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The Role of Linear Electric Field Effects in Halogen Induced ^{13}C Chemical Shifts in Cyclohexanes and Methylenecyclohexanes

Marianne E. van Dommelen, Jan W. de Haan* and Henk M. Buck

Laboratories of Organic Chemistry and Instrumental Analysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

The ^{13}C NMR chemical shifts of methylenecyclohexane at low temperature are compared with those of 4-chloro- and 4-bromo-methylenecyclohexane under the same conditions. It is concluded that the halogen induced shift differences at the double bond are to be ascribed largely to linear electric field (LEF) effects. At the same time, doubt is expressed concerning similar explanations for C-4 in halo-substituted cyclohexanes. The large influence of using different values of longitudinal bond polarizabilities is demonstrated. Finally, some remarkable long-range shift effects on double bonds are described for geranyl chloride and geranyl bromide.

Recently, Wiberg *et al.*¹ concluded that linear field effects (LEF effects) do not contribute significantly to γ - and δ -substituent effects in the ^{13}C NMR spectra of halobicyclic hydrocarbons. Schneider and Freitag,^{2a} on the other hand, described a linear correlation between observed δ -substituent effects in halocycloalkanes and calculated values of $\Sigma\Delta q$, using the C—X group as the perturbing dipole and adding the repolarizations over all four bonds concerned. The relationship obtained between $\Delta\delta^{13}\text{C}$ and $\Sigma\Delta q$ was 400 ppm/electron. The polarizability of an unsaturated carbon-carbon bond is considerably higher than that of saturated carbon-carbon or carbon-hydrogen bonds.³ Recently, the spectra of 4-chloro- and 4-bromo-methylenecyclohexane were reported⁴ at low temperatures, allowing the separate measurements of the shifts of axially and equatorially substituted compounds. In view of the existing uncertainties of the role of the LEF effect and the large C=C polarizability it is of interest to compare the shifts in methylenecyclohexyl halides (I) (see Fig. 1) with those of the parent hydrocarbon measured under the same conditions. Resulting differential shifts are given in Table 1.

For the α - and β -effects we obtain values within 15% of those of cyclohexyl halides (II).^{2a,2b} The halogen induced shifts in II are given in Table 2 for comparison. The γ -effects differ far more on a percentage basis but will not be discussed here in view of the existing difficulties in their interpretation and the possible influence of the nearby $=\text{CH}_2$ group. In I there are

Figure 1. Axial and equatorial 4-halo-1-methylenecyclohexane.

* Author to whom correspondence should be addressed.

Table 1. ^{13}C NMR shifts of methylenecyclohexyl halides in ppm with respect to methylenecyclohexane;^a (e = equatorial, a = axial).

	Cl-e	Cl-a	Br-e	Br-a
α	+33.7	+34.4	—	—
β	+9.2	+6.2	+10.1	+6.7
γ	−1.6	−6.9	−0.5	−6.2
δ	−5.0	−3.1	−5.2	−3.7
ϵ	+2.1	+0.8	+1.9	+0.7

^a Negative values indicate shielding effects.

considerable shielding δ -effects and deshielding ϵ -effects, in contrast with results obtained on 4-halo-*tert*-butylcyclohexanes.^{2c} The ratio of $\Delta\text{C}-\delta\text{sp}_2$ in I versus $\Delta\text{C}-\delta\text{sp}_3$ in II is 2 to 2.5. There are some examples in the literature of experimentally obtained shift differences, described in the LEF formalism, from which relative sensitivities of sp_2 -carbons and sp_3 -carbons can be derived.^{5,6b,7}

A complication is often caused by the different conformational equilibria of alkenes and alkanes. From the measurements of Bus⁵ it is clear that the influence of the terminal methoxycarbonyl group in a

Table 2. ^{13}C NMR shifts of cyclohexyl halides in ppm with respect to cyclohexane;^a (e = equatorial, a = axial).

	Cl-e	Cl-a	Br-e	Br-a
α	+32.32	+32.32	+24.59	+27.51
β	+10.51	+6.74	+11.20	+7.23
γ	−0.57	−7.10	+0.34	−6.48
δ	−2.19	−1.44	−2.45	−1.54

^a From Ref. 2b.

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Table 3. Bromine induced ^{13}C substituent effects of 5-bromo-1-pentene [A] and 1-bromopentane [B] in ppm relative to 1-pentene and *n*-pentane, respectively.^a

	[A]	[B]
α	+21.32	+19.11
β	+11.11	+8.20
γ	-5.67	-2.76
δ	-2.29	-0.53
ϵ	+1.19	0 $\pm$ 0.2

^a All compounds measured as 5-10 mol% in *n*-hexane.^b Assignments may be reversed.

