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Abstract

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CORRELATION OF THE DISSOCIATION CONSTANTS OF CARBOXYLIC ACIDS RCOOH AND TAFT' S σ^* CONSTANTS WITH THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF HALIDES IN COMPOUNDS OF THE TYPE RHal

Nuclear quadrupole resonance (N.Q.R.) is caused by the interaction of the electric quadrupole moment of the nucleus (eQ is a nuclear constant) with the inhomogeneous electric field surrounding the atomic nucleus, the measure of which is the gradient of the electric-field strength q_{zz}. Therefore the N.Q.R. frequency, to a first approximation proportional to eQq_{zz}, is a measure of the anisotropy of the electronic environment of the atomic nucleus (see (1)).

For an atom whose nucleus possesses a quadrupole moment, for example a chlorine atom in R—Cl, the N.Q.R. frequencies will be determined not only by the nature of this atom and its valence state, but also by the nature of the atom bonded to it (in our example, carbon), by its valence state, and by the character of the other atoms entering into the molecule (substituents in the radical R). The influence of substituents on the form of the electron-density distribution finds quantitative expression in changes in the N.Q.R. frequencies. It is natural to suppose that the influence of substituents on the N.Q.R. frequencies of some atom and the properties of functional groups located in place of this atom in analogously constructed molecules will be largely of the same type; changes in the N.Q.R. frequencies should correlate with changes in the parameters characterizing the functional groups.

The literature describes attempts to establish such correlations with Hammett' s σ in the aromatic series ($^{2-4}$). In five examples it has been shown that there is a linear dependence between the N.Q.R. frequencies of primary, secondary, and tertiary alkyl chlorides and the Taft σ^* constants of the corresponding alkyl radicals (^{5}).*

We attempted to compare the N.Q.R. frequencies of halogen-containing compounds of the type RX with the pK_a values of the corresponding carboxylic acids RCOOH. We found a satisfactory linear dependence covering aliphatic and aromatic compounds (see Table 1, Nos. 1 and 2, and Fig. 1). All the data were treated by the method of least squares. All conclusions concerning the influence of structure on the N.Q.R. frequencies are made below on the basis of the equation of Table 1, No. 1. As follows from Fig. 1, A, the compounds that best satisfy the dependence found are those in which R is some substituted methyl or ortho-substituted aromatic radical, as well as aromatic radicals having electron-acceptor substituents. Large deviations are observed in the case of aromatic radicals having substituents with lone pairs of electrons (RO, HO, CH_3COO, $HNCOCH_3$, F, etc.—see points 61-64, 69), and in the case of elements of the third and other periods (Cl, Br, J) smaller deviations are observed (points 17, 72, 18), lying within the limits of the mean statistical deviation.

The reason for these deviations apparently lies in the different electronic nature of the carboxyl group and the chlorine atom, and in the different character of the sensitivity of these "reaction centers" to the electronic influence of substituents. The carboxyl group and, to an even greater extent, its anion are conjugated with the phenyl nucleus and, in a number of cases, also with the substituent; therefore, a change in the dissociation constant, which is a measure of the difference in the influence of substituents on the acid and its anion, is very sensitive to effects transmitted through the π-electron system, especially in the case of donor substituents. In contrast to the carboxyl group, the halogen atom,

Table 1

No.	Equation	Mean deviation	Correlation coefficient	Note
1	$pK'_a = 22.89 - 0.55\,\nu\nu = 40.67 - 1.56\,pK_a$	0.420.71	0.9250.925	Cl^{35}. Number of points 90
2	$pK_a = 19.11 - 0.06\,\nu\nu = 319.31 - 12.58\,pK_a$	0.456.70	0.8420.842	Br^{79}. Number of points 34
3	$\Delta pK_a = -0.08 + 1.12\,\Delta\sigma\Delta\sigma = 0.02 + 0.67\,\Delta pK_a$	0.150.12	0.8650.865	Number of points 19

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* For aliphatic and aromatic compounds, the question of the dependence of N.Q.R. frequencies on structure was considered earlier (^{6}).

