Notes

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Electronic Indices of Cations of Monosubstituted Benzene Derivatives by *omega*- Technique

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In the preceding paper[2] in this series on the relations between the H-1 chemical shifts of aromatic ring systems and substituent constants σ_π,[3] numerous electronic indices were presented, and it was shown that these are reliable for the chemical reaction mode ——for example, the cleavage reaction mode of the aromatic ether linkage by metallic sodium in liquid ammonia.[4] In this work, numerous electronic indices for the cationic species of monosubstituted benzene derivatives were estimated with a localization model[5a–d] by *omega*-technique. The mathematical treatments were carried out on an NEAC 7040 Electronic Computer at Osaka University Computer Center using the parameters as in our previous work.[6]

As shown in the following Figures,[7] the *pi*-electron charge density, *pi*-bond order, free valence and electrophilic superdelocalizabilities, other than those of the *meta*-localized species, afforded linear relations with the substituent constants σ_π in the electron releasing substituent group site, whereas the free radical and nucleophilic superdelocalizabilities did not show definite relations, though these are of little practical significance.

Next, the *pi*-electron energies of monosubstituted benzene derivatives and their cations were estimated and then the localization energies were calculated. These localization energies were also found to be linearly related with the substituent constants σ_π in the electron releasing substituent group site, and the magnitudes of these decrease in the order: *meta*>*para*>*ortho*.

pi-Electron Charge Density (*cf.* Fig. 1).

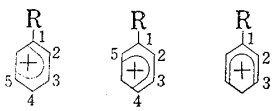
pi-Bond Order (*cf.* Fig. 2).

Free Valence (*cf.* Fig. 3).

Electrophilic Superdelocalizability $S_r^{(E)}$ (*cf.* Fig. 4).

omega Localization Energy L_+^{ω} (*cf.* Fig. 5).

1) Location: *Toneyama 1-1, Toyonaka, Osaka.*
2) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1759 (1970).
3) Y. Yukawa and Y. Tsuno, *Nippon Kagaku Zasshi*, **86**, 873 (1965).
4) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1 (1970).
5) *a*) M.J.S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952); *b*) E.L. Mackor, A. Hofstra and J.H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958); *c*) G.W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); *d*) A. Streitwieser Jr., "Molecular Orbital Theory for Organic Chemists," Wily, New York, 1961, pp. 307—448.
6) Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1090 (1969).
7) Abbreviations: L.O., L.M. and L.P. Localization at the *ortho*, *meta* and *para* position, respectively. The numbers of the carbon atoms are as follows:



