and from the oligomers prepared in the presence of nitrogen was found to be 85 and 8.1 mg/L of the oligomerization mixture, respectively.

Urea Analysis of HCN Oligomer Hydrolyzates. Sublimed HCN oligomers (50 mg) were hydrolyzed with 6 N HCl, and half of the hydrolysate was subjected to paper chromatography on Whatman 3MM paper using ethyl acetate/formic acid/water (7:2:1 by volume) as the developing solvent. One-quarter of the hydrolysate was analyzed by TLC using butanol/acetic acid/water (12:3:5 by volume) as the developing solvent. Both chromatograms were sprayed with the p-dimethylaminobenzaldehyde reagent.[35] No urea was detected in either chromatogram above the limit of detection of 2–5 μg. It was determined that urea is stable under the acid hydrolysis conditions used.

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Registry No.—**1**, 1726-32-5; **2**, 5181-05-5; **3**, 1187-42-4; hydrogen cyanide, 74-90-8; cyanide, 57-12-5; urea, 57-13-6.

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Steric Effects. 13. Composition of the Steric Parameter as a Function of Alkyl Branching

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The υ steric parameters for alkyl, alkoxy, thioalkyl, dialkylamino, and oxyalkyl groups and the υ' values of alkyl groups were correlated with equations derived from the relationship $\upsilon = an_\alpha + bn_\beta + cn_\gamma + dn_\delta + i$, with excellent results. The parameters n_α, n_β, n_γ, and n_δ represent the number of α, β, γ, and δ carbon atoms, respectively. The correlation equations make possible the estimation of υ values for a very large number of groups. The $E_S{}^c$ values of Hancock and the $E_S{}^o$ values of Palm are simply steric parameters with different values of a from that obtained for the υ values. Rate constants for nucleophilic substitution of benzyl chloride by alkoxide ions, of allyl bromide and of 1-chloro-2,4-dinitrobenzene by alkylamines, of alkaline hydrolysis of ethyl 4-nitrophenyl alkyl phosphonates, C-substituted amides, O-substituted esters, and dialkylphenylacetonitriles, of acidic hydrolysis of C-substituted amides, and of the reaction of alcohols with 4-nitrobenzoyl chloride have been successfully correlated with the equation $Q_{Ak} = an_\alpha + bn_\beta + cn_\gamma + i$. Evaluation of the effect on branching shows clearly that for alkyl groups which are not symmetric, no one set of steric parameters will be effective in all types of reactions.

We have calculated in our previous work in this series[1-5] υ steric parameters for 232 substituents and υ' steric parameters for nine substituents.[6,7] In this paper we investigate the dependence of the steric parameter, υ, on the degree of branching in the alkyl group. We would also like, if possible, to be able to estimate υ values for many additional groups.

In commencing this work, we note that Bowden and Woolridge[8] have reported a poor but significant correlation of E_S values with the equation

$$E_S = m_1 n_C + m_2 n_H + m_3 \qquad (1)$$

where n_C and n_H are the number of carbon and hydrogen atoms in the sixth position (with the carbonyl oxygen atom in the ester used to define E_S being considered atom number 1). Let us define the following quantities: $n_\alpha \equiv$ the number of C atoms bonded to the α carbon atom of an alkyl group; $n_\beta \equiv$ the number of C atoms bonded to the β carbon atoms; $n_\gamma \equiv$ the number of C atoms bonded to the γ carbon atoms; $n_\delta \equiv$ the total number of carbon atoms bonded to the δ carbon atoms. Thus, for example, the group t-BuCH(Me(CH(Et)CMe$_2$–has values of 3, 2, 3, 3 for n_α, n_β, n_γ, n_δ, respectively, while for the cyclohexyl group, the corresponding values are 2, 2, 1, 0.

Newman[9] had suggested long before that the "six number", n_6, is the major factor in the steric effect. This quantity is defined by the equation

$$n_6 = 3n_\beta \qquad (2)$$

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Table I. υ Values Used in the Correlations

1. Alkyl groups: Me, 0.52; Et, 0.56; Pr, 0.68; Bu, 0.68; BuCH$_2$, 0.68; BuCH$_2$CH$_2$, 0.73; Bu(CH$_2$)$_3$, 0.73; Bu(CH$_2$)$_4$, 0.68; *i*-Pr, 0.76; *sec*-Bu, 1.02; c-C$_6$H$_{11}$CH$_2$, 0.97; *i*-Bu, 0.98; *t*-Bu, 1.24; *t*-BuCH$_2$, 1.34; Et$_2$CH, 1.51; Pr$_2$CH, 1.54; Bu$_2$CH, 1.56; *t*-BuCH$_2$Me$_2$C, 1.74; *t*-BuMeCH, 2.11; *i*-PrEtCH, 2.11; *t*-BuMe$_2$C, 2.43; Et$_3$C, 2.38; *i*-PrCH$_2$CH$_2$, 0.68; *t*-BuCH$_2$CH$_2$, 0.70; (*i*-PrCH$_2$)$_2$CH, 1.70; (*t*-BuCH$_2$)$_2$CH, 2.03; *t*-BuCHEtCH$_2$CH$_2$, 1.01; c-C$_6$H$_{11}$CH$_2$CH$_2$, 0.70; c-C$_6$H$_{11}$(CH$_2$)$_3$, 0.71; *sec*-BuCH$_2$, 1.00; *t*-BuCH$_2$CHMe, 1.41; MePrCH, 1.05; Me-*i*-PrCH, 1.29; *i*-BuCH$_2$CH$_2$, 0.68; MeBuCH, 1.07; Me-*i*-BuCH, 1.09; EtBuCH, 1.55; *n*-C$_9$H$_{19}$, 0.68; *n*-C$_{11}$H$_{23}$, 0.68; *n*-C$_{13}$H$_{27}$, 0.68; *n*-C$_{15}$H$_{31}$, 0.68; *n*-C$_{17}$H$_{35}$, 0.68; c-C$_4$H$_9$; 0.51; c-C$_5$H$_9$, 0.71; c-C$_6$H$_{11}$, 0.87; c-C$_7$H$_{13}$, 1.00

