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A CORRELATION BETWEEN SUBSTITUENT EFFECTS ON CHEMICAL SHIFTS IN CONJUGATED SYSTEMS AND COUPLING CONSTANTS

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The correlation of chemical shifts with structures is a longstanding quest, important successes in which have been Shoolery's rules (1, 2) for alicyclic compounds and, in the benzenoid field, the results of work by Corio and Dailey (3a), Bothner-By and Glick (3b), and Diehl (4). An important area for which correlations have yet to be established is that of polycyclic aromatic and heteroaromatic systems : in recent work (5, 6) we have found that the effect of substituents varies according to ring systems and position of substitution.

We now show that the effect $\Delta\tau$ on the chemical shift of an aromatic ring proton at ring position a by a substituent X at an ortho position b is related linearly to the ortho coupling constant J_{ab} between the protons in these positions in the corresponding unsubstituted compound :

$$(\Delta\tau)_{aXb} = n_x J_{ab} + t_x$$

In this equation n_x and t_x are constants for each substituent X. Figures A - C demonstrate the relationship for nitro and methoxy substituents, and for the substitution of CH in a six membered ring by a sp^2 hybridised nitrogen atom. The graphs give the following values for the constants (solvent indicated) :

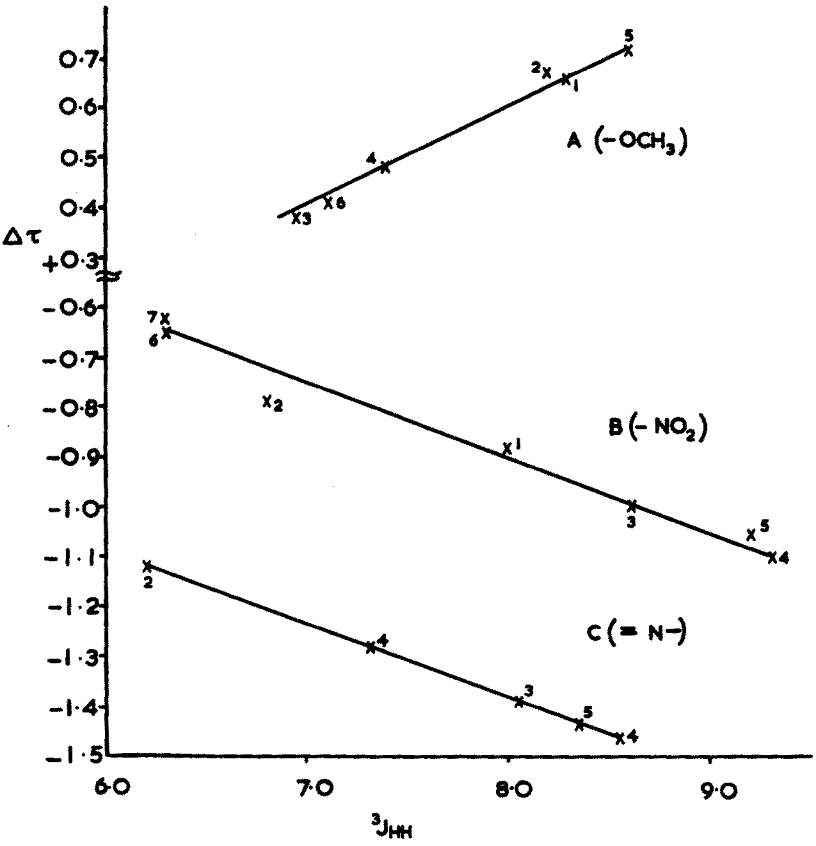
	NO_2 (acetone)	OMe (acetone, CCl_4)	N (cyclohexane)
n_x	-0.130	+0.230	-0.138
t_x	-0.134	-1.226	-0.279

The following reasoning led us to seek the present correlation. A substituent will affect the chemical shift of an ortho proton by diamagnetic anisotropy, electric field, inductive, and mesomeric effects. To a first approximation, all these will be constant for a given substituent except the last, because the distances and steric orientation between the substituent and an ortho proton in general vary but little. The mesomeric effect will depend on bond order; Jonathan, Gordon and Dailey (7) have related bond order P_{ij} to coupling constant by the equation :

$$^3J_{HH} = 12.7\, P_{ij} - 1.1$$

If one assumes that the bond orders in an aromatic compound will not be significantly altered by a substituent, then a relation of the form found should follow, provided the measurements are carried out in a constant, non-interacting solvent.

Our constants n_x should be a measure of the mesomeric effect of the substituents, and we plan to measure a variety of n_x and seek a relation between them and σ^o_R constants (8). The constants t_x should in principle be divisible into a component measuring the inductive effect and another caused by direct field and magnetic anisotropy effects. We plan to measure further systems to test the limits of applicability of our relation.



FIGURE

Dependence of chemical shifts of protons (A) ortho to an -OCH$_3$ group and (B) ortho to a-NO$_2$ group on the ortho coupling constant in the corresponding aromatic hydrocarbon.

(C) Dependence of chemical shifts of protons ortho to an sp hybridised N-atom in a six-membered ring on the ortho coupling constant in the corresponding carbocyclic aromatic compound.

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REFERENCES

1. J.N.Shoolery, *Technical Bulletin, Varian Associates, Palo Alto, Calif.*, **2**, No. 3 (1959).
2. B.P.Dailey and J.N.Shoolery, *J.Amer.Chem.Soc.*, **77** 3977 (1955).
3. a P.L.Corio and B.P.Dailey, *J.Amer.Chem.Soc.*, **78**, 1071 (1956).
   b A.A.Bothner-By and R.E.Glick, *J.Amer.Chem.Soc.*, **78**, 1071 (1956).
4. P. Diehl, *Helv.Chim.Acta.*, **44**, 829 (1961), **45**, 568 (1962); *cf* also G.W.Smith, *J.Mol.Spectroscopy*, **12**, 146 (1964).
5. R.K.Harris, A.R.Katritzky, S.Øksne, A.S.Bailey and W.G.Paterson, *J.Chem.Soc.*, 197 (1963).
6. A.R.Katritzky, R.E.Reavill and F.J.Swinbourne, *J.Chem.Soc.* in press.
7. N.Jonathan, S.Gordon and B.P.Dailey, *J.Chem.Phys.*, **36**, 2443 (1962).
8. R.T.C.Brownlee, A.R.Katritzky and R.D.Topsom, *J.Amer.Chem.Soc.*, **87**, 3260,(1965).