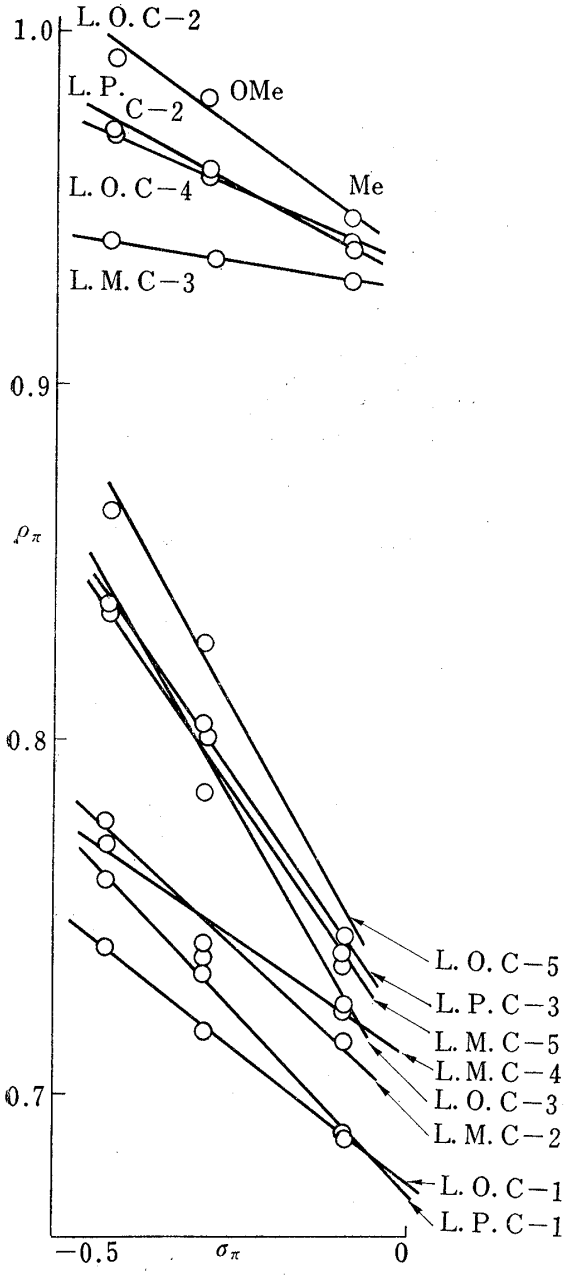


Fig. 1. *pi*-Electron Charge Densities for Cations of Monosubstituted Benzene Derivatives and Substituent Constants σ_π

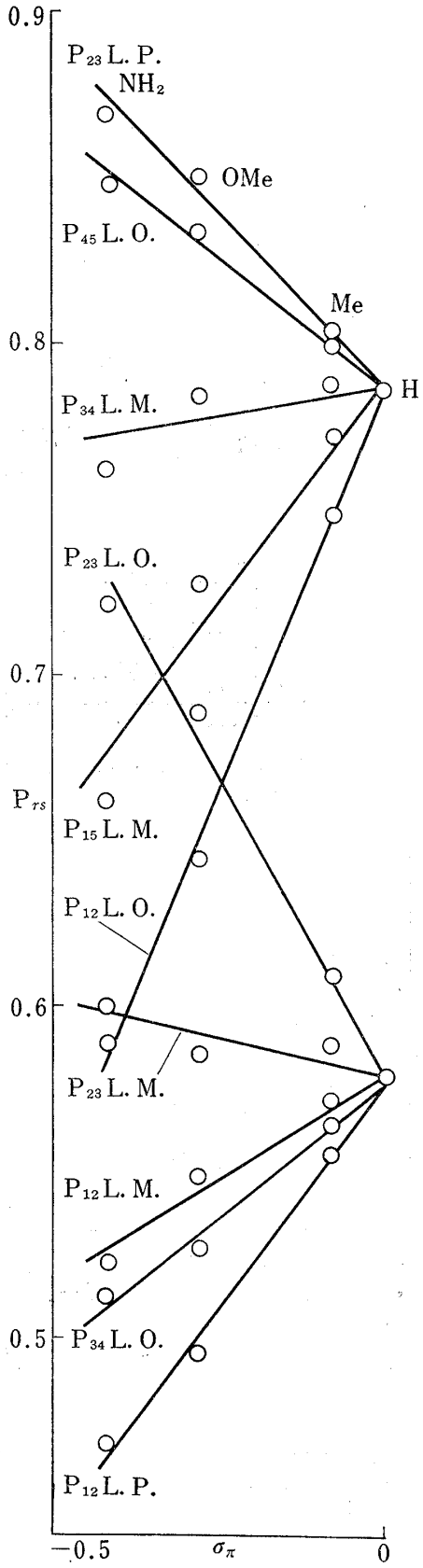


Fig. 2. *pi*-Bond Orders of Cations of Monosubstituted Benzene Derivatives and Substituent Constants σ_π

