we use the bond moment for Si–F of 2.3 D along with the observed dipole moments, then with tetrahedral bonding, $\mu_{\text{SiH}} = 1.0$ or 3.6 D. However, the higher value of 3.6 D appears quite unreasonably large for a slightly polar bond with only a moderate $\overset{\underset{-\ +}{\longrightarrow}}{\text{H–Si}}$ homopolar moment supplementing the very small $\overset{\underset{-\ +}{\longrightarrow}}{\text{H–Si}}$ ionic moment. Therefore, it may be reasonably concluded that Si–H has a bond moment around 1.0 D. Such a conclusion is dependent, as is generally so, on the assumptions of bond additivity and the fairly close association of infrared bond moments with observed dipole moments.

Since methylsilane has a dipole moment[3] of 0.73 D and the butylsilanes and triethylsilane have dipole moments of 0.75–0.85 D, then with tetrahedral bonding, the Si–R bond has a moment of either 0.2 D or 1.8 D with the direction $\overset{\underset{-\ +}{\longrightarrow}}{\text{R–Si}}$.

The R–Si bond moment is made up of the Si–C bond moment and the C(sp^3)–H bond moments. From infrared absorption and dispersion measurements,[22–25] the bond moments of C(sp^3)–H, C(sp^2)–H and C(sp)–H obtained are ±0.31, ±0.63 and ±1.05, respectively. The C(sp)–H bond moment direction probably is $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–H}}$.[25] The C(sp^2)–H bond moment would also appear to have the direction $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–H}}$.[24] The C–H bond in substituted benzenes has been found to be $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–H}}$.[26,27] Recently Barrow and McKean[28] have determined the infrared absorption intensities in the methyl halides and concluded that in these compounds, the C(sp^3)–H bond moment has the direction $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–H}}$ with a magnitude around 0.4 D.[29] The experimental evidence thus favors a small C(sp^3)–H bond moment of about 0.4 D with the hydrogen positive.[30]

If we use a $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–H}}$ bond moment of 0.4 D, with a $\overset{\underset{-\ +}{\longrightarrow}}{\text{R–Si}}$ bond moment of 0.2 or 1.8 D, the $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–Si}}$ bond moment would be either 0.6 or 2.2 D. The latter value seems excessively large for the C–Si bond moment considering the electronegativity difference of only 0.7 and the radius difference of only 0.83 Å. (proportional to the homopolar moment). Thus a $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–Si}}$ bond moment of 0.6 D and a $\overset{\underset{-\ +}{\longrightarrow}}{\text{R–Si}}$ bond moment of 0.2 D seem reasonable.

On the basis of the foregoing discussion, the following bond moment magnitudes and directions may be assigned: $\overset{\underset{-\ +}{\longrightarrow}}{\text{H–Si}} = 1.0\ D$, $\overset{\underset{-\ +}{\longrightarrow}}{\text{R–Si}} = 0.2\ D$, $\overset{\underset{-\qquad +}{\longrightarrow}}{\text{C(sp}^3\text{)–H}} = 0.4\ D$ and $\overset{\underset{-\ +}{\longrightarrow}}{\text{C–Si}} = 0.6\ D$.

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[22] A. M. Thorndike, *J. Chem. Phys.*, **15**, 868 (1947).

[23] C. F. Hammer, Ph.D. Thesis, Univ. of Wisconsin, 1948.

[24] R. L. Kelly, R. Rollefson and B. S. Schurin, *J. Chem. Phys.*, **19**, 1595 (1951).

[25] G. E. Hyde and D. F. Hornig, *ibid.*, **20**, 647 (1952).

[26] R. P. Bell, H. W. Thompson and E. E. Vago, *Proc. Roy. Soc.* (*London*), **A192**, 498 (1948).

[27] A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).

[28] G. M. Barrow and D. C. McKean, *Proc. Roy. Soc.* (*London*), **A213**, 27 (1952).

[29] It is also of interest to note that if the bond moments of the C–H bonds with sp^3, sp^2 and sp hybridization are assumed to be of the same sign and if these bond moments are plotted against their bond order, a straight line relationship results. See also ref. 25.

[30] Coulson, ref. 18, calculated theoretically a C–H bond moment of 0.3 D with the hydrogen *negative*. At the present time, the experimental evidence given above does not support this conclusion. Bell, *et al.*, ref. 26, argue that Coulson's results for a rigid molecule cannot be closely related to the bond moments obtained from bending vibrational modes in infrared intensity studies.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

On the Separation of Inductive and Mesomeric Effects by Molecular Orbital Theory[1]

BY H. H. JAFFÉ[1a]

RECEIVED JULY 15, 1954

Calculations of electron densities and localization energies by perturbation theory applied to the semi-empirical LCAO molecular orbital method are analyzed into four separate steps. The individual steps are used to separate the various effects used by the English school in the qualitative interpretation of the reactivity of conjugated organic compounds.

Theoretical treatments of the reactivity of conjugated and aromatic organic compounds by molecular orbital (MO) theory have been performed by use of two fundamentally different semi-empirical approaches—the electron density (static), and the localization methods.[2] It appeared of interest to examine whether an analysis of such calculations would permit a quantitative separation of the various effects which have been introduced in the qualitative interpretation of reactivity.[3] The crude calculations by the LCAO method, neglecting overlap integrals, are best suited for such an analysis, and in particular the perturbation treatment introduced by Coulson and Longuet-Higgins[4]

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[1] Theoretical Considerations Concerning the Hammett Equation. VII. For the previous paper in this series see H. H. Jaffé, THIS JOURNAL, **76**, 5843 (1954).

