The Inductive Effect and Chemical Reactivity. I. General Theory of the Inductive Effect and Application to Electric Dipole Moments of Haloalkanes

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The Inductive Effect and Chemical Reactivity. I. General Theory of the Inductive Effect and Application to Electric Dipole Moments of Haloalkanes

BY RICHARD P. SMITH, TAIKYUE REE, JOHN L. MAGEE[1] AND HENRY EYRING

The inductive effect is discussed qualitatively in terms of bond orbital theory, and the main features of the effect are pointed out. A simple semi-classical model for the inductive effect is then introduced, and the analysis of this model leads to a method for calculating approximately net charges on atoms in molecules having no conjugation. All of the parameters are obtained from accepted longitudinal polarizabilities, screening constants, covalent bond radii and electric dipole moments. The method is checked by comparing calculated and observed electric dipole moments of some halogen substituted alkanes, and excellent agreement is found. The method will be shown, in succeeding papers, to be of great utility in understanding relative organic reaction rates and equilibria.

Introduction

The inductive effect has long been recognized as playing a prominent role in determining relative rates of organic reactions. The extent of this role has heretofore been impossible to determine, inasmuch as steric and resonance effects often overshadow—or have been thought to overshadow—the inductive effect, and lack of understanding of the nature of the effect has prohibited the calculation of its magnitude.

The successful correlation of relative amounts of ortho, meta and para nitration of substituted benzenes with empirically calculated charges[2] indi-

cates that rough calculations of charges can be useful for discussing chemical reactivity semi-quantitatively. In this paper we propose to develop a general, approximate theory for calculating the magnitudes of charges on atoms in molecules having no conjugation. The theory will be checked by comparing a number of calculated and observed dipole moments. Succeeding papers in this series will show how reaction rates and equilibria may be semi-quantitatively correlated with charges calculated on the basis of our model for the inductive effect and improvements on it.

The principal inductive effect theories in existence are those of Branch and Calvin[3] and

(1) Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

(2) T. Ri (Ree) and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

(3) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 217ff.

Remick.[4] Branch and Calvin followed ideas similar
to those of Ingold and collaborators,[5] who suppose
that substituent effects are propagated principally
along chemical bonds in molecules. Using the ob-
servations of Derick[6] and others, they developed an
empirical method for calculating acid strengths.
"Inductive constants" were assigned to various
groups, and rules for their application were given.
A number of acid strengths were calculated on the
basis of this theory, and rough accord with experi-
ment was obtained. The theory of Remick is less
empirical, being based largely on electronic polari-
zations of bonds and changes in effective kernel
charges; it was used for discussing the dipole mo-
ments of some polyhalogeno alkanes. This theory
bears some resemblance to the theory which we
shall develop here; a further discussion of Remick's
theory and its relationship to ours will be given la-
ter in this paper.

The problem of charge distribution in molecules
is of course a quantum mechanical problem; con-
sequently we shall first discuss the inductive ef-
fect quantum mechanically. This will lead to a
simple picture for the inductive effect, but the ap-
proximations necessary for the development of a
general theory will not permit its actual numerical
application. Consequently, we shall use a semi-
classical model, and thereby develop a simple
method for calculating charge distributions; the
results of the application of this method will, we be-
lieve, amply justify its use.

Bond Orbital Treatment of the Inductive Effect

We now discuss the inductive effect quantum me-
chanically, considering the electron pair of each
bond as moving in a molecular orbital which may be
written as a linear combination of atomic orbitals
(L.C.A.O.) of the two atoms between which the
electrons move. This localized electron pair,
L.C.A.O. model seems necessary for simplicity in
developing a general theory which readily permits
approximate identification of net charges associ-
ated with individual atoms. Thus in the conveni-
ent notation of Mulliken,[7] we write

$$\varphi_B = a_B \chi_a + b_B \chi_b \qquad (1)$$

for the bonding (lower energy) orbital in which the
two electrons of a bond a–b are supposed to move.
Here χ_a and χ_b are the atomic orbitals and a_B and
b_B are numerical coefficients obtained by normaliza-
tion of (1) and minimization of the energy with re-
spect to the coefficients. When the coefficients are
thus obtained and inserted into the expressions

