Relationship Between Dipole Moments and Inductive Substituent Constants

Bo-Long Poh

School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia.

Abstract

A linear relationship between μ/d (where μ is the C–X bond dipole moment and d is a distance parameter) and the inductive substituent constant, σ_I, for substituted acetic acids, XCH_2COOH, is derived from a combination of Taft and Kirkwood–Westheimer equations. This linear relationship is similar to the empirical relationship relating μ/d and σ_I observed in monosubstituted alkanes.

Several empirical correlations of dipole moments of organic molecules with substituent constants have been given by various workers.[1-6] Some[1] used μ, some[2] used $\log \mu$, and some[5,6] used μ/d in the correlations (μ refers to the dipole moment of the molecule and d is a distance parameter[6]). It was found[6] that good correlations of μ/d with the inductive substituent constant, σ_I, were obtained in monosubstituted alkanes though this approach was criticized as being physically meaningless.[7] The purpose of this short paper is to show that a similar linear relationship between μ/d and σ_I in substituted acetic acids, XCH_2COOH, can be derived from a combination of Taft and Kirkwood–Westheimer equations.

From a simple combination of Taft[8] and Kirkwood–Westheimer[9] equations relating the ionization constants of substituted acetic acids, XCH_2COOH, in water at 25°C we obtain

$$\mu/R^2 = 2 \cdot 3 k_B T D_e \sigma^* \rho^* / e \cos \theta \qquad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, D_e is the effective dielectric constant, e is the electronic charge, R is the distance between the ionizing proton and the centre of the dipole, θ is the angle between the dipole axis and the line joining the ionizing proton to the centre of the dipole, σ^* is the substituent constant,

[1] Taft, R. W., Jr, *J. Am. Chem. Soc.*, 1953, **75**, 4231.
[2] Petkovic, D. M., Kezele, B. A., and Rajic, D. R., *J. Phys. Chem.*, 1973, **77**, 922.
[3] Rao, C. N. R., Wahl, W. H., and Williams, E. J., *Can. J. Chem.*, 1957, **35**, 1575.
[4] Charton, M., *J. Org. Chem.*, 1965, **30**, 552.
[5] Exner, O., *Collect. Czech. Chem. Commun.*, 1960, **25**, 642.
[6] Deady, L. W., Kendall, M., Topsom, R. D., Jones, R. A. Y., *J. Chem. Soc., Perkin Trans. 2*, 1973, 416.
[7] Exner, O., 'Dipole Moments in Organic Chemistry' Ch. 3 (Georg Thieme: Stuttgart 1975).
[8] Taft, R. W., Jr, and Lewis, I. C., *J. Am. Chem. Soc.*, 1959, **81**, 5343.
[9] Kirkwood, J. G., and Westheimer, F. H., *J. Chem. Phys.*, 1938, **6**, 506, 513.

ρ^* is the rho parameter, and μ is the C–X bond dipole moment. Inserting numerical values into equation (1) for k_B, e, T (298 K), ρ^* (1·72),[1] $D_e/\cos\theta$ (6·62, Table 1) and replacing[10] σ^* by $2\cdot22\sigma_I$ and R^2 by $6\cdot46d$ (Table 2) transform equation (1) into the approximate equation (2)

$$\mu/d = 3\cdot22\sigma_I \qquad\qquad (2)$$

which predicts a linear relationship between μ/d and σ_I with a slope of 3·22. The C–X bond dipole moments[9] of XCH_2COOH are close to the dipole moments of

Table 1. Values of $\cos\theta$, R, and D_e for some XCH_2COOH compounds in water

X	$\cos\theta^A$	$R\,(\text{Å})^A$	$D_e^{B,C}$	$D_e/\cos\theta$	X	$\cos\theta^A$	$R\,(\text{Å})^A$	$D_e^{B,C}$	$D_e/\cos\theta$
CN	0·737	4·20	4·622	6·27	Br	0·566	3·44	3·748	6·62
NO2	0·573	3·46	3·761	6·56	Cl	0·584	3·39	3·681	6·72
I	0·586	3·50	3·805	6·49	F	0·506	3·29	3·584	7·08

average $D_e/\cos\theta$ 6·62±0·27

[A] Values of $\cos\theta$ and R calculated from the geometry of the molecule with the carboxyl proton at 1·45 Å beyond the carboxyl carbon atom (ref.[9]).
[B] Values of D_e calculated according to Tanford, C., J. Am. Chem. Soc., 1957, **79**, 5348.
[C] Data of D_e from Edward, J. T., Farrell, P. G., and Job, J. L., J. Chem. Phys., 1972, **57**, 5251.

Table 2. A comparison of R^2 and d

X	$d\,(\text{Å})^A$	$R^2/d\,(\text{Å})$	X	$d\,(\text{Å})^A$	$R^2/d\,(\text{Å})$
CN	2·62	6·73	Br	1·94	6·10
NO2	2·02	5·93	Cl	1·78	6·46
I	2·14	5·72	F	1·38	7·84

average R^2/d 6·46±0·77

[A] Data taken from ref.[6], which also gives the definition of d.

alkanes containing the corresponding substituents X and we find that the predicted value of 3·22 in equation (2) is also in close agreement with the reported values[6] of 2·74 (CH_3X), 2·77 (Bu^tX), 2·94 (cyclohexyl-X), 2·61 (cyclopentyl-X), and 3·03 (1-adamantyl-X) obtained from plots of μ/d against σ_I in monosubstituted alkanes.

Acknowledgment

[10] Ritchie, C. D., and Sager, W. F., Prog. Phys. Org. Chem., 1964, **2**, 323.