2. Alkoxy groups: Me, 0.36; Et, 0.48; Pr, 0.56; *i*-Pr, 0.75; Bu, 0.58; *i*-Bu, 0.62; *sec*-Bu, 0.86; *t*-Bu, 1.22; CH$_2$Bu, 0.58; CH$_2$-*sec*-Bu, 0.62; CH$_2$-*i*-Bu, 0.62; CH$_2$-*t*-Bu, 0.70; CHEt$_2$, 1.00; CHMePr, 0.90; CHMe-*i*-Pr, 0.91; CMe$_2$Et, 1.35; CH$_2$CH$_2$Bu, 0.61; CHEtPr, 1.04; CH$_2$CH$_2$-*t*-Bu, 0.53; CH$_2$CHEt$_2$, 0.71; CH$_2$CMe$_2$Et, 0.78; CH$_2$CHMe-*i*-Pr, 0.64; CHEt-*i*-Pr, 1.18; CEt$_2$Me, 1.52; CPrMe$_2$, 1.39; CHMe-*t*-Bu, 1.19; CHMeBuCH$_2$, 0.90; CH$_2$CHEt-*i*-Pr, 0.76; CH$_2$CHMe-*t*-Bu, 0.66; CH$_2$CMeEt$_2$, 0.82; *n*-C$_8$H$_{17}$, 0.61; CH$_2$CHEtBu, 0.76; CHMe(BuCH$_2$CH$_2$), 0.92; CH$_2$CHEt-*t*-Bu, 0.96; CH$_2$CH-*i*-Pr$_2$, 0.89; CH-*i*-Bu$_2$, 1.28; *n*-C$_{12}$H$_{25}$, 0.65; c-C$_5$H$_9$, 0.77; c-C$_6$H$_{11}$, 0.81; CH$_2$-c-C$_3$H$_5$, 0.48; CH$_2$-c-C$_5$H$_9$, 0.58; CH$_2$-c-C$_6$H$_{11}$, 0.65; CH$_2$CEt$_3$, 0.97

3. Alkylamino and dialkylamino groups: NHMe, 0.39; NHEt, 0.59; NHPr, 0.64; NH-*i*-Pr, 0.91; NHBu, 0.70; NH-*i*-Bu, 0.77; NH-*sec*-Bu, 1.12; NH-*t*-Bu, 1.83; NHCH$_2$Bu, 0.64; NHCH$_2$-*i*-Bu, 0.65; NHCH$_2$CH$_2$Bu, 0.66; NMe$_2$, 0.43; NMeEt, 0.87; NEt$_2$, 1.37; NPr$_2$, 1.60; NiPr$_2$, 2.01; NHcC$_6$H$_{11}$, 0.92

4. Alkylthio groups: Me, 0.64; Et, 0.94; *i*-Pr, 1.19; Pr, 1.07; Bu, 1.15; *i*-Bu, 1.15; *sec*-Bu, 1.36; *t*-Bu, 1.60

5. Oxyalkyl groups: MeOCH$_2$, 0.63; EtOCH$_2$, 0.61; PrOCH$_2$, 0.65; *i*-PrOCH$_2$, 0.67; BuOCH$_2$, 0.66; *i*-BuOCH$_2$, 0.62; EtCHOMe, 1.22; PrCHOMe, 1.22; BuCHOMe, 1.20; CH$_2$OH, 0.53; MeCHOH, 0.50; EtCHOH, 0.71; PrCHOH, 0.71; BuCHOH, 0.70; BuCH$_2$CHOH, 0.71; *t*-BuCH$_2$OCMe$_2$, 1.23

6. Alkyl groups: Me, 0.35; Et, 0.38; Pr, 0.42; Bu, 0.42; *i*-PrCH$_2$, 0.55; *i*-Pr, 0.62; *t*-Bu, 1.23; *sec*-Bu, 0.66

while

$$n_C = n_\gamma \tag{3}$$

Furthermore,

$$n_6 = nC + n_H \tag{4}$$

Thus, from eq 2, 3, and 4, we obtain

$$n_H = 3n_\beta - n_\gamma \tag{5}$$

Substituting eq 3 and 5 in eq 1 gives

$$E_S = 3m_2n_\beta + (m_1 - m_2)n_\gamma - m_3 \tag{6}$$

Thus, the work of Bowden and Woolridge indicates a dependence of the Taft steric parameter, E_S, on the degree of branching. This work is extended by a report of Rybkov, Gankin, and Gurevich,[10] which states that the rate of esterification of RCO$_2$H is dependent on n_5 as well as n_6, as n_5 is given by the equation

$$n_5 = 3n_\alpha \tag{7}$$

It seemed reasonable, therefore, to examine the correlation of all available υ values for alkyl groups with the equation

$$\upsilon = an_\alpha + bn_\beta + cn_\gamma + dn_\delta + i \tag{8}$$

The υ values were taken from our previous work.[1,2] The groups studied are set forth in Table I (set 1). The cyclopropyl group was not included in this correlation as we have already suggested that υ for this group includes a significant resonance effect contribution. The results of the correlation by least mean squares with eq 8 are reported in Table II (set 1A). The results are significant at the 99.9% confidence level (CL). The value of r^2, however, is only 0.7909. Thus, only about 79% of the data are accounted for by the correlation. Seven of the 46 data points are apparently outliers. These points include Me, Et, *t*-BuEtCHCH$_3$CH$_2$, c-C$_4$H$_7$, c-C$_5$H$_9$, c-C$_6$H$_{11}$, and c-C$_7$H$_{13}$. The deviation of the cyclic substituents is reasonable as the steric effect of these groups is undoubtedly different from that of the corresponding open chain analogues. Comparing *sec*-Bu with c-C$_4$H$_7$, the υ values are 1.02 and 0.51, respectively. This is certainly due to greater freedom of motion in an acyclic group than is possible in a cyclic group. The υ values for the Me and Et apparently deviate because they are not substituted sufficiently compared to the other groups studied. The deviation of υ for the *t*-BuEtCHCH$_2$CH$_2$ group may be due simply to experimental error.

