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# The mode of transmission of electrical effects: evidence from infrared stretching frequencies

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**epoc** ABSTRACT: The transmission of the universal electrical effect in infrared stretching frequencies is well fit by the modified field effect model with $m \approx -1.5 \pm 0.2$. The considerable variation in $r_{m/p}$, the ratio of transmission of the electrical effect through meta-substituted benzene derivatives to that through para-substituted benzene derivatives and $r_{c/t}$, the ratio of the transmission of the electrical effect through the s-cis conformer to that through the s-trans conformer and the failure of these ratios to show a Gaussian distribution provides further evidence against the existence of the inductive effect. The values of $r_{m/p}$ obtained show that, in the general case, the Hammett equation is inferior to either di- or tri-parametric equations, as it assumes the equality of $\rho_m$ and $\rho_p$. This is also true of the Yukawa–Tsuno equation. It has been shown that the inductive effect does not fit the experimental data on the transmission of electrical effects in a range of chemical reactions and in infrared stretching frequencies. Recent quantum chemical calculations support the field effect as the mode of electrical effect transmission. The inductive effect model of electrical effect transmission should be abandoned. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: electrical effect; inductive effect; field effect; infrared stretching frequencies; Hammett equation; Yakawa–Tsuno equation

## INTRODUCTION

Our objective in this work is to provide further evidence from infrared stretching frequencies on the mode of electrical effect transmission. There is a universal electrical effect that occurs in all XGY systems (where X, G, and Y are substituent, skeletal group, and active site). It is due to the action of X on Y. It is the only electrical effect observed when X is bonded to two or more $sp^3$-hybridized C atoms of G. The universal effect of X can be represented by a substituent constant $\sigma_U$. Our overall 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 (CFE; Kirkwood–Westheimer);[1–4]
(b) the classical inductive effect (CIE);[1,5–7]
(c) the modified inductive effect (MIE; Exner–Fiedler);[8]
(d) the modified field effect (MFE; Charton);[9,10]
(e) some combination of the field and the inductive effects;
(f) an entirely new model required due to the failure of all of the other models.

We have already presented evidence that the dependence of substituent electrical effect transmission on substituent–reaction site distance and on the charge on reactant and product or transition state can best be described by the MFE model.[9,10] The systems studied were X–G–Y and X–Y. Reaction types considered were molecule–molecule (MM), molecule–ion (MI), and molecular ionization (Mi). MM reactions included proton transfer equilibria (p$K_a$) of compounds with Y = $CO_2H$, OH, $SO_2NH_2$, $NR_2H^+$, 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 $K_e$ for XGCN (p$K_{HB}$). MI included rates of base-catalyzed ester hydrolysis, nucleophilic substitution of $PhCOCH_2Br$ by $XGCO_2^-$,and protodetritiation of T-substituted arenes. Mi reactions were solvolyses of XGCHLgMe (where Lg is a leaving group), $XGCMe_2Cl$, and XGLg where G is norbornyl. We have also presented evidence showing that neither the CIE or the MIE models are in agreement with experiment.[11] Here we make use of infrared stretching frequencies to generalize our results further. It will be necessary to show that:

(1) the transmission of electrical effects on infrared spectra can be described successfully by the MFE model but not by the CFE model;

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(2) the transmission of electrical effects on infrared spectra cannot be described successfully by the CIE or MIE models.

In order to achieve these objectives it is necessary to have a measure of the magnitude of the electrical effect transmission. In linear free energy relationships (LFERs), for substituent effects the magnitude of the universal (polar/field/inductive/localized) electrical effect of a substituent X acting on an active site Y usually, though not always, through an intervening skeletal group G on some measurable property $Q$ is given by either $\rho$, $C$, or $L$ depending on the choice of the correlation equation. $\rho$, $C$, and $L$ are equivalent to each other. It is possible to account for electrical effects in all types of system in terms of the 'pure' parameters:

$\sigma_l$, the localized (polar/field/inductive or universal) electrical effect constant;

$\sigma_d$, the delocalized (resonance) electrical effect constant;

$\sigma_e$, the electronic demand electrical effect constant.

