Long-range σ-inductive interactions through saturated C–C bonds in polymethylene chains

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Analysis of the NMR shifts of unsaturated carbon in monounsaturated linear long-chain esters, alcohols and acids, including data from jojoba oil, shows a highly linear dependence of the logarithm of the shift separation in the C=C bond upon the number of bonds separating this from the ester moiety. Both the linearity of this dependence, and the observation that it does not change sign upon reversal of the ester grouping, rule out the 'electric field effect' as an explanation, but are semi-quantitatively consistent with a remarkably simple, 'σ-inductive' through-bond mechanism. Semi-empirical MO calculations support this conclusion. The attenuation factor is 1.75 per saturated C–C bond in each class of compound, although the actual shift separations, for a given chain length, vary up to twofold with changes in the polarizing group and with (*Z*)–(*E*) isomerism at the C=C bond. Other series of compounds show the same attenuation factor.

Introduction

Although NMR shifts should ideally be predicted by *ab initio* quantum mechanical calculations, these are still not practical for relatively large molecules such as lipids, even though the details of their shifts contain much useful structural information.[1] One must therefore still resort to empirical correlations having only partial theoretical justifications, and within these one must select only those with the power to give reliable shift predictions for unknown materials. The present paper aims to establish one such correlation empirically, which has analytical applications to many long-chain molecules. It offers a semi-quantitative justification which rules out any significant contribution from supposed 'through-space' effects, and which conversely shows that inductive 'through-bond' effects attenuate far less sharply with distance than is commonly supposed.

The effect of a substituent in an organic molecule on a probe group in the same molecule, at which the effect can be measured (*e.g.* an ionisable group having a detectable pK_a) has been analysed in various ways.[2] A division into polar and steric effects is possible, at least in principle, though it has proved more difficult in practice.[3] It is also generally accepted that polar substituent effects may be sub-divided further into resonance effects, where the substituent and probe group are linked by a conjugated π-system, and another effect, often known loosely as an inductive effect, where the link is a saturated system or contains only unconjugated double bonds. It is these latter effects which have proved most controversial, with two models being proposed. Many of the early data were interpreted in terms of a 'through bond' (TB) inductive interaction, in which the polarization of a carbon-substituent bond is transmitted in attenuated form to the next C–C bond, and so on, down the chain. More recently, the generally accepted explanation has been a 'through space' (TS) field effect,[4] in which there is a charge–dipole interaction between the substituent and an ionizing probe group or in which the electric dipole of the substituent directly polarizes the electron density surrounding a neutral probe group. As recently as 1993, however, two articles in the same issue of one review journal came to different conclusions on this issue.[4,5]

The evidence which has led to general acceptance of the field effect (TS) mechanism is of several types, but none is irrefutable. Firstly, in its simplest form, the σ-inductive (TB) interaction should depend only on the number of intervening bonds and not on the geometric relationship between the substituent and the probe, whereas a field effect would be expected to show an angular dependence. Such angular dependence has indeed been observed and the field effect has been used to account for it, at least semi-quantitatively.[4]

More recently, however, Exner *et al.*,[5] by considering multiple transmission paths, have shown that some cases of apparent angular dependence can equally well be accounted for, even semi-quantitatively, by a TB interaction. Furthermore, Hoffmann's original discussion of TB and TS interactions led to the 'all-*trans* rule' that coupling through a bridge is maximized for an all-*trans* (antiperiplanar) configuration of bridge bonds.[6] This has been verified for rates of electron transfer, by Paddon-Row's recent studies of norbornylogous bridges.[7] Whilst this theory is difficult to apply quantitatively, it does show that the original prediction, of no angular dependence for the TB inductive effect, is naive and that an inductive effect can accommodate an angular dependence.

Secondly, most estimates of the attenuation factor[8] implicit in the inductive effect lead to the prediction that the effect will fall off to insignificance within a very few bonds, whereas the field effect is expected to operate over longer distances. However, these small perturbations are notoriously hard to calculate. Furthermore, Paddon-Row[9] has used photoelectron and electron transmission spectroscopy to demonstrate orbital interactions over eight saturated C–C bonds, with attenuation factors (the reciprocal of his β^0 parameter) of 1.67 and 2.50 per bond. He has also used photoinduced electron transfer rates to estimate orbital interactions over as many as 13 bonds, with attenuation factors of 1.64, 2.00 and 2.17 per bond.

