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THE EFFECTS OF NON-BONDED INTERACTIONS IN SOLUTION ON PROTON RESONANCE SHIFTS

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Abstract The magnitude of bulk susceptibility (σ_B), dispersion force (σ_W), magnetic anisotropy (σ_A) and reaction field (σ_E) contributions to proton resonance shifts are estimated for selected situations. σ_B, σ_W and σ_E are shown to be capable of quite reasonable quantitative prediction for simple systems, whereas theoretical estimates of σ_A are shown to be, as yet, inaccurate. An experimental method for determining σ_A is described. The influence of the non-bonded interactions on chemical shifts is discussed by reference to the methyl proton shifts of hexamethyldisiloxane and tetramethylsilane.

THE use of internal reference compounds in NMR has been generally accepted for some time. Probably the most significant reason for adopting this form of referencing is that it avoids the necessity of correcting for differences in sample and external reference bulk susceptibility when the latter type of reference is used. The internal reference method affords a simple way of assessing and correlating shifts for routine analysis. It is, however, apparent that there is a tendency, when making detailed comparisons of internally referenced shifts, to overlook solution effects other than bulk susceptibility. The present work indicates the possible sources and magnitudes of error that can occur in making shift comparisons for molecules not involved in specific intermolecular bonding.

Proton resonance measurements, because of the relatively small natural shifts, are most likely to be significantly affected by solution effects. In the proton resonance field tetramethylsilane (TMS) is widely used as internal reference and for convenience the present work deals with measurements made relative to the methyl proton resonance of this compound. There are two conventional and essentially arbitrarily chosen scales based on TMS. One is the delta (δ) scale for which δ_{TMS} is defined as zero and the other the tau (τ) scale for which the τ value of TMS is 10 in carbon tetrachloride.[1] The τ scale will in preference to the δ scale be used herein. Unknown resonance positions should, in general, be determined relative to TMS at infinite dilution in carbon tetrachloride for the resulting τ values to have a consistent basis and be meaningful. For experimental convenience quoted τ values infrequently correspond to the infinite dilution criterion and to a first approximation these values, based on the position of TMS in low concentration (usually 0·5%), are acceptable. However, shifts relative to TMS in solvents other than carbon tetrachloride are also quoted in τ units and used indiscriminately for shift comparison. Whilst they may be satisfactory for approximate shift correlations solvent effects make accurate shift comparisons difficult because a specific solute resonance measured relative to TMS in different solvents may be found to have differing apparent τ values. Examples of

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[1] G. V. D. Tiers, *J. Phys. Chem* **62**, 1151 (1958).

this effect have been reported recently[2] for the methyl resonances of the methyl phenyldisiloxanes (Me_nPh_{3-n} Si—O—Si $Ph_{3-m}Me_m$ where m and $n \leqslant 3$ and may or may not be equal) which conventional measurement gave for each compound different apparent τ values for each resonance when studied in carbon tetrachloride, chloroform, cyclohexane and benzene as solvents. Even hexamethyldisiloxane, an apparently simple molecule, provided a spread of about 0·06 ppm on the measured values at infinite dilution in the different solvents.

In general, solvents can contribute to the shielding of solute molecules, relative to that in the gas phase, in four ways in the absence of specific intermolecular bonds. The contributions are due to (i) the bulk susceptibility of the solvent, (ii) the magnetic anisotropy of the solvent, (iii) the Van der Waals or dispersion forces between the solute and solvent molecules, and (iv) the influence of the reaction field, set up in the solvent, on the electron distribution in the solute when the latter is a polar molecule. The associated shielding contributions σ_B, σ_A, σ_W, and σ_E respectively, are related to the screening constant in the gas phase (σ_{gas}) and that observed in solution (σ_{obs}) by Eq. 1. As mentioned previously the choice of internal reference compounds

$$\sigma_{obs} = \sigma_{gas} + \sigma_B + \sigma_A + \sigma_W + \sigma_E \tag{1}$$

eliminates the necessity of correcting for σ_B. However, each of the contributions arising from (ii) to (iv) which modify the shielding of the solute and reference differently should be accounted for when making shift comparisons.

