Aromatic Solvent Induced Shifts in Molecules with and without a Permanent Electric Dipole Moment

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It is shown that there is little justification for regarding aromatic solvent induced shifts as being of a chemical origin. A literature method of determining the direction of molecular dipole moments is criticised. Data are presented for molecules which have no net dipole moment, and for some which do; the latter are analysed in terms of the approach of Laszlo and Engler.

WORK by Verkade *et al.*[1-3] advocates the use of aromatic solvent induced (chemical) shifts (ASIS) to determine the direction of electric dipole moments in molecules. This is an important problem, and it is necessary to examine the validity of the method in order to assess the possibility of wider application. Since the interpretation of ASIS is still controversial [4] we shall examine in the wider sense the fundamental assumptions made in such studies.

The method is based upon consideration of ASIS observed in [$^2H_6$]benzene and hexafluorobenzene as solvents, with CCl_4 as a reference 'non-interacting' solvent. In order to interpret such data a dipole induced-dipole model, based upon that of Schneider [5] is used in which one or more aromatic solvent molecules tend to associate with the solute dipole. It is postulated that benzene tends to lie as far away as possible from the negatively charged region of the dipole (hence inducing high-field shifts of protons at the 'positive' end) while hexafluorobenzene has the opposite preference and induces high-field shifts of protons at the *negative* end. The validity of such a model has recently been criticised,[6] but the usefulness of the approach seems to be unquestioned.

It is clear that ASIS derives mainly from a large diamagnetic anisotropy ($\psi_{\parallel} - \psi_{\perp}$) in the solvent. It is an inherent (though unstated) assumption that the diamagnetic anisotropy of C_6F_6 is of the same sign as in benzene. The former ring carbon skeleton is very electron deficient however (as witnessed by chemical as well as spectroscopic evidence) and it is at least arguable that the diamagnetic anisotropy may be of *opposite* sign. We know of no evidence to support either standpoint, but the consequence of such a sign reversal would be a high-field induced shift without there being any difference in the relative orientations of the solute and solvent molecules.

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[1] R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 2702.

[2] J. Mosbo and J. G. Verkade, *J. Magnetic Resonance*, 1972, **8**, 250.

[3] T. J. Barton, R. W. Roth, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1972, **94**, 8854.

[4] M. I. Foreman, 'Nuclear Magnetic Resonance,' Specialist Periodical Reports, The Chemical Society, London, 1976, vol. 5, p. 295.

[5] W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

[6] M. I. Foreman, 'Nuclear Magnetic Resonance,' Specialist Periodical Reports, The Chemical Society, London, 1974, vol. 3, p. 347 *et seq.*

It is well established that non-dipolar molecules, such as symmetrical *para*-disubstituted benzenes which have significant electric *quadrupole* moments but no dipole moment, also show ASIS.[7-9] It is the object of the present work to examine ASIS in several dipolar and non-dipolar solutes, using C_6D_6 and C_6F_6 as solvents and to examine the basis of the models and interpretations given elsewhere.[1-3]

EXPERIMENTAL

All solutes and solvents were commercially obtained, and used without further purification. Spectra were recorded with a Varian Associates HA 100 n.m.r. spectrometer using frequency sweep. Line positions were recorded by the frequency difference technique using a RACAL frequency counter (801R). All samples were examined as a series of dilute solutions in the various solvents, and chemical shift measurements (from internal tetramethylsilane) were extrapolated to infinite dilution.

RESULTS AND DISCUSSION

Table 1 lists the chemical shifts of the protons in cyclohexane, 1,4-dioxan, benzene, *p*-difluorobenzene, *p*-dimethoxybenzene, and *p*-dinitrobenzene; data are given for solutions in CCl_4, C_6D_6, and C_6F_6, and the magnitudes of the ASIS (positive to high field) are quoted. Also included in Table 1 are data, taken from the literature, for some other dipolar and quadrupolar molecules.

