Correlation of Nuclear Quadrupole Resonance Frequencies with σ_I and σ_C the Taft–Hammett Parameters for the Series of Tetrahedral Molecules of Group IVB and Quinquevalent Phosphorus

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FOLLOWING the first correlations of n.q.r. frequencies of halides of tetrahedral derivatives of Group IVB with Taft's σ^*,[1] an attempt was made to introduce an additional parameter accounting for the coupling or conjugation for such a type of correlation.[2]

Here, we have used the equation

$$\frac{\nu - \nu_0}{\nu_0} = (\alpha\Sigma\sigma_I + \beta\Sigma\sigma_C) \pm \mu$$

which connects the change in the n.q.r. frequencies ν at temperature 77°K with the σ_I, σ_C parameters, using the same scale. In the series of tetrahedral molecules belonging to Group IVB, the following elements were examined as substituents for the central atom: H,Alk, Ar, Hal, and a series of ethers. For the correlations, the values for the σ parameters, determined by the chemical shift ^{19}F of fluorine-substituted benzenes in inert solvents, were used.[3] The values for the induction constants σ_I for Et and Pr[i] were calculated by the formula[3]

$$\sigma_I = \frac{\sigma^* - 0{\cdot}49}{6{\cdot}23}$$

The changes in the parameters α and β, which characterize the system transmitting the effect, show that peculiarities of the radial distribution of the halide p-electrons, as well as the presence of free d-orbitals on the central atom, make an essential contribution in relation to the transmission coefficients of the conjugation (β) and induction (α) effects. The n.q.r. data, used to derive the equations, were partly obtained by us, partly extracted from reviews.[4]

As well as examination of the halogenoalkylaryl derivatives of the Group IVB elements, correlations were determined for the tetrahedral derivatives of quinquevalent phosphorus $R^1R^2P(O)Cl$ and $R^1R^2P(S)Cl$, where R^1,R^2 = Alk, Ar, or Hal. The results, shown in the Table, confirm the large double bond character of the P–S bond as compared with P–O.

The results obtained enables the effect of the substituent on the n.q.r. frequency of a haloid atom to be represented as the sum of the induction and conjugation substituents ($\Delta\nu_1 = \alpha\sigma_I + \beta\sigma_C$), they also confirm the additivity of changes in n.q.r. frequencies $\nu = \nu_0 + \Sigma\Delta\nu_1$ (*vide e.g.* ref. 5). At the same time, low correlation coefficients and

Correlation of equation's parameters $\nu - \nu_0/\nu_0 = [(\alpha\Sigma\sigma_I + \beta\Sigma\sigma_C) \pm \mu]\cdot10^{-3}$*

	$R^1R^2R^3M$ Hal	ν_0(Mc./sec.)	α	β	α/β	μ	τ
1.	$R^1R^2R^3C$-^{35}Cl	33·72	197	+ 64	+ 3·05	± 8·3	0·9916
2.	$R^1R^2R^3C$-^{79}Br	261·54	188	+124	+ 1·56	±14·5	0·9722
3.	$R^1R^2R^3C$-^{127}I	264·56	240	+218	+ 1·10	± 8·6	0·9948
	$(\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2})$						
4.	$R^1R^2R^3Si$-^{35}Cl	17·12	159	− 11	−12·10	± 9·3	0·9821
5.	$R^1R^2R^3Si$-^{81}Br	105·31	210	−253	− 0·83	± 3·0	0·9996
6.	$R^1R^2R^3Si$-^{127}I	129·12	283	−399	− 0·71	± 4·5	0·9996
	$(\pm\frac{1}{2} \longleftrightarrow \pm\frac{3}{2})$						
7.	$R^1R^2R^3Ge$-^{35}Cl	18·46	296	− 40	− 7·29	±13·5	0·9973
8.	$R^1R^2R^3Ge$-^{81}Br	118·75	300	−176	− 1·70	± 1·9	0·9999
9.	‡$R^1R^2R^3Sn$-^{35}Cl	9·91	845	−795	− 1·06	±19·0	0·9958
10.	‡$R^1R^2R^3Sn$-^{81}Br	103·23	393	−161	− 2·44	± 0·3	0·9999
11.	R^1R^2OP-^{35}Cl	22·89	224	−247	− 0·91	± 6·4	0·9946
12.	R^1R^2SP-^{35}Cl	23·52	146	−408	− 0·36	± 5·1	0·9948

* ν—N.q.r. frequency; σ_I, σ_C—induction and conjugation constants of the substituents; α,β transmission coefficients; μ—average absolute error; τ—correlation coefficient.

‡ The preliminary data.

large deviations would result if an attempt is made to correlate n.q.r. values only with inductivity parameters of substituents (*vide e.g.* refs. 1 and 6).

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