Some Studies of the Inductive Effect

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Inductive effect has long been recognized as a useful idea in organic chemistry, particularly in relation to chemical reactivity problems. We can see the occurrence of this effect among the values of electric dipole moment of various molecules, most remarkably in some chain homologues.

In most cases, it is relatively a simple matter to take this effect qualitatively into consideration, but rather difficult quantitatively. In recent years, some developments were brought about on the latter point. Morino, Miyagawa and Oiwa[1] have established an empirical rule successfully applicable to the electric moments of various haloalkanes. Smith, Ree, Magee and Eyring[2] have developed a semi-classical theory advantageous for the application to chemical reactivity problems. Cahill and Mueller[3] have treated the effect of carboxylic group on the adjacent C-C bond quantum-mechanically.

For all these and previous studies, however, the theoretical basis of inductive effect can not yet be considered to be well established enough for quantitative applications. Now, in this paper, an approximate method will be developped to

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[1] Y. Morino, I. Miyagawa and J. Oiwa, *Botyu-kagaku*, **15**, 181 (1950). I. Miyagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 1061 (1954).

[2] R. P. Smith, T. Ree, J. L. Magee and H. Eyring, *J. Am. Chem. Soc.*, **73**, 2263 (1951).

[3] J.M. Cahill and C.R. Mueller, *J. Chem. Phys.*, **24** 513 (1956).

estimate the details of induced electric moment in non-conjugate systems, with some illustrative applications to haloalkane molecules.

An Approximate Expression of the Polarity of Bond

The object of the present work is the description of saturated systems such as substituted paraffin compounds. It is a conclusion of chemical experiences that the bonding electron pair of each separate bond in such a molecule can be regarded as fairly well localized. For such systems, the treatment based on bond orbital wave functions may be a fairly good approximation.

The bond orbital ϕ_i of the i-th bond A-B may be approximated by the localized molecular orbital as given by Eq. 1,

$$\phi_i(1)=a_i\chi_{\mathrm{A}i}(1)+b_i\chi_{\mathrm{B}i}(1) \qquad (1)$$

where $\chi_{\mathrm{A}i}$ and $\chi_{\mathrm{B}i}$ are the valence atomic orbitals of both atoms. Each ϕ_i is subjected to the normalization condition, Eq. 2.

$$\int\phi_i^*(1)\phi_i(1)d\tau_1=a_i^2+2a_ib_iS_i+b_i^2=1 \qquad (2)$$

$$S_i=\int\chi_{\mathrm{A}i}^*(1)\chi_{\mathrm{B}i}(1)d\tau_1$$

A quantity Q_i is also used as defined in Eq. 3, named "bond charge" by Mulliken[4], in the present formulation as the principal parameter.

$$Q_i=a_i^2-b_i^2=(a_i^2+a_ib_iS_i)-(b_i^2+a_ib_iS_i) \qquad (3)$$

Now, when the complete localization of bond obitals were assumed, the electronic energy of a molecule may be approximately expressed by Eq. 4, the basic elucidation for which is given in appendix.

$$E=2\sum H_i+\sum_{i,j}(2-\delta_{ij})J_{ij} \qquad (4)$$

$$H_i=\int\phi_i^*(1)h_1\phi_i(1)d\tau_1 \qquad (5)$$

$$J_{ij}=\int\phi_i^*(1)\phi_j^*(2)(e^2/r_{12})\phi_i(1)\phi_j(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (6)$$

In Eq. 4, H_i and J_{ij} are the bare-nuclear field orbital energy and the coulomb integral as given in Eqs. 5 and 6 respectively, where h_1 is the bare nuclear field energy Hamiltonian, r_{12} the interelectronic distance, and $\delta_{ij}=1$ or 0 for $i=j$ or $\neq j$.

With the ϕ_i given in Eq. 1, H_i can be written as Eq. 7 taking Eq. 2 into consideration.

$$\begin{aligned}H_i=&(1/2)(\alpha_{\mathrm{A}}^i+\alpha_{\mathrm{B}}^i)\\&+(1/2)Q_i(\alpha_{\mathrm{A}}^i-\alpha_{\mathrm{B}}^i)+2a_ib_i\beta_i\end{aligned} \qquad (7)$$

$$\left.\begin{aligned}\alpha_{\mathrm{A}}^i&=\int\chi_{\mathrm{A}i}^*(1)h_1\chi_{\mathrm{A}i}(1)\mathrm{d}\tau_1,\\ \alpha_{\mathrm{B}}^i&=\int\chi_{\mathrm{B}i}^*(1)h_1\chi_{\mathrm{B}i}(1)\mathrm{d}\tau_1\\ \beta_i&=\int\chi_{\mathrm{A}i}^*(1)h_1\chi_{\mathrm{B}i}(1)\mathrm{d}\tau_1\\&\qquad-(1/2)S_i(\alpha_{\mathrm{A}}^i+\alpha_{\mathrm{B}}^i)\end{aligned}\right\} \qquad (8)$$

