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Linear Electric Field (LEF) Effects in ^{13}C NMR. Some Model Calculations on 5-Chloro-1-pentene

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The usefulness and some of the limitations of the linear electric field (LEF) effect in ^{13}C NMR are illustrated by means of model calculations on the ^{13}C NMR chemical shifts of C-1 and C-2 in 5-chloro-1-pentene in nine different conformations. Two different concepts are used in order to calculate the electric fields near C-1 and C-2 caused by the C-5—Cl dipole. It is also demonstrated that, when using charges calculated by CNDO/2, the influences of the hydrogen atoms at C-5 cannot be neglected. The use of the dipole-dipole interaction formula is advocated. The consequences of taking into account the additional contributions of the vinylic bonds to the accumulated charges at C-1 and C-2 are described. The results with the dipole-dipole formula show that the same signs and similar magnitudes of the LEF effects are calculated in seven out of nine conformations of 5-chloro-1-pentene. This reduces the LEF to a means of confirming, rather than deducing, conformational equilibria in acyclic flexible compounds. The usefulness of some recently published applications of the LEF concept to explain some short range substituent effects is critically discussed, mainly in view of the inhomogeneities of the calculated electric fields.

INTRODUCTION

The concept of linear electric field (LEF) effects in ^{13}C NMR was first introduced by Batchelor *et al.*^{1,2} in order to explain long-range influences of highly polar end groups on the olefinic ^{13}C NMR shifts of unsaturated fatty acids. It was anticipated that, together with steric factors, LEF effects would provide a powerful tool for conformational analysis by ^{13}C NMR, mainly because both geometric and distance factors are involved.^{1b} The LEF effect was described as $\Delta\delta = A \cdot E_z$ where E_z is the electric field strength along the bond concerned and A is the sensitivity factor.

There are some obvious weaknesses in the LEF concept. First, a straightforward, linear relationship between accumulated atomic charges for the C atoms and the ^{13}C NMR chemical shifts is inherent in the method.³ Second, the sensitivity factors of the carbon atoms are mainly comprised of longitudinal bond polarizabilities, which are by no means well-defined data.⁴ Moreover, the direct calculation by semi-empirical MO calculations of changes in the atomic charges on the double bond is obviously not possible. The first mentioned difficulty was partially alleviated by the recent work of Seidman and Maciel who calculated, by SCF finite perturbation methods,⁵ the ^{13}C NMR chemical shifts of ethane and ethene subjected to electric mono- or dipoles.

Some applications of the LEF concept have been published recently for rather small distances of the electric dipole and the repolarized moiety. A semi-quantitative conformational analysis of the C-10 side

chain of cholest-5-en-3 β ,19-diol was partially based on a comparison of ^{13}C NMR chemical shift differences observed at the C-5=C-6 double bond with LEF effects calculated for different conformers on C-19 —OH substitution.⁶ Similar comparisons were made for 19-iodocholest-5-en-3 β -ol and 6 β -iodomethyl-19-norcholest-5(10)-en-3 β -ol. In these cases the polarizing dipole is only two bonds away from the double bond. Moreover, a second dipolar group is present at C-3, at the same distance from the double bond. Even smaller distances are involved in a number of systems described by Schneider *et al.* The differences in β -effects in halocyclohexanes and at C-2 in 2,2-dimethylhalocyclohexanes were explained^{7a} by applying the LEF point-dipole approach postulated earlier.^{7b} The non-additivities of the substituent induced shifts in *cis*- and *trans*-2,3-dihalocyclohexanes were also explained by the same procedure.^{7c} An extreme case seems to be the application of the point-dipole approximation to a C- α —C- β bond in order to explain, semi-quantitatively, the larger discrepancies in the substituent induced shift (SIS) values of carbons which carry a more electronegative substituent.^{7c} It was admitted, however, that the point-dipole approximation could be problematic because of the inhomogeneity of the electric fields.

We recently compared the ^{13}C NMR SIS values of axial and equatorial 4-chloro- and 4-bromo-*exo*-methylenecyclohexane with those in the appropriately substituted cyclohexanes.⁴ We also calculated the $\Delta\delta$ values on the double bond following the LEF concept with $\Delta\delta_{\text{C}} = A \cdot E$.¹⁻³ Special attention was paid to the difficulty of obtaining reasonable estimates for the sensitivity factors (A values). In this study we concentrate on the different formulae for calculating the

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electric fields which are presently available in the literature.^{1,2,7b,8} Certain consequences with respect to recent LEF applications are also discussed.