$$Q_a = Q = -2e(a_B{}^2 + a_B b_B S) + e \qquad (2)$$

and

$$Q_b = -Q = -2e(a_B b_B S + b_B{}^2) + e \qquad (3)$$

for the approximate net charges on atoms a and b,
respectively, it is found[7] that

$$Q = (\delta/\beta)[1 - {}^1/_2(1 - S^2)(\delta^2/\beta^2) + \ldots] \qquad (4)$$

where

$\delta = {}^1/_2(\alpha_b - \alpha_a)$, $\alpha_a = \int \chi_a{}^* h \chi_a d\tau$, $\alpha_b = \int \chi_b{}^* h \chi_b d\tau$,
$\beta = \gamma - {}^1/_2 S(\alpha_a + \alpha_b)$, $\gamma = \int \chi_a{}^* h \chi_b d\tau$, $S = \int \chi_a{}^* \chi_b d\tau$

(4) A. E. Remick, *J. Chem. Phys.*, **9**, 653 (1941).

(5) C. K. Ingold, *Chem. Rev.*, **15**, 225 (1934).

(6) C. G. Derick, THIS JOURNAL, **33**, 1152 (1911).

(7) R. S. Mulliken, *Colloques intern. centre natl. recherche sci.*, No. **18**, *Liaison chim.*, **1948**, 158 (1950); *J. chim. phys.*, **46**, 497 (1949).

where h is the S.C.F. (self consistent field) one-elec-
tron Hamiltonian. In general it should be a satis-
factory approximation to drop all terms in (4) but
the first. Now Mulliken finds that the integral β
is remarkably invariant with respect to a number of
factors, including the polarity of the bond.[7] Hence
Q should be approximately linear in δ, which for
bonds of the type we are considering has been shown
by Mulliken to be given approximately by

$$\delta = {}^1/_2 A[(I_a - {}^1/_2 J_{aa}) - (I_b - {}^1/_2 J_{bb})] \qquad (5)$$

Here I_a and I_b are the ionization potentials for
atoms a and b, respectively, in the appropriate va-
lence states; A is roughly constant, being about 0.5
for the bonds studied by Mulliken; and J_{aa} and J_{bb}
are integrals defined by

$$J_{ii} = \int \chi_i{}^{*(1)} \chi_i \frac{e^2}{r_{12}} \chi_i{}^{*(2)} \chi_i{}^{(2)} d\tau_1 \, d\tau_2 \qquad (6)$$

where the subscripts and superscripts (1) and (2)
refer to the individual electrons of the bond.

Substitution of (5) into (4), neglecting higher or-
der terms, gives

$$Q = Q_a = {}^1/_2 |\beta^{-1}| A[(I_b - {}^1/_2 J_{bb}) - (I_a - {}^1/_2 J_{aa})] \qquad (7)$$

since β is negative. Equation (7) permits us to see,
qualitatively, the nature of the inductive effect.
The quantity I_b is positive and roughly proportional
to the square of the effective nuclear charge of
atom b, while J_{bb} is positive and roughly propor-
tional to the nuclear charge of b. Similar state-
ments apply to I_a and J_{aa}. Suppose a substituent
removes charge from b. This will increase the ef-
fective nuclear charge of b, and therefore $(I_b -
{}^1/_2 J_{bb})$, since I_b predominates over ${}^1/_2 J_{bb}$. Hence
Q increases, *i.e.*, electrons are pulled from a onto b;
the resulting increase of the effective nuclear charge
of a will cause a to pull electrons from the other
atoms to which it is attached, and so on. The ap-
proximations made in the derivation of (7), to-
gether with the uncertainties in the quantities in
the right-hand side of this equation, prevent us, at
present, from actually using this formulation of the
theory for numerical calculations.

"Semi-classical" Treatment of the Inductive Effect

We now proceed to develop the theory of the in-
ductive effect on the basis of a simple model. Al-
though the model used is probably only a rough
approximation to the situation, its use permits cal-
culation of the parameters involved in terms of
quantities whose values are known empirically, and
the numerical results obtained are surprisingly good.

