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UNUSUAL CONFORMATIONALLY DEPENDENT SUBSTITUENT EFFECTS UPON THE ^{13}C CHEMICAL SHIFTS OF β ALKYL CARBONS OF PHENYLALKANES.

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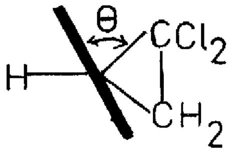
An inverse substituent dependence (i.e. NO_2 derivative to high field of NH_2) has been noted for the methyl ^{13}C chemical shifts for a series of compounds $Z\text{-}C_6H_4Y(CH_3)_3$ (Y = C, Si, Ge)[1]. More recently a similar inverse substituent dependence was reported for the β-methylene carbons for compounds $Z\text{-}C_6H_4CH_2CH_2X$ (X = Br, SMe_2^+)[2]. While inverse substituent effects might reasonably be expected at α carbons[3], it is most unusual to note this effect at β carbons. While no explanation was offered in the first case[1], Blackwell et al suggested that the inverse substituent dependence might possibly reflect hyperconjugative interactions between the phenyl group and the $CH_2\text{-}CH_2$ bond[2].

We now report results which indicate that the substituent dependence of β-carbon ^{13}C chemical shifts in phenylalkanes varies with alkyl conformation and may not reflect ground state electron density changes.

Alkyl ^{13}C chemical shifts for a series of 4-substituted ethylbenzenes and (2,2-dichlorocyclopropyl) benzenes are given in Table I. The α-carbons show an irregular trend with the unsubstituted derivative at lowest field (similar results have been reported previously[2]). Both the β-CH_3 group of ethylbenzene and the β-CCl_2 group of (2,2-dichlorocyclopropyl) benzene show an inverse substituent dependence, ie. NO_2 derivative to high field of NH_2. However, the β-CH_2 group of (2,2-dichloropropyl) benzene shows normal substituent effects.

It seems reasonable to assume that ethylbenzene prefers a conformation in which the C(α)-C(β) bond is at right angles to the plane of the phenyl group, to minimize steric hindrance. In the case of (2,2-dichlorocyclopropyl) benzene, it has been reported that the cyclopropyl group adopts a conformation with the α C-H bond at 60° to the plane of the phenyl group[4], 1 Based on the microwave geometry for phenylcyclopropane[5], this corresponds to dihedral angles, Θ, of 86° and 23° for the C(α)-CCl_2 bond and the C(α)-CH_2 bond respectively, relative to the plane of the phenyl group. This suggests that the substituent dependence varies with conformation with inverse effects when



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the C(α)-C(β) bond is at right angles to the plane of the phenyl group and normal effects when the bond is near the plane of the ring. ^{13}C chemical shifts for selected isopropylbenzene and t-butylbenzene derivatives support this suggestion (Table II).

These results could possibly be attributed to a combination of hyperconjugative interactions (varying as $\sin^2\Theta$) which cause inverse substituent effects on ^{13}C chemical shifts and conjugative interactions (varying as $\cos^2\Theta$) which cause normal effects. However, considerable caution is necessary in interpreting these results in terms of ground state electron density changes. CNDO/2 calculations for these compounds reproduce the normal substituent dependence for $C(\beta)H_2$ of (2,2-dichlorocyclopropyl) benzene with fair accuracy (see Table I):

$$\delta_{CH_2} = 390\ q_{CH_2} \qquad (r = 0.956)$$

However, the calculated excess charges for the other carbons are anomalous. They predict an inverse substituent dependence for C(α) in each case while $C(\beta)H_3$ and $C(\beta)Cl_2$ show an odd pattern in which all derivatives show increased electron density relative to the parent compound. It is amusing to note that if C(α) and C(β) charge densities (or chemical shifts) were switched, then there would be a reasonable agreement between charge densities and chemical shifts. It is entirely possible that the calculations do not correctly predict the electronic interaction of the C(α)-C(β) bond for $\Theta \simeq 90°$, although the hydrogen charge densities from the same calculations (not shown) accurately predict the ^1H chemical shifts for ethylbenzenes[6,7] and (2,2-dichlorocyclopropyl) benzenes[8] (all of which show normal substituent effects). Alternatively, it is possible that the observed chemical shifts do not accurately reflect ground state electron density changes. While there is substantial evidence for a linear relationship between ^{13}C chemical shifts and carbon electron densities in aromatic derivatives[9], there is much less evidence in the case of saturated carbons and strained rings. This is clearly an area where further experimental work (to further elucidate the apparent conformational effects) and more sophisticated theoretical calculations (to investigate chemical shift-charge density relationships in alkyl side chains) would be desirable[10].

