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THEORETICAL INVESTIGATION OF THE SYMMETRIC TRISUBSTITUTED BORAZINES

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Abstract—The bonding in borazine and four symmetric tri-substituted derivatives, B-trifluoroborazine, N-trifluoroborazine, B-trimethylborazine and N-trimethylborazine, is discussed by means of all electron *ab initio* SCF–MO calculations. B-trifluoroborazine is predicted to be 12·9 eV more stable than the N-trifluoro derivative and B-trimethylborazine 2·8 eV more stable than the N-trimethyl derivative. The calculated wavefunctions are used to interpret the low energy photoelectron spectra of these molecules. The calculated sequence for the three highest filled orbitals is $\pi\sigma\pi$ in all derivatives except B-trifluoroborazine, where the sequence $\pi\pi\sigma$ is realised.

Borazines can be formulated as either cyclic triamines or as cyclic compounds incorporating a π system similar to that found in benzene. A variety of physio-chemical experiments[1] suggests that the borazine nucleus in several compounds is planar; moreover, the B–N internuclear distance measured in, for example, N-trimethylborazine (1·42 Å)[2] is shorter than that expected for a single bond (1·59 Å).[3] However, some chemical evidence suggests that the nitrogen sites in a borazine ring retain some basic character. Thus the empirical formula of the adduct formed by reacting the N-trimethyl derivative with hydrogen chloride suggests that the ring nitrogen atoms have been protonated.[4] Although the borazines have been the subject of numerous approximate molecular orbital investigations,[5–15] in which the bonding has often been compared to that in the corresponding isoelectronic substituted benzenes, studies of the electronic structure by all electron *ab initio* self-consistent field molecular orbital (SCF–MO) calculations have been limited to unsubstituted borazine, $(BHNH)_3$.[16,17] Investigations of the electronic structure of substituted borazines by photoelectron (PE) spectroscopy[18–21] have relied heavily on the use of semi-empirical calculations in assigning the spectra. The failure of such calculations[13–15] to yield an orbital sequence in agreement with the spectrum of borazine itself highlights the need for accurate calculations to assist in the assignment of the spectra of the substituted borazines. In this paper we report a theoretical study of bonding in the borazines by means of *ab initio* SCF–MO calculations on borazine itself, and the B-trifluoro, $(BFNH)_3$, N-trifluoro, $(BHNF)_3$, B-trimethyl, $(BCH_3NH)_3$ and N-trimethyl, $(BHNCH_3)_3$, derivatives.

Computational details

Ab initio SCF–MO calculations were performed in bases of contracted Gaussian type functions (GTF), such functions being used to expand Slater-type orbitals (STO). The boron, carbon, nitrogen and fluorine 1s and 2s orbitals were represented by a single STO expanded in three GTF[22] by the least squares method, with best atom exponents.[23] A double zeta[24] basis of STO was used for the valence 2p and hydrogen 1s orbitals, each STO being expanded in two GTF.[25] Exponents of 0·9 and 1·4 were used for the hydrogen 1s orbitals, while the 2p exponents were those due to Clementi.[24] The borazine ring bond angles were taken[26] as 120°, with bond lengths: B–N, 1·44; B–H, 1·20; N–H, 1·02; N–C, 1·47; B–C, 1·56; C–H, 1·09; B–F, 1·31; and N–F, 1·37 Å. The methyl HCH angles were assumed tetrahedral.

RESULTS AND DISCUSSION

We first discuss the calculated electronic structure of the substituted borazines, followed by an interpretation of the low energy PE spectra in terms of these calculations.

Calculated electronic structure of the borazines

The results of the SCF–MO calculations are summarised in Table 1. The calculated molecular energies predict B-trimethylborazine to be 2·8 eV more stable than the N-trimethyl substituted derivative, and B-trifluoroborazine to be 12·9 eV more stable than N-trifluoroborazine. The relative instability of the N-trifluoro derivative is consistent with the ease of synthesis of these compounds, for although B-fluoro substitution has been known since the synthesis of B-trifluoroborazine by Niedenzu,[27] N-fluoro substitution has only been reported recently.[28]

