C-13 NMR Chemical Shifts and Charge Densities of Substituted Thiophenes—The Effect of Vacant d$^\pi$ Orbitals

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The effect of vacant d$^\pi$ orbitals on the charge distributions of heteroatomic systems containing sulfur and halogens is discussed. From an appropriate estimation of the Coulomb and resonance integrals associated with the vacant d$^\pi$ orbitals, a linear relationship is obtained between charge density and C-13 chemical shift. For a discussion of the reactivity for electrophilic substitution of thiophene, the contribution of d$^\pi$ orbitals of sulfur atom should be taken into account.

The C-13 NMR chemical shift can be empirically correlated with the charge density on a given carbon atom in a molecule.[1] Since charge density is an important quantity for the study of the chemical reactivity of molecule, an investigation of a relationship between the C-13 chemical shift and the charge density will greatly contribute to theoretical organic chemistry. For aromatic hydrocarbons, substituted benzenes and aromatic heterocyclic compounds containing oxygen or nitrogen atoms, π-electron densities calculated by the MO method have a nearly linear relationship with the C-13 chemical shifts.[1] However, such linear correlation has not yet been obtained for the organic compounds containing halogen and sulfur atoms. The reason for this may be due to the contribution of the vacant d-orbitals to the electronic structure of these compounds. In order to elucidate the effect of vacant d-orbitals of sulfur, chlorine, and bromine atoms on the charge distributions, we carried out a MO calculation based on the σ-included ω-HMO method.[2] We have studied the relationship between C-13 NMR chemical shifts and charge densities for pyrrole, furan, thiophene, and its derivatives.

Theoretical

NMR Chemical Shift and Local Charge Density. The quantum theory of NMR chemical shift was developed by Ramsey.[3] He calculated the shielding parameter σ by means of the second order perturbation theory. However, it is difficult to apply his equation to large molecules. The total shielding constant can be expressed by a sum of local contributions. The expression of shielding constant is divided into the following three terms: 1) The diamagnetic contribution or Lamb term for the atom being considered, σ_d. 2) The paramagnetic term for the same atom, σ_p. 3) The contribution from other atoms, σ'. Thus

$$\sigma = \sigma_d + \sigma_p + \sigma' \tag{1}$$

The diamagnetic term, σ_d, can be given by

$$\sigma_d = \frac{e}{3mc^2}\sum_i \langle r_i^{-1} \rangle \tag{2}$$

where $\langle r_i^{-1} \rangle$ is the mean inverse distance of electron i from the nucleous, and the summation is taken over the electrons in the atom considered.

Karplus and Pople[4] pointed out that in a C-13 NMR chemical shift, σ_d makes no significant contribution. The neighbor atom term, σ', is also very small. Thus, the main contribution to the C-13 chemical shift arises from the paramagnetic term, σ_p. Since the NMR measurement in liquid sample deals with a rotational average, σ_p^A associated with a given atom A can be represented by

$$\sigma_p^A = -\frac{e^2h^2}{2m^2c^2\Delta E}\langle r^{-3} \rangle_{2p} \sum_B Q_{AB} \tag{3}$$

where

$$\begin{aligned} Q_{AB} = {} & \frac{4}{3}\delta_{AB}(P_{x_Ax_B}+P_{y_Ay_B}+P_{z_Az_B}) - \frac{2}{3}(P_{y_Ay_B}P_{z_Az_B} \\ & +P_{z_Az_B}P_{x_Ax_B}+P_{x_Ax_B}P_{y_Ay_B}) + \frac{2}{3}(P_{y_Az_B}P_{z_Ay_B} \\ & +P_{z_Ax_B}P_{x_Az_B}+P_{x_Ay_B}P_{y_Ax_B}). \end{aligned} \tag{4}$$

ΔE is a mean excitation energy, and $\langle r^{-3} \rangle_{2p}$ is the mean cube inverse distance of a 2p electron from the nucleous. Σ extends over the atom considered and the neighboring atoms, P_{ab} being the element of charge density and bond order matrix in the unperturbed molecule.