The resulting relationship is the LDR equation.[12,13] $L$ is the coefficient of $\sigma_l$ in the L, LD and LDR equations, $C$ is the coefficient of $\sigma_C$ in the CR equation, and $\rho$ is the coefficient of the Hammett $\sigma$ constants in the Hammett and the modified Yukawa–Tsuno equations. The $\sigma_D$, $\sigma_C$, and Hammett $\sigma$ constants are composite parameters consisting of a combination of $\sigma_d$ and $\sigma_e$, of $\sigma_l$ and $\sigma_d$, and of $\sigma_l$, $\sigma_d$ and $\sigma_e$ respectively. All of these LFERs can be derived from the LDR equation:

$$Q_X = L\sigma_{lX} + D\sigma_{dX} + R\sigma_{eX} + h \qquad (1)$$

## Field effect

The field effect is primarily dependent on the distance $r$ between the substituent and the nearest atom of the active site Y, and the cosine of the angle formed by $r$ and the X–G or, in the absence of a skeletal group, the XY bond. As a measure of $r$ we have again used $n$, the number of bonds on the shortest path between X and the nearest atom of Y (designated $Y^1$) (Fig. 1). The cos $\theta$, where $\theta$ is the angle $GXY^1$, may be neglected to a first approximation if only XGY with angles 45° or less are included in data sets, as cos $\theta$ must then lie in the range 0.707 to 1 and is roughly constant. When experimental conditions are held constant the variation of $L$ with G should be given by Eqn. (2). We have again carried out correlations with Eqn. (3). We have used the $m$ values $-2$, $-1.5$ and $-1$, and examples of the determination of $n$ are given in Fig. 1.

$$L_G = \hat{C}n^m \qquad (2)$$

$$L_G = \hat{C}n^m + a_o \qquad (3)$$

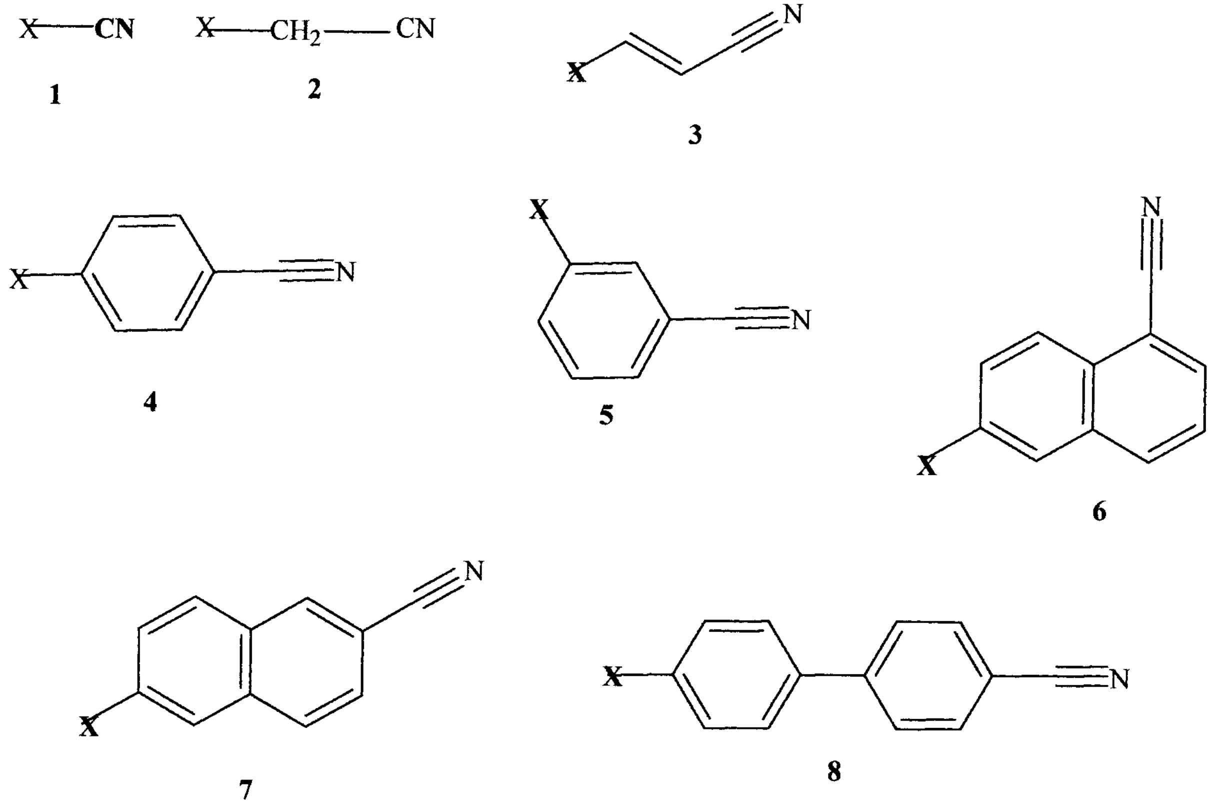


**Figure 1.** Examples of the determination of $n$. $n$ values are **1**: 1; **2**: 2; **3**: 3; **4**: 5; **5**: 4; **6**: 6; **7**: 8; **8**: 9

