Tetrahedron Letters No.26, pp. 2521-2527, 1967. Pergamon Press Ltd. Printed in Great Britain.

CORRELATION OF THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF Cl^{35} MONOSUBSTITUTED CHLOROBENZENES WITH σ-HAMMETT CONSTANTS

E.N.Tsvetkov, G.K.Semin, D.I.Lobanov, M.I.Kabachnik
Institute of Organo-element Compounds
Academy of Sciences, USSR, Moscow

(Received 7 April 1967)

Hammett "substituent constant is a measure of the effect of the substituent on the activation energy of the reaction of the unsubstituted compound" or it "measures the effect of the substituent on the electron density at the reaction site".[1] The change in halogenobenzenes nuclear quadrupole resonance (NQR) frequency according to the sort of substituent introduced into a benzene ring shows an effect of the latter on the anisotropy of the halogen atom's electron environment. A correlation between these two functions of electron distribution in the side chain of aromatic nucleus is, undoubtedly, of certain interest.

The connection between the NQR frequencies of substituted halogenobenzenes and the σ Hammett constants of substituents was reported[2-4]. The main drawback of the correlations suggested is a significant standard deviation from a linear relationship. Even by the most satisfactory Bray and Barnes[4] correlation, the σ constants can be calculated only to $\pm$ 0.50 accuracy.

We made an attempt to find more precise correlations, suitable for calculating σ constants by using the NQR frequencies values available. As the previous works show, it appears to be impossible to obtain such a correlation by a direct comparison of the NQR frequencies with σ values. Earlier we have pointed out[5], that the NQR frequencies have rather poor sensitivity to the double-bond character of the C-Cl bond; hence it follows that within a first approximation, the influence of the substituents upon the NQR frequencies is governed by their inductive effect. Therefore it might be supposed that, the σ constant values are linearly dependent on the values of Cl^{35} NQR frequencies only for meta-substituted chlorobenzenes. A comparison between those two series of values gave a fairly strict linear relationship between them (Fig.1):

$$\sigma_m = (-26.71 + 0.7735\nu_m) \pm 0.07;\ r=0.973 \qquad (1)$$

$$\nu_m = (34.55 + 1.223\,\sigma_m) \pm 0.09;\ r=0.973 \qquad (2)$$

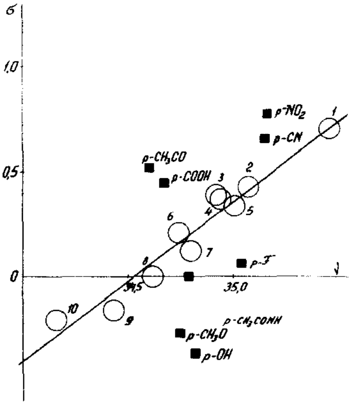

Fig.1. A correlation of Cl^{35} NQR frequencies for meta-substituted chlorobenzenes with the σ_m constants of the substituents.

The values of σ_m constants for 10 substituents (mainly from McDaniel and Brown data[6]) and the averaged values of NQR frequencies (at 77°K) for the corresponding substituted chlorobenzenes (Tabl.I) have been used at deducing the equation (1) and (2). The values of σ_m constant, calculated by the equation (1) are given in Table I. The standard deviation of σ is within the usual limits of accuracy (from 0.02 to 0.1)[1,6]. Only one significant deviation (0.17) is observed in the case of m -HOOC group, the latter not having been used at the calculation of the parameters of the equations (1) and (2).

No general linear relationship between the NQR frequencies of para-substituted chlorobenzenes and the σ constants has been obtained. The points, corresponding to either non-conjugated substituents or weakly-conjugated ones with lone-pair electrons (Cl, Br, I, $OCOCH_3$, i.e. substituents with

$\sigma_R \sim -0.2$, or less) satisfy the abovementioned relationship. The σ_p constants of those groups can be calculated by the equation (1) to a fairly high accuracy (Tab.I, No. 12-18), although the deviations exceeding 0.1 (points No.17 and 18) have been observed. The points conformable to both the strongly conjugated substituents of the first type and to all the second type substituents do not satisfy the equation (1). The points corresponding to the electron-accepter groups lie above and those corresponding to the electron-donor groups lie below the line obtained (Fig.1). It might be accounted for the fact, that the σ Hammett constants are affected by both the inductive and the resonance influence of the substituents, while the NQR frequencies values depend mainly on the inductive effect. A comparison of the deviations from the ordinate-axis ($\Delta\sigma = \sigma - \sigma_{cal}$) with the Taft resonance parameters σ_R [7] brings us to the linear relationship (Fig.2)

