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The Nature of the *ortho* Effect. II. Composition of the Taft Steric Parameters

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Abstract: The Taft E_S values are shown to be a linear function of the van der Waals radii. They are independent of electrical effects. The Taft $E°_S$ values intended for use with *ortho* substituents are completely independent of the van der Waals radius; they are solely a function of electrical effects. The *ortho* effect for most substituents is electrical rather than steric in nature.

The most widely used quantitative measures of steric effects among organic chemists are the E_S and $E°_S$ values proposed by Taft.[1] Numerous papers have appeared reporting correlations with these "steric effect" constants.[2] Taft, in his review,[1] reported that the E_S values parallel the van der Waals radii. It has been suggested that these parameters may include electrical as well as steric effects.[3] Koppel[4] has reported that for alkyl groups the equations

$$E_S = a + b\sigma^* + c\Delta n \qquad (1)$$

and

$$E°_S = a + b\sigma^* + c\Delta n \qquad (2)$$

are obeyed. Other substituents generally did not follow eq 1 and 2.

In view of the uncertainty regarding the nature of the E_S and $E°_S$ values it seemed of interest to investigate their composition. To this end we have carried out correlations of E_S and $E°_S$ values with the equations

$$E_{SX} = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_{V,X} + h \qquad (3)$$

$$E°_{SX} = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + \psi r_{V,N} + h \qquad (4)$$

where σ_I and σ_R are the localized (field and/or inductive) and delocalized (resonance) effect substituent constants, and r_V is the van der Waals radius. The σ_I constants required are taken from our compilation;[5] the σ_R constants were obtained from the equation[6]

$$\sigma_R = \sigma_p - \sigma_I \qquad (5)$$

The σ_p constants are from McDaniel and Brown[7] or from Exner and Jonás.[7] Constants from other sources are given in Table I. The atomic van der Waals radii are from the excellent study of Bondi[8,9] (Table II). For symmetric top substituents of the type CX_3 (*e.g.*, Me, CF_3, *t*-Bu, CCl_3,...) radii for the entire group were calculated. For such a substituent there are four quantities of interest. They are shown in Figures 1 and 2. These quantities are: (1) $r_{V,min}$, minimum perpendicular to CX_3, minimal van der Waals radius perpendicular to the group axis; (2) $r_{V,max}$, maximum

Table I. Substituent Constants[a]

X	σ_I	Ref	σ_p	Ref
CH_2SMe	0.07	*a*	0	*b*
CBr_2H	0.28	*c*	0.34	*d*
CBr_3	0.38	*c*	0.57	*f*
CCl_2H			0.36	*e*
CF_2H			0.41	*e*

[a] Calculated from the equation $\sigma_{I.XCH_2} = 0.369\sigma_{I.X} - 0.02$. [b] Calculated from the equation $\sigma_{p.XCH_2} = 0.522\sigma_{I.X} - 0.13$. [c] Calculated from the equation $\sigma_{I.X_2CH} = 0.324\epsilon\sigma_{I.X} - 0.01$. [d] Estimated from the equation $\sigma_{p.X_2CH} = 0.522\epsilon\sigma_{I.X} - 0.13$. [c] Calculated from the equation $\sigma_{I.CX_3} = 0.308\epsilon\sigma_{I.X} - 0.03$. [f] Estimated from the equation $\sigma_{p.X_3C} = 0.522\epsilon\sigma_{I.X} - 0.13$.

Table II. van der Waals Radii Used in Correlations[a]

X	F	Cl	Br	I	O	S	H
r_v	1.47	1.75	1.85	1.98	1.52	1.80	1.20

[a] See ref 8 and 9.

(1) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., JohnWiley & Sons, Inc., New York, N. Y., 1965, p 565.
(2) See references cited in the review by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 342 (1964); R. T. M. Fraser, *Nature*, **205**, 1207 (1965); K. Bowden, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 5239 (1963); 3370 (1964). (This is only a sampling of references using E_S values in correlations.)
(3) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 228; C. K. Hancock, E. A. Myers, and B. J. Yager, *J. Am. Chem. Soc.*, **83**, 4211 (1961).
(4) I. Koppel, *Reakts. Sposobnost. Org. Soedin.*, **2** (2), 24 (1965).
(5) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).
(6) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).
(7) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); O. Exner and J. Jonás, *Collection Czech. Chem. Commun.*, **27**, 2296 (1962).
(8) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(9) Complete tables of the correlations obtained have been deposited as Document No. NAPS-00156 with the ASIS National Auxiliary Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

