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GEOMETRY OPTIMISED AB INITIO MOLECULAR ORBITAL STUDIES OF THE SERIES A_nBF_{3-n} ($A = CH_3, C_2H_3$; n = 0-3)

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Summary

Geometry optimised ab initio calculations are reported for two series of trigonal boron compounds. The extent of π bonding between boron and carbon for the vinyl series is shown to be much less than between boron and fluorine but nevertheless to exert a strong influence on the B—C bondlength. Good linear correlations between NMR experimental parameters and electronic populations for B and F are noted and some predictions are made.

The extent of π bonding between trigonal boron and carbon has long been of interest. Coyle, Stafford and Stone [1] discussed the chemical and spectroscopic evidence for such bonding. More recently, Holliday and Reade [2], through a comparison of the photoelectron spectra of $(C_2H_3)_3B$ and $(C_2H_5)_3B$, suggested that there was limited conjugation in the former. However, evidence for B—C π bonding was later presented from infrared, Raman and electron diffraction data [3]. Geometry optimised ab initio studies of ABF_2 ($A = H, CH_3, C_2H_3, C_2H_5, F$) have been reported [4].

Method

The Gaussian-70 computer program of Pople and coworkers [5] with a minimal STO-3G basis set [6] was used. C—H bond distances (1.09 Å), tetrahedral (109.5°) angles at carbon and trigonal (120°) angles at C and at B in A_3B were preserved constant throughout. D_{3h} symmetry was used in $(C_2H_3)_3B$ and substituting F for a vinyl group gave the conformation of $(C_2H_3)_2BF$ — the so-called 'swastika' conformation.

Results and discussion

Geometry. The optimised bond lengths and angles are in Tables 1 and 2. In all compounds r(B—F) is approximately constant. The insensitivity of the B—F

TABLE 1

BOND LENGTHS (Å)

	A	BF_3	ABF_2	A_2BF	A_3B
r(B—F)	CH_3	1.309	1.307	1.300	—
r(B—C)		—	1.590	1.592	1.587
r(B—F)	C_2H_3	1.309	1.310	1.308	—
r(B—C)		—	1.564	1.569	1.571
r(C—C)		—	1.319	1.319	1.321

TABLE 2

BOND ANGLES (°)

	A	ABF_2	A_2BF
FBF	CH_3	117.0	—
FBC		121.5	119.1
CBC		—	121.8
FBF	C_2H_3	116.8	—
FBC		121.6	117.9
CBC		—	124.1

TABLE 3

GROSS ATOMIC CHARGES

	A	BF_3	ABF_2	A_2BF	A_3B
q_B	CH_3	0.652	0.556	0.479	0.409
q_F		−0.217	−0.213	−0.196	—
q_C		—	−0.315	−0.309	−0.300
q_A		—	−0.130	−0.141	−0.136
q_B	C_2H_3	0.652	0.542	0.443	0.342
q_F		−0.217	−0.214	−0.200	—
$q_{C\alpha}$		—	−0.196	−0.187	−0.174
$q_{C\beta}$		—	−0.107	−0.110	−0.108
q_A		—	−0.114	−0.122	−0.114

TABLE 4

GROSS ORBITAL POPULATIONS

Atom	A	BF_3	ABF_2	A_2BF	A_3B
σ B	CH_3	3.839	4.032	4.237	4.489
π		0.509	0.412	0.285	0.102
σ F		7.387	7.406	7.424	—
π		1.830	1.807	1.772	—
Total C			6.315	6.309	6.300
In plane H			0.940	0.948	0.951
Out of plane H			0.937	0.942	0.943
σ B	C_2H_3		4.021	4.211	4.430
π			0.437	0.346	0.228
σ F			7.403	7.417	—
π			1.811	1.783	—
σ Cα			5.204	5.205	5.198
π			0.992	0.982	0.976
σ Cβ			5.158	5.157	5.160
π			0.949	0.953	0.948

bondlength to change in electronic environment was also noted by Becher [7] in a force constant study of methylboranes. The significant decrease in r(B—C) from methyl to vinyl series has been noted experimentally [3] as also the increase in r(C—C) relative to ethylene (optimised r(C—C) in ethylene is 1.310 Å [8]). These effects can be explained by a closer look at the electronic structures of the compounds.