Several expressions have been derived for predicting the magnitudes of σ_A, σ_W and σ_E. Buckingham *et al.*[3] have shown that the anisotropic shielding of spherical molecules by firstly, disc shaped and secondly, rod shaped molecules may be calculated simply, but only semi-quantitatively, using Eqs 2 and 3 respectively. $\Delta\chi$ is the difference in magnetic susceptibilities parallel and perpendicular to the symmetry axis of the magnetically anisotropic molecule, R the distance from the centre of the

$$\sigma_A\,(\text{disc}) \approx \frac{-2n\,\Delta\chi}{3R^3} \tag{2}$$

$$\sigma_A\,(\text{rod}) \approx \frac{+n\,\Delta\chi}{3R^3} \tag{3}$$

anisotropic molecule to the centre of the resonating nucleus, n the number of molecules in the effective range of R, and θ the angle between the axis of the solvent molecule and the line joining the centre of the solvent and the nucleus under consideration. Eqs 2 and 3 result from limiting conditions for Eq. 4, which was also deduced by Buckingham *et al.*,[3] and is effectively equivalent to the more explicit

$$\sigma_A = \tfrac{1}{3}nR^{-3}\,\Delta\chi(1 - 3\cos^2\theta) \tag{4}$$

expression given by Stephen.[4] Abraham[5] has suggested Eq. 5 as a less qualitative and more generally applicable expression than Eqs 2 and 3.

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[2] J. Homer, A. W. Jarvie, A. Holt and H. J. Hickton, *J. Chem. Soc.* B, 67 (1967).

[3] A. D. Buckingham, T. Schaeffer and W. G. Schneider, *J. Chem. Phys.* **32**, 1227 (1960).

[4] M. J. Stephen, *Mol. Phys.* **1**, 223, (1958).

[5] R. J. Abraham, *Mol. Phys.* **4**, 369 (1961).

$$\sigma_A = -10^{30} \cdot \tfrac{2}{3}\Delta\chi \cdot \frac{r-h}{(r+2h)(r^2+h^2)^{\frac{1}{2}}} \tag{5}$$

This was derived by considering the anisotropic molecule to be a cylinder of effective radius r (Å) and height $2h$ (Å) with different magnetic suceptibilities $\chi_{||}$ and $\chi_{\perp}$ along and perpendicular to the cylinder axis, considered arising from an equivalent dipole acting along this axis. Eq. 5 does, however, only provide an estimate of the shielding contribution from a single anisotropic molecule.

The contribution of Van der Waals or dispersion forces to the shielding of a molecule has been shown[6] to be represented by

$$\sigma_W = \tfrac{3}{4}\phi\, hg[v_1 v_2 (v_1 + v_2)] \tag{6}$$

where

$$g = [(2n^2 - 2)(2n^2 + 1)]\, a^3, \tag{7}$$

n is the refractive index of the solvent and a the radius of the solute which can be deduced from its molar volume. v, a mean absorption frequency (the subscripts 1 and 2 refer respectively to solvent and solute) can be deduced from Eq. 8 or often more conveniently from Eq. 9. In these expressions I is the ionization potential, α the

$$v = \frac{I}{h} \tag{8}$$

$$v = -[4\mathrm{mc}^2\, hN_o\alpha]\chi \tag{9}$$

optical polarizability and χ the molar diamagnetic susceptibility of the appropriate solution component. The value of ϕ in Eq. 6 is characteristic of the nuclear species. Marshall and Pople[7] indicate that $\phi = -0{\cdot}74 \times 10^{-12}$ cm^2 esu^{-1} ppm for the hydrogen atom whereas -1×10^{-12} cm^2 esu^{-1} ppm has been used[8,9] for bonded hydrogen.

When polar solutes are being studied the surrounding medium is polarized and the solute experiences a reaction field which modifies the electron distribution within the solute molecule and, therefore, the shielding of the nuclei. A similar effect can also occur for non-polar solutes containing highly polar groups because a quadrupole moment in the solute can lead to reaction fields that modify the solute resonance condition. The shielding contribution σ_E due to a reaction field E has been shown[8] to be expressed approximately in the form of Eq. 10 where, for a sufficiently

$$\sigma_E = -2 \times 10^{-12} E\cos\theta - 10^{-18} E^2 \tag{10}$$

symmetrical solute, θ is the angle between the dipole axis and the H—X bond for the solute proton considered. The most significant reaction field normally encountered for solutions of polar molecules has been defined in two ways. Firstly, Buckingham[8] followed the approach of Onsager[10] to define E in the form of Eq. 11 where ε is the medium dielectric constant and n and α the refractive index and polarizability of the

$$E = \frac{2(\varepsilon - 1)(n^2 - 1)\mu}{3(2\varepsilon + n^2)\alpha} \tag{11}$$

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[6] B. B. Howard, B. Linder and M. T. Emerson, *J. Chem. Phys.* **36**, 485, (1962).

