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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE RELATION OF THE PROTON CHEMICAL SHIFT TO TAFT INDUCTIVE σ^*-CONSTANTS

(Presented by Academician V. V. Voevodsky, December 23, 1964)

An estimate of the polar influence of substituents on the reaction center of a molecule can be made by means of Taft inductive σ^*-constants ([1]). The polar influence of substituents is due to a change in the electron density at the reaction center. Therefore attempts ([2]) to establish a relation between σ^*-constants and proton chemical shifts (for example, in the presence of a reaction center of the type CHXYZ), which are directly related to the density of the electron cloud at the hydrogen atom, appear quite well founded.

Direct comparison of the chemical shift with σ^*-constants, however, as a rule does not give the expected dependences. Fig. 1 demonstrates the absence of a clear dependence between the quantities $\sum \sigma^*$ (calculated on the basis of data taken from ([3]), see Table 1) and the proton chemical shifts for compounds of the type CHXYZ listed in Table 2. In the light of modern theories of the proton chemical shift, these results are not unexpected. The proton chemical shift is determined not only by the "chemical component," associated with the density of the electron cloud at the hydrogen atom, but also by a number of other components. The most significant "side effect" is the influence of magnetically anisotropic chemical bonds or groups located in the immediate vicinity of the hydrogen atom under consideration. Until recently it had not been possible to exclude this effect with any rigor, since theoretical estimates of anisotropic effects were insufficiently accurate, and direct experimental methods for determining them were lacking.

Fig. 1. Comparison of the observed chemical shifts with Taft $\sum \sigma^*$. The

numbering of the points corresponds to the numbering of the compounds in Table 2.

Recently Goldstein and Reddy ([4]) proposed a semiempirical method for determining anisotropic corrections, based on a linear dependence of the proton chemical shift on the spin-spin coupling constant J ($C^{13}H$). The corrections $\Delta\delta$ found by Goldstein and Reddy are given in Table 1. Using these data, we attempted to isolate the "chemical component" of the shift in the CHXYZ compounds listed in Table 2. The corrected chemical shift was determined by the formula

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \sum \Delta\delta_i,$$

Table 1

σ^* Taft constants and corrections for anisotropy of chemical shifts $\Delta\delta$

No.	Substituent	σ^* (3)	$\Delta\delta$, ppm (4)	No.	Substituent	σ^* (3)	$\Delta\delta$, ppm (4)
1	H	0.49	0	6	–C CR	1.30	−0.25
2	CH_3	0.00	−1.00	7	–C N	3.60	−0.25
3	Cl	2.90	+0.37	8	–C_6H_5	0.60	−1.65
4	Br	2.80	+0.62	9	–$CH{=}CH_2$	0.653	−1.00
5	J	2.36	+0.87				

where $\Delta\delta_i$ are corrections for the anisotropy of substituents X, Y, and Z, taken from Table 1. Some of the compounds considered by us contain substituents different from those given in Table 1. For such substituents, only the anisotropy of the bond nearest to the CH group was taken into account.

