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*Review Commentary*

# The nature of electrical effect transmission

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**epoc** ABSTRACT: Methods of distinguishing between the field and inductive modes of electrical effect transmission are derived and applied. They show clearly that neither the classical inductive effect nor the Exner–Fiedler inductive effect can be the mode of transmission of electrical effects. This transmission is best described by a modified field effect model. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: electrical effects; inductive effect; field effect; electrical effect transmission; meta-para ratio; *LL* relationship; polarizability dependence; path dependence

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## INTRODUCTION

For many years, the mode of transmission of electrical effects has been a problem of great significance to those interested in structural effects on chemical reactivities, chemical and physical properties and biological reactivities. By 1950, two different models had been suggested, the classical inductive effect (CIE)[1,2] and the classical field effect (CFE).[3–5] Reynolds[6] has reviewed the mode of transmission. Bowden and Grubbs[7,8] have reviewed the evidence for the angular dependence of the electrical effect. This evidence supports some type of field effect as the mode of transmission. Exner and Fiedler[9] suggested a modified inductive effect model. Exner and Friedl[10] have argued that the evidence is unclear and can be just as well accounted for by this modified form of the inductive effect (EFIE model). We have shown (M. Charton and B. I. Charton, unpublished results) that a modified field effect (MFE) model can account for the available data on the transmission of electrical effects. The dependence of substituent electrical effect transmission on substituent–reaction site distance was studied in the systems X–G–Y and X–Y where X is a variable substituent, Y a reaction site and G a skeletal group. Reaction types were molecule–molecule (MM), molecule–ion (MI) and molecular ionization (Mi). MM reactions include proton transfer equilibria (p$K_a$s) of compounds with Y = $CO_2H$, OH, $SO_2H$, $NR_2H^+$, azarenes, $PO_2(OH)^-$ and SH, gas-phase $\Delta G_{acid}$ values for Y = $CO_2H$ and OH and proton affinities for $NR_2H^+$, proton transfer reaction rates for $XGCO_2H$ with $Ph_2CN_2$ and hydrogen bonding equilibria for XGCN (p$K_{HB}$). Mi include rates of base-catalyzed ester hydrolysis, nucleophilic substitution of $PhCOCH_2Br$ by $XGCO_2^-$ and protodetritiation of T-substituted arenes. All Mi reactions were solvolyses of XGCHLgMe (Lg is a leaving group) and $XGCMe_2Cl$. The measure of electrical effect magnitude used was *L*, the coefficient of the localized (field and/or inductive) effect obtained from correlation of appropriate data sets with linear free energy relationships. The substituent–reaction site distance was parameterized by *n*, the number of bonds between the substituent and the nearest atom of the reaction site undergoing bond change ($Y^1$). Correlations of *L* with $1/n^2$ and $1/n$ and of log $|L|$ with log *n* by simple linear regression analysis determined the dependence of *L* on *n*. Data sets with very large values of $\theta$, the angle between the X–G bond and the line joining X and $Y^1$ were excluded. Data in aqueous–organic solvent mixtures can be combined into a single data set regardless of the solvent composition, probably due to preferential solvation by water. The results support a modified field effect as the mode of transmission. This model differs from that of Kirkwood and Westheimer[3] as *m* seems to depend on the charge difference between initial and final states. In this paper we do not intend to review the dependence of electrical effect transmission on $\theta$ as Bowden and Grubbs[7,8] have already described it in detail. Here we present the results of several tests which should distinguish between the two types of model.

Our objective in this work may be summed up as follows. There is a *universal* electrical effect which occurs in all XGY systems (where X, G and Y are substituent, skeletal group and reaction site, respectively). It is due to the action of X on Y. It is the only electrical effect observed when X is bonded to an $sp^3$-

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hybridized C atom of G. The universal effect of X can be represented by a substituent constant $\sigma_U$. Our goal is to determine which of the following possible models best represents the mode of transmission of the universal electrical effect:

(a) the classical field effect (Kirkwood–Westheimer);
(b) the classical inductive effect;
(c) the modified inductive effect (Exner–Fiedler);
(d) the modified field effect (Charton);
(e) a new model, neither field nor inductive, required owing to the failure of all of the other models.

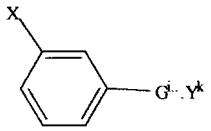
## DISTINGUISHING THE MODE OF ELECTRICAL EFFECT TRANSMISSION

### The *meta–para* ratio

Let us define the ratio

$$r_{m/p} \equiv L_m/L_p \tag{1}$$

where $L_m$ and $L_p$ are the localized electrical effect coefficients for skeletal groups **1** and **2**. The $G^i$ in these

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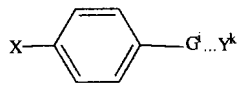



2

structures are the atoms of the skeletal group G between the benzene ring and the closest atom of the reaction site, $Y^1$. Values of $r_{m/p}$ are reported in Table S1 (supplementary material). There are now two models of the inductive effect; the classical (CIE) model and the Exner–Fiedler (EFIE) model. In both models transmission through an acyclic skeletal group is given simply by the equation

$$t_a = f^n \tag{2}$$

where $t_a$ is the contribution to the overall transmission, $f$ is the fall-off factor and $n$ is the number of bonds in the path between X and $Y^1$. If a skeletal group includes a ring then there are three contributions to the transmission: (1) $t_{a1}$, due to the acyclic bonds between X and the ring; (2) $t_c$, the sum of the paths through the ring bonds, each paths contribution being given by Eqn. (2); The total contribution $t_c$ is

$$t_c = \sum_{j=1}^{l} (f^n)_j \tag{3}$$

(3) $t_{a2}$, the contribution due to the acyclic bonds between the ring and $Y^1$.

The overall transmission, of which $L$ is a measure, is then the product of the $t_{ai}$ and the $t_{ci}$. Thus, in the general case for $m$ rings separated by $m-1$ acyclic segments the maximum total number of acyclic segments is $m-1+2$ or $m+1$. $L$ will be given by

$$L_G = \prod_{i=1}^{l} t_{aj} \prod_{j=1}^{m} t_{cl} \tag{4}$$

From Eqns (2), (3) and (4) we have

$$L_G = \prod_{i=1}^{l} (f^b)_i \prod_{j=1}^{m} \sum_{k=1}^{n} (f^b)_{j,k} \tag{5}$$

The EFIE model differs in its treatment of rings. Kirchoffs laws are assumed to apply to G that include rings.