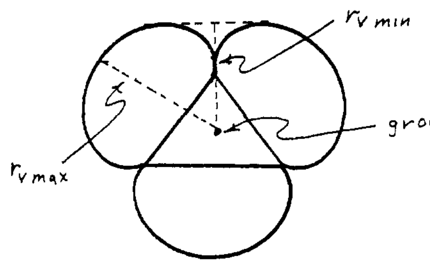

Figure 1. Bottom view of CX_3 group.

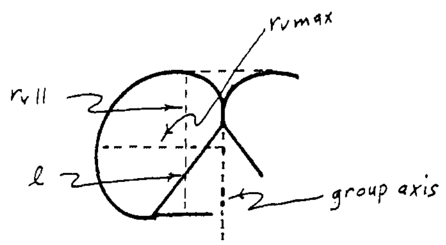

Figure 2. Side view of CX_3 group.

perpendicular to CX_3, maximal van der Waals radius perpendicular to the group axis; (3) $r_{V,||}$, van der Waals radius parallel to the group axis; (4) l, equivalent to a covalent radius for the entire group, CX_3.

By means of simple geometry and trigonometry these quantities can be calculated. Values for some common groups are given in Table III. The values for the t-Bu and NMe_3^+ groups were obtained using for the van der Waals radius of X the value of $r_{V,min}$ calculated for the Me group.

Table III. van der Waals Parameters for BA_3 Symmetric Top Substituents

X	$l_{X,G}$	$r_{V,\|\|}$	$r_{V,max}$	$r_{V,min}$
Me	1.912	1.575	2.23	1.715
CF_3	1.933	1.866	2.743	2.107
Me_3Si		2.12	3.987	2.60
SO_3^-	2.332	2.077	2.852	2.186
t-Bu	2.100	2.283	3.150	2.435
NMe_3^+	1.973	2.214	3.114	2.417
CCl_3	2.144	2.357	3.408	2.579
CBr_3	2.157	2.470	3.670	2.760
CI_3	2.251	2.684	3.996	2.988
CO_3	2.013	1.996	2.864	2.192
CS_2	2.247	2.510	3.473	2.637

For purposes of correlation with eq 3 E_S values were divided into three categories: CH_2X, CHX_2, and symmetric top (CX_3 and H) substituents. Correlations were then made with each set using r_V, $r_{V,max}$, and $r_{V,min}$ as steric parameters. The sets studied are listed in Table IV. The E_S values are taken from Taft;[1] the values used are given in Table V.

In correlating the E_S values for $MeOCH_2$ and $MeSCH_2$ in set 1, it was assumed that the OMe and SMe groups would be oriented in such a way as to minimize their size. Thus r_V values for O and S, respectively, were used for these groups. For the Me group, the van der Waals radius was taken to be the value of $r_{V,min}$.

Table IV. Sets of E_S Parameters Studied

Set	Substituent type	Parameters
1	CH_2X	σ_I, σ_R, $r_{V,X}$
2		σ_I, σ_R, $r_{V,min}$
3		σ_I, σ_R, $r_{V,max}$
4		$r_{V,X}$
5		$r_{V,min}$
6		$r_{V,max}$
7	CHX_2	σ_I, σ_R, $r_{V,X}$
8		σ_I, σ_R, $r_{V,min}$
9		σ_I, σ_R, $r_{V,max}$
10		$r_{V,X}$
11		$r_{V,min}$
12		$r_{V,max}$
13	CX_4	σ_I, σ_R, $r_{V,X}$
14		σ_I, σ_R, $r_{V,min}$
15		σ_I, σ_R, $r_{V,max}$
16		$r_{V,X}$
17		$r_{V,min}$
18		$r_{V,max}$
19[a]	X	σ_I, σ_R, $r_{V,X}$
20[a]	X	σ_I, σ_R

[a] Sets 19 and 20 represent correlations of E°_S constants defined for *ortho* substituents in benzene derivatives. All other sets represent correlations of E_S values defined for aliphatic systems.