No.	Equation	Mean deviation	Correlation coefficient	Note
4	$\sigma^* = -9.70 + 0.29\,\nu\nu = 33.19 + 2.99\,\sigma^*$	0.260.82	0.9380.938	Cl^{35}. Number of points 25

which has lone pairs of electrons, is usually an electron donor in conjugation with π-bonds.

On the other hand, as follows from theory (see, for example, (^{1})), NQR frequencies depend little on the degree of double-bond character of the halide, which is characterized by the asymmetry parameter

$$\nu = 0.5\,eQq_{zz}\,{(1+\eta^2/3)}^{1/2}; \quad \eta = |q_{xx} - q_{yy}|/q_{zz},$$

where e is the charge of the electron, Q is the electric quadrupole moment of the nucleus, and q_{zz}, q_{yy}, q_{xx} are components of the electric-field-gradient tensor; the directions q_{zz} coincide with the direction of the C—Hal bond axis.

The maximum value of the asymmetry parameter for this type of bond is $\sim 20\%$*. It is easy to see from the formula given above that, even at the maximum value of η, the entire radical expression will differ little from 1. It follows from this that the asymmetry parameter, and consequently the degree of double-bond character, does not substantially affect the NQR frequency.

Thus, deviations from linear dependence in the case of aromatic radicals are probably associated with conjugation, which has little effect on the NQR frequencies of halides and exerts a substantial influence on the dissociation constants of acids. According to Taft (^{5}), an approximate measure of conjugation is the difference between Hammett constants σ and constants σ' for bicyclo-$(2,2,2)$-octane systems, for which transmission of influence occurs only by the inductive route. Comparison of $\Delta\sigma = \sigma - \sigma'$ with deviations from the found linear dependence $\Delta pK_a = pK_{a\,\mathrm{calc}} - pK_{a\,\mathrm{expt}}$ showed that an approximate linear dependence exists between the indicated differences, with a fairly good correlation coefficient (see Table 1, No. 3, and Fig. 2).

Deviations in the series of aliphatic compounds are associated with the presence in the α-positions of electron-donor substituents: alkyl, alkoxyl—

* For para-, meta-, and some ortho-disubstituted benzenes $\eta = 5 \pm 2.5\%$ (^{7}). It should be noted that, in those cases where η has been determined, it becomes possible to estimate the degree of double-bond character of the C—Hal bond.

Figure 1

Figure 1: Figure 1

Fig. 1. Relationship between the pK_a values of acids RCOOH and (A) the NQR frequencies of Cl^{35} in compounds RCl; (B) the NQR frequencies of Br^{79} in compounds RBr.