**Table 1.** Results of correlations with Eqns (3), (4), (6), and (7)

| Set | $m$ | $\hat{C}/m$ | $S$[d] | $s$ | $S$[d] | $a_C$ | $S$[d] | $a_o/\log \hat{C}$ | $S$[d] | $100r^2/$ $100R^2$[e] | $A100$ $R^2$[f] | $F$[g] | $S_{est}$[h] | $S^o$[i] | $N_{dp}$[j] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CN1A | −2 | 97.8 | 9.08 | – | – | – | – | 2.11 | 0.709 | 91.24 | – | 116.0 | 1.84 | 0.319 | 13 |
| CN2A | −1.5 | 75.1 | 6.38 | – | – | – | – | −0.371 | 0.639 | 92.21 | – | 130.3 | 1.84 | 0.303 | 13 |
| CN3A | −1 | 62.1 | 8.78 | – | – | – | – | −5.66 | 4.35 | 91.31 | – | 115.6 | 1.95 | 0.320 | 13 |
| CN4A[a] | – | −1.50 | 0.222 | – | – | – | – | −1.50 | 0.222 | 82.14 | – | 45.78 | 0.122 | 0.463 | 12 |
| CN1B | −2 | 93.0 | 8.26 | – | – | – | – | 2.57 | 0.809 | 94.77 | – | 126.9 | 1.73 | 0.259 | 9 |
| CN2B | −1.5 | 71.7 | 4.41 | – | – | – | – | −0.0393 | 0.682 | 97.42 | – | 264.7 | 1.22 | 0.182 | 9 |
| CN3B | −1 | 59.8 | 2.53 | – | – | – | – | −5.22 | 7.87 | 98.76 | – | 557.8 | 0.844 | 0.126 | 9 |
| CN4B[a] | – | −1.77 | 0.210 | – | – | – | – | 2.01 | 0.145 | 91.08 | – | 2.01 | 0.145 | 0.339 | 9 |
| CN1C | −2 | 95.7 | 5.88 | – | – | – | – | 2.29 | 0.510 | 92.98 | – | 264.9 | 1.78 | 0.278 | 22 |
| CN2C | −1.5 | 73.4 | 3.90 | – | – | – | – | −0.195 | 0.540 | 94.66 | – | 354.2 | 1.55 | 0.242 | 22 |
| CN3C | −1 | 60.9 | 3.19 | – | – | – | – | −5.44 | 7.07 | 94.78 | – | 363.5 | 1.53 | 0.240 | 22 |
| CN4C[a] | – | −1.62 | 2.29 | – | – | – | – | 7.93 | 0.107 | 86.19 | – | 118.6 | 0.116 | 0.391 | 21 |
| Bz1 | −2 | 133 | 6.84 | – | – | – | – | 3.57 | 0.665 | 96.70 | – | 380.9 | 2.13 | 0.195 | 15 |
| Bz2 | −1.5 | 99.4 | 5.41 | – | – | – | – | −1.15 | 0.786 | 96.30 | – | 338.3 | 2.26 | 0.207 | 15 |
| Bz3 | −1 | 74.8 | 5.04 | – | – | – | – | −4.46 | 5.04 | 95.07 | – | 250.7 | 2.60 | 0.239 | 15 |
| Bz4[a] | – | −1.39 | 0.116 | – | – | – | – | 1.98 | 0.0961 | 91.60 | – | 141.8 | 0.105 | 0.311 | 15 |
| NCS1 | −2 | 377 | 34.9 | – | – | – | – | 19.4 | 25.6 | 90.68 | – | 116.8 | 9.98 | 0.330 | 14 |
| NCS2 | −1.5 | 276 | 24.9 | – | – | – | – | −12.8 | 2.87 | 91.13 | – | 123.3 | 7.79 | 0.321 | 14 |
| NCS3 | −1 | 212 | 21.7 | – | – | – | – | −1.29 | 4.36 | 88.80 | – | 95.17 | 8.76 | 0.361 | 14 |
| NCS4[a] | – | −1.02 | 0.130 | – | – | – | – | 2.32 | 0.111 | 86.13 | – | 62.10 | 0.101 | 0.408 | 12 |
| $CO_2Ak1$[b] | −2 | 212 | 8.83 | 3.14 | 1.26 | 3.68 | 1.15 | −4.44 | 2.13 | 97.21 | 96.91 | 197.8 | 2.61 | 0.185 | 21 |
| $CO_2Ak2$[b] | −1.5 | 163 | 6.95 | 3.39 | 1.26 | 3.48 | 1.18 | −9.62 | 2.26 | 97.07 | 96.74 | 187.4 | 2.68 | 0.190 | 21 |
| $CO_2Ak3$[b] | −1 | 134 | 7.46 | 3.63 | 1.63 | 3.23 | 1.52 | −20.7 | 3.18 | 95.14 | 94.60 | 110.9 | 3.44 | 0.245 | 21 |
| $CO_2Ak4$[c] | – | −1.59 | 0.132 | 0.0804 | 0.0581 | 0.150 | 0.0541 | 1.91 | 0.150 | 86.47 | 84.96 | 36.21 | 0.123 | 0.409 | 21 |