Thirdly, where it has proved possible to study compounds in which the substituent and probe group are the same, but the distance between them varies, the observed effects have been claimed to correlate better with distance than with the number of intervening bonds.[10] This conclusion disagrees with the data presented below.

Fourthly, the field effect theory has been used to explain, at least qualitatively, the observed effect of the bulk dielectric constant (relative permittivity) of the solvent on the transmission of a substituent effect,[11] whereas, at least on a simplistic model, an inductive effect should be independent of the bulk dielectric constant. There have been problems in making the TS model fully quantitative, since it is difficult to define an effective dielectric constant of the medium, *i.e.* the molecule and solvent, through which the effect is transmitted. The normal approach is to use this as an adjustable parameter, limiting quantitative applications.[4,5] However, a TB model will also show a dependence on solvent, if solvation attenuates the effective dipole moment of the polarizing group.

A fifth argument has been constructed by Bachelor *et al.*, from the ^{13}C NMR shifts at the double bond in long-chain mono-unsaturated esters.[12] The purpose of the present paper is to extend these shift observations, and thus to challenge their interpretation. Our counter-arguments are also supported by a query raised some years ago against the importance of non-covalent, TS effects, namely that the ^{13}C NMR shifts in metal complexes of edta (ethylene diamine tetraacetate) and related ligands do not show any obvious dependence on the metal charge. One notes that in these cases the M–O bonds are at best only weakly covalent, as judged by the small *J*-couplings to metal.[13]

A final problem with the TS electric field theory in its naive form is that it predicts different shift-dependences for esters and acids. The esters are largely monomeric in organic solvents, and so experience a dipole field from the ester moiety, whereas the carboxylic acids are very largely dimeric, and so must create a quadrupole field. This falls off more steeply with distance than a dipole field. All experiments to date in fact show that esters and acids show very similar dependence of C=C shift difference with distance.[12]

^{13}C Chemical shifts at unsaturated C are very suitable as a probe for long-range polar effects, because they are extremely sensitive to charge distribution, with a positive partial charge giving a positive shift increment. A typical proportionality factor of + 180 ppm per electron removed from an sp^2 carbon[14] means that, at 9.3 Tesla (400 MHz for protons), a difference in charge density of 10^{-4} electrons corresponds to 1.8 Hz, which is readily resolved. This contrasts with the use of most reactivity-based probes, such as the recent unsuccessful search for a ζ-hyperconjugative interaction of tin through six σ-bonds,[15] which could not distinguish such a small effect. It has been known for some time[12,16] 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. Bachelor *et al.* interpreted the data for acids in terms of the prevailing field effect theory.[12] His theory implies, using reasonable assumptions concerning chain conformations, that alcohols and reversed ester groupings (*e.g.* ROCOMe) should, at distance, show algebraically opposite shift differences from acids and acid esters (*e.g.* RCO_2Me). In other words, the carbon with the highest shift should now be the one nearest to the oxygen. This implication has not been explored to date. However, it can now be studied by using modern 2D assignment methods. Also, the much higher 1D resolution now available makes it possible to extend the ^{13}C shift data to include double bonds with greater separation from the ester group, and hence to subject the distance-dependence of the TS and TB theories to a much more severe test. Here we report new studies of such compounds, including, in particular, results for esters, acids and alcohols in which the polar group and the double bond are separated by up to 14 saturated C–C bonds. We argue that when the published data are reanalysed together with our new results, they are quantitatively consistent with the TB σ-inductive effect alone, and also algebraically inconsistent with any dominant TS interaction.