[1a] Department of Chemistry, Univ. of Cincinnati, Cincinnati, Ohio.

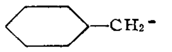
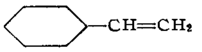
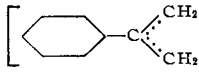
[2] R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter II-7.

[4] (a) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); (b) **A192**, 16 (1947).

TABLE I

RELATION BETWEEN REFERENCE COMPOUNDS AND ACTUAL COMPOUNDS THEY REPRESENT[a]

Ref. cpd.				
# of π electrons	6	8	8	10
Cpd. represented	C_5H_5N $C_6H_5NH_3^+$ $C_6H_5CH_3$	$C_6H_5X^b$ C_6H_5OR C_6H_5SR $C_6H_5NR_2$ $C_6H_5PR_2$ C_6H_5NO	C_6H_5CN $C_6H_5N{=}NR$ C_6H_5NO $C_6H_5CH{=}CH_2$ C_6H_5COR $C_6H_5CH_3^c$	$C_6H_5NO_2$ C_6H_5COOR $C_6H_5CONH_2$

[a] R represents H or alkyl; hyperconjugation is neglected unless otherwise noted. [b] X = Halogen [c] Including hyperconjugation; in this case, however, M_β is important.

lends itself admirably to the desired calculations.

The MO calculations of properties of a conjugated organic compound by perturbation theory can be divided into four distinct steps: (1) the calculation, by standard variational methods, of the properties of a reference compound; (2) the perturbations effected by the assignment of realistic resonance integrals to those bonds in the molecules which differ appreciably from the "standard" bonds; (3) the perturbations effected by assigning realistic Coulomb integrals to heteroatoms; (4) the perturbations effected by permitting the heteroatoms to affect the Coulomb integrals of the carbon atoms. We must now examine these four steps separately, and attempt to relate any differences found in each step between parent and substituted compound with the effects introduced by the English school. Our discussion will be based on the influence of substituents in benzene, since the concepts of inductive and conjugative effects have found their widest application in the chemistry of aromatic compounds. First we shall deal with the calculations by the electron density method, evaluating the various effects in terms of electron density changes induced by substituents. Later, we shall examine the localization energy calculations and compare the results obtained by the two methods.

The Pure Conjugative Effect.—The *first step* in the application of perturbation theory to the LCAO MO method (neglecting overlap integrals) consists in the calculation of orbital energies, electron densities and bond orders in a reference compound (unperturbed structure). In evaluating the effect of a substituent X on a parent compound (say benzene) by perturbation theory, the reference compound is the parent compound substituted by an idealized substituent X° (*cf.* Table I) and X° is formed from X by replacing all conjugated atoms by "standard" carbon atoms, and by assuming all bonds to be equal.[4] The introduction of idealized substituent X° into the parent compound *may* produce changes in the electron distribution. Such electron density changes are clearly caused by a conjugative effect, which we shall call the *pure conjugative* effect and denote by M_π. According to the Coulson-Rushbrooke theorem,[5] M_π vanishes whenever the parent compound and the reference compound both are alternant hydrocarbons. The changes in electron distribution for compounds containing a number of π-electrons different from the number of atoms in the conjugate system (alternant hydrocarbon ions)[6] are evaluated readily following the method outlined by Longuet-Higgins.[7]

The *second step* in the perturbation treatment involves the assignment of realistic resonance integrals to all bonds which appreciably differ from the "standard" carbon–carbon bonds. The changes of electron densities effected by this perturbation will be denoted as M_β. This quantity vanishes identically in the case of alternant hydrocarbons,[4] and under special circumstances in alternant hydrocarbon ions.[6] It has generally been assumed that the corrections due to this perturbation are small, and hence we shall neglect them in this paper. Since they are a correction to the pure conjugative effect, they should be included in the latter.

The Effect of Coulomb Integrals.—The *third step* in the perturbation treatment involves assignment of realistic Coulomb integrals to all heteroatoms.[8] Since so far no satisfactory theoretical procedure for the evaluation of such integrals has been found, recourse is generally made either to rough but reasonable estimates[9] or to empirical evaluation from experimental data.[1,10] We shall for the moment assume that the necessary integrals have been, or can be, evaluated in this manner; they are then considered as perturbation parameters, and their effect on the electron density of a given atom r in the molecule is given by[4]

$$\delta q_r = \sum_s \pi_{r,s}\delta\alpha_s \qquad (1)$$

Here, $\delta\alpha_s$ is the difference in Coulomb integrals of atom s between the actual and the reference compound. The $\pi_{r,s}$ are the mutual atom polarizabilities.[4] δq_r in equation 1 represents an effect of the difference of electron attracting (or repelling) nature of the carbon and heteroatoms, and is obviously an inductive effect of the heteroatom on the π-electron system. We shall call it the *π-Coulombic effect*, and denote it by I_π.

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(5) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

(6) H. H. Jaffé, *J. Chem. Phys.*, **22**, Nov. (1954).

(7) H. C. Longuet-Higgins, *ibid.*, **18**, 265 (1951).

(8) Carbon atoms in the substituent are in a different environment and frequently in a different state of hybridization from carbon atoms in the parent compound, and hence will be considered as heteroatoms.