Correlations are with Eqn. (3) unless otherwise noted. CNA sets are in $CHCl_3$, CNB sets in $CCl_4$, CNC sets include all $L$ values.

[a] Correlation with Eqn. (4).

[b] Correlation with Eqn. (6).

[c] Correlation with Eqn. (7).

[d] Standard errors of the coefficients.

[e] Percent of the variance of the data accounted for by the regression equation.

[f] $100R^2$ corrected for the number of independent variables.

[g] $F$ test for the significance of the coefficients.

[h] Standard error of the estimate.

[i] The ratio $S_{est}$/root-mean-square of the data.

[j] Number of data points in the data set.

Further evidence can be acquired by writing Eqn. (2) in logarithmic form, giving:

$$\log |L_{GY}| = m \log n_{GY} + \log \hat{C} \qquad (4)$$

Correlation of the $L$ values with Eqn. (4) is a method of determining the exponent $m$ and the coefficient $\hat{C}$. The data generally fit Eqn. (3) much better than they do Eqn. (4). There are two possible reasons for this behavior.

(1) A disadvantage of Eqn. (3) is that $L$ values for $n = 1$ or 2 have a disproportionate effect on the model. The data points for $n > 5$ tend to form a cluster. The coefficient $\hat{C}$ tends to be large, resulting in better fit.

(2) The logarithmic nature of Eqn. (3) results in a range for the independent variable of only one order of magnitude when $n$ varies from one to ten, whereas for the same range of $n$ the independent variable of Eqn. (4) has a range of two orders of magnitude.

Data for four sets of infrared stretching frequencies have been studied, with Y equal to CN, COPh, NCS, and $CO_2Ak$ (Ak is alkyl). The $L$ values used are given in Table S1 and the data sets from which they were obtained are reported in Table S2 of the supplementary material. Correlation of $L$ values for $\Delta\nu_{CN}$ in $CHCl_3$ (set 1a, Table S1) with Eqns (3) and (4) by means of simple linear regression analysis gave the regression equations CN1A through CN4A. The statistics obtained for all regression equations are reported in Table 1. The results show an $m$ value of −1.5.

Correlation of $L$ values for $\Delta\nu_{CN}$ in $CCl_4$ (set 1b, Table S1) with Eqns (3) and (4) gave the regression equations CN1B to CN4B. In this solvent $m$ has a value of about −1.8. It seemed reasonable to attempt to combine the two data sets into a single data set (set 1, Table S1) by introducing an indicator variable Sv, which takes the value one for $CHCl_3$ and zero for $CCl_4$. These solvents differ greatly in dipole moment (that of $CCl_4$ is zero) and in hydrogen bonding capability ($CCl_4$ does not hydrogen bond significantly, whereas $CHCl_3$ is a hydrogen donor).

$$L_G = \hat{C}n^m + s\mathrm{Sv} + a_o \qquad (5)$$

Correlation of the data with Eqn. (5) by means of multiple linear regression analysis gave as the best results the regression equations CN1C through CN3C. No dependence on solvent type was observed. Correlation was, therefore, also carried out with Eqn. (4), giving the regression equation CN4C after the exclusion of the value for 3-Xpn(NC)C=CHPh in $CHCl_3$. The value of $m$ is about $-1.6$, in reasonable agreement with the values found in the single solvent correlations. We have correlated $\Delta\nu_{CO}$ for XGCOPh in $CHCl_3$ and $CCl_4$ (set 2, Table S1) with Eqn. (5), giving the regression equations Bz1 through Bz3. Again, no dependence on the solvent type was observed. This may be due to the fact that the majority of the $L$ values (11 of 15) were determined in $CCl_4$. The data set was then correlated with Eqn. (4), giving the regression equation Bz4. An $m$ value of about $-1.5$ is observed.