TABLE 1

Chemical shifts of solute protons in various solvents

Solute	Site of ^1H	δCCl_4	δC_6D_6	$\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$	δC_6F_6	$\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6F_6}}$	Reference
Benzene		7.263	7.149	+0.114	7.197	+0.066	
p-Difluorobenzene		6.970	6.509	+0.461	6.810	−0.011	
p-Dimethoxybenzene	Ring	6.692	6.759	−0.067	6.513	+0.179	
	OCH_3	3.706	3.348	+0.358	3.746	−0.040	
1-4-Dioxan		3.571	3.356	+0.215	3.466	+0.105	
Cyclohexane		1.434	1.402	+0.032	1.434	0.000	
p-Benzoquinone				+0.50			8
p-Dinitrobenzene		8.402	7.328	1.074	8.595	−0.193	
Pyrazine				+0.50			*a*
Tetrahydrofuran	β	1.794	1.433	+0.361	1.845	−0.051	3
	α	3.619	3.573	+0.046	3.514	+0.105	
Furan	β	6.299	6.084	+0.215	6.283	+0.016	3
	α	7.363	7.135	+0.228	7.254	+0.109	
Pyrrolidine	β	1.625	1.396	+0.229	1.738	−0.113	3
	α	2.772	2.648	+0.124	2.809	−0.037	
Pyrrole	β	6.087	6.314	−0.227	5.885	+0.202	3
	α	6.606	6.381	−0.225	6.610	−0.004	
Tetrahydrothiophen	β	1.915	1.479	0.436	1.998	0.083	3
	α	2.752	2.547	0.205	2.714	0.038	
Thiophen	β	7.064	6.847	0.217	7.028	0.036	3
	α	7.221	6.905	0.316	7.167	0.054	

[a] J. N. Murrell and V. M. S. Gil, *Trans. Faraday Soc.*, 1965, **61**, 402.

Consideration of these data, together with the diagram in ref. 9, leads to several conclusions. (a) The sign of $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$ * for the ring protons in the symmetrical *para*-disubstituted aromatic molecules is negative if the substituents are electron releasing (OMe), and positive for benzene itself and for benzene bearing electron-withdrawing groups. It may be numerically larger than in the *dipolar* ' aromatic ' heterocyclic molecules. (b) The sign and magnitude of $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$ in the saturated quadrupolar molecule 1,4-dioxan (+0.215) is the same as in the saturated dipolar molecules tetrahydrofuran (α +0.046; β +0.361) and pyrrolidine (α +0.124; β +0.229). (c) The non-polar molecules cyclohexane and benzene have small ASIS (+0.032, +0.0114) but nevertheless they are comparable to the α-protons in the dipolar tetrahydrofuran (+0.046) or pyrrolidine (0.124). (d) $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6F_6}}$ for quadrupolar aromatic molecules may be negative or positive (*p*-dinitrobenzene −0.193, *p*-dimethoxybenzene +0.179), as is also the case for the dipolar heterocyclic aromatic species (pyrrole, α −0.004, β +0.202). (e) $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6F_6}}$ for 1,4-dioxan is positive (+0.102) and in the saturated dipolar heterocycles it may be positive (tetrahydrofuran, α +0.105) or negative (tetrahydrofuran, β −0.051, pyrrolidine, α −0.037, β −0.113). (f) There is the well established [1-3,9] relationship between the signs and magnitudes of $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6F_6}}$ for the different situations (thus in *p*-dinitrobenzene $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$ is positive and $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6F_6}}$ negative, while in *p*-dimethoxybenzene the converse is true).

It is obvious from these data however that there is little justification for relating ASIS in either C_6D_6 or C_6F_6 to the direction or magnitude of molecular *dipole* moments, and conclusions reached by such a procedure (*e.g.* that the direction of the dipole moment in furan is not the same as in pyrrole [3] must be treated with caution. especially in cases where a dipolar molecule also has a significant quadrupole moment.

It is possible that the ASIS observed for molecules with finite electric quadrupole moments may arise from a ' quadrupole induced-quadrupole ' interaction with the

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* $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$ = Chemical shift difference for a solute in these two solvents.

[7] P. Diehl, *Helv. Chim. Acta*, 1962, **45**, 568.

[8] J. V. Hatton and W. G. Schneider, *Canad. J. Chem.*, 1962, **40**, 1285.

[9] K. Nikki, N. Nakahata, and N. Nakagawa, *Tetrahedron Letters*, 1975, 3811.

aromatic solvent as suggested by Schneider.[5] Alternatively, Ronayne and Williams [10] suggest that there is a ' stereospecific solvation at the most important electron-deficient sites ' in such molecules. Nikki *et al.*[9,11,12] specify dipole (solute)–quadrupole (solvent) or quadrupole (solute)–quadrupole (solvent) interactions as being responsible for the association.