For $r_{m/p}$, we have from structures **1** and **2**

$$L_m = fb_m f^{n'} \tag{6a}$$

$$L_p = fb_p f^{n'} \tag{6b}$$

and

$$r_{m/p} = \frac{L_m}{L_p} = \frac{fb_m f^{n'}}{fb_p f^{n'}} = \frac{b_m}{b_p} \tag{7}$$

where $b_m$ and $b_p$ represent the contributions of transmission through the *meta*- and *para*-substituted benzene rings, respectively, and $n'$ is the number of bonds between the benzene ring and the nearest reacting atom of the reaction site. The classical inductive effect (CIE) model predicts that $r_{m/p}$ is constant for all values of $n'$.

The EFIE model represents transmission through two or more paths by an expression analogous to Kirchoff's law for the resistance of parallel resistors. Transmission through a single path is represented in the same manner as the CIE model. We may represent transmission through the benzene ring in this model as $B_m$ and $B_p$. Then,

$$r_{m/p} = \frac{L_m}{L_p} = \frac{fB_m f^{n'}}{fB_p f^{n'}} = \frac{B_m}{B_p} \tag{8}$$

Again, the model predicts that $r_{m/p}$ is constant for all values of $n'$.

Both the classical field effect model and any modification of it require that the transmission of the field effect have a dependence on both the angle $\theta$ and on

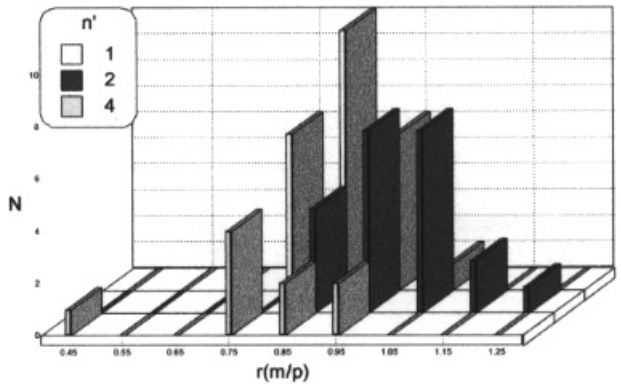



**Figure 1.** The distribution of $r_{m/p}$ as a function of $n'$, the number of bonds between the ring and the reaction site

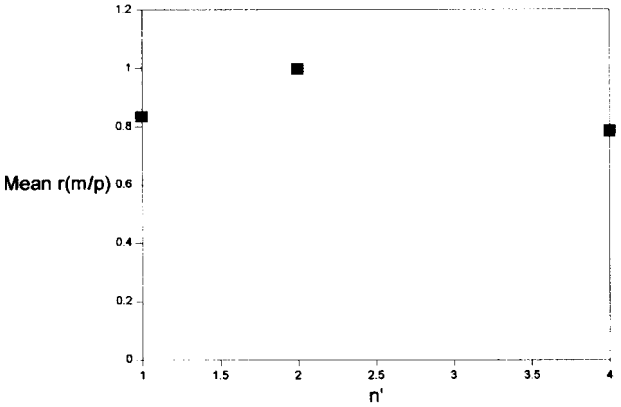



**Figure 2.** The variation of the mean values of $r_{m/p}$ at constant $n'$ with $n'$

the distance parameter $r^{-m}$ and therefore $r_{m/p}$ need not be constant as a function of $n'$. Values of $r_{m/p}$ are best compared for reactions of the same type. As the largest number of values available for proton transfer equilibria this reaction was chosen. The available values are reported in Table S1. It seems clear from these results that $r_{m/p}$ is not constant. Mean values and their standard deviations in parentheses of $r_{m/p}$ for proton transfer equilibria with $n' = 1$, 2 and 4 are 0.834 ($\pm$0.0739), 0.996 ($\pm$0.111) and 0.784 ($\pm$0.144), respectively. The distribution of $r_{m/p}$ values is shown in Fig. 1 and a plot of the mean values against $n'$ is shown in Fig. 2. The results are in accord with the MFE but not with either the CIE or the EFIE.

## The *L,L* relationship

Consider the MFE equation:

$$L = \hat{C}n^{-m} + a_0 \tag{9}$$

where $\hat{C}$ is the slope, $a_0$ the intercept, $m$ the exponent and $n$ the number of bonds between the first atom of the reaction site and the first atom of the substituent. In each case the first atom is that closest to the skeletal group; $m$ may have values of 1 or 2.

If it is written for a reaction site Y and a reference reaction site $Y^0$:

$$L_{GY} = C_Y n^{-m} + a_{0Y} \tag{10}$$

$$L_{GY^0} = C_{Y^0} n^{-m} + a_{0Y^0} \tag{11}$$

Solving Eqn. (11) for $1/n^m$ gives

$$n^{-m} = (L^0_{GY} - a_{0Y^0})/C_{Y^0} \tag{12}$$

Substituting Eqn. 12 in Eqn. 10, we have

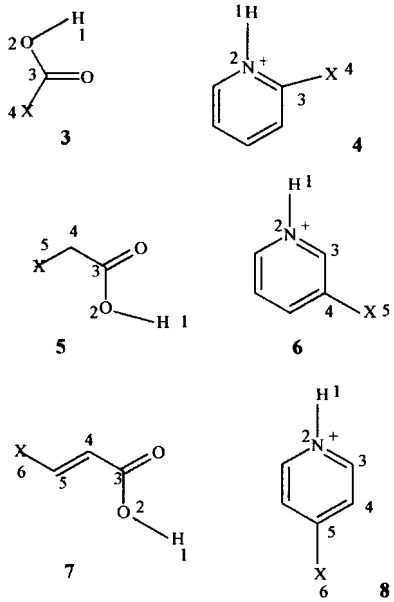
$$L_{GY} = (C_Y/C_{Y^0})(L_{GY^0} - a_{0Y^0}) + a_{0Y} \tag{13}$$

$$= (C_Y/C_{Y^0})L_{GY^0} + a_{0Y} - a_{0Y^0}/C_{Y^0} \tag{14}$$

or

$$L_{GY} = a_1 L_{GY^0} - a_o \tag{15}$$

Equation (15) predicts a linear relationship between the $L$ values for data sets XGY having some reaction site of interest and those of data sets $XGY^0$ of reference reaction sites which have the same geometry. Data sets are considered to have the same geometry when each atom of XGY can mapped on to a corresponding atom of $XGY^0$. Three such pairs of data sets are shown in **3**–**8**. Clearly, if