A. R: 1 –iso-C_3H_7; 2 –$(CH_3)_2(C_2H_5)C$; 3 –tert-C_4H_9; 4 –sec-C_4H_9; 5 –$Cl(CH_2)_4$; 6 –$Cl(CH_2)_3$; 7 –$CH_2{=}CH$; 8 –*n*-$ClC_6H_4CH_2$; 9 –$HOOCCH_2CH_2$; 10 –CH_3SCH_2; 11 –*o*-$ClC_6H_4CH_2$; 12 –$(C_6H_5)_2CH$; 13 –*m*-$O_2NC_6H_4CH_2$; 14 –$ClCH_2CH_2$; 15 –*n*-$O_2NC_6H_4CH_2$; 16 –2,4,6-trimethylphenyl; 17 –*n*-ClC_6H_4; 18 –*n*-JC_6H_4; 19 –naphthyl-1; 20 –*n*-$CH_3COC_6H_4$; 21 –*n*-$(C_2H_5O)_2P(O)C_6H_4$; 22 –*n*-$HOOCC_6H_4$; 23 –H_2NCOCH_2; 24 –*m*-$(CH_3)_3\overset{+}{N}C_6H_4J$; 25 –*o*-$CH_3CONHC_6H_4$; 26 –*m*-$HOOCC_6H_4$; 27 –$(CH_3)_2CCl$; 28 –*n*-$(CH_3)_3\overset{+}{N}C_6H_4J$; 29 –*β*-anthraquinonyl; 30 –*o*-NC_6H_4; 31 –*o*-$HOOC_6H_4$; 32 –$HC{\equiv}CCH_2$; 33 –ClC_6H_4; 34 –$ClCH_2$; 35 –$BrCH_2$; 36 –$HOOCCH_2$; 37 –2-chloro-4-nitrophenyl; 38 –2-carboxy-5-chlorophenyl; 39 –2,4-dinitrophenyl; 40 –HOOCCHCl; 41 –Cl_2CH; 42 –$Cl_2C{=}CCl$; 43 –2,6-dinitrophenyl; 44 –2,4,6-trinitrophenyl; 45 –Cl_3C; 46 –C_2H_5; 47 –$(CH_3)_2CHCH_2$; 48 –*n*-C_3H_7; 49 –*n*-C_8H_{17}; 50 –*n*-C_8H_{18}; 51 –$(CH_3)_3SiCH_2CH_2$; 52 –*n*-C_7H_{15}; 53 –*n*-C_5H_{11}; 54 –*n*-C_4H_9; 55 –$(CH_3)_3SiCH_2$; 56 –cyclopropyl; 57 –CH_3; 58 –*n*-$C_2H_5OC_6H_4$; 59 –$CH_2{=}CHCH_2$; 60 –$C_6H_5CH_2$; 61 –*n*-$HOOC_6H_4$; 62 –*n*-$CH_3OC_6H_4$; 63 –*n*-$CH_3COOC_6H_4$; 64 –*n*-$CH_3CONHC_6H_4$; 65 –C_6H_5; 66 –$Cl_3CCH_2CH_2$; 67 –naphthyl-2; 68 –*m*-$ClC_6H_4CH_2$; 69 –*n*-FC_6H_4; 70 –*m*-HOC_6H_4; 71 –*m*-$CH_3CONHC_6H_4$; 72 –*n*-BrC_6H_4; 73 –$(C_6H_5)_3C$; 74 –*m*-FC_6H_4; 75 –*m*-ClC_6H_4; 76 –*m*-$F_3CC_6H_4$; 77 –trans-*β*-chlorovinyl; 78 –CH_3COCH_2; 79 –*m*-$O_2NC_6H_4$; 80 –$C_2H_5OCCH_2$; 81 –*o*-FC_6H_4; 82 –F_3CCH_2; 83 –JCH_2; 84 –*o*-$HOOCC_6H_4$; 85 –$NCCH_2$; 86 –$CH_3SO_2CH_2$; 87 –*o*-$O_2NC_6H_4$; 88 –2-chloro-5-nitrophenyl; 89 –2-nitro-5-chlorophenyl; 90 –$F_2C{=}CF$; 91 –CF_3; 92 –CH_3OCH_2; 93 –$C_4H_9OCH_2$.

B. R: 1 –C_2H_5; 2 –*n*-C_4H_9; 3 –$Br(CH_2)_4$; 4 –*n*-C_3H_7; 5 –*n*-$CH_3C_6H_4CH_2$; 6 –$HOOCCH_2CH_2$; 7 –$BrCH_2CH_2$; 8 –CH_3; 9 –*n*-$C_2H_5OC_6H_4$; 10 –*n*-HOC_6H_4; 11 –*n*-$CH_3OC_6H_4$; 12 –*n*-$C_6H_5OC_6H_4$; 13 –C_6H_5; 14 –*n*-$CH_3CONHC_6H_4$; 15 –$(C_6H_5)_3C$; 16 –*n*-FC_6H_4; 17 –*m*-HOC_6H_4; 18 –*o*-$CH_3OC_6H_4$; 19 –*n*-BrC_6H_4; 20 –*m*-BrC_6H_4; 21 –*α*-$C_{10}H_7$; 22 –*n*-$CH_3COC_6H_4$; 23 –*n*-$HOOCC_6H_4$; 24 –*m*-$O_2NC_6H_4$; 25 –*n*-$O_2NC_6H_4$; 26 –2,4,6-trimethylphenyl; 27 –*o*-$HOOCC_6H_4$; 28 –$HOOCCHCH_3$; 29 –$HOOCCH_2$; 30 –*o*-BrC_6H_4; 31 –*o*-$O_2NC_6H_4$; 32 –$BrCH_2$; 33 –*o*-HOC_6H_4; 34 –2,4-dinitrophenyl.