Experimental

Spectra

1D ^{13}C NMR spectra were obtained at 100.6 MHz from a Bruker ACP400 spectrometer, using 128k data points, which were zero-filled to 512k data points to maximize the resolution, typically 0.3 Hz. Some of the smaller splittings were resolved by the deconvolution and peak-fitting method, using Bruker WIN-NMR. 2D ^{1}H–^{1}H and ^{1}H–^{13}C shift correlations were obtained by standard methods, using the same instrument. Shifts are relative to Me_4Si, in solutions *ca.* 5% by weight in $CDCl_3$, at 298 K. Absolute shifts depend on concentration and temperature, as observed previously and are ±0.1 ppm, but shift differences are ±0.001 ppm. Curve fitting used Microsoft Excel ver. 4 with Solver, and linear regression used Systat ver. 5, and was carried out independently for each line shown.

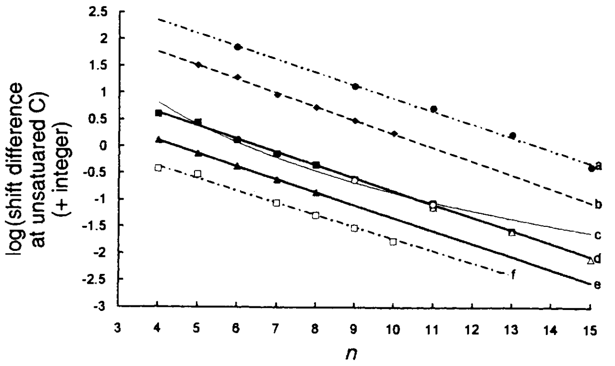


Fig. 1 Experimental variation of log (shift difference between the unsaturated carbons) with *n*, the position of the multiple bond in monounsaturated linear chains. Integers are added to a, b and f, for clarity. a alcohols, +2; b (*E*)-acids, +1; c electric field theory with optimized exponents; d (*Z*)-acids and esters (either moiety); e selenophenes ($\delta_{n+3} - \delta_n$); f alkyne acids, −1.

Materials

Jojoba oil was supplied by the COMSA cooperative, Ordona, Foggia, Italy, and was obtained from the ground seeds by ether extraction and decolourisation. Our analysis showed it to have a composition very similar to that reported by Miwa[17] and by Spencer and Plattner.[18] Little variation in composition was found between plants, beyond slight variations in average chain length. 8-, 11- and 13-icosenoic acids, icos-11-enyl acetate, (*Z*)-dec-5-enyl acetate, petroselinic [(*Z*)-octadec-6-enoic] acid ethyl ester, and petroselinyl, palmitoleyl [(*Z*)-hexadec-9-enyl], oleyl, ico-11-enyl, erucyl [(*Z*)-docos-13-enyl] and nervonyl [(*Z*)-tetracos-15-enyl] alcohols were obtained from Sigma Ltd.

Computational studies

All calculations were carried out using the AM1[19] Hamiltonian in MOPAC[20] ver. 6, and the PRECISE keyword, on either a MicroVax II or a Silicon Graphics Indigo workstation.

Results

NMR studies

Carbon-13 NMR spectra were obtained for the esters and alcohols listed along with their ethylenic carbon shifts in Table 1. Some of the data come from a sample of jojoba oil. The C=C portion of the ^{13}C NMR spectrum of this sample is shown in Fig. 1 of a preliminary communication.[21] As expected, the resonances are found to form pairs, distributed with a consistent asymmetry on either side of the shift value (129.835 ppm) anticipated for an infinitely large separation of the C=C and ester bonds. They may be assigned readily from the shifts of known compounds, and also on the basis of the typical composition of jojoba oil.

The experimental data are also shown graphically in the present Fig. 1, as plots of log (C=C shift difference) against *n*, the number of C atoms between O and the double bond.