Further, it is transformed to Eq. 9 by expanding $2a_ib_i$ into a power series of Q_i.

$$\begin{aligned}H_i=&(1/2)(\alpha_{\mathrm{A}}^i+\alpha_{\mathrm{B}}^i)+(\beta_i/1+S_i)\\&-(1/2)(\alpha_{\mathrm{A}}^i-\alpha_{\mathrm{B}}^i)Q_i-(1/2)\beta_iQ_i^2\\&-(1/8)(1-S_i^2)\beta_iQ_i^4\cdots\cdots\end{aligned} \qquad (9)$$

In order to express J_{ij} by a simple function of Q_i's, we shall adopt the approximate equation (10)[4].

$$\phi_i^*\phi_i\approx(1+Q_i)\chi_{\mathrm{A}i}^*\chi_{Ai}+(1-Q_i)\chi_{\mathrm{B}i}^*\chi_{\mathrm{B}i} \qquad (10)$$

Then Eq. 11 is obtained, where the coefficients C^{ij}'s take the form of Eq. 12.

$$J_{ij}=C_0^{ij}+C_i^{ij}Q_i+C_j^{ij}Q_j+C_{ij}^{ij}Q_iQ_j \qquad (11)$$

$$\left.\begin{aligned}C_0^{ij}&=(1/4)[(ii/jj)+(ii/j'j')\\&\qquad+(i'i'/jj)+(i'i'/j'j')]\\ C_i^{ij}&=(1/4)[(ii/jj)+(ii/j'j')\\&\qquad-(i'i'/jj)-(i'i'/j'j')]\\ C_j^{ij}&=(1/4)[(ii/jj)-(ii/j'j')\\&\qquad+(i'i'/jj)-(i'i'/j'j')]\\ C_{ij}^{ij}&=(1/4)[(ii/jj)-(ii/j'j')\\&\qquad-(i'i'/jj)+(i'i'/j'j')]\end{aligned}\right\} \qquad (12)$$

$$(pq/rs)=\int p^*(1)s^*(2)(e^2/r_{12})q(1)r(2)\mathrm{d}\tau_1\mathrm{d}\tau_2,$$

(i, i', j, j' represent $\chi_{\mathrm{A}i}$, $\chi_{\mathrm{B}i}$, $\chi_{\mathrm{A}'j}$, $\chi_{\mathrm{B}'j}$, respectively).

Consequently, the total energy E is approximately given by Eq. 13.

$$\begin{aligned}E=\sum_i\{&(\alpha_{\mathrm{A}}^i+\alpha_{\mathrm{B}}^i)+(2\beta_i/1+S_i)+\sum_j(2-\delta_{ij})C_0^{ij}\\&+Q_i[(\alpha_{\mathrm{A}}^i-\alpha_{\mathrm{B}}^i)+2\sum_j(2-\delta_{ij})C_i^{ij}]\\&-(\beta_i-C_{ij}^{ij})Q_i^2+\sum_{j\neq i}2C_{ij}^{ij}Q_iQ_j\\&-(1/4)(1-S_i^2)\beta_iQ_i^4\cdots\cdots\}\end{aligned} \qquad (13)$$

Now, in Eq. 13, each Q_i has to take the value so as to minimize E, according to the variation principle; that is, Eq. 14 must be fulfiled by all Q_n's.

$$\partial E/\partial Q_n=0 \qquad (14)$$

This equation takes the form of an infinite series in Q's in the present formulation. But, the Q's appearing in the

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[4] R. S. Mulliken, *J. chim. phys.*, **46**, 497, 675 (1949).

systems in which we are interested are supposed to be fairly small against unity, and the approximate equation 15 may serve the purpose, where the quadratic and successive higher terms were neglected, and $\gamma_n = -\beta_n + C_{nn}^{nn}$.

$$[(\alpha_A^n - \alpha_B^n) + \sum_i 2(2-\delta_{ni})C_n^{ni}] + 2\gamma_n Q_n + 4\sum_{i \neq n} C_{ni}^{ni} Q_i = 0 \tag{15}$$

If we could solve the simultaneous equations resulting from Eq. 15, approximate $Q's$ for all separate bonds might be determined. But it seems hardly possible, at present, because of the difficulty in fixing the values of necessary integrals, especially α and γ. In the present calculation, however, we do not look for the $Q_i's$ themselves, but their changes due to some change in molecular constitution.

