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Steric Effects. V. Barriers to Internal Rotation

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Abstract: Values of $\Delta G^\ddagger$ for the barriers to internal rotation in 11 sets of compounds were correlated with the modified Taft equation, $\Delta G^\ddagger = \psi\nu_X + h$. With sets including more than four points, correlations were generally successful. The steric parameter (ν), is valid both for substituents bonded to aromatic rings and substituents bonded to aliphatic carbon atoms. The ψ values constitute a measure of the sensitivity to steric effects of a set of $\Delta G^\ddagger$ values for internal rotational barriers. The methyl group is found to behave as a symmetrical substituent with no noticeable "gear effect".

Recently, Nilsson et al.[1] have determined values of $\Delta G^\ddagger$ for barriers to internal rotation in substituted 1,3,5-trineopentylbenzenes (I). Attempts were then made to correlate these $\Delta G^\ddagger$ values with van der Waals volumes (V_W) and with $\Delta G^\ddagger$ values for rotational barriers in 2-substituted 2,3,3-trimethylbutanes[2] (II) by means of the linear free energy relationship

$$\Delta\Delta G^\ddagger{}_{IX} = \gamma\Delta\Delta G^\ddagger{}_{IIX} \tag{1}$$

where $\Delta\Delta G^\ddagger = \Delta G^\ddagger{}_X - \Delta G^\ddagger{}_H$. Good results were obtained with eq 1. An attempt to correlate $\Delta\Delta G^\ddagger$ values (with $\Delta\Delta G^\ddagger = \Delta G^\ddagger{}_X - \Delta G^\ddagger{}_{Me}$) with the Taft[3] $E^\circ{}_S$ values obtained from the acid catalyzed hydrolysis of 2-substituted benzoate esters and esterification of 2-substituted benzoic acids was unsuccessful. It seemed of interest to us to examine the correlation of all available data on barriers to internal rotation as a function of substituent with the modified Taft equation

$$\Delta G^\ddagger{}_X = \psi\nu_X + h \tag{2}$$

which is analogous to the equations used to correlate steric effects in previous papers of this series.[4-7] In eq 2, the ν values are steric parameters which are defined by the equation

$$\nu_X \equiv r_{VX} - r_{VH} = r_{VX} - 1.20 \tag{3}$$

where r_{VX} and r_{VH} are the van der Waals radii of the X group and the hydrogen atom, respectively. The ν values are from ref 4 or from our compilation.[8] The value of ν used for the Ph group was 0.57. Correlations were carried out by the method of least-squares. Data used in the correlations are set forth in Table I. Results of the correlations with eq 3 are set forth in Table II.

Of the 11 sets of data studied, 4 gave excellent, 1 gave good, and 1 gave poor correlation. The remaining five sets did not give significant correlation. It should be noted, however, that four of these sets had only three points. Of the six sets with four or more points, five gave correlations ranging from excellent to good and only one did not give significant results. It seems likely therefore that the four three-point sets would have given much better results had more data been available.

Sets 3 and 7 both report $\Delta G^\ddagger$ values for barriers to internal rotation in 2-substituted 2-chloro-3,3-dimethylbutanes. The values obtained for the ethyl and *tert*-butyl groups in set 3 are in good agreement with those obtained in set 7, for which excellent correlation was obtained with eq 2. The values reported in set 3 for methyl and chloro agree fairly well with the value for methyl and chloro calculated from the correlation line for set 7. The value reported in set 3 for bromo is significantly larger than the value obtained from the correlation line for set 7. Furthermore in set 2, which reports $\Delta G^\ddagger$ values for internal rotational barriers in 2-substituted 2,3,3-trimethylbutanes, a system very similar to that studied in sets 3 and 7, the value of $\Delta G^\ddagger$ for the bromo substituent is only 0.3 kcal/mol greater than that of the

Table I. Data Used in Correlations

1 $\Delta G^{\ddagger}$ for rotational barriers in substituted 1,3,5-trineopentylbenzenes[a]
H, 5.4; F, 9.0; Cl, 14.7; Br, 16.6; I, 18.8; Me, 15.4
2 $\Delta G^{\ddagger}$ for rotational barriers in 2-substituted 2,3,3-trimethylbutanes[b]
H, 7.0; F, 8.0; Cl, 10.4; Br, 10.7; I, 11.1
3 $\Delta G^{\ddagger}$ for rotational barriers in 2-substituted 2-chloro-3,3-dimethylbutanes[c]
Me, 9.82; Cl, 10.81; Br, 11.90; Et, 10.87; *t*-Bu, 11.42
4 $\Delta G^{\ddagger}$ for rotational barriers in 2-substituted 2-bromo-3,3-dimethylbutanes[c]
Me, 10.80; Br, 12.27; Cl, 11.90
5 E_a for rotational barriers in 2,4-di-*tert*-butyl-6-methylbenzyl-halides[d]
Cl, 11.3; Br, 12.5; I, 15.9
6 $\Delta G^{\ddagger}$ for rotational barriers in substituted benzylmesitylenes[e]
OMe, 9.2; OH, 9.5; SH, 11.4; CN, 10.4; Me, 11.2; Cl, 11.4; Br, 12.7
7 $\Delta G^{\ddagger}$ for rotational barriers in 2-substituted 2-chloro-3,3-dimethylbutanes[f,g]
H, 8.32; Me, 10.43; Et, 10.82; $PhCH_2$, 10.85; *t*-Bu, 11.43; Ph, 10.19; *t*-$BuCH_2$, 11.80
8 $\Delta G^{\ddagger}$ for rotational barriers in 2-substituted methyl-2-chloro-3,3-dimethylbutanes[g]
H, 10.43; Me, 10.82; Ph, 10.85; *t*-Bu, 11.80
9 ΔG_c for rotational barriers in 2-substituted 2,11-dithia[12]-metacyclophane[h]
Cl, 15.4; Me, 16.6; Br, 22.5
10 ΔG_c for rotational barriers in 2-substituted 2,12-dithia[13]-metacyclophane[h]
Cl, 11.6; Me, 12.0; Br, 15.4
11 ΔG_c for rotational barriers in 9-substituted 9-(2',6'-dimethoxyphenyl)fluorene[i]
H, 20.6; OH, 14.4; Cl, 9.2