Comparable literature data[12,16] are also included. The resulting shift separations for the unsaturated *cis* carbon pairs in the esters are very similar, whichever side of the ester grouping is involved, but they depend strongly upon *n*. Thus for $n = 11$ (*i.e.* for 20:1 chains) the separations are 0.084 ppm (acid moiety) and 0.075 ppm (alcohol moiety), but for $n = 12$ they are both 0.026 ppm, within experimental error. The data from Gunstone *et al.*[16] for (*E*)-acids is also shown in Fig. 1, with 1 added to log ($\Delta\delta_{C=C}$) for visual clarity. Similarly, the data for the simple alcohols is shown with 2 added, plus that for monoyne acids, with 1 subtracted,[22] and also for the unsaturated carbons flanking Se in a series of methyl esters in which a 2,5-selenophene unit is inserted into the otherwise saturated chain (no vertical increment on graph).[23] A simple TB theory predicts a constant attenuation factor for $\Delta\delta_{C=C}$, so that $\Delta\delta_{C=C} \propto \varepsilon^{-n}$. It also implies the same attenuation factor for the alkyne and the selenophene series. The straight lines are independent best fits to this theory, and their statistical data are listed in Table 2. The correlations are excellent. In contrast, Fig. 1 also contains a curve (thin continuous line) representing the best fit to Bachelor's TS theory,[12] after allowing a variable exponent. In its simplest form, this theory predicts that the shift separation should vary as n^{-3} for an all-*trans* methylene chain, and that the exponent will reduce towards -1.5 to the extent that *gauche* rotamers are permitted. More sophisticated calculations predict more negative exponents. Thus, approximate exponents of -3.44 have been calculated for the distance-dependence of the shift perturbation of Ar by an Na^+ ion, and also -4.94 for perturbation of Ar by NaH at distances not larger than 5 Å, with evidence of a lower exponent at greater distances.[24] But even our freely optimised exponent of -4.23 yields a far inferior fit, particularly at large *n*, as shown in Fig. 1. If one were to use the exponent of -3.5 claimed by Bachelor *et al.*,[12] then the fit would be considerably worse. An attempt was also made to fit to a variably-weighted combination of TS + TB theories, but the TS component was consistently reduced to zero by the least-squares fitting process.

One might still object that this analysis is unduly dismissive of the TS model because it takes inadequate account of possible geometric factors. Perhaps the dominant geometry makes the two chains lie nearly parallel, so that they each experience much the same dipolar interaction? A complete modelling study of this possibility would require more sophistication than is currently available, particularly as it would require the inclusion of solvent. However, two lines of argument converge to cast severe doubt on this apparent geometric possibility. Firstly, modelling studies make it very clear that the C1–C2 bond in the acyl chain and the O–C1 bond in the alkyl chain are necessarily antiparallel. The next bonds in each chain are also energetically likely to be nearly antiparallel, albeit with less strong geometric constraints. Beyond this, there is little conformational preference other than the general favouring of *trans*-conformers. These together make near-parallel acyl and alkyl chains most unlikely, and argue instead for a molecule which is extended on average into a nearly linear shape with antiparallel chains.

Secondly, if any unusual geometric preferences contributed to $\Delta\delta$ for the unsaturated carbons, then one would expect $\Delta\delta$ to alternate in magnitude, or even sign, between odd and even *n*, as this would vary the angle of the C=C bond in the field of the ester dipole. Fig. 1 shows that this is not the case, which also argues strongly against any TS model other than a highly artificial one.

In addition, the individual double-bond carbon shifts in the esters can also be readily fitted to a simple TB-type formula, although fully reliable individual shifts can only be obtained from mixtures of esters containing unequal amounts, in order to avoid the small but noticeable effects of concentration. There is no assignment problem with esters (or with acids), because the two shifts can readily be distinguished from each other in a given compound. In the case of the acid moieties, biosynthetic labelling has been used previously to show that the carbon nearer to the carboxylate always shifts to higher field, whereas the more distant carbon always shifts to lower field, by a somewhat smaller amount.[12] We have checked, and can confirm this order for the cases $n = 5$ [methyl (*Z*)-icos-5-enoate] and $n = 6$ (ethyl petroselinate), by using H–H and H–C shift correlation spectra. There is thus no experimental evidence for an alternation of charge density suggested by our calculations and attributed to an artefact as discussed below. Using this assignment, we find that the shifts of carbon *n* in the acid esters fit well to the formula (1) and those for carbon ($n + 1$) to eqn. (2).