CALCULATIONS

5-Chloro-1-pentene is used as a model compound in this study to illustrate different aspects of the calculations of LEF effects. For comparisons of calculated results (LEF) with experimentally observed substituent effects (e.g. using 1-pentene as a reference, where the experimentally observed substituent effects of the Cl atom on the shifts of C-1 and C-2 in 5-chloro-1-pentene are +1.2 ppm and -1.8 ppm, respectively^{9,10}) it is important that effects through σ -bonds are negligibly small. Even so, conformations with relatively short distances between the C-5—Cl bond and the C-1=C-2 bond are feasible, see for example conformations 6 and 8 in Fig. 1. (In all conformers, one of the allylic hydrogens is defined as *syn* to the double bond¹¹).

Calculations of electric fields were carried out by means of the usual dipole-dipole interaction formula^{1,2} and via calculations of the electric potentials at the two carbons defining a given bond. In the latter procedure the contributions of $C_5^{\delta+}$, $Cl^{\delta-}$ and the two hydrogen atoms at C-5 to the electric potentials at C-1 and C-2 were calculated separately, and subsequently added. Atomic charges for C-5, Cl and the two hydrogens at C-5 were taken from CNDO/2 and INDO calculations on ethyl chloride as a model compound. The results are given in Fig. 2.

The electric field at the bond centre is then obtained by dividing the difference between the electric potentials at the two carbons by the length of their connecting bond, thus assuming uniformity. The calculation can be repeated for the two H—C-1 bonds, the C-2—H and the C-2—C-3 bonds.

In the dipole-dipole interaction formula a bond dipole of 1.54 D was taken for C-5—Cl. This value was derived from the molecular dipole of methyl chloride, assuming the C—H bond dipoles to be 0.4 D (hydrogen positive).^{4,12,13} Larger values of the C—Cl bond dipole have been used previously.^{7b,9} Replacing the value of 1.54 D by a different number would only affect comparisons with the experimentally obtained substituent effects in 5-chloro-1-pentene. The major aim of the present study, however, is a comparison of the relative magnitudes of the LEF effects calculated for the different conformations of 5-chloro-1-pentene (see Fig. 1), and an estimate of the possible errors involved by assuming that the fields are uniform. In order to check this latter point the dipole calculations

Figure 1. Conformations of 5-chloro-1-pentene. Cl atom at positions indicated.

Figure 2. CNDO and INDO charges in me from geometrically optimized ethyl chloride calculations (INDO results in parentheses).

were carried out not only at the centre of the C-1=C-2 bond, but also at two points located along the C-1=C-2 bond, or on its extension at small, equal distances on either side of C-1 and C-2. The inhomogeneities can therefore be estimated.

The A factors in the LEF equation $\Delta\delta = E_z \cdot A$ were derived as follows. The δ/e values were taken as 200 ppm/e for a C=C bond and as 400 ppm/e for C—C and C—H bonds. As stated already in the Introduction, there is an element of ambiguity in the selection of these numbers. The present values, however, correspond approximately to those generally assumed^{4,7b,14} for the types of bond involved and, together with values for the longitudinal bond polarizabilities,^{1a,4} they produce the following A values: $A_{C=C} = 0.418 \times 10^{-19} \text{ cm}^2/\text{e}$, $A_{C-C} = 0.258 \times 10^{-19} \text{ cm}^2/\text{e}$ and $A_{C-H} = 0.238 \times 10^{-19} \text{ cm}^2/\text{e}$ (bond lengths: 1.34 Å, 1.54 Å and 1.08 Å, respectively). Standard bond lengths and angles were used both with the dipole-dipole formula and with the electric potential procedure.

RESULTS AND DISCUSSION

Dipole calculations

Table 1 summarizes our results with the dipole-dipole interaction formula together with typical distances from the centre of the C-5—Cl dipole to the centre of C-1=C-2. Details of the calculations were described in the previous section.

