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AN INVERSE SUBSTITUENT EFFECT IN THE ^{13}C NMR CHEMICAL SHIFTS FOR THE ETHANO CARBON ATOMS OF PHENETHYL BROMIDES AND DIMETHYLPHENETHYLSULPHONIUM BROMIDES

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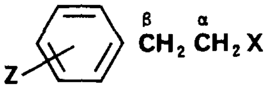
There have been some recent reports [1-3] that substituent induced variations in ^{13}C chemical shifts (SCS), show an alternation of sign along a carbon chain. For a series of trans 1-substituted butadienes[1] the ^{13}C resonances for the δ and β carbons show shifts to lower field for electron withdrawing substituents as expected[4], but for the α and γ carbons the reverse was found to be the case. A similar inversion of the normal substituent effect has been recently reported[2] for substituted benzonitriles but so far such an inversion has not been noted for saturated hydrocarbon side chains.

Such inverse substituent effects are theoretically respectable[5] and the above examples may be considered as a vindication of the theory. Pople and Gordon's CNDO calculations[5] were based on both saturated and unsaturated hydrocarbons but so far the alternation of induced charge (AIC) is suggested as a general phenomenon only for carbon atoms in π systems[6].

We wish now to report results of ^{13}C SCS obtained for the saturated α and β carbon atoms of the ethano group in some substituted phenethyl bromides and dimethylphenethylsulphonium bromides



where Z = a meta or para substituent and X = Br or $\overset{+}{\mathrm{S}}\mathrm{Me}_2$.

The results are shown in Table For both series of compounds (X = Br and X = $\overset{+}{\mathrm{S}}\mathrm{Me}_2$) the chemical shifts of the β carbon atoms remain virtually constant. The scatter of the data is significantly larger than the experimental error of the measurements (0.03 ppm) but there is no apparent trend with substituent polarity.

Table. Observed ^{13}C Chemical Shifts[a] for $Z-C_6H_4CH_2CH_2X$ in 50 mole % $(CD_3)_2SO-D_2O$

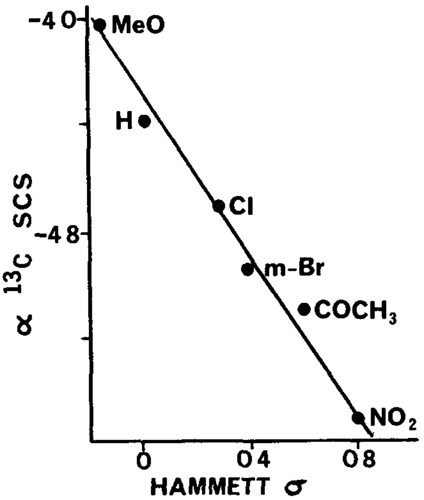
Z	p-MeO	H	p-Cl	m-Br	m-NO_2	p-$COCH_3$	p-NO_2
X = Br							
C-α	-4.05	-4.38	-4.70	-4.95	-5.03	-5.11	-5.51
C-β	-1.46	-0.73	-1.62	-	-1.70	-1.06	-1.38
$X = \overset{+}{S}Me_2$							
C-α	4.80	4.39	4.03	3.87		3.74	3.41
C-β	-10.55	-9.82	-10.51	-10.32		-9.90	-10.06

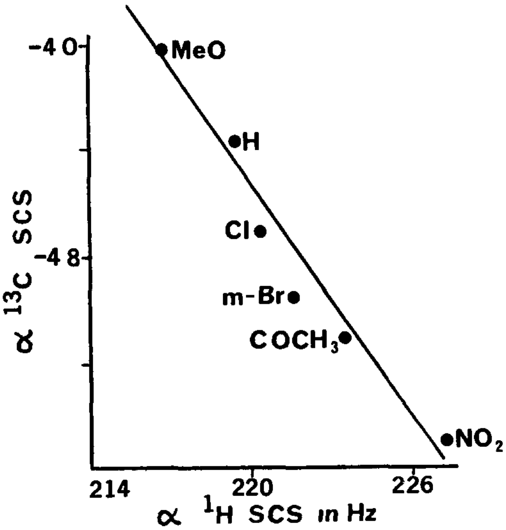
[a] Shifts in ppm from $(CD_3)_2SO$, measured for 5% solutions on a JEOL-FX-60 PFT-NMR spectrometer. Negative values indicate resonance to fields higher than the reference. Unambiguous assignments were made by comparison with the β - $[D_2]$ derivatives.

Fig. 1. Hammett plot of α ^{13}C SCS for $Z-C_6H_4CH_2CH_2Br$

Fig. 2. Plot of α ^{13}C SCS against the α ^1H SCS for $Z-C_6H_4CH_2CH_2Br$.

X=Br



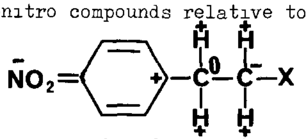


(All substituents are para unless otherwise stated)

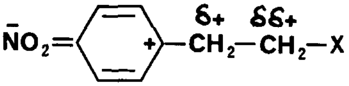
If the ^{13}C chemical shifts are proportional to the total carbon electron density[6] then presumably there is a near constant level of electron density at the β carbon atoms. The shifts for the α carbon atoms on the other hand show an inverse linear relationship with the electron withdrawing power of the substituents. This can be seen from the negative slope for the plot of the chemical shifts versus Hammett σ shown for the phenethyl bromides (Fig. 1). This observation appears to be the first documented case of an inverse substituent effect for the chemical shifts of a saturated side chain. That similar behaviour is observed for $X = \overset{+}{S}Me_2$ can be seen from the Table and confirms that it is a general effect for phenethyl groups.

The α and β ^{1}H chemical shifts for the same compounds show good linear correlations with reactivity parameters[7] in the normal sense and a plot of the α ^{1}H SCS against the α ^{13}C SCS is satisfactorily linear (Fig. 2). Thus it seems reasonable to consider the SCS as a measure of the electron density in the ethano group caused by ring substitution.

A comparison of the ^{1}H and ^{13}C results for the ethano groups indicates that charge densities in the p-nitro compounds relative to hydrogen are as shown in the resonance structure below.



The reverse situation of course applies for electron donating substituents (p-$MeOC_6H_4$ -). Such a development of alternating induced charges is inconsistent with the usual idea of a simple attentuation of charges.



The most likely explanation of the results would seem to be in terms of hyperconjugation[5,8] involving the - CH_2CH_2 - side chain and the substituted phenyl ring, but whatever the explanation may be, it seems clear that the - CH_2CH_2 - group of phenethyl compounds is not behaving as a typical saturated group. The role of the X groups in this effect must await a comparison of the present results with the ^{13}C SCS for substituted ethyl benzenes.

Acknowledgement

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