The role of linear electric field effects in halogen induced 13C chemical shifts in cyclohexanes and methylenecyclohexanes

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

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The $^{13}$C NMR chemical shifts of methylenecyclohexane at low temperature are compared with those of 4-chloro- and 4-bromo-methylene cyclohexane 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. concluded that linear field effects (LEF effects) do not contribute significantly to $\gamma$- and $\delta$-substituent effects in the $^{13}$C NMR spectra of halobicyclic hydrocarbons. Schneider and Freitag, on the other hand, described a linear correlation between observed $\delta$-substituent effects in halocycloalkanes and calculated values of $\Sigma \pi q$, using the C—X group as the perturbing dipole and adding the repolarizations over all four bonds concerned. The relationship obtained between $\Delta \delta^{13}$C and $\Sigma \pi q$ 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. Recently, the spectra of 4-chloro- and 4-bromo-methylenecyclohexane were reported 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 $\alpha$- and $\beta$-effects we obtain values within 15% of those of cyclohexyl halides (II). The halogen induced shifts in II are given in Table 2 for comparison. The $\gamma$-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 —CH$_2$ group. In II there are considerable shielding $\delta$-effects and deshielding $\epsilon$-effects, in contrast with results obtained on 4-halo-tert-butylcyclohexanes. The ratio of $\Delta C-\delta p_2$ in I versus $\Delta C-\delta p_3$ 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.

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

![Figure 1. Axial and equatorial 4-halo-1-methylenecyclohexane.](image)

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

<table>
<thead>
<tr>
<th></th>
<th>CI-e</th>
<th>CI-a</th>
<th>Br-e</th>
<th>Br-a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>33.7</td>
<td>34.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\beta$</td>
<td>9.2</td>
<td>6.2</td>
<td>10.1</td>
<td>+6.7</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-1.6</td>
<td>-6.9</td>
<td>-0.5</td>
<td>-6.2</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-5.0</td>
<td>-3.1</td>
<td>-5.2</td>
<td>-3.7</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>2.1</td>
<td>+0.8</td>
<td>1.9</td>
<td>+0.7</td>
</tr>
</tbody>
</table>

* Negative values indicate shielding effects.

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

<table>
<thead>
<tr>
<th></th>
<th>CI-e</th>
<th>CI-a</th>
<th>Br-e</th>
<th>Br-a</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>32.3</td>
<td>32.3</td>
<td>24.6</td>
<td>27.5</td>
</tr>
<tr>
<td>$\beta$</td>
<td>10.5</td>
<td>6.7</td>
<td>11.2</td>
<td>7.2</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>-0.5</td>
<td>-7.1</td>
<td>+0.3</td>
<td>-6.4</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-2.2</td>
<td>-1.4</td>
<td>-2.4</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

* From Ref. 2b.

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resulting in a ratio of 4.3 at C-6. Moreover, Seidman et al. reported a value of 1.5 in fatty acids. In Table 3, bromine induced shifts in 5-bromopentene and 1-bromopentane, compared in 5-bromopentene and 1-bromopentane, respectively. A large number of unsaturated fatty acid methyl esters were taken from the dipoles of CH₃Cl and CH₂Br with the assumption that the CH bond dipole amounts to 0.4 D¹⁰ (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=K bond generates a larger LEF effect than an axial C=K bond. The calculated orders 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 ΔC-δ and ΔC-ε are, however, rather large. According to Eqn (2) of Ref. 6a, a LEF induced shift can be written as: ΔC-x = 3(μ * R_x * dR) / R_x^3, where E_x 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_x at C-δ and C-ε in I, according to Eqn (4) of Ref. 6a:

\[
\bar{E}_x(C-x) = 3(\mu \times \bar{R}_x)(\bar{R}_x \times d\bar{R}) / R_x^3
\]

where \( \mu \) 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 dipole moments of CH₃Cl and CH₂Br with the assumption that the CH bond dipole amounts to 0.4 D¹⁰ (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.

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\]

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

| 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 |
| C-6 | 5.207 | 0 | 2.444 |
| C-7 | 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-methylenehexanes [Å].
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.$^a$

<table>
<thead>
<tr>
<th>X = Cl</th>
<th>X = Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>+26.55 or +26.82$^b$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>+3.09</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>+5.96</td>
</tr>
<tr>
<td>$\delta$</td>
<td>-0.35 or -0.62$^b$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>-0.53</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>-0.97</td>
</tr>
<tr>
<td>$\eta$</td>
<td>-0.93</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>+0.05</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

$^a$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 $\delta$-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-dihydro-squalene,$^{14b}$ 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-di-methyloctadi-2,6-ene, see Table 5. Clearly, the large $\zeta$- and $\eta$-effects are not caused by inductive, steric or squared electric field effects, ($E^2$), because of the large halogen C-$\zeta$ = C-$\eta$ distances. Also, in view of these large distances, it is reasonable to assume uniform fields along C-$\zeta$ = C-$\eta$. The induced shifts do indeed have different signs and equal magnitudes, which demonstrates equal A values for C-$\zeta$ and C-$\eta$. (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.)

Acknowledgement

The authors wish to thank Jan Schreurs for technical assistance. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES


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APPENDIX

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

$$A = \delta/e \times \frac{b_{C-X}}{l_{C-X}}$$

$\delta/e = 182$ ppm/e.

$\begin{array}{c}
 l_{C-X} \times 10^8 \text{ cm}^3: \\
 l_{C-H}: 1.09 \\
 l_{C-C}: 1.54 \\
 l_{C-c}: 1.34 \\
 b_{C-X} \times 10^{24} \text{ cm}^3: \\
 b_{C-H} 0.64 \\
 b_{C-C} 0.99 \\
 b_{C-c} 2.8 \\
 A_{C-X} \times 10^{11} \text{ esu:} \\
 A_{C-H} 2.22 \\
 A_{C-C} 2.44 \\
 A_{C-c} 7.92 \\
\end{array}$

$\begin{array}{cccc}
 A^5 & B^6 & C^6 & D^{2,2d} \\
 0.64 & 1.30 & 9.4 & 0.79 \\
 0.99 & 0.99 & 7.2 & 1.12 \\
 2.8 & 2.8 & 3.4 & \\
\end{array}$

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

$A \hat{\text{C}} = A_{C-c} - [2 \cos 58.4 ] A_{C-c}$

$= A_{C-c} - 1.048 A_{C-c}$

$A \hat{\text{H}} = A_{C-c} - [2 \cos 58.4 ] A_{C-c}$

$= A_{C-c} - 1.048 A_{C-c}$

$A^* \text{ values} \times 10^{11} \text{ esu}$

$\begin{array}{cccc}
 A & B & C & D \\
 A \hat{\text{CH}}_2 & -0.25 & 2.4 & 17.3 & -0.01 \\
 A \hat{\text{C}} & 5.4 & 5.4 & - & 6.7 \\
 A \hat{\text{H}} & 5.6 & 3.2 & - & 6.7 \\
\end{array}$