For the sake of simplicity, we make the following approximations; 1) σ-AO of carbon atom can be represented by a sp^2 hybridization. Thus, each σ-AO can be expressed as follows.

$$\left.\begin{aligned} \sigma_1 &= \frac{1}{\sqrt{3}}\phi(2s) + \frac{2}{\sqrt{6}}\phi(2p_x) \\ \sigma_2 &= \frac{1}{\sqrt{3}}\phi(2s) - \frac{1}{\sqrt{6}}\phi(2p_x) + \frac{1}{\sqrt{2}}\phi(2p_y) \\ \sigma_3 &= \frac{1}{\sqrt{3}}\phi(2s) - \frac{1}{\sqrt{6}}\phi(2p_x) - \frac{1}{\sqrt{2}}\phi(2p_y) \end{aligned}\right\} \tag{5}$$

2) ΔE is assumed to be constant for each molecule. The assumption does not seem to be unreliable, since the C-13 NMR chemical shifts of aromatic hydrocarbons are almost constant, in spite of the fact that the average excitation energy changes considerably with the size of molecule. 3) Bond order dependence of the chemical shift is neglected. The C-13 chemical shifts should depend on the bond orders. However, Olah and Mateescu[5] showed that in a series of stable carbonium ions the C-13 chemical shifts can be fairly well correlated with only the charge densities, in spite of the fact that their bond orders vary considerably. Let us assign the charge densities q_1, q_2 and q_3 to each σ-AO's, σ_1, σ_2, and σ_3 of a given carbon atom and q^π to the π-AO, respectively.

If we use the expression

TABLE 1. PARAMETERS ASSOCIATED WITH π AND σ AO's

Atom	δ^{π}_{μ}	ω	Bond	$k^{\pi}_{\mu\nu}$	Atom	δ^{σ}_{μ}	ω
C·	0.0	0.5	C$\equiv$C	1.0	C(sp^2)	0.0	0.25
N·	0.5	0.5	C=C	1.1	C(sp^3)	−0.05	0.25
N:	0.8	0.5	C-C	0.9	O	0.5	0.25
O·	1.0	0.5	C-NO$_2$	0.9	N	0.25	0.25
O:	1.4	0.5	N$\equiv$O	1.1	H	−0.1	0.43
S:	1.0	0.5	C=O	1.2	S	−0.06	0.17
Cl:	1.7	0.5	C-O	0.7	Cl	0.0	0.17
Br:	1.3	0.5	C-S	0.5	Br	−0.2	0.12
			C-Cl	0.6			
			C-Br	0.5		$\beta^{\sigma}_{\mu\nu}=\beta$	

$$\Delta q_i = q_i - 1 \tag{6}$$

we obtain

$$\left.\begin{aligned} \Delta P_{xx} &= \frac{1}{6}(\Delta q_1+4\Delta q_2+\Delta q_3) \\ \Delta P_{yy} &= \frac{1}{2}(\Delta q_1+\Delta q_3) \\ \Delta P_{zz} &= \Delta q^{\pi} \end{aligned}\right\} \tag{7}$$

$$P_{xy}P_{yx} = \frac{(q_3-q_1)^2}{12}.$$

Assuming Slater's rule, the integral $\langle r^{-3}\rangle_{2p}$ can be easily represented by

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24a_0^3}(3.25-0.35\Delta Q)^3 \tag{8}$$

where

$$\Delta Q = \Delta q_1 + \Delta q_2 + \Delta q_3 + \Delta q^{\pi}$$

a_0 means the Bohr radius. Substituting Eqs. (4), (7), and (8) into Eq. (3), we obtain

$$\begin{aligned} \sigma^{A}_{p} = &-K(1-0.108\Delta Q)^3\{9-\Delta q^{\pi}(\Delta q_1+\Delta q_2+\Delta q_3) \\ &-(\Delta q_1\Delta q_2+\Delta q_2\Delta q_3+\Delta q_3\Delta q_1\} \end{aligned} \tag{9}$$

where

$$K = \frac{e^2h^2}{m^2c^2\Delta E}\,\frac{3.25^3}{216a_0^3}$$

Since Δq_i is usually very small, we can, to a first approximation, neglect higher terms. Consequently, Eq. (9) can be rewritten as

$$\sigma^{A}_{p} = -9K(1-0.324\Delta Q) \tag{10}$$

showing a linear relationship between C-13 NMR chemical shift and charge density. The present expression is the same as that obtained by Yonezawa *et al.*[6] for saturated hydrocarbon systems. As Alger *et al.*[7] pointed out, when orbital contraction of σ-AO is considered, Eq. (10) is modified as follows:

$$\sigma_{C^{13}} = a\Delta q^{\pi} + b\Delta Q - c\Delta P \quad (a=b) \tag{11}$$