A Mulliken analysis of borazine (Table 1) suggests, in agreement with the calculations of Ref. 16, that the boron atoms are significantly positive as a consequence of the overall B → N charge transfer (0·46e) in the ring system, with the N → B π-charge transfer (0·40e) outweighed by the B → N transfer in the σ-MO's (0·86e). This charge distribution is consistent with the chemistry of borazine where addition of a hydrogen halide to the system results in proton attachment to nitrogen and halide to boron.[4] Furthermore, the boron $2p_\pi$ population compares favourably with the value of 0·45e determined from the NQR spectra of laminar boron nitride by Silver and Gray.[29] The population analysis of the trisubstituted borazines suggests that methyl substitution has a considerably smaller effect on the electronic structure of the ring relative to fluorine substitution. In $(BFNH)_3$ the fluorine causes a σ-electron shift of 0·56e towards the fluorine in

Table 1. Total energy and electronic structures of the borazines $(BXNY)_3$

	Borazine	Tri-substituted borazines			
		tri-fluoro		*tri-methyl*	
	$(BHNH)_3$	$(BFNH)_3$	$(BHNF)_3$	$(BCH_3NH)_3$	$(BHNCH_3)_3$
	(i) Total energy*/a.u.				
	−238·3580	−531·9055	−531·4316	−354·1474	−354·0438
	(ii) Population analysis†				
boron					
2s	0·897	0·644	0·892	0·783	0·890
$2p_\sigma$	1·319	0·959	1·299	1·128	1·282
$2p_\pi$	0·399	0·453	0·365	0·400	0·406
charge	0·39e	0·95e	0·45e	0·70e	0·43e
nitrogen					
2s	1·607	1·602	1·582	1·604	1·600
$2p_\sigma$	2·590	2·586	2·212	2·566	2·497
$2p_\pi$	1·601	1·668	1·647	1·622	1·579
charge	−0·79e	−0·85e	−0·44e	−0·79e	−0·67e
substituent, X‡					
ns	0·931	1·917	0·842	1·424	0·935
$2p_\sigma$		3·646		2·272	
$2p_\pi$		1·880		1·123	
charge	0·07e	−0·44e	0·16e	−0·81e	0·07e
substituent, Y					
ns	0·668	0·659	1·953	0·685	1·374
$2p_\sigma$			3·233		1·956
$2p_\pi$			1·987		1·139
charge	0·33e	0·34e	−0·17e	0·31e	−0·46e
	(iii) Bond overlap populations				
boron nitrogen					
2s 2s	0·055	0·078	0·049	0·064	0·049
2s $2p_\sigma$	0·212	0·231	0·195	0·217	0·218
$2p_\sigma$ 2s	0·156	0·120	0·125	0·152	0·143
$2p_\sigma$ $2p_\sigma$	0·228	0·227	0·204	0·237	0·232
$2p_\pi$ $2p_\pi$	0·196	0·168	0·186	0·194	0·199

*Unit of energy, hartree $\simeq 4{\cdot}359828 \times 10^{-18}$J.

†e = elementary change $\simeq 1{\cdot}602192 \times 10^{-19}$C.

‡Valence shell orbitals. For the methyl borazines the populations refer to the carbon atoms of each methyl group. The average methyl hydrogen populations are 0·804e in $(BCH_3NH)_3$ and 0·786e in $(BHNCH_3)_3$.

the F–B–N–H bond system, resulting in a positive increase in charge for B, N and H as compared to borazine. The fluorine also participates in significant $p\pi$–$p\pi$ bonding with boron, resulting in a π-donation of 0·12e from the fluorine into the π-ring system. Both mechanisms are significantly reduced on methyl substitution, the methyl group in $(BCH_3NH)_3$ gaining 0·25e by a σ-mechanism while back-donating 0·02e into the π-ring system. When considering trisubstitution at the nitrogen ring atoms, it is clear that the π-donation into the borazine ring system, facilitated by the vacant boron $2p\pi$ orbital in the B-trisubstituted derivatives, will be markedly reduced since the $2p_\pi$ orbital on nitrogen is formally doubly occupied. Thus in $(BHNCH_3)_3$ the nitrogen actually donates 0·02e by a π-mechanism to the methyl group. The σ-electron shift from the borazine ring to the substituent is also reduced because of the greater electronegativity of nitrogen relative to boron. Thus the σ-electron shift of 0·56e in $(BFNH)_3$ decreases to 0·18e in $(BHNF)_3$, while the shift is reversed in $(BHNCH_3)_3$, the nitrogen gaining 0·20e from the methyl group. The considerably greater effect of fluorine substitution on the electronic structure of the ring is also seen in the components of B–N overlap populations (Table 1). While methyl substitution leads to little change in the overlap populations relative to borazine, fluorine substitution at the ring nitrogen results in a marked decrease in all components of the B–N overlap population, a further pointer to the relative instability of $(BHNF)_3$.