The moment μ induced in a system by a field of
strength E is

$$\mu = \alpha E \qquad (8)$$

where α is the polarizability tensor; the non-diago-
nal components of α will vanish if the axes of the
system are properly chosen. An approximation
frequently used for chemical bonds is the assump-
tion that the diagonalized polarizability tensor has
one component b_l and two components b_t where b_l
is the "longitudinal polarizability," *i.e.*, the polariz-
ability in the direction of the bond, and where b_t
is the "transverse polarizability" which is perpen-
dicular to the bond direction. This assumption

has been discussed and applied by Wang[8] and by Denbigh.[9]

Let us now consider the application of the bond-direction component of (8) to the electron cloud of the two bonding electrons of a bond a–b. It seems reasonable to write

$$-Q_a{}^b R_{ab} = (b_1)_{ab} \left(\frac{z_a e}{R_a 2} - \frac{z_b e}{R_b 2} \right) \qquad (9)$$

where $Q_a{}^b$ is the net charge on atom a due to the polarization of the electron pair of a–b, R_{ab} is the internuclear distance and $(b_1)_{ab}$ the longitudinal polarizability of a–b, z_a and z_b are the effective nuclear charges of a and b, respectively, in the molecule, and R_a and R_b are the covalent bond radii of a and b, respectively. The minus sign was introduced for consistency between the direction of the field and the induced moment. The principal assumptions embodied in (9) are (a) that a bond dipole moment may be represented by equal and opposite net charges localized on the atomic nuclei, and (b) that the dipoles are induced by a net force of the form represented in (9). Assumption (a) seems necessary in any simple treatment of the inductive effect. Assumption (b) amounts to assuming spherical potential fields for atoms a and b, neglecting asymmetry due to the fact that the bonding electrons have a greater probability of being found between the atoms than elsewhere, and that the conducting spheres on which the electrons move have, on the average, radii equal to the covalent bond radii.

According to Slater,[10] one electron on atom a exerts a screening of s_a on another in the same valence shell, where s_a is 0.35 unless the electron is in the $1s$ group, in which case 0.30 is used; hence we write

$$z_a = z_a{}^0 + \frac{s_a}{e} \epsilon_a \qquad (10)$$

where $z_a{}^0$ is a constant for atom a, and ϵ_a is the *total* net charge on this atom (sum of net charge contributions from all bonds joined to a). Substitution of (10) and a similar equation for z_b into (9) yields

$$Q_a{}^b = \alpha_{ab} + \beta_b{}^a \epsilon_b - \beta_a{}^b \epsilon_a \qquad (11)$$

where

$$\alpha_{ab} = - \frac{(b_e)_{ab} e}{R_{ab}} \left[\frac{Z_a{}^0}{R_a{}^2} - \frac{Z_b{}^0}{R_b{}^2} \right] \qquad (12)$$

$$\beta_b{}^a = \frac{S_b (b_e)_{ab}}{R_{ab} R_b{}^2} \qquad \beta_a{}^b = \frac{S_a (b_e)_{ab}}{R_{ab} R_a{}^2} \qquad (13)$$

It is of interest to note, at this point, the relationship of the theory of Remick[4] to ours. Remick considered only C–C bonds and C–X bonds where X was hydrogen or halogen. For the carbon–halogen bonds Remick derived the equation

$$\bar{\mu}_{cx} - \bar{\mu}^0{}_{cx} = -1.583 \times 10^{-24} (P_{E}')_{cx} \Delta q_c{}^{\sharp} / R^2{}_{cx}$$

where $\bar{\mu}^0{}_{cx}$ is a "standard bond moment," $\bar{\mu}_{cx}$ is the moment under the influence of a change $\Delta q_c{}^{\sharp}$ in the effective kernel charge of the carbon, R_{CX} is the C–X bond length, and $(P_{E}')_{cx}$ is the electronic polarization of the electron pair of C–X. Using the relations

$$\frac{4\pi N}{3} \alpha = P_{E}' \qquad \frac{b_1 + 2b_t}{3} = \alpha$$

and the following relation, found empirically by Denbigh[9] for carbon–halogen bonds

$$b_t = 0.57 b_1$$

(8) S. Wang, *J. Chem. Phys.*, **7**, 1012 (1939).