[7] T. W. Marshall and J. A. Pople, *Mol. Phys.* **1**, 199 (1958).

[8] A. D. Buckingham, *Canad. J. Chem.* **38**, 300 (1960).

[9] A. A. Bothner-By, *J. Mol. Spec.* **5**, 52 (1960).

[10] L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).

solute respectively. The solute is considered as a sphere having a point electric dipole effective from its centre with μ the gas phase value. Diehl and Freeman[11] have accounted for the shape of the solute molecules in Eq. 12 by considering the dipole to act from the centre of a non-spherical cavity with semi-axes a, b and c.

$$E = \frac{\mu}{abc}\, 3\xi_a[1 + (n^2 - 1)\xi_a]\left[\frac{(\varepsilon - 1)}{\varepsilon + (n^2\xi_a)/(1 - \xi_a)}\right] \qquad (12)$$

ξ_a is a shape factor for the solute which can be deduced by the method of Ross and Sack.[12] The choice of Eqs. 11 and 12 to best represent E can be decided readily by considering a simple polar solute such as chloroform in a non-polar solvent such as cyclohexane. Using the values $\mu_{gas} = 1{\cdot}01 \times 10^{-18}$ esu,[13] $\xi_a = 0{\cdot}364$, $a = 2{\cdot}05$ Å, $b = c = 3{\cdot}25$ Å,[13] $n_{18} = 1{\cdot}44643$,[14] and $\alpha = 0{\cdot}819 \times 10^{-23}$ cc for chloroform[15] and $\varepsilon_{20} = 2{\cdot}023$ for cyclohexane[14] enables the values $14{\cdot}96 \times 10^3$ and $22{\cdot}61 \times 10^3$ for E to be deduced respectively from Eqs. 11 and 12. Taking $\cos\theta = +1$ and neglecting the second term of equation 10 the respective corresponding values of σ_E are $-0{\cdot}030$ ppm and $-0{\cdot}045$ ppm. The quantitative significance of these values may be ascertained by considering the dipole moment of chloroform in cyclohexane relative to the gas phase value. The measured solution dipole moment μ_m is defined[11] by

$$\mu_m = \mu + \alpha_1 E \qquad (13)$$

in which α_1 is the polarizability of the solute along the dipole axis; α_1 is required by the model used to derive Eq. 12, whereas α, the normal polarizability, is required by that used in the derivation of Eq. 11. The value of α_1 for chloroform[15] is $0{\cdot}588 \times 10^{-23}$ cc and μ_m is $1{\cdot}196 \times 10^{-18}$ esu.[16] Substitution of these values in Eq. 13 yields a value for E of $31{\cdot}63 \times 10^3$. Alternatively, using $\alpha = 0{\cdot}819 \times 10^{-23}$, E is found to be $22{\cdot}71 \times 10^3$. It would appear, therefore, that (12) should be used in preference to (11) when predicting absolute values for σ_E. However, because σ_E values are generally required for comparison purposes the use of Eq. 11 will not invoke serious errors but will beneficially avoid the necessity of assessing ξ_a for each solute molecule. Eq. 11 will accordingly be used in the following discussion.

It is possible to test experimentally the quantitative accuracy of the expressions predicting σ_A, σ_W, and σ_E. The terms σ_W and σ_E will be considered first. If, for example, the methyl proton shifts of hexamethyldisiloxane relative to TMS are measured in the solvents cyclohexane, carbon tetrachloride, chloroform, benzene and carbon disulphide the only terms of Eq. 1 that can modify the shifts are σ_W and σ_E assuming the anisoptropic effect of a solvent is independent of the shape of the solute. The measured shifts of hexamethyldisiloxane at the same mole concentration as TMS are respectively 9·947, 9·947, 9·939, 9·885 and 9·961 τ. If Eqs. 6 and 11 leading to σ_W and σ_E respectively are quantitatively acceptable for comparative correction purposes then each shift

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[11] P. Diehl and R. Freeman, *Mol. Phys.* **4**, 39 (1961).

[12] I. G. Ross and R. A. Sack, *Proc. Phys. Soc.* **B63**, 893 (1950).