The low energy photoelectron spectra of the borazines

The vertical valence ionization potentials (I.P's) from the He(I) spectra of Lloyd and Lynaugh[18,19] are presented in Table 2, together with the Koopman's theorem (KT) I.P's from the present calculations. It has been found that the orbital energies from near double zeta calculations are often in good agreement with experiment if reduced by 8%;[30] thus the KT I.P's in Table 2 are the orbital energies multiplied by this empirical 0·92 factor. The He(I) PE spectrum of borazine has been recorded by several groups[15,18–21] and has consequently been assigned in several ways. Frost *et al.*[15] assigned the first I.P. to ionization from the $6e'\sigma$ B–H bonding orbital, while Lloyd and Lynaugh[18,19] and Bock *et al.*[20,21] concluded from

Table 2. Vertical ionization potentials of the borazines/eV

Orbital	(i) Borazine Experimental	Calculated[a]
$1e''(\pi)$	10·14	10·21
6e'	11·44	11·50
$1a_2''(\pi)$	12·83	13·05
$5a_1'$	13·82	13·81
5e'	14·75	15·19
$1a_2'$		15·21
4e'	17·47	18·08
$4a_1'$	18·0	18·57

Orbital	(ii) Trifluoroborazines $(BFNH)_3$ Experimental	Calculated	Orbital	$(BHNF)_3$ Calculated
$2e''(\pi)$	10·79	10·75	$2e''(\pi)$	11·14
$2a_2''(\pi)$	12·98	12·84	9e'	13·03
$2a_2'$	13·53	13·41	$2a_2''(\pi)$	13·55
9e'	14·29	14·07	$2a_2'$	14·52
8e'	15·85	16·20	$7a_1'$	15·09
$1e''(\pi)$	16·20	16·20	8e'	15·68
$1a_2''(\pi)$	16·87	16·63	7e'	17·42
7e'		16·85	$1e''(\pi)$	17·80
$7a_1'$	17·73	17·84	$1a_2''(\pi)$	18·18
$1a_2'$		18·27	$6a_1'$	19·28
$6a_1'$	19·0	19·18	$1a_2'$	19·32
6e'		19·40	6e'	20·67

Orbital	(iii) Trimethylborazines $(BCH_3NH)_3$ Experimental	Calculated	Orbital	$(BHNCH_3)_3$ Experimental	Calculated
$2e''(\pi)$	9·64	9·85	$2e''(\pi)$	9·28	9·30
9e'	10·90	10·95	9e'	11·14	11·52
$2a_2''(\pi)$	11·87	12·13	$2a_2''(\pi)$	11·48	11·75
$2a_2'$	12·46	12·62	$2a_2'$	12·41	12·61
$7a_1'$		12·76	8e'	12·96	13·27
8e'		13·48	$7a_1'$		13·89
$1e''(\pi)$		13·75	7e'		14·17
$1a_2''(\pi)$	14·07	14·21	$1e''(\pi)$	14·05	14·91
7e'		14·70	$1a_2''(\pi)$		15·37
$1a_2'$	15·24	15·79	$6a_1'$	15·93	16·25
6e'	16·68	17·30	$1a_2'$		16·64
$6a_1'$	17·65	18·22	6e'	17·51	18·49

