered.

The shift in charge in N-trifluoroborazine is unusual in that nitrogen now has a net positive charge. This is due to the decrease in the σ-charge on nitrogen as compared to borazine and B-trifluoroborazine as a result of the highly electronegative fluorine on nitrogen. The total charges of B, N and H have increased as compared to the corresponding atoms in borazine. The π-ring population is only slightly larger than borazine due to a small fluorine to nitrogen π-bond contribution.

The fluorine charges on hexafluoroborazine are almost identical to the charges on the corresponding fluorines of B-trifluoroborazine and N-trifluoroborazine. This similarity is also seen in the B–N bond polarity if one compares the average sum of the difference in the total charge on boron and nitrogen in B-trifluoroborazine (0.41) and N-trifluoroborazine (0.15) with hexafluoroborazine (0.31).

Table. Mulliken population analysis of borazine and fluoroborazines

Analysis	$B_3H_3N_3H_3$		H(N)	H(B)	$B_3H_3N_3F_3$		F	H	$B_3F_3N_3F_3$		F(N)	F(B)
	N	B			N	B			N	B		
π-population	1.3838	0.6162			1.4668	0.5588	1.9625		1.4842	0.7444	1.9694	1.7781
π-charge	0.6162	−0.6162			0.5332	−0.5588	0.0375		0.5158	−0.7444	0.0306	0.2219
σ-population	3.7614	2.2723	0.9116	1.0548	3.4862	2.2495	5.2528	1.0238	3.4452	1.8750	5.2286	5.4755
σ-charge	−0.7614	0.7277	0.0884	−0.0548	−0.4862	0.7505	−0.2528	−0.0238	−0.4452	1.1250	−0.2286	−0.4755
Total ring population	24.1011				23.2839				22.6464			
π-ring population	6.0000				6.0768				6.6858			

| Analysis	$B_3F_3N_3H_3$		F	H	$B_3F_3N_3H_2CH_3$		B_1	B_2, B_3	F_1	F_2, F_3	CH_3
	N	B			N_1, N_2	N_3					
π-population	1.3968	0.8008	1.7903		1.3989	1.3600	0.8091	0.8141	1.8007	1.7989	1.0945
π-charge	0.6032	−0.8008	0.2097		0.6011	0.6400	−0.8091	−0.8141	0.1993	0.2011	−0.0945
σ-population	3.7143	1.8919	5.5014	0.8969	3.7176	3.7629	1.8911	1.8891	5.4975	5.4980	5.7518
σ-charge	−0.7143	1.1081	−0.5014	0.1031	−0.7176	−0.7629	1.1089	1.1109	−0.4975	−0.4980	0.2482
Total ring population	23.4114				23.4625						
π-ring population	6.5928				6.5951						
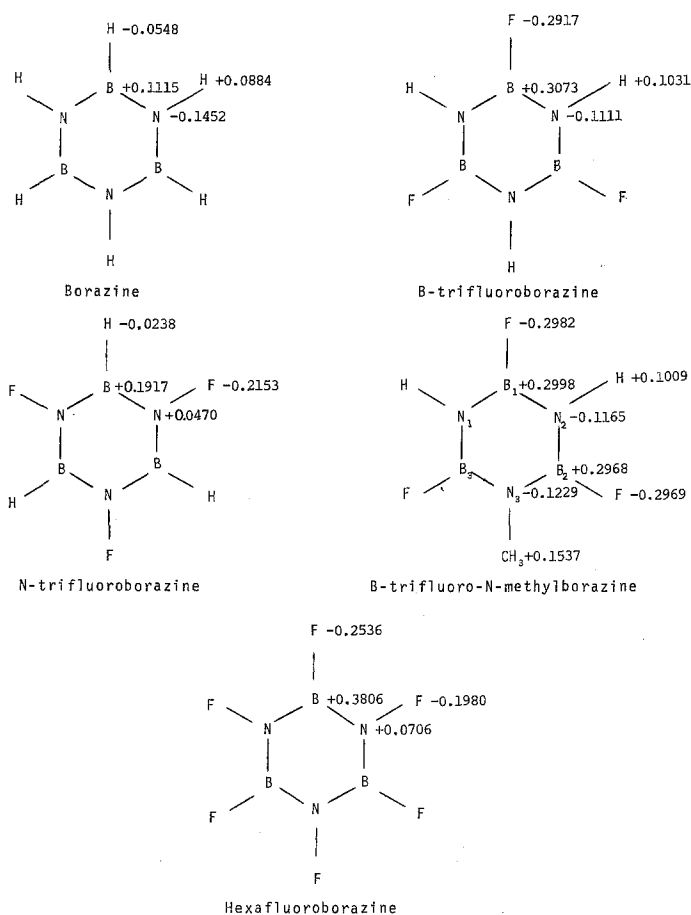
Fig. 1. Net charges from Mulliken population analysis of borazine and fluoroborazines

The π-ring population increases over borazine in hexafluoroborazine (0.69) as compared to B-trifluoro- (0.60) and N-trifluoroborazine (0.08) also indicates that the population analysis of hexafluoroborazine may be considered a composite of these fluoroborazines.