(9) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

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

Remick's equation reduces to

$$\bar{\mu}_{cx} - \bar{\mu}^0{}_{cx} = -2.95 (b_1)_{cx} \frac{\Delta q_c{}^{\sharp}}{R^2{}_{cx}}$$

If we make the approximation $R_C \approx R_X \approx \frac{1}{2} R_{CX}$, our theory gives us the corresponding equation

$$\delta\mu_{cx} = -4(b_1)_{cx} \frac{Z_c' e}{R^2{}_{cx}}$$

for the change, $\delta\mu_{cx}$, in the C–X moment due to a change z_c' in the effective charge of the carbon. We use $z_c' e = 0.35 \epsilon_0'$, where ϵ_0' is the change in electronic charge on the carbon, the factor 0.35 naturally arising from Slater's screening rules, while Remick empirically uses $\Delta q_c{}^{\sharp} = \frac{1}{2} \epsilon_0'$. Similar considerations apply to the other bonds discussed by Remick. Thus our theory has much in common with Remick's, although we believe ours to be a more *direct* theory, being based on a simpler model, and not requiring empirical corrections as did the former theory.

The α_{ab} defined by (12) depend on small differences between large quantities, and are therefore very sensitive to the values of the $z_i{}^0$ and the R_i. In view of the uncertainties in these quantities, the α_{ab} are best determined from measured electric dipole moments, as will be explained later.

The $\beta_a{}^b$, on the other hand, present no such problem. It is found that our calculated charge distributions are sufficiently insensitive to small changes in the $\beta_a{}^b$ that the approximate values obtained in the following way are satisfactory. We use $R_{ab} = R_a + R_b$, and use Pauling's covalent bond radii[11] for the R_i. We use values of b_1 from Denbigh.[9] The results for a number of bonds are summarized in Table I. Note that our theory from the field-polarizability viewpoint is immediately applicable to double bonds.

TABLE I

SOME CALCULATED VALUES OF $\beta_a{}^b$ AND $\beta_b{}^a$

Bond a–b	$b_1 \times 10^{24}$, cc.	R_a, Å.	R_b, Å.	$\beta_a{}^b$	$\beta_b{}^a$
C–C	1.88	0.771	0.771	0.718	0.718
C–F	0.96[a]	.771	.64	.401	.581
C–Cl	3.67	.771	.99	1.23	.744
C–Br	5.04	.771	1.14	1.55	.710
C–I	8.09[a]	.771	1.33	2.27	.762
C–H	0.79	.771	0.30	0.434	2.46
C–O	.84[a]	.771	.66	.346	0.472
C–N	.86[a]	.771	.70	.344	.418
N–H	.58	.70	.30	.414	1.93
S–H	2.30	1.04	.30	.555	5.72
C=O	1.99	0.665	.55	1.30	1.90
C=C	2.86	.665	.665	1.70	1.70
C=S	7.57	.665	.94	3.73	1.87
N≡N	2.43	.547	.547	2.60	2.60
C≡N	3.1	.602	.547	2.61	3.16
C≡C	3.54	.602	.602	2.84	2.84
C_{ar}–C_{ar}[b]	2.25	.695[c]	.695[c]	1.17	1.17

[a] These values calculated assuming $b_t/b_1 = 0.57$, a relationship Denbigh[9] found for C–Cl and C–Br bonds, and using bond refraction values given by Denbigh. [b] Nuclear bond in benzene and derivatives. [c] One-half carbon–carbon distance in benzene.

Application of the Theory to Organic Molecules

Basically, application of our charge distribution theory to a molecule involves the solution of simultaneous equations of the form of (11), one for each bond, subject to the restriction that the sum of the

(11) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

net charges must be zero. In practice, it is apparent that there will in general be fewer equations to solve for a given molecule than there are bonds in the molecule, if use is made of obvious charge equalities—for example, each of the three hydrogens in CH_3X has the same net charge.