[a]Koopmans' theorem I.P.'s scaled by 0·92.[30]

the recognisable fine structure that the 10·14 eV band arose from the $1e''\pi$ B–N bonding orbital. Bock and Fuss[20] then assigned the 11·44 eV band to ionization from the $6e'\sigma$ orbital and the 12·83 eV ionization to the $1a_2''\pi$ B–N bonding orbital, giving the sequence $\pi\sigma\pi$. Lloyd and Lynaugh, however, observed a further ionization at 12·06 eV and, assigning this to the $1a_2''$ orbital and the 11·44 eV ionization to the 6e' orbital, again found a $\pi\sigma\pi$ sequence. The He(I) spectra of $(BHNH)_3$ and $(BFNH)_3$ were further analysed by Brundle, Robin and Kuebler[31] who, using the perfluoro effect (whereby σ MO's are stabilized relative to π MO's on fluorination), arrived at an assignment for borazine identical to that of Bock and Fuss, thus overlooking the feature at 12·06 eV. It is possible that this feature is just a part of the high energy fall-off of the band at 11·44 eV, and indeed a study of the spectrum suggests that the first two bands do display a similar shape on the high binding energy side, suggesting that the true third ionization is at 12·83 eV. The calculated I.P.'s from the present calculations provide a good agreement with experiment only if we assume that the 12·06 eV feature does not correspond to a true ionization of the molecule. Although KT predictions have proved unreliable in certain cases, the general good agreement between theory and experiment in the present assignment, coupled with the variation in the form of the 12·06 eV feature from spectrum to spectrum, would seem to rule out any further ionization at this energy. The assignment of the remaining bands from the KT I.P's follows closely that due to Bock and Fuss.[20] The fourth band at 13·82 eV with significant vibrational fine structure may be assigned to ionization from the $5a_1'$ B–H bonding orbital. The band at 14·75 eV is assigned to ionization from the accidentally degenerate 5e' and $1a_2'$ orbitals, the 5e' exhibiting both N2p–H and B2p–N2p bonding character while the $1a_2'$ is exclusively N2p–B2p bonding. Although the sixth band at 17·47 eV was originally assigned by Bock and Fuss[20] to ionization from the 4e' and $4a_1'$ orbitals, a further weak band at 18·0 eV has been observed in the spectrum due to Kroner *et al.*[21] The calculated separation of the 4e' and $4a_1'$ orbitals in the present study is such that an assignment of the 17·47 eV band to the 4e' and the 18·0 eV band to the

$4a_1'$ may be made. The 4e' orbital, with significant B2s character, is both B2s–H and B2s–N2p bonding, while the $4a_1'$ orbital, with little boron character, is predominantly N2p–H bonding. Some doubt must remain over the assignment of these two bands, however, since the more extensive calculations of Ref. 16 interchange the order of the $4a_1'$ and 4e' orbitals.

Turning to the PE spectra of the substituted borazines, we find that the He(I) spectrum of $(BFNH)_3$[18-21] has been tentatively assigned on the basis of CNDO calculations[21] and by an analysis based on the perfluoro effect.[31] The latter assignment suggests that the first band at 10·79 eV corresponds to ionization from the $2e''\pi$ orbital and the second band at 12·98 eV to ionization from the $2a_2''\pi$ orbital, realising the order $\pi\pi\sigma$ for the three highest occupied MO's, in contrast to borazine. This order is also predicted from the present calculations, where the third band is assigned to ionization from the $2a_2'\sigma$ orbital and the more intense band, at 14·29 eV, to ionization from the doubly degenerate 9e' orbital. Although the modified CNDO calculations of Ref. 21 also predict the $\pi\pi\sigma$ ordering of the three highest levels, an assignment based on these calculations suggests that the third band arises from ionization from the accidentally degenerate 9e' and $2a_2'$ orbitals, while the fourth band is assigned to ionization from the 8e' N–H bonding orbital. Conventional CNDO calculations[18] predict a $\pi\sigma\pi$ ordering of the three highest occupied MO's. The assignment of the remaining bands from the present calculations leads to significant differences from that based on semiempirical calculations. The fifth and sixth bands at 15·85 and 16·20 eV are assigned to ionization from the 8e' N–H bonding orbital and the 1e'' B–F π-bonding orbital, although a definitive assignment cannot be made owing to the accidental degeneracy of these levels. The seventh band at 16·87 eV is assigned to ionization from the $1a_2''$ B–N π-bonding orbital and the 7e' B–N σ-bonding orbital, while the band at 17·73 eV is assigned as $7a_1' + 1a_2'$, both orbitals exhibiting B–F σ-bonding character. The final band at 19·0 eV may be assigned to ionization from the $6a_1'$ and 6e' σ-orbitals: the $6a_1'$ is predominantly N2p–H bonding, while the 6e', with a significant B2s component, is both B2s–N2p and B2s–F2p bonding. In the absence of the spectrum of $(BHNF)_3$ we omit a detailed discussion of the KT I.P.'s (Table 2), but note that the order of the three highest occupied MO's is predicted to be $\pi\sigma\pi$, as in borazine.