A further point is that the "student t" test shows that d is not significant and therefore n_δ is not required. The remaining 39 data points were therefore correlated with the equation

$$\upsilon = an_\alpha + bn_\beta + cn_\gamma + i \tag{9}$$

with excellent correlation (set 1B). Again, the correlation was significant at the 99.9% CL. The value of r^2 obtained was 0.9722. Thus, the correlation accounts for about 97% of the variation. The success of eq 9 led us to applying this method to υ values for alkoxy, dialkylamino, and alkylthio substituents. Values of the υ constants used in the correlations are set forth in Table I and results of the correlations in Tables II and III. The υ values for the alkoxy groups were correlated with the equation

$$\gamma = bn_\beta + cn_\gamma + dn_\delta + i \tag{10}$$

This equation was obtained by dropping the n_α term in eq 8. The n_α term is not required for alkoxy groups as the α atom is the oxygen atom which of course can form only one bond to a carbon atom. Correlation of all 44 available υ values for alkoxy groups gave a result (set 2A) significant at the 99.9% CL with a value for r^2 of 0.8633. Thus, the correlation accounted for about 86% of the variation. Examination of the calculated υ values showed that the OMe, OCH$_2$CH$_2$-*t*-Bu, OcC$_5$H$_9$, OcC$_6$H$_{11}$, OCH$_2$-c-C$_3$H$_5$, OCH$_2$-c-C$_4$H$_7$, and OCH$_2$-c-C$_5$H$_9$ groups deviate considerably from the experimental values. Exclusion of these values gave an excellent correlation (set 2B) which was again significant at the 99.9% CL with an r^2 value of 0.9491. Thus, the correlation accounts for about 95% of the variation. The most probable cause for the deviation of the groups indicated above from the correlation is experimental error with the exception of the OME groups. The deviation of the OMe group is reasonable in view of the deviation of the υ value for the Et group from the correlation line for alkyl groups.

It must be noted that the successful correlation obtained with eq 10 shows that the n_δ term is required. We believe that this is due to the fact that the alkoxy groups available had much more variation in n_δ than did the alkyl groups available. Thus, seven alkoxy groups had n_δ values ≥ 3 whereas only one alkyl group had such a value. We believe that if υ values for suitably substituted alkyl groups were available, the n_δ term would have been significant.

Since the dialkylamino and alkylamino groups can undergo variable substitution at N, we have correlated υ values for them with eq 8. An excellent correlation was obtained (set 3A), significant at the 99.9% CL, with an r^2 value of 0.0258, thereby accounting for about 93% of the variation. Examination of calculated υ values showed that those for the NHMe, NH-*i*-Pr, and NH-c-C$_6$H$_{11}$ groups deviated considerably from the experimental υ values. The deviation of the NHMe group is in agreement with the previously observed deviations of the OMe and Et groups. The NH-*i*-Pr and NH-c-C$_6$H$_{11}$ groups pre-

Table II. Results of Correlations

set	a	b	c	d/b'	c	i	R^{a}	F^{b}
1A	0.397	0.347	0.0614	0.0158		−0.101	0.889	38.76^{e}
1B	0.497	0.409	0.0608			−0.309	0.986	408.0^{e}
2A		0.372	0.0787	0.0528		0.0795	0.929	84.18^{e}
2B		0.406	0.108	0.0594		−0.0084	0.974	204.9^{e}
3A	0.227	0.415	0.0467	−0.0737		0.0357	0.962	37.41^{e}
3B	0.200	0.453				0.0407	0.969	85.58^{e}
4		0.318	0.108	0.0897		0.635	0.999	476.9^{e}
5A	0.262	0.186	−0.0153	0.417	−0.0551	0.309	0.957	21.91^{e}
5B	0.303	0.255		0.484		0.159	0.997	612.9^{e}
6A	0.280	−0.0127				0.202	0.900	10.65^{f}
6B	0.386	0.0760				−0.0502	0.950	18.53^{g}
6C	0.349					0.0638	0.935	34.87^{h}
11	0.346					0.345	0.997	397.7^{e}

set	$s_{est}{}^{c}$	$s_{a}{}^{c}$	$s_{b}{}^{c}$	$s_{c}{}^{c}$	$s_{d}{}^{c}/s_{b'}$	$s_{c'}{}^{c}$	$s_{i}{}^{c}$	n^{d}
1A	0.249	0.616^{e}	0.0497^{e}	0.0303^{i}	0.0483^{j}		0.118^{k}	46
1B	0.0927	0.0230^{e}	0.0199^{e}	0.0118^{e}			0.0457^{e}	39
2A	0.103		0.0240^{e}	0.194^{e}	0.0140^{e}		0.0543^{l}	44
2B	0.0623		0.0167^{e}	0.0128^{e}	0.00934^{e}		0.0400^{m}	37
3A	0.151	0.0896^{i}	0.0388^{e}	0.0534^{k}	0.0716^{k}		0.143^{m}	17
3B	0.136	0.0779^{i}	0.0380^{e}				0.114^{j}	14
4	0.0197		0.00854^{e}	0.00903^{e}	0.0212^{n}		0.0161^{e}	8
5A	0.0936	0.0471^{e}	0.0875^{o}	0.0786^{m}	0.0584^{e}	0.0559^{k}	0.0595^{e}	16
5B	0.0230	0.0119^{e}	0.0148^{e}		0.0146^{e}		0.0165^{e}	15
6A	0.0148	0.0621^{g}	0.0764^{m}				0.117^{l}	8
6B	0.112	0.0681^{g}	0.0709^{k}				0.146^{j}	7
6C	0.114	0.0590^{e}					0.102^{j}	7
11	0.0145	0.0141^{e}					0.0184^{e}	6

[a] Correlation coefficient. [b] F test for significance of regression. Superscripts indicate confidence levels (CL). [c] Standard errors of the estimate and the regression coefficients. Superscripts indicate confidence level of the "student t" test. [d] Number of points in set. [e] 99.9% CL. [f] 97.5% CL. [g] 99.0% CL. [h] 99.5% CL. [i] 95.0% CL. [j] 20.0% CL [k] 50.0% CL. [l] 80.0% CL. [m] <20.0% CL. [j] 98.0% CL. [o] 90.0% CL.