Results

E_{S,CH_2X} Values. The results of the best correlations with eq 3 and 4 are given in Table VI. The correlations of the E_{X,CH_2X} values with $r_{V,X}$, $r_{V,min}$ and $r_{V,max}$ (Figure 1, sets 1, 2, and 3, respectively) all gave significant, although poor, correlation with eq 3. The t test shows that ψ is much more significant than is α or β. Elimination of the E_S value for X = Me gave slight improvement in the case of correlation with $r_{V,X}$ (set 1A) and slightly worse results with $r_{V,min}$ and $r_{V,max}$ (sets 2A and 3A). Again t tests showed ψ to be the most significant coefficient. This suggests a far greater dependence of the E_S values on r_V than upon σ_I or σ_R. To determine whether this is indeed the case correlations were carried out with the equation

$$E_S = \psi r_V + h \qquad (6)$$

The results of these correlations are presented in Table VII. A good correlation of E_{S,CH_2X} with $r_{V,X}$ was obtained (set 4); exclusion of the value for X = Me gave excellent results (set 4A). Very good correlations with eq 6 were obtained using $r_{V,min}$ and $r_{V,max}$ (sets 5 and 6). Exclusion of the value for X = Me gave excellent correlations (sets 5A and 6A).

E_{S,CH_2X} Values. Correlations with $r_{V,X}$, $r_{V,min}$, and $r_{V,max}$ (sets 7, 8, and 9) gave no significant, poor but significant, and fair results, respectively. The value for hydrogen (H in place of CHX_2) was included in sets 8 and 9. The van der Waals parameter used for the hydrogen substituent was its r_V value. Exclusion of the value for hydrogen from set 8 gave a nonsignificant correlation (set 8A) whereas exclusion of the value for X = Me gave fair results (set 8B). Exclusion of the value for hydrogen from set 9 also gave a nonsignificant correlation (set 9A) whereas exclusion of the value for X = Me gave good results (set 9B). Again, in all correlations, ψ was the most significant coefficient as shown by the t tests. Correlations were therefore carried

Table V. E_S Values Used in Correlations[1]

				Sets 1–6				
X	Me	Et	CH_2F	CH_2Cl	CH_2Br	CH_2I	CH_2OMe	CH_2SMe
E_S	0	−0.07	−0.24	−0.24	−0.27	−0.37	−0.19	−0.34

			Sets 7–12			
X	Me	Me_2CH	F_2CH	Cl_2CH	Br_2CH	H
E_S	0	−0.47	−0.67	−1.54	−1.86	1.24

			Sets 13–18			
X	Me	CF_3	CCl_3	CBr_3	CMe_3	H
E_S	0	−1.16	−2.06	−2.43	−1.54	1.24

				Sets 19 and 20					
X	MeO	EtO	F	Cl	Br	I	Me	NO_2	Ph
$E°_S$	0.99	0.90	0.49	0.18	0	−0.20	0	−0.75	−0.90

Table VI. Results of Correlations with Eq 3 and 4

Set	α	β	ψ	h	R^a	F^b	r_{12}^c	r_{13}^c	r_{23}^c
1A	−0.139	−0.476	−0.361	0.347	0.931	6.454	0.738	0.685	0.390
2A	−0.126	−0.648	−0.216	0.262	0.922	5.649	0.738	0.674	0.354
3	−0.552	−0.410	−0.119	0.187	0.908	6.250	0.794	0.560	0.319
7	−3.71	3.12	−1.69	2.44	0.935	2.307	0.992	0.468	0.408
8B	−1.49	2.87	−1.81	3.39	0.9997	499.0	0.890	0.820	0.534
9B	0.289	−0.641	−1.28	2.78	0.9999	2510.	0.890	0.797	0.483
13	−0.662	−0.374	−3.12	3.71	0.9991	185.8	0.814	0.437	0.408
14	−0.604	1.32	−2.20	3.81	0.999	308.8	0.766	0.573	0.311
15	−0.401	−0.300	−1.44	3.01	0.998	196.8	0.766	0.574	0.295
19	−0.687	−3.11	0.484	−1.23	0.990	50.66	0.191	0.0695	0.886
20A	−0.433	−2.45		−0.279	0.990	122.0	0.191		