$$\delta_n = 129.835 - 22.930\,(1.754^{-n}) \qquad (1)$$

$$\delta_{(n+1)} = 129.835 + 14.543\,(1.754^{-n}) \qquad (2)$$

Secondly, we find almost exactly the same dependence for the alcohol moieties in jojoba oil. This asymmetric dependence points to their shifts having the same signs as the corresponding acid moiety shifts. We have confirmed this conclusion by

Table 1 ^{13}C NMR shifts for ethylenic C in compounds (re)measured in the present work

Compound	n	$\delta_{C\text{-}(n+1)}$	$\delta_{C\text{-}n}$	$\Delta\delta$
Methyl (*Z*)-icos-5-enoate	5	131.184	128.288	2.896
Ethyl petroselinate	6	130.431	129.080	1.351
Petroselinyl alcohol	6	130.152	129.456	0.696
Methyl (*Z*)-icos-8-enoate	8	130.062	129.613	0.449
Palmitoleyl alcohol	9	129.929	129.796	0.133
Oleyl alcohol	9	129.919	129.780	0.139
Jojoba C_{18} (acid) esters[a,b]	9	129.922	129.684	0.238
Icos-11-enol	11	129.897	129.844	0.053
Icos-11-enoyl acetate	11	129.905	129.832	0.073
Methyl (*Z*)-icos-11-enoate	11	129.923	129.834	0.089
Jojoba C_{20} (acid) esters[a,b]	11	129.859	129.775	0.084
Jojoba C_{20} (alcohol) esters[a,b]	11	129.859	129.784	0.075
Methyl (*Z*)-icos-13-enoate	13	129.895	129.877	0.018
Methyl erucate[a]	13	129.841	129.815	0.026
Erucyl alcohol	13	129.889	129.872	0.017
Jojoba C_{22} (both) esters[a,b]	13	129.838	129.811	0.027
Nervonyl alcohol[b]	15	129.892	129.888	0.004
Jojoba C_{24} (alcohol) esters[a,b]	15	129.830	129.823	0.007

[a] Concentration significantly greater than 5% w/w. [b] Splitting checked by deconvolution/curve fitting.

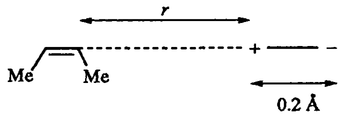
Table 2 Statistical data for the fitted lines in Fig. 1

Class	Slope	Intercept	N	r	s	F	Attenuation factor
Alcohols	−0.242 ± 0.009	3.321 ± 0.105	5	0.998	0.065	676	1.746 ± 0.036
(*E*)-acids	−0.255 ± 0.006	2.783 ± 0.050	6	0.999	0.027	1 536	1.800 ± 0.025
Alkynes	−0.232 ± 0.009	1.564 ± 0.066	6	0.997	0.046	686	1.706 ± 0.035
Selenophenes	−0.242 ± 0.002	1.079 ± 0.011	5	0.999	0.006	17 024	1.746 ± 0.008
(*Z*)-esters	−0.247 ± 0.003	1.614 ± 0.027	14	0.999	0.031	8 512	1.766 ± 0.012

carrying out ^1H and ^{13}C assignments, *via* 2D shift correlation methods, for C1–C10 of (*Z*)-dec-5-enyl acetate. The relevant shifts are reported in Table 3. However, we note that the size of the splitting is consistently less for free alcohols and for acetates than for alcohols esterified with longer chain acids (Table 1).

Computational studies

We recognized that the small shift differences (as little as 0.01 ppm) and relatively large molecules ($\geqslant C_{18}$) being discussed here were beyond the power of even current *ab initio* methods for the calculation of shifts.[1] We also considered that such long-range shift perturbations in otherwise very similar molecules must measure local differences in charge density at alkene carbon, even though this may not be true more generally. Thus we expected the dominant factor determining the shift differences to be the differences in charge density induced by the substituent at one end of the chain. We thus sought to explore the implications of the TB and TS models computationally by using semi-empirical MO methods to calculate differences in charge density between the alkene carbon atoms and comparing them with differences in charge density deduced from the NMR shift differences. Firstly, to confirm our expectation that the simplest field effect should show an r^{-3} dependence on distance, we used the 'sparkle' facility in MOPAC to calculate the effect of a dipole on the charge distribution in (*Z*)-but-2-ene. Calculations were performed using the optimised geometry of (*Z*)-but-2-ene, in which a pair of charges, of one electron each, were placed on the extension of the C=C axis, with the positive charge at a variable distance, *r*, from the nearer carbon atom, and the negative charge 0.2 Å further away, as shown in Scheme 1. Charge densities were calculated without further optimization of geometry. The difference in charge, Δq, between the two olefinic carbon atoms was fitted to eqn. (3). As shown in