Table III. Partial Correlation Coefficients [a]

set	r_{12}	r_{13}	r_{14}	r_{23}	r_{24}	r_{34}
1A	0.372^{b}	0.042	0.369^{b}	0.106	0.195	0.126
1B	0.265	0.009		0.096		
2A	0.109	0.344^{c}		0.247		
2B	0.241	0.421^{b}		0.280		
3A	0.218	0.264	0.387	0.052	0.187	0.369
3B	0.228					
4	0.145	0.114		0.061		
5A	0.552^{d}	0.422	0.269	0.764^{e}	0.358	0.313
5B	0.523^{d}	0.395		0.472		
6A	0.183					
6B	0.520					

set	r_{15}	r_{25}	r_{35}	r_{45}
5A	0.406	0.633^{b}	0.484	0.556^{c}

[a] Superscripts indicate significance of partial correlation coefficients. Lack of superscripts indicates less than 90% CL. [b] 98.0% CL. [c] 95.0% CL. [d] 90.0% CL. [e] 99.5% CL.

sumably deviate due to experimental error. The correlation obtained with eq 8 shows (from the "student t" tests) that c and d are not significant and therefore the n_{γ} and n_{γ} terms are not required. We have therefore correlated the data, after the exclusion of the values for NHMe, NH-i-Pr, and NH-c-C_6H_{11}, with the equation

$$\upsilon = an_{\alpha} + bn_{\beta} + i \tag{11}$$

once more resulting in a correlation (set 3B) significant at the 99.9% CL, with an r^2 value of 0.9396, accounting for about 94% of the variation.

The υ values for alkylthio groups were correlated with eq 10 as no n_{α} term is required, as was the case for alkoxy groups, and for the same reason. An excellent correlation was obtained, significant at the 99.9% CL, with r^2 equal to 0.9972. Surprisingly the SMe group does not deviate greatly from the correlation line for thioalkyl groups, in contrast to the behavior of the Et, OMe, and NHMe groups.

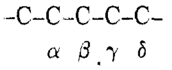
We have also examined the effect of branching on oxyalkyl groups of the type $CR^1R^2(OR^3)$. We first attempted correlation with

$$\upsilon = an_{\alpha} + bn_{\beta} + cn_{\gamma} + b'n_{O\beta} + c'n_{O\gamma} + i \tag{12}$$

where $n_{O\beta}$ is the number of carbon atoms bonded to O (either 0 or 1, keeping in mind that the lettering of C atoms is as shown in (I) with the oxygen atom replacing Cβ), and $n_{O\gamma}$ is the number of γ carbon atoms attached to the β carbon atom, which is bonded to an oxygen atom.

Table IV. Values of υ_{CHX_2} and υ_{CX_3}

X	H	Me	F	Cl	Br	I
υ_{CHX_2}	0.52	0.76	0.68	0.81	0.89	0.97
υ_{CX_3}	0.52	0.24	0.91	1.38	1.56	1.79



$$\underset{}{-C}\underset{\alpha}{-C}\underset{\beta}{-C}\underset{\gamma}{-C}\underset{\delta}{-C-}$$

(I)

The result obtained from correlation with eq 12 (set 5A) was significant at the 99.9% CL, with a value of r^2 of 0.9164, accounting for about 92% of the variance. The "student t" tests showed that c and c' were not significant. Furthermore, the calculated value of υ for the CH_2OH group deviated greatly from the experimental value. This is in accord with our previous results for the Et, OMe, and NHMe groups. The remaining 12 values of υ were correlated with the equation

$$\upsilon = an_\alpha + bn_\beta + b'n_{0\beta} + i \qquad (13)$$

with excellent results (set 5B). Once again, the correlation was significant at the 99.9% CL, with an r^2 value of 0.9941, accounting for essentially all the variation.

Finally, we have examined the few available values of υ' for alkyl groups. As no υ' values were available for groups with significant values of n_γ or n_δ, the data were correlated with eq 11 (set 6A). The correlation obtained was good and the results were significant at the 95% CL with an r^2 value of 0.8099, accounting for about 81% of the variation. A "student t" test showed that b was not significant. Exclusion of the υ value for Me gave an improved correlation with eq 11, significant at the 99.0% CL, with an r^2 value of 0.9026, accounting for about 90% of the variation. Again, however, b was not significant. Data were therefore correlated with the equation

$$\upsilon' = an_\beta + i \qquad (14)$$

giving an excellent correlation, significant at the 99.5% CL with an r^2 value of 0.8746, accounting for about 87% of the variation. The lack of significance of b is probably due to the small number of points in the set.

The successful correlation of υ values with the degrees of alkyl branching makes possible the estimation of ν values for a large number of substituents and thereby greatly expands the utility of the modified Taft equation. The preferred equations for the estimation of new υ constants are:

$$\upsilon_R = 0.497n_\alpha + 0.409n_\beta + 0.0608n_\gamma - 0.309 \qquad \text{(i)}$$

$$\upsilon_{OR} = 0.406n_\beta + 0.108n_\gamma + 0.059n_\delta - 0.00839 \qquad \text{(ii)}$$

$$\upsilon_{NR^1R^2} = 0.200n_\alpha + 0.453n_\beta + 0.0407 \qquad \text{(iii)}$$

$$\upsilon_{SR} = 0.318n_\beta + 0.108n_\gamma + 0.089n_\delta + 0.635 \qquad \text{(iv)}$$

$$\upsilon_{CR^1R^2(OR^3)} = 0.303n_\alpha + 0.255n_\beta + 0.484n_{0\beta} + 0.159 \qquad \text{(v)}$$

Our results also shed light on the composition of the "corrected" $E_S{}^c$ values of Hancock and co-workers[11] and $E_S{}^o$ values of Palm.[12]

Let us establish the freedom of the υ parameters for alkyl groups from resonance effects. We propose to do this by showing that they are obtained by calculation from van der Waals radii, or by linear relationships with υ values which were calculated from van der Waals radii. It will be convenient to review at this point the difference between electrical and steric effects. Both effects are of course electrical in orgin. The electrical effect of a substituent is due to the charge (usually partial) on the substituent. It is conveniently factored into a localized effect and a delocalized effect. The steric effect is dependent on the size and shape of the substituent, whereas the electrical effect is not. Thus, it is quite possible to have groups which are isoelectronic (have a constant electrical effect) and show a widely varying steric effect, or are isosteric and have a widely varying electrical effect. The origin of the steric effect lies in repulsions between nonbonding atoms. The origin of the electrical effect lies in the effect of the substituent upon the electron distribution at the active site (the atom or group of atoms at which some measurable phenomenon occurs). As van der Waals radii are a measure of size, not charge, we believe that υ parameters which are calculated from these radii or are a linear function of parameters calculated from these radii are pure steric parameters.

