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Simple HMO Calculation of the Substituent Effects in Tropolone Derivatives*[1]

Kimiaki IMAFUKU and Hisashi MATSUMURA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto

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It is well known that the observations concerning the effects of substituents on the rates and equilibrium data for the reaction of benzene derivatives are correlated by the Hammett equation.[1] Further, this equation was found to be applicable to some heterocyclic aromatic compounds, such as pyridines,[2] furans,[3] thiophenes,[4] *etc.*

For tropolone derivatives, which have a seven-membered ring structure, their dissociation constants have been reported to be linearly correlated with Hammett's substituent constants.[5] The chemical shifts of their acidic protons measured in the binary systems of tropolones-pyridine in infinite dilutions were found to be linear with their dissociation constants.[6]

On the other hand, the Hammett equation has been studied with molecular orbital theory in recent years, and it has been found that substituent constants are related to π-electron density[7] as well as localization energy[8] pertinent to reactions.

In order to explain the linearity of pK_a values

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6) Y. Ikegami, T. Ikenoue and S. Seto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 105 (1965).

7) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 285, 1554 (1952); **21**, 415 (1953).

8) F. L. J. Sixma, *Rec. trav. chim.*, **72**, 673, (1953); *Chem. Abstr.*, **47**, 11935[f] (1953); *Rec. trav. chim.*, **73**, 243 (1954); *Chem., Abstr.*, **49**, 6893[g] (1955).

in the dissociation of tropolone derivatives with σ constants, we calculated the π-electron densities of some of 4- and 5-substituted tropolones by using the simple Hückel molecular orbital method, and examined whether or not these calculated values may be correlated with the substituent constants. The substituent constants of *m*- and *p*-positions of benzenes were used for 4- and 5-positions in tropolone derivatives, respectively.

Calculation

Treatment of Oxygen Atoms. The oxygen atoms of tropolones were treated according to Kubo *et al.*[9] The numbering of each atom is shown in Fig. 1. Although the two oxygen atoms are not

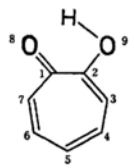

Fig. 1. The numbering for each atom.

identical, they are almost equivalent, owing to the hydrogen bonding and resonance. The molecule is assumed to be symmetrical with respect to a plane which involves the C_5-atom and the middle point of C_1- and C_2-atoms and is perpendicular to the ring. Molecular orbitals are constructed from the π-orbitals of the seven carbon atoms and of the two oxygen atoms. The number of the π-electrons which occupy these orbitals is ten.

The Coulomb integral for the oxygen atoms and the resonance integral for the oxygen-carbon bonds were obtained by repeating calculations until the dipole moment calculated for tropolone agreed reasonably with its observed value. Thus, the finally calculated dipole moment was 3.96 Debyes (observed, 3.53 Debyes[10]). The Coulomb integral for oxygen atoms and the resonance integral for the oxygen-carbon bonds were $\alpha+1.31\beta$ and 1.27β, respectively. The parameter of the Coulomb integral for the carbon atoms attached to the oxygen atoms was assumed to be one-tenth of the value of the latter atoms.

Integral Parameters for Substituents. The integral parameters for substituents were exactly those adopted by Fueno *et al.*[11] in the calculations of the molecular orbitals of benzene derivatives.

Results and Discussion

The π-electron densities q_C and q_O of C_1- or C_2-atoms and O_8- or O_9-atoms, respectively, were calculated and listed in Table 1. When these values are plotted against the Hammett substituent constants σ, linearity among them is obtained as shown in Fig. 2.

Table 1. π-Electron densities

No.	Substituent	σ	q_C	q_O
1	5-OCH_3	−0.268	0.9022	1.7196
2	5-CH_3	−0.170	0.8821	1.7065
3	4-CH_3	−0.069	0.8780	1.7031
4	H	0.000	0.8691	1.6954
5	5-Cl	0.227	0.8459	1.6696
6	5-Br	0.232	0.8431	1.6675
7	5-NO_2	0.778	0.7955	1.5970

No. of substituents are referred to Fig. 2.

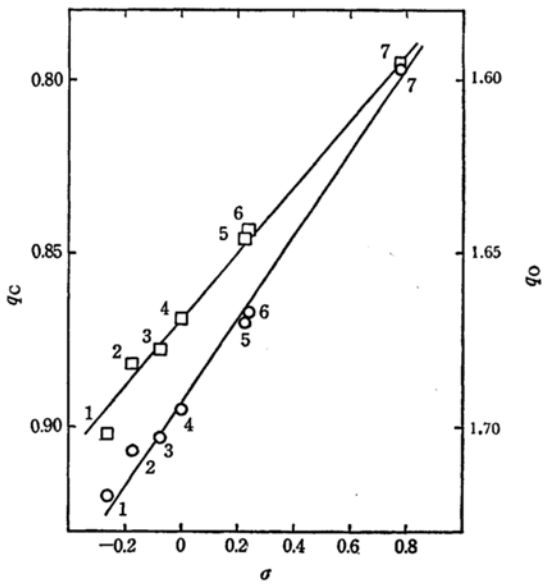

Fig. 2. The relation of π-electron densities of oxygen atoms (○) and adjacent carbon atoms (□) to substituent constants.

The linear correlations of q_C and q_O with σ are compatible with the experimental results that the pK_a values fit the Hammett plot. The linearity of q_O also illustrates the correlation of the chemical shifts of the acidic protons to the substituent constants, since their chemical shifts are influenced by the screening effect of the electrons around the oxygen atom.

Thus, it may be concluded that, for molecular orbital calculations of the seven-membered tropolone derivatives, the integral parameters for substituents obtained in benzene derivatives can be used as they are.

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