B. MO calculation

In the present study, the charge densities were calculated by the σ-included ω-HMO method which is summarized as follows: As σ-bonds are almost localized between two atoms, we can approximately describe them by means of the two center MO. ω-Technique is used in order to take so-called inductive effect of a heteroatom through bonds into account. Thus, the polarized σ-framework is determined by the two center ω-HMO method. The π-electrons are regarded as moving over this σ-framework. The π-densities, then are dependent on the σ- and π-charge densities. We neglect the effect of π-charge densities on the σ-bonds. The net charge ΔQ_{μ} on the atom μ is given by

$$\Delta Q_{\mu} = \Delta Q^{\sigma}_{\mu} + \Delta q^{\pi}_{\mu}. \tag{12}$$

The Coulomb integrals associated with the σ- and π-AO's of the μ-th atom, α^{σ}_{μ} and α^{π}_{μ} are expressed as follows:

$$\begin{aligned} \alpha^{\sigma}_{\mu} &= \alpha^{\sigma}_{c} + \delta^{\sigma}_{\mu}\beta + \omega^{\sigma}\Delta Q^{\sigma}_{\mu} \\ \alpha^{\pi}_{\mu} &= \alpha^{\pi}_{c} + \delta^{\pi}_{\mu}\beta + \omega^{\pi}\Delta Q_{\mu} \end{aligned}$$

The resonance integral for the μ-ν bond, $\beta_{\mu\nu}$, is represented by

$$\beta^{\sigma}_{\mu\nu} = k^{\sigma}_{\mu\nu}\beta, \qquad \beta^{\pi}_{\mu\nu} = k^{\pi}_{\mu\nu}\beta.$$

The values of ω's, δ_{μ}'s and $k_{\mu\nu}$'s, used are summarized in Table 1.

Since the compounds we considered include sulfur and halogen atoms, the contribution of d-orbitals should be taken into account. We consider only the vacant d$^{\pi}$AO's in our MO calculation. The Coulomb and resonance integrals associated with d$^{\pi}$AO's are estimated with use of atomic energy levels[8] and overlap integrals between 2pπ and 3dπ AO's. Their values are given in Table 2.

TABLE 2. PARAMETERS ASSOCIATED WITH d$^{\pi}$ ORBITALS

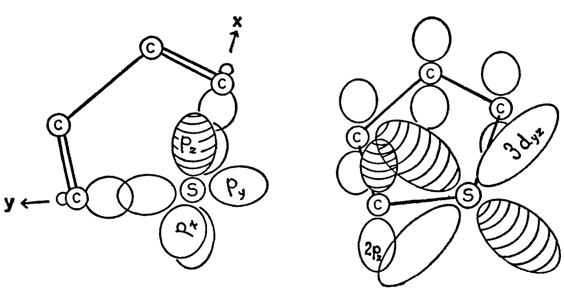
Atom	$\delta^{\pi}_{\mu d}$	ω	Bond	$k_{\mu\nu}$
S	−1.0	0.4	C-S	0.5
Cl	−0.8	0.4	C-Cl	0.5
Br	−0.7	0.4	C-Br	0.5

Results and Discussion

Charge Density and C-13 *NMR Chemical Shift.* The effect of substitution on the electron distribution is quite important for discussing the chemical reactivity of a substituted compound. The influence of the heteroatoms on the charge density of a given carbon atom can be described in terms of mesomeric and inductive effects. Takahashi *et al.*[9] reported the C-13 NMR chemical shifts of thiophene and its derivatives and presented some interesting results. However, they could not obtain inter-relationship between the charge density and the chemical shift. In this paper, the experimental data are quoted from their work. From the NMR measurements, it is expected that in pyrrole and furan the charge densities of C_2 positions are smaller than those of C_3 positions, because of the lower chemical shifts. However, in thiophene the chemical shifts of both positions are almost the same.

