A Correlation between Solvent Shifts of Proton Resonances and Steric Environment

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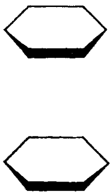
The screening constant (σ_{solvent}) which determines the difference in chemical shifts of a proton in a molecule in the gas phase and in a solvent has been expressed in terms of four contributions: σ_b (bulk magnetic susceptibility effect), σ_a (the effect due to the anisotropy in the molecular susceptibility of the solvent molecules), σ_W (the effect due to van der Waals forces between the solvent and the solute), and σ_E (the polar effect).[1] These are purely "physical effects" and act independently of "chemical association" between solvent and solute:

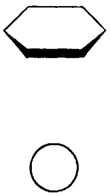
$$\sigma_{\text{solvent}} = \sigma_b + \sigma_a + \sigma_W + \sigma_E$$

If the difference in chemical shift to be considered is between a molecule in the gas phase relative to a gas-phase reference and the molecule in a solvent relative to the same *internal* reference, then the bulk susceptibility correction (σ_b) will be zero (*i.e.*, the corrections for sample and reference will cancel out). Moreover, if all the molecules involved (the molecule under investigation, the solvent and the reference) are relatively nonpolar, the σ_E terms will be insignificant. Under these circumstances, the difference in chemical shift alluded to above will therefore largely reflect anisotropy and van der Waals effects.

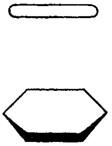
Disc-shaped solvent molecules lie closer to disc-shaped or spherical solutes when in the configuration (I) or (II) (as opposed to alternative configurations), and rod-shaped solvent molecules lie closer to disc-shaped or spherical solutes in the configuration (III) or (IV).[1] Hence the σ_a term for benzene (disc-shaped) as solvent will correspond to a shielding effect on solute protons relative to the gas phase, whereas the σ_a term for carbon disulphide (rod-shaped) as solvent will correspond to a deshielding effect.



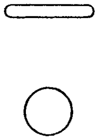
(I)



(II)



(III)



(IV)

van der Waals forces cause deshielding effects relative to the gas phase; an important contribution to this deshielding effect increases with increasing number of electrons in the solvent molecule.[1] Hence the van der Waals deshielding effect is greater for methylene iodide than for carbon tetrachloride, and is in turn greater for carbon tetrachloride than hexane.

If the approach of bulk solvent to a solute proton is inhibited due to steric effects, then the "surface protons" of the internal reference (usually tetramethylsilane) will be affected more by the σ_a and/or σ_W terms of a given solvent than will the sterically hindered protons of the solute, *i.e.*, the sterically hindered protons will have an environment which approximates more nearly to that in the gas phase. Therefore, as the environment of a given solute proton becomes more sterically hindered, relative to internal Me_4Si (i) methylene iodide and carbon tetrachloride as solvents will cause an apparent upfield shift of the solute proton, with the effect being $CH_2I_2 > CCl_4$ (σ_W effects), (ii) carbon disulphide as solvent will cause an apparent upfield shift of the solute proton (largely a σ_a effect), and (iii) benzene will cause an apparent downfield shift of the solute proton (largely a σ_a effect). The term "apparent" is used since the predictions reflect actual shifts of the internal reference in the opposite sense.

To test these predictions, the chemical shifts (relative to internal Me_4Si) of the aromatic protons of benzene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene have been compared in hexane, carbon tetrachloride, methylene iodide, carbon disulphide, and $[^2H_6]$benzene as solvents.† Since hexane has a negligible σ_a term and a relatively small σ_W term,[1] the chemical shifts are all recorded relative to the values observed in this solvent.

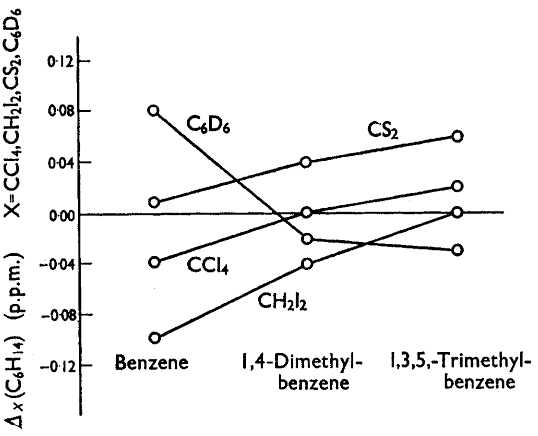


FIGURE 1

