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A SIMPLE METHOD OF OBTAINING σ^* VALUES OF ALKYL SUBSTITUENTS

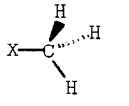
Bo-Long Poh

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

The Taft's σ^* value of any given alkyl substituent can be calculated from the equation $\sigma^* = -0.255\ \sigma_b + 0.461$ since the value of σ_b, an alkyl substituent constant, of any alkyl group can be obtained from the C-C and C-H bond refractions.

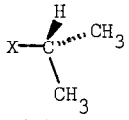
Taft's σ^* values of alkyl substituents,[1] obtained mainly from the data on the hydrolyses of esters, have found wide applications in correlation analysis.[2] However, the σ^* values of many alkyl substituents are still not available in the literature. Therefore, it is desirous to have a simple method that will enable one to obtain the σ^* value of any given alkyl substituent. Such a method is given below.

Based on the facts that alkyl substituent effects are (1) attenuating[3] and (2) mainly polarizing effects,[4] we have calculated a set of alkyl substituent constants, σ_b, by projecting successively along the C-X bond the C-C and C-H bond refractions in a given alkyl substituent (X is the atom to which the alkyl substituent is attached). The use of successive projection[5] takes care of fact (1) and the use of C-C and C-H bond refractions accounts for fact (2), of alkyl substituent effects. Two examples illustrating the method of calculating σ_b are given below. The bond refractions (R_D) of C-H (1.676) and C-C (1.296) are taken from the work of Vogel and co-workers,[6] and all bond angles are assumed to be tetrahedral. The σ_b value of H is zero.



(1)

$$\sigma_b(\text{Me}) = 3R_D(\text{C-H})\cos 70.5^\circ = 1.678$$



(2)

$$\sigma_b(\underline{i}\text{-Pr}) = 2(3R_D(\text{C-H})\cos 70.5^\circ + R_D(\text{C-C}))\cos 70.5^\circ + R_D(\text{C-H})\cos 70.5^\circ = 2.545$$

Some calculated σ_b values are given in Table 1, together with the available σ^* values. The two parameters are related as follows

$$\sigma^* = -0.255\ \sigma_b + 0.461 \quad (1) \quad (n = 16,\ r = 0.992)$$

Therefore, equation (1) can be used to obtain the σ^* values of all the alkyl substituents that are still not available in the literature.

Table 1. σ_b and σ^* values of H and alkyl substituents

Substituent	σ_b	σ^* [a]	Substituent	σ_b	σ^* [a]
H	0	0.490	t-Bu	2.979	-0.300
Me	1.678	0	n-Pe	2.320	-0.16[b]
Et	2.112	-0.100	i-Pe	2.353	-0.162[b]
n-Pr	2.256	-0.115	t-Pe	3.123	-0.33[d]
i-Pr	2.545	-0.190	$CHEt_2$	2.834	-0.225[e]
n-Bu	2.304	-0.130	neo-Pe	2.546	-0.165
i-Bu	2.401	-0.125	n-Hex	2.326[c]	-0.165[b]
s-Bu	2.690	-0.210	CH(Me)t-Bu	2.979	-0.285

[a] Ref.1. [b] Ref.7. [c] Constant for all straight-chain alkyl groups with six or more carbon atoms. [d] Ref.3. [e] Ref.8.

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