$XGY^0$ and XGY have the same geometry they will have the same values of $n$ and $\theta$. As the reference reaction site we have chosen the nitrogen atom of azarenonium ions in water. We have obtained significant correlations with

**Table 1.** Data sets correlated with Eqn. (15)[a]

**CA1**. p$K_a$, XGCO$_2$H vs p$K_a$ XG$_{Azrn}$, water, 20–25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 9.63, *2-Py, 11.3*; none, 9.63, *2-Qu, 11.1*; $CH_2$, 4.05, *3-Py, 6.54*; $CH_2$, 4.05, *3-Py, 6.22*[20]; $CH_2$, 4.05, *2-$CH_2$Py, 5.51*; $CH_2$, 4.05, *3-Qu, 4.87*; CHMe, 4.04, *3-Py, 6.54*; CHMe, 4.04, *3-Py, 6.22*[20]; CHMe, 4.04, *2-$CH_2$Py, 5.51*; CHMe, 4.04, *3-Qu, 4.87*; 1-Vn, 4.14, *3-Py, 6.54*; 1-Vn, 4.14, *3-Py, 6.22*[20]; 1-Vn, 4.14, *2-$CH_2$Py, 5.51*; 1-Vn, 4.14, *3-Qu, 4.87*; E-2-Vn, 2.41, *4-Py, 5.22*; E-2-Vn, 2.41, *4-Qu, 5.27*; E-2-Vn, 2.41, *5-Qu, 3.13*; E-2-Vn, 2.41, *7-Qu, 3.63*; (*E*)-2-Vn, 2.41, *3-$CH_2$Py, 3.15; (E)-CMe=CH—, 2.84; 4-Py, 5.22; (E)-CMe=CH—, 2.84; 4-Qu, 5.27; (E)*-CMe=CH—, 2.84; *5-Qu, 3.13*; (*E*)-CMe=CH—, 2.84; *7-Qu, 3.63*; (*E*)-CMe=CH—, 2.84; *3-$CH_2$Py, 3.15*; (E)-Vn$CH_2$, 1.18; *4-$CH_2$Py, 3.19*; 3-Pn, 0.943, *4-$CH_2$Py, 3.19*; 4-Pn, 0.976, *6-iQu, 2.50*; (*E*)-4′-Pn-2-Vn, 0.446, *(E)-4″-Pn-2′-Vn-2-Py, 0.949*.

**CA2**. p$K_a$, XGCO$_2$H vs p$K_a$, XG$_{Azrn}$, AE, 20–25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 12.0, *2-Py, 11.3*; none, 12.0, *2-Qu, 11.1*; $CH_2$, 4.52, *3-Py, 6.54*; $CH_2$, 4.52, *3-Py, 6.22*[20]; $CH_2$, 4.52, *2-$CH_2$Py, 5.51*; $CH_2$, 4.52, *3-Qu, 4.87*; $CH_2$, 4.47, *3-Py, 6.54*; $CH_2$, 4.47, *3-Py, 6.22*[20]; $CH_2$, 4.47, *2-$CH_2$Py, 5.51*; $CH_2$, 4.47, *3-Qu, 4.87*; $CH_2$, 5.44, *3-Py, 6.54*; $CH_2$, 5.44, *3-Py, 6.22*[20]; $CH_2$, 5.44, *2-$CH_2$Py, 5.51*; $CH_2$, 5.44, *3-Qu, 4.87*; (*E*)-2-Vn, 2.89, *4-Py, 5.22*; (*E*)-2-Vn, 2.89, *4-Qu, 5.27*; (*E*)-2-Vn, 2.89, *5-Qu, 3.13*; (*E*)-2-Vn, 2.89, *7-Qu, 3.63*; (*E*)-2-Vn, 2.89, *3-$CH_2$Py, 3.15*; $CH_2CH_2$, 2.24, *4-Py, 5.22*; $CH_2CH_2$, 2.24, *4-Qu, 5.27*; $CH_2CH_2$, 2.24, *5-Qu, 3.13*; $CH_2CH_2$, 2.24, *7-Qu, 3.63*; $CH_2CH_2$, 2.24, *3-$CH_2$Py, 3.15*; 3,1-And, 1.47, *4-$CH_2$Py, 3.19*; 3-Pn, 1.58, *4-$CH_2$Py, 3.19*; 3,1-Azn, 1.61; *4-$CH_2$Py, 3.19*; 4-Pn, 1.57, *6-iQu, 2.50*; 4,1-Nn, 1.75, *6-iQu, 2.50*; (*Z,E*)-4″-Pn-2′-Vn-2-Vn, 0.527, *(E)-4″-Pn-2′-Vn-4-Py, 0.813;* (E)-4′-Pn-2-Vn, 0.809, *(E)-4″-Pn-2′-Vn- 2-Py, 0.949*.

**CA3**. p$K_a$, XGCO$_2$H vs p$K_a$, XG$_{Azrn}$, AMCS, 25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 11.8, *2-Py, 11.3*; none, 11.8, *2-Qu, 11.1*; $CH_2$, 4.58, *3-Py, 6.54*; $CH_2$, 4.58, *3-Py, 6.22*[20]; $CH_2$, 4.58, *2-$CH_2$Py, 5.51*; $CH_2$, 4.58, *3-Qu, 4.87*; (*E*)-2-Vn, 3.41, *4-Py, 5.22*; (*E*)-2-Vn, 3.41, *4-Qu, 5.27*; (*E*)-2-Vn, 3.41, *5-Qu, 3.13*; (*E*)-2-Vn, 3.41, *7-Qu, 3.63*; (*E*)-2-Vn, 3.41, *3-$CH_2$Py, 3.15*; $CH_2CH_2$, 1.81, *4-Py, 5.22*; $CH_2CH_2$, 1.81, *4-Qu, 5.27*; $CH_2CH_2$, 1.81, *5-Qu, 3.13*; $CH_2CH_2$, 1.81, *7-Qu, 3.63*; $CH_2CH_2$, 1.81, *3-$CH_2$Py, 3.15*; 3,1-bc[2.2.2]Ocn, 1.38, *4-$CH_2$Py, 3.19*; 3-Pn, 1.80, *4-$CH_2$Py, 3.19*; 4-Pn, 1.89, *6-iQu, 2.50*.