Let us now consider the application of the theory to some simple molecules with two purposes in mind: Illustration of the method of application, and determination of some of the parameters. First, let us make our notation more compact by introducing the quantities

$$\gamma_{ab} = \frac{\alpha_{ab}}{1 + \beta_a{}^b} \qquad \beta_{ab} = \frac{\beta_b{}^a}{1 + \beta_a{}^b} \quad (14)$$

Then if a is an atom which is attached *only* to a particular carbon atom (a = F, Cl, Br, I, H, O of O=C, etc.), and b is carbon, then $Q_a{}^b = \epsilon_a$ and (11) becomes, using definitions (14)

$$\epsilon_x = \gamma_{xc} + \beta_{xc}\epsilon_c \quad (15)$$

Using the $\beta_a{}^b$ of Table I, we find $\beta_{HC} = 0.13$, $\beta_{FC} = 0.25$, $\beta_{ClC} = 0.71$, $\beta_{BrC} = 0.91$, and $\beta_{IC} = 1.29$. For the molecules CH_3X, then, we have the equations

$$\epsilon_x = \gamma_{xc} + \beta_{xc}\epsilon_c \quad (16a)$$
$$\epsilon_H = \gamma_{HC} + \beta_{HC}\epsilon_c \quad (16b)$$

to be solved subject to the condition that

$$\epsilon_c + \epsilon_x + 3\epsilon_H = 0 \quad (16c)$$

The solution of the set of equations (16) is

$$\epsilon_H \Delta = (1 + \beta_{XC})\gamma_{HC} - \beta_{HC}\gamma_{XC} \quad (17a)$$
$$\epsilon_C \Delta = -\gamma_{XC} - 3\gamma_{HC} \quad (17b)$$
$$\epsilon_X \Delta = (1 + 3\beta_{HC})\gamma_{XC} - 3\beta_{XC}\gamma_{HC} \quad (17c)$$

where

$$\Delta = 1 + \beta_{XC} + 3\beta_{HC} \quad (17d)$$

Now the methyl halide bond angles are undoubtedly very close to tetrahedral[12,13]; assuming them
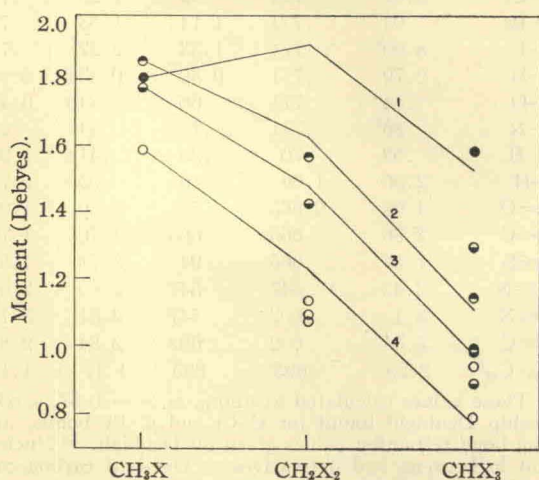

Fig. 1.—Calculated and observed moments for halogen substituted methanes. Lines are calculated, assuming no methane CH moment, and fitting experimental points for CH_3X molecules. Points are experimental. Lines 1, 2, 3 and 4, are for X = F, Cl, Br and I, respectively.

to be tetrahedral, we have, for the methyl halide electric dipole moments

$$\mu_{CH_3X} = -\epsilon_X R_{CX} + \epsilon_H R_{CH} \quad (18)$$

where R_{CX} and R_{CH} are the C–X and C–H internuclear distances, respectively. Combining (18) with equations (17), we have

$$\mu_{CH_3}(1 + \beta_{XC} + 3\beta_{HC}) = \gamma_{HC}[3\beta_{XC} R_{CX} + (1 + \beta_{XC})R_{CH}] - \gamma_{XC}[(1 + 3\beta_{HC})R_{CX} + \beta_{HC}R_{CH}] \quad (19)$$

