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TRANSMISSION OF INDUCTIVE EFFECT AND POLAR RESONANCE EFFECT THROUGH THE BENZENE AND THE FURAN RING IN PMR SPECTRA

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Assuming the independence and additivity of the inductive and polar resonance effects, experimental data for chemical shifts in proton magnetic resonance (PMR) spectra of mono and disubstituted benzene and furan derivatives are used to calculate transmission coefficients for the inductive and polar resonance effects due to any substituent for a proton in the 2, 3, or 4 position in the ring. Values of ρ^* and ρ^c are tabulated. With benzene compounds transmission of the polar resonance effect decreases on passing from the p and o to the m position. The coefficient of transmission of the inductive effect to a proton in the m or p position is negligible.

With furan compounds the values of the coefficient ρ^c for 2, 5 and 2, 4 ring positions are close to the corresponding values for benzene compounds. In the furan ring a considerable part of the polar resonance is transmitted through the heteroatom. The ρ^* coefficients are appreciably greater with furan than with benzene compounds, because the ring carbon atoms screen the proton less from the substituent. Most of the inductive effect from the 2 to the 5 position in the furan ring is direct (transmitted through space).

A number of authors [1-3] have attempted to separate transmissions of inductive and polar resonance effects in the aromatic ring by considering reactivity data. Pal'm and Tuulmets [4] established the validity of the following equation:

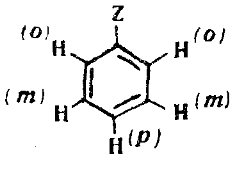
$$\sigma^\circ = z^*\sigma^* + z^c\sigma^c, \qquad (1)$$

where z^* and z^c are the "conductivities" of p and m substituted systems in the transmission of the inductive and polar resonance effects, respectively, while the various σ constants for substituents are calculated from the reactivities of various series of derivatives and tabulated [4].

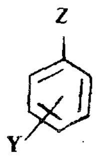
The present paper is concerned with values of chemical shifts of proton magnetic resonance (PMR) signals for substituted derivatives of benzene and furan, with the object of discovering regularities similar to those previously described [4] and evaluating the individual transmissions of the various effects in the heterocyclic system by various possible routes, viz., a conjugated diene system, through the oxygen hetero atom, and directly through space.

Taft [5] has previously carried out similar work on shifts of signals from the flurorine nucleus for a series of monosubstituted benzene derivatives, but the shift of PMR signals has not, as far as is known, been used for such calculations.

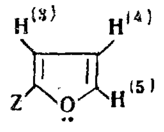
In searching for correlations, we used values of the chemical shifts δ of the signals of non-equivalent protons in the o, p, and m positions in relation to various substituents taken from papers [6] which give the PMR spectra of monosubstituted benzene derivatives (I). Since the PMR spectra of monosubstituted benzene derivatives are complex (type AB_2C_3 or AB_2X_2), and the signals found cannot always be unequivocally assigned to definite protons, we also analyzed data on chemical shifts S[7], calculated from the PMR spectra of disubstituted benzene derivatives (II), where the degree of effect of substituents Z and Y can be individually evaluated by calculating additively. It has been found that chemical shifts δ and S, and hence all the parameters that can be calculated therefrom, agree within the limits of error (Table 1, plots A and B). The starting data for calculating the transmissions of inductive and polar resonance effects in the furan series are taken from a paper [8] that gives the PMR spectra of monosubstituted furan derivatives (III). The experimental data in papers [6-8] relate to the media cyclohexane and benzene, where there is not any significant intermolecular interaction.



I



II



III

PMR chemical shifts and σ° constants in the series of compounds investigated are approximately related by the equation:

$$\delta = \rho\sigma^\circ + C, \qquad (2)$$

which has already been noted [6, 7, 9]. Values of ρ and C for the furan and benzene series are given in Tables 1 and 2.

TABLE 1

Transmission of inductive effect and polar resonance in the benzene ring, calculated from PMR spectra

Graph A shows the variation of the chemical shift δ of the proton signal for a monosubstituted derivative according to [6]. Graph B shows the variation of the chemical shifts of the proton signal for a disubstituted derivative according to [7].