Now, we shall consider about the changes of Q of residual C–H or C–C bonds, due to subsitution by some polar group. In such a case, a hydrocarbon molecule before the substitution is taken as the reference constitution, for which Eq. 15 is written as Eq. 16; where Q_i^0 represents the magnitude in the reference constitution.

$$[(\alpha_A^n - \alpha_B^n) + \sum_i 2(2-\delta_{ni})C_n^{ni}] + 2\gamma_n Q_n^0 + 4\sum_{i \neq n} C_{ni}^{ni} Q_i^0 = 0 \tag{16}$$

When m C–H bonds corresponding to 1-st to m-th in reference constitution were replaced by other kind of polar bond, e. g. $CX_1 \cdots\cdots CX_m$, then Eq. 15 is written as Eq. 17 for each C–H or C–C bond in substituted constitution;

$$[(\overline{\alpha}_A^n - \overline{\alpha}_B^n) + \sum_{i=1}^m 4\overline{C}_n^{ni} + \sum_{i=m+1}^z 2(2-\delta_{ni})C_n^{ni}] + 2\gamma_n Q_n + 4\sum_{\substack{i=m+1 \\ \neq n}}^z C_{ni}^{ni} Q_i + 4\sum_{i=1}^m \overline{C}_{ni}^{ni} Q_i = 0 \tag{17}$$

(z: the final number of bonds).

where the bar above some quantities implies the change due to substituion. It is to be noted, here, that β (and consequently γ) may be taken as fairly invariable at the substitution⁴⁾. Subtracting Eq. 16 from Eq. 17, Eq. 18 is obtained.

$$[(\overline{\alpha}_A^n - \alpha_A^n) - (\overline{\alpha}_B^n - \alpha_B^n) + 4\sum_{i=1}^m (\overline{C}_n^{ni} - C_n^{ni})] + 2\gamma_n (Q_n - Q_n^0) + 4\sum_{i=1}^m (\overline{C}_{ni}^{ni} Q_i - C_{ni}^{ni} Q_i^0) + 4\sum_{\substack{i=m+1 \\ \neq n}}^z C_{ni}^{ni} (Q_i - Q_i^0) = 0 \tag{18}$$

In this equation, the braced term, which represents the change of penetration energy due to the substitution (cf. Eq. 12), may well be neglected as fairly small. Thus, Eq. 18 may be simplified as follows:

$$\gamma_n (Q_n - Q_n^0) + 2\sum_{i=1}^m (\overline{C}_{ni}^{ni} Q_i - C_{ni}^{ni} Q_i^0) + 2\sum_{\substack{i=m+1 \\ \neq n}}^z C_{ni}^{ni} (Q_i - Q_i^0) = 0 \tag{19}$$

(for every unsubstituted bond, n).

On the other hand, for change of Q of the substituent bond C–X, the simplest molecule CH_3X is taken as the reference constitution. Then the similar procedure as above gives Eq. 20 finally.

$$\gamma_n (Q_n - Q_n^0) + 2\sum_{\substack{i=1 \\ \neq n}}^z (\overline{C}_{ni}^{ni} Q_i - C_{ni}^{ni} Q_i^0) = 0 \tag{20}$$

(for every substituted bond, n).

In the following calculation, Eqs. 19 and 20 shall be used together to calculate the approximate magnitudes of induced polarity $(Q_n - Q_n^0)$.