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Table II. Results of Correlations With Equation 2

Set	ψ	h	r[a]	F[b]	s_{est}[c]	s_{ψ}[c]	s_h[c]	n[d]
1	17.8	5.09	0.992	243.5[e]	0.720	1.14[e]	0.604[g]	6
2	5.72	6.87	0.985	96.15[f]	0.366	0.583[g]	0.309[e]	5
3	1.20	10.1	0.467	0.837[l]	0.795	1.31[n]	0.988[g]	5
4	9.39	6.27	0.836	2.323[l]	0.593	6.16[n]	3.55[n]	3
5	20.3	−0.165	0.981	25.84[l]	0.651	3.99[m]	2.66[p]	3
6	8.84	6.59	0.971	82.40[e]	0.319	0.973[e]	0.483[e]	7
7	2.28	8.95	0.925	29.82[f]	0.468	0.417[g]	0.343[e]	7
8	1.12	10.3	0.981	50.27[i]	0.140	0.158[h]	0.116[e]	4
9	51.8	−11.6	0.928	6.242[l]	2.00	20.7[n]	12.0[o]	3
10	29.1	−3.71	0.950	9.222[l]	0.924	9.59[n]	5.53[o]	3
11	−20.6	20.7	0.999	525.5[j]	0.352	0.900[j]	0.331[h]	3

[a] Correlation coefficient. [b] F test for significance of correlation. Superscripts indicate confidence levels. [c] Standard errors of the estimate, ψ, and h. Superscripts indicate confidence levels of "Student t" test. [d] Number of points in the set. [e] 99.9% confidence level (CL). [f] 99.5% CL. [g] 99.0% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95% CL. [k] 90.0% CL. [l] <90% CL. [m] 80.0% CL. [n] 50.0% CL. [o] 20% CL. [p] 20.0% CL.

chloro substituent whereas, in set 3, the difference between the values for the chloro and bromo substituents is 1.1 kcal/mol. It seems likely, therefore, that the value reported in set 3 for the bromo substituent is in error, being about 1 kcal/mol too large. This explains the lack of significant correlation of set 3 with eq 2.

Our results show that, in many cases, the barrier to internal rotation is a true steric effect and can be successfully represented by eq 2. These results also provide further evidence that van der Waals radii in the form of ν parameters are widely useful measures of steric effects. In this context, it is of interest and importance that successful correlations were obtained in both aromatic (set 1) and nonaromatic sets (2, 6, 7, 8, 11). This suggests the general applicability of the ν values.

The ψ values obtained from correlations with eq 2 are a measure of the sensitivity of a set of internal rotational barriers to steric effects. Of the sets which are successfully correlated by eq 2, set 11 has the greatest magnitude of ψ. It is somewhat puzzling that ψ for the 2-substituted 2,3,3-trimethylbutanes (set 2) is greater than ψ for the 2-substituted 2-chloro-3,3-dimethylbutanes (set 7). The values are 5.72 and 2.28, respectively. We are unable to explain this observation at the present time. The value of ψ for the 2-substituted methyl-2-chloro-3,3-dimethylbutanes, 1.12, is as expected, less than the value of ψ for the 2-substituted 2-chloro-3,3-dimethylbutanes.

Nilsson et al.[1] have suggested that there is a qualitative difference in steric effect between the methyl group and the halogens. They suggest that a comparison between these substituents requires that the methyl group be a more or less cylindrically symmetrical or pear-shaped substituent, and that this does not take into account "the actual 'three-pronged' nature of the methyl and its consequent tendency to become involved in 'gear effects' ". Of the six sets we have examined with four or more substituents, five include the methyl group (sets 1, 3, 6, 7, 8). Four of these sets gave good to excellent correlations with eq 2, using a value of ν for the methyl group which was calculated on the assumption that Me is a symmetrical substituent (and therefore the "gear effect" is negligible). The success of these correlations including the methyl group strongly implies that the "gear effect" is unimportant and that the methyl group behaves as a symmetrical substituent. Furthermore, the ν value successfully represents the steric effect of the *tert*-butyl group, although this group should be even more susceptible to a "gear effect" than is the methyl group.

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