Coefficient ρ		Coefficient C		para-				meta-				ortho-	
				ρ_p^c		ρ_p^*		ρ_m^c		ρ_m^*		ρ_o^c	ρ_o^*
A	B	A	B	A	B	A	B	A	B	A	B	A	A
−0.80	−0.86	+0.15	+0.18	−0.42 ±0.01 (correlation 1.0)	−0.46	0 ±0.02	0	−0.18 (correlation 0.91)	−0.20	0 ±0.02	0	−0.58 (correlation 0.94)	**−0.07** **±0.02**

TABLE 2

Transmission of inductive effect and polar resonance in the furan ring, as calculated from PMR spectra [8]

Coefficients		2, 5 positions		2, 4 positions		2, 3 positions	
ρ	C	$\rho_{2,5}^c$	$\rho_{2.5}^*$	$\rho_{2.4}^c$	$\rho_{2.4}^*$	$\rho_{2.3}^c$	$\rho_{2.3}^*$
−1.1±0.2	0.5	−0.48 (correlation coefficient 0.73)	+0.07	−0.20 (correlation coefficient 0.96)	+0.01	−1.57 (correlation coefficient 0.99)	+0.06

Equation 3 below, analogous to Eq. (1), has been derived by the authors; in it the value of the σ constant is fixed in relation to log K/K_0 for the dissociation constant of substituted benzoic acids:

$$\delta = \rho^* \sigma^* + \rho^c \sigma^c, \tag{3}$$

where ρ^* characterizes the transmission of the inductive effect, and ρ^c that of the polar resonance due to any substituent, to the corresponding proton in the ring, as calculated from the PMR chemical shifts.

Equation (3) was used to calculate values of ρ^* and ρ^c from the experimental data for the systems investigated. The average values were found by the method of least squares while the errors $\Delta\rho^*$ and $\Delta\rho^c$ were obtained by putting the corresponding parameters for the individual points in Eq. (3). Tables 1 and 2 give the calculated values of ρ^* and ρ^c. Figures 1-6 give examples of correlation.

The values ρ^c of the resonance effect in the benzene series, calculated from the PMR chemical shifts, decrease on passing from the o and p positions to the m position. In magnitude the numerical values of ρ_p^c and ρ_m^c are close to the calculated "absolute conductivities" of polar resonance z_p^c and z_m^c given in [4], and the ratio $(\rho_p^c/\rho_m^c) \approx (z_p^c/z_m^c)$. Consequently, application of the universal σ constants makes it possible to give a correct estimate of the polar resonance fraction from chemical shifts in PMR spectra of benzene derivatives.

Actually, the values of the inductive effect transmission ρ^*, as found from the PMR spectra for benzene compounds, are considerably less than the values of z^*; ρ_p^* and ρ_m^* are practically zero, so that transport of the electronic effect of a substituent to a proton in the p and m positions is, for the given series of compounds, wholly due to transmission of polar resonance. When explaining the difference it must be borne in mind that the chemical shift δ relates not to the carbon atom in the m or p position with respect to the substituent, but to the hydrogen atom attached to the carbon atom, screened by the skeleton of the molecule from the "transmitter," i. e., the substituent. Because there is screening in the benzene molecule between substituent and proton, there is no direct transmission of the inductive effect, to carry the main part of the total transmission of the inductive effect, while the fraction of the inductive effect transmitted by the benzene σ-bond system is negligible and is wiped out by the experimental error.