The υ values for Me and t-Bu were directly calculated from van der Waals radii and are therefore pure steric parameters. The values of υ for i-Pr and $CHCl_2$ lie on the correlation line of the equation

$$\upsilon_{CHX_2} = m\upsilon_{CX_3} + c \qquad (15)$$

All of the υ values for the CX_3 groups involved were obtained by calculation from van der Waals radii. The υ values used are given in Table IV and results of the correlation in Table II (set 11). The results of the correlation are excellent; it was significant at the 99.9% CL with $r^2 = 0.9936$. Thus, the υ_{CHX_2} parameters are completely accounted for by a relation with pure steric parameters and are therefore themselves pure steric parameters. We have previously shown[1] that when X = Cl, an excellent correlation with the equation

$$\upsilon_{CX_nH_{e-n}} = m\upsilon_{CMe_nH_{3-n}} \qquad (16)$$

was obtained, significant at the 99.9% CL with $r^2 = 0.9986$.

We have also pointed out above that υ_{Me}, υ_{CHCl_3}, υ_{CHMe_2}, and υ_{CMe_3} are pure steric parameters. Since the point for υ_{CH_2Me}, υ_{CH_eCl} lies on this line, both of these υ values must be pure steric parameters. Thus, we have now shown that the ν values for Me, Et (or CH_2Me), i-Pr (or $CHMe_2$), and t-Bu (or CMe_3) are all related to van der Waals radii and may therefore be considered pure steric parameters.

Significant correlations obtained with eq 16 when X = Pr or Et suggest that υ values for the CH_2Et, CH_2Pr, $CHEt_2$, and $CHPr_2$ groups are also pure steric parameters. We feel, therefore, that as all of these alkyl groups are pure steric parameters, and as they cover the complete range of number of α hydrogen atoms, the υ parameters for alkyl groups are free of hyperconjugative effects in particular and electrical effects in general. We conclude therefore that as the left side of eq 8 represents only steric effects, the right side of eq 8 must also represent only steric effects. Let us now consider the "corrected" $E_S{}^c$ values of Hancock. They are defined by the equation

$$E_S = E_S{}^c + h(n_{H\text{-}3}) \qquad (17)$$

where n_H is the number of α hydrogen atoms. From the definition of E_S values and that of υ values it can be seen that neglecting errors in the definition of E_S, $E_S = s\upsilon$. Furthermore, $n_H = 3 - n\alpha$. Thus,

$$E_S{}^c = E_S - h(n_{H\text{-}3}) \qquad (18)$$

$$E_S{}^c = s\upsilon - h(3 - n_{\alpha-3}) \qquad (19)$$

$$E_S{}^c = s\upsilon + hn_\alpha \qquad (20)$$

From eq 8

$$E_S{}^c = s(an_\alpha + bn_\beta + cn_\gamma + i) + hn_\alpha \qquad (21)$$

$$E_S{}^c = (sa + h)n_\alpha + sbn_\beta + scn_\gamma + si \qquad (22)$$

It follows then that the $E_S{}^c$ values are not freer of electrical effects than E_S or υ, as claimed by Hancock, but are steric parameters which differ from υ in the coefficient of n_α. Thus, they are not better or worse steric parameters, they are steric

Table V. Composition of the υ Parameters

type of group	a	b	c	d	b'
R	0.497	0.409	0.0608		
OR		0.406	0.108	0.0594	
NR^{1}R^2	0.200	0.453			
SR		0.318	0.108	0.0897	
CR^{1}R^2 (OR^3)	0.303	0.255			0.484
R[a]	0.348				

[a] υ^1 values.

Table VI. Data Used in Correlation with (30)