Some Reference to Molecular Polarizability

Now, it is helpful for the present study to treat the molecular polarizability from the same point of view as above. The polarizability along one of the principal axes y of a molecule is given by Eq. 21, where f is a homogeneous electric field parallel to y-axis.

$$\alpha_y = -(\mathrm{d}^2 E / \mathrm{d}f^2)_{f=0} \tag{21}$$

The total energy E under the field is written as Eq. 22 which includes several f-dependent terms in addition to Eq. 13.

$$E = \sum_i \{(\alpha_A^i + \alpha_B^i) + (2\beta_i / 1 + S_i) + \sum_j (2-\delta_{ij}) C_0^{ij} - f(y_A^i + y_B^i) + Q_i[(\alpha_A^i - \alpha_B^i) + \sum_j 2(2-\delta_{ij}) C_i^{ij} - f(y_A^i - y_B^i)] + \gamma_i Q_i^2 + \sum_{j \neq i} 2C_{ij}^{ij} Q_i Q_j - (1/4)(1-S_i^2)\beta_i Q_i^4 \cdots\} \tag{22}$$

where y_A^i and y_B^i denote the average positions of electrons as given by

$$y_A^i = \int \chi_{Ai}^*(1) y_1 \chi_{Ai}(1) \mathrm{d}\tau_1 ,$$

and $$y_B^i = \int \chi_{Bi}^*(1) y_1 \chi_{Bi}(1) \mathrm{d}\tau_1 \tag{23}$$

where y_1 is the y-coordinate of electron 1. Then, Eq. 24 results from Eqs. 21 and 22.

$$\alpha_y = \sum_i \{2Q_i (y_A^i - y_B^i - 2\sum_{j \neq i} C_{ij}^{ij} \dot{Q}_j)$$

$$+\dot{Q}_i^2[-2\gamma_i+3(1-S_i^2)\beta_i Q_i^2+\cdots]$$
$$-\ddot{Q}_i[\alpha_A^i-\alpha_B^i+2\textstyle\sum_j(2-\delta_{ij})C_i^{ij}+2\gamma_i Q_i$$
$$+4\sum_{j\neq i}C_{ij}^{ij}Q_j-(1-S_i^2)\beta_i Q_i^3+\cdots]\}_{f=0} \tag{24}$$

$$\dot{Q}=(\mathrm{d}Q_i/\mathrm{d}f)_{f=0}, \quad \ddot{Q_i}=(\mathrm{d}^2Q_i/\mathrm{d}f^2)_{f=0} \tag{25}$$

On the other hand, all $Q's$ have to satisfy Eq. 26 which corresponds to Eq. 14 in the last section.

$$\partial E/\partial Q_i=\alpha_A^i-\alpha_B^i+\textstyle\sum_j 2(2-\delta_{ij})C_i^{ij}-f(y_A^i-y_B^i)$$
$$+2\gamma_i Q_i+\sum_{j\neq i}4C_{ij}^{ij}Q_j-(1-S_i^2)\beta_i Q_i^3+\cdots=0 \tag{26}$$

Since this equation should hold for arbitrary value of f, Eq. 27 is available also.

$$[\mathrm{d}(\partial E/\partial Q_i)/\mathrm{d}f]_{f=0}=-(y_A^i-y_B^i)+2\gamma_i\dot{Q}_i$$
$$+\sum_{j\neq i}4C_{ij}^{ij}\dot{Q}_j-3(1-S_i^2)\beta_i(Q_i)_{f=0}^2\dot{Q}_i+\cdots=0 \tag{27}$$

Thus, Eq. 28 is obtained finally from the combination of Eqs. 24 and 27. It shows also that the approximation employed thus far is consistent with the expression of bond moment given by Eq. 29.

$$\alpha_y=\textstyle\sum_i\dot{Q}_i(y_A^i-y_B^i) \tag{28}$$

$$m_i=Q_i(y_A^i-y_B^i) \tag{29}$$

The values of γ_i, which is essential to carry out the calculation formally given in the last section, can be determined by solving Eq. 28 simultaneously with Eq. 27′,

$$(y_A^i-y_B^i)-2\gamma_i\dot{Q}_i-\sum_{j\neq i}4C_{ij}^{ij}\dot{Q}_j=0 \tag{27′}$$

where the fourth and further terms in Eq. 27 have been neglected. It must be noticed here, however, that the α_y in Eq. 28 represents only longitudinal contributions of bond polarizabilities dismissing the transverse; that is, as to methane, for example, $\alpha_y=(4/3)\alpha_{L(CH)}$, where $\alpha_{L(CH)}$ is the longitudinal bond polarizability determined empirically for CH bond. We solve Eqs. 28 and 27′ with such an α_y and theoretically calculated C_{ij}^{ij} and $(y_A^i-y_B^i)$, giving γ_{CH}. Next, γ_{CC} can be determined by similar calculation for ethane molecule, where γ_{CH} obtained above be available. In this way, the values of γ_i for several bonds were evaluated presuming that they are actually definite by bond species, and given in Table I.