$$\Delta\sigma = (0.12 + 1.495\,\sigma_R) \pm 0.06; \quad r=0.990$$

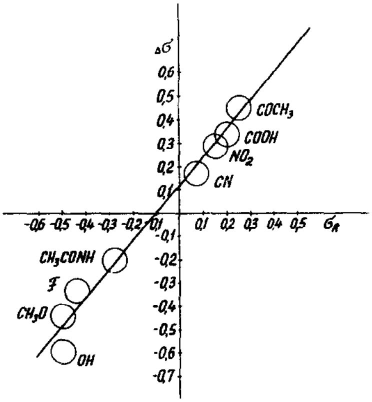

Fig.2. A correlation of σ_R of substituents with deviations $\Delta\sigma$ from the linear dependence σ_m (ν_m) (Fig.1) for the para-substituted chlorobenzenes with the strongly conjugated substituents of the first type and for the second type substituents.

An analogous equation gives the deviations from the abscissa

$$\Delta\nu = (0.15 + 1.466\ \sigma_R) \pm 0.07; \quad r=0.990$$

The above relationships for calculating the corrections $\Delta\sigma$ and $\Delta\nu$ together with the equations (1) and (2) enable us to determine the σ_p constants as well as the NQR frequencies values of the corresponding substituted chlorobenzenes for the second group para-substituents (Tabl.2).

$$\sigma_p = \sigma_{cal} + \Delta\sigma \quad \text{or}$$

$$\sigma_p = (-26.59 + 0.7735\nu_p + 1.195\,\sigma_R) \pm 0.06; \quad r=0.990 \qquad (3)$$

$$\nu_p = \nu_{cal} - \Delta\nu \quad \text{or}$$

$$\nu_p = (34.40 + 1.223\,\sigma_p - 1.466\,\sigma_R) \pm 0.07; \quad r=0.990 \qquad (4)$$

In that case the exceptions are the p-amino and p-dimethylamino groups ($\nu = 34.15$[2] and 33.94*) megacycles per sec.). The σ_p constants calculated from the equation (3), have the excessive absolute values (-1.08 and -1.45 respectively). If both the σ_p value and the NQR frequency for the given parasubstitued chlorobenzene are available, the relationship obtained can be used to determine the resonance parameter σ_R (Tabl.2)

$$\sigma_R = (21.80 + 0.820\,\sigma_p - 0.6342\nu_p) \pm 0.05; \quad r=0.990 \qquad (5)$$

Similar relationships can be obtained if the Taft constants σ° and σ_R°[8,9] are used instead of the σ Hammett constants and the σ_R constants respectively and in that case, both the correlation coefficient and the standard deviation have the values close to those obtained above.

It is of interest that there is a difference between the influence of a substituent up on F^{19} NMR resonance frequency and its influence upon Cl^{35} NQR resonance frequency in the corresponding aromatic compounds. Taft[10] has shown that the chemical shifts of F^{19} resonance signals for fluorobenzene meta-derivatives are linearly related with the values of the σ_I constants of the substituents, while the chemical shifts for para-derivatives are affected by both the inductive effect of the substituents and its resonance influence; the contribution of the latter being three times as large as that of the inductive effect.

---

*) Authors data.

When trying to establish a correlation of meta-substituted chlorobenzenes' NQR frequencies with the σ_I constants we 've obtained rather rough linear relationship (r=0.928); hydrogen and carboxylic group deviating considerably from the line obtained ($\Delta\sigma$ =0.23 and 0.25 respectively). Para-isomers, in fact, do satisty the very same relationship, in contrast to what has been observed for F^{19} chemical shifts. This confirms the conclusion, that the inductive influence of substituents is predominant; although the relationship being not a strict one.

REFERENCES

1. H.H.Jaffe, Chem.Rev., **53**, 191 (1953).
2. H.C.Meal, J.Am.Chem.Soc., **74**, 6121 (1952).
3. P.J.Bray, J.Chem.Phys., **22**, 1787 (1954); P.A.Cassabela, P.J.Bray, S.L.Segel, R.G.Barnes, J.Chem.Phys., **25**, 1280 (1956); H.O.Hooper, P.J.Bray, J.Chem.Phys., **33**, 334 (1960).
4. P.J.Bray, R.G.Barnes, J.Chem.Phys., **27**, 551 (1957).
5. E.N.Tsvetkov, G.K.Semin, D.I.Lobanov, M.I.Kabachnik, Dokl.Akad.Nauk SSSR, **161**, 1102 (1965).
6. D.H.McDaniel, H.C.Brown, J.Org.Chem., **23**, 420 (1958).
7. R.W.Taft,Jr., in "Steric Effect in Organic Chemistry", M.S.Newman ed. Wiley, New York, 1956.
8. R.W.Taft,Jr., J.Phys.Chem., **64**, 1805 (1960).
9. R.W.Taft,Jr., S.Ehrenson, I.C.Lewis, R.E.Glick, J.Am.Chem.Soc., **81**, 5352 (1959).
10. R.W.Taft,Jr., J.Am.Chem.Soc., **79**, 1045 (1957).
11. R.W.Taft,Jr., I.C.Lewis, J.Am.Chem.Soc., **80**, 2436 (1958).