Table 2

Compound No.	Formula	δ_{obs} (ppm from TMS)	Compound No.	Formula	δ_{obs} (ppm from TMS)
	Chemical shifts in compounds of type CHXYZ (protons whose resonance is observed are printed in boldface)				
1	CH_4	0.25 (*)	37	$CHCl_3$	7.27 (6)
2	C_2H_6	0.88 (5,7)	38	$CHBr_3$	6.85 (8)
3	CH_3Cl	3.05 (5,7)	39	CH_3CN	1.96 (4)
4	CH_3Br	2.68 (5,7)	40	$ClCH_2CN$	4.04 (4)
5	CH_3J	1.98 (4)	41	$CH_2=CHCH_2CN$	3.15 (4)
6	$CH_3C_6H_5$	2.34 (5)	42	CH_3OCH_2CN	2.62 (6)
7	$CH_3CH_2CH_3$	0.90 (5)	43	CH_3OCH_2CN	4.20 (6)
8	$(CH_3)_2C=CH_2$	1.67 (4)		Chemical shifts for α-protons in alcohols and simple ethers containing substituents from Table 1	
9	$CH_3C\ CH$	1.66 (4)	44	$(CH_3)_2CHOCH_3$	3.38 (8)
10	$CH_3CH=CHCH_3$	1.65 (4)	45	CH_3OH	3.47 (6)
11	$CH_3CH_2CH_3$	1.25 (5)	46	C_2H_5OH	3.70 (6)
12	$CH_3CH_2C_6H_5$	2.60 (5)	47	$CH\ CCH_2OH$	4.28 (6)
13	$CH_2(C_6H_5)_2$	3.92 (5)	48	$CH_2=CHCH_2OH$	4.13 (6)
14	CH_3CH_2Cl	3.50 (4)	49	$C_2H_5CH_2OH$	3.58 (6)

Compound No.	Formula	δ_{obs} (ppm from TMS)	Compound No.	Formula	δ_{obs} (ppm from TMS)
15	CH_3CH_2Br	3.33 (4)	50	$(CH_3)_2CHOH$	4.00 (6)
16	CH_3CH_2J	3.08 (4)	51	$C_6H_5CH_2OH$	4.58 (6)
17	CH_2Cl_2	5.33 (5,7)	52	CH_3OCH_3	3.27 (8)
18	CH_2Br_2	4.94 (5,7)	53	$CH_3CH_2OCH_2CH_3$	3.36 (8)
19	CH_2J_2	3.90 (5,7)	54	$CH_3OC_6H_5$	3.72 (8)
20	CH_2BrJ	4.40 (4)	55	$C_6H_5CH_2OCH_3$	4.41 (7)
21	CH_2ClBr	5.00 (4)	56	$CH_3CH_2OCH_3$	3.37 (7)
22	CH_2ClJ	4.99 (7)	Chemical shifts for the CH group in ω-substituted acetophenones RCHXY, where R = C_6H_5CO		
23	$CH_2Cl-C\equiv C-CH_2Cl$	3.98 (7)	57	RCH_2OCH_3	5.10
24	$CH\equiv C-CH_2Cl$	3.96 (4)	58	RCH_3	2.80
25	$CH_2=CH-CH_2J$	3.87 (6)	59	RCH_2CH_3	3.15
26	$CH_2Br-C\equiv C-CH_2Br$	3.74 (4)	60	$RCH(CH_3)_2$	3.66
27	$CH_2=CH-CH_2Br$	3.86 (7)	61	$RCH_2C_3H_7$	3.15
28	$C_6H_5CH_2Cl$	4.51 (7)	62	RCH_2Cl	5.01
29	$C_6H_5CH_2Br$	4.42 (7)	63	RCH_2Br	4.83
30	$CH(CH_3)_3$	1.50 (5)	64	RCH_2J	4.42*
31	$CH(CH_3)_2C_6H_5$	2.78 (5)	65	$RCHCl_2$	7.66*
32	$ClCH(CH_3)C_2H_5$	3.90 (5)			
33	$BrCH(CH_3)C_4H_9$	4.03 (5)			
34	$CH(CH_3)_2Cl$	4.13 (5)			
35	$CH(CH_3)_2Br$	4.20 (5)			
36	$CH(CH_3)_2J$	4.24 (5)			

Fig. 2. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft (the numbering of the points corresponds to Table 2)

Figure 2: Fig. 2. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft (the numbering of the points corresponds to Table 2)

* Calculated according to Shulery' s rule (7).

Figure 2 shows the results of comparing δ_{corr} and $\Sigma\sigma^*$ for all the compounds listed in Table 2. Only compounds containing a CN group, which deviate from the general regularity and will be discussed separately, were excluded from consideration.