The problem with these suggestions is that they do not lend themselves to quantitative assessment of the magnitudes of ASIS to be expected in a given situation. It seems unlikely to the present authors that the direct dipole–quadrupole or quadrupole–quadrupole interactions suggested by Nikki *et al.* could be sufficiently large to cause significant association. The quadrupole moment of benzene is very small [13] and benzene itself, viewed as a solute in [$^2H_6$]benzene, has an ASIS ($\Delta^{CCl_4}_{C_6D_6}$) which is comparable to that in many dipolar species! These authors have recently attempted to calculate the energy of interaction between a solute and solvent benzene, arising from dipole induced-dipole and dipole–quadrupole terms.[14] They then proceed to calculate the resultant ASIS, and conclude that the latter term dominates both orientation and ASIS. This is, however, open to question. The calculation is necessarily complex, and the approximations of point dipole and quadrupole in spherical molecules critical. The major difficulty arises in evaluating an integration over a volume of space which does not include the solute cavity; equal weight is given to a distance between molecular centres (4.5 Å) which brings the solute and solvent closer together than the sum of their van der Waals radii, and all distances up to 10.5 Å at which point the interaction is essentially zero. The very short distances completely dominate the calculated values of ASIS, and a more realistic appraisal allowing for the increased *repulsions* as the molecules approach collision (*e.g.* by limiting the closest approach to 5.5—6.0 Å) would result in estimated ASIS, an order of magnitude less than experimental.

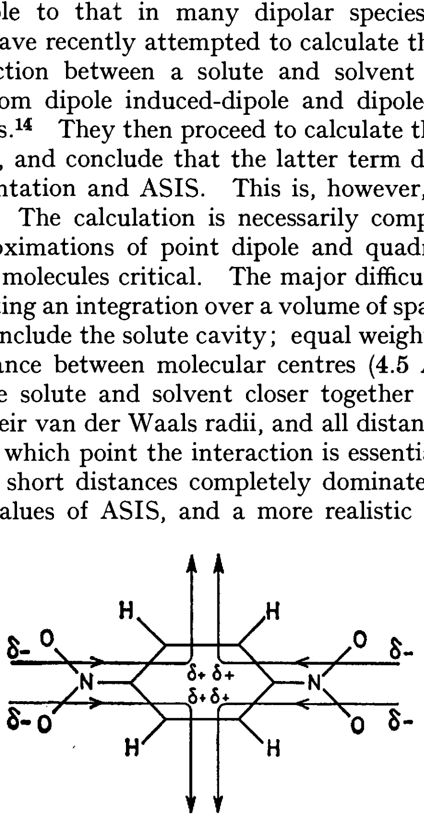

FIGURE 1

Similarly, difficulties befall the quadrupole induced-quadrupole picture. For example, in *p*-dinitrobenzene the quadrupolar field has the shape shown in Figure 1 and the ring is electron deficient. The quadrupolar field induced in the planar solvent molecules may cause some degree of association to occur, with a corresponding high-field ASIS. *para*-Dimethoxybenzene is somewhat different. It is generally recognised that the direction of the dipole moment of anisole (and hence of the Ar–OMe bond) is of opposite sign to that of nitrobenzene; this is demonstrated by the fact that the dipole moment of *p*-nitroanisole is given approximately by the sum of the dipole moments of anisole and nitrobenzene and not by the difference between these values [μ($PhNO_2$) 4.22, μ(PhOMe) 1.38, μ(*p*-$NO_2C_6H_4OMe$) 5.26 D].[15] The quadrupolar field of *p*-dimethoxybenzene has the form shown in Figure 2.

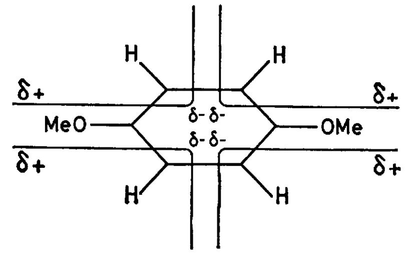

FIGURE 2

There is no apparent reason, however, why this molecule should not also induce a quadrupolar field in the benzene solvent, albeit in the opposite sense to that induced by *p*-dinitrobenzene. This would still lead to a degree of association between solute and solvent and give a high-field ASIS, which is of course not observed.