Table I. Correlations of Cl^{35} NQR frequencies for meta- and para-substituted chlorobenzenes RC_6H_4Cl with the σ constants of the substituents

No.	R	ν in Mc/s	$\nu_{calc.}$	$\nu-\nu_{calc.}$	σ 6)	σ_{calc}	$\sigma-\sigma_{calc.}$
1.	m-NO_2	35.46 2)	35.42	0.04	0.710	0.72	0.01
2.	m-CF_3	35.07 2)	35.08	-0.01	0.43	0.41	0.02
3.	m-Br	34.92 a)	35.03	-0.11	0.391	0.30	0.09
4.	m-Cl	34.94 2)	35.01	-0.07	0.373	0.32	0.05
5.	m-F	35.01 a)	34.96	0.05	0.337	0.37	-0.03
6.	m-CH_3CONH	34.74 4)	34.81	-0.07	0.21	0.16	0.05
7.	m-OH	34.80 4)	34.70	0.10	0.121	0.21	-0.09
8.	H	34.62 2)	34.55	0.07	0.000	0.08	-0.08
9.	m-NH_2	34.43 4)	34.35	0.08	-0.16	-0.08	-0.08
10.	m-$(CH_3)_2N$	34.16 a)	34.29	-0.13	-0.211 1)	-0.29	0.08
11.	m-HOOC	35.23 2)	35.00	0.23	0.37	0.54	-0.17
12.	p-Cl	34.77 2)	34.83	-0.06	0.227	0.18	0.05
13.	p-Br	34.80 a)	34.83	-0.03	0.232	0.21	0.02
14.	p-I	34.77 a)	34.77	0.00	0.18	0.18	0.00
15.	p-CH_3COO	34.93 a)	34.93	0.00	0.31	0.31	0.00
16.	p-CH_2CN	34.61 4)	34.56	0.05	0.007 1)	0.06	-0.05
17.	p-CH_2Cl	34.57 2)	34.77	-0.20	0.184 1)	0.03	0.15
18.	p-$(CH_3)_3\overset{+}{N}$	35.41 a)	35.55	-0.14	0.82	0.68	0.14

---

a) The authors data.

Table 2. Correlation of Cl^{35} NQR frequencies for para-substituted chlorobenzenes RC_6H_4Cl with the σ and σ_R constants of the substituents.

№	R	$\nu_{Mc/s}$	ν_{calc}	$\nu-\nu_{calc}$	σ [6]	σ_{calc}	$\sigma-\sigma_{calc}$	σ_R [7,8]	$\sigma_{R\,calc}$	$\sigma_R-\sigma_{R\,calc}$
1.	p-CH_3CO	34.62 2)	34.66	-0.04	0.516 1)	0.49	0.03	0.25	0.26	-0.01
2.	p-COOH	34.67 2)	34.66	0.01	0.45	0.47	-0.02	0.20	0.18	0.02
3.	p-NO_2	35.16 a)	35.13	0.03	0.778	0.79	-0.01	0.15	0.14	0.01
4.	p-CN	35.15 a)	35.11	0.04	0.660	0.68	-0.02	0.07	0.05	0.02
5.	p-OH	34.82 2)	34.68	0.14	-0.37	-0.26	-0.11	-0.50	-0.58	-0.08
6.	p-OCH_3	34.75 2)	34.80	-0.05	-0.268	-0.31	0.04	-0.50	-0.46	-0.04
7.	p-F	35.04 a)	35.11	-0.07	0.062	-0.02	0.08	-0.44	-0.37	-0.07
8.	p-CH_3CONH	34.79 4)	34.81	-0.02	0.00	-0.01	0.01	-0.28 b)	-0.26	-0.02

a) The authors data

b) Found as the difference $\sigma_p - \sigma_I$; $\sigma_I = 0.28$ 11)