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Relationes

The Electronic Structures of Substituted Benzenes and Borazines

D. A. Brown and C. G. McCormack

Department of Chemistry, University College, Belfield, Dublin 4. Ireland

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The electronic structure of borazine has been discussed in terms of both simple and extended Hückel molecular orbital theory [*1, 2, 4*] and the more sophisticated S.C.F. method [*1, 3*]; however, few calculations of substituted borazines have been reported [*3*]. In the former case [*4*], correlation of reduction potentials of a series of phenyl substituted borazines was made in terms of Hückel theory and extended to a discussion of the charge-transfer spectra of some phenyl and methyl substituted borazines. Whilst the present work was in progress detailed S.C.F. calculations of borazine, N-trimethylborazine, B-trimethylborazine and B-trichloroborazine have appeared [*3*]. The main purpose of the present work was to test whether substituent parameters for the methyl group and chlorine atom obtained by fitting the observed ionization potentials of 1, 3, 5 trichlorobenzene and hexamethylbenzene could be used in similar calculations of ionization potentials and electronic energies of a series of methyl and chloro-substituted borazines. Both methyl and chloro-groups were considered as inductive groups only; it was hoped that any conjugation or hyperconjugation effects could be included in this simple manner.

Method

All calculations were made by the standard Hückel L.C.A.O. M.O. method [*5*]. The Coulomb term of a heteroatom X was taken as:

$$H_{\mathrm{XX}} = H_{\mathrm{CC}} + \delta_{\mathrm{X}}\,\beta_{\mathrm{CC}} \tag{1}$$

and the resonance integral β_{XY} between p_π orbitals of adjacent atoms X and Y as:

$$\beta_{\mathrm{XY}} = k\,\beta_{\mathrm{CC}}\,. \tag{2}$$

The effect of methyl and chloro substitution upon an adjacent atom was assumed to modify its Coulomb term according to the expression:

$$H_{\mathrm{X'X'}} = H_{\mathrm{XX}} + \delta_s\,\beta_{\mathrm{CC}}$$

where δ_s is a substituent parameter. Within this framework three approximations were used.

Approximation 1

In this case, it was assumed that $k = 1$ for all substituted borazines. Values of δ_{Me} and δ_{Cl} were obtained by equating the energy of the highest occupied orbital of hexamethylbenzene [6] and of 1, 3, 5 trichlorobenzene [7] with the observed ionization potentials of 7.9 eV [6] and 9.9 eV [7] respectively. A value of 7.1 eV was assigned to H_{CC} and of 2.5 eV to β_{CC} since these values give a good fit to the ionization potentials of a wide range of conjugated hydrocarbons [7]. The value of δ_{B} (assumed equal to $-\delta_{\mathrm{N}}$ because of the relative electronegatives of boron and nitrogen) was obtained as above from the observed ionization potential [7] of borazine (10.3 eV). These values of δ_{B}, δ_{N}, δ_{Me}, and δ_{Cl} were then used to calculate the ionization potentials and one-electron transition energies of a series of substituted benzenes and borazines; the results are given in column three of Tab. 1 and 2 and compared with experimental values in column eight. The δ values are listed in Tab. 3.

Approximation 2

In this approximation, allowance was made for a variation in the resonance integral β_{BN} between the adjacent boron and nitrogen $2p\pi$ orbitals by assuming direct proportionality to the respective overlap integrals:

$$k = \frac{S_{\mathrm{BN}}}{S_{\mathrm{CC}}}\,. \tag{3}$$

Using Slater functions, one obtains a value of 0.888 for k which agrees well with previous values [4]. Values of $\delta_{\mathrm{B}}(-\delta_{\mathrm{N}})$ were then recalculated from the observed ionization potential of borazine and with these new values the data for the substituted borazines were recalculated.

Approximation 3

Finally, the resonance integral β_{XY} was expressed in terms of the Wolfsberg-Helmholtz approximation [8]:

$$\beta_{\mathrm{XY}} = K S_{\mathrm{XY}} \left(\frac{H_{\mathrm{XX}} + H_{\mathrm{YY}}}{2}\right).$$

As shown by Shriver [4], this equation together with equations 1, 2 and 3, leads to the expression:

$$k_{\mathrm{BN}} = \frac{S_{\mathrm{BN}}}{S_{\mathrm{CC}}} [1 + (\delta_{\mathrm{N}} + \delta_{\mathrm{B}})] \frac{\beta_{\mathrm{CC}}}{2H_{\mathrm{CC}}}\,.$$

