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THEORETICAL STUDIES OF THE INDUCTIVE EFFECT - 3. A THEORETICAL SCALE OF FIELD PARAMETERS[1]

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Summary: *It is shown that theoretical calculations on simple systems at the ab initio 4-31G level are capable of reproducing inductive field parameters and can be used to extend the scale to substituents whose values are less well established.*

The transmission of polar effects in σ-bonded systems continues to attract interest.[2-6]. It is now well established[2,5,6] that the predominant mechanism of transmission involves a direct through space electrostatic interaction, generally referred to as a field effect (F). Positive evidence for transmission via the alternative σ-inductive effect, a progressive but diminishing relay of polar effects along a chain of carbon atoms, is hard to find except possibly in physical properties at very short distances.[5] Such sigma-inductive effects arise from substituent electronegativities (χ). In a recent communication[4] we have shown that the charge on the hydrogen atom in compounds HX provides a measure of substituent group electronegativity. Here we show that field effects, as measured by σ_F values, can equally be obtained from theoretical results.

In earlier work we have shown[7] that polar substituent constants are approximately proportional to calculated values of ΔE^o for the proton transfer reaction (1),

$$XCH_2NH_3^+ + CH_3NH_2 \rightleftharpoons X\,CH_2NH_2 + XCH_2NH_2 \qquad (1)$$

and also for the corresponding equilibrium with the β-substituted ethylamines. We later showed[9] that isolated molecule calculations using the methylammonium ion could also be used as a measure of field effects. For example, the field effects of <u>para</u>-substituted anilines can be simulated[6] using the isodesmic process below (2),

$$CH_3NH_3^+/CH_3X + CH_3NH_2/CH_4 \rightleftharpoons CH_3NH_3^+/CH_4 + CH_3NH_2/CH_3X \qquad (2)$$

where the distances between the isolated molecules were equivalent to those in the corresponding anilines. The dual substituent parameter[10] analysis was given by (3).

$$\Delta E^o = 10.1\sigma_I + 2.00\sigma_R^- \qquad (3)$$

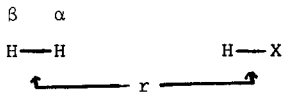
It was suggested that the resonance term was not significant but its presence together with the only moderate statistical fit ($f^9 = 0.21$) precluded the method being used as a theoretical basis for a scale of inductive parameters.

We are examining various series of isolated molecules and have found some that are particularly suitable as a theoretical basis for scales of field effects. We have made these calculations at the ab inito 4-31G level and have looked at both electron densities and energies. We briefly discuss one example of each. The series have been selected to avoid secondary

effects[6,8] arising from the polarisation of bonds in between the substituent and the measurement site.

A. Polarisation of hydrogen by HX.

We have made a series of calculations on the very simple system (4) below with various values of r from 4A° to 7A°. We have used the charge at hydrogen atom α as a measure of the



(4)

polarisation of the hydrogen molecule caused by HX. Since this should be proportional to the dipole in the HX, it provides a measure of the substituent field effect. Values are given in Table 1. A dsp analysis leads to (5) with an excellent fit (f = 0.08).

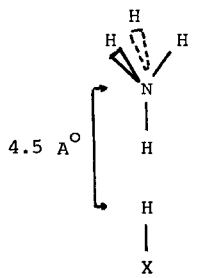
$$10^3 q_H = -26.0\sigma_I + 0.06\sigma_R^{\circ} \qquad (5)$$

B. ΔE° for the proton exchange of NH_4^+/HX.

Here the isodesmic process is (6).

$$NH_4^+/HX + NH_3/HH \rightleftharpoons NH_4^+/HH + NH_3/HX \qquad (6)$$

The results used the geometry below (7)



(7)

The ΔE° values are shown in Table 1. A dsp analysis gives equation (8) with both a very low resonance component and an excellent fit (f = 0.09).

$$\Delta E^{\circ} = -12.63\sigma_I + 0.29\sigma_R^{\circ} \qquad (8)$$

Results from the two methods are proportional and can be used to obtain values at σ_F for other substituents. Thus values obtained using method B and equation (9) are shown in Table 2.

$$\Delta E^{\circ} = -12.6\sigma_F \qquad (9)$$

In the figure, we show a plot of these σ_F values against the σ_I values given in reference 10. The good correlation shows the utility of the method.

Acknowledgement. We are grateful to the Australian Research Grants Committee for financial assistance.