[13] A. D. Buckingham and R. J. W. Le Fèvre, *J. Chem. Soc.* 1932 (1952).

[14] *Handbook of Chemistry and Physics*, The Chemical Rubber Publishing Co. (1961).

[15] C. G. Le Fèvre and R. J. W. Le Fèvre, Rev. *Pure and Applied Chem.* **5**, 261 (1955).

[16] R. P. Young, A. Holt and S. Walker, *Tetrahedron* **20**, 2351 (1964).

should be capable of correction within experimental error to the same value. The characteristic data of each compound necessary for the calculations are given in Table 1. The σ_W contributions to the shielding of TMS and hexamethyldisiloxane can be computed readily for the different solvents and have the values given in Table 2. The evaluation of the σ_E contributions to the shielding of hexamethyldisiloxane in the various solvents is not simple because of the difficulty in obtaining a value for θ

TABLE 1. MOLECULAR DATA[l] USED IN THE CALCULATION OF THE VALUES GIVEN IN TABLE 2

Compound	Molar volume	Refractive index	Optical polarizibility	Molar diamagnetic susceptibility	Dielectric constant	Dipole moment
	cc		× 10^{24} cc	× − 1 × 10^6 cc cc/mole		Debyes
Tetramethylsilane	137·62[a]	—	12·78[e]	72·16[i]		
Hexamethyldisiloxane	214·23[a]	1·3741[b]	21·83[f]	119·34[i]		0·77[k]
Cyclohexane		1·42354[c]	10·87[c]	68·13[c]	2·015[d]	
Carbon tetrachloride		1·45759[c]	10·24[c]	66·6[c]	2·228[d]	--
Chloroform		1·44643[d]	8·32[c]	59·3[c]	4·718[d]	
Benzene		1·50112[d]	9·87[g]	54·84[j]	2·274[d]	
Carbon disulphide	--	1·6295[d]	8·32[h]	41·0[j]	2·628[d]	

[a] Calculated from densities taken from *b*.

[b] V. Bažant, V. Chvalovský and J. Rathouský. *Organosilicon Compounds*. Czechoslovak Academy of Sciences (1965).

[c] Ref. 6.

[d] Ref. 14.

[e] Calculated from the data of A. P. Altshuller and L. Rosenblum, *J. Am. Chem. Soc.* **77**, 272 (1955).

[f] Calculated from the data of R. S. Holland and C. P. Smyth, *J. Am. Chem. Soc.* **77**, 268 (1955).

[g] Ref. 15.

[h] Calculated from data given by C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.* 487 (1936).

[i] Estimated from Pascal's constants.

[j] Ref. 18.

[k] The average of values given by H. Freiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.* **75**, 2824 (1953); R. O. Sauer and D. J. Mead, *Ibid.*, **68**, 1794 (1946) and A. A. Gundyrev, N. S. Nametkin and A. V. Topchiev, *Dokl. Akad. Nauk. S.S.S.R.* **121**, 1031 (1958).

[l] All temp dependent data are quoted for 25° or as close thereto as possible.

TABLE 2. CALCULATED SOLUTE–SOLVENT INTERACTION CONTRIBUTIONS (ppm) TO THE SHIELDING OF TETRAMETHYLSILANE AND HEXAMETHYLDISILOXANE IN SELECTED SOLVENTS

Solvent	TMS	Hexamethyldisiloxane	
	σ_W	σ_W	σ_E
Cyclohexane	−0·090	−0·057	−0·007
Carbon tetrachloride	−0·097	−0·061	−0·008
Chloroform	−0·099	−0·063	−0·014
Benzene	−0·095	−0·060	−0·008
Carbon disulphide	−0·103	−0·065	−0·010

in Eq. 10. Furthermore, in view of the uncertainty regarding the geometry of hexamethyldisiloxane, it could be misleading to assess a definite value for θ. In fact if all rotations in the molecule are considered perfectly unrestricted θ could vary between 0 and 180° resulting in a zero σ_E contribution. If however, as is possible, small steric interactions preclude certain geometric arrangements a real and effective value for θ could arise. The σ_E contributions to the shielding of hexamethyldisiloxane which are given in Table 2 for the various solvents are the maximum values possible. Using the appropriate values from Table 2 the observed shifts are readily corrected assuming negligible solute solute interactions at the low concentration used. The shifts, corrected to the τ scale in carbon tetrachloride, are