The π-ring population increases in the order: borazine < N-trifluoroborazine < B-trifluoroborazine $\simeq$ B-trifluoro-N-methylborazine < hexafluoroborazine. This is almost the inverse of the total ring population order where borazine > B-trifluoroborazine $\simeq$ B-trifluoro-N-methylborazine > N-trifluoroborazine > hexafluoroborazine. It may be concluded that substitution of fluorine at boron and/or nitrogen enhances the σ-shift towards fluorine, thus decreasing the total ring population. Clearly, fluorine on boron has good $p_\pi - p_\pi$ bonding due to the empty p-orbital on boron; whereas, a small π-bond contribution is made from fluorine to the filled p-orbital on nitrogen. π-bonding to nitrogen from fluorine can only be accomplished after $p_\pi - p_\pi$ bonding from nitrogen to boron is completed.
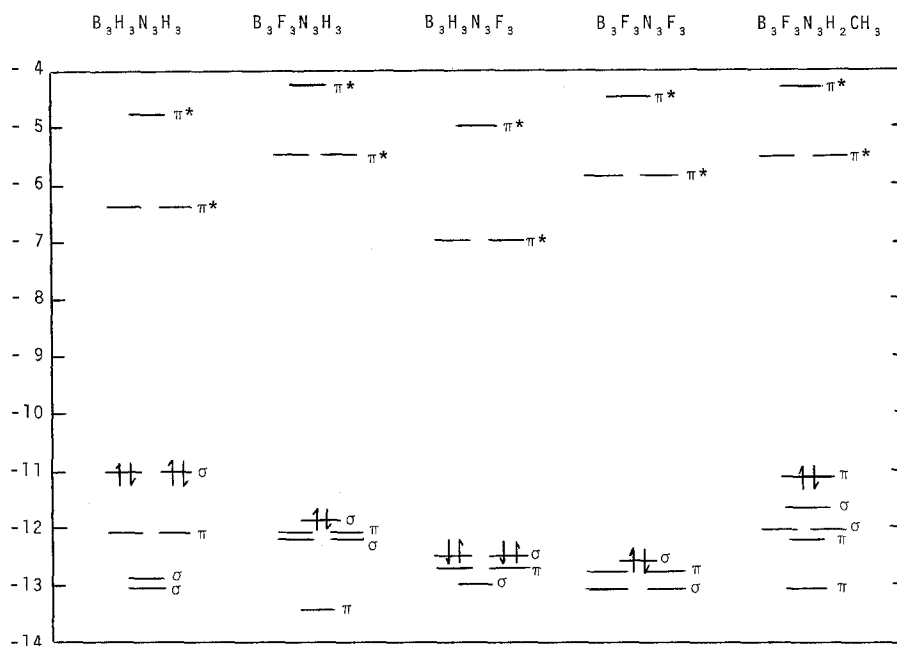
Fig. 2. Molecular orbital energy diagrams of borazine and fluoroborazines resulting from MWH calculations (eV)

The studies undertaken here indicate: (1) that it is not feasible to rely solely on π-populations and π-charges to account for the charge distribution in borazine and substituted borazines; (2) the migration of electron density with fluorine substitution decreases the total ring population and increases the π-ring population; (3) the aromaticity is increased by fluorine on boron to a larger degree than fluorine on nitrogen; (4) hexafluoroborazine may be considered a "50 − 50 equilibrium mixture" of B-trifluoroborazine and N-trifluoroborazine when examining the electron population analysis of the various atoms; (5) methyl substitution at nitrogen is rather ineffective at transmitting electronic effects.

Orbital energies of the high energy bonding orbitals and the low lying anti-bonding orbitals are diagrammed in Fig. 2. B-trifluoro substitution increases the energy separation of bonding and antibonding orbitals, giving a stabilization to the borazine system. This bonding stabilization is predicted to be characteristic of N-trifluoroborazine also, though this molecule has been reported only as a product of mass spectrometry [2].

Calculations of borazine and the three symmetrically-substituted fluoro-borazines result in a σ-type highest filled molecular orbital (HFMO). This was the result of previous calculations of borazine and B-trifluoroborazine [3, 8]. However, the HFMO's of borazine and B-trifluoroborazine are known to be π-MO's from photoelectron spectroscopy (ESCA) [3]. This incorrect ordering of orbital type is a well-known weakness of semiempirical calculations, as it is of minimal basis set complete SCF–MO calculations of some systems [9]. There

is correspondence for the types of bonding orbitals and the range of ionization potentials (negative of orbital energies) between photoelectron spectroscopy and semiempirical results. For example, ESCA [3], CNDO [8] and our MWH studies of borazine result in three doubly-degenerate σ-MO's, one doubly-degenerate π-MO, one non-degnerate π-MO and two non-degenerate σ-MO's. The correspondence between experiment and calculation is also found for B-trifluoroborazine, and may be expected for the other members of this series. Thus, direction of change of orbital energies and types of bonding orbitals involved may be predicted by MWH.

N-methyl substitution of B-trifluoroborazine results in a lifting of orbital degeneracy and a separation of orbital energies, giving a π-HFMO.

A consideration of the orbital energies predicts the wavelength of the first $\pi \rightarrow \pi^*$ electronic transition to be: borazine $\simeq$ N-trifluoroborazine $>$ B-trifluoroborazine $\simeq$ hexafluoroborazine. Thus, N-trifluoro substitution has almost no effect on the $\pi \rightarrow \pi^*$ transition, whereas a blueshift is predicted for B-trifluoro substitution.

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