The $\Delta\nu_{NCS}$ values for XGNCS in $CHCl_3$ and $CCl_4$ (set 3, Table S1) were correlated with Eqn. (5), giving the regression equations NCS1 through NCS3. Once more the term in Sv was not significant. It must be noted that for the 4-substituted-1-isothiocyanato-azobenzenes the solvent was benzene, which, as it is nonpolar and has about the same polarizability as $CCl_4$, was assumed to have a value of Sv equal to zero. The data set was then correlated with Eqn. (4) after the exclusion of the $L$ values for the 4-substituted-1-isothiocyanato-stilbenes and the 4-substituted methyl benzene isothiocyanates, giving the regression equation NCS4. The $m$ value is about $-1.3$.

In order to obtain a data set large enough for statistical analysis, $\Delta\nu_{CO}$ for $XGCO_2Ak$ in $CHCl_3$ and $CCl_4$ (set 4, Table S1), where Ak is methyl or ethyl, were correlated with Eqns (6) and (7), in which the effect of the alkyl group is accounted for by $n_C$, the number of carbon atoms it contains. This variable is a measure of both polarizability and mass of the alkyl group.

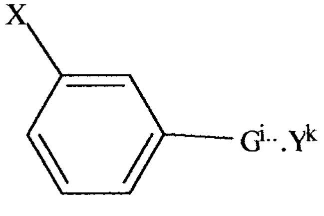
$$L_G = \hat{C}n^m + s\mathrm{Sv} + a_C n_C + a_o \tag{6}$$

$$\log|L_G| = m\log n + s\mathrm{Sv} + b_C n_C + b_o \tag{7}$$

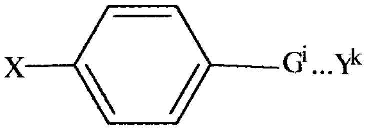
The regression equations $CO_2Ak1$ through $CO_2Ak4$ were obtained on exclusion of the value for methyl 4″-substituted-5,2-furanyl-2-ethenyl carboxylates.

This data set is the only one in which a dependence on the nature of the solvent is observed. As is shown by the values of $C$, the solvent effect is small, as is also the effect of variation in the carbalkoxy group. As the alkoxy group bonded to the carbonyl group is a strong delocalized (resonance) effect donor it should increase the electron density on the carbonyl oxygen atom, making it a better hydrogen bond H acceptor. This seems the most likely way to account for the solvent dependence. The value of $m$ is about $-1.6$.

The overall value of $m$ obtained for all of these sets is about $-1.5 \pm 0.2$. As the CFE (Kirkwood–Westheimer) model does not allow for values of $m$ between $-1$ and $-2$ it could not represent the data.



**1**



**2**

**Figure 2.** Skeletal groups of meta- and para-substituted benzene derivatives

## INDUCTIVE EFFECT MODELS

Unlike the field effect, which is dependent on molecular geometry, the inductive effect is dependent only on path length and the number of paths.

### The meta–para ratio

The meta–para ratio $r_{m/p}$ is defined as:

$$r_{m/p} \equiv L_m/L_p \tag{8}$$

where $L_m$ and $L_p$ are the localized electrical effect coefficients for skeletal groups **1** and **2** (Fig. 2) The $G^i$ in these structures are the atoms of the skeletal group G between the benzene ring and the closest atom of the reaction site, In both inductive-effect models, transmission through an acyclic skeletal group is given by:

$$t_a = f^n \tag{9}$$

where $t_a$ is the contribution to the overall transmission, $f$ is the falloff 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 inductive effect transmission according to the CIE model.

(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

path's contribution being given by Eqn. (2). The total contribution $t_c$ is:

$$t_c = \sum_{i=1}^{p} (f^n)_j \tag{10}$$

where $p$ is the number of paths.

(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 most general case for $r$ rings separated by $l-1$ acyclic segments, the maximum total number of acyclic segments is $l-1+2$ or $l+1$. The maximum occurs when X and Y are both attached to rings by acyclic segments. $L$ will be given by:

$$L_G = \prod_{i=1}^{l} t_{ai} \prod_{i=1}^{r} t_{cl} \tag{11}$$

From Eqns (9)–(11) we have:

$$L_G = \prod_{i=1}^{l} (f^n)_i \prod_{i=1}^{r} \sum_{k=1}^{p} (f^n)_{j,k} \tag{12}$$

The MIE model differs in its treatment of rings. Kirchoff's laws are assumed to apply to transmission through rings.

From the CIE we have for structures **1** and **2**:

$$L_m = fb_m f^n \tag{13a}$$

$$L_p = fb_P f^n \tag{13b}$$

Then $r_{m/p}$ is:

$$r_{m/p} = \frac{L_m}{L_p} = \frac{fb_m f^n}{fb_p f^n} = \frac{b_m}{b_p} \tag{14}$$

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 CIE model predicts that $r_{m/p}$ is constant.