**CA4**. p$K_a$, XGCO$_2$H vs p$K_a$, XG$_{Azrn}$, AM, 20–25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 7.47, *2-Py, 11.3*; none, 7.47, *2-Qu, 11.1*; $CH_2$, 4.15, *3-Py, 6.54*; $CH_2$, 4.15, *3-Py, 6.22*[20]; $CH_2$, 4.15, *2-$CH_2$Py, 5.51*; $CH_2$, 4.15, *3-Qu, 4.87*; $CH_2$, 3.74, *3-Py, 6.54*; $CH_2$, 3.74, *3-Py, 6.22*[20]: $CH_2$, 3.74, *2-$CH_2$Py, 5.51*; $CH_2$, 3.74, *3-Qu, 4.87*; 3-Pn, 1.66, *4-$CH_2$Py, 3.19*; 4-Pn, 1.39, *6-iQu, 2.50*.

**CA5**. p$K_a$, XGCO$_2$H vs p$K_a$, XG$_{Azrn}$, MeOH, 20–25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 9.20, *2-Py, 11.3*; none, 9.20, *2-Qu, 11.1*; $CH_2$, 3.60, *3-Py, 6.54*; $CH_2$, 3.60, *3-Py, 6.22*[20]; $CH_2$, 3.60, *2-$CH_2$Py, 5.51*; $CH_2$, 3.60, *3-Qu, 4.87*; $CH_2CH_2$, 1.29, *4-Py, 5.22*; $CH_2CH_2$, 1.29, *4-Qu, 5.27*; $CH_2CH_2$, 1.29, *5-Qu, 3.13*; $CH_2CH_2$, 1.29, *7-Qu, 3.63*; $CH_2CH_2$, 1.29, *3-$CH_2$Py, 3.15*; 3-Pn, 1.49, *4-$CH_2$Py, 3.19*; 4-Pn, 1.45, *6-iQu, 2.50*.

**CA10**. $\Delta G_{acid}$, XGCO$_2$H vs p$K_a$, XG$_{Azrn}$, MeOH, 20–25 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 46.7, *2-Py, 11.3*; none, 46.7, *2-Qu, 11.1*; $CH_2$, 26.1, *3-Py, 6.54*; $CH_2$, 26.1, *3-Py, 6.22*[20]; $CH_2$, 26.1, *2-$CH_2$Py, 5.51*; $CH_2$, 26.1, *3-Qu, 4.87*; $CH_2CH_2$, 11.5, *4-Py, 5.22*; $CH_2CH_2$, 11.5, *4-Qu, 5.27*; $CH_2CH_2$, 11.5, *5-Qu, 3.13*; $CH_2CH_2$, 11.5, *7-Qu, 3.63*; $CH_2CH_2$, 11.5, *3-$CH_2$Py, 3.15*; 3-Pn, 13.6, *4-$CH_2$Py, 3.19*; 4-Pn, 15.8, *6-iQu, 2.50*.

**CD1**. Log $k$, XGCO$_2$H + $Ph_2CN_2$ vs p$K_a$, XG$_{Azrn}$, EtOH, 30 °C. $G_{CO_2H}$, p$K_{a_{CO2H}}$, $G_{Azrn}$, p$K_{a_{Azrn}}$: none, 4.74, *2-Py, 11.3*; none, 4.74, *2-Qu, 11.1*; $CH_2$, 2.50, *3-Py, 6.54*; $CH_2$, 2.50, *3-Py, 6.22*[20]; $CH_2$, 2.50, *2-$CH_2$Py, 5.51*; $CH_2$, 2.50, *3-Qu, 4.87*; (*E*)-2-Vn, 1.81, *4-Py, 5.22*; (*E*)-2-Vn, 1.81, *4-Qu, 5.27*; (*E*)-2-Vn, 1.81, *5-Qu, 3.13;* (*E*)-2-Vn, 1.81, *7-Qu, 3.63*; (*E*)-2-Vn, 1.81, *3-$CH_2$Py, 3.15*; 3-Pn, 0.891, *4-$CH_2$Py, 3.19*; 4-Pn, 0.865, *6-iQu, 2.50*; (*E*)-4′-Pn-2-Vn, 0.378, *(E)-4″-Pn-2′-Vn-2-Py, 0.949*.

[a] Abbreviations: Vn, vinylene; Pn, phenylene, Nn, naphthylene, Azn, azulylene, Fln, fluorenylene; cPrn, cyclopropylene; cBun, cyclobutylene, cPen, cyclopentylene, cHxn, cyclohexylene; s[3.3]Hpn, spiro[3.3]heptylene; bc[2.2.1]Hpn, bicyclo[2.2.1]heptylene; bc[2.2.2]Oen, bicyclo[2.2.2]octylene; bc[2.2.2]Ocn, bicyclo[2.2.2]octylene; Adn, adamantylene; Cbn, cubanylene, Fn, furylene; Tn, thiophenylene; Spn, selenophenylene; Tpn, tellurophenylene; Prn, pyrrolene, Pyn, pyridylene, Ozn, oxazolylene; Tzn, thiazolylene; Bfn, benzofurylene; Btn, benzothiophenylene; Pnn, pyrenylene; Idn, indolylene; Py, pyridyl, Qu, quinolyl; iQu, isoquinolyl. Absence of a skeletal group is indicated by 'none.'