Electronic distributions. The gross atomic charge on boron is positive in all cases and decreases (linearly for the vinyl series) as fluorines are substituted by A moieties. As expected, the fluorine charges are negative and their absolute values decrease from BF_3 to A_2BF, the variations being essentially the same in both series. Thus the absolute A charges are higher in the methyl series. The variations in q_A across the series are not monotonic, A_2BF having the largest absolute value in both cases. Cβ in the vinyl series has a constant negative charge whose absolute value is less than that on each C in ethylene ($q_C = -0.125$) [8]. The absolute values of $q_{C\alpha}$ and q_C decrease with increasing vinylation and methylation respectively.

Further insight into the charge distribution is obtained from the σ and π gross atomic populations (Table 4). The total electronic population on B is due to increasing σ and decreasing π contributions across both series. The former dominates and thus q_B decreases. The greater total atomic populations for the vinyl borons result from the π electron delocalization from the vinyl group. The similarities in q_F arise from increasing σ and decreasing π populations almost cancelling each other in both series.

The general decreases in the F π gross atomic populations across each series are due to a decrease in the number of F atoms bonded to B thus allowing increasing F→B π donation across the series. Since F is a stronger π donor than either of the organic moieties (Table 5), the B π populations decrease from BF_3 to A_3B. The decreased F π donation with coordinated vinyl groups compared to methyl groups is a direct result of greater π donation to B from the vinyls. The constant σ and π gross orbital populations are reflected in the charge on Cβ while the decreasing absolute charge on Cα shows the increased delocalization with increased vinylation. The trend in σ electron flow follows from variations in electronegativity of the atoms bonded directly to B.

The overlap populations show definite trends (Table 6). Both σ and π, B—F and B—C, overlap populations (o.p.'s) increase as the number of F atoms decreases. The B—C π o.p.'s are less than half the B—F π values. The total o.p.'s

TABLE 5

ELECTRON DONATIONS

	A	BF_3	ABF_2	A_2BF	A_3B
$(F\rightarrow B)_\pi$	CH_3	0.170	0.193	0.228	
	C_2H_3		0.189	0.217	
$(A\rightarrow B)_\pi$	CH_3		0.026	0.029	0.034
	C_2H_3		0.059	0.065	0.076
F σ acceptance	CH_3	0.387	0.406	0.424	
	C_2H_3		0.403	0.417	
A σ acceptance	CH_3		0.156	0.170	0.170
	C_2H_3		0.163	0.186	0.190

TABLE 6

OVERLAP POPULATIONS

		A	BF_3	ABF_2	A_2BF	A_3B
σ	B—F	CH_3	0.420	0.431	0.441	—
π			0.120	0.137	0.162	—
Total	B—C			0.729	0.748	0.775
σ	B—F	C_2H_3		0.435	0.448	
π				0.132	0.149	
σ	B—C			0.729	0.747	0.768
π				0.049	0.055	0.063
σ	C—C			0.805	0.806	0.808
π				0.378	0.376	0.371

for the methyl series are equal to the corresponding σ o.p.'s in the vinyl series; thus the decreases in B—C bondlengths from methyl to vinyl are due to π overlap contributions. The C—C π o.p. is less than the corresponding ethylene value (0.400) [8].

The ionization potentials (Koopmans' Theorem) for $(CH_3)_nBF_{3-n}$ (n = 1-3) are 10.83, 9.83 and 10.45 eV respectively, where ionization in each case is from a σ orbital. The corresponding values in the vinyl series are 9.14, 8.63 and 8.40 eV where ionization is from a C—C bonding π orbital.