The MIE model represents transmission through two or more paths by an expression analogous to Kirchoff's law for the resistance of parallel resistors. Transmission through an acyclic 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 $B_p$ respectively. Then:

$$r_{m/p} = \frac{L_m}{L_p} = \frac{fB_m f^n}{fB_p f^n} = \frac{B_m}{B_p} \tag{15}$$

Again, the model predicts that $r_{m/p}$ is constant.

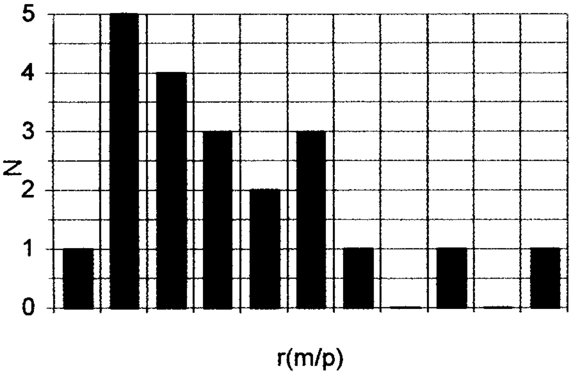


**Figure 3.** Histogram of $r_{m/p}$ values for $\Delta\nu_{CO}$

Both the CFE model and any modification of it require that the transmission of the field effect have a dependence on both the angle $\theta$ and on 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 or properties of the same type. Values of $r_{m/p}$ are presented in Table 2.

That the $r_{m/p}$ values are not constant is shown by comparing the mean values of $r_{m/p}$ obtained for phenylene systems with different Y. The values and their standard errors for Y = OH or OD, NH or ND, NCS and CN are 0.691 ± 0.0712, 0.750 ± 0.0890, 1.05 ± 0.145; and 1.38 ± 0.0820 respectively. There is no significant different difference between the values for $\nu_{OH}$ and $\nu_{NH}$. The means for OH and NH are 2.5 and 2.1 standard deviations from that for NCS, whereas the values for CN are 4.0, 7.7, and 8.4 standard deviations respectively from those for NCS, NH, and OH.

Inspection of the histogram for $\nu_{CO} r_{m/p}$ values (Fig. 3) shows clearly that $r_{m/p}$ is not constant. If it were, the values observed would be subject to random error and, therefore, should follow a Gaussian distribution. It is obvious from the histogram that they do not do so. A histogram of $\nu_{CN} r_{m/p}$ values also shows no Gaussian distribution (Fig. 4). We conclude that this evidence shows that neither inductive effect model is obeyed.

