Dependence of Nuclear Magnetic Resonance Solvent Anisotropy Shifts on the Size of the Solute Molecule

By J. K. BECCONSALL*
(*Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box* 11, *The Heath, Runcorn, Cheshire*)

and T. WINKLER and W. VON PHILIPSBORN
(*Organisch-Chemisches Institut der Universität Zürich,* 8001 *Zürich, Switzerland*)

Summary Solvent magnetic anisotropy shifts for non-polar solutes in benzene show a systematic decrease with increasing size of the solute molecule, in agreement with theoretical predictions based on a geometrical model.

THE effects of solvents with magnetically anisotropic molecules (*e.g.* benzene) on n.m.r. chemical shifts are an aid to structure determination.[1-4] The resonance positions in the anisotropic solvent are compared with those for the same solute in an isotropic solvent (*e.g.* carbon tetrachloride), with an internal tetramethylsilane (TMS) reference in both solutions. For non-polar solutes, the collision complex model[1] successfully applied to solutes with polar groups is inappropriate, and the shifts depend mainly on the size and shape of the solute molecules.

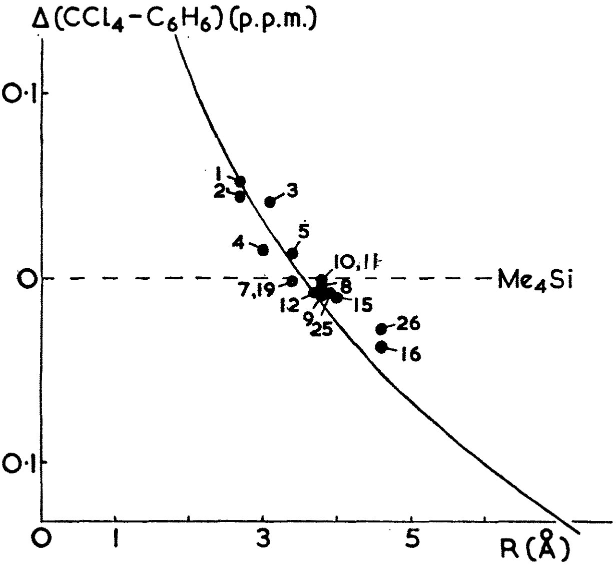

FIGURE. *Predicted and observed solvent shifts* Δ (CCl_4–C_6H_6) *relative to TMS internal reference as a function of the "core" radius* R. *The experimental points are for the following solutes*: (1) 1,1-*dimethylcyclopropane*; (2) *methylcyclobutane*; (3) 1,1-*dimethylcyclobutane*; (4) *methylcyclopentane*; (5) 1,1-*dimethylcyclopentane*; (7) *methylcyclohexane*; (8) 1,1-*dimethylcyclohexane*; (9) cis-1,3-*dimethylcyclohexane*; (10) trans-1,3-*dimethylcyclohexane*; (11) cis-1,4-*dimethylcyclohexane*; (12) trans-1,4-*dimethylcyclohexane*; (15) cis-1-*isopropyl*-4-*methylcyclohexane*; (16) trans-1-*isopropyl*-4-*methylcyclohexane*; (19) *methylcycloheptane*; (25) *methylcyclo-octane*; (26) *methylcyclohendecane*

It has been shown[5] that the benzene-induced solvent shifts for the methyl group protons in methyl cycloalkanes are simply related to the molecular diameters. A calculation[6] of the solvent anisotropy shift for spherical non-polar solute molecules also predicted such a relationship, which was confirmed by measurements on methane, cyclohexane and TMS. A generalisation of these calculations now accounts adequately for the results on methylcycloalkanes.

For a single solute molecule, the neighbouring solvent molecules contributing to the anisotropy term in the nuclear screening are those whose centres lie within a shell of uniform thickness surrounding the exclusion surface defined by the atomic van der Waals radii. The time-averaged volume magnetic susceptibility tensor in the shell is assumed to have an axis of symmetry along the normal to the nearest point on the exclusion surface, with susceptibilities χ_{vr} and $\chi_{v\theta}$ along this normal and perpendicular to it respectively. Then the magnetic anisotropy contribution to the screening of the ith nucleus in the solute molecule, assuming a point dipole field configuration from each volume element, is

$$\sigma_{ai} = \int_{\text{shell}} (\chi_{vr} - \chi_{v\theta})_j \, \frac{3\cos^2\theta_{ij} - 1}{3r_i^3} \, dv \qquad (1)$$

where the anisotropy $(\chi_{vr} - \chi_{v\theta})_j$ is assumed to be a function of the radius of the exclusion sphere j nearest to the volume element dv, θ_{ij} is the angle between the vectors from the ith and jth centres to the element dv, and r_i is the distance from the ith centre (*i.e.* the nucleus).

For molecules having a methyl substituent attached to an approximately spherical cycloalkane core, it is convenient to treat this core (together with any substituents other than the single methyl group under consideration) as if it were a single large atom, whose radius R is half the overall van der Waals diameter of the molecule without the methyl substituent. The integral (1) for the methyl group protons in such a molecule has been evaluated numerically for a range of radii R. By subtracting from the resulting anisotropy shifts the value calculated for the protons of TMS in benzene solution by the same method, we obtain the predicted shift relative to the TMS internal reference; this gives the curve of the Figure. The experimental points in the Figure are for 14 of the substituted cycloalkanes previously reported[5] (those omitted do not contain a simple methyl substituent), together with two more (25 and 26). The radii R, defined as above, were estimated with the aid of Dreiding molecular models; for flexible molecules the measurements were made for the most sterically favoured configurations.

It has already been pointed out[5] that this correlation can be used in some circumstances for assigning structures to geometrical isomers. Further studies[7] have shown that these solvent shifts can be used to locate methyl groups in complex hydrocarbons, and in solutes containing polar functional groups, the non-specific shifts arising as above and those originating from complex formation[1] are additive.

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