

CORRELATION OF THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES
WITH σ^* TAFT CONSTANTS

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The correlations between the nuclear quadrupole resonance (NQR) frequencies and constants characterizing the electron influence of substituents^{1,2}, are for different reasons (poor accuracy or being of restricted use), valid only in some cases.

Recently we have shown³ that there exists an approximately linear relationship of a rather general nature between the NQR frequencies of Cl^{35} of RCl type compounds and Taft constants of R radicals. With a view to finding some more accurate correlations, we have chosen the following two groups of radicals: unsubstituted alkyl R radicals and XCH_2 groups containing electronegative substituents X . In recent years the principal differences between the inductive effects of alkyl radicals and the electronegative substituents, have been a point of discussion^{4,5}. In case of alkyl groups we have obtained the following dependence between the NQR frequencies of RCl compounds and σ^* constants of R radicals ($\text{R}=\text{CH}_3$, C_2H_5 , C_3H_7 , iso- C_3H_7 , cyclo- C_3H_5 , n- C_4H_9 , sec- C_4H_9 , cyclo- C_6H_{11}).

$$\sigma^* = (-3.75 + 0.1110) \pm 0.05; r=0.929 \quad (1)$$

Most of the deviations are within 0.02-0.03 range while only the points corresponding to cyclopropyl and n-butyl radicals have larger deviations, 0.08 and 0.07 respectively. The relationship is analogous to that suggested previously by Taft² but it covers a larger number of compounds.

The σ^* constants of electronegative groups XCH_2 are connected with the NQR frequencies of XCH_2Cl compounds by the equation (2) where X is an electronegative substituent not containing an atom with lone-pair electrons in an α -position relative to chlorine atom (Fig.1). The σ^* constants of 21 groups

satisfy the relationship (2)

$$\sigma^* = (-7.27 + 0.2237\nu) \pm 0.07; r=0.983 \quad (2)$$

The σ^* values for many groups have been calculated from the ionization constants of carboxylic acids in water at 25°C: $\sigma^* = (2.64 - 0.561 \text{ p}K_a) \pm 0.02$; $r=0.9998$. Unlike Taft², who first used correlation $\text{p}K_a$ of RCOOH with σ^* constants of R, we have used only electronegative R to derive the equation: $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$, $\text{C}_6\text{H}_5\text{CH}_2$, $\text{CF}_3\text{CH}_2\text{CH}_2$, ClCH_2CH_2 , $(\text{C}_6\text{H}_5)_2\text{CH}$, $\text{NO}_2\text{CH}_2\text{CH}_2$, CH_3COCH_2 , ICH_2 , $\text{C}_6\text{H}_5\text{OCH}_2$, CF_3CH_2 , BrCH_2 , ClCH_2 , HOOCCH_2 , CNCH_2 , $\text{CH}_3\text{SO}_2\text{CH}_2$, CHCl_2 , CCl_3 . The $\text{p}K_a$ values have been taken from monographs⁷, handbooks⁸ and some other works⁹ (for CCl_3 group); the σ^* values and other reaction constants have been taken from V.A.Palm's review⁴.

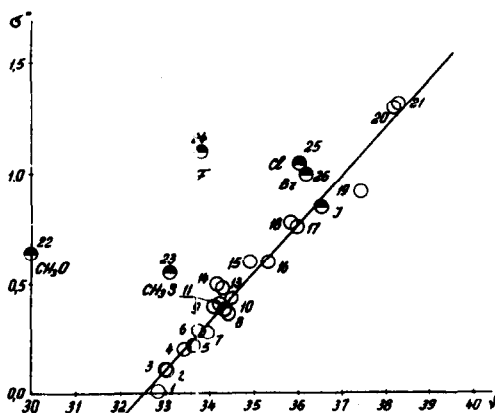


Fig 1.

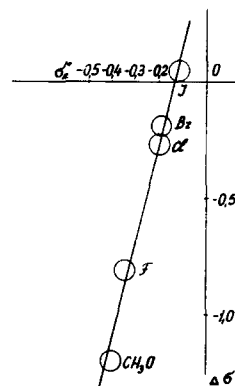


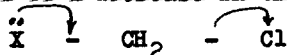
Fig 2.

