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HMO-EIP TREATMENT OF THE NMR PROTON CHEMICAL SHIFTS OF MONOSUBSTITUTED THIOPHENES

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In spite of extensive investigation of the proton NMR spectra of monosubstituted derivatives of thiophene[1)], no simple quantum-chemical interpretation of the substituent effects in this system is known. The only correlation observed[2)] was a linear relationship between the chemical shifts of the corresponding protons in thiophenes and furans. The purpose of this paper is to demonstrate the application of simple HMO-theory to predict the substituent effects in thiophenes.

In our investigations we used HMO methods employing two sets of parameters for Coulomb and resonance integrals, i.e. that of Streitwieser[3)] and that of Derflinger and Lischka[4)], but the relations between pi-electron densities q_r and chemical shifts τ_r were far from linear. Much better correlations were obtained using the so-called HMO-EIP method[5,6,7)]. The pi-electron densities in the positions r are calculated according to the formula[8)]:

$$q_r = q_r^o + \pi_{r,t} \, d\alpha_t(X)$$

where q_r^o is the pi-electron density in position r of unsubstituted molecule, t is the position of substituent X, $\pi_{r,t}$ is the atom-atom polarisability and $d\alpha_t$ (X) is a correction to the Coulomb integral at the t position due to substituent X. Using the EIP-model within the HMO method we obtained:

$$q_r = q_r^o + \pi_{r,t} \, \mathrm{EIP}(X)_t$$

where $\mathrm{EIP}(X)_t$ is the value of the effective inductive parameter (a collection of these values has been published[7)]) of substituent X connected to the ring at position t. The results are collected in Table I for equation $\tau_r = a\, q_r + b$; R denotes the correlation coefficient. The experimental τ_r values for substituted thiophenes with substituents X = H, NO_2, CN, CH_3CO, J, Br, CH_3, CH_3O, NH_2 were taken from the literature[1,2)].

For the protons in ortho- and para-type positions to the substituent (taking into account only the bonds being the hydrocarbon part of the molecule) the correlation coefficients are satisfactory or good according to the Jaffe classification[9)]. The HMO-EIP method is equivalent to the Hammett interpretation of the problem[5,6,7)]

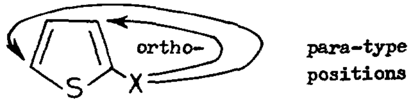

Table I

$$\tau_r = a\, q_r + b$$

Type of compounds	position	slope a	intercept b	correlation coefficient R
2-X-derivatives	3	4.83	- 2.47	0.962
	4	5.88	- 3.66	0.751
	5	9.78	- 8.45	0.901
3-X-derivatives	2	5.95	- 3.97	0.969
	4	3.37	- 8.26	0.937
	5	4.20	- 2.03	0.791
2-X-derivatives, all positions		5.27	- 3.04	0.875
3-X-derivatives, all positions		4.71	- 2.51	0.900
2- and 3-X-deriv.all positions		4.94	- 2.72	0.879

when the para-constants of substituents are used. In fact[10] such correlations between $\tau_r(X)$ and $\sigma_{para}(X)$ were found to have correlation coefficients similar to those in Table I. This observation confirms the suggestion[11] that the substituent effects in thiophene are transmitted through hydrocarbon part of the molecule rather than through the long C-S bonds.

References

(1) S.Gronowitz and R.A.Hoffman, Arkiv Kemi 13,279(1958); 15,45(1959); 16,501 (1960); 16,515(1960); 16,539(1960); 16,563(1960); S.Gronowitz, P.Moses and R.Hakansson, ibid. 16,267(1960); S.Gronowitz, P.Moses and A.Hornfeldt, ibid. 17,237(1961); S.Gronowitz and B.Gestblom, ibid. 18,513(1962); S.Gronowitz and R.A.Hoffman, Acta Chem.Scand. 13,1687(1959); S.Gronowitz, B. Gestblom and R.A.Hoffman, ibid. 15,1201(1961); S.Gronowitz and A.Bugge, ibid. 22,59(1968).
(2) H.Suhr, Anwendungen der kernmagnetischen Resonanz in der organischen Chemie, Springer-Verlag, Berlin, (1965), p.217-221.
(3) A.Streitwieser, Molecular Orbital Theory, J.Wiley, (1961), p.135.
(4) G.Derflinger and H.Lischka, Monatsh.Chem. 100,1003(1969).
(5) W.Kemula and T.M.Krygowski, Tetrahedron Letters, 5135(1968).
(6) T.M.Krygowski, P.Tomasik, Bull.Acad.Polon.Sci.,Ser.Sci.Chim. 18,303(1970).
(7) W.Kemula and T.M.Krygowski, ibid. 15,479(1967).
(8) C.A.Coulson and H.C.Longuet-Higgins, Proc.Roy.Soc. A193,447(1948).
(9) H.H.Jaffe, Chem.Rev. 53,191(1953).
(10) T.M.Krygowski, unpublished results.
(11) E.Scriven and P.Tomasik, Application of Hammett Equation to the Heterocyclic Systems, to be published.