Charge Demands of Electron-withdrawing Groups: Evidence for a Saturation Effect

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Estimates of charge demands q_X (the fraction of π charge withdrawn by the electronegative functionalities X in X_2CH^-) are obtained through a charge–δ(^{13}C) relationship and are shown to be additive for predicting the ^{13}C shift of the carbanionic carbon atom in $XYCH^-$: the facts that such values are less than those for $PhCH^-X$ and that the combined effect of the two phenyl groups in Ph_2C^-X is almost the same as that of one phenyl in $PhCH^-X$ in delocalizing the charge are attributed to saturation phenomena.

Equation (1)[1] allows the prediction of the ^{13}C chemical shift of a charged trigonal carbon atom on the basis of the π electron density q_C, of the carbon shift of ethylene (122.8 p.p.m.), and of the shielding effects A_i exerted by the neighbouring groups: k is the sensitivity of the carbon shift to charge (160 p.p.m. per electron).

$$\delta_{\pm}(^{13}C) = 122.8 + \Sigma A_i - k \, (q_C - 1) \tag{1}$$

The use of such an equation for benzyl carbanions $PhCH^-X$ has provided access[2] to experimental charge demands q_X of electron-withdrawing functionalities X: charge demand has been defined as the fraction of π negative charge delocalized by the group X. We have now applied equation (1) to carbanions $YXCH^-$ diactivated with equal (X = Y) or different (X $\neq$ Y) groups. In symmetrically disubstituted carbanions X_2CH^- the π electron density q_C residing on the carbanionic carbon is $q_C = 2 - 2q_X$. Thus, from the experimental ^{13}C shifts of the carbanions X_2CH^- in Me_2SO,

and on the basis of the previously reported A_X values,[2] the charge demands q_X may be evaluated through equation (1) as $q_X = \frac{1}{2} [1 - (122.8 + 2A_X - \delta_{\pm})/k]$. Table 1 reports the q_X
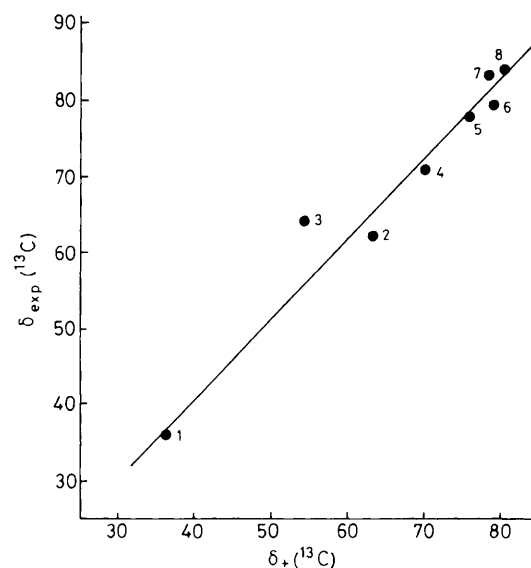
X–CH–Y

1 X = CO_2Me, Y = $PO(OEt)_2$
2 X = CO_2Me, Y = SO_2Me
3 X = $COMe$, Y = $PO(OEt)_2$
4 X = CO_2Me, Y = $SOPh$
5 X = CO_2Me, Y = $COPh$
6 X = CO_2Me, Y = $COMe$
7 X = $COPh$, Y = SO_2Ph
8 X = $COMe$, Y = SO_2Ph

$\delta_{exp.} = 1.01\delta_{\pm} + 2.58$; $r = 0.973$

Figure 1. Experimental ^{13}C shifts of the carbanionic carbon atoms in $XYCH^-$ *vs.* the values calculated as $\delta_{\pm} = 122.8 + A_X + A_Y - 160$ $[(2 - q_X - q_Y) - 1]$.

Table 1. π Charge demands of electron-withdrawing groups X in $PhCH^-X$ and X_2CH^-.

X	$PhCH^-X$[a]	X_2CH^-
Ph	0.286	0.286
CO_2Me	0.404	0.268
$CONMe_2$	0.418	0.275
COMe	0.509	0.325
COPh	0.563	0.340
CN	0.283	0.207
SO_2Me	0.281	0.225
SO_2Ph	0.282	0.206
SOPh	0.264	0.233
$PO(OEt)_2$	0.256	0.127
2-Pyridyl	0.411	
4-Pyridyl	0.408	

[a] From ref. 2.