According to the picture of Ronayne and Williams,[10] the electron rich character of the ring shown in Figure 2 causes a repulsion of solvent (benzene) molecules. The electron deficient ring in Figure 1 causes an attraction, and the different geometries for the resultant ' complexes ' lead to ASIS of opposite sign. This picture presumably implies a sort of electrostatic interaction. Although ASIS is not *dependent* upon the existence of a net molecular dipole moment, it does seem to be related to association of aromatic molecules with electron deficient regions of a molecule. Surprisingly, many correlations *do* exist between dipole moments and ASIS [5,9,16-18] and they are often an additive property of the nature and environment of polar functional groups.[18-21] Let us therefore consider what factors are necessary for the observation of ASIS.

In the present work, as in that of Verkade, the internal reference tetramethylsilane is used. As has been pointed

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[10] J. Ronayne and D. H. Williams, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 83.

[11] N. Nakagawa, K. Nikki, Y. Takeuchi, and I. Kumagai, *Chem. Letters*, 1972, 1239.

[12] K. Nikki and N. Nakagawa, *Chem. Letters*, 1974, 699.

[13] T. H. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, 1972, **94**, 330.

[14] K. Nikki, N. Nakagawa, and Y. Takeuchi, *Bull. Chem. Soc. Japan*, 1975, **48**, 2902.

[15] ' Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 50th edn., 1969—1970, E71.

[16] J. A. Mosbo, J. R. Pipal, and J. G. Verkade, *J. Magnetic Resonance*, 1972, **8**, 243.

[17] T. L. Brown and K. Stark, *J. Phys. Chem.*, 1965, **69**, 2679.

[18] P. Diehl, *J. Chim. Phys.*, 1964, **61**, 199.

[19] D. H. Williams and N. S. Bhacca, *Tetrahedron*, 1965, **21**, 2021.

[20] M. Fetizon and J. C. Gramain, *Bull. Soc. chim. France*, 1966, 2289, 3444.

[21] P. Diehl, *Helv. Chim. Acta*, 1961, **44**, 829.

out elsewhere [22,23] the observed $\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}$ is actually the difference between the *absolute* effect of aromatic solvent upon the shielding constant of the protons in the solute, compared with that upon the shielding constant of the protons in tetramethylsilane. Buckingham *et al.*[24] long ago produced a theory which enables these effects to be calculated. The approach is essentially a statistical one, which allows for non-random orientations between the solute and solvent molecules, arising from their anisotropic properties. In this work, the effects of benzene upon the shielding of protons in the *isotropic* molecule methane are considered, and rationalised in terms of a statistically greater probability of collisions of type (a) than of type (b) (Figure 3). There is no explicit consideration of the consequences of departure from spherical symmetry in the solute molecule, beyond a statement that the shape must be important and that disc-like solutes would probably have enhanced positive solvent effects in benzene.

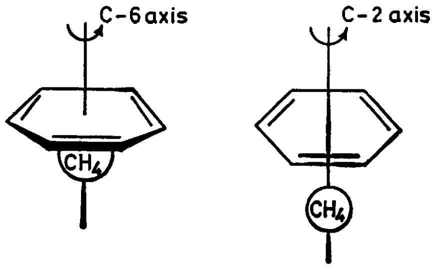

FIGURE 3

These workers point out that exceptionally large ASIS are observed for small highly polar molecules, such as CH_3CN, as solutes and in later work Hatton and Schneider examine the effects upon other solutes containing polar substituent groups.[8] They suggest that in general in such circumstances a chemical association between solute and aromatic solvent is involved, a suggestion which has led to the vast amount of literature which speculates about the nature of such interactions (*e.g.* refs. 9, 25—27, and references cited therein). The hypothesis stems from the belief that the approach of Buckingham *et al.*[24] is adequate to account for all ' non-chemical ' solvation effects due to aromatic molecules, and that any unusually large solvent effects due to the aromatic nature of the solvent must be chemical in nature. However, it is clearly warned in this work that there are ' severe approximations inherent in the model ',[24] and in fact the equation derived to quantify ASIS contains parameters which are sufficiently flexible to account for the observed magnitude in all cases! For a small, hard, spherical solute in a disc-shaped solvent equation (1)

$$\sigma_a = -2_n\,(\psi_{\parallel} - \psi_{\perp})/3R^3 \qquad (1)$$

holds where σ_a is the contribution, to the observed shielding constant of a nucleus in the solute, which arises from the solvent anisotropy, $\chi_{\parallel} - \chi_{\perp}$ is the difference in the two principle components of the magnetic susceptibility tensor of the solute and n is the number of solvent molecules within a sphere of radius R from the nucleus. For $n = 2$ and $R = 4.5$ Å (*i.e.* $n/R^3 = 2.198 \times 10^{-2}$), $\sigma_a = 1.3$ p.p.m.

