# Calculation of $^{11}$B Chemical Shifts in Mixed Halides of Boron

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THE chemical shifts in the $^{11}$B nuclear magnetic resonance spectra of a series of fluoroboron halides have been reported.[1] In this communication we present the results of calculations of these quantities using the molecular orbital theory of $^{13}$C chemical shifts recently formulated by Karplus and Pople.[2]

In this treatment it was deduced that the local paramagnetic effect is the chief contributor to the shift and hence the mean value of the shielding constant is dominated by the term, $\sigma_p^{AA}$ (for carbon atom A). This has the general form,

$$\sigma_p^{AA} = -[e^2\hbar^2/2m^2c^2(\Delta E)] < r^{-3} >_{2p} \sum_{B} Q_{AB} \tag{1}$$

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[1] K. M. Harmon, J. R. Spielman, and R. E. Williams, A. D. 603782 O.N.R. Technical Report No. **1**, 1964.
[2] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.

$$Q_{AB} = 4/3\, \delta_{AB}(P_{X_AX_B} + P_{Y_AY_B} + P_{Z_AZ_B}) - 2/3(P_{Y_AY_B}\, P_{Z_AZ_B} + P_{Z_AZ_B}\, P_{X_AX_B} + P_{X_AX_B}P_{Y_AY_B})$$
$$+ 2/3(P_{Y_AZ_B}\, P_{Z_AY_B} + P_{Z_AX_B}\, P_{X_AZ_B} + P_{X_AY_B}\, P_{Y_AX_B}) \qquad (2)$$

where $\sum\limits_{B}$ ranges over all atoms and $P_{\mu\nu}$ is the element of the density matrix corresponding to different $2p$ atomic orbitals designated by the subscripts: $\Delta E$ is an average electronic excitation energy, and $<r^{-3}>_{2p}$ the mean inverse cube of the radial co-ordinate.

In order to apply (1) to the calculation of $^{11}B$ chemical shifts in the mixed boron halides we assume $sp^2$ hybridization on the boron atom in each case. The boron–halogen $\sigma$-bonds are represented by,

$$\Psi\,(\text{B–hal1}) = 2^{-\frac{1}{2}}[(1-\lambda_1)^{\frac{1}{2}}\ \ (\text{B};sp^2) + (1+\lambda_1)^{\frac{1}{2}}\ \ (\text{hal } 1;\, p)] \qquad (3)$$

in which $\lambda_1$ is a polarity parameter and $sp$ hybridization in the halogen is assumed negligible. Choosing the $\pi$-orbitals to lie in the $z$-direction, for the molecule B(hal 1 hal 2 hal 3), $Q$ is given by an expression which requires only the three polarity parameters and the spinless $\pi$-electron density matrix elements.

*$^{11}B$ shielding constants and chemical shifts of fluoroboron halides (p.p.m.)*

| | | $BF_3$ | | $BF_2Cl$ | | $BF_2Br$ | | $BFCl_2$ | | BFClBr | | $BFBr_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | c | d | c | d | c | d | c | d | c | d | c | d |
| $\sigma_p(1)$ | a | −108·33 | −127·98 | −132·65 | −156·60 | −139·74 | −165·90 | −137·46 | −162·70 | −143·59 | −169·65 | −147·59 | −174·45 |
| | b | 0 | 0 | − 24·32 | − 28·62 | − 31·41 | − 37·92 | − 29·13 | − 34·72 | − 35·26 | − 41·67 | − 39·26 | − 46·47 |
| $\sigma_p(2)$ | a | −108·33 | −127·98 | −119·41 | −140·89 | −121·72 | −143·83 | −131·28 | −154·42 | −135·27 | −158·83 | −139·52 | −163·52 |
| | b | 0 | 0 | − 11·08 | − 12·91 | − 13·39 | − 15·85 | − 22·95 | − 26·44 | − 26·94 | − 30·85 | − 31·19 | − 35·54 |
| $\sigma_p(3)$ | a | −103·52 | −121·45 | −111·22 | −130·31 | −112·25 | −131·66 | −119·40 | −139·62 | −121·62 | −141·96 | −123·95 | −144·46 |
| | b | 0 | 0 | − 7·70 | − 8·86 | − 8·73 | − 10·21 | − 15·88 | − 18·17 | − 18·10 | − 20·51 | − 20·44 | − 23·01 |
| $\sigma$(obs.) relative to $BF_3$ | | 0 | | −10·6 | | −10·1 | | −21·8 | | −21·7 | | −20·2 | |

$\sigma_p(1)$ $\Delta E$ was taken as the first singlet–singlet transition energy.
$\sigma_p(2)$ $\Delta E$ was taken as the average of the first and second transitions.
$\sigma_p(3)$ $\Delta E$ was taken as the average of the first, second, and third transitions.

a—absolute shielding constant.
b—relative to $BF_3$
c—Mataga repulsion integrals.
d—Mataga 'refined' repulsion integrals.

The $\lambda_j$ and $\sigma$-population drifts were estimated from the electronegativities of the atoms forming the particular $\sigma$-bond under consideration and the $\pi$-density matrix calculated using a modification of the Pariser–Parr–Pople LCAO–MO–SCF treatment[3] for unsaturated systems. The two-electron repulsion integrals necessary for the above method were obtained essentially from the Mataga approximation.[4] In the orbital expansion[5] of $<r^{-3}>_{2p}$ account was taken of both the $\sigma$- and $\pi$-electron distributions *via* the effective Slater nuclear charge on the atoms.

Calculations of chemical shifts usually employ a $\Delta E$ which is constant for a particular series of related compounds but in the present work the change in this quantity from compound to compound was allowed for by using the calculated singlet–singlet transition energies in each case.

The best agreement is thus obtained using the higher $\Delta E$ values and the second form of integrals. The shielding constants are obtained in the wrong order if a $\Delta E$ value common to all members of the series is employed.

Further preliminary investigation indicates that the diamagnetic and neighbour magnetic anisotropy contributions to the shielding constants will be small. We are, however, studying this aspect further.

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[3] J. A. Pople, *Trans. Faraday Soc.*, **1953**, **49**, 1375; R. Pariser and R. G. Parr, *J. Chem. Phys.*, **1953**, **21**, 466.
[4] K. Nishimoto and N. Mataga, *Z. phys. Chem.* (*Frankfurt*), 1957, **13**, 140.
[5] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw Hill Book Company Inc., New York, 1955, Chap. 9.