large number of unsaturated fatty acid methyl esters on an sp_3 -carbon is smaller than that on an sp_2 -carbon by a factor 4 ± 1 . Batchelor^{6b} reported a value of c. 5 in fatty acids. In Table 3, bromine induced shifts are compared in 5-bromopentene and 1-bromopentane, resulting in a ratio of 4.3 at C- δ . Moreover, Seidman and Maciel⁷ carried out SCF finite perturbation ^{13}C shift calculations on ethane and ethene subjected to fields generated by monopoles and dipoles. Rather large effects were obtained for the ethene system, only small effects (0.5 ppm or less) were found for the ethane system, implying an unfavourable prognosis for the use of LEF effects in saturated hydrocarbon frameworks. The ratio of LEF effects for sp_2 - and sp_3 -carbons deduced from semiempirical relationships such as those of Horsley and Sternlicht⁸ is too dependent on parameters which cannot be defined with enough precision for the present problem (see footnote †). Summarizing, it seems most unlikely that the observed ratio of 2 to 2.5 of $\Delta\text{C-}\delta$ in I versus $\Delta\text{C-}\delta$ in II is large enough to be accounted for solely by LEF

	X	Y	Z
C-1	0	0	0
C-2	1.330	0	0
C-3	2.136	1.265	0
C-4	3.156	1.266	1.141
C-5	4.015	0	1.109
Cl-e	5.207	0	2.444
Cl-a	5.105	0	-0.311
Br-e	5.321	0	2.570
Br-a	5.208	0	-0.445

(composed from the data of Refs 11 and 12 and from the standard values of Ref. 13).

Figure 2. Atomic co-ordinates of 4-halo-1-methylenecyclohexanes [A].**Table 4.** Calculated LEF induced ^{13}C shifts on C- δ and C- ϵ in 4-halo-1-methylenecyclohexanes in ppm. Experimental values in parentheses; (e = equatorial, a = axial)

	C- δ	C- ϵ
Cl-e	-3.6 (-5.0)	+1.6 (+2.1)
Br-e	-3.1 (-5.2)	+1.4 (+1.9)
Cl-a	-2.7 (-3.1)	+1.1 (+0.8)
Br-a	-2.5 (-3.7)	+1.0 (+0.7)

effects in both systems. In I the induced effects on C- δ and C- ϵ have different signs, which points strongly to significant contributions from LEF effects; the differences between $\Delta\text{C-}\delta$ and $\Delta\text{C-}\epsilon$ are, however, rather large. According to Eqn (2) of Ref. 6a, a LEF induced shift can be written as: $\Delta\text{C-x} = A \times E_z$, where E_z is the value of the electric field along the bond and A is the sensitivity of a nucleus to the field. We calculated the value of E_z at C- δ and C- ϵ in I, according to Eqn (4) of Ref. 6a:

$$\bar{E}_z(\text{C-x}) = 3 \frac{(\bar{\mu} \times \bar{R}_x)(\bar{R}_x \times d\bar{R})}{R_x^5} - \frac{(\bar{\mu} d\bar{R})}{R_x^3}$$

where $\bar{\mu}$ is the carbon-halogen dipole, $\bar{R}_x$ is the vector from the middle of the carbon-halogen bond to C- δ and C- ϵ , respectively, and $d\bar{R}$ is the unit vector along the double bond. The carbon-halogen bond dipoles were taken from the dipoles of CH_3Cl and CH_3Br ⁹ with the assumption that the CH bond dipole amounts to 0.4 D^{10} (hydrogen positive). For geometrical details see Fig. 2. The assumption of equal A values† at C- δ and C- ϵ of 6.7×10^{-11} esu (see Appendix) yields the results summarized in Table 4.

The calculations confirm the experimental fact that in I an equatorial C-X bond generates a larger LEF effect than an axial C-X bond. The calculated orders

† Batchelor^{6c} uses different values for A and

A $\text{C}=\text{C}$, based on the assumption that $A_{\text{C-H}} \neq A_{\text{C-C}}$. The

calculation of $A_{\text{C-H}}$ is, however, strongly dependent on the values of the longitudinal bond polarizabilities of C-H and C-C bonds: $b_{\text{C-H}}$ and $b_{\text{C-C}}$. The values of Le Fevre³ for $b_{\text{C-C}}$ and $b_{\text{C-H}}$ are based on an isotropic C-H bond. Batchelor recalculated the values of $b_{\text{C-H}}$ and $b_{\text{C-C}}$ twice,^{6b,c} assuming that C-H and C-C bonds do have the same axial polarizability ratios. The influence of the different values of $b_{\text{C-H}}$ and $b_{\text{C-C}}$ is clearly demonstrated in the Appendix but the choice of the correct values of $b_{\text{C-H}}$ and $b_{\text{C-C}}$ is not obvious. However, the fact that $b_{\text{C=C}} \gg b_{\text{C-C}}$, $b_{\text{C-H}}$ does, in our opinion, imply that A values for unsaturated carbons should be larger than for saturated carbons. In Ref. 6c, on the other hand,

A CH_2 is almost equal to A $\text{C}=\text{C}$. Taking into account the large number of assumptions inherent in this concept, we prefer to take equal values for A $\text{C}=\text{C}$ and A $\text{C}=\text{C}$.