Fig.1. Correlations of Taft σ^* constants of XCH_2 radicals with NQR frequencies of XCH_2Cl . Where X represents: 1- $\text{ClCH}_2\text{CH}_2\text{CH}_2$; 2- ClCH_2CH_2 ; 3- HOCH_2 ; 4- $\text{CH}_2=\text{CH}$; 5- C_6H_5 ; 6- *p*- ClC_6H_4 ; 7- HOOCCH_2 ; 8- *o*- ClC_6H_4 ; 9- CNCH_2 ; 10- CH_3ClCH ; 11- *m*- $\text{NO}_2\text{C}_6\text{H}_4$; 12- ClCH_2 ; 13- *p*- $\text{NO}_2\text{C}_6\text{H}_4$; 14- NO_2CH_2 ; 15- NH_2CO ; 17- $\text{C}_2\text{H}_5\text{OOC}$; 18- $\text{CH}\equiv\text{C}$; 19- CF_3 ; 20- CN ; 21- CH_3SO_2 .

Fig.2. Correlation of deviation ($\Delta\sigma^*$) from linear dependence $\sigma^*_{\text{XCH}_2} - \nu_{\text{XCH}_2\text{Cl}}$ (Fig.1) for X having lone-pair electrons with resonance parameters σ^0_R of X substituents.

The equations (1) and (2) allow us to calculate Taft σ^* constants from the NQR frequencies to an accuracy which, in most cases, can compare very well with the values determined by the chemical methods. Somewhat larger deviations are observed for the substituents $\text{X}=\text{NO}_2\text{CH}_2$ (0.15) and $\text{X}=\text{CF}_3$ (0.17).

Significant deviations from relationship (2) occur in substituents with lone-pair electrons (X=NO₂, F, NH₂, Cl, Br, see Fig. 1, No. 22-26). This is due to a decrease in NQR frequencies when substituents with lone-pair electrons are introduced in the α -position relative to chlorine atom. As stated by Lucken⁶ this may result from the overlapping of the lone-pair electron orbital with the C-Cl σ -orbital (p- σ conjugation) which leads to an increase in the polarity of the C-Cl bond, and to a decrease in the NQR frequency of chlorine.



Thus, p- σ conjugation affects the frequencies in direction opposite to the changes in electronegativity of the substituents. This is especially evident in a substitution of Fluorine by Iodine: in a series of XCH_2Cl (where X=F, Cl, Br, I) with a decrease in electronegativity of X the NQR frequency of Cl³⁵ does not decrease but increases. On the contrary, the σ^* constants decrease with a drop in electronegativity of the halogen. It is this disparity that causes deviations in substituents with lone-pair electron. These deviations are of a regular nature and increase with the α -effect of the X-substituent: I < Br < Cl < F. If the magnitude of σ^0_R ¹⁰ is taken as a measure of this effect and comparing their deviations from the relationship (2), we get a good correlation between the above quantities:

$$v_{\text{cal.}} - v = \Delta v = (-2.65 - 18.747 \sigma^0_R) \pm 0.30; \quad r=0.994 \quad (3)$$

This confirms the resonance nature of the deviations discussed. In calculating σ^* by the equation (2) for X with lone pair electrons v should be replaced by $v + \Delta v$. The deviations from the Y-axis which shows a similar dependence on resonance parameters σ^0_R can also be found (Fig. 2):

$$\sigma_{\text{cal.}}^* - \sigma^* = \Delta \sigma^* = (0.57 + 4.164 \sigma^0_R) \pm 0.06; \quad r=0.995 \quad (4)$$

and the σ^* constants can be calculated from the equation (5) which is a combination of equations (2) and (4):

$$\sigma^* = (-7.84 + 0.2237 \cdot v) - 4.164 \cdot \sigma^0_R \pm 0.06; \quad r=0.995 \quad (5)$$

The existence of a linear correlation between the value $\Delta \sigma^*$ (or Δv) and the resonance parameters, σ^0_R of X substituents, gives us an unexpected possibility to calculate the latter to high degree of accuracy from the σ^* constants of XCH_2 and from NQR frequencies of XCH_2Cl , i.e. from the chemical and physical characteristics of saturated compounds.

$$\sigma_R^0 = (-1.87 + 0.0532 \cdot \gamma) - 0.238 \sigma^* \pm 0.01; r=0.995 \quad (6)$$

The parameter σ_R^2 can be used instead of σ_R^0 . With this substitution similar, but somewhat less accurate correlations (7) and (8) are obtained. The equation (8) may be used to calculate, with sufficient accuracy, the constants σ_R :

$$\sigma^* = (-7.65 - 0.2237 \cdot \gamma) - 2.960 \sigma_R \pm 0.10; r=0.979 \quad (7)$$

$$\sigma_R = (-2.49 - 0.0724 \cdot \gamma) - 0.324 \sigma^* \pm 0.03; r=0.979 \quad (8)$$

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