Eqn. (15) for p$K_a$s of carboxylic acids in water, aqueous ethanol, aqueous methyl Cellosolve, aqueous methanol and methanol, $\Delta G_{acid}$ values in the gas phase and log $k$ values for the reaction of carboxylic acids with $Ph_2CN_2$. The data used in correlations with Eqn. (15) are given in Table 1, the results of the correlations in Table S2 (supplementary material). All of the seven sets studied gave significant results. We now derive a similar relationship from the classical inductive effect for XGY$^0$ and XGY sets with $k$ paths of the same length.

$$L_{GY} = \zeta_{GY} k_{GY} f^n \quad (16a)$$

$$L_{GY^0} = \zeta_{GY^0} k_{GY^0} f^n \quad (16b)$$

$$(L_{GY}/\zeta_{GY} k_{GY}) = f^n = (L_{GY^0}/\zeta_{GY^0} k_{GY^0}) \quad (17)$$

$$L_{GY} = (\zeta_{GY}/\zeta_{GY^0})(k_{GY}/k_{GY^0}) L_{GY^0} \quad (18)$$

where $\zeta_{GY}$ and $\zeta_{GY^0}$ are constants and $k_{GY}$ and $k_{GY^0}$ are variables. If the CIE is valid, a significant correlation should not be observed as the ratio $k_{GY}/k_{GY^0}$ varies from data point to data point. This is equally true in the case where the paths are of different length.

## X— ZCH$_2$—CO$_2$H data sets

Another test for the validity of the CIE and EFIE results

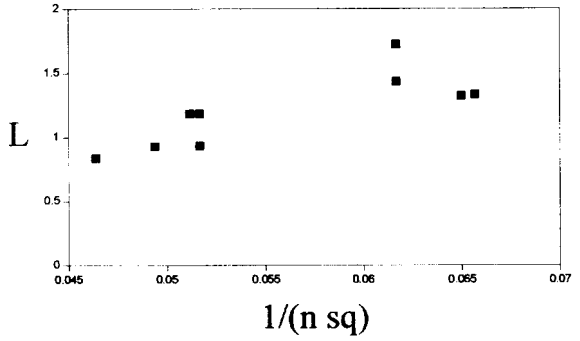



**Figure 3.** *L* as a function of $1/n^2$ for 3-substituted-3-*Z*-propanoic acids

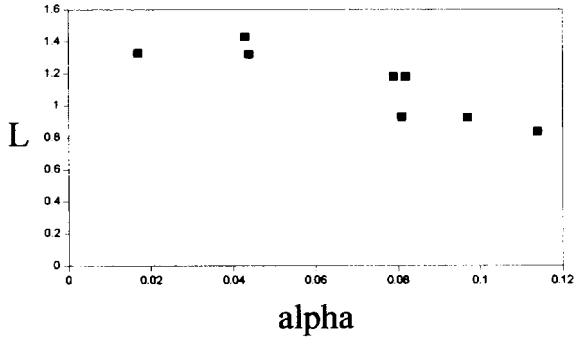



**Figure 4.** *L* as a function of α for 3-substituted-3-*Z*-propanoic acids

from the *L* values for the system X—$ZCH_2$—$CO_2H$, where Z, itself a part of the skeletal group, may be $CH_2$, O, S, S(O), $S(O)_2$, Se, NH, and P(O). Z is constant within a data set. For all compounds of this type *n*, the number of bonds between the substituent X and the O atom to which H is bonded, is 4. Presumably, any difference in the inductive effect in these systems is due to a difference in the polarizability of Z,[11–14] with *L* increasing as polarizability increases. As a measure of the polarizability of Z we have used α, defined as the group molar refractivity of Z divided by 100.[6] Any difference in the field effect should be due to differences in bond length of the XZ and CZ bonds, as the remainder of the geometry is very similar throughout the different Z groups. The field effect should decrease as the ZX and CZ bond lengths increase; it is linear in $n^{-2}$ for molecule–molecule reactions such as carboxylic acid ionization in which the product has a diffuse charge. A plot of *L* versus α is shown in Fig. 3; it shows a rough relationship but with a negative slope rather than the positive slope that is expected. *L* decreases as α increases. Correlation of *L* with the equation

$$L = A\alpha + a_o \tag{19}$$

gave, after the exclusion of the *L* value for $Z = CH_2$ at 18°, the equation

$$L = -6.01(\pm 1.42)\alpha + 1.56(\pm 0.108) \tag{20}$$
$$100r^2, 74.89; F, 17.89; S_{\text{est}}, 0.119; S^0, 0.579; N, 8$$

A plot of *L* versus $n^{-2}$ shows the expected linear relationship (Fig. 4). Correlation with Eqn. (21) gave Eqn. (22) as the best regression equation:

$$L = \hat{C}n^{-2} + a_0 \tag{21}$$
$$L = 26.5(\pm 5.49)n^{-2} - 0.345(\pm 0.309) \tag{22}$$
$$100r^2, 79.59; F, 23.40; S_{\text{est}}, 0.108; S^0, 0.522; N, 8$$

again on exclusion of the value (*L* = 1.72 at 18°) for $Z = CH_2$. Values of *n* for the XZ and CZ bonds were obtained by dividing their bond lengths by the average bond length in skeletal groups that contain no heteroatoms (assumed to be 150 pm). Values of the CZ bond length (assumed equal to the XZ bond length), $n_Z$, *L*, *n*, $1/n^2$ and α are reported in Table S3 (supplementary material).

Equation (22) is significant at the 99.5% confidence level. In view of the narrow range of *n*, the results are very good. Equation (20) not only gives a much poorer fit but, more importantly, has the wrong sign for the slope. That the polarizability α and *L* are related is not surprising as α is a linear function of the bond length of the C—Z bond:

$$l_{\text{CZ}} = 6.30(\pm 0.507)\alpha + 1.27(\pm 0.0386) \tag{23}$$
$$100r^2, 96.26; F, 154.6; S_{\text{est}}, 0.0426; S^0, 0.223; N, 8.$$

Clearly, the results agree best with some form of the field effect.