1. k_r, AkPhCHCN + OH$^-$ in isoamyl alcohol at 99.8 °C:[a] Pr, 0.121; *i*-Pr, 0.013; Bu, 0.082; *sec*-Bu, 0.013; *i*-Bu, 0.095; BuCH$_2$, 0.137; *i*-PrCH$_2$CH$_2$, 0.095; c-C$_5$H$_9$, 0.019; BuCH$_2$CH$_2$, 0.119; c-C$_6$H$_{11}$, 0.010
2. k_r, AkPhCHCN + OH$^-$ in isoamyl alcohol at 117 °C:[a] Pr, 0.250; *i*-Pr, 0.044; Bu, 0.256; *sec*-Bu, 0.045; *i*-Bu, 0.225; BuCH$_2$, 0.423; *i*-PrCH$_2$CH$_2$, 0.260; c-C$_5$H$_9$, 0.058; BuCH$_2$CH$_2$, 0.308; c-C$_6$H$_{11}$ 0.018
3. k_r, AkNH$_2$ + CH$_2$═CHCH$_2$Br in PhH at 100 °C:[b] H, 1.380; Me, 8,302; Et, 3.807; Pr, 3.783; Bu, 3.896; BuCH$_2$, 3.790; Bu(CH$_2$)$_3$, 3.537; *i*-Pr, 1.257; *sec*-Bu, 1.240; *i*-Bu, 2.759; *i*-PrCH$_2$CH$_2$, 2.985; *i*-PrMeCH, 0.586; *t*-Bu, 0.314
4. k_r, AkO$^-$ + PhCH$_2$Cl in AkOH at 50 °C:[c] Pr, 0.530; Bu, 0.460; BuCH$_2$, 0.350; BuCH$_2$CH$_2$, 0.270; *i*-Pr, 0.334; Bu, 0.229; *t*-Bu, 0.132
5. k_r, AkO$^-$ + PhCH$_2$Cl in AkOH at 60 °C:[c] Pr, 1.31; Bu, 1.02; BuCH$_2$, 0.830; BuCH$_2$CH$_2$, 0.620; *i*-Pr, 0.662; *sec*-Bu, 0.458, *i*-Bu, 0.907; *i*-PrCH$_2$CH$_2$, 0.697; *t*-Bu, 0.250
6. k_r, AkO$^-$ + PhCH$_2$Cl in AkOH at 70 °C:[c] Pr, 2.96; Bu, 2.33; BuCH$_2$, 1.77; BuCH$_2$CH$_2$, 1.33; *i*-Pr, 1.43; *sec*-Bu, 0.845; *i*-Bu, 1.89; *i*-PrCH$_2$CH$_2$, 1.54; *t*-Bu, 0.523
7. k_r, AkO$^-$ + PhCH$_2$Cl in AkOH at 80 °C:[c] Pr, 6.39; Bu, 4.96; BuCH$_2$, 3.65; BuCH$_2$CH$_2$, 2.77; *i*-Pr, 2.55; *sec*-Bu, 1.60; *i*-Bu, 3.92; *i*-PrCH$_2$CH$_2$, 3.35; *t*-Bu, 0.910;
8. k_r, AkNH$_2$ + 1-Cl-2,4-(NO$_2$)$_2$C$_6$H$_3$ in EtOH at 25 °C:[d] Et, 9.2; Pr, 9.6; *i*-Pr, 1.0; Bu, 10.0; *sec*-Bu, 0.91; *t*-Bu, 0.038; Me, 31.6; *i*-Bu, 6.8; Bu(CH$_2$)$_3$, 10.0; H, 0.04
9. k_r, Ak(PO)(O-C$_6$H$_4$NO$_2$-4)(OEt) + OH$^-$ in water (pH 8.3) at 37.5 °C:[e] Me, 24.2; Et, 5.06; Pr, 4.17; Bu, 4.23; BuCH$_2$, 3.62; BuCH$_2$CH$_2$, 3.56; *i*-Pr, 1.07; *i*-Bu, 2.34; *i*-PrCH$_2$CH$_2$, 2.45; *i*-Pr(CH$_2$)$_3$, 3.62; *t*-Bu, 0.032; *t*-Bu(CH$_2$)$_3$, 3.41; c-C$_6$H$_{11}$, 0.307
10. k_r, PhCAK^{1}AK^{2}CN + OH$^-$ in isoamyl alcohol at 99.8 °C:[a] H, H, 0.505; Me, H, 0.411; Et, H, 0.316; Pr, H, 0.121; Bu, H, 0.082; Me, Me, 0.148; Et, Me, 0.057; Pr, Me, 0.073; Bu, Me, 0.058; Et, Et, 0.046; Pr, Et, 0.021; Bu, Et, 0.007
11. k_r, PhCAk^{1}Ak^{2}CN + OH$^-$ in isoamyl alcohol at 117 °C:[a] H, H, 1.221; Me, H. 0.695; Et, H, 0.600; Pr, H, 0.250; Bu, H, 0.256; Me, Me, 0.341; Me, Et, 0.107; Pr, Me, 0.141; Bu, Me, 0.134; Et, Et, 0.109; Pr, Et, 0.056; Bu, Et, 0.035;
12. $10^4\,k_r$, AkCONH$_2$ + H$_3$O$^+$ in H$_2$O at 75 °C:[f] Me, 10.3; Et, 12.0; Pr, 5.99; Bu, 5.93; *i*-Bu, 1.29; *t*-BuCH$_2$, 0.193; *i*-Pr, 6.06; Et$_2$CH, 0.176; *sec*-Bu, 1.51; *t*-Bu, 2.26
13. 10^4k_r, AkCONH$_2$ + OH$^-$ in H$_2$O at 75.0 °C:[g] Me, 13.6; Et, 13.1; Pr, 7.05; Bu, 5.52; *i*-Bu, 1.97; *sec*-Bu, 1.65; *i*-Pr, 6.61; *t*-Bu, 2.57
14. k_r, AkOBz + OH$^-$ in 56% w/w MeAc–H$_2$O at 25 °C:[h] Me, 9.022; Et, 2.891; Pr, 1.932; Bu, 1.667; AmCH$_2$, 1.274; Am(CH$_2$)$_3$, 1.263; *i*-Pr, 0.4644; *i*-Bu, 1.429; *sec*-Bu, 0.2259; *t*-Bu, 0.01327; *i*-BuCH$_2$, 1.200; MePrCH, 0.1487; Me$_2$EtC, 0.005024
15. 10^3k_r, AkOH + 4-O$_2$NC$_6$H$_4$COCl in Et$_2$O at 25 °C:[i] Me, 184; Et, 84.5; Pr, 65.9; *i*-Pr, 10.1; Bu, 70.3; *sec*-Bu, 7.35; *t*-Bu, 2.70; *i*-Bu, 30.8; Am, 79; AmCH$_2$, 85; Am(CH$_2$)$_2$, 69; *sec*-BuCH$_2$, 36; *i*-BuCH$_2$, 73; *i*-Bu(CH$_2$)$_2$, 68; MePrCH, 5.9; MeBuCH, 65; Et$_2$CH, 36; Pr$_2$CH, 2.7

[a] D. Zavoianu, *Ann. Univ. Bucuresti. Ser. Stiint. Natur. Chim.*, **17,** 41, 123 (1968); *Chem. Abstr.*, **71,** 112064, 112065. [b] Menschutkin, *Z. Phys. Chem.*, **17,** 193 (1895); *Ber.*, **30,** 2775, 2966 (1897). [c] I. G. Murgulescu and D. Dancea, *Rev. Roum. Chim.*, **16,** 1625 (1971). [d] O. L. Brady and W. H. Cropper, *J. Chem. Soc.*, 507 (1950). [e] T. R. Fukuto and R. L. Metcalf, *J. Am. Chem. Soc.*, **81,** 372 (1959). [f] P. D. Bolton, *Aust. J. Chem.*, **22,** 527 (1969); **24,** 471 (1971). [g] P. D. Bolton and G. L. Jackson, *ibid.*, **24,** 969 (1971). [h] E. Tommila, *Ann. Acad. Sci. Fenn., Ser. A3,* **59,** 3 (1942); *Chem. Abstr.*, **38,** 6172b (1944). [i] J. F. Norris and A. A. Ashdown, *J. Am. Chem. Soc.*, **47,** 837 (1925); J. F. Norris and F. Cortese, *J. Am. Chem. Soc.*, **49,** 2340 (1927).