Since for TMS the observed value of σ_a (relative to solution in CCl_4) is 0.7 p.p.m.,[28] this model can account for an ASIS (relative to internal tetramethylsilane) of up to 0.6 p.p.m.

The largest ASIS ($\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6H_6}}$, relative to internal tetramethylsilane) reported in the review by Laszlo [25] is 1.4 p.p.m.; this corresponds to $n/R^3 \simeq 3.55 \times 10^{-2}$, which is realised for example if $n = 2.3$ and $R = 4$ Å. What is a reasonable value for n/R^3 however? The specific density of benzene is 0.00679 molecule Å^{-3}, implying that each molecule occupies *ca.* 147 Å^3. Assuming a cubic lattice-like distribution, each molecule of solute has six benzene molecules 5.3 Å distant ($n/R^3 = 4.0 \times 10^{-2}$), twelve at 7.5 Å ($n/R^3$ 2.8×10^{-2}), and eight at 10.6 Å (n/R^3 0.6×10^{-2}). Thus, even the largest ASIS may be accounted for by perfectly realistic parameters in equation (1).

The approach of Buckingham *et al.* is not able to take account of the fact that ' n/R^3 ' will be different for chemically different protons in a molecule, and will thus be a function of the molecular geometry and the disposition of these protons with respect to functional groups in the solute.

The general principles governing the description of intermolecular effects are well understood. For an isolated molecule it is possible to write an exact Hamiltonian but obtaining an exact (or even good approximate) wavefunction poses great computational problems. The same is true for intermolecular effects, because the problem is basically the same but the Hamiltonian must include at least some neighbouring molecules. The difficulties arise because of the large numbers of molecules which ought to be considered, plus the large numbers of different arrangements of these molecules which must be allowed for in order to approximate to the true liquid state. The usual way of approaching such a problem is to apply perturbation methods, because the intermolecular terms in the Hamiltonian are much smaller than the intramolecular ones, and to drastically simplify the problem by treating the intermolecular effects as arising from the effect of a surrounding solvent continuum upon a discrete solute molecule.

The approach used by Buckingham *et al.* introduces some structuring into the continuum, in the simplest possible way, by considering only two solvent molecules within a sphere of influence, each of which has two

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[22] F. H. A. Rummens and R. H. Krystynak, *J. Amer. Chem. Soc.*, 1972, **94**, 6914.

[23] P. Laszlo, A. Speert, R. Ottenger, and J. Reisse, *J. Chem. Phys.*, 1968, **48**, 1732.

[24] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

[25] P. Laszlo, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 348.

[26] J. Ronayne and D. H. Williams, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 97.

[27] E. M. Engler and P. Laszlo, *J. Amer. Chem. Soc.*, 1971, **93**, 1317.

[28] C. Barbier, J. Delman, and G. Bené, *J. Chim. Phys.*, 1961, **58**, 764.

possible relative orientations with respect to the solute (considered as a hard sphere).

The difficulties in generalising this approach are enormous, and beyond the scope of the present work. Some attempts have recently been made however to consider in this way the effect of solvent upon nuclear spin–spin coupling constants, and the reader is referred to this work in order to illustrate the magnitude of the problem.[29-33] What is certainly true, however, is that the magnitudes of ASIS observed in this work and elsewhere are too small for it to be possible to deduce that they arise from chemical interactions, *i.e.* non-statistical associations between solvent and solute arising from such phenomena as dipole induced-dipole or quadruple induced-quadrupole interactions.

Engler and Laszlo [27] have shown how ASIS may be explained in terms of the time averaged solvation pattern around a molecule, and have introduced the dependence upon the chemical nature of the proton in terms of a ' site factor ' which describes the geometrical disposition of the site with respect to a functional group. The approach succeeds remarkably well, for example, in predicting the values of ASIS for the various protons in camphor and related molecules, and the authors give a highly critical and authoritative condemnation of the huge volume of work which has been centred around the assumption and subsequent ' identification ' of chemical complexation in aromatic solvents (see references quoted in ref. 27). Probably this work is the most thorough and realistic appraisal yet offered, although the idea of specific complexation still appears to be widespread; [24] it does not enable predictions to be made concerning ASIS in situations such as the quadrupolar molecules described in Table 1, but it does enable the relative values of ASIS in the dipolar molecules listed in the same Table to be examined.