## The significance of path dependence

The classical inductive effect requires a dependence on the number of paths. This dependence can be tested for by considering the special case in which all of the paths in a system are of the same length. Then, for a data set consisting of systems of this type, the inductive effect is given by the equation

$$L = Çkf^n \tag{24}$$

where *n* is the number of bonds between the substituent X and the atom of the reaction site nearest to it, *k* is the number of paths, *f* is the fall-off factor and *Ç* is a constant. Writing Eqn. (24) in logarithmic form gives

$$\log|L| = n \log f + \log k + \log Ç \tag{25}$$

or

**Table 2.** Data sets used in correlations with Eqns (26), (27), (29) and (36)[a]

**CA1**. $XGCO_2H$, water, 25 °C. G,L:4,1-bc[2.2.1]Hpn, 1.12[b](0.0515); 4-$PnOCH_2$, 0.317(0.0749); C≡C, 2.40(0.249); (*E*)-2-Vn, 2.41(0.0985); 4-Pn[c], 0.963(0.0607); 4-$PnCH_2$, 0.557(0.0216); none, 9.63(0.696); 4-Pn[c], 0.976(0.0262); 4-$PnSCH_2$, 0.359(0.0654); 4-$PnS(O)CH_2$, 0.221(0.0158); 4-$PnS(O)_2CH_2$, 0.258(0.0523); $CH_2$, 4.05(0.0529); 1-Vn, 4.14(0.234); (*E*)-4-cHxn[c], 0.747(0.0320); (*E*)-4-Pn-2-Vn, 0.446(0.0277); 4-$PnOCH_2$, 0.352(0.0568); 4-$PnSeCH_2$, 0.399(0.0252); CHMe, 4.04(0.101); (*E*)-CX=CHPh, 4.25(0.643); (*E*)-CX=CHMe, 3.55(0.251); $CX=CMe_2$; 3.56(1.42); (*E*)-MeC=CXH, 2.58(0.245); (*E*)-CH=CXMe, 2.84(0.159); (*E*)-2-$VnCH_2$[c]; 1.18(0.131); 4,1-bc[2.2.2]Ocn[c], 0.878(0.0311); $(CH_2)_4$, 0.840(0.104); $(CH_2)_2$[a], 1.43(0.0935); 5,2-Fn, 1.37[b]; 5,2-Tn[b], 1.24; 5,2-Spn[b], 1.27; 5,2-Tpn[b], 1.18; 5,2-Prn[b], 1.40; 3-Pn[b], 0.943; $(CH_2)_3$[b], 0.698(0.0533).

**CA2**. L, $XGCO_2H$, p$K_a$, aq. EtOH, 25 °C. G, L: 4-Pn[d], 1.57(0.0363); 4-$PnCH_2$, 0.793(0.0328); 4-$PnCMe_2CH_2$, 0.433(0.0169); 3,1-Azn[e], 1.61(0.0891); (*E*)-2-Vn, 2.89(0.310); 4,1-bc[2.2.2]Ocn[d], 1.44(0.0862); 6,2-s[3.3]Hpn, 0.738(0.0353); 4,1-Cbn[d], 1.43(0.0972); 3,1-And[e], 1.47(0.190); 4,1-cHxn[d], 1.10(0.0741); $CH_2$, 4.52(0.145); 4,1-bc[2.2.2]Ocn[d], 1.56(0.0509); 4-$CH_2$Pn, 0.905(0.0442); 3,1-bc[2.1.0]Pen[f], 2.25; $(CH_2)_3$[e], 1.17; none, 12.0((1.21); $CH_2$, 5.44(0.516); 3-Pn[e], 1.39(0.0730); 3-Pn[e], 1.60(0.0906); 3-Pn[e], 1.59(0.0879); 4-Pn[d], 1.42(0.0137); 4-Pn[d], 1.74(0.101); 4-Pn[d], 1.59(0.144); 4-$PnCOCH_2CO$, 0.416(0.0502); 4′-Pn-(*E*)-2-Vn, 0.807(0.0308); $CH_2$, 4.47; 3,1-And[e], 1.39(0.0799); 4,2-Nn[e], 1.14(0.0999); 4′-PnS-(*E*)-2-Vn, 0.709(0.00310); 4′-PnS(O)-(*E*)-2-Vn, 0.279(0.0322); 4′-$PnS(O)_2$-(*E*)-2-Vn, 0.380(0.0684); 4-$PnCH_2CH_2$, 0.405(0.0160); 3,1-Nn[e], 1.38(0.136); 3-Pn[e], 1.58; 6,2-Nn, 0.857(0.0517), $(CH_2)_4$[d], 1.65(0.389).

**CA3**. L, $XGCO_2H$, p$K_a$, 80% aq. $MeOCH_2CH_2OH$, 25 °C. G, L: 4-Pn, 1.89(0.127); (*E*)-2-Vn, 3.41(0.227); 4-$CH_2$Pn, 0.964(0.120); $CH_2$, 4.58(0.134); none, 11.8(0.853); 4,1-bc[2.2.2]Ocn, 1.20(0.0279).

**CA4**. L, $XGCO_2H$, p$K_a$, aq. MeOH, 25 °C. G, L, $\varphi_M$: none, 7.47(1.21); $CH_2$, 4.15(0.374); 4,1-bc[2.2.2]Ocn[g], 0.982; 4-Pn[g], 1.33(0.146); 4-Pn[g], 1.39(0.0127); 4-Pn[g], 1.36(0.122); (*E*)-4-cHxn[g], 0.774(0.0875); $CH_2$, 3.74(0.388); 4,1-bc[2.2.2]Ocn[g], 1.06(0.0368); 4″-Pn-(*E*)-2′-CH=N-4-Pn, 0.125(0.0119); 4″-Pn-(*E*)-2′-N=CH-4-Pn, 0.271(0.0504).

**AB1**. L, $XGNH_3^+$, p$K_a$, aq., 25 °C. G, L: none, 24.9; $CH_2$, 9.16(0.283); $CH_2CH_2$, 4.82(0.268); 4-Pn, 3.74(0.118); 4-Pn, 3.87(0.132); 4-Pn, 3.81(0.218); 4-$PnCH_2$, 1.09(0.0922); 4-$PnCH_2CH_2$, 0.400(0.019); $(CH_2)_3$, 2.17(0.227); $(CH_2)_4$, 1.40(0.203); 4′4-$Pn_2$, 0.735(0.0933); 4′4-PnOPn, 0.639(0.0982).

