σ-Inductive Interaction Through up to Fourteen Saturated C–C Bonds

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Analysis of the NMR shifts of unsaturated carbon atoms in monounsaturated linear long-chain esters and acids, including new data from jojoba oil, rules out any explanation in terms of an 'electric field effect', but is semi-quantitatively consistent with a 'σ-inductive' mechanism, having an attenuation factor of 1.75 per saturated C–C bond.

It has been known for some time[1,2] that the ^{13}C chemical shifts of the double-bond carbons in monounsaturated esters and acids are sensitive to the separation of the double bond from the carboxylate moiety, even when this separation is comparatively large. Biosynthetic labelling has been used to show that the carbon nearer to the carboxylate is always the more shielded, and we have confirmed this in two cases by 2D assignment methods. The current explanation of this observation is that the dipole of the ester exerts an 'electric field effect' through space, so as to induce a dipole in the C=C bond. This π-charge separation is reflected in a proportional separation of shift. In its simplest form the theory predicts a symmetrical separation of shifts, and in a more sophisticated form it predicts an asymmetry biassed towards higher frequency.[2]

The arguments used by Batchelor *et al.* in favour of an electric field effect[2] were (*i*) an approximately exponential fall-off of shift separation with n, the number of carbons between the polar group and the π-bond, (*ii*) an appropriate influence of solvent dielectric on the shifts, and (*iii*) the supposed improbability of measurable through-bond σ-inductive effects over such long ranges. However, all these arguments are open to challenge. Paddon-Row has used photoelectron spectroscopy to demonstrate orbital interactions through up to eight saturated C–C bonds.[3]

The solvent effect could be to reduce the effective dipole moment of the ester group, rather than to change the transmission of a field by changing the intervening dielectric. Electric field effects have also been brought into question by studies of complexes between diamine tetraacetates and metal ions with different formal charges,[4–6] because these reveal little effect of metal charge upon the carbon shifts of the carboxylates.

Therefore, it seems appropriate to submit the supposed 'electric field effect' to more stringent scrutiny, especially now that ^{13}C NMR spectroscopy can resolve the C=C shifts in compounds with larger values of n. Some of these compounds are readily available, and we have measured other shifts from a very high resolution study of jojoba oil, whose approximate composition is known from mass spectrometry.[7,8] The C=C portion of the ^{13}C NMR spectrum of jojoba oil is shown in Fig. 1(*a*). As expected,[1] the resonances are found to form pairs, distributed with a consistent asymmetry on either side of the shift value (δ 129.736) anticipated for $n = \infty$. They may be assigned readily from the reported composition of jojoba oil,[7,8] using deconvolution. Fig. 1(*b*) shows the equivalent resonances for an artificial mixture of alkyl esters of monounsaturated acids, with (outer to inner pairs) n = 5, 6, 8. The same pattern is evident, albeit on a tenfold wider scale. The asymmetry itself is opposite to that predicted by the electric field theory. The resulting shift separations for the unsaturated carbon pairs depend to a surprisingly small extent upon which side of the ester grouping is involved, but they do depend strongly upon n. Thus for $n = 11$ (*i.e.* for 20:1 chains) the separations are δ 0.084 (acid moiety) and δ 0.075 (alcohol moiety), but for $n = 13$ they are both 0.026 ppm, within experimental error.

The electric-field theory proposed by Batchelor *et al.* predicts that this shift separation will vary as n^{-3} for an all-*trans* methylene chain, and that this exponent will reduce towards $n^{-1.5}$ to the extent that *gauche* rotamers are permitted. The authors also observe that their data fits best with an exponent of −3.5. We plot their data, extended by our data, in Fig. 2. It diverges substantially from the above proposal (light curve). However, the logarithm of the shift separation varies almost linearly with n (heavy line). The experimental data in the plot include our measurements of C=C shift separation for the methyl esters of the following acids: 8-eicosenoic, Δδ 0.449 ppm, 11-eicosenoic = 0.089, 13-eicosenoic = 0.017, and also for 11-eicosenyl acetate = 0.073. The log-linear dependence on n has an attenuation factor of 1.754 per intervening methylene group. Its remarkable linearity argues for a through-bond interaction, because one

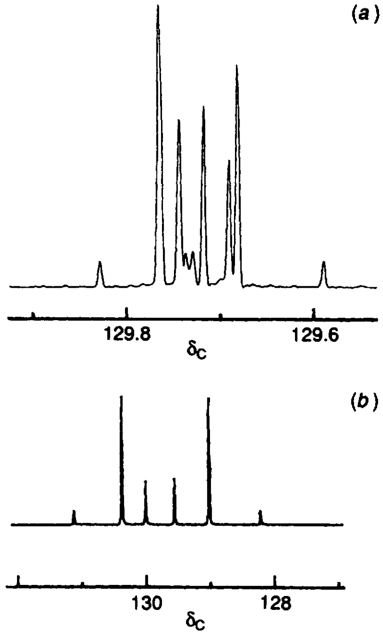

Fig. 1 Ethylenic portions of the 100.6 MHz ^{13}C{^{1}H} NMR spectra of (*a*) jojoba oil and (*b*) a prepared mixture of (in descending order of concentration) ethyl petroselinate, methyl-8-eicosenoate and methyl-5-eicosenoate

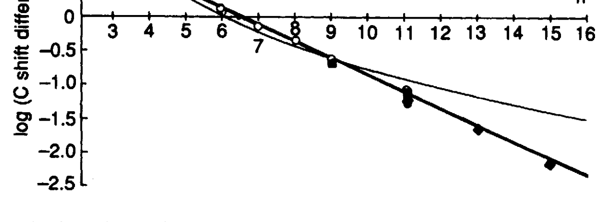

Fig. 2 Plot of $\log_{10}$(C=C shift separation) against n, the double bond position, for both the alcohol (■) and the acid (◆) moieties of jojoba esters, and of other esters described in the text or in ref. 1 (○). The heavier line is the best linear fit, and the lighter line is that predicted by the electric-field theory of ref. 2.

would expect almost all the methylene groups to provide the same attenuation.

The electric-field theory also predicts that the shift separation should reverse in sign between the acid and the alcohol moieties. To the extent that the dominant rotamers for the first few bonds of either chain type, out from the ester group, are *trans*, the electric dipole associated with the entire ester grouping has opposite orientation with respect to the acid or the alcohol moieties. The consistent asymmetry of the shift separations in Fig. 1(*a*) led us to suspect that this prediction runs counter to experiment, and our suspicions were confirmed by a full ^{13}C and ^{1}H shift assignment of *cis*-5-decenyl acetate. This had C(5) to low frequency of C(6), as with the fatty acid esters quoted above. It follows that the shifts of the C=C bond carbons arise from the carbon to oxygen bond(s) nearest to this C=C bond, rather than from the overall ester dipole.

Although it may be surprising that a separation of charge is transmitted through up to 14 C–C single bonds, one should note that the shifts of the C=C carbons provide an exquisitely sensitive probe. The attenuation factor of 1.75 is not improbable, although it is at the lower end of the published experimental values for inductive effects, *ca.* 2–3.[9] Our results cannot rule out all possible effects of electric fields on chemical shifts,[10] but they do show these to be at most minor, in the present case. Our measurements also offer a useful alternative method for analysing the main components of unsaturated oils such as jojoba.

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