Scheme 1 Polarization of butene by 'sparkles'

$$\log(\Delta q) = -x \log(r) \qquad (3)$$

Fig. 2, for $r \geqslant 3.5$ Å, the fit is excellent, with $\rho = 0.999$ (22 points) and $x = 2.56 \pm 0.03$, confirming our expectation.

Secondly, we sought to confirm our alternative expectation that, if a TB effect operates, then both a fatty acid methyl ester and a reversed ester should show the same direction of polarization of the C=C bond, since both functional groups are electron withdrawing with respect to the long carbon chain. (In contrast, if a TS effect were to operate, then since the group dipoles are oriented in opposite directions with respect to the chain, the two series should show opposite directions of polarization of the C=C bond.) To this end, we carried out calculations for methyl (*Z*)-tridec-7-enoate and (*Z*)-dodec-6-enyl acetate, in which the only geometric constraint applied was that the heavy atoms were coplanar. In both cases, the difference in charge, Δq, between the two olefinic carbon atoms was $+0.0039$, with the proximal carbon atom more negative, indicating that the effect of the two polarizing groups had the same magnitude for both orientations of the ester group, and, more significantly, had the same, correct sign. To construct a model for the corresponding TS effects, we removed three of the methylenes separating the groups, and four methylenes from the ω-end, to leave, in both cases (*Z*)-but-2-ene and methyl acetate, as shown in Scheme 2. The remaining heavy atoms were constrained to be not only coplanar, but also to retain the same geometric relationships as in the TB models. For the truncated methyl ester, $\Delta q = +0.0023$, whereas, for the truncated acetate $\Delta q = -0.0029$, *i.e.* opposite in sign, as anticipated. The experimental results agree with the TB model. This approach is closely similar to the 'isolated molecule' calculations of Reynolds.[25]

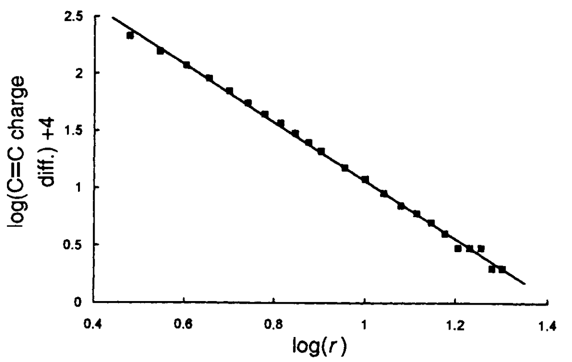


Fig. 2 Calculated variation of log(Δq), the C=C charge difference, +4, correlated with log(distance to the perturbing *ca.* 1 debye dipole) in an electrostatic model

