All-valence-electron CNDO/2 Calculations of Substituent Effects upon Localisation Energies for Electrophilic Aromatic Substitution

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Summary All-valence-electron CNDO/2 calculations correctly predict the directional and reactivity effects of substituents upon electrophilic aromatic substitution, and indicate that alternation of charge-density in the ring system is a feature of both σ- and π-type molecular orbitals.

THE qualitative theory of substituent effects upon rates of electrophilic aromatic substitution as developed by Ingold and his co-workers[1] was of very great importance in developing the electronic theory of organic chemistry. Subsequent attempts to give quantitative expression to such theories have met with limited success.[2,3] Those that give the most accurate predictions usually incorporate separate and semi-empirical expressions for the mesomeric effect, inductive effect, *etc.*[4,5] This type of separation is of necessity an approximation, since the total energy of the ground and transition states is in reality a single expression, namely the eigenvalue of the appropriate energy operator.

We now report results obtained using the CNDO/2 all-valence-electron treatment of Pople, Santry, and Segal,[6] for localisation energies for *o*-, *m*-, and *p*-substituted benzenes. The model used for the transition state was a protonated σ-complex (the Wheland intermediate.[7])

The Table shows the predicted effect of some substituents upon the rate of electrophilic hydrogen exchange relative to a single position in benzene, "plus" indicating an increase in rate, "minus" a decrease. The predictions agree with the experimental results[1,8] in every case *e.g.* the chloro-group is deactivating but is *ortho–para* directing.

TABLE

Substituent	*ortho*	*meta*	*para*
F	+	−	+
Cl	−	− −	−
Me	+ +	+	+ +
MeO	+	−	+
CF_3	− −	−	− −
NO_2	− −	−	− −

The second important result from these calculations is that in ground and transition states both σ and π charge densities show a regular alternation in magnitude around the ring system.[9] This is in obvious contradiction to the classical concept of a σ inductive effect where the σ charge should fall off sequentially and exponentially through the chain of carbon atoms.[10]

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell, London, 1963, ch. 6.

[2] A. Streitwieser jun., "Molecular Orbital Theory for Organic Chemists," John Wiley, New York and London, 1961, chs. 5 and 11, and references therein.

[3] S. Ehrenson, *Progr. Phys. Org. Chem.*, 1964, **2**, 195.

[4] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3548; and preceding papers.

[5] K. C. C. Bancroft and G. R. Howe, *Tetrahedron Letters*, 1967, 4207.

[6] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 5129; J. A. Pople and G. A. Segal, *ibid.*, p. 5136; *ibid.*, 1966, **44**, 3289.

[7] G. W. Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[8] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[9] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[10] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice Hall, New York, 1941.