In Fig. 1, the charge densities of substituted thiophenes calculated by σ-included ω-HMO method are plotted against the chemical shifts, neglecting the contribution of d-orbitals. The plots deviate considerably from lineality. This might be caused by the neglect of contribution of vacant d-orbitals. The results of thiophene derivatives calculated by CNDO/2 method are shown in Fig. 2. The CNDO/2 method takes explicitly the contribution of d-orbitals into account. However, no improvement could be obtained. This could be attributed to an overestimation of the contribution of d-orbitals at C_3 and C_4 positions. The failure is due to the estimation of parameters associated with d-orbitals.

In our calculations, the resonance integrals between $d\pi$ and $2p\pi$ AO's of non-neighbors are completely neglected. In thiophene, the C–S–C bond angle is known to be almost 90°.[10] We, therefore, assumed σ AO's of sulfur atom are not hybridized but are pure $3p_x$ or $3p_y$ AO's. Thus, $3d_{xz}$ and $3d_{yz}$ should be directed toward each C-S bonds as shown in Fig. 3. We considered only one $d\pi$ AO in a halogen atom, Cl or Br. In Figs. 4 and 5, the charge densities calculated by σ-included ω-HMO method, including



(a) (b)

Fig. 3. p and d orbital profile for thiophene. (a) 3p-sp^3 overlap, (b) $3d_{yz}$-$2p^{\pi}$ overlap.

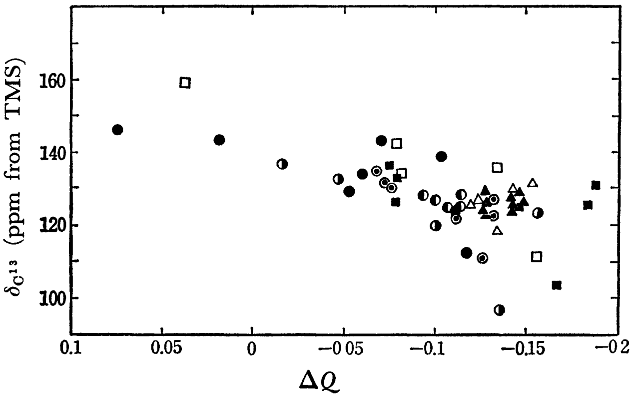


Fig. 1. C-13 NMR chemical shifts *vs.* charge densities of substituted thiophenes (σ-included ω-HMO method without d orbitals).

● C_2 of 2-substituted thiophene, ■ C_3 of 2-substituted thiophene, ▲ C_4 of 2-substituted thiophene, ⊙ C_5 of 2-substituted thiophene, ◑ C_2 of 3-substituted thiophene, □ C_3 of 3-substituted thiophene, △ C_4 of 3-substituted thiophene, ◐ C_5 of 3-substituted thiophene.

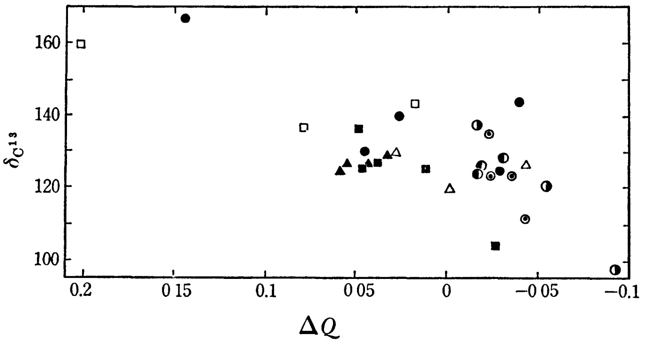


Fig. 2. C-13 NMR chemical shifts *vs.* charge densities of substituted thiophenes (CNDO/2 method).