parameters which differ from E_S or υ in their sensitivity to branching at the first carbon atom of the alkyl group. The same treatment can be applied to the $E_S{}^\circ$ values of Palm

$$E_S = E_S{}^\circ - j(n_{H\text{-}3}) - kn_C \tag{23}$$

where n_H is the number of α hydrogen atoms and n_C the number of α carbon atoms. With $E_S = s\upsilon$, $n_H = 3 - m_\alpha$, $n_C = n_\alpha$, we obtain

$$E_S{}^\circ = s\upsilon + j(3 - n_\alpha - 3) - kn_\alpha \tag{24}$$

$$E_S{}^\circ = s - (j + k)n_\alpha \tag{25}$$

From eq 8

$$E_S{}^\circ = s(an_\alpha + bn_\beta + cn_\gamma + i) - (j + k)n_\alpha \tag{26}$$

$$E_S{}^\circ = (sa - j - k)n_\alpha + sbn_\beta + scn_\gamma + si \tag{27}$$

Again, $E_S{}^\circ$ is not more or less free of electrical effects than is υ. It differs from E_S and υ in its sensitivity to branching at the first carbon of the alkyl group. As to the use of the $E_S{}^c$ and $E_S{}^\circ$ values, it is certainly true that different reactions may have a different composition of the steric effect. Differences in the geometry of the transition state would lead us to expect this. Thus, for example, the υ values for many groups were defined from rates of esterification of carboxylic acids and have a value of a in eq 8 of 0.497 while the υ values defined from a bimolecular nucleophilic substitution have a value of a in eq 14 of 0.348. It is entirely likely that for some particular reaction a correlation with $E_S{}^\circ$ or $E_S{}^c$ (or their equivalents, υ° or υ^c) would be best. As more data become available, we expect to find a wide variation in a, b, and c with reaction type.

It is of interest to compare the composition of the various types of υ values studied here. Values of a, b, c, d, and b are given in Table V. The values of a are easily understandable for the υ_R, $\upsilon_{NR^1R^2}$, and $\upsilon_{CR^1R^2(OR^3)}$ parameters, all of which are determined from analogus reactions (esterification or acid catalyzed amide hydrolysis). The υ_R values in which hindrance to α substitution is greatest show the highest sensitivity to n_α. The $\upsilon_{CR^1R^2(OR^3)}$ values should be less senitive than the υ_R values to n_α because the oxygen atom is significantly smaller than a CH$_2$ group and this is indeed the case. The $\upsilon_{NR^1R^2}$ values should be the least sensitive to n_α because only two N–C bonds can be formed, the remaining tetrahedral orbital being occupied by a pair of nonbonding electrons. Again, this is what is observed.

The υ_R, υ_{OR}, and $\upsilon_{NR^1R^2}$ values all show about the same sensitivity to n_β. The υ_{SR} values are less sensitive to n_β, possibly due to the longer C–S bonds which would tend to remove the alkyl moiety of the thioalkyl group from the vicinity of the reaction site. We are unable at the present time to account for the smaller sensitivity to n_γ of υ_R as compared with υ_{OR}. The value of b' obtained for $\upsilon_{CR^1R^2(OR^3)}$ values is somewhat larger than but comparable to the values of b obtained for the υ_R, $\upsilon_{NR^1R^2}$, and υ_{OR} constants.

Our rests suggest the possibility, when a sufficiently large data set is available, of correlating the data with the equation

$$Q = S(an_\alpha + bn_\beta + cn_\gamma + dn_\delta + i) + h \tag{28}$$

where Q is some quantity to be correlated, such as the logarithm of a rate or equilibrium constant. This equation simplifies to

$$Q = a'n_\alpha + b'n_\beta + c'n_\gamma + i \tag{29}$$

Table VII. Results of Correlation with (30)[o]

set	$-a$	$-b$	$-c$	i	R^{a}	F^{b}	$r_{12}{}^{c}$	$r_{13}{}^{c}$
1	0.985	0.0606	0.0374	0.114	0.9882	55.67^{g}	0.577	0.518
2	0.815	0.0531	−0.0242	0.305	0.9798	32.00^{g}	0.577	0.518
3	0.500	0.0688	−0.0329	1.056	0.9779	58.36	0.542	0.291
4	0.384	0.164	0.188	0.282	0.943	8.026^{l}	0.806^{l}	0.679
5	0.410	0.136	0.143	0.628	0.956	17.67^{g}	0.732^{l}	0.526
6	0.452	0.176	0.145	1.05	0.949	14.97^{i}	0.732^{l}	0.526
7	0.487	0.165	0.135	1.39	0.954	16.86^{g}	0.732^{l}	0.520
8	0.968	0.0822	−0.148	1.74	0.981	43.60	0.204	0.218
9	0.940	0.0955	0.0284	1.59	0.974	49.50	0.306	0.221
10	0.328	0.330	0.227	−0.101	0.926	18.12	0.536^{l}	0.187
11	0.341	0.291	0.181	0.200	0.962	33.38	0.548	0.258
12	0.308	0.561	−0.322	1.320	0.951	18.92^{g}	0.125	0.167
13	0.281	0.353	−0.0815	1.294	0.937	9.577^{m}	0.183	0.165
14	1.04	0.106	0.0505	1.346	0.971	49.84	0.098	0.255
15	0.809	0.220	0.0545	2.704	0.959	53.66	0.000	0.082

set	$r_{23}{}^{c}$	$s_{est}{}^{d}$	$s_{a}{}^{d}$	$s_{b}{}^{d}$	$s_{c}{}^{d}$	$s_{i}{}^{d}$	$100r^{2}$ ^{e}	n^{f}
1	0.000	0.0867	0.112	0.0832^{h}	0.0570^{h}	0.231^{h}	97.66	8
2	0.000	0.100	0.130^{i}	0.0962^{h}	0.0660^{h}	0.268^{j}	96.00	8
3	0.158	0.0993	0.0402	0.0423^{k}	0.0475^{h}	0.0759	95.63	12
4	0.548	0.0951	0.0951^{m}	0.135^{h}	0.0990^{k}	0.247^{j}	88.92	7
5	0.159	0.0783	0.0705^{i}	0.0734^{k}	0.0487^{m}	0.176^{n}	91.38	9
6	0.159	0.0909	0.0818^{i}	0.0852^{l}	0.0565^{l}	0.205^{i}	89.98	9
7	0.159	0.0973	0.0876^{i}	0.0913^{k}	0.0605^{l}	0.219^{i}	91.00	9
8	0.267	0.215	0.0910	0.113^{j}	0.182^{j}	0.174	96.32	9
9	0.383	0.178	0.0793	0.0966^{j}	0.0877^{h}	0.145	94.89	12
10	0.454	0.224	0.116^{m}	0.120^{n}	0.140^{k}	0.166^{h}	85.79	13
11	0.471	0.145	0.0777^{i}	0.0777^{i}	0.0952^{l}	0.108^{k}	92.60	12
12	0.000	0.251	0.101^{m}	0.0801	0.269^{j}	0.195	90.44	10
13	0.204	0.164	0.0695^{n}	0.0862^{n}	0.181^{h}	0.133	87.88	8
14	0.292	0.255	0.0869	0.129^{j}	0.120^{h}	0.187	94.32	13
15	0.375	0.190	0.0663	0.0725^{i}	0.0728^{j}	0.126	92.00	18