Comparison of Figs. 1 and 2 shows that introduction of anisotropic corrections leads to a clear linear dependence between the chemical shifts and $\Sigma\sigma^*$. This dependence is described by the equation:

$$\Sigma\sigma^* = 0.92 + 0.85\delta,$$

obtained by the least-squares method (correlation coefficient 0.985, standard deviation—0.4).

As is seen from Fig. 2, some points do not fall on the straight line; moreover, the deviations apparently lie beyond the limits of experimental error. The largest deviations are observed in those cases where the compounds contain two or three bulky substituents (I, Br, CH_3), with at least one of them being strongly electronegative. Modern radiospectroscopic measurements ([9]) show that in

Fig. 2. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft (the numbering of the points corresponds to Table 2)

halogen derivatives of methane the tetrahedral geometry of the bonds is appreciably changed (the hydrogen atoms are displaced toward the halogen). Bulky substituents can impede these changes. It may be assumed that the deviations mentioned are caused precisely by these steric hindrances.

The dependence found, after clarification of the limits of its applicability, can be used to determine Taft constants from the values of proton chemical shifts. At present, however, this possibility is limited by the fact that anisotropy corrections are known only for a small number of substituents. In this connection the inverse problem may also be of interest—the determination of anisotropy corrections for substituents with known Taft σ^*-constants. As an illustration of these possibilities we considered literature data on chemical shifts in alcohols and simple ethers, as well as data obtained by us for substituted acetophenones (Table 2). As is seen from Fig. 3, the points for alcohols and ethers fall on the straight line (b), parallel to the straight line (a), corresponding to the compounds considered above. The anisotropy correction for the C—O bond is equal to the displacement of the two straight lines along the δ axis, since the straight

Fig. 3. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft: a —straight line from Fig. 2; —alcohols and ethers (Table 2); —acetophenone derivatives (Table 2); —compounds containing the C N group (Table 2)

Figure 3: Fig. 3. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft: a —straight line from Fig. 2; —alcohols and ethers (Table 2); —acetophenone derivatives (Table 2); —compounds containing the C N group (Table 2)

line (b) was constructed without taking this correction into account. The correction found in this way is −1.2 ppm. To verify the correctness of the result obtained, we used literature data on chemical shifts ([8]) and spin-spin coupling $J(^{13}H)$ ([10]) in methanol and anisole and calculated the anisotropy correction by the method of Goldstein and Reddy. The correction proved to be −1.24 ppm, which is in good agreement with the result given above. The straight line for acetophenone derivatives (c) is also parallel to the straight line (a). The magnitude of the displacement in this case, however, does not make it possible to obtain any information on the properties of the substituent C_6H_5CO, since

the shift is caused by two unknown factors—the induction properties of this substituent and its magnetic anisotropy, which were not taken into account in constructing line ( ). It should be noted that the point for methoxyacetophenone falls on line ( ) only after introducing the correction we found for the anisotropy of the C—O bond, which is an additional confirmation of the correctness of the value of this correction.

Fig. 3. Comparison of corrected chemical shifts with $\Sigma\sigma^*$-Taft: *a* —straight line from Fig. 2; —alcohols and ethers (Table 2), —acetophenone derivatives (Table 2), —compounds containing the C N group (Table 2)

As already noted, compounds containing the CN group fall outside the general regularity. The points corresponding to the compounds of this group form a straight line ( ) that does not coincide with line (a), but is parallel to it. The simplest explanation of this anomaly might be the assumption that the values of the σ^*-constant or of the anisotropy correction for this group are erroneous. However, another possibility appears more probable, namely that in the case of the strongly polar π-electron cloud of the C N group there are additional interactions whose influence on the chemical shift is not reducible to an inductive one. To clarify this latter possibility it is necessary to compare the σ^*-constants, proton chemical shifts, and spin-spin coupling constants $J(C^{13}H)$ for a broader range of substituents, and especially for substituents containing polar multiple bonds.

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Note: Figure translations are in progress. See original paper for figures.