The difference between the numbers in columns 3 and 5 for C-1 and those in columns 4 and 9 for C-2 is caused by the assumption of uniform fields along the entire C-1=C-2 bond in the former case. The errors thus incurred do not exceed *c.* 25% for conformations 1 and 2, which have relatively large dipole-double bond distances. This distance is, however, not the only important factor, as can be clearly seen by comparing conformations 3, 7, 9 and 4 in the same way. These conformations have dipole-double bond distances of 4.1 ± 0.3 Å. By assuming uniform fields, the LEF effects are overestimated at C-1 in conformations 3, 7 and 9 by *c.* $33 \pm 3\%$ whereas the value at C-2 is consistently underestimated by *c.* $52 \pm 3\%$. The opposite situation holds in conformation 4. The angles between $\vec{\mu}$, $\vec{R}$ and $\vec{dR}$ ^{1,2,8} probably determine the discrepancies. In conformations 5 and 8 the absolute value of the electric field at the centre of C-1=C-2 is calculated to be larger than at either end point. Calculations for conformation 6 yield the unlikely result of the electric fields at C-1 and C-2 being of opposite signs, i.e. both directed towards the bond centre. Obviously, distances in this situation are too small for

Table 1. Calculated LEF effects (in ppm) on C-1 and C-2 of 5-chloro-1-pentene in nine conformations,^a using the dipole-dipole formula^b

Conformation No. ^a	R ^c (Å)	C _M ^d		C-1				C-2			
		C-1	C-2	C-1=C-2 ^e	C-1-H-1 ^f	C-1-H-1 ^f	Total	C-1=C-2 ^e	C-2-H-2 ^f	C-2-C-3 ^f	Total
1	4.98	+1.23	-1.23	+1.01	+0.13	-0.73	+0.41	-1.40	-0.54	+1.48	-0.45
2	4.60	+0.48	-0.48	+0.48	+0.15	-0.44	+0.19	-0.35	-0.51	+0.77	-0.09
3	4.44	+1.55	-1.55	+1.00	-0.60	+0.09	+0.49	-2.19	+0.59	+0.77	-0.83
4	4.02	+1.71	-1.71	+1.84	+0.10	-1.19	+0.75	-1.01	-0.89	+1.61	-0.28
5	3.34	+3.13	-3.13	+2.43	-1.46	+0.01	+0.98	-2.93	+0.82	+1.00	-1.11
6	2.77	—	—	—	+1.63	-1.08	—	—	-1.58	+3.79	—
7	4.32	+2.97	-2.97	+1.99	-0.56	-0.63	+0.80	-4.53	+1.21	+1.61	-1.70
8	3.19	-1.38	+1.38	-1.16	+1.55	-0.85	-0.46	+0.92	-4.05	+3.79	+0.66
9	3.88	+1.80	-1.80	+1.20	-0.34	-0.38	+0.48	-2.81	+0.75	+1.00	-1.06

^a See Fig. 1.

^b See text.

^c Distance between centres of the C-5—Cl and C-1=C-2 bonds.

^d Obtained by calculating the electric field at the centre of the C-1=C-2 bond and taking $\Delta\delta_{\text{C-1}} = -\Delta\delta_{\text{C-2}}$.^{1,2}

^e Obtained by calculating the fields at C-1 and C-2 along C-1=C-2 (see text).

^f Obtained by calculating the fields at C-1 and C-2 along the vinylic bonds, see Fig. 3.

comparison of observed shift differences with values calculated by means of the LEF formulae. A uniform field or, at least, a monotonically changing field is required. An additional point is that quadratic field effects cannot be neglected in this conformation.*

Table 1 also shows the influence of extending the dipole-dipole calculations to the four vinylic bonds depicted in Fig. 3. It should be realized that in some conformations the C-5—Cl bond is rather close to C-2—H-2 and C-2—C-3. In principle, these calculations are therefore sometimes subject to the same limitations as noted above for the C-1=C-2 bond in conformation 6. This point has been checked by performing a number of calculations along the vinylic bonds. Opposing directions of electric fields at either end of the C-2—C-3 bond are calculated, for example, in conformations 4, 5 and 9; rather strong gradients are calculated in some of the other conformations. The numbers in Table 1 should thus be considered as only first order indications of the vinylic contributions to the total LEF shifts at C-1 and, in particular, at C-2.

Generally, the vinylic contributions to the total LEF effects at C-1 and C-2 tend to 'mask' the patterns given with the C-1=C-2 bond only. This masking is particularly clear in conformations 7 and 9 where C-5—Cl is almost 'in line' with C-1=C-2.

Table 2 shows some results calculated for C-1=C-2 in 4-chloro-1-butene with the dipole-dipole approach. The *g*⁺-conformation, in particular, shows a rather large field inhomogeneity. Since field homogeneity is a basic assumption for the LEF concept, applications to such conformations⁶ are potentially dangerous. For the same reason, separate calculations on the vinylic bonds in order to correct for their influences on the calculated LEF shifts seem useless.