TABLE I

Bond A-B	C-H	C-C	C-Cl	C-Br	unit
γ_{AB}	0.396	0.309	0.368	0.388	e^2/a_0
α_L(AB)	7.9*	18.8*	36.7*	50.4*	10^{-25} cc.
$y_A^{AB}-y_B^{AB}$	1.291	1.372	2.461	2.915	a_0**

* H. A. Stuart, "Die Struktur des freien Molekuls" pp. 449, Springer, (1952).

** Bohr radius.

Illustrative Examples

Some examples of the calculation for the systems of the simplest type will be shown. Throughout them, Q_{CH}^0 and Q_{CC}^0 have presumably been taken equal to zero, and, necessary integrals such as $C_{ij}^{ij}(i\neq j)$, y_A^i and y_B^i were computed with Slater atomic orbitals[5] assuming sp^3 tetrahedral hybridization for carbon, except C_{ij}^{ij} of non-neighbors which were approximated by point charge model.

Example I. CH_3X (cf. Fig. 1)

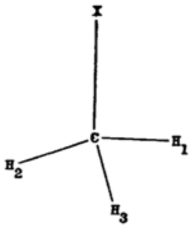

Fig. 1

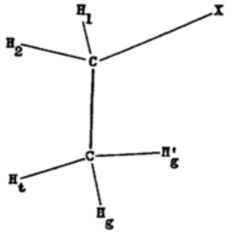

Fig. 2

For the CH bond of this type of molecule, Eq. 19 is written as Eq. i,

$$\gamma_{CH}Q_{CH}+2(C_{CH,CX}Q_{CX}+2C_{1,2}Q_{CH})=0 \tag{i}$$

where the superscripts in C_{ij}^{ij} were dropped.

On the other hand, this type is taken as the reference constitution for all other X-substituted systems in the sense stated under Eq. 19. Therefore, Q_{CX} is taken so as the electric moment to be in accord with observed value. That is, Eq. ii is adopted as the second condition,

$$M_{exp}(CH_3X)=M_{cal}(CH_3X)=m_{\overrightarrow{CX}}+m_{\overleftarrow{CH}} \tag{ii}$$

where each bond moment is given by Eqs. iii and iv.

$$m_{\overleftarrow{CH}}=(1+Q_{CH})y_C^{CH}+(1-Q_{CH})y_H^{CH} \tag{iii}$$

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5) J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

$$m_{\overrightarrow{\mathrm{CX}}}=(1-Q_{\mathrm{CX}})y_{\mathrm{C}}^{\mathrm{CX}}+(1+Q_{\mathrm{CX}})y_{\mathrm{X}}^{\mathrm{CX}} \qquad \text{(iv)}$$

Then, Q_{CH} and Q_{CX} can be determined from these equations, and induced bond moment is given by Eq. v.

$$\Delta m_{\mathrm{CH}}=Q_{\mathrm{CH}}(y_{\mathrm{C}}^{\mathrm{CH}}-y_{\mathrm{H}}^{\mathrm{CH}}) \qquad \text{(v)}$$

Example II. C_2H_5X (cf. Fig. 2)

The staggered form is assumed in this case. Then, Eq. 19 is written down as Eqs. iv∼ix for the adjacent, *trans*, and *gauche* C–H bonds as to C–X bond respectively.

$$\begin{aligned}&\gamma_{\mathrm{CH}}Q_{\mathrm{CH}}+C_{1,\mathrm{CX}}Q_{\mathrm{CX}}+C_{1,2}Q_{\mathrm{CH}}+C_{\mathrm{CH,CC}}Q_{\mathrm{CC}}\\&\quad+C_{1,g}(Q_{\mathrm{CH}g}+Q_{\mathrm{CH}t})+C_{1,t}Q_{\mathrm{CH}g}=0 \qquad \text{(vi)}\end{aligned}$$

$$\begin{aligned}&\gamma_{\mathrm{CH}}Q_{\mathrm{CH}g}+C_{g,\mathrm{CX}}Q_{\mathrm{CX}}+(C_{1,g}+C_{1,t})Q_{\mathrm{CH}}\\&\quad-C_{\mathrm{CH,CC}}Q_{\mathrm{CC}}+C_{1,2}(Q_{\mathrm{CH}g}+Q_{\mathrm{CH}t})=0 \qquad \text{(vii)}\end{aligned}$$