···and methylmercapto groups, as well as fluorine atoms. In the case of alkyl radicals, the relationship found is well satisfied by compounds with primary radicals, beginning with ethyl (points 46–50, 52–54). Secondary and tertiary radicals, as well as methyl and cyclopropyl radicals, give deviations (points 1–4, 57, 56). In essence, alkyl radicals form another straight line with a different

Fig. 2 and Fig. 3: plotted dependencies

Figure 2: Fig. 2 and Fig. 3: plotted dependencies

slope. Sharp deviations are observed for methoxy- and butoxy-methyl radicals and fluorine-containing methyl groups (points 92, 93, and 91). These points were not included in the statistical treatment. Smaller deviations are given by methylmercapto and trimethylsilyl groups (points 10 and 55).

Consideration of the types of compounds satisfying the dependence suggests that the NQR frequencies should be linearly related to Taft' s σ^* constants not only in the case of unsubstituted alkyl radicals (^{5}). Indeed, as follows from Fig. 3 (see also Table 1, No. 4), comparison of the NQR frequencies of 25 compounds of the type RCl with the corresponding Taft σ^* constants confirms this idea. Here deviations analogous to those in the case of the dependence of ν on pK_a are observed. The falling out of point 7, corresponding to the vinyl group, is probably connected with an overestimated value of σ^* for this radical, which has already been noted in the literature (^{8}).

Fig. 2. Dependence between $\Delta pK_a = pK_{a\,\mathrm{calc}} - pK_{a\,\mathrm{exp}}$ and $\Delta\sigma = \sigma - \sigma'$ of Taft

R: 1—*p*-HO; 2—*p*-CH_3O; 3—*n*-F; 4—*n*-$NHCOCH_3$; 5—*m*-F; 6—*n*-Cl; 7—*m*-HO; 8—*n*-Br; 9—*n*-J; 10—*m*-Cl; 11—*m*-CH_3CONH; 12—H; 13—*m*-F_3C; 14—*n*-$(CH_3)_3N^+$; 15—*m*-HOOC; 16—*m*-O_2N; 17—*m*-$(CH_3)_3N^+$; 18—*n*-HOOC; 19—*n*-CH_3CO

Fig. 3. Dependence between the constants σ^* of radicals R and NQR frequencies of Cl^{35} in compounds RCl

R: 1—*tert*-C_4H_9; 2—$(CH_3)(C_2H_5)CH$; 3—iso-C_3H_7; 4—C_2H_5; 5—C_3H_7; 6—*n*-C_4H_9; 7—$CH_2{=}CH$; 8—$C_6H_5CH_2$; 9—$(C_6H_5)_2CH$; 10—$ClCH_2CH_2$; 11—C_6H_5; 12—CH_3; 13—$(CH_3)_3SiCH_2$; 14—trans-β-chlorovinyl; 15—CH_3COCH_2; 16—$ClCH_2$; 17—$BrCH_2$; 18—$HOOCCH_2$; 19—JCH_2; 20—Cl_2CH; 21—Cl_3C; 22—$CH_3SO_2CH_2$; 23—$NCCH_2$; 24—F_3CCH_2; 25—$O_2NCH_2CH_2$; 26—CH_3OCH_2

Thus, NQR spectra make it possible to judge the inductive influence of substituents. Assuming that deviations from the linear dependence found are connected with conjugation effects and differences in spatial and intermolecular interactions in crystals and solutions, it should be recognized that, in a number of cases, NQR can serve as a reliable means for studying the nature of the mutual influence of atoms.

In this work use has been made of literature material on NQR spectra measured at 77° K (^{1}), and data obtained by the authors. The pK_a values were taken from monographs ($^{9-11}$).

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Note: Figure translations are in progress. See original paper for figures.