**AB2**. L, $XGNH_3^+$, p$K_a$, aq. EtOH, 25 °C. G, L: none, 28.9; 4-Pn, 4.82(0.564); 4′-PnC≡CPn-4, 0.360(0.011); 4″-Pn-(*E*)-2′-Vn-4-Pn, 0.422(0.018); 4′-$PnCH_2O$-4-Pn, 0.195(0.011); 4′-Pn-4-Pn, 0.755(0.0635).

**BEH1**. L, $XGCO_2Et$, log *k*, $OH^-$, aq. EtOH, 24–30 °C. G, L: 4,1-bc[2.2.2]-Ocn[h], 2.19(0.154); 4,1-Nn, 2.37; 4′-Pn-4-Pn, 0.607(0.0802); 4-PnC≡C, 1.00(0.0579); 4-$PnCH_2$, 1.14(0.0249); 4-$PnCH_2$, 1.07(0.0486); (*E*)-4′-Pn-2-Vn, 1.14(0.0717); 4-$PnCH_2CH_2$, 0.642(0.0284); none, 12.6(1.49); (*E*)-4′-Pn-2-cHxn, 0.769(0.0529); none, 10.5(0.834); 4-Pn[h], 2.31(0.134); 4-Pn[h], 2.33(0.145); 4-$PnCH_2$, 1.04(0.0364).

**BEH45**. L, $XGCO_2Ak$, $OH^-$, log *k*, aq. dioxane, 20–35 °C. L, G, Ak = Et: $CH_2$, 4.28(0.884); 5,2-Tn, 2.79(0.138); 3-Pn, 1.38(0.210); 4-Pn, 2.30(0.0639); 4-Pn, 2.33(0.0515); (*E*,*E*)-4″-Pn-2′-Vn-2′-Vn, 0.724(0.0453). Ak = Me: (*E*)-2-Vn, 4.07(0.300); 6,2-Nn, 1.79(0.0851); 7,2-Nn, 1.46(0.166); 4-Pn, 3.00(0.0457); (*E*)-4′-Pn-CO-2-Vn, 0.605(0.0679); 3-Pn, 2.18(0.106); 4-Pn, 2.26(0.0789); 4,1-cHxn[h], 1.47(0.0947); 4,1-cHxn[h], 1.46(0.0496).

**CD1**. L, $XGCO_2H$, DDM, log *k*, EtOH, 25–30 °C. L, G: $CH_2$, 2.50(0.0729); 4,1-bc[2.2.2]-Ocn, 0.686(0.0182); 4-$PnCH_2$, 0.370(0.0269); (*E*)-4,1-cHxn, 0.410(0.0297); 4′-Pn-(*E*)-2-Vn, 0.378(0.0210); (*E*)-2-Vn, 1.81(0.172); (*Z*)-4′-Pn-2-Vn, 0.430; none, 4.74; 4-Pn, 0.865(0.0753).

[a] For abbreviations, see Table 1. Standard errors of *L* ($S_L$) are given in parentheses when available.
[b] In subset CA1-5 only.
[c] In set CA1 and subset CA6.
[d] In set CA2 and subset CA2-6.
[e] In subset CA2-5 only.
[f] In set CA2 and subset CA2-5.
[g] In set 4 and subset CA4-6.
[h] In set BEH1 and subset BEH1-6.

$$\log|L| = a_1 n + a_2 \log k + a_0 \quad (26)$$

$$\log|L| = a_1 n + a_0 \quad (27)$$

where $a_1 = \log f$, $a_2 = 1$ and $a_0 = \log Ç$. Correlation of the data sets reported in Table 2 with Eqns (26) and (27) gave the results in Table S4 (supplementary material). Of the nine sets studied, none gave a statistically significant value of $a_2$. No conclusion can be drawn from eight of these data sets as log *k* is highly collinear in *n*. In the remaining set, CA4, the coefficient is not significant. In a first attempt to solve the problem, Eqn. (26) was rearranged, giving

$$\log|L| - \log k = n \log f + \log Ç \quad (28)$$

or

$$\log|L| - \log k = a_1 n + a_0 \quad (29)$$

Comparisons of values of $100r^2$, $F$ and $S^0$ from correlations with Eqns (27) and (29) were used to detect a dependence on log $k$. The results of these correlations are also reported in Table S4. The tests used to make the comparisons are as follows. For $100r^2$, we define[5]

$$\Delta^* = \Delta 100r^2 = (100r^2)_{29} - (100r^2)_{27} \tag{30}$$

Introducing a weighting factor for the number of degrees of freedom in the data set, given by $N_{\mathrm{DF}}^{1/2}$, we have

$$\tau_r \equiv \Delta^* N_{\mathrm{DF}}^{1/2} \tag{31}$$

If $\tau_{\mathrm{r}} < -2$, Eqn. (29) is obeyed; if $-2 < \tau_{\mathrm{r}} < 2$, no conclusion can be drawn; if $\tau_{\mathrm{r}} > 2$, Eqn. (27) is obeyed. For $F$ we define

$$r_F \equiv \frac{F_{27} - F_{29}}{F_{27} + F_{29}} \tag{32}$$

Then, on introducing the weighting factor, we obtain

$$\tau_F \equiv r_F N_{\mathrm{DF}}^{1/2} \tag{33}$$

If $\tau_{\mathrm{F}} < -0.250$, then Eqn. (29) is obeyed; if $-0.250 < \tau_{\mathrm{F}} < 0.250$, then no conclusion can be drawn; if $\tau_{\mathrm{F}} > 0.250$, then Eqn. (27) is obeyed.

For $S^0$ we define

$$\Delta^0 \equiv \Delta S^0 = {S_{27}}^0 - {S_{29}}^0 \tag{34}$$

On introducing the weighting factor, we have

$$\tau_S \equiv \Delta^0 {N_{\mathrm{DF}}}^{1/2} \tag{35}$$

If $\tau_{\mathrm{S}} < -0.100$, then Eqn. (27) is obeyed; if $-0.100 < \tau_{\mathrm{S}} < 0.100$, then no conclusion can be drawn; if $\tau_{\mathrm{S}} > 0.100$, then Eqn. (29) is obeyed.