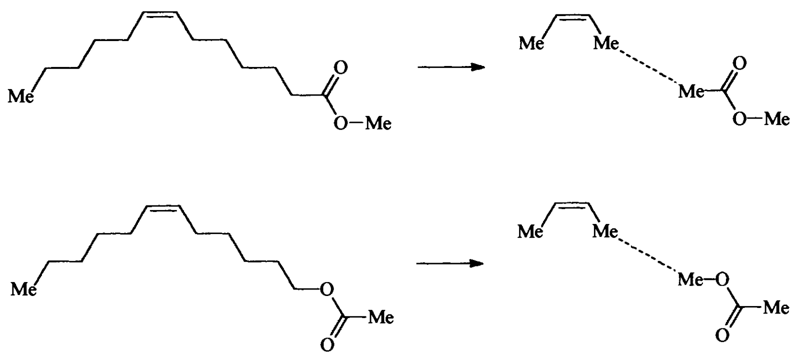
Thirdly, we wished to test the TB effect. For this, the obvious targets for calculation would be unsaturated fatty esters, themselves. However, we were aware that MO calculations had shown that a polar substituent, at one end of a chain, led to oscillation of charge density along the chain.[26] These results have normally been dismissed as artefacts of the calculation, though they persist in *ab initio* calculations with basis sets up to 6-31G.[27] Having confirmed that this still obtained at the AM1 level by performing a calculation for a saturated long-chain ester, we did carry out calculations for the series of methyl (*Z*)- and (*E*)-hexadec-*n*-enoates, in which the heavy atoms were constrained to be coplanar. The results showed three features: (*i*) the proximal carbon atoms were consistently more negative, (*ii*) Δq fell off with *n*, and (*iii*) the values for odd and even *n* oscillated about a mean fall-off curve. This oscillation precluded a meaningful test of the functional dependence of Δq on *n*, such as we had carried out for the experimental data, but the best fit of log (Δq) against *n* led to a fall-off factor of 1.45 ± 0.05 for the (*Z*) series (see Fig. 3) and 1.44 ± 0.04 for the (*E*) series. Furthermore, if we combine a typical value of *q*, *e.g.* for $n = 6$, with the empirical estimate quoted above, of 180 ppm per electron, we obtain estimated C=C shift separations of 1.4 ppm (*Z*) and 1.5 ppm (*E*). The experimental values are unexpectedly close to the smoothed values taken from the lines in Fig. 1, *viz.* 1.39 and 1.80 ppm respectively.

Discussion

Our experimental data and the semi-empirical calculations show that the shift dependence of the unsaturated carbons is inconsistent with a TS field effect, both numerically and algebraically, but is highly consistent with a TB mechanism. The slope of each fitted line in Fig. 1 is the same, within the very small experimental error, which shows that ε, the ÷1.75 attenuation factor for each additional saturated C–C bond, is a property of those bonds rather than of the dipolar group which generates $\Delta\delta_{C=C}$. The nature of the dipolar group does, however, determine the intercept of the line. If we give the (*Z*)-ester/ester line a normalized intercept of zero, then the corresponding intercept for (*E*)-acids is 0.169 and for simple (*Z*)-alcohols is -0.293. These correspond to shift factors of ×1.48 and ×0.51 respectively. In the (*E*) case, the increased shift differences must arise from a more ready polarization of the π-electrons in the C=C bond, under the influence of the TB

Table 3 ^1H and ^{13}C NMR shifts for (*Z*)-dec-5-enyl acetate in $CDCl_3$, 298 K

	CO	1	2	3	4	5	6	7	8	9	10
δ_H	—	4.24	1.66	1.38	2.04	5.31	5.35	2.00	1.29	1.29	0.86
δ_C	171.33	64.47	28.09	25.92	26.63	128.93	130.47	26.84	31.81	22.24	13.89



Scheme 2 Truncated molecule calculations

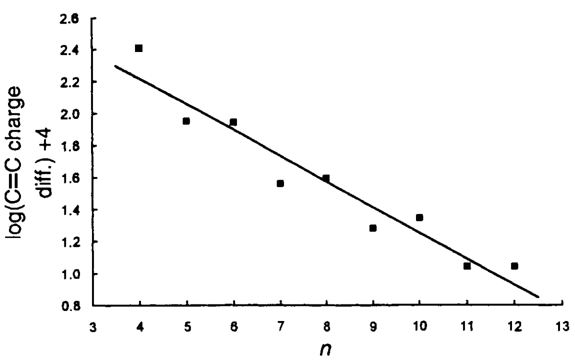


Fig. 3 Calculated variation of log(Δ*q*), the C=C charge difference, + 4, correlated with *n* in a through-bond model