(9) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(10) (a) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952); (b) **20**, 778 (1952); (c) **20**, 1554 (1952); (d) THIS JOURNAL, **76**, 3527 (1954); (e) P.-O. Löwdin, *J. Chem. Phys.*, **19**, 1323 (1951).

The σ-Inductive Effect.—The heteroatoms in the substituent also effect the electron distribution in σ-bonds. This effect is difficult to treat adequately in terms of molecular orbital theory, since only the π-electrons are considered. The present author has proposed to express the inductive effect on *all* carbon atoms through the equation[10a–d,11]

$$\delta\alpha_{\mathrm{C}} = \mathcal{E}^{n}\,\delta\alpha_{\mathrm{Y}} \qquad (2)$$

where n is the number of bonds between the carbon atom and the heteroatom Y along the shortest path. A value of $\mathcal{E} = {}^1/_3$ has been recommended.[12] On the basis of equation 2 and the value $\mathcal{E} = {}^1/_3$, the effect of σ-bond polarization of the π-electron density at any atom r can be evaluated by the equation

$$\delta q_{\mathrm{r}} = \sum_{s} \mathcal{E}^{n_s}\pi_{\mathrm{r,s}}\delta\alpha_{\mathrm{Y}} \qquad (3)$$

where the summation extends over all carbon atoms, including r, which are not considered as heteroatoms.[8]

Although the effect discussed in this section also represents changes in π-electron densities, these changes are the direct consequence of induction through σ-bonds; hence, we shall call this effect the *σ-inductive effect* and denote it by I_σ.

Although the above four steps do not represent a complete solution to the problem of a MO treatment of the compounds under investigation, any attempts at separation of the various effects after further refinements, such as inclusion of overlap integrals, antisymmetrization, or making the solutions self-consistent, is doomed to failure since all such corrections necessarily depend on the interaction of the separate effects.

Inductomeric and Electromeric Effects.—Finally, the English school recognizes two polarizability effects: the inductomeric and the electromeric effects. These effects represent the knowledge that the polarizability of the parent compound under the influence of the attacking reagent is affected by the introduction of the substituent X. Since we have made a greatly simplifying assumption concerning the polarizability of the σ-electrons (*cf.* equation 2), the inductomeric effect is, in our approximation, proportional to the inductive effect. This can only be a crude approximation since undoubtedly σ-bond polarizabilities for different bonds vary considerably.

The electromeric effect (E) is the difference in polarizability by an attacking reagent of the parent compound and its substituted derivative, and hence is given by

$$E = \Big(\sum_{\mathrm{r}\neq\mathrm{s}} \pi_{\mathrm{r,s}}\Big)_{\mathrm{subst}} - \Big(\sum_{\mathrm{r}\neq\mathrm{s}} \pi_{\mathrm{r,s}}\Big)_{\mathrm{unsubst}} \qquad (4)$$

where s is the atom at which reaction occurs, and the atom bond polarizabilities are again neglected. Since

$$\sum_{\mathrm{r}} \pi_{\mathrm{r,s}} = 0$$

when the summation extends over all r, equation 4 reduces to[2]

$$E = -(\pi_{\mathrm{s,s}})_{\mathrm{subst}} + (\pi_{\mathrm{s,s}})_{\mathrm{unsubst}} = \Delta\pi_{\mathrm{s,s}} \qquad (5)$$

It should be noted that the values for $(\pi_{\mathrm{s,s}})_{\mathrm{subst}}$ are polarizabilities, not of the reference compound, but of the actual perturbed compound. Calculation of these quantities is possible by perturbation theory[6] or by direct computation, but in either case is tedious. In compounds derived from alternant hydrocarbons, and for certain atoms in compounds derived from alternant hydrocarbon ions the self-polarizabilities are independent of the Coulomb integrals of all atoms in the molecule.[6] As a first approximation one may assume that the self-polarizabilities are independent of all Coulomb and resonance integrals, and hence are the same in the actual compound and the unperturbed structure. This assumption leads to equal electromeric effects for all substituents X derived from the same idealized substituent X° (*cf.* Table I), but probably gives values of correct order of magnitude. In the approximation used here, the electromeric effect is evaluated as a differential polarizability, and hence is obtained with equal magnitude operating in both (electron repelling or withdrawing) directions (*cf.* ref. 3).

The Localization Method.—Although consideration of electron density changes is consistent with the line of thought underlying the definitions of the effects studied,[3] their manifestations are found in reactivities. Since MO theory provides a second approach to the treatment of reactivities, the localization method,[2] it appeared desirable to investigate whether this method also permits the separation of these effects.

The localization energy L is the difference between the π-electron energies $\mathfrak{E}^{L}$ and $\mathfrak{E}^{NL}$ of the localized or "transition" and the initial (non-localized) states. The desired effects are the difference between the localization energies for the substituted compound and the parent compound, with the values for the substituted compound being evaluated at various stages in the perturbation calculations. Thus

$$M_\pi = L_{\mathrm{R}} - L_{\mathrm{P}} = \mathfrak{E}^{L}_{\mathrm{R}} - \mathfrak{E}^{NL}_{\mathrm{R}} + \mathfrak{E}^{L}_{\mathrm{P}} + \mathfrak{E}^{NL}_{\mathrm{P}}, \text{ with} \qquad (6)$$
$$\mathfrak{E} = \Sigma_{\mathrm{j}}\, n_{\mathrm{j}}\, \epsilon_{\mathrm{j}}$$