The results of these tests are presented in Table S5 (supplementary material). Of the nine sets studied, four obey Eqn. (27), two obey Eqn. (29) and three are indeterminate.

In order to provide further evidence on this point, we have correlated subsets of sets CA1, CA2, CA4 and BEH1 for which $n = 6$ with the equation

$$\log |L| = a_1 \log k + a_0 \tag{36}$$

where $a_1 = 1$ and $a_0 = 6 \log f + \log Ç$. Equation (36) is obtained from Eqn. 26 by holding $n$ constant; it provides a direct test for the dependence on the number of paths. Results of the correlations are given in Table S4 and the subsets are indicated in Table S3. None of the four subsets gave anything close to a significant correlation.

Of the nine data sets studied, five have been shown to have no dependence on path number. The CIE predicts such a dependence. We are forced to conclude that the CIE does not exist.

Up to this point we have considered only the case in which all of the skeletal groups have one or more paths of the same length. We may now consider a test of the proposal that trsnsmission depends on the shortest path, and not on the number and length of any remaining paths. We consider here subsets CA1-5 and CA2-5 (Table 2) which contain all of the systems for which the shortest path length is 5. The skeletal groups in set CA1-5 include 5,2-furylene, 5,2-thienylene, 5,2-selenophenylene, 5,2-tellurophenylene, 5,2-pyrrolene, 3-phenylene, 3,1-propanylene, (*E*)-2-propenylene and bicyclo[2.2.1]heptanylene. Those in set CA2-5 include 3,1-azulylene, 3,1-naphthylene, 4,2-naphthylene, 3-phenylene, propanylene, 3,1-adamantylene and 3,1-bicyclo[1.1.1]pentanylene. All of these systems share a shortest path with $n = 5$ and with the exception of 3,1-propanylene and 3,1-(*E*)-2-propenylene they have varying numbers of longer paths. For set CA1-5 the mean value of $L$ is $1.16 \pm 0.219$. On exclusion of the $L$ value for 3,1-propanylene the mean value of $L$ is $1.21 \pm 0.146$. We believe that this is due to a conformation in which $\theta$ is unacceptably large. The mean of the $L$ values for set CA2-5 is $1.51 \pm 0.296$. On exclusion of the $L$ value for 3,1-bicyclo[1.1.1]pentanylene the mean is $1.43 \pm 0.173$. As 3,1-bicyclo[1.1.1]pentanylene is the system in which the distance is shortest and the angle $\theta$ is zero, it is an outlier. Clearly $L$ is constant for the remaining members of the susbset. This differs from the result expected for the CIE.

Finally, there is one more point of importance. From the correlations with Eqn. 26 we may obtain values of $f$ ($a_1 = \log f$). The mean value of $f$ for the nine data sets studied is $0.662 \pm 0.0410$. This value is significantly different from the value of 1/3 first reported by Derick[1] or the value of 1/2.8 given by Branch and Calvin.[2] This differs significantly from what is expected for both the CIE and the EFIE.

## CONCLUSION

Part of the difficulty in separating the two modes of transmission is due to the high degree of collinearity between $f^n$ and $n^{-m}$, as is shown by correlations with the equation

$$f^n = b_1 n^{-m} + b_0 \tag{37}$$

with values of the falloff factor of 0.2, 0.4 and 0.6. Results of the correlations are presented in Table S6 (supplementary material). Distinction between models of transmission of electrical effects must therefore be made on properties other than the dependence on distance. The problem is further complicated by the fact that both the CIE and the CFE are classical models whose application on the atomic scale is suspect.

In Table S7 (supplementary material) are summarized the predictions of the various models of the transmission of electrical effects as a function of the skeletal group G and the observed behavior. Both inductive effect models disagree with the results obtained for the dependence of transmission on $\Delta q$, the difference in charge between initial (reactant) and final (product or transition state) states. Neither inductive effect model can account for the dependence on $\theta$. Both inductive effect models cannot account for the failure of $r_{m/p}$ to be constant. The CIE model cannot account for the lack of dependence on path number. Neither inductive effect model can account for the observed value of the fall-off factor. It is clear, then, that the inductive effect is not the mode of transmission of the localized electrical effect. The CFE model exemplified by the Kirkwood–Westheimer equation is so sensitive to the choice of cavity shape that it cannot account for the observed results. We can best describe the transmission of the localized electrical effect in terms of some type of modified field effect (MFE) model:

$$L_{GY} = \acute{C} \cos\theta d^{-m} \qquad (38)$$

It is always very difficult to discard a popular idea regardless of its lack of validity. Conceptually the inductive effect is a delight. It is simple and easy to understand. This undoubtedly accounts for the numerous and passionate attempts to defend it and for the unjustifiable conclusion that it must be present in some attenuated form or that it simply cannot be distinguished from the field effect. As was noted above, both inductive and field effects are classical macroscopic electrostatic models. Their application on the molecular scale can be justified only by success. Of the two models, the field effect accounts for the observed dependence of electrical effect transmission to some extent; the inductive effect is very much poorer as a model. According to Occam's Razor we should choose the simplest model that accounts for all the observations. In view of the fact that the MFE model successfully describes all of the available chemical reactivity data on the transmission of electrical effects while neither of the inductive effect models does so, it seems clear that the inductive effect model should be discarded. There is no point in making further attempts to revive it. As the classical field effect (Kirkwood–Westheimer) model predicts a sensitivity to the chosen cavity shape and charge location which simply does not exist, it too must be discarded. To avoid endless discussions revolving about semantics and the 'soft' science to which they lead, we propose that some new name be given to the universal electrical effect that we now refer to as inductive or field.

To sum up, transmission of this universal electrical effect is a function of three parameters: (1) the shortest distance, *r*, from substituent to reaction site; (2) the angle between the substituent–skeletal group bond and *r*; and (3) the charge difference between reactant and product in the case of equilibria or transition state in the case of rate. It is not a function of (1) the number of paths between substituent and the reaction site or (2) the choice of cavity shape and charge location required by the classical field effect (Kirkwood–Westheimer) model.

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