The values for the inductive effect and polar resonance, calculated from proton signal shift, differ from the results [5] calculated from the signal shift for the fluorine nucleus. Displacement of the signal from the F^{19} atom in the meta position to the substituent, is completely determined by the inductive effect of the substituent, while displacement of the

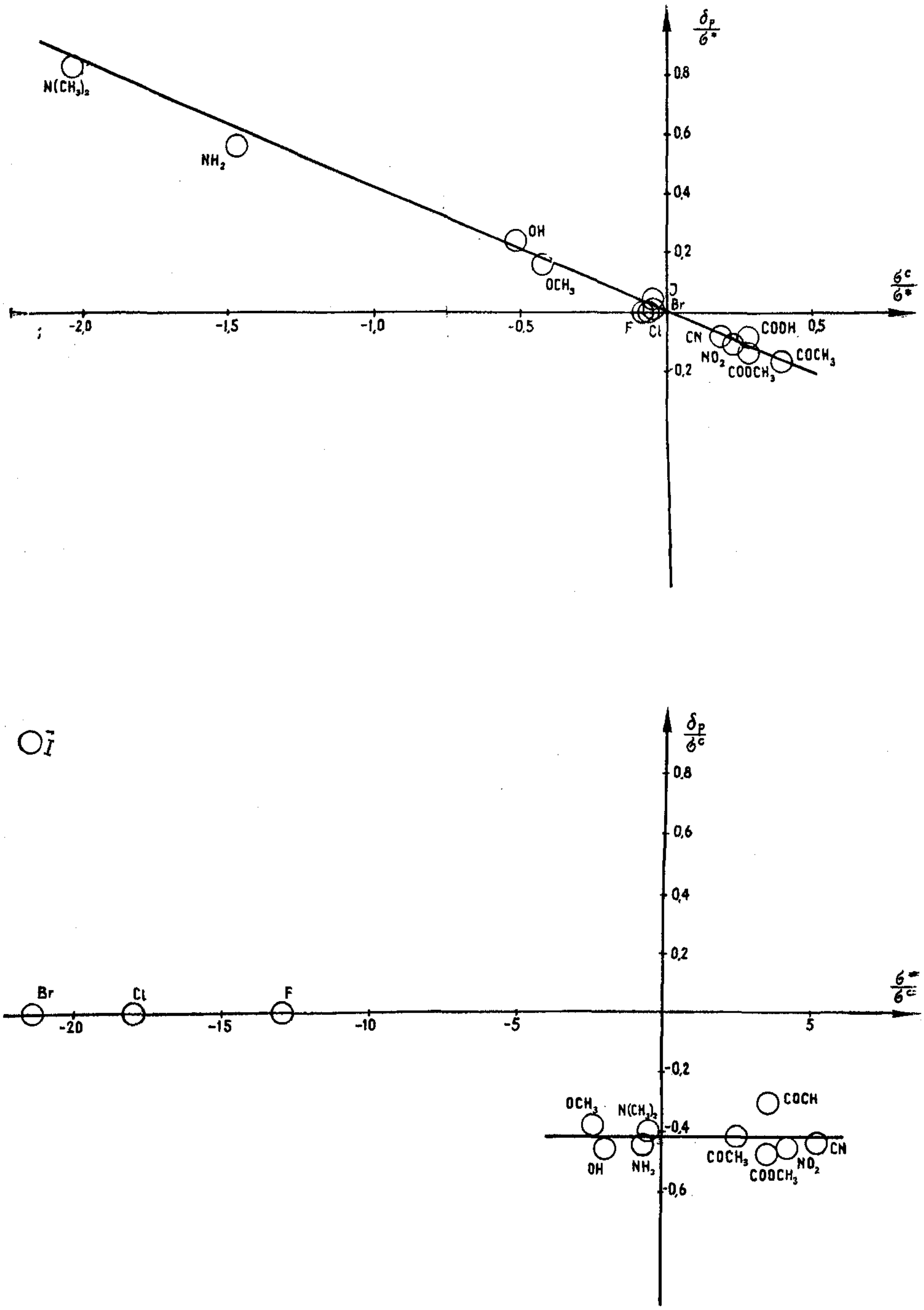


Fig. 1. Calculation of the conductivity of inductive effect ρ_p^* and polar resonance ρ_p^c for the p position of the benzene ring:

$$\text{a)}\quad \frac{\delta_p}{\sigma^*}=\rho^*_p+\rho^c_p\,\frac{\sigma^c}{\sigma^*}\ ;$$