where ϵ_{j} is the energy of the j'th MO, and n_{j} the number of π-electrons assigned to this MO according to the Aufbau principle. The subscripts P and R refer to the parent and unperturbed reference structures, respectively. Further, since

$$\mathfrak{E} = \mathfrak{E}_{\mathrm{R}} + \sum_{\mathrm{r<s}}\Delta p_{\mathrm{r,s}}\,\delta\beta_{\mathrm{r,s}} + \sum_{\mathrm{r}} \Delta q_{\mathrm{r}}\delta\alpha_{\mathrm{r}}$$

we have

$$\begin{aligned} M_\beta = L_\beta - L_{\mathrm{R}} &= \mathfrak{E}^{L}_{\beta} - \mathfrak{E}^{NL}_{\beta} - \mathfrak{E}^{L}_{\mathrm{R}} + \mathfrak{E}^{NL}_{\mathrm{R}} \qquad (7)\\ &= \sum_{\mathrm{r<s}} \Delta\, p_{\mathrm{rs}}\,\delta\beta_{\mathrm{rs}} \end{aligned}$$

$$\begin{aligned} I_\pi = L_\pi - L_{\mathrm{R}} &= \mathfrak{E}^{L}_{\pi} - \mathfrak{E}^{NL}_{\pi} - \mathfrak{E}^{L}_{\mathrm{R}} + \mathfrak{E}^{NL}_{\mathrm{R}} \\ &= \sum_{\mathrm{r}} \Delta q_{\mathrm{r}}\delta\alpha_{\mathrm{r}} \qquad (8) \end{aligned}$$

$$\begin{aligned} I_\sigma = L_\sigma - L_{\mathrm{R}} &= \mathfrak{E}^{L}_{\sigma} - \mathfrak{E}^{NL}_{\sigma} - \mathfrak{E}^{L}_{\mathrm{R}} + \mathfrak{E}^{NL}_{\mathrm{R}} \\ &= \sum_{\mathrm{s}} \Delta q_{\mathrm{s}}\delta\alpha_{\mathrm{s}} \qquad (9) \end{aligned}$$

In equations 7 to 9 the subscripts β, π and σ under the energy quantities refer to the perturbation of resonance integrals, of heteroatomic Coulomb

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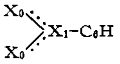
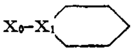
(11) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415(1953).

(12) A variation of $\mathcal{E}$ is examined in reference 11. See also references 10a–c for further justification of the value $^1/_3$.

TABLE II

SEPARATION OF THE EFFECTS OF SUBSTITUENTS ON THE ELECTRON DENSITIES AT THE *ortho, meta* AND *para* POSITIONS IN MONOSUBSTITUTED BENZENE DERIVATIVES[a]

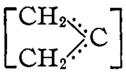
Ref. cpd.[b]	*Ortho*				*Meta*				*Para*			
	$M\pi$	$I\pi$	$I\sigma$	E	$M\pi$	$I\pi$	$I\sigma$	E	$M\pi$	$I\pi$	$I\sigma$	E
$X\text{–}C_6H_5$	0.143	-0.072α	0.012α	0.071	0	-0.010α	-0.014α	-0.005	0.143	-0.116α	-0.019α	0.040
$X_0\text{–}X_1\text{–}C_6H_5$	0	$\begin{Bmatrix} -\ .075\alpha_0 \\ .010\alpha_1 \end{Bmatrix}$	$-\ .014\alpha_1$	.041	0	$\begin{Bmatrix} .002\alpha_0 \\ -\ .001\alpha_1 \end{Bmatrix}$	$-\ .014\alpha_1$	$-\ .002$	0	$\begin{Bmatrix} -\ .065\alpha_0 \\ .009\alpha_1 \end{Bmatrix}$	$-\ .032\alpha_1$	.026
	0	$\begin{Bmatrix} -\ .046\alpha_0 \\ .008\alpha_1 \end{Bmatrix}$	$-\ .008\alpha_1$	.030	0	$\begin{Bmatrix} .002\alpha_0 \\ -\ .001\alpha_1 \end{Bmatrix}$	$-\ .013\alpha_1$	$-\ .001$	0	$\begin{Bmatrix} -\ .038\alpha_0 \\ .003\alpha_1 \end{Bmatrix}$	$-\ .034\alpha_1$	.021
$X\ldots C_6H_5$[c]	0	0	$-\ .017\alpha$	0	0	0	$-\ .013\alpha$	0	0	0	$-\ .039\alpha$	0
	0	$-\ .157\alpha$	$.107\alpha$	0	0	$.009\alpha$	$-\ .047\alpha$	0	0	$-\ .102\alpha$	$-\ .014\alpha$	0
	.143	$\begin{Bmatrix} -\ .072\alpha_0 \\ -\ .073\alpha_1 \end{Bmatrix}$	$.109\alpha_1$	.071	0	$\begin{Bmatrix} -\ .010\alpha_0 \\ .005\alpha_1 \end{Bmatrix}$	$-\ .049\alpha_1$	$-\ .005$	.143	$\begin{Bmatrix} -\ .038\alpha_0 \\ .003\alpha_1 \end{Bmatrix}$	$-\ .034\alpha_1$	.040

[a] All entries in this table are in the units of the charge of an electron, except that E does not have these units until multiplied by the perturbing factor α. In conformance with customary practice, α_C for "standard" carbon atoms is equated to zero, thus defining the origin of the energy scale; hence all $\delta\alpha_r$ terms are replaced by α_r in this table, and all α_r are in units of β, the "standard" C–C resonance integral. [b] The X are the atoms considered as heteroatoms, *cf.* Table I. The subscripts on the X serve to connect the Coulomb integrals α_r with the corresponding atoms X_r. [c] A compound in which X is not conjugated with the ring.

integrals, and of ring atom Coulomb integrals, respectively. The summation in equation 7 extends over all bonds, in equation 8 over all atoms of the substituent, and in equation 9 over all other atoms. The Δp_{rs} are the differences in bond orders between localized and non-localized structures, and the Δq are similar differences in electron densities. The $\delta\beta_{rs}$ and $\delta\alpha$ are the usual perturbation parameters.