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Table I: Substituent-induced ^{13}C chemical shifts for alkyl carbons of 4-substituted ethylbenzenes and (2,2-dichlorocyclopropyl) benzenes and calculated CNDO/2 excess charges ($x10^4$) for the same carbons[e].

X	Ethylbenzenes				(2,2-dichlorocyclopropyl)benzenes					
	$\delta_{C(\alpha)}$	$q_{C(\alpha)}$	$\delta_{C(\beta)}$	$q_{C(\beta)}$	$\delta_{C(\alpha)}$	$q_{C(\alpha)}$	δ_{CCl_2}	q_{CCl_2}	δ_{CH_2}	q_{CH_2}
H	(28.80)[a]	-	(15.59)	_	(35.07)[d]	-	(60.17)[d]	-	(25.64)[d]	-
$N(CH_3)_2$	-0.98[b]	+44[c]	+0.40	-12	-0.30	+47	+0.64	-9	-0.30	-7
NH_2	-0.88	+37	+0.34	-10	-0.28	+37	+0.49	-9	-0.30	-4
OCH_3	-0.88	+35	+0.31	-10	-0.35	+34	+0.25	-11	-0.07	-3
CH_3	-0.43	+12	+0.12	-2	-0.05	+14	+0.25	-2	-0.05	-2
$C(CH_3)_3$	-0.53	+17	+0.07	-3	-0.14	+17	+0.10	-1	-0.08	-3
F	-0.78	+22	+0.12	-11	-0.50	+17	-0.32	-8	+0.11	+1
CF_3	-0.12	-19	-0.38	-1	-0.10	-32	-0.58	-5	+0.24	+10
CN	+0.08	-7	-0.63	-2	+0.01	-15	-0.50	-7	+0.29	+6
NO_2	-0.09	-27	-0.56	-2	-0.15	-43	-0.59	-5	+0.59	+14

[a] ^{13}C chemical shifts measured at 25.16 MHz using 0.4 M solutions in CCl_4. Chemical shifts were measured relative to tetramethylsilane.

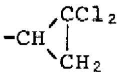
[b] Chemical shift relative to unsubstituted derivative. Low field shifts positive.

[c] Excess charges relative to unsubstituted derivative. Positive sign indicates decreased electron density.

[d] Chemical shifts assigned by off-resonance decoupling.

[e] Calculations carried out assuming standard geometries (J.A. POPLE and D.L. BEVERIDGE) Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970.

Table II. β alkyl carbon chemical shifts for 4-NH_2 and 4-NO_2 derivatives of phenylalkanes.

Alkyl group	$\delta^{a}_{4-NH_2}$	$\delta^{a}_{4-NO_2}$	$\Delta\delta^{b}$	$\sin^2\Theta$
CH_2CH_3	+0.40	-0.56	+0.96	1 [c]
	+0.64	-0.59	+1.23	.99[d]
	-0.30	+0.59	-0.89	.16[d]
$-CH(CH_3)_2$	+0.20	-0.45	+0.65	0.75[c]
$-C(CH_3)_3$	+0.20	-0.32	+0.52	0.50[c]

[a] Chemical shift relative to unsubstituted compound, low field shift positive.

[b] $\Delta\delta = \delta_{NH_2} - \delta_{NO_2}$.

[c] Assuming conformations which minimize β alkyl steric interactions with ring, eg. C(α)-C(β) bond of ethyl group at right angles to plane of ring ($\Theta = 90°$), C(α)-H bond of isopropyl group in plane of ring ($\Theta_{CH_3} = 60°$). $\langle \sin^2\Theta \rangle = 0.50$ for $C(CH_3)_3$, independent of conformation.

[d] See text.

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