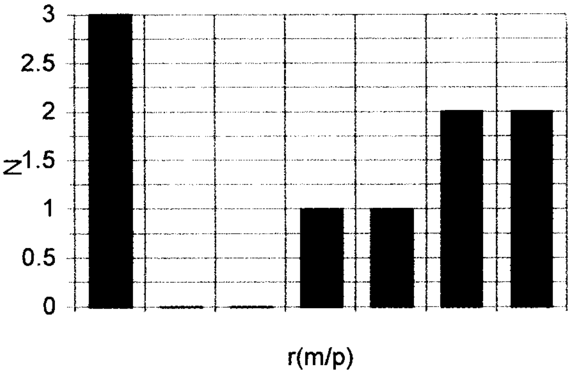


**Figure 4.** Histogram of $r_{m/p}$ values for $\Delta\nu_{CN}$

**Table 2.** Values of the meta–para ratio $r_{m/p}$

| G | Y | Sv[b] | *n* | $L_m$ | $L_p$ | $r_{m/p}$ |
|---|---|---|---|---|---|---|
| $\Delta\nu_{CN}$ | | | | | | |
| Pn[a] | CN | $CCl_4$ | 1 | 10.1 | 7.46 | 1.35 |
| Pn[a] | CN | $CHCl_3$ | 1 | 9.15 | 7.11 | 1.29 |
| Pn[a] | CN | $CCl_4$ | 1 | 9.73 | 6.57 | 1.48 |
| Pn[a] | CN | DMSO | 1 | 12.2 | 9.12 | 1.34 |
| Pn[a] | CN | HMPA | 1 | 11.8 | 8.06 | 1.46 |
| *E*-CH=CPh— | CN | $CCl_4$ | 3 | 3.50 | 4.05 | 0.864 |
| CH=CPh— | CN | $CHCl_3$ | 3 | 4.04 | 4.77 | 0.847 |
| CH=CPh— | CN | $CHCl_3$ | 3 | 4.72 | 4.05 | 1.17 |
| —C=CHPh | CN | $CHCl_3$ | 2 | 2.46 | 2.87 | 0.857 |
| $\Delta\nu_{NCS}$ | | | | | | |
| Pn[c] | NCS | $CCl_4$ | 1 | −48.1 | −42.0 | 1.15 |
| Pn[c] | NCS | $CHCl_3$ | 1 | −36.0 | *−38.1* | 0.945 |
| $\Delta\nu_{NH}$ | | | | | | |
| Pn[d] | $NH_2$ (s) | $CS_2$ | 1 | 17.5 | 21.7 | 0.806 |
| Pn[d] | $NH_2$ (as) | $CS_2$ | 1 | 21.4 | 30.1 | 0.711 |
| Pn[d] | NH**D** | $CS_2$ | 1 | 12.5 | 19.9 | 0.628 |
| Pn[d] | N**H**D | $CS_2$ | 1 | 18.8 | 28.9 | 0.651 |
| Pn[d] | NHAc | $CCl_4$ | 1 | *−3.11* | −4.73 | 0.658 |
| $\Delta\nu_{OH}$ | | | | | | |
| Pn[e] | OH | $CCl_4$ | 1 | −11.9[f] | −18.0 | 0.661 |
| Pn[e] | OH | $CCl_4$ | 1 | −14.0[f] | −18.7 | 0.749 |
| Pn[e] | OD | $CCl_4$ | 1 | −9.90[f] | −11.8 | 0.839 |
| PnCO[e] | OH | $CCl_4$ | 2 | −11.4[f] | −12.4 | 0.919 |
| $PnCH_2CO$[e] | OH | $CCl_4$ | 3 | −7.42[f] | −7.28 | 1.02 |
| PhNH | OH | $CCl_4$ | 2 | −16.3[f] | −16.1 | 1.01 |
| $\Delta\nu_{CO}$ | | | | | | |
| Pn | H[g] | $CCl_4$ | 1 | 10.4 | 13.8 | 0.754 |
| t-Pn-*E*-2-Vn | H[g] | $CCl_4$ | 3 | *8.37* | *5.73* | *1.46* |
| Pn | Me[g] | $CCl_4$ | 1 | 14.9 | 15.4 | 0.968 |
| Pn | Me[g] | $CCl_4$ | 1 | 14.3 | *8.66* | *1.65* |
| c-Pn-*E*-2-Vn | $^t$Bu[g] | $CCl_4$ | 3 | 5.39 | 6.55 | 0.823 |
| c-Pn-*E*-2-Vn | 2-Tn[g] | $CH_2Cl_2$ | 3 | 5.69 | 6.61 | *0.861* |
| Pn | c-*E*-2-Vn-Ph[g] | $CCl_4$ | 1 | 8.86 | 7.37 | 1.20 |
| Pn | c-*E*-2-Vn-Ph[g] | $CCl_4$ | 1 | 7.08 | 6.14 | 1.15 |
| Pn | c-*E*-2-Vn-Fc[g] | $CCl_4$ | 1 | 7.99 | 9.03 | 0.885 |
| Pn-5,2-Frn-2-Vn- | Ph[g] | $CCl_4$ | 6 | *2.66* | 3.81 | *0.698* |
| Pn | t-*E*-2-Vn-Ph[g] | $CCl_4$ | 1 | 8.88 | 11.3 | 0.786 |
| Pn | t-*E*-2-Vn-Ph[g] | $CCl_4$ | 1 | 7.44 | 9.20 | 0.809 |
| Pn | $NMe_2$[g] | $CCl_4$ | 1 | 8.12 | 8.42 | 0.964 |
| *E*-Pn-2-Vn | $NMe_2$[g] | $CCl_4$ | 3 | 5.40 | 4.84 | 1.12 |
| Pn | OH[g] | $CCl_4$ | 1 | 10.7 | 14.1 | 0.759 |
| Pn | OH[g] | $CCl_4$ | 1 | *11.8* | 16.0 | 0.738 |
| Pn-2-Vn | OH[g] | $CCl_4$ | 3 | 10.4 | 11.1 | 0.937 |
| Pn | OMe[g] | $CCl_4$ | 1 | 9.07 | 11.4 | 0.796 |
| Pn | OMe[g] | $CCl_4$ | 1 | 13.6 | 11.4 | 1.19 |
| t-6,2-/6,3-Pyn | OMe[g] | $CCl_4$ | 1 | 10.2 | 9.83 | 1.04 |
| c-6,2-/6,3-Pyn | OMe[g] | $CCl_4$ | 1 | 12.6 | 11.8 | 1.07 |
| $\nu_{CO_2^-}$ | | | | | | |
| $PnCH_2$ | $CO_2^-$[g] | $D_2O$ | 2 | 8.82 | 10.6 | 0.832 |

Values in italics are unreliable.