Set	s_{est}^d	s_α^d	s_β^d	s_ψ^a	s_h^d	n^e	CL^f
1A	0.0626	0.583	1.29	0.134	0.203	7	90.0
2A	0.0663	0.628	1.38	0.0872	0.191	7	90.0
3	0.0701	0.536	1.45	0.0583	0.188	8	90.0
7	0.548	13.4	23.7	1.36	2.22	5	<90.0
8B	0.0644	0.873	1.30	0.134	0.171	5	95.0
9B	0.0287	0.442	0.669	0.0422	0.0579	5	97.5
13	0.0795	0.270	0.480	0.169	0.266	5	90.0
14	0.101	0.339	0.567	0.0967	0.185	6	99.5
15	0.127	0.431	0.716	0.0793	0.191	6	99.0
19	0.0919	0.230	0.539	0.495	0.955	7	99.5
20A	0.0970	0.173	0.172		0.0940	8	99.9

Set	t_α^g	CL^h	t_β^g	CL^h	t_ψ^g	CL^h	t_h^g	CL^h
1A	0.238	<20.0	0.469	20.0	2.694	90.0	1.709	80.0
2A	0.201	<20.0	0.470	20.0	2.477	90.0	1.372	50.0
3	1.030	50.0	0.283	20.0	2.041	80.0	0.995	50.0
7	0.277	<20.0	0.132	<20.0	1.243	50.0	1.099	50.0
8B	1.707	50.0	2.208	50.0	13.51	95.0	19.82	95.0
9B	0.654	20.0	0.958	20.0	30.33	95.0	48.01	98.0
13	24.52	80.0	0.779	20.0	18.46	99.0	13.95	99.0
14	1.782	50.0	2.328	80.0	22.75	99.0	20.59	99.0
15	0.930	50.0	0.419	20.0	18.16	99.0	15.76	99.0
19	2.987	90.0	5.769	98.0	0.988	50.0	1.288	50.0
20A	2.503	90.0	14.24	99.9			2.968	95.0

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficients of σ_I on σ_R, σ_I on r_V, and σ_R on r_V, respectively. [d] Standard errors of the estimate, α, β, ψ, and h, respectively. [e] Number of points in the set. [f] Confidence level of significance of correlation. [g] t tests for significance of α, β, ψ, and h. [h] Confidence levels for significance of α, β, ψ, and h.

Table VII. Results of Correlations with Eq 6

Set	$-\psi$	h	r^a	t^b	s_{est}^c	s_ψ^c	n^d	CL^e
4A	0.412	0.445	0.915	5.085	0.0533	0.0810	7	99.0
5A	0.248	0.366	0.899	4.591	0.0580	0.0540	7	99.0
6A	0.179	0.334	0.894	4.472	0.0593	0.0399	7	99.0
10A	2.88	3.49	0.998	24.75	0.0590	0.116	4	99.0
11B	1.95	3.49	0.998	25.32	0.0982	0.0772	5	99.9
12B	1.26	2.77	0.9998	91.59	0.0272	0.0138	5	99.9
16	3.49	4.14	0.978	8.031	0.229	0.435	5	99.0
17	2.33	3.99	0.996	21.38	0.144	0.109	6	99.9
18	1.51	3.14	0.995	19.91	0.154	0.0760	6	99.9

[a] Correlation coefficient. [b] t test for significance of ψ. [c] Standard error of the estimate and of ψ. [d] Number of points in the set. [e] Confidence level for significance of correlation.

out with eq 6. The correlation with $r_{V,X}$ gave poor but significant results (set 10); exclusion of the value for X = Me gave an excellent correlation (set 10A). The correlations with $r_{V,min}$ and $r_{V,max}$ (sets 11 and 12) gave excellent results. Exclusion of the value for hydrogen from these sets gave only fair correlation (sets 11A and 12A). Exclusion of the value for X = Me from sets 11 and 12 gave excellent results (sets 11B and 12B) as did exclusion of both the hydrogen value and the value for X = Me (sets 11C and 12C). The good agreement between ψ and h values for sets 11B and 11C and for sets 12B and 12C indicates that the E_S value for hydrogen definitely lies on the line for X_2CH groups.