Figure 3. Arrangement of atoms and bonds in the LEF calculations.

* We acknowledge this suggestion from one of the referees.

Table 2. Results of calculations of LEF effects on C-1=C-2 of 4-chloro-1-butene in three conformations, using the dipole-dipole formula^a

Conf.	Distance dipole-centre C-1=C-2 (Å)	LEF effects (ppm) via $\vec{E}$ at M ^b		LEF effects (ppm) via $\vec{E}$ at C-1 and C-2	
		C-1	C-2	C-1	C-2
<i>anti</i>	3.74	+3.71	-3.71	+2.67	-4.76
<i>gauche</i> ⁺	3.02	+4.26	-4.26	+2.06	-7.21
<i>gauche</i> ⁻	3.25	+1.76	-1.76	+1.43	-1.47

^a See text and Fig. 4.

^b M denotes the centre of the C-1=C-2 bond.

Electric potential calculations

Table 3 summarizes the calculated LEF shifts on C-1 and C-2 of 5-chloro-1-pentene by taking charges of equal magnitudes (230 me) but different signs on C-5 and Cl.^{7b} The first set was obtained by considering only C-1=C-2 and, therefore, the close resemblance to the 3rd and 4th columns of Table 1 is not surprising. The second set was calculated by also considering the vinylic bonds. The changes with respect to the first set of LEF shifts in Table 3 are, qualitatively, the same as those between 'vinyl corrected' and 'uncorrected' results with the dipole formula. Because the calculations with the potentials method have been applied to complete bonds rather than to small sections around the terminal atoms, and also because the C-2—C-3 bond is generally much closer to the C-5—Cl dipole than C-1=C-2, the balance of LEF shifts calculated for C-2 sometimes becomes positive. In some other cases, e.g. conformation 4, the contributions from C-2—H-2 and C-2—C-3 nearly cancel, and thus the difference with respect to the uncorrected LEF shift is only small. As with the dipole-dipole interaction formula the 'correction' for C-2 is the sum of two relatively large amounts for the C-2—C-3 and C-2—H-2

Figure 4. Conformations of 4-chloro-1-butene.

Table 3. Results of calculations of LEF effects on C-1=C-2 of 5-chloro-1-pentene in nine conformations via the electric potentials method^a with $q_{(C-5)} = -q_{(Cl)} = 230$ me

Conformation no. ^a	LEF effects considering only the olefinic bond (ppm)		LEF effects considering also the vinylic bonds (ppm)	
	C-1	C-2	C-1	C-2
1	+1.53	-1.53	+0.84	+0.95
2	+0.50	-0.50	+0.19	+0.32
3	+1.86	-1.86	+1.02	-0.04
4	+2.12	-2.12	+0.42	-2.60
5	+3.49	-3.49	+1.41	-3.07
6	+1.33	-1.33	+2.92	+2.83
7	+4.11	-4.11	+2.58	-1.86
8	-1.15	+1.15	-0.43	-0.72
9	+2.06	-2.06	+1.19	-1.68

^a See text.

bonds. The calculated contribution of the vinylic bonds in this case is only a very rough indication of direction and order of magnitude (see also the corresponding corrections for the dipole calculations).

Instead of the rather arbitrary values of +230 me and -230 me for C-5 and Cl, results of INDO or CNDO procedures can also be used as input for calculations of the LEF effects, see Fig. 2 for values of charges. Because the absolute value of the negative charge calculated on the Cl atom exceeds that of the positive charge on C-5, the characteristic '+-picture' of the resulting LEF effects at C-1 and C-2 is attenuated; see, for example, the results for conformation 1 in columns 3 and 4 of Table 4. The difference in magnitude of the positive and negative charges is more pronounced with CNDO. The effect of the negative monopole on C-1=C-2 may now override that of the positive monopole, in spite of the shorter distance to C-1=C-2 of the latter. In some conformations this may lead to a reversed sign of the calculated LEF effects; see, for example, conformations 1 and 2. In conformation 7, the combined effects of C-5 and Cl would cause no LEF effect using CNDO charges. It is thus obvious that charges should be specified, and that

CNDO charges yield completely different results compared with those using +230 me and -230 me.^{7b}

The influence of also taking into account the vinylic bonds is evident from a comparison of the columns 3, 4, 5 and 6 of Table 4. INDO calculations yield only small positive charges on the hydrogen atoms at C-5, in contrast to CNDO where these amount to c. +30 me (Fig. 2). Accordingly, inclusion of these positive poles into the LEF calculations causes little change to the INDO results but the sign of the calculated LEF effect may be changed on using CNDO charges (for example, conformation 1 in Table 4). The last two columns of Table 4 illustrates the effect of taking into account a combination of both hydrogens at C-5 and the vinylic bonds.

