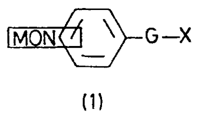
Substituent Effects in Benzyl Carbanions and in Nitrogen Analogues by Linear Extrathermodynamic Relationships

By (Mrs.) Silvia Bradamante, Federico Gianni, and Giorgio A. Pagani*

(*Istituto di Chimica Industriale dell'Universita', C.N.R., Centro di Studio sulla sintesi e stereochimica speciali sistemi organici, via Golgi* 19, *Milano, Italy*)

Summary Chemical shifts of spin-active nuclei at the *para* position of ω-substituted benzyl carbanions, *N*-substituted anilines, and sodium *N*-substituted anilides are sensitive monitors of effects induced by substituents directly bonded to the carbanionic carbon atom and the nitrogen: the $MeSO_2$, MeSO, and CN groups show incoherent effects in the three types of compounds.

Extrathermodynamic linear correlations have recently provided a deeper insight into substituent effects[1] than was possible previously. We present evidence that the substrates (**1**) are successful models for studying substituent effects, induced by the electron-withdrawing groups X, on the remote spin-active nuclei (^1H, ^{19}F, ^{13}C) which act as monitors (MON).



(1)

a; G = NH
b; G = N^-
c; G = CH^-

X = (H), Ph, $CONMe_2$, CO_2Me, CHO, COMe, COPh, CN, SOMe, SO_2Me, NO_2

MON = ^1HC, ^{19}FC, and $H^{13}C$

In the models (**1**) the interactions of the 'cavity'[2] G with the mesomeric groups X are transmitted to the monitors MON, the variations in n.m.r. resonances of which allow the extent of electron withdrawal from the cavity to be estimated. This approach thus allows a comparative study of substituent effects in benzyl carbanions (**1c**) with the isoelectronic *N*-substituted anilines (**1a**) and with the analogous sodium *N*-substituted anilides (**1b**) and complements Taft's studies[3] in which the cavities were phosphorus[4] and sulphur[5] functional groups. N.m.r. spectra were recorded in Me_2SO; the anions (**1b**,**c**) were prepared using dimsyl sodium as a base. It is found that: (a) within each group of compounds, variations of shifts induced by different groups X on the monitor (*e.g.* ^1H) are linearly correlated with variations induced on different monitors (*e.g.* ^{19}F, ^{13}C). As an example the slope of the plot for ^1H *vs.* ^{13}C shifts for

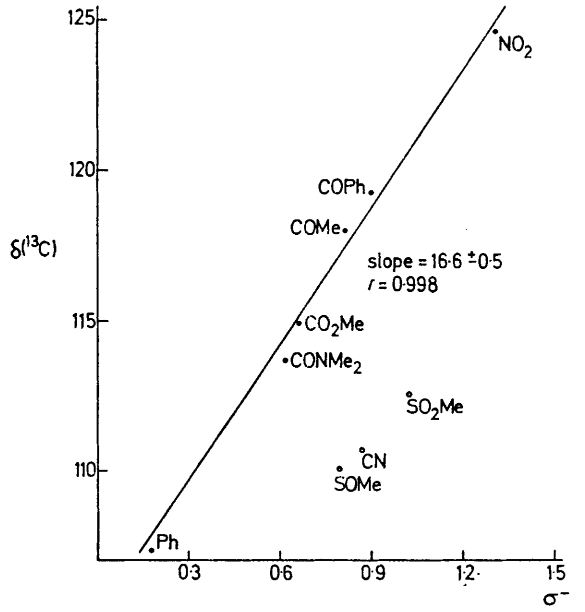


Figure. Plot of shifts for *para*-^{13}C for ω-substituted benzyl carbanions $PhCH^-X$ in Me_2SO *vs.* σ^- values of X groups. ^{13}C shifts are relative to $Me_3SiCH_2CH_2CH_2SO_3Na$.

anilines (**1a**) is 12·8 ± 0·3 (*r* 0·993 for 10 points) and for benzyl carbanions (**1c**) is 13·0 ± 0·2 (*r* 0·999 for 9 points); for anilines the slope of the plot for ^1H *vs.* ^{19}F shifts is 17·8 ± 0·7 (*r* 0·993 for 10 points). (b) Variations of the shifts induced on the monitor by groups X in *N*-substituted anilines (**1a**) can be correlated reasonably well with variations induced in the sodium *N*-substituted anilides (**1b**). Anilides (**1b**) are always more sensitive to substituents than anilines (**1a**): *e.g.* using ^1H the slope is 1·8 ± 0·1 (*r* 0·980 for 10 points). (c) Variations of the shifts in *N*-substituted anilines can be correlated with variations induced in benzyl carbanions (**1c**), with the exceptions of $MeSO_2$, MeSO, and CN substituent groups. Carbanions are more sensitive than anilines to substituent effects: *e.g.*, using ^{13}C the slope is 2·4 ± 0·2 (*r* 0·980 for 6 points). (d) For the three series of compounds, (**1a—c**) the variations of the shifts (^1H, ^{13}C, ^{19}F) are related linearly to σ^- values:[1] in the case of benzyl carbanions (**1c**) the $MeSO_2$, MeSO, and CN groups deviate substantially from the line, irrespective of the monitor used (see Figure for ^{13}C).

Our results lead to the following conclusions: (i) substituent effects exerted by nitro and carbonyl-type substituents are coherent among the three series of compounds (**1a—c**); (ii) since in benzyl carbanions (**1c**) the substituent effects of the MeSO, $MeSO_2$, and CN groups are not accounted for by tabulated σ^- values and are not coherent with the effects in anilines and anilides (**1b,c**), the mechanism of interaction of the $MeSO_2$, MeSO, and CN groups with an adjacent carbanionic centre must be different from that occurring with an adjacent nitrogen atom: these substituents exert a weaker electron-withdrawing effect in benzyl carbanions than in anilines; (iii) chemical shifts of *para* spin-active labelled phenyl derivatives (**1**) are sensitive monitors of the interactions taking place between the substituent groups X and the 'cavities' G.

(*Received*, 15*th March* 1976; *Com.* 260.)

---

[1] 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972.

[2] S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 9113.

[3] P. R. Welles, R. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1968, **6**, 147.

[4] J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1968, **90**, 5236.

[5] W. A. Sheppard and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 1919.