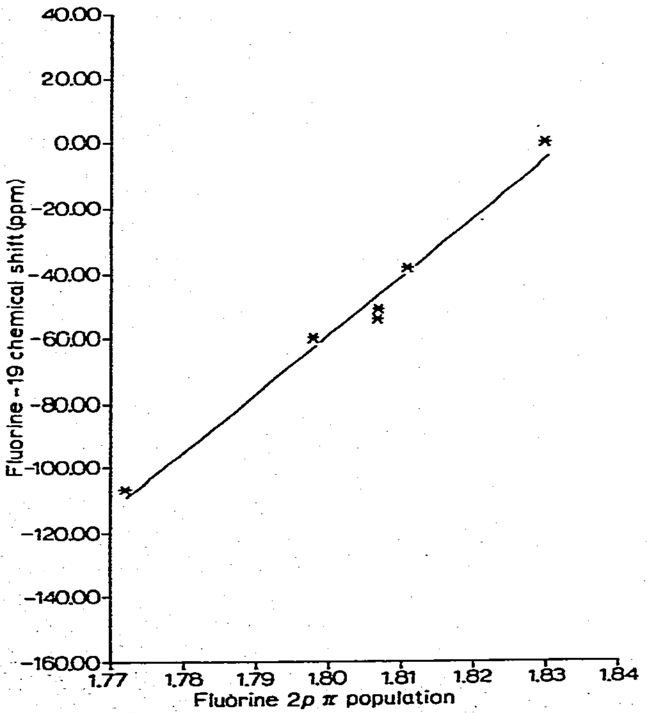

Fig. 1. Regression analysis between δ(^{19}F) and total F 2pπ overlap population for BF_3, CH_3BF_2, $(CH_3)_2BF$, $C_2H_3BF_2$, $C_2H_5BF_2$ and HBF_2.

NMR

A number of regression analyses were performed to study the relations between published NMR parameters and the ab initio populations.

(a). An analysis on BF_3, CH_3BF_2, $(CH_3)_2BF$, $C_2H_3BF_2$, $C_2H_5BF_2$ and HBF_2 showed a good linear correlation ($r = 0.965$) between $J(^{11}B—^{19}F)$ and total B—F overlap population.

(b). For the same series of compounds an analysis of $\delta(^{19}F)$ against F $2p\pi$ gross orbital populations gave a strong linear correlation (Fig. 1).

$$\delta(^{19}F) = 1804\ (F\ 2p\pi\ o.p.) - 3307 \qquad (r = 0.991).$$

Thus for $(C_2H_3)_2BF$ the predicted value of the fluorine chemical shift is —89.9 ppm.

(c). To the above series was added $(CH_3)_3B$ and $(C_2H_3)_3B$ for an analysis of $\delta(^{11}B)$ against B $2p\pi$ gross orbital populations.

$$\delta(^{11}B) = 189\ (B\ 2p\pi\ o.p.) - 87 \qquad (r = 0.985).$$

The boron chemical shift for $(C_2H_3)_2BF$ is therefore predicted to be 22 ppm. The intercept gives the chemical shift for BH_3 as —87 ppm (Fig. 2).

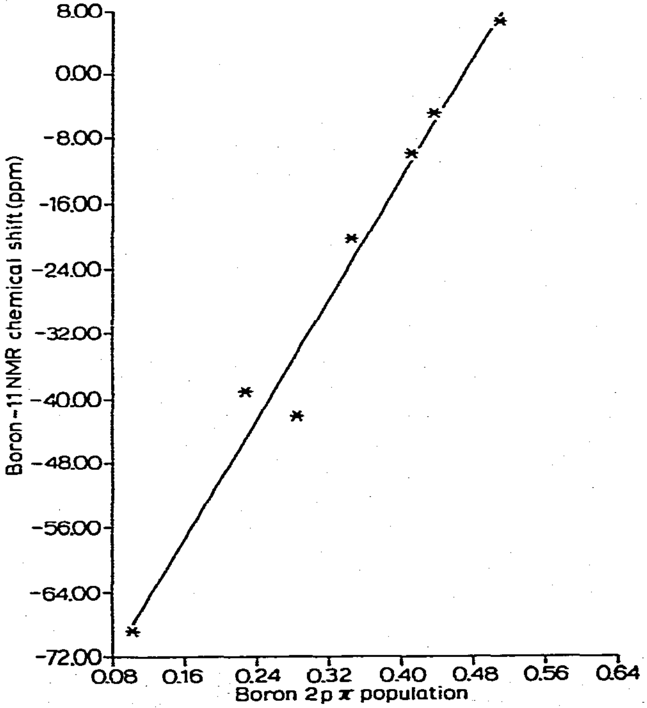

Fig. 2. Regression analysis between $\delta(^{11}B)$ and total B $2p\pi$ population for BF_3, CH_3BF_2, $(CH_3)_2BF$, $C_2H_3BF_2$, $C_2H_5BF_2$, HBF_2, $(CH_3)_3B$ and $(C_2H_3)_3B$.

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