Equation (19) may be used to calculate the γ_{XC} for the carbon–halogen bonds from the parameters given previously, the measured internuclear distances,[12] the measured electric dipole moments as given in Table II, and γ_{HC}. The value of γ_{HC} may be determined from the moment of the C–H bond in methane as follows. In equations (17) if X is H (methane) we find $\epsilon_H = \gamma_{HC}/(1 + 4\beta_{HC})$ or $\gamma_{HC} = 1.52 \epsilon_H$. Using 0.3 debye for the moment of the CH bond in methane[14,15,16] and 1.09 Å. as the length of this bond[11] we find, assuming a direction C^+H^-, that $\gamma_{HC} = -0.418 \times 10^{-10}$ e.s.u. There is some possibility that the CH bond moment is in the opposite direction[16]; in this case we find $\gamma_{HC} = 0.418 \times 10^{-10}$ e.s.u. for a moment of the same magnitude. In our calculations in this paper we have used both of the above values of γ_{HC} and also $\gamma_{HC} = 0$ corresponding to no C–H bond moment in methane.

The results of our calculations are summarized in Table II. We now have the values of all the parameters necessary for the calculation of charge distributions for all haloalkanes. The distributions may be tested by comparing the calculated and observed electric dipole moments; some results of such tests are summarized in Table II. The results for the series CH_3X, CH_2X_2, CHX_3 are shown graphically in Fig. 1. In these calculations, all bond angles have been assumed tetrahedral, and the bond distances have been assumed to be the same as in the corresponding methyl halides. The carbon–carbon distance has been taken as 1.54 Å.[11] Note, from its definition, that $\alpha_{CC} = 0$; hence application of (11) to the carbon–carbon bond in ethyl chloride, for example, yields

$$Q_2{}^1 = \beta_c{}^c(\epsilon_1 - \epsilon_2) \quad (20)$$

where $Q_2{}^1$ is the net charge contribution to carbon 2 of the carbon–carbon bond; the carbons are numbered 1, 2 starting from the substituent. We note that carbon 2, having three hydrogens substituted on it, each with charge ϵ_b, has the total net charge

$$\epsilon_2 = -3\epsilon_b + Q_2{}^1 \quad (21)$$

Hence, using (20)

$$\epsilon_2 + 3\epsilon_b = \beta_c{}^c(\epsilon_1 - \epsilon_2) \quad (22)$$

Hence for ethyl chloride the charge distribution is found by solving (22) simultaneously with

$$\epsilon_{Cl} = \gamma_{ClC} + \beta_{ClC}\epsilon_1 \quad (23)$$
$$\epsilon_a = \gamma_{HC} + \beta_{HC}\epsilon_1 \quad (24)$$
$$\epsilon_b = \gamma_{HC} + \beta_{HC}\epsilon_2 \quad (25)$$
$$\epsilon_1 + \epsilon_2 + 2\epsilon_a + 3\epsilon_b + \epsilon_{Cl} = 0 \quad (26)$$

where ϵ_a is the charge on each hydrogen attached

(12) W. Gordy, J. W. Simmons and A. G. Smith, *Phys. Rev.*, **74**, 243 (1948).

(13) H. A. Skinner, *J. Chem. Phys.*, **16**, 553 (1948).

(14) R. Rollefson and R. Havens, *Phys. Rev.*, **57**, 710 (1940).

(15) C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

(16) W. L. G. Gent, *Quarterly Reviews* (London), **2**, 383 (1948).