[a] For G = Pn, $r_{m/p} = 1.38 \pm 0.0820$.

[b] DMSO: dimethyl sulfoxide; HMPA: hexamethylphosphamide; Fc: ferrocenyl; Pyn: Pyridinylene.

[c] For G = Pn, $r_{m/p} = 1.05 \pm 0.145$.

[d] For G = Pn, $r_{m/p} = 0.691 \pm 0.0712$.

[e] For G = Pn, $r_{m/p} = 0.750 \pm 0.0890$.

[f] $L_m$CO.

[g] Z in COZ. c = s-cis, t = s-trans.

**Table 3.** Values of the cis–trans conformational ratio $r_{c/t}$

| G | Z in COZ | Sv | $L_c$ | $L_t$ | $r_{c/t}$ |
|---|---|---|---|---|---|
| 6,2-Pyn | OMe | $CCl_4$ | 10.2 | 12.4 | 1.24 |
| 6,3-Pyn | OMe | $CCl_4$ | 11.8 | 9.83 | 1.20 |
| *E*-4′-Pn-2-Vn | Ph | $CCl_4$ | 6.91 | 7.91 | 0.877 |
| Pn | *E*-Ph-2-Vn | $CCl_4$ | 6.14 | 9.20 | 0.668 |
| Pn | *E*-Ph-2-Vn | $CCl_4$ | 7.37 | 11.3 | 0.652 |
| *E*-4′-Pn-2-Vn | Ph | $CCl_4$ | 8.44 | 8.12 | 1.04 |
| *E*-4″-Pn-5′,2′-Tpn-2-Vn | Ph | $CCl_4$ | 3.49 | 3.17 | 1.10 |
| *E*-3″-Pn-5′,2′-Frn-2-Vn | Ph | $CCl_4$ | *2.66* | *4.65* | *0.572* |

## Conformation

Both the CIE and the MIE models predict that different conformers of G will have the same $L$ values. This is because the same path between X and Y is traversed in each conformer, only the arrangement in space differs and the inductive effect is independent of spatial arrangement. Then for G, which can exist in s-cis and s-trans conformations, the ratio $r_{c/t}$, given by Eqn. (16), must equal unity.

$$r_{c/t} \equiv L_c/L_t \qquad (16)$$

Values of $r_{c/t}$ are reported in Table 3. Again, examination of the histogram (Fig. 5) shows that they are not constant, they do not have the expected Gaussian distribution and do not equal unity. Thus, neither inductive-effect model accounts for transmission of the electrical effect in infrared stretching frequencies.

## Validity of the Hammett and Yukawa–Tsuno equations

The Hammett and Yukawa–Tsuno equations assume $r_{m/p} = 1$. We have presented evidence that this is not generally the case for either chemical reactivities or for infrared stretching frequencies. It follows, then, that correlations of data sets containing both meta- and para-substituted benzene derivatives must frequently be subject to error. It would be best to avoid the use of these equations in such cases.

## CONCLUSIONS

(1) The transmission of the universal electrical effect in infrared spectra is well fit by the MFE model with $m \approx -1.5 \pm 0.2$.

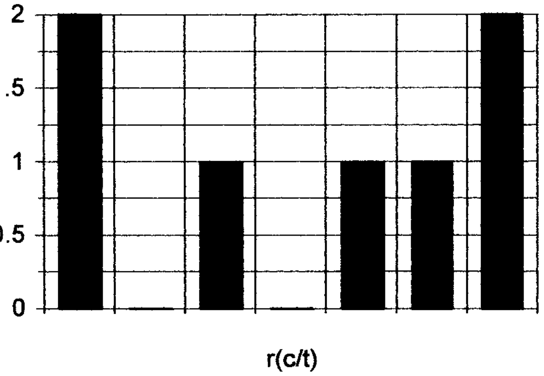


**Figure 5.** Histogram of $r_{c/t}$ values

(2) The considerable variation in $r_{m/p}$ and $r_{c/t}$ values and their failure to show a Gaussian distribution provide further evidence against the existence of the inductive effect.

(3) The values of $r_{m/p}$ obtained show that, in the general case, the Hammett equation is inferior to either di- or tri-parametric equations, as it assumes the equality of $\rho_m$ and $\rho_p$. This is also true of the Yukawa–Tsuno equation.

We have now shown that the inductive effect does not fit the experimental data on the transmission of electrical effects in a range of chemical reactions and in infrared stretching frequencies. Recent quantum chemical calculations support the field effect as the mode of electrical effect transmission.[14] Now is the time to abandon the inductive effect as a model of electrical effect transmission. It has long outlived its usefulness.

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