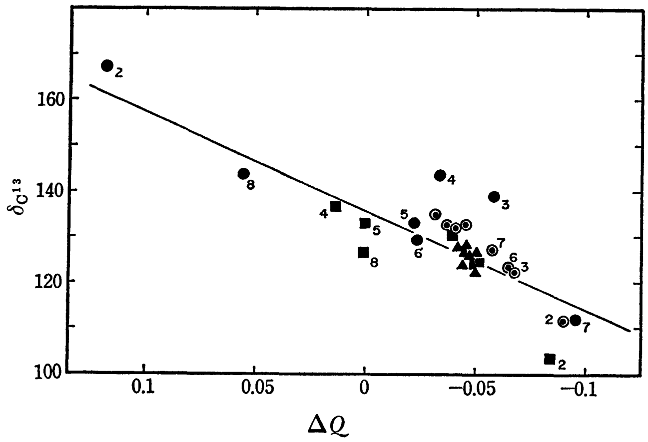


Fig. 4. C-13 NMR chemical shifts *vs.* charge densities of 2-substituted thiophenes (σ-included ω-HMO method considering d^{π} orbitals). 1; H, 2; OCH_3, 3; CH_3, 4; CHO, 5; $COOCH_3$, 6; Cl, 7; Br, 8; NO_2.

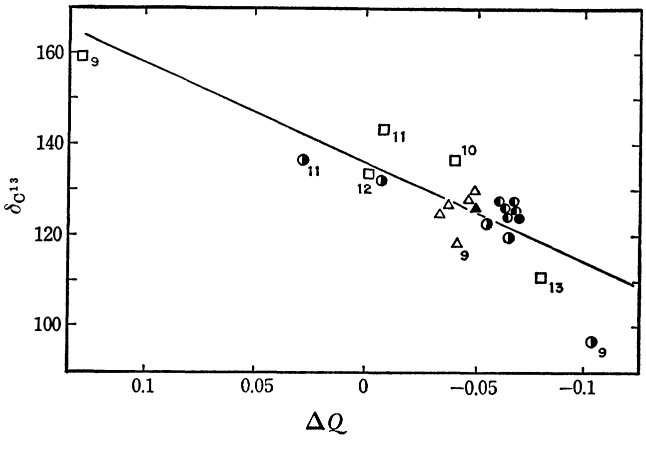
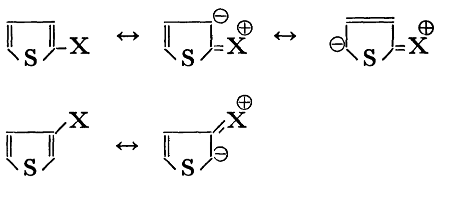


Fig. 5. C-13 NMR chemical shifts *vs.* charge densities of 3-substituted thiophenes (σ-included ω-HMO method considering d^{π} orbitals). 9; OCH_3, 10; CH_3, 11; CHO, 12; $COOCH_3$, 13; Br.

dπ orbitals, are plotted against the chemical shifts. We see a better correlation than the results without dπ orbitals. The plots of α-positions of methyl, carbonyl, and cyano derivatives deviated considerably. This deviation may be caused by another factor, such as anisotropy effect.

The mesomeric effect of a substituent on the charge distribution is an important problem in theoretical organic chemistry. The resonance structure of thiophene derivative having an electron donating group can be written as follows:



Thus, the π-electron densities on the β and δ carbons vary a great deal with mesomeric effect of substituent. In the case of δ-carbon of 2-substituted thiophene, a plot of π-electron density against the corresponding C-13 NMR chemical shift has distinct lineality, as shown in Fig. 6. A similar plot shows no lineality, when the contribution of dπ orbitals is neglected. This fact suggests us that, in order to investigate the mesomeric effect in a heteroatomic system containing S, P, Cl, or Br atoms, the contribution of the vacant dπ orbitals should be taken into consideration. When we take dπ orbitals of sulfur atom into consideration, the plots of pyrrole, furan, and thiophene show a better lineality.

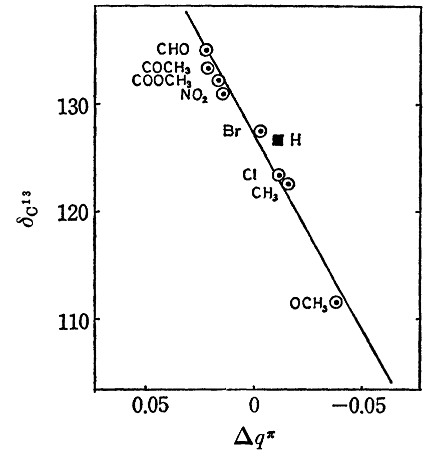


Fig. 6. C-13 NMR chemical shifts *vs.* π-charge densities on δ-carbons in substituted thiophenes.