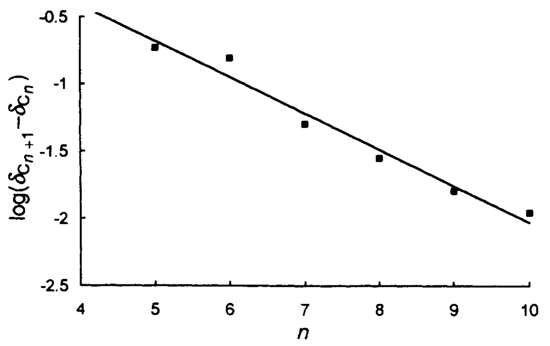


Fig. 4 $\log(\delta_{C-(n+1)} - \delta_{C-n})$ *vs. n*, the carbon position, for the central methylene resonances in palmitic acid

field. In the alcohol case, the source is likely to be the known, lower polarity of the C–OH bond relative to the C–OCOR bond. Our measured attenuation factor, $\varepsilon = 1.75$, agrees well with those measured in a quite different way by Paddon-Row.[9] It is also supported semi-quantitatively by our MOPAC calculations.

Very similar data are available for monoene chains in glyceryl triesters.[28] The attenuation factors are essentially identical, in both chains, to those listed above. However, most of the shift differences between the unsaturated carbons in the central, β chain are slightly greater than in the α chains, even at large *n*. The reasons for this are not fully known, but may in part be related to the additional electron-withdrawing effects of the more distant oxygens in the glycerol moiety.

Some care is necessary when interpreting the shifts at unsaturated carbon. Our MOPAC calculations show a decreasing gradient of induced net positive charge at the methylene groups, which originates at C-1. This gradient is consistent with an intuitive understanding of inductive effects. Each positive charge at C-*n* attracts a significantly smaller negative charge from C-($n + 1$), thus also rendering C-($n + 1$) positive, but less so than C-*n*. However, the unequal positive charges that result in the region of the double bond(s) also induce a reversed π-polarization of charge, which evidently dominates δ_C here, so that this is lowest at the unsaturated carbon nearest to O.

One might also enquire whether the charge gradient at saturated C is reflected at all in the methylene shifts. There is some evidence for this, even though the shift mechanism is unclear. Bengsch *et al.*[29] have published a comprehensive analysis of the carbon shifts in saturated long-chain fatty acids. Their most surprising observation, for which they offer no explanation, is that the shifts of the central carbons in all these chains increases monotonically with carbon number. Thus, if we take their data for palmitic acid (C_{16}) there is a steady increase in δ_C from C-5 to C-11. In fact, if we plot $\log_{10}(\delta_{C-(n+1)} - \delta_{C-n})$ against *n* for these carbons (Fig. 4), we obtain a reasonably straight line, with a gradient corresponding to an attenuation factor of ÷ 1.85 per added methylene. This equals the ÷ 1.75 factor deduced above, when allowance is made for possible errors arising from end-chain effects. Almost identical shifts are also observed for stearic acid (our data). It thus appears that the shifts at saturated C may be influenced by the same charge gradient as for unsaturated C, albeit to about $+\frac{1}{20}$ of the extent and with end-chain effects superimposed. Also, the same shifts at saturated carbon have the correct dependence on *n*, sign and approximate magnitude to offer a possible qualitative explanation of the slight asymmetry in the shifts at the double bond carbon pairs about their $n = \infty$ value, evident from eqns. (1) and (2).

Conclusions

All the above series of compounds show the same attenuation factor per intervening methylene, within experimental error, which must indicate that the mechanism of attenuation is independent of the 'reporter group' which senses it. This has useful implications for the analysis of *e.g.* unsaturated natural oils, for if any one member of a series of general formula R–(reporter group)–$(CH_2)_m$–(polar group) can be identified, with $m > 3$, then the carbon shift difference in the reporter group can be predicted for any other value of m, if this is also > 3, without recourse to any further experimental data, and without ambiguity. Other data also show that the size of the linear alkyl group R is unimportant if it is larger than butyl. We are currently seeking to extend our analysis to other chain types.

Our data also strongly support the dominance of the TB inductive effect in determining carbon shifts, although of course they cannot rule out competing TS effects below a level of about 10%. Thus we challenge the widely held assumption that TB effects attenuate rapidly.

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