$$\text{б)}\quad \frac{\delta_p}{\sigma^c}=\rho^c_p+\rho^*_p\,\frac{\sigma^*}{\sigma^c}\ ;$$

$$\rho^*_p=0;\qquad \rho^c_p=-0.42.$$

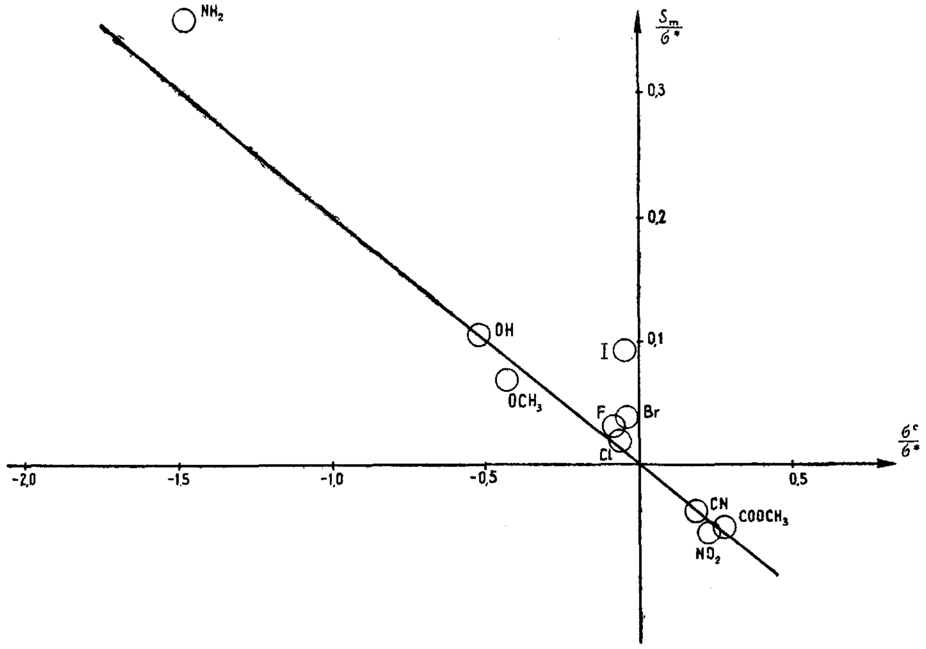


Fig. 2. Calculation of the conductivity of inductive effect ρ^*_m and polar resonance ρ^c_m for the m position of the benzene ring:

$$\frac{S_m}{\sigma^*} = \rho^*_m + \rho^c_m \frac{\sigma^c}{\sigma^*};$$

$$\rho^c_m = -0.2; \quad \rho^*_m = 0.$$

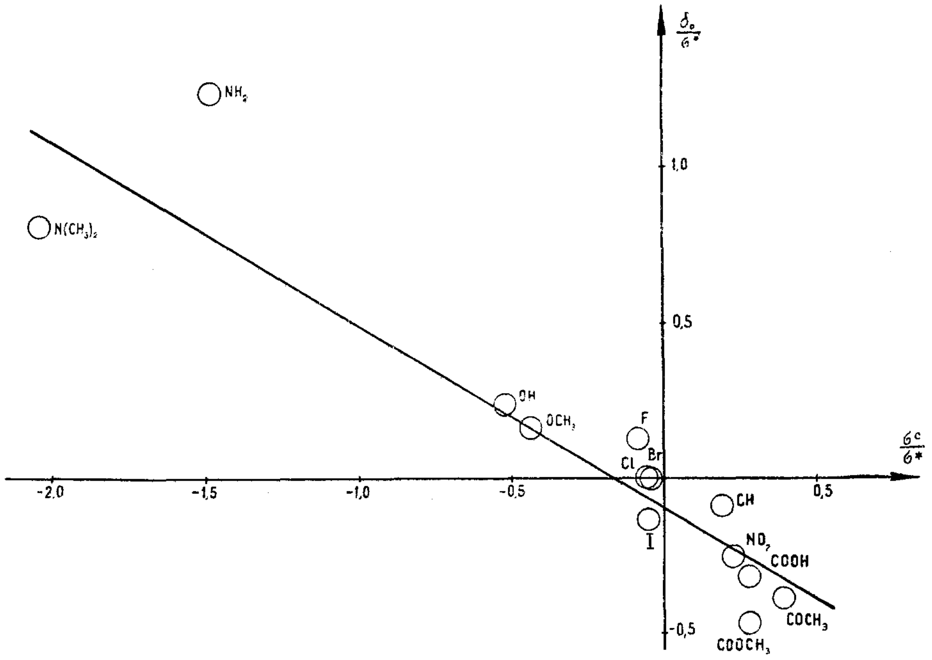


Fig. 3. Calculation of the conductivity of inductive effect ρ^*_o and polar resonance ρ^c_o for the o position of the benzene ring:

$$\frac{\delta_o}{\sigma^*} = \rho^*_o + \rho^c_o \frac{\sigma^c}{\sigma^*};$$

$$\rho^c_o = -0.58; \quad \rho^*_o = -0.07.$$

signal from atoms in the p and o positions is completely determined by a linear combination of inductive and mesomeric effects. In the actual PMR spectra the displacement of a signal from a proton in the m and p positions is almost completely determined by the polar resonance effect, and the inductive effect is appreciably exerted only in the o position; however, in [5] the author uses a σ-constant of a different and not universal type for evaluating the inductive and mesomeric effects.

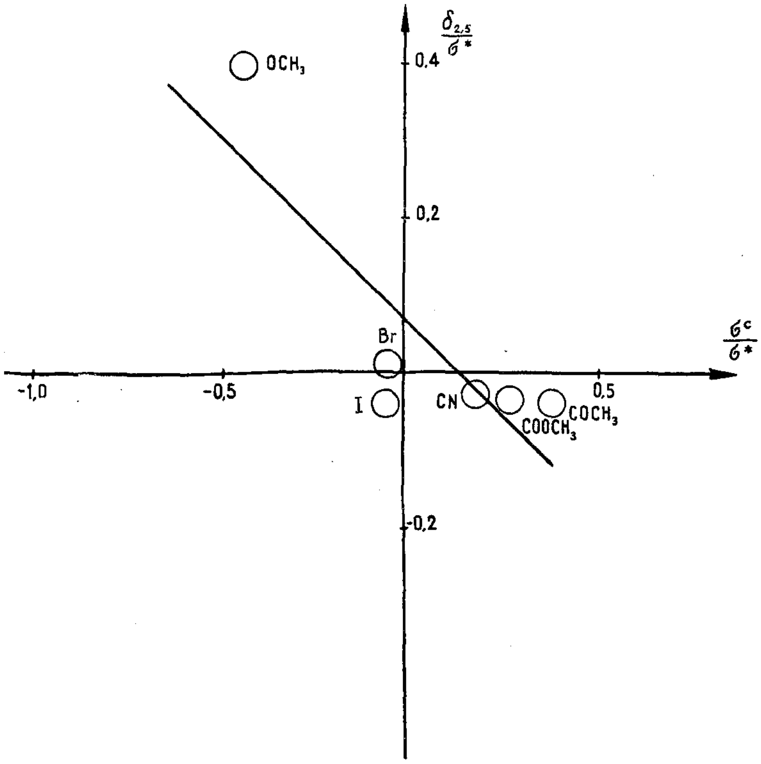


Fig. 4. Calculation of the conductivity of inductive effect $\rho^*_{2,5}$ and polar resonance $\rho^c_{2,5}$ for the 2, 5 positions of the furan ring:

$$\frac{\delta_{2,5}}{\sigma^*} = \rho^*_{2,5} + \rho^c_{2,5}\frac{\sigma^c}{\sigma^*};$$

$$\rho^c_{2,5} = -0.48; \quad \rho^*_{2,5} = +0.07.$$

Experimental values of the PMR chemical shifts are scarcer for the furan series, and not all members of the series show good agreement with the correlations; in particular, values for electron donor substituents (OCH_3 and halogens) tend to deviate.