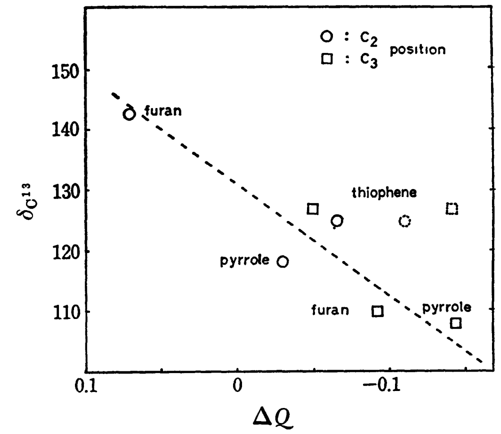


Fig. 7. C-13 NMR chemical shifts *vs.* charge densities of pyrrole, furan, and thiophene. ○ and □ represent the results of thiophene, neglecting d^π orbitals.

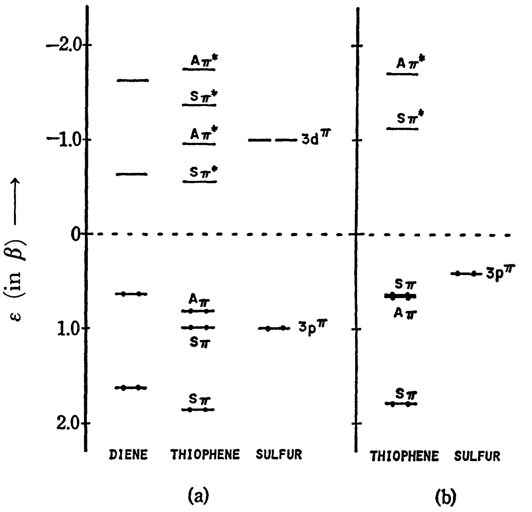


Fig. 8. Correlation diagram of π-MO's of diene fragment, sulfur atom, and thiophene. (a) With d^π orbitals, (b) without d^π orbitals.

TABLE 3. MO AND MO ENERGIES OF THIOPHENE

			Case i); without d^π orbitals				
MO energy	$\alpha+1.793\beta$	$\alpha+0.678\beta$	$\alpha+0.668\beta$	$\alpha-1.107\beta$	$\alpha-1.705\beta$		
Symmetry	S	A	S	S	A		
S	0.419	0.0	0.815	0.401	0.0		
C_2	0.423	0.588	0.059	−0.563	0.392		
C_3	0.483	0.392	−0.405	0.320	−0.588		
			Case ii); with d^π orbitals				
MO energy	$\alpha+1.872\beta$	$\alpha+0.992\beta$	$\alpha+0.806\beta$	$\alpha-0.563\beta$	$\alpha-0.958\beta$	$\alpha-1.379\beta$	$\alpha-1.772\beta$
Symmetry	S	S	A	S	A	S	A
S(p^π)	0.495	−0.816	0.0	−0.241	0.0	0.175	0.0
C_2	0.410	0.043	0.581	0.388	0.009	−0.424	−0.404
C_3	0.452	0.406	0.369	−0.296	−0.299	0.207	0.524
S(d^π)	0.072	0.011	0.164	0.483	0.641	0.512	0.250

Contribution of dπ Orbital to Frontier MO's. The chemical reactivity of conjugated system can be interpreted, to a first approximation, by the frontier MO's, HOMO and LUMO.11) The MO's and their energies of thiophene are summarized in Table 3. MO spacings are shown in Fig. 8. We see that if dπ orbitals are neglected, ϕ_2 and ϕ_3 are almost degenerate each other. The frontier electron densities at C_2 and C_3 are calculated to be 0.350 and 0.318, respectively. It is known experimentally that the C_2 position is most reactive. Thus, this tendency can not be interpreted by the calculation of case i) in Table 3. On the other hand, in the calculation of case ii), the orbital degeneracy of HOMO's is removed by the contribution of vacant dπ orbitals. The frontier electron density at C_2 becomes much larger than that at C_3. This shows that in order to explain the reactivity of electrophilic substitution of thiophene, we should consider vacant dπ orbitals. In the discussion of the Diels-Alder reaction, Lert and Trindle12) pointed out the importance of the contribution of dπ orbitals in thiophene.

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