CONCLUSIONS

Calculations of the electric field along a bond by means of the dipole-dipole interaction formula is, in our opinion, to be favoured over the electric potential method. This conclusion is drawn mainly from the fact that better agreement with experiment is achieved with the dipole-dipole formula. *A posteriori*, this is not very surprising, since dipole moments are also experimental properties. For electric potential calculations, the results depend rather strongly on the exact locations and magnitudes of the contributing atomic charges. Even the signs of the calculated LEF effects may depend on which particular semi-empirical MO method is being used. The differences between, for example, the CNDO/2 and INDO methods are severe. Although the use of charge distribution should, therefore, in principle, yield better results, the present calculations do not apparently yield results realistic enough to warrant their use in LEF calculations.

As stated in the Introduction, the LEF concept was originally introduced in order to draw conclusions regarding conformational equilibria in unsaturated systems carrying polar rest groups.^{1,2} From the present study it becomes clear that, as long as the dipole

Table 4. Comparison of calculations of LEF effects on C-1=C-2 of 5-chloro-1-pentene in some conformations via the electric potentials method with different charges at C-5 and Cl

Conformation no.	Charge calc. ^a	Calculated LEF effects on C-1 and C-2 (ppm)							
		C-1 ^{a,c}	C-2 ^{a,c}	C-1 ^{b,c}	C-2 ^{b,c}	C-1 ^{a,d}	C-2 ^{a,d}	C-1 ^{b,d}	C-2 ^{b,d}
1	[230 me]	+1.53	-1.53	+0.84	+0.95	—	—	—	—
	INDO	+0.60	-0.60	+0.37	+0.77	+0.70	-0.70	+0.42	+0.79
	CNDO	-0.39	+0.39	-0.13	-0.52	+0.33	-0.33	+0.22	+0.64
2	[230 me]	+0.50	-0.50	+0.19	+0.32	—	—	—	—
	INDO	-0.34	+0.34	-0.22	+0.20	-0.24	+0.24	-0.18	+0.20
	CNDO	-1.14	+1.14	-0.61	+0.06	-0.53	+0.53	-0.33	+0.08
7	[230 me]	+4.11	-4.11	+2.58	-1.86	—	—	—	—
	INDO	+2.18	-2.18	+1.46	-0.99	+2.45	-2.45	+1.61	-1.10
	CNDO	+0.07	-0.07	+0.23	-0.05	+1.83	-1.83	+1.23	-0.76
8	[230 me]	-1.15	+1.15	-0.43	-0.72	—	—	—	—
	INDO	-2.58	+2.58	-1.25	+0.03	-2.39	+2.39	-1.15	-0.04
	CNDO	-3.79	+3.79	-1.98	+0.78	-2.58	+2.58	-1.32	+0.34

^a Considering only the C-1=C-2 bond.^b Taking also into account the vinylic bonds.^c Taking only C-5 and Cl.^d Also considering the C-5—H atoms.^e See text and Fig. 2.

method is used (or when charges of equal absolute magnitudes are inserted in the potential method), similar characteristic induced shifts are calculated in seven out of nine possible conformations of 5-chloro-1-pentene. Thus, the application of the method to conformationally mobile systems is useful only in conjunction with other methods (e.g. ^1H NMR) to confirm rather than to deduce conformational equilibria.

In conformations with small dipole-double bond distances, such as conformation 6, no physically meaningful results can be obtained. Applications of LEF in butene-like fragments, as presented recently⁶ for some substituted steroids, are unfeasible at present: first, because of the large field inhomogeneities, second, because of the probable influence of quadratic electric field effects and, finally, because interactions between electric field effects and other factors such as steric influences have not been taken into account at all, neither here nor in previous publications.^{1,2,5} Such an interaction is also conceivable when the chlorine atom

in 5-chloro-1-pentene approaches the double bond. Definite quantitative data about these interactions are, however, not available. Similar reservations about possible interaction terms are certainly in order in the case of applications of the LEF formula when the distances between the dipole and repolarized bonds are extremely short.^{7a,7b} In these cases the consideration of charge polarization caused by a dipole as an independent shift inductor seems rather optimistic. The LEF effect, as predictable, does not offer an alternative for the description of the total substituent effect or the lack of additivities in these cases.

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