The values of the coefficient ρ^c for the 2, 5 and 2, 4 positions of the furan ring lie close to the values of the coefficient ρ^c for the p and m positions of benzene, respectively, and this agrees well with the results of a polarographic study of five substituted derivatives of 2-nitrofuran [10, 11].

The actual inductive effect transmission coefficient $\rho^*_{2,5}$ for the 2, 5 position in furan is considerably greater than the coefficient ρ^*_p for the benzene series, since here the proton is less screened from the substituent by the carbon atoms of the ring.

If an attempt is made to separate polar resonance transmission for the 2, 5 position of the furan ring, $\rho^c_{2,5}$, into its components, viz., transmission through the system of diene bonds ρ^c_{diene} and transmission through the oxygen heteroatom ρ^c_{het}, when the component for the system of double bonds ρ^c_{diene} is taken as one half the ρ^c_p for benzene, the following is obtained:

$$\rho^c_{\mathrm{het}} = -0.48 - (-0.21) = -0.27,$$

i. e., the polar resonance in the furan ring is to a considerable extent transmitted through the hetero atom. However, it is to be borne in mind that transmission of the polar effect through the system of diene bonds, ρ^c_{diene}, cannot with certainty be put equal to half the value of ρ^c_p, and that it is necessary to take into account the charges and the actual types of bonds in the furan molecule, as computed by the method of molecular orbitals [12].

If, then, the transmission of the inductive effect through the furan ring $z^*_{2,5}$ is split into its components, viz., direct transmission through space and transmission through the bond system [13], a theoretical calculation using the most recent bond lengths and values of the angles in the furan ring gives:

$$z^*_{2,5}=z^*_{\text{пр}}+z^*_{\text{св}}=q\sum_i \frac{1}{l_i^2}\Pi\cos\varphi_{ij}+\sum_i 0.36^{n_i}=$$

$$=0.6\cdot\frac{1}{9.77}\cdot\cos 27^0 21+0.36^5+0.36^4=$$

$$=0.054+0.006+0.017=0.077.$$

The calculated value of $z^*_{2,5}$ and the value of $\rho^*_{2,5}$ found from experimental data are close to each other, hence the main part of the inductive effect (70%) from positions 2 and 5 is transmitted through space, over 20% through the oxygen atom, only an insignificant fraction through the ring bond system. On the other hand, there is no direct transmission of the inductive effect from positions 2 and 4, because of screening of the protons by the ring atoms, so that only the component transmitted through the ring appears, and its numerical value shows it to be negligible.

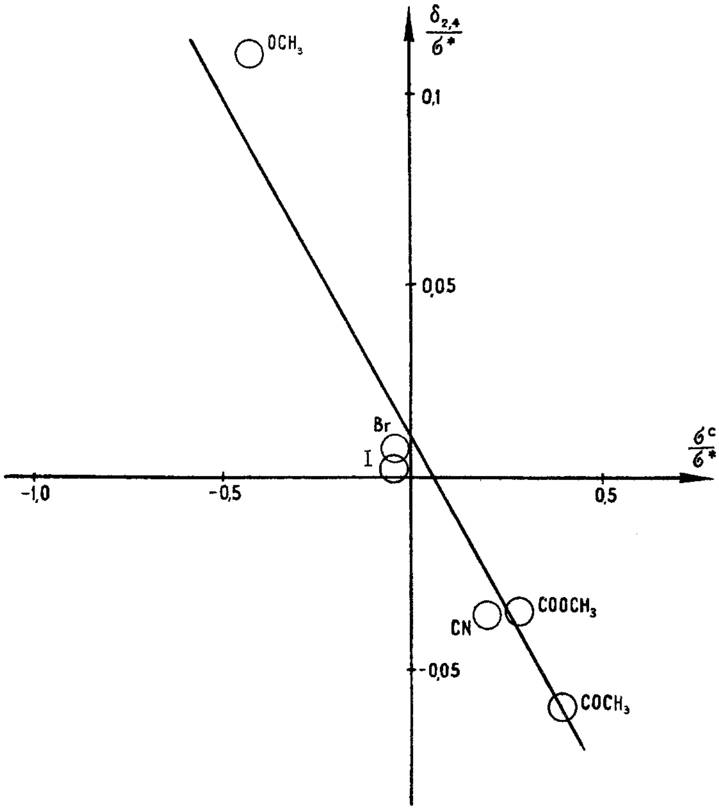


Fig. 5. Determination of the conductivity of the inductive effect $\rho^*_{2,4}$ and polar resonance $\rho^C_{2,4}$ for the 2, 4 positions of the furan ring:

$$\frac{\delta_{2,4}}{\sigma^*}=\rho^*_{2,4}+\rho^c_{2,4}\frac{\sigma^c}{\sigma^*};$$

$$\rho^c_{2,4}=-0.20;\qquad \rho^*_{2,4}=+0.01.$$

Analogous preliminary calculations for thiphene derivatives (the data will be published in another paper) give values of ρ^* and ρ^C close to those for the benzene and furan systems.

Our results show that when using PMR data for the quantitative partition of the transmission of inductive effect and polar resonance in ring systems, a cautious approach is necessary, and that it must be borne in mind that the values of ρ^C and ρ^* relate to transmission of the effect from substituent to a proton occupying a particular position in the ring, and not to transmission to a carbon atom, i. e., possible screening of the proton by the ring carbon atoms must be considered, as well as attenuation through the C-H bond. The transmission of the inductive effect and polar resonance, as manifested in PMR spectra, is not identical with the manifestation of these effects in series of kinetic measurements or measurements of acid-base equilibrium constants, for which universal σ-constants are fixed.

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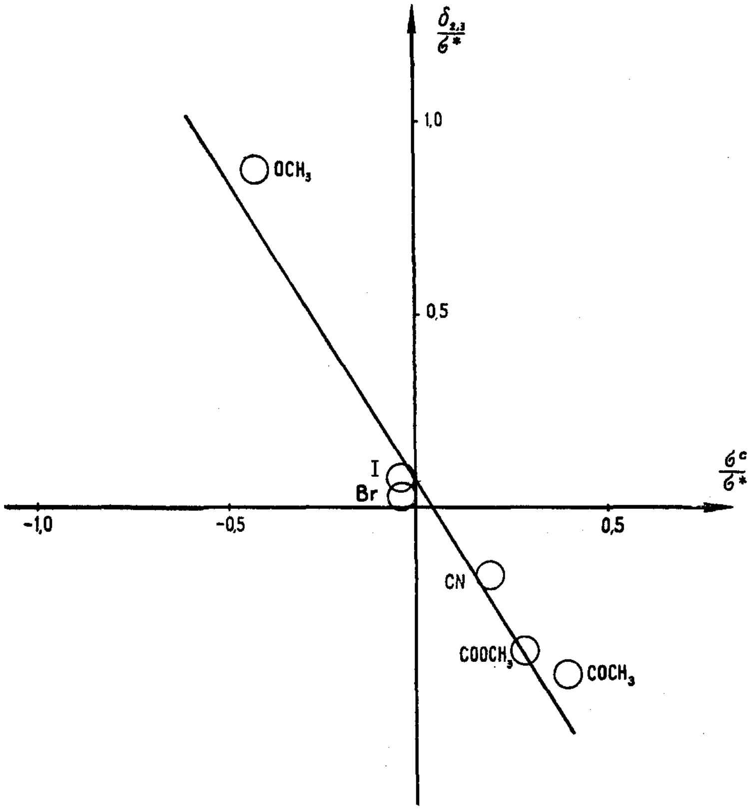

Fig. 6. Determination of conductivity of inductive effect $\rho^*_{2,3}$ and polar resonance $\rho^c_{2,3}$ for the 2, 3 positions of the furan ring:

$$\frac{\delta_{2,3}}{\sigma^*} = \rho^*_{2,3} + \rho^c_{2,3}\frac{\sigma^c}{\sigma^*};$$

$$\rho^c_{2,3} = -1{,}57; \qquad \rho^*_{2,3} = +0{,}06.$$

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