A difficulty arises with $\delta\alpha$ in equation 9 since the non-localized structure contains more atoms in the conjugated system than the localized one. However, $\delta\alpha$, as evaluated for this atom from equation 2, is usually negligible.[1] Also, the inductive effect of the atom at which the localization occurs is neglected.[10d]

Results and Discussion

Electron Density Method.—The values of the quantities M_π, I_π, I_σ and E calculated by the electron density (static) method for the *ortho*, *meta* and *para* positions of monosubstituted benzene derivatives are listed in Table II, and for side chain atoms of disubstituted derivatives of benzene in Table III. I_π and I_σ are given in terms of the Coulomb integrals of the heteroatoms. The M_π vanish identically for all positions for which resonance theory does not predict any mesomeric effect, with the single exception of the compounds *m*- and *p*- $^-CH_2C_6H_4CH_2^-$, which are complicated by the fact that they are doubly charged ions, with both CH_2^- groups donating electrons to the ring. However, the M_π also vanish for all positions of all compounds not having a CH_2^- group as substituent. This fact arises from the assumption, in the first step of the perturbation treatment, that substituent atoms have the same electron affinity as the ring atoms, and from the necessity of assigning the extra electron in the  group to a MO antisymmetric with respect to the bisector of the angle $CH_2\text{—}C\text{—}CH_2$, and consequently isolated on the two CH_2 groups.

From this discussion it appears fruitless to attempt to identify M_π (or $M_\pi + M_\beta$) with the mesomeric effect as defined by Ingold,[3] since this identification would lead to a vanishing mesomeric effect in such compounds as benzonitrile, nitrobenzene and pyridine. However, the effect which we have denoted by I_π is an effect due exclusively to π-electrons. Examination of Tables II and III also shows that I_π is quite small, although not vanishing, for all positions for which resonance theory predicts no mesomeric effect, and takes appreciable values for the other positions in the majority of the cases considered. Hence, it appears reasonable to conclude that the mesomeric effect is represented by

$$M = M_\pi + M_\beta + I_\pi \qquad (10)$$

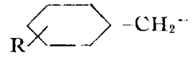
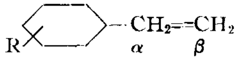
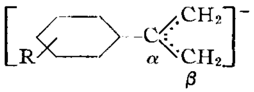
With this definition, it becomes apparent from Tables II to V that the mesomeric effect is not identical for the *ortho* and *para* positions, as commonly assumed in the use of resonance theory. However, there is no theoretical reason for expecting such an equality. It may be noteworthy, however, that M_π-values are equal for these positions.

Once the definition of the mesomeric effect through equation 10 has been made, the inductive effect I must be equated to I_σ. The data in Tables II to V indicate that the inductive effect in aromatic compounds, in general, does not fall off smoothly with distance from the heteroatom, as has frequently been assumed. This conclusion is a direct consequence of the law of alternating polarities,[4] as evidenced in the alternating magnitudes of mutual atom polarizabilities. However, the treatment of the inductive effect remains the least certain step in the present calculations (*cf.* also the discussion of actual compounds below), and the conclusions in this connection seem the least compelling. Nevertheless, it is hard to visualize *any* set of assumptions concerning the inductive effect, short of a virtually complete neglect, which would substantially alter the above conclusions.

A careful examination of Tables II and III shows that the inductive effects are far from negligible, even for the positions for which the resonance effects are of importance. This fact indicates that great caution should be exercised in interpreting experimental results on the basis of

TABLE III

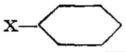
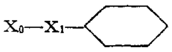
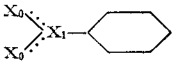
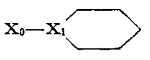
SEPARATION OF THE EFFECTS OF SUBSTITUENTS ON THE ELECTRON DENSITIES AT SIDE-CHAIN ATOMS IN DISUBSTITUTED BENZENE DERIVATIVES[a]