TABLE II

VALUES OF γ_{XC} FOR CX BONDS AND DIPOLE MOMENTS OF HALOALKANES

| Molecule | $\gamma_{XC} \times 10^{10}$, e.s.u. | | | $\mu_{calcd.}$ (D) | | | $\mu_{obsd.}$ (D)[a] | Ref. |
	C^-H^+	O	C^+H^-	C^-H^+	O	C^+H^-		
CH_3F	−0.944	−1.44	−1.93	(1.81	1.81	1.81)	1.81	17, 21
CH_2F_2				1.91	1.91	1.93	..	
CHF_3				1.51	1.53	1.54	1.59	19
CH_3Cl	−0.584	−1.49	−2.40	(1.86	1.86	1.86)	1.86	20
CH_2Cl_2				1.58	1.63	1.68	1.57	20
$CHCl_3$				1.04	1.12	1.19	1.01, 1.15	20, 22
CH_3Br	−0.354	−1.44	−2.53	(1.78	1.78	1.78)	1.78	17
CH_2Br_2				1.40	1.48	1.55	1.43	19
$CHBr_3$				0.88	0.98	1.08	1.3, 0.99, 0.90	18, 19, 22
CH_3I	0.081	−1.73	−2.82	(1.59	1.59	1.59)	1.59	17
CH_2I_2				1.12	1.23	1.34	1.10B, 1.08B, 1.14H	18
CHI_3				0.63	0.78	0.93	0.8B, 0.95B, 1.00H	18
$CFCl_3$				1.00	0.95	0.88	.45	21
CF_2Cl_2				1.23	1.18	1.12	.51	21
CCl_3Br				0.61	0.59	0.57		18
C_2H_5F				2.01	2.05	2.08	1.92	17
C_2H_5Cl				1.98	2.13	2.28	2.03	17
C_2H_5Br				1.85	2.05	2.25	2.02	17
C_2H_5I				1.57	1.86	2.15	1.90	17

[a] Gas values, if not otherwise indicated (B, benzene; H, hexane).

to carbon 1. Charge distributions for each halo-alkanes are obtained similarly.

Discussion

Inspection of Table II reveals that the value of the methane C–H bond moment, which indirectly enters the calculations through γ_{HC}, does not make as much difference in the calculated dipole moments as might be expected. In fact, it is difficult to say which of the three "calculated" columns in Table II gives the best agreement with the observed values. As far as the four series CH_3X, CH_2X_2, CHX_3 are concerned it may be said that any of the three "calculated" columns gives satisfactory agreement with experiment, with the column corresponding to no CH moment probably giving the best agreement. For the ethyl halides the zero CH moment column represents the best agreement for ethyl bromide and ethyl iodide while the C^-H^+ column gives the best agreement for ethyl fluoride and ethyl chloride. The smallness of the moments of $CFCl_3$, CF_2Cl_2 and CCl_3Br as compared to all the calculated values can probably be attributed to a large extent to bond shortening and angle spreading in these molecules.

It is not to be concluded, however, that the CH bond in methane has no moment, particularly in view of the large amount of evidence supporting a moment.[16] The consistently high dipole moments calculated for a C^+H^- moment may be due to inaccuracies in the calculations from other sources, e.g., the values we have used for the screening constants s_a may not be the "correct" values. Other inaccuracies are inherent in the theory, e.g., the approximation that the electron distributions may be con-

sidered as point charges localized on nuclei as we have assumed, and that the potential fields of the atoms are spherical.

Needless to say, the results obtained for the ethyl halides do not warrant dipole moment calculations for other alkyl halides. However, it must be remembered that the primary importance of our theory is not the calculation of dipole moments, although we believe the theory does give a clear qualitative picture of "induction of bond moments" which results in such phenomena as a lower dipole moment for chloroform than for methyl chloride. The main purpose of this work is the approximate calculation of charge shifts in molecules due to substituents. In succeeding papers in this series, we shall be interested primarily in *differences* in charges on various atoms in molecules, and these are far less sensitive than dipole moments to inaccuracies in the parameters of the theory. As an illustration of this point, consider ethyl iodide, the molecule listed in Table II where the value of the methane CH moment makes the most difference in the value of the calculated moment of the molecule. Here the quantity $\epsilon_1 - \epsilon_2$ (where ϵ_1 is the charge on the carbon attached to the iodine and ϵ_2 is the charge on the other carbon) has the values 0.301, 0.298, and 0.295 (in units of 10^{-10} e.s.u.) for C^-H^+ moments of 0.3 D, 0, and −0.3 D, respectively. Similar small variations in charge *differences* will occur for the other ethyl halides as the methane CH moment is varied. This result is of great importance, for it will enable us to calculate fairly accurately the differences in charges on atoms in molecules due to the induction of some substituent, such as a halogen. These charge differences are very important in determining relative reaction rates, as Ri and Eyring[2] have shown for the nitration of substituted benzenes, and as we shall further demonstrate in future papers in this series.

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