The Laszlo approach is to consider that the time-averaged solvation ' sphere ' around a molecule is distorted by the presence of a substituent (*i.e.* a polar grouping) in the solute, which results in apparently specific solvation at that site. Within such a molecule, the relative chemical shifts of the various protons are decided by a perturbation to their environment which is defined by their structural relationship to this site. Solvation causes a change in the perturbation which is solely a function of the relative geometrical disposition of the substituent and the various protons and is defined by a site factor $(3\cos^2\theta-1)/r^3$ (r is the distance vector between a convenient point in the polar group and the site, and θ is the angle between this vector and a suitable norm, *e.g.* the direction of a point dipole centred in the grouping).

Such a model is very difficult to test in molecules where there are only two chemically different types of proton to consider; indeed, it seems only to have been applied with success in the case of camphor and similar molecules were there are many non-equivalent protons.[27] We adopt a pragmatic approach here, and presume that it is reasonable that the ' origin of the perturbation ' lies along the C-2 axis of each of the six molecules under consideration,* furan, thiophen, pyrrole, and their hydrogenated derivatives tetrahydrofuran, tetrahydrothiophen, and pyrrolidine.

It is obviously possible, in each case, to find a position along this axis which satisfies the requirement that the ratios of the site factors for the two types of proton is the same as that of their respective ASIS, *i.e.* equation (2).

$$\frac{(3\cos^2\theta_1-1)}{r_1^3}\Big/\frac{(3\cos^2\theta_2-1)}{r_2^3} = \Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}(1)/\Delta^{\mathrm{CCl_4}}_{\mathrm{C_6D_6}}(2) \quad (2)$$

The question we ask is, ' Do the distances thus calculated make chemical sense? ' Using widely accepted values for bond lengths and bond angles [35] to approximate to the geometry of the molecule, the distances d were calculated, and Table 2 shows the results for the six molecules. In the case of unsaturated compounds the values of d are relatively larger than in their saturated counterparts. According to the principles of Engler and Laszlo [27] these distances may be interpreted as indicating the seat of the perturbation causing the chemical non-equivalence of the two sets of protons in each molecule, which may be influenced by solvent. In terms of hybrid orbitals, the O and S atoms in tetrahydrofuran and tetrahydrothiophen are conveniently regarded as being sp^3, with two of the hybrid orbitals being involved in σ bonding to ring carbons, and two bearing each a non-bonding lone pair of electrons. In pyrrolidine, the nitrogen is also sp^3 hybridised but has only one lone pair, with the remaining orbital involved in bonding to hydrogen. In the unsaturated analogues, the atoms are supposedly sp^3 hybridised; this results in greater electron density along the direction of the C-2 axis (for O and S, a non-bonding lone pair, for N a bond to H). It is reasonable, therefore, that the ' seat of the perturbation ' should move further away from the rings and result in larger d values, as observed.

TABLE 2

Molecule	d/Å
Tetrahydrofuran	1.20
Furan	1.50
Tetrahydrothiophen	1.20
Thiophen	2.00
Pyrrolidine	1.46
Pyrrole	1.60

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* For the saturated systems, rapid ring inversion produces an effective C-2 axis.

[29] G. E. Maciel, J. W. McIver, N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 1.

[30] M. Barfield and M. D. Johnston, *Chem. Rev.*, 1973, **73**, 53.

[31] M. Barfield and M. D. Johnston, *J. Chem. Phys.*, 1971, **55**, 3483.

[32] M. Barfield and M. D. Johnston, *Mol. Phys.*. 1971, **22**, 831.

[33] M. Barfield and M. D. Johnston, *J. Chem. Phys.*, 1971, **54**, 3083.

[34] N. E. Alexandrou, N. A. Rodios, and C. P. Hadjiantoniou-Louizon, *Org. Magnetic Resonance*, 1973, **5**, 579.

[35] L. E. Sutton, ' Tables of Interatomic Distances,' Chemical Society Special Publication, 1958; Supplement, 1964.

Conclusions.—Non-polar, dipolar, and quadrupolar molecules all have measurable ASIS. There is no need to invoke special associative interactions in order to account for the magnitude of these effects since the statistical method of Buckingham *et al.*[24] is probably adequate to account for the observed values. The method of Engler and Laszlo[27] may be applied to dipolar solutes and gives reasonable results.

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