References

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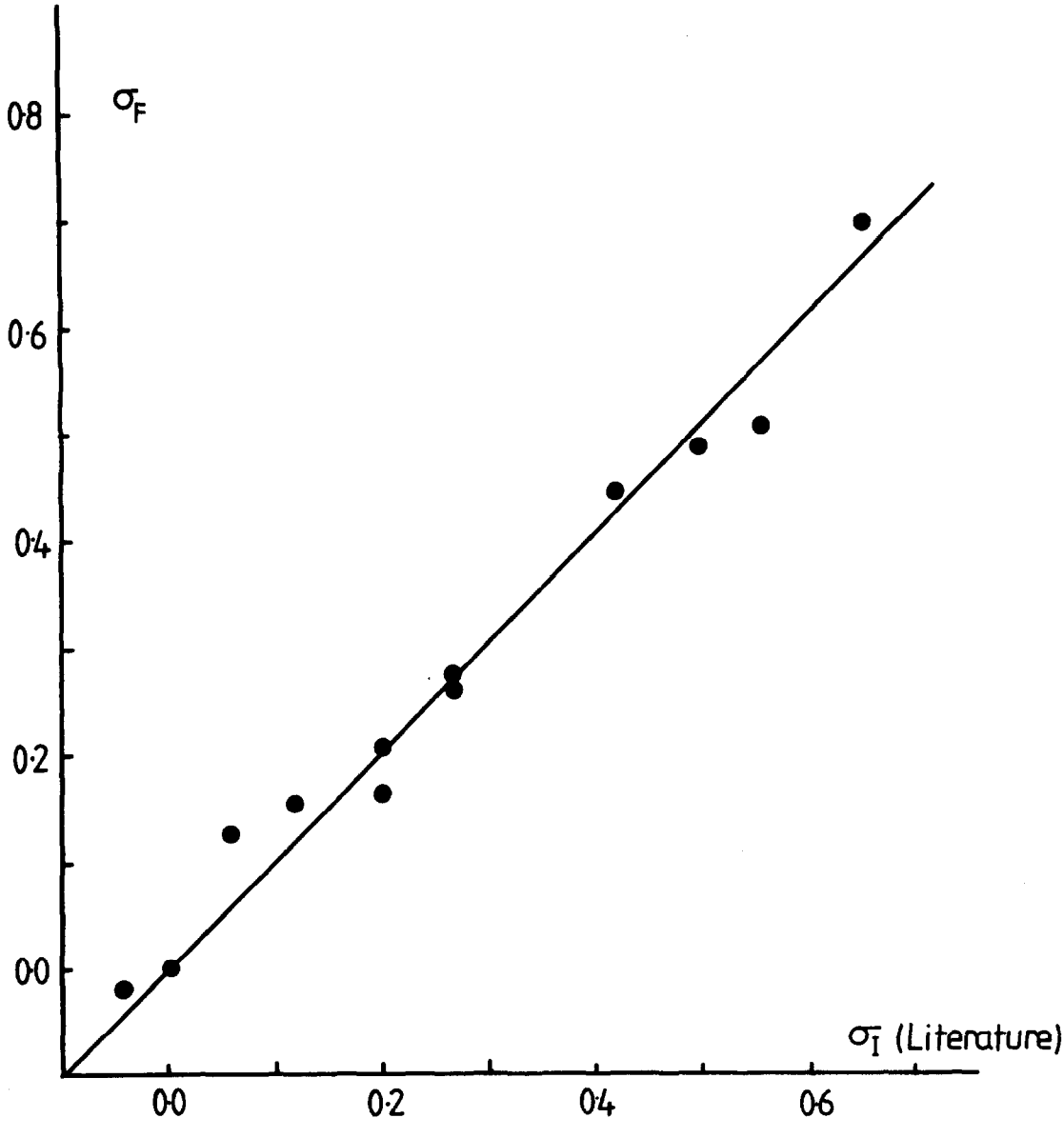
Table 1. Values for Polarisation of H_2 by HX (A in text) and of the Effect of HX on the Isodesmic Proton Transfer from the Ammonium Ion (B in text). Calculations using ab initio 4-31G basis.

Subst.	A $-\Delta q_{H(\alpha)}$ [a] 10^3 electrons	B $-\Delta E^o$ kcal mol^{-1}	σ_I (ref.9)
Me	-0.25	-0.27	-0.04
H	0.00	0.00	0.00
NH_2	4.15	2.04	0.12
OMe	8.15	3.29	0.27
CF_3	11.75	5.64	0.45
F	12.75	6.22	0.50
CN	12.65	6.39	0.56
NO_2	18.45	8.92	0.65

[a] $r = 4A^o$ in (4) - see text.

Table 2. Field Parameters, σ_F, derived from the Effect of Isodesmic Proton Exchange on (NH_4^+/HX).

Subst.	σ_F	Subst.	σ_F	Subst.	σ_F
Me	-0.02	NH_2	0.16	CF_3	0.45
H	0.00	CO_2Me	0.17	COF	0.48
$CHCH_2$	0.01	COMe	0.21	F	0.49
CH_2OH	0.06	OMe	0.26	CN	0.51
CCH	0.12	CHO	0.27	NO	0.58
NMe_2	0.13	OH	0.29	NO_2	0.71
CH_2F	0.16				



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