[a] Multiple correlation coefficient. [b] F test for significance of correlation. [c] Partial correlation coefficients of n_α on n_β, n_α on m_γ, and n_β on n_γ. [d] Standard errors of the estimate, a, b, c, and i. [e] Percent of data accounted for by correlation equation. [f] Number of points in set. [g] 99.5% CL. [h] 20.0% CL. [i] 99.0% CL. [j] 50.0% CL. [k] 80.0% CL. [l] 90.0% CL. [m] 95.0% CL. [n] 98.0% CL. [o] Superscripts indicate confidence levels of F, "student t" test of a, b, c, i, and of r. No superscript indicates 99.9% CL for F or the "student t" test, <90.0% CL for r.

Table VIII. Values of P_n

set	P_a	P_b	P_c
1	91.0	5.60	3.45
2	93.9	6.1	
3	87.9	12.1	
4	52.2	22.3	25.5
5	59.5	19.7	20.8
6	58.5	22.8	18.8
7	61.9	21.0	17.2
8	92.2	7.8	
9	88.4	8.98	2.67
10	35.5	40.0	24.5
11	41.9	35.8	22.3
12	35.4	64.6	
13	44.3	55.7	
14	86.9	8.86	4.22
15	74.7	20.3	5.03

We may now examine the application of equations such as eq 29. In order to provide a good test of the applicability of this type of correlation we have examined a wide range of reaction types. They include rate constants for nucleophilic substitution of benzyl chloride by alkoxide ions and of allyl bromide and 1-chloro-2,4-dinitrobenzene by alkylamines for alkaline hydrolysis of ethyl 4-nitrophenyl alkyl phosphonates, C-substituted amides, O-substituted esters and $PhCAk^1Ak^2CN$, acidic hydrolysis of C-substituted amides, and finally for reactions of alcohols with 4-nitrobenzoyl chloride.

The data used in the correlations are set forth in Table VI. As the data available were insufficient to provide a test of the effect of branching at the δ atom, the correlation equation used was

$$Q = a'n_\alpha + b'n_\beta + c'n_\gamma + i' \qquad (30)$$

Results of the correlations are set forth in Table VII. In the case of sets 10 and 11, a justification of this equation is necessary. In these sets the substrate has the form XCN where CN is the active site and X may be written $Z^0Z^1Z^2C$ where Z^1 and Z^2 are alkyl groups or H and Z^0 is a constant substituent, in this case a phenyl group.

We have shown elsewhere that a single sp^3-hybridized carbon atom suffices to prevent the existence of a delocalized electrical effect. Then we may write as a correlation equation for these sets

$$Q_X = L(\sigma_{I,Z^0} + \sigma_{I,Z^1} + \sigma_{I,Z^2}) + s\upsilon_X + h \qquad (31)$$

We have presented evidence which indicates that $\sigma_{I,Ak}$ is constant, with an average value of -0.01 ± 0.02,[13] that is, alkyl groups do *not* have a variable localized electrical effect.[13,14] For H, $\sigma_I \equiv 0.00$. Thus, $\sigma_{I,Ak}$ and $\sigma_{I,H}$ are essentially equal. It then follows that $\sigma_{I,Z^1} = \sigma_{IZ^e}$ = constant. As S^0 is constant throughout, σ_{I,Z^0} is constant and $L\sum\sigma_{IZ}$ is constant, then

$$Q_X = S\upsilon_X + h \qquad (32)$$

where $h' = h + L\sum\sigma_{IZ}$.

We have demonstrated that for a substituent of the type WZ^1Z^2 we may write

$$\upsilon_{WZ^1Z^2} = m\upsilon_{CHZ^1Z^2} + b \qquad (33)$$

where W is some constant atom or group of atoms. Extending this relationship we obtain

$$\upsilon_{Z^0Z^1Z^2C} = m\upsilon_{Z^1Z^8CH} = b \qquad (34)$$

Substituting eq 34 in eq 32 we obtain

$$Q = Sm\upsilon_{Z^1Z^3CH} + Sb + h' \qquad (35)$$

or

$$Q = S'\upsilon_{X^1} + h'' \qquad (36)$$

where X^1 is Z^1Z^2CH. Then on substituting eq 8 into eq 36 we obtain, after simplification, eq 30.

All of the sets studied gave significant correlations with eq 30. Significant branching effects at the α carbon atom were observed in all of the sets studied. Six sets (6, 10–13, 15) showed significant branching effects at the β carbon atom, and sets 5–7 and 11 showed significant branching effects at the γ carbon atom. The first conclusion we may reach is that for the use of eq 30 in determinating the effect of alkyl branching on reactivity, sufficient variation at the β and γ carbon atoms is required to permit conclusions to be drawn. The interpretation of the branching effects can be simplified by considering the quantities:

$$P_n = \frac{n \cdot 100}{\Sigma n} \qquad (37)$$

where n is a', b', or c'. These quantities are reported in Table VIII. When c differed in sign from a' and b' we assumed that it was an artifact and considered only a' and b' in the calculations of P_n. Those sets which differed only in temperature provide a test for the variation in P_n to be expected when steric requirements of the transition state are essentially the same. Consideration of the P_n values for sets 1 and 2, 4–7, and 11 and 12 indicates that P_n values for reactions passing through the same type of transition state may differ by as much as about 10%. Certain patterns of behavior emerge from our examination of the P_n values. Thus, the reactions of alkylamines with allyl bromide and with 1-chloro-2,4-dinitrobenzene show the same type of behavior with substitution at the α carbon atom being by far predominant in determining the steric effects. The acid- and base-catalyzed hydrolysis of amides show about the same dependence of the steric effect on branching. The reaction of alkoxide with benzyl chloride shows predominance of α substitution with significant and equal effects of β and γ substitution. Overall, the results show that the steric effect of an alkyl group depends on the degree of branching, and the nature of the dependence varies from one reaction to another. This observations supports the concept that the steric effect of an alkyl group is dependent on the geometry of the transition state. It leads to the very important conclusion that *no one set* of steric parameters for alkyl groups will work for all types of reactions.

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