	R in *meta* position								R in *para* position							
R[b]	M_π		I_π		I_σ		E		M_π		I_π		I_σ		E	
A. Reference compound  -CH$_2$-																
X–	0.012		-0.008α		-0.025α		-0.015		0.094		-0.056α		-0.024α		-0.087	
X_0-X_1-	0		$\left\{\begin{matrix}-.006\alpha_0\\ .001\alpha_1\end{matrix}\right\}$		$-.024\alpha_1$		.009		$-.071$		$\left\{\begin{matrix}-.141\alpha_0\\ -.019\alpha_1\end{matrix}\right\}$		$-.041\alpha_1$		.129	
$\begin{matrix}X_0\\X_0\end{matrix}\!>\!X_1-$	0		$-.004\alpha_0$		$-.025\alpha_1$		.005		$-.038$		$\left\{\begin{matrix}-.077\alpha_0\\ .006\alpha_1\end{matrix}\right\}$		$-.044\alpha_1$		.064	
X. . . .[e]	0		0		$-.025\alpha$		0		0		0		$-.046\alpha$		0	
X$<$[c]	0		$-.040\alpha$		$-.003\alpha$		0		0		$-.116\alpha$		$-.002\alpha$		0	
B. Reference compound 																
	α[d]	β[d]	α	β	α	β	α	β	α	β	α	β	α	β	α	β
X–	0	0	0.001α	-0.006α	-0.023α	-0.018α	-0.003	0.001	0	0.125	-0.019α	-0.141α	0.001α	-0.016α	0.006	0.045
X_0-X_1-	0	0	0	$.001\alpha_0$	$.006\alpha_1$	$-.017\alpha_1$	0	$-.001$	0	0	$\left\{\begin{matrix}.004\alpha_0\\ -.001\alpha_1\end{matrix}\right\}$	$\left\{\begin{matrix}-.049\alpha_0\\ .004\alpha_1\end{matrix}\right\}$	$.004\alpha_1$	$-.024\alpha_1$	$-.003$	.012
$\begin{matrix}X_0\\X_0\end{matrix}\!>\!X_1-$									0	0	$\left\{\begin{matrix}.002\alpha_0\\ -.001\alpha_1\end{matrix}\right\}$	$\left\{\begin{matrix}-.028\alpha_0\\ .001\alpha_1\end{matrix}\right\}$	$.004\alpha_1$	$-.025\alpha_1$	$-.002$	.007
X. . .[e]	0	0	0	0	$.005\alpha$	$-.017\alpha$	0	0	0	0	0	0	$.005\alpha$	$-.027\alpha$	0	0
X$<$[c]	0	0	$-.013\alpha$	$.002\alpha$	$.015\alpha$	$-.054\alpha$	0	0	0	0	$.009\alpha$	$-.065\alpha$	$.005\alpha$	$-.017\alpha$	0	0
C. Reference compound 																
X–	0	0	0	$-.002\alpha$	$.001\alpha$	$-.006\alpha$	0	$-.004$	0	.033	$-.006\alpha$	$-.034\alpha$	$.001\alpha$	$-.005\alpha$	$-.003$	$-.066$
X_0-X_1-									0	0	$\left\{\begin{matrix}.001\alpha_0\\ -.001\alpha_1\end{matrix}\right\}$	$\left\{\begin{matrix}-.014\alpha_0\\ .001\alpha_1\end{matrix}\right\}$	$.002\alpha_1$	$-.007\alpha_1$	$-.001$	.015
$\begin{matrix}X_0\\X_0\end{matrix}\!>\!X_1-$	0	0	$\left\{\begin{matrix}-.001\alpha_0\\ .003\alpha_1\end{matrix}\right.$	$\left.\begin{matrix}.001\alpha_0\\ -.001\alpha_1\end{matrix}\right\}$	$.003\alpha_1$	$-.005\alpha_1$	.003	$-.001$	0	0	$.001\alpha_0$	$\left\{\begin{matrix}-.008\alpha_0\\ .001\alpha_1\end{matrix}\right\}$	$.002\alpha_1$	$-.007\alpha_1$	$-.001$	.009
X. . .[e]	0	0	0	0	$.003\alpha$	$-.005\alpha$	0	0	0	0	0	0	$.002\alpha$	$-.008\alpha$	0	0
X$<$[c]	0	0	$-.001\alpha$	$.001\alpha$	$.009\alpha$	$-.017\alpha$	0	0	0	0	$.003\alpha$	$-.019\alpha$	$.003\alpha$	$-.005\alpha$	0	0

[a] *Cf.* footnote *a*, Table II. [b] *Cf.* Footnote *b*, Table II. [c] The ring is X. [d] α and β refer to the positions indicated in the headings of sections b and c. [e] X not conjugated with the ring.

TABLE IV

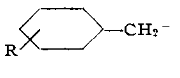
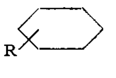
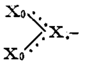
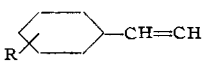
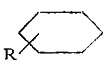
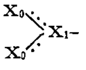
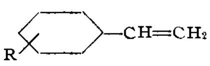
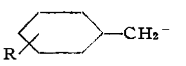
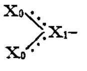
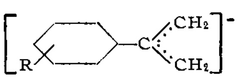
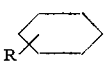
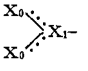
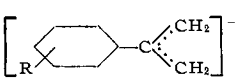
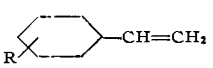
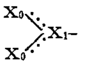
SEPARATION OF THE EFFECTS OF SUBSTITUENTS ON THE LOCALIZATION ENERGY FOR NUCLEOPHILIC AND ELECTROPHILIC SUBSTITUTION AT THE *ortho, meta* AND *para* POSITION IN MONOSUBSTITUTED BENZENE DERIVATIVES[a]