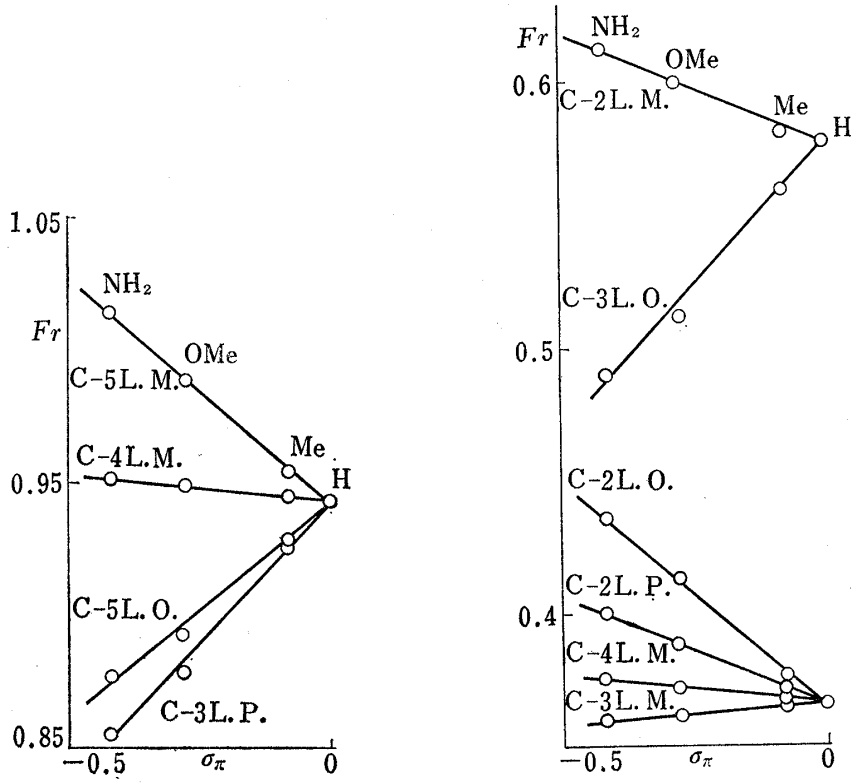


Fig. 3. Free Valences of Cations of Monosubstituted Benzene Derivatives and Substituent Constants, σ_π

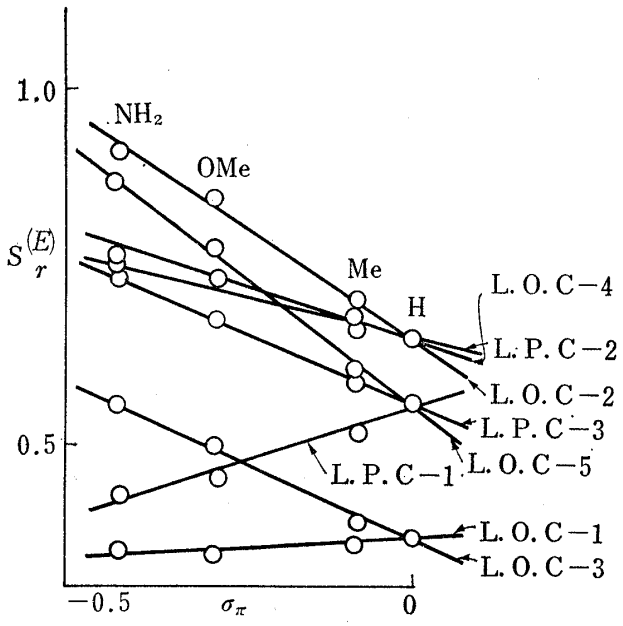


Fig. 4. Electrophilic Superdelocalizabilities $S_r^{(E)}$ of Cations of Monosubstituted Benzene Derivatives and Substituent Constants, σ_π

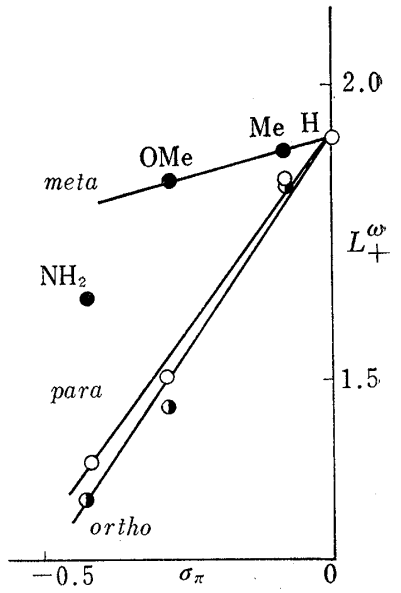


Fig. 5. *omega*-Localization Energies of Cations of Monosubstituted Benzene Derivatives and Substituent Constants, σ_π