However, the above authors assigned a value of 0.40 to the ratio $\beta_{\mathrm{CC}}/2H_{\mathrm{CC}}$ whereas we calculate a value of 0.18 from the above values of β_{CC} and H_{CC}. In this approximation, the value of k_{BN} for borazine is identical with that of approximation 2 but will vary for substituted borazines because of its dependence upon δ_{N} and δ_{B} and hence upon δ_{Me} and δ_{Cl} as shown in column six of Tabs. 1 and 2. The values of δ_{Me} and δ_{Cl} appropriate to this case were calculated as before from the observed ionization potentials of hexamethylbenzene and 1, 3, 5, trichlorobenzene. These values were then used to calculate ionization potentials and one-electron transition energies for the remaining compounds which are given in column seven of Tabs. 1 and 2.

Discussion

The general agreement between calculated and observed values of ionization potentials and one-electron transition energies is most encouraging and suggests

Table 1. *Ionization Potentials* (eV)

Compound	Approximation 1		Approximation 2		Approximation 3		Experimental
	k	I.P.	k	I.P.	k	I.P.	
I[a]	1.000	9.6	1.000	9.6	1.000	9.6	9.6 [7]
II[a]	1.000	7.9	1.000	7.9	0.823	7.9	7.9 [6]
III	1.000	8.89	1.000	8.89	0.911	8.84	8.9 [7]
IV[a]	1.000	9.90	1.000	9.90	1.030	9.90	9.9 [7]
V	1.000	9.28	1.000	9.28	0.942	9.19	—
VI[a]	1.000	10.3	0.888	10.3	0.888	10.3	10.3 [7]
VII	1.000	10.04	0.888	10.11	0.809	10.03	9.8 [7]
VIII	1.000	8.60	0.888	8.60	0.731	8.78	8.6 [9]
IX	1.000	10.41	0.888	10.39	0.915	10.41	10.9 [7]
X	1.000	9.17	0.888	9.04	0.836	9.24	—
XI	1.000	9.00	0.888	8.90	0.809	9.09	

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[a] Used for calculation of parameters.

Table 2. *Electronic Energies* (eV)

Compound	Approximation 1	Approximation 2	Approximation 3	Experimental
I	5.00	5.00	5.00	4.92 [10]
II	5.00	5.00	4.11	4.53 [12]
III	5.28	5.28	4.73	4.68 [10]
IV	5.03	5.03	5.17	4.55 [11]
V	5.49	5.49	5.00	—
VI	6.40	6.40	6.40	6.37 [10]
VII	7.57	7.72	7.13	6.50 [10]
VIII	6.40	6.40	5.88	—
IX	6.06	6.00	6.20	6.52 [10]
X	5.29	5.02	5.10	—
XI	5.50	5.31	5.25	5.54 [10]

Table 3. *Parameters*

	δ_B	δ_N	δ_{Me}	δ_{Cl}
Approximation 1	−.799	.799	−.680	.227
Approximation 2	−.922	.922	−.680	.227
Approximation 3	−.922	.922	−.503	.171

I[a]	benzene.
II[a]	hexamethylbenzene.
III	2:4:6-trimethylbenzene.
IV[a]	2:4:6-trichlorobenzene.
V	1:3:5-trimethyl, 2:4:6-trichlorobenzene.
VI[a]	borazine.
VII	B-trimethylborazine.
VIII	hexamethylborazine.
IX	B-trichloroborazine.
X	B-trichloro-N-trimethylborazine.
XI	N-trimethylborazine.

[a] Used for calculation of parameters.

that it is indeed possible to carry over substituent parameters obtained from conjugated hydrocarbons to heteroaromatic systems such as borazine. The calculated ionization potentials are relatively insensitive to the different approximations but in view of the generally good agreement it does appear that the experimental value of 10.9 eV for B-trichloroborazine may be in error. The long wavelength band in the electronic spectrum is predicted best by approximation 3, viz. that of a variation in the resonance integral according to the Wolfsberg-Helmholtz formula.

Finally, mention should be made of the value of δ_{Me} of -0.54 obtained by STREITWIESER [*13*] by correlation with the ionization potential of toluene and a series of conjugated hydrocarbons. We found a slight numerical error in this paper so that the correct value is -0.580 which agrees well with our value of -0.503 according to approximation 3.

It should be noted that our value of δ_{Cl} is much smaller than that suggested for calculations involving conjugation of the chlorine lone pair [*5*]; this result is hardly surprising since δ_{Cl} is now an effective parameter embracing two opposing effects (inductive and mesomeric).

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Prof. D. A. BROWN
Department of Chemistry
University College
London, England