C_6H_{12}	CCl_4	$CHCl_3$	C_6H_6	CS_2
9·949	9·947	9·945	9·886	9·961

The shifts in the first three solvents correspond within the limits set by the experimental accuracy. The value in benzene remains low. This is probably due to dipole-induced dipole association of the hexamethyldisiloxane with the benzene in such a way that a complex is formed with the hexamethyldisiloxane oxygen on the benzene six-fold axis. This could place the methyl protons in a relatively deshielded region and give the lower than normal shift as observed. The corrected value in carbon disulphide is still unaccountably high. If this discrepancy is attributed to the dependence of solvent effective anisotropy on solute shape the shielding observed is contrary to that predicted[3] for rod-shaped solutes in rod-shaped solvents.

It appears from the preceding evidence that the σ_W and σ_E contributions to the shifts of simple non-bonded solutes in solution may be corrected for in a reasonably quantitative manner. On the other hand, the several expressions for predicting σ_A invariably produce only semi-quantitative agreement with the few experimentally determined solvent magnetic anisotropies. For example, Stephen[4] predicts a value of +0·47 ppm for benzene using an expression similar to Eq. 4, Buckingham *et al.*[3] 1·3 ppm for benzene and −0·5 ppm for carbon disulphide using Eqs. 2 and 3 respectively, Abraham[5] +0·08 ppm and −0·046 for single benzene and carbon disulphide molecules using Eq. 5. The value obtained by Bothner-By and Glick[17] for benzene was corrected by Abraham[5] to 1·51 ppm. The experimental values determined previously for benzene are quoted as +0·6 ± 0·05 ppm,[17] +0·33 ppm,[3] and +0·42 to +0·43 ppm,[5] and those for CS_2 −0·42 ppm,[3] and −0·13 to −0·14 ppm.[5] The procedure adopted by Abraham[5] for determining σ_A appears satisfactory to a point since he compared the shift of a non-polar solute in the anisotropic solvent with that of the same solute in a similarly constituted solvent of identical bulk susceptibility. This procedure eliminates the uncertainty due to bulk susceptibility corrections. However, whilst it was claimed by him that σ_W corrections are also avoided it is apparent from Eqs. 7 and 9 that unless the refractive index and optical polarizability of the two solvents are also identical this is not true. Furthermore, the method is based on the assumption that the magnetic anisotropy of the normal solvent, e.g. cyclohexane, is negligible. To ascertain the approximate order of magnitude of the magnetic anisotropic shielding by the so-called normal solvent cyclohexane, its shift at low concentration in carbon tetrachloride was measured relative to neat cyclohexane as external reference. After correcting for bulk susceptibility differences and

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[17] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.* **26**, 1651 (1957).

neglecting σ_W contributions the shift indicates that the anisotropic shielding of cyclohexane is of the order of +0·1 ppm. In view of the possible deficiencies in Abraham's method an alternative procedure is now proposed which does necessitate correction for σ_B and σ_W. The shift of a non-polar and isotropic solute (TMS) is measured in the various solvents relative to the same solute in carbon tetrachloride which is taken as the isotropic standard. The same low concentration of solute is used in each of the solvents. For each anisotropic solvent two samples are prepared. One consists of the solute in the anistropic solvent contained in a normal precision cylindrical tube in which is sited a precision capillary filled with the solute—carbon tetrachloride solution. The other sample contains the carbon tetrachloride solution in the main tube and the anisotropic solvent solution in the capillary. The solute resonances in the two solutions of one sample can be identified on relative intensity grounds. The shifts obtained using TMS as isotropic solute with the five solvents studied herein are recorded in Table 3. It can be seen that the magnitudes of the two shifts obtained for each anisotropic solvent system differ. These shift differences are expected because, in general, if the shift between two samples A and B, with volume susceptibilities χ_A and χ_B respectively, is measured first with B in the main tube and A in a reference vessel and then with the sample positions reversed the two observed shifts (δ^o_{B-A} and δ^o_{A-B}) are related to the true shift ($\delta^T_{B-A} = -\delta^T_{A-B}$) by different equations which are 14a and 14b in which α_1 and α_2 are shape factors characteristic of the internal and external surfaces of the reference vessel. These expressions, which were