	X		X
1	CN	6	Ph
2	SO₂Ph	7	4Py
3	SOPh	8	2Py
4	CONMe₂	9	COMe
5	SOMe		

$\delta_\pm = 1.2093\delta_{exp} - 16.72; r = 0.983$
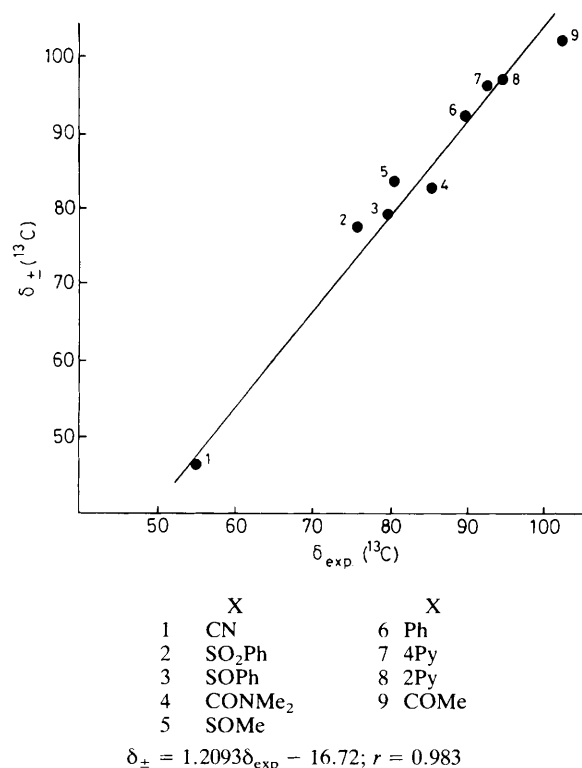
Figure 2. Experimental ^{13}C shifts of the carbanionic carbon atoms in Ph_2C^-X vs. the values calculated as $\delta_\pm = 122.8 + A_X + 2A_{Ph} - 160$ $[(2 - q_{Ph}) - 1]$.

values for a number of functionalities X in both X_2CH^- and $PhCH^-X$.[2] It is immediately evident that the q_X values for X_2CH^- are less than those for $PhCH^-X$: this result is regarded as a manifestation of a saturation phenomenon operating in X_2CH^- on the electron-withdrawing power of the X functionality. It can be explained by considering that while in X_2CH^- the charge must be partitioned between two strong electron-withdrawing groups, in $PhCH^-X$ the charge is partitioned

between two groups of unequal power: the stronger group is favoured and exerts a higher charge demand. The weak charge demands of SO_2Ph, $SOPh$, CN, and $PO(OEt)_2$ are in line with previous findings,[2] and with X-ray structural results for benzyl anions substituted with such groups,[3] and confirm the proposal that such groups stabilize the adjacent carbanionic charge by forming a π-bond associated with a weak transfer to the electronegative atom (oxygen or nitrogen).[2] In the carbanions $XYCH^-$, diactivated with different groups X and Y, both of which are however strongly electronegative, the effects of X and Y are additive. This is clearly demonstrated in Figure 1, which shows the straight line obtained by plotting the experimental ^{13}C shift of the carbanionic carbon atoms of some $XYCH^-$ carbanions vs. the shift calculated equation by (1) as $\delta_\pm(^{13}C) = 122.8 + A_X + A_Y - k [(2 - q_X - q_Y) - 1]$, where q_X and q_Y are the charge demands of the groups X and Y. The goodness of the fit supports the reliability of equation (1).

Figure 2 shows the straight line obtained by plotting the ^{13}C shifts of the carbanionic carbon atoms of Ph_2C^-X against the ^{13}C values calculated as $\delta_\pm(^{13}C) = 122.8 + 2A_{Ph} - k [(2 - q_X - q_{Ph}) - 1]$, where q_{Ph} is the fraction of π charge delocalized by the phenyl group in $PhCH^-X$.

Surprisingly, relative to the $PhCH^-X$ systems, the second phenyl group in Ph_2C^-X is 'active' only as far its shielding effect is concerned, but has practically no effect in withdrawing charge. This must be considered as an average effect: two twisted[4] phenyl rings in Ph_2C^-X exert the same charge demand as one, almost planar,[2] phenyl group. This is another manifestation of saturation resulting from steric compression.

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