E_{S,CX_3} **Values.** Correlation with $r_{V,X}$ values gave poor although significant results (set 13). The E_S value for hydrogen was included in sets 14 and 15. Excellent results were obtained for set 14 and very good results for set 15. Elimination of the hydrogen value from these sets gave poorer correlation, due at least in part to the small size of the set (sets 14A and 15A). Once more, the most significant coefficient as determined by t tests was ψ. The data were therefore correlated with eq 6. Correlation with $r_{V,X}$ values gave excellent results (set 16). Still better results were obtained from correlations with $r_{V,min}$ and $r_{V,max}$ (sets 17 and 18). Exclusion of the value for hydrogen from sets 17 and 18 gave excellent correlations (sets 17A and 18A). The values of ψ and h for sets 17 and 17A and for sets 18 and 18A were essentially the same, indicating that the hydrogen E_S value lies on the line for the CX_3 values.

$E^{\circ}_{S,X}$ **Values.** The phenyl and nitro groups were excluded from the correlation for lack of a suitable van der Waals parameter. Correlation of the remaining groups with eq 4 using the $r_{V,X}$ values as the steric parameter gave an excellent correlation (set 19). The t tests show that β *and, to a lesser extent,* α *are significant whereas* ψ *is not.* Correlation of the data with the equation

$$E_S = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{7}$$

gave excellent results (set 20). Inclusion of the value for X = NO_2 gave improved results. The results show clearly that the E°_S values can be accounted for solely by the σ_I and σ_R parameters.

Discussion

Our results show clearly that E_S values for CH_3X, CHX_2, and CX_3 substituents are a linear function of van der Waals radii. *They are independent of electrical effect.* The five correlations obtained show that the van der Waals radius can account completely for the E_S values, and no dependence on other quantities is required. The different substituent types do lie on different lines. The line for CHX_2 substituents and the line for CX_3 substituents intersect at the point for the hydrogen substituent. The fact that the hydrogen lines on the CX_3 group line can be explained in terms of the fact that the CX_3 substituents are roughly spherically symmetric, as is also the hydrogen substituent. The CHX_2 substituents present a face which is equivalent to one face of the CX_3 substituents. We may account for the hydrogen substituent lying on the CHX_2 line in terms of this picture. The question now arises as to what is the cause of the nonadditivity of the steric effects. We believe that this may be accounted for in terms of conformational effects. Thus in the case of the CH_2X group a conformation is possible in which the X substituent is rotated as far from the site of steric interaction as is possible. In the case of the CHX_2 group two of the conformations will have less steric interactions than will the third. In the case of the CX_3 group all three conformations will be equivalent, with maximal steric interaction. Thus it seems reasonable to us to consider each group type separately, and not to expect additivity for the steric effects observed.

All of the van der Waals parameters studied gave approximately the same results. We prefer the $r_{V,min}$ parameter because it seems to us likely that a group will preferentially take up a position which will minimize the degree of steric interaction.

In sharp contrast to the behavior of the E_S values which are a function only of the van der Waals radii, *the* E°_S *values intended for use with ortho substituents are completely independent of the van der Waals radii and may be completely accounted for (with the exception of the Ph group) in terms of electrical effect parameters.* We conclude from this that the *ortho* effect for most substituents is an electrical rather than a steric effect.

It is convenient to describe the composition of "compound" substituent constants (substituent constants composed of localized and delocalized effects) by the parameter ϵ where

$$\epsilon \equiv \frac{\delta}{\lambda} = \frac{\beta}{\alpha} \tag{8}$$

and

$$\sigma_X = \lambda\sigma_{I,X} + \delta\sigma_{R,X} \tag{9}$$

Values of ϵ for substituent constants[10] are $\sigma_m = 0.33$; $\sigma_p{}^0 = 0.65$; $\sigma_p = 1.00$; $\sigma_p{}^+ = 1.60$; as compared with $E^{\circ}_S = 4.62$. A number of authors have correlated data with the equation

$$Q_X = \rho\sigma_X + sE^{\circ}_{S,X} + h \tag{10}$$

From eq 10, 7, and 9 we obtain

$$Q_X = (\rho\lambda + \alpha)\sigma_{I,X} + (\rho\delta + \beta)\delta_{R,X} + h \tag{11}$$

$$Q_X = \alpha'\sigma_{I,X} + \beta'\sigma_{R,X} + h \tag{12}$$

Thus eq 10 is equivalent to correlation with the extended Hammett equation (eq 12).

(10) M. Charton, *J. Org. Chem.*, 30, 3341 (1965).