TABLE 3. THE PROTON SHIFTS OF TMS IN SELECTED ANISOTROPIC SOLVENTS RELATIVE TO THAT IN CARBON TETRACHLORIDE

Solvent in Capillary	Solvent in Main tube	δ (ppm)*	Solvent in Capillary	Solvent in Main tube	δ (ppm)*	δ average, corrected for $\Delta\sigma_B$
CCl_4	CCl_4	Not detected				
CCl_4	C_6H_{12}	+0·253	C_6H_{12}	CCl_4	0·259	+0·122
CCl_4	$CHCl_3$	0·074	$CHCl_3$	CCl_4	+0·077	+0·027
CCl_4	C_6H_6	+0·654	C_6H_6	CCl_4	−0·662	+0·490
CCl_4	CS_2	−0·132	CS_2	CCl_4	+0·149	−0·124

* These shifts are, for convention, given relative to the resonance of TMS in the capillaries.

$$\delta^T_{B-A} = \delta^0_{B-A} - \left[\left(\frac{4\pi}{3} - \alpha_1\right)\chi_A + (\alpha_1 - \alpha_2)\chi_g + \left(\alpha_2 - \frac{4\pi}{3}\right)\chi_B\right] \tag{14a}$$

$$\delta^T_{A-B} = \delta^0_{A-B} - \left[\left(\frac{4\pi}{3} - \alpha_1\right)\chi_B + (\alpha_1 - \alpha_2)\chi_g + \left(\alpha_2 - \frac{4\pi}{3}\right)\chi_A\right] \tag{14b}$$

deduced by Frost and Hall,[19] are independent of the geometry of the main tube. However, depending on the geometry of the reference vessel, they show that the corrections to the observed shifts, necessary to obtain the true shift, can depend on the susceptibilities of A,B and the material from which the reference vessel is constructed (χ_g). For a perfectly spherical vessel $\alpha_1 = \alpha_2 = (4\pi/3)$ and no correction is necessary.

For a perfectly cyclindrical vessel, with length large compared with radius, $\alpha_1 = \alpha_2 = 2\pi$ and the well-known susceptibility correction is necessary and Eqs 15a and 15b are applicable. If $\alpha_1 \neq \alpha_2$ the measured shifts should ideally be corrected according

$$\delta^{T}_{B-A} = \delta^{0}_{B-A} + (2\pi/3)(\chi_A - \chi_B) \tag{15a}$$

$$\delta^{T}_{A-B} = \delta^{0}_{A-B} - (2\pi/3)(\chi_A - \chi_B) \tag{15b}$$

to either Eq. 14a or 14b as appropriate. However, it is possible to express the true shift (now denoted by δ^{T1}_{B-A}) in terms of the two observed shifts in the form of Eq. 16

$$\delta^{T1}_{B-A} = \tfrac{1}{2}(\delta^{0}_{B-A} - \delta^{0}_{A-B}) + \tfrac{1}{2}(\chi_A - \chi_B)[\alpha_1 + \alpha_2 - (8\pi/3)] \tag{16}$$

which is independent of χ_g. If a perfectly cylindrical vessel is used Eq. 16 reduces to Eq. 17.

$$\delta^{T2}_{B-A} = \tfrac{1}{2}(\delta^{0}_{B-A} - \delta^{0}_{A-B}) + (2\pi/3)\ (\chi_A - \chi_B) \tag{17}$$

Consequently, if as is the normal practice, imperfect cyclindrical reference vessels are assumed to be perfect the approximately correct shift (δ^{T2}_{B-A}), obtained from Eq. 17, differs from the actual shift by the amount given by

$$\delta^{T1}_{B-A} - \delta^{T2}_{B-A} = \tfrac{1}{2}(\chi_A - \chi_B)[\alpha_1 + \alpha_2 - 4\pi] \tag{18}$$

One further general point is also apparent. This is that because for most capillaries $\alpha_1 \neq \alpha_2$ any single externally referenced shift corrected using Eqs 15a or 15b will provide an apparent true shift which can be subject to appreciable error. In the case of the observed shifts given in Table 3 each value was obtained using a different capillary. Therefore, if in the two experiments we assume the shape factors for the capillary containing A to be α_1 and α_2 and α^1_1 and α^1_2 for that containing B, the equations analogous to 16 and 18 are respectively