Ref. cpd.[b]	Type of substitution[c]	*Ortho*			*Meta*			*Para*		
		$M\pi$	$I\pi$	$I\sigma$	$M\pi$	$I\pi$	$I\sigma$	$M\pi$	$I\pi$	$I\sigma$
	N	-0.321	-0.028α	0.091α	-0.030	0.029α	0.060α	-0.086	0.218α	0.096α
	E	$.805$	$-.571\alpha$	$-.018\alpha$	$-.030$	$-.171\alpha$[d]	$-.038\alpha$[d]	$.714$	$-.571\alpha$	$-.032\alpha$
	N	$.112$	$.250\alpha_0$	$.102\alpha_1$	$-.007$	0	$.078\alpha_1$	$.166$	$.250\alpha_0$	$.102\alpha_1$
	E	$.112$	$-.250\alpha_0$	$-.102\alpha_1$	$-.007$	0	$-.078\alpha_1$	$.166$	$-.250\alpha_0$	$-.102\alpha_1$
	N	$.119$	$.071\alpha_0$	$.116\alpha_1$	$.004$	0	$.078\alpha_1$	$.077$	$.071\alpha_0$	$.116\alpha_1$
	E	$.119$	$-.071\alpha_0$[d]	$-.116\alpha_1$[d]	$.004$	0[d]	$-.078\alpha_1$[d]	$.077$	$-.071\alpha_0$[d]	$-.116\alpha_1$
[e]	N	0	0	$.136\alpha$	0	0	$.222\alpha$	0	0	$.136\alpha$
	E	0	0	$-.136\alpha$	0	0	$-.222\alpha$	0	0	$-.136\alpha$
	N	0	$.333\alpha$	$.041\alpha$	0	0	$.235\alpha$	0	$.333\alpha$	$.074\alpha$
	E	0	$-.333\alpha$	$-.041\alpha$	0	0	$-.235\alpha$	0	$-.333\alpha$	$-.074\alpha$
	N	$-.321$	$-.028\alpha_0$ $.108\alpha_1$	$.167\alpha_1$	$-.030$	$.029\alpha_0$	$.181\alpha_1$	$-.086$	$.218\alpha_0$ $.211\alpha_1$	$.063\alpha_1$
	E	$.805$	$-.571\alpha_0$	$-.053\alpha_1$	$-.030$	$-.171\alpha_0$[d]	$-.115\alpha_1$[d]	$.714$	$-.571\alpha_0$	$-.095\alpha_1$

[a] All entries in the table are in units of β, the ring carbon–carbon resonance integral. It should be noted that this is a negative quantity and hence a positive entry in the table corresponds to a negative contribution to the activation energy, and thus facilitates reaction. The $\delta\alpha_r$ terms have been replaced by α_r, *cf.* footnote *a* of Table II. [b] *Cf.* footnote *b*, Table II. [c] N = nucleophilic, E = electrophilic. [d] In the localized reference structure, two electrons are assigned to two degenerate orbitals. Since most heteroatoms are more electronegative than carbon, the degeneracy is split on perturbation in such a manner that the MO having a higher contribution from the heteroatom acquires lower energy. Hence, the correct unperturbed wave function is the one in which both electrons are assigned to the MO having the larger contribution from the atomic orbital of the heteroatom. This assumption was used in the calculations. [e] X not conjugated with the ring.

TABLE V

SEPARATION OF THE EFFECTS OF THE SUBSTITUENTS ON THE LOCALIZATION ENERGY FOR NUCLEOPHILIC SUBSTITUTION AT SIDE-CHAIN ATOMS IN DISUBSTITUTED DERIVATIVES OF BENZENE[a]

Compound			R in *meta* position			R in *para* position		
Non-localized	Localized	R[b]	$M\pi$	$I\pi$	$I\sigma$	$M\pi$	$I\pi$	$I\sigma$
		$X-$	0.010	-0.012α	0.034α	-0.094	0.239α	0.031α
		X_0-X_1-	$.003$	0	$-.033\alpha_1$	$-.045$	$.125\alpha_0$	$-.051\alpha_1$
		 $\begin{matrix}X_0\\ \rangle X_1-\\ X_0\end{matrix}$	$-.009$	0	$-.033\alpha_1$	$-.037$	$.033\alpha_0$	$-.054\alpha_1$
		$X-$	$.003$	0	0	$-.045$	$.071\alpha$	$-.004\alpha$
		X_0-X_1-	$.001$	0	0	$-.009$	0	0
		 $\begin{matrix}X_0\\ \rangle X_1-\\ X_0\end{matrix}$				$-.016$	0	0
		$X-$	$-.007$	$-.012\alpha$	$.019\alpha$	$-.184$	$.168\alpha$	$.033\alpha$
		X_0-X_1-	$.002$	0	$-.033\alpha_1$	$.036$	$-.125\alpha_0$	$-.051\alpha_1$
		 $\begin{matrix}X_0\\ \rangle X_1-\\ X_0\end{matrix}$				$.020$	$-.033\alpha_0$	$-.031\alpha_1$
		$X-$	$-.009$	0	0	$-.037$	$.038\alpha$	$-.002\alpha$
		X_0-X_1-				$-.016$	0	0
		 $\begin{matrix}X_0\\ \rangle X_1-\\ X_0\end{matrix}$	$-.021$	0	0	$-.025$	0	0
		$X-$	$-.012$	0	0	$.008$	$.033\alpha$	$.002\alpha$
		X_0-X_1-				$-.007$	0	0
		 $\begin{matrix}X_0\\ \rangle X_1-\\ X_0\end{matrix}$				$-.009$	0	0

[a] *Cf.* footnote *a*, Table IV. [b] *Cf.* footnote *b*, Table II.

resonance effects alone, a procedure which has sometimes been adopted.