The He(I) PE spectra of $(BCH_3NH)_3$ and $(BHNCH_3)_3$ have been reported by Lloyd and Lynaugh[19] and Kroner *et al.*[21] CNDO calculations being used in each case to aid the assignment. Although the two molecules do not exhibit the full symmetry of the D_{3h} point group due to the methyl hydrogens, the MO's in Table 2 are assigned assuming D_{3h} to allow a ready comparison with the other borazines. The calculated I.P's suggest that the sequence for the three highest occupied orbitals for both isomers is as in borazine, $\pi\sigma\pi$, the first ionization arising from the B–N π-bonding 2e'' orbital, the second from the 9e' σ-orbital, (B–H bonding in $(BHNCH_3)_3$ and B–C bonding in $(BCH_3NH)_3$), and the third from the B–N π-bonding $2a_2''$ orbital. While the second band of $(BCH_3NH)_3$ is similar to that in borazine, $(BHNCH_3)_3$ has a shoulder on the low I.P. side of the maximum.[19] The conclusion of Lloyd and Lynaugh, that the a and e components of the second band in $(BHNCH_3)_3$ are closer in energy than in $(BHNH)_3$ and $(BCH_3NH)_3$, is borne out by the calculations, since the 9e'–$2a_2''$ separation is calculated to be 1·2 eV in $(BCH_3NH)_3$ but only 0·2 eV in $(BHNCH_3)_3$. As noted previously,[19] B-trimethylation is predicted to destabilise both the e'' and e' orbitals, whilst N-trimethylation is predicted to destabilise e'' considerably while leaving the energy of the e' orbitals almost unchanged. The remainder of both spectra may be satisfactorily assigned from the KT I.P's. Thus in $(BHNCH_3)_3$ the third band at 12·41 eV may be assigned to ionization from the $2a_2'$ orbital and the fourth band (12·96 eV) to ionization from 8e', both orbitals exhibiting C–H bonding character. The broad band centred at 14·05 eV is assigned to ionization from the B–H bonding $7a_1'$ orbital, the C–H and C–N π-bonding orbitals (1e'' and $1a_2''$) and the C–N σ-bonding 7e' orbital. The sixth band at 15·93 eV is assigned as $6a_1' + 1a_2'$, and the final weak band at 17·51 eV to the 6e' orbital which, with significant B2s character, is predominantly B2s–N2p bonding. In $(BCH_3NH)_3$ we assign the fourth band to the accidentally degenerate $2a_2'$ and B–C bonding $7a_1'$ orbitals and the extremely broad and intense band at 14·07 eV to the 8e', 1e'' and $1a_2''$ C–H bonding orbitals and the N–H 7e' orbital. The sixth band at 15·24 eV is assigned to the $1a_2'$ orbital, the weak band at 16·68 eV to the 6e' B–N bonding orbital and the final band at 17·65 eV to the $6a_1'$ orbital.

CONCLUSIONS

The SCF-MO calculations reported here predict B-trimethyl borazine to be more stable than N-trimethyl borazine and B-trifluoroborazine to be substantially more stable than the N-trifluoro derivative. Fluorine substitution is predicted to have a far greater effect on the electronic structure of the borazine ring relative to methyl substitution, while the π-donation into the borazine ring system is markedly reduced on N-trisubstitution relative to B-trisubstitution. The excellent agreement between the Koopmans' theorem and experimental I.P's for the substituted borazines suggests that the 12·06 eV feature in the PE spectrum of borazine does not correspond to a true ionization of the molecule. The calculated sequence for the three highest occupied valence MO's is $\pi\sigma\pi$ for all derivatives exept B-trifluoroborazine, where the sequence $\pi\pi\sigma$ is realised.

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