$$\begin{aligned}\delta^{T1'}_{B-A} = \tfrac{1}{2}(\delta^{0}_{B-A} - \delta^{0}_{A-B}) + \tfrac{1}{2}\chi_A[\alpha_1 + \alpha^1_2 - (8\pi/3)] - \tfrac{1}{2}\chi_B[\alpha_2 + \alpha^1_1 - (8\pi/3)]\\ - \tfrac{1}{2}\chi_g(\alpha_1 - \alpha_2 - \alpha^1_1 + \alpha^1_2)\end{aligned} \tag{19}$$

and

$$\begin{aligned}\delta^{T1'}_{B-A} - \delta^{T2}_{B-A} = -2\pi(\chi_A - \chi_B) + \tfrac{1}{2}\chi_A(\alpha_1 + \alpha^1_2) - \tfrac{1}{2}\chi_B(\alpha_2 + \alpha^1_1) - \tfrac{1}{2}\chi_g(\alpha_1 - \alpha_2\\ - \alpha^1_1 + \alpha^1_2)\end{aligned} \tag{20}$$

In order to test the departure of the reference vessels from perfectly cylindrical geometry Eq. 21, which gives the difference in magnitude of the observed shifts, can be used. The discrepancies between each pair of shift values given in Table 3 indicate,

$$\delta^{0}_{B-A} + \delta^{0}_{A-B} = \chi_g(\alpha_1 - \alpha_2 + \alpha^1_1 - \alpha^1_2) - \chi_A(\alpha_1 - \alpha^1_2) - \chi_B(\alpha^1_1 - \alpha_2) \tag{21}$$

because none of the susceptibilities are zero, that the capillaries are not perfect cylinders. Because of the difficulty in estimating α_1, α_2, α^1_1 and α^1_2 and the fact that the currently proposed method for estimating σ_A is inherently subject to errors by virtue of the uncertainty in the corrections for σ_W it will suffice to assume that since precision capillaries were used the condition $\alpha_1 = \alpha^1_1 = \alpha_2 = \alpha^1_2 = 2\pi$ is valid. Approximately correct shifts can then be estimated using Eq. 17. The values obtained in each case differ from the actual values by amounts defined by Eq. 20. The average shifts, corrected for bulk susceptibility differences, are shown in Table 3. Correction for differences in σ_W, predicted in Table 2, enable the effective solvent anisotropies to be calculated. The final σ_A contributions for each solvent, given in Table 4, should only be considered significant within a range defined by the difference in the two uncorrected δ values for each system given in Table 3. The values for benzene ($+0{\cdot}488$ ppm) and carbon disulphide ($-0{\cdot}118$ ppm) agree favourably with those reported by Abraham, although agreement in the case of benzene is perhaps fortuitous in view of the assumption of negligible anisotropy of the normal solvent standard cyclohexane, made by Abraham. It is worthy of emphasis that cyclohexane which is generally considered a normal solvent does provide a large (0·115) positive magnetic anisotropic shielding.

TABLE 4. THE ANISOTROPIC SHIELDING EFFECTS (σ_A) OF SOME SOLVENTS

Solvent	σ_A (ppm)
Cyclohexane	+0·115
Chloroform	+0·029
Benzene	+0·488
Carbon disulphide	0·118

One final point now becomes apparent. This is that if the strict definition[1, 18] of the τ scale is adhered to, the reference shifts of TMS in solvents other than carbon tetrachloride should not be taken as 10 but that shift appropriately corrected for σ_B, σ_A and σ_W relative to the carbon tetrachloride scale. That is, in cyclohexane, chloroform, benzene and carbon disulphide the absolute shifts of TMS should be 10·256, 9·924, 10·658 and 9·859 τ respectively. However, for internal reference purposes the bulk susceptibility corrections included in the above values are unnecessary and, furthermore, unless the lengthy corrections for all other solute-solvent effects relative to the conventional scale are undertaken the measured shifts will still not be related directly to the inferred[1] absolute scale.

EXPERIMENTAL

The proton resonance spectra were obtained at 34° using a Perkin-Elmer R10 spectrometer operating at 60·004 Mc/s. Shift measurements were made using the conventional sideband technique employing a Muirhead-Wigan D-890-A oscillator to provide the calibration signals, the frequencies of which were assessed with a Venner 3336 frequency counter. The shift values quoted were measured to an estimated accuracy of ±0·004 ppm. Precision drawn cylindrical (0·181 inch) sample tubes containing precision 2 mm diameter reference capillaries were used for all measurements.

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[18] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1. Pergamon Press (1965).

[19] D. J. Frost and G. E. Hall, *Mol. Phys.* **10**, 191 (1966).