The values of E listed in Tables II and III are extremely small, although not identically vanishing, for all positions for which resonance theory predicts the absence of an electrometric effect. Thus, the results of our analysis are consistent with expectations. Again values for *ortho* and *para* position differ.

Localization Method.—The effects of the substituents on nucleophilic and electrophilic substitution at the *ortho, meta* and *para* position in monosubstituted benzenes are separated in Table IV into the effects M_π, I_π and I_σ. In Table V, a similar separation is performed for the effect of one substituent on the nucleophilic substitution in an atom in the other substituent in disubstituted derivatives of benzene. As in Tables II and III, I_π and I_σ are given in terms of the Coulomb integrals of the heteroatoms.

The M_π calculated by the localization method do *not* vanish identically, although they are quite small, whenever resonance theory predicts no mesomeric effect for the atom undergoing substitution (localization). The M_π are larger for positions for which a mesomeric effect is predicted, and, in general, are largest in those cases where static M_π-values do not vanish. The localization method does not permit the separation of polarization and polarizability effects, since the calculations actually take account of polarization occurring under the influence of the attacking reagent. Accordingly, it was expected that localization M_π-values for nucleophilic and electrophilic substitution would differ. In spite of this fact agreement is observed in Table IV, except where CH_2^- is the substituent. This fact arises out of the presence, in all localized structures not involving this substituent, of at least one MO of zero energy, which accommodates the two electrons distinguishing the localized and non-localized structures in the two types of reaction.

The I_π calculated by the localization method for substituents containing two heteroatoms usually depend only on the Coulomb integral of one of them (*cf.* Tables IV and V). This is in contrast with the electron density method, where I_π depends on the Coulomb integrals of all heteroatoms. Table IV also shows the importance of the electromeric effect in the calculations by the localization method. Unless the substituent is CH_2^-, due to the presence of the zero energy MO discussed above, I_π has equal magnitude, but opposite sign, for electrophilic and nucleophilic substitution.

It has been noted that the static and localization methods *usually* lead to the same predictions about reactivity,[2] particularly for hydrocarbons, and some theoretical basis for this generalization has been given.[13] The difference in the separated effects between the two methods makes it appear surprising that this generalization should hold at all. And the fact that the static value of I_π depends on the Coulomb integrals of all substituent atoms, while the localization value does not, suggests that the agreement between the two methods should be the worse, the less the compound resembles an alternant hydrocarbon. In agreement with this expectation we found, in the investigation of pyridine 1-oxide,[10d] that a region could be defined, in terms of the two Coulomb integrals, in which predictions of the position of greatest reactivity made by the two methods disagree. This region was characterized by a rather large difference between the two Coulomb integrals.

Actual Compounds.—The Coulomb integrals derived for some actual compounds from Hammett substituent constants (σ)[1,10a–d] have been introduced into the expressions given in Tables II to V. The use of parameters derived from the static method in calculations by the localization method cannot be justified *a priori* in view of the poor theoretical basis of the calculations; the only justification for this procedure, aside from expediency, is found in the successful treatment of the multiplicity of Hammett substituent constants[1] and of the electrical effect of the N-oxide group[10b] achieved by use of this assumption. The use of the same parameters in localized and non-localized structures appears *a priori* more reasonable, and also is justified empirically. The over-all electron density changes are, in most cases, of the sign and magnitude expected from a knowledge of the physical and chemical properties of the compounds concerned. The major exception is that the electron density changes calculated for the *ortho* position frequently appear unreasonable. This fact is not an unexpected finding, since the *ortho* position has long given trouble in MO calculations of chemical reactivity.[10a,d,14] Brown has suggested that the difficulties are not inherent in the MO treatment, but arise from steric effects of special importance in this position.[14] On the other hand, it is not impossible that the difficulties are also connected with the assumptions about the inductive effect, particularly with the value chosen for the parameter $\mathcal{E}$, with the form of equation 2, or with the assumption that the Coulomb integral of a carbon atom attached to a heteroatom of Coulomb integral $\delta\alpha_Y$ is $^1/_3\delta\alpha_Y$.[15] It should be noted, in particular, that *ortho:para* ratios calculated from data such as those of Tables II to V must be regarded with caution. The question of the *ortho* position undoubtedly merits further considerations. Due to these difficulties, results of the calculations of the various effects for specific compounds are not tabulated in this paper.

Calculations

In the calculations of the data in Tables II and III, mutual atom polarizabilities in all of the reference compounds were required. These quantities were calculated by standard methods.[4] The values for the benzyl anion, $C_6H_5CH_2^-$,[11d] for benzene[4d] and for the disubstituted compounds containing the CH_2^- group[1] have been tabulated earlier; all other values are listed in the appendix,[16] together with the orbital energies and the wave functions for the compounds involved.

The calculations of the data in Tables IV and V required the orbital energies and electron densities in both the localized and non-localized structures considered. These data were calculated by standard methods, and are also tabulated in the appendix, and in earlier papers.[1,10d]

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(13) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 585 (1952).

(14) R. D. Brown, THIS JOURNAL, **75**, 4077 (1953).

(15) I am indebted to Dr. C. A. Coulson for suggesting this possibility.

(16) The appendix has been deposited as Document number 4349 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $2.50 for photoprints, or $1.75 for 35 mm. microfilm, by check or money order, payable to: Chief, Photoduplication Service, Library of Congress.