$$\begin{aligned}&\gamma_{\mathrm{CH}}Q_{\mathrm{CH}t}+C_{t,\mathrm{CX}}Q_{\mathrm{CX}}+2C_{1,g}Q_{\mathrm{CH}}\\&\quad-C_{\mathrm{CH,CC}}Q_{\mathrm{CC}}+2C_{1,2}Q_{\mathrm{CH}g}=0 \qquad \text{(viii)}\end{aligned}$$

$$\begin{aligned}&\gamma_{\mathrm{CC}}Q_{\mathrm{CC}}+C_{\mathrm{CC,CH}}Q_{\mathrm{CX}}\\&\quad+C_{\mathrm{CH,CC}}(2Q_{\mathrm{CH}}-2Q_{\mathrm{CH}g}-Q_{\mathrm{CH}t})=0 \qquad \text{(ix)}\end{aligned}$$

On the other hand, Eq. 20 is written as Eq. x for CX bond,

$$\begin{aligned}&\gamma_{\mathrm{CX}}(Q_{\mathrm{CX}}-Q'_{\mathrm{CX}})+2C_{1,\mathrm{CX}}(Q_{\mathrm{CH}}-Q'_{\mathrm{CH}})\\&\quad+C_{\mathrm{CC,CX}}Q_{\mathrm{CC}}-C_{1,\mathrm{CX}}Q'_{\mathrm{CH}}\\&\quad+2C_{t,\mathrm{CX}}Q_{\mathrm{CH}g}+C_{t,\mathrm{CX}}Q_{\mathrm{CH}t}=0 \qquad \text{(x)}\end{aligned}$$

where the primed quantities represent the corresponding values in reference constitution CH_3X. In this way, all Q values can be determined.

For the other type of molecules, a similar procedure can be applied.

Results and Discussion

The theory has really been applied to the inductive effect occurring in some haloalkane molecules, the results of which are given in Table II and Fig. 3. For the present time, we have dealt with chloro- and bromo derivatives for which reliable experimental data could be obtained.

Looking at the Table II, the correspondence between the calculated and the experimental electric moments may be called fairly good in spite of several shortcomings in this treatment as mentioned below. Therefore, it may be permissible to

TABLE II

Molecule	Δm_{CH}	m^*_{CX}	M_{cal}		M_{exp}	Reference
CH_3Cl	0.186 D.	1.674 D.	(1.86) D.		1.86, 1.87 D.	1) 2), 3)
CH_3Br	0.167	1.623	(1.79)		1.78, 1.79, 1.80	4), 5), 3)
CH_2Cl_2	0.299	1.148	1.671		1.57, 1.62	1), 6)
CH_2Br_2	0.252	1.044	1.496		1.43	7)
$CHCl_3$	0.377	0.797	1.174		1.01, 1.15	1), 8)
$CHBr_3$	0.313	0.700	1.013		0.90, 0.99, 1.3	8), 9), 10)
C_2H_5Cl		1.773	2.029		1.98, 2.00, 2.02, 2.03	11), 12), 2), 4)
C_2H_5Br		1.739	1.966		1.92, 1.99, 2.01	4), 12), 5)
i-C_3H_7Cl		1.853	2.131		2.15	5)
n-C_3H_7Cl t		1.794	2.178	2.044**	2.03, 2.04	7), 12)
g		1.825	1.974			

* The value subtracted by the atomic dipole of carbon tetrahedral orbital.

** Mean value for the abundance ratio *gauche*/*trans*=2/1[13].

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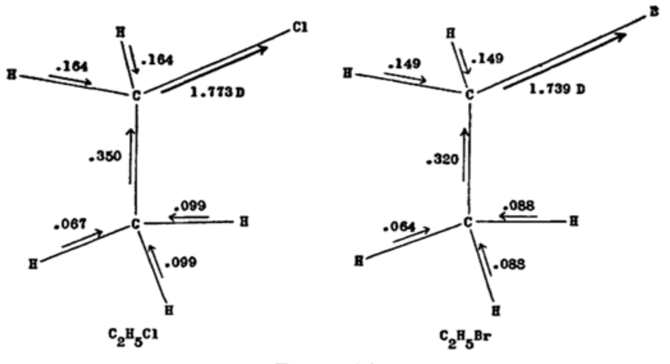
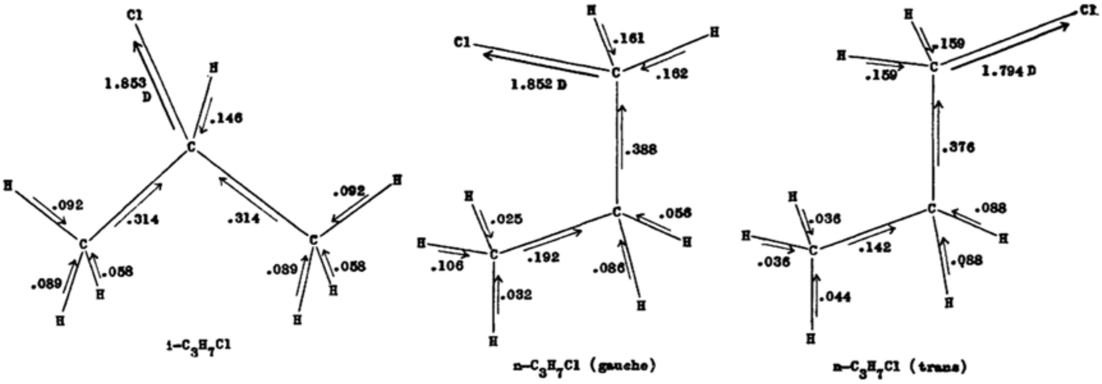


C_2H_5Cl　　C_2H_5Br

Fig. 3 (a)



i-C_3H_7Cl　　n-C_3H_7Cl (gauche)　　n-C_3H_7Cl (trans)

Fig. 3 (b)

discuss the detailed features of inductive effect somewhat quantitatively through the present treatment. It is also noticeable that Table II and Fig. 3 show fairly good agreement, in principal parts, with the preceding works[1,2]. In the present calculation, however, all inductive interaction terms have been included, and then, any change in the relative arrangement of bonds is reflected upon the whole results more or less, as can be observed at the difference between the *trans* and *gauche* forms of n-C_3H_7Cl in Fig. 3. The larger moment induced on γ-CH parallel to C-X than the β-C-H's may be understood as the marked consequence of direct effect. It must be noticed also that the *trans* form gives somewhat greater value of total moment than the *gauche* form in which actual induction is stronger than the *trans*. This means that the observed value of dipole moment can not always be taken as the measure of inductive effect without consideration about the abundance ratio of rotational isomers.

For the present calculation, we have assumed $Q^0_{\mathrm{CH}}=0$ somewhat arbitrarily. It can readily be shown, however, that the different choice of Q^0_{CH}, which is smaller enough than Q_{CX} anyway, does not affect the results very much. Now, there may arise a question as to whether the inductive effect can be properly described with such a simple LCAO wave function as one which includes no polarization of atomic orbitals. This difficulty has essentially been avoided in the above treatment by employing the γ values determined from experimental bond polarizabilities, which are closely related phenomenally with the inductive effect. But yet, it is doubtful whether the bond polarizability data corresponding to vanishing field strength be efficient to estimate finite magnitudes of polarization. At present, little comment can be given on this problem. But the numerical results seem to permit the adoption of the data.

There still remains, however, an important problem; that is, the neglect of the possibility of transverse polarization. Considerable explanation against it might be found in the situation that the greater portion of general inductive effect is still attributable to the electronegativity change of end atoms; that is, the inductive effect in the narrower sense, which causes mainly longitudinal polarization. However, the datails of the affair are yet an open question.

In practice of calculation, we must be concerned with the valence electronic configuration of substituent atoms. The present calculation has been carried out for $(ns)^2(np\sigma)(np\pi)^2(np\pi')^2$ configuration of halogen atoms. However, the possibility of mixing $(ns)(np\sigma)^2(np\pi)^2(np\pi')^2$ can not be ignored as has often been pointed out. After the mixing, the C-X bond moment becomes able to comprise the contribution from σ-type lone pair dipole in addition to the one from bonding pair expressed by Eq. ii, where the value of $y_{\mathrm{X}}^{\mathrm{CX}}$ also changes with the mixing. This modification changes the formal expression of γ_{CX} and $C_{\mathrm{X}i}$'s in Eqs. 19 and 20. The formal change in γ_{CX} is not very significant, because it is determined empirically in practical calculations, as if it were a simple empirical parameter. The change in $C_{\mathrm{X}i}$'s, however, may possibly lead to markedly different results. There is no doubt that this effect might be most obvious on the neighboring bonds, and, the test-calculation has been carried out for methyl chloride and bromide. The result given in Fig. 4 shows that the effect seems not very serious.

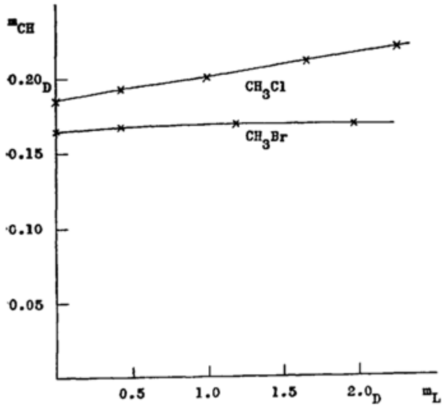


Fig. 4. The calculation has been carried out by the same procedure as in Example I, except that the lone pair dipole of X-atom, m_{L}, was added to M_{cal}. The bonding and lone pair orbitals of X-atom have been taken to be orthogonal with each other.

m_{L} can exceed the values of m_{CX} in Table II, because the latter is subtracted by the atomic dipole of carbon tetrahedral orbital.

Appendix

In SCF MO theory, the electronic energy of a molecule in closed shell state is expressed by Eq. I[4], where H_i, J_{ij}, and K_{ij} are bare nuclear field orbital energy, coulomb integral, and exchange integral

$$E=2\sum_i H_i+\sum_{i,j}(2J_{ij}-K_{ij}) \tag{I}$$

$$H_i=\int\phi_i^*(1)\,h_1\phi_i(1)\,\mathrm{d}\tau_1 \tag{II}$$

$$J_{ij}=\int\phi_i^*(1)\,\phi_j^*(2)\,(e^2/r_{12})\,\phi_i(1)\,\phi_j(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{III}$$

$$K_{ij}=\int\phi_i^*(1)\,\phi_j^*(2)\,(e^2/r_{12})\,\phi_i(2)\,\phi_j(1)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{IV}$$

as given by Eqs. II~IV respectively. Now, an SCF MO ϕ_i may approximately be expressed by the linear combination of bond orbitals localized at each bond, as given by Eq. V.

$$\phi_i=\sum_r c_{ir}\phi_r \tag{V}$$

Then, we assume two approximate conditions as follows:

(1) There exists little overlapping between two different ϕ_r's, and therefore those integrals which include the product $\phi_r^*\phi_s$ $(r\neq s)$ such as S_{rs}, H_{rs}, and electronic interaction energy integrals other than coulomb type may be neglected. Then, Eq. VI may be taken as an approximate orthonormality condition.

$$\sum_r c_{ir}^*c_{jr}=\delta_{ij} \tag{VI}$$

(2) The electron density at each bond orbital and the bond order* between different bond orbitals remain constantly equal to 2 and 0 respectively, as expressed by Eq. VII.

$$\sum_i c_{ir}^*c_{is}=\delta_{rs} \tag{VII}$$

Under these assumptions, Eqs. II~IV can be written as follows:

$$H_i=\sum_r\sum_s c_{ir}^*c_{is}H_{rs}=\sum_r c_{ir}^2H_{rr} \tag{VIII}$$

$$\begin{aligned}J_{ij}&=\sum_r\sum_s\sum_t\sum_u c_{ir}^*c_{js}^*c_{it}c_{ju}(rt/su)\\&=\sum_r\sum_s c_{ir}^2c_{js}^2(rr/ss)\end{aligned} \tag{IX}$$

$$\begin{aligned}K_{ij}&=\sum_r\sum_s\sum_t\sum_u c_{ir}^*c_{js}^*c_{it}c_{ju}(ru/st)\\&=\sum_r\sum_s c_{ir}^*c_{js}^*c_{is}c_{jr}(rr/ss)\end{aligned} \tag{X}$$

where

$$H_{rs}=\int\phi_r^*(1)\,h_1\phi_s(1)\,\mathrm{d}\tau_1 \tag{XI}$$

$$(rt/su)=\int\phi_r^*(1)\,\phi_s^*(2)\,(e^2/r_{12})\,\phi_t(1)\,\phi_u(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2\,. \tag{XII}$$

Then, the total energy E can be given by Eq. XIII taking Eqs. VI and VII into consideration.

$$\begin{aligned}E&=2\sum_i\sum_r c_{ir}^2H_{rr}+\sum_i\sum_j\sum_r\sum_s(2c_{ir}^2c_{js}^2\\&\quad-c_{ir}^*c_{js}^*c_{is}c_{jr})\,(rr/ss)\\&=2\sum_r H_{rr}+\sum_r\sum_s(2-\delta_{rs})\,(rr/ss)\,.\end{aligned} \tag{XIII}$$

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* Similarly defined as in LCAO approximation.

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