Table 5. Chlorine and bromine induced ^{13}C substituent effects in geranyl chloride and geranyl bromide in ppm relative to 2,6-dimethyl-2,6-octadiene.^a

	X = Cl	X = Br
α	+26.55 or +26.82 ^b	+13.58 or +13.89 ^c
β	+3.09	+3.22
γ	+5.96	+6.75
δ	-0.35 or -0.62 ^b	-0.27
ϵ	-0.53	-0.27 or -0.58 ^c
ζ	-0.97	-0.97
η	+0.93	+0.97
ν_c	+0.05	+0.05
ν_t	-0.05	0

^a All compounds measured as 5 mol% in *n*-hexane.

^b Assignments may be reversed.

^c Assignments may be reversed.

of magnitude compare favourably with the experimental values but residual discrepancies remain to be accounted for. It has already been mentioned that there are also sizeable shielding δ -effects, whatever their origin, in substituted cyclohexanes. It would be unwarranted to assume that comparable effects could not also occur in substituted methylenecyclohexanes. Also, the dependability of our LEF calculations has obvious limits, see above. The background of our

interest in halogen induced shifts is their application to our study of the conformational aspects of steroid precursors, such as squalene and squalene derivatives.¹⁴ In 3-bromo-2-hydroxy-2,3-dihydrosqualene,^{14b} in particular, large parts of the shifts induced on the double bonds can be ascribed to LEF effects. The phenomenon of sizeable chemical shift effects of halogen substituents, even on remote double bonds, can be shown by comparing the shifts of geranyl chloride and geranyl bromide with 2,6-dimethyloctadi-2,6-ene, see Table 5. Clearly, the large ζ - and η -effects are not caused by inductive, steric or squared electric field effects, $\langle E^2 \rangle$, because of the large halogen C- ζ = C- η distances. Also, in view of these large distances, it is reasonable to assume uniform fields along C- ζ = C- η . The induced shifts do indeed have different signs and equal magnitudes, which demonstrates equal A values for C- ζ and C- η . (See footnote on page 448). We conclude that the linear electric field effect is a major contributor to halogen induced shifts in unsaturated carbon-carbon bonds on positions at least three single bonds from the place of substitution, but in the case of saturated groups other factors prevail.¹ (The suggestion of Wiberg *et al.*¹ of induced magnetic fields near C-4 in 1-halobicyclo[2.2.2.]octanes is reminiscent of magnetic susceptibilities. It would be of interest to know the effect on the proton at C-4. No effect on the olefinic protons in 5-bromopent-1-ene was observed in this study.)

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APPENDIX

^{13}C uniform field LEF coefficients calculated according to Ref. 6c with different values of longitudinal bond polarizabilities.

$$A = \delta/e \times \frac{b_{\text{C-X}}}{l_{\text{C-X}}} \quad \delta/e = 182 \text{ ppm/e.}$$

$l_{\text{C-X}} \times 10^8 \text{ cm:}$	$l_{\text{C-H}}: 1.09$				
	$l_{\text{C-C}}: 1.54$				
	$l_{\text{C=C}}: 1.34$				
$b_{\text{C-X}} \times 10^{24} \text{ cm}^3:$	A^{6a}	B^{6c}	C^{6b}	$D^{2a,2d}$	
	$b_{\text{C-H}}$	0.64	1.30	9.4	0.79
	$b_{\text{C-C}}$	0.99	0.99	7.2	1.12
	$b_{\text{C=C}}$	2.8	2.8		3.4
$A_{\text{C-X}} \times 10^{11} \text{ esu:}$	A	B	C	D	
	$A_{\text{C-H}}$	2.22	4.52	32.68	2.75
	$A_{\text{C-C}}$	2.44	2.44	17.72	2.76
	$A_{\text{C=C}}$	7.92	7.92		9.61

$$A \text{ } ^*\text{CH}_2 = (2/\sqrt{3})(A_{\text{C-H}} - A_{\text{C-C}})$$

$$A \begin{array}{c} \text{C} \\ \diagup \\ \text{C}^*=\text{C} \\ \diagdown \\ \text{C} \end{array} = A_{\text{C=C}} - [2 \cos 58.4] A_{\text{C-C}} \\ = A_{\text{C=C}} - 1.048 A_{\text{C-C}}$$

$$A \begin{array}{c} \text{H} \\ \diagup \\ \text{C}^*=\text{C} \\ \diagdown \\ \text{H} \end{array} = A_{\text{C=C}} - [2 \cos 58.4] A_{\text{C-H}} \\ = A_{\text{C=C}} - 1.048 A_{\text{C-H}}$$

$A^* \text{ values} \times 10^{11} \text{ esu}$	A	B	C	D
$A \text{ } ^*\text{CH}_2$	-0.25	2.4	17.3	-0.01
$A \begin{array}{c} \text{C} \\ \diagup \\ \text{C}^*=\text{C} \\ \diagdown \\ \text{C} \end{array}$	5.4	5.4	—	6.7
$A \begin{array}{c} \text{H} \\ \diagup \\ \text{C}^*=\text{C} \\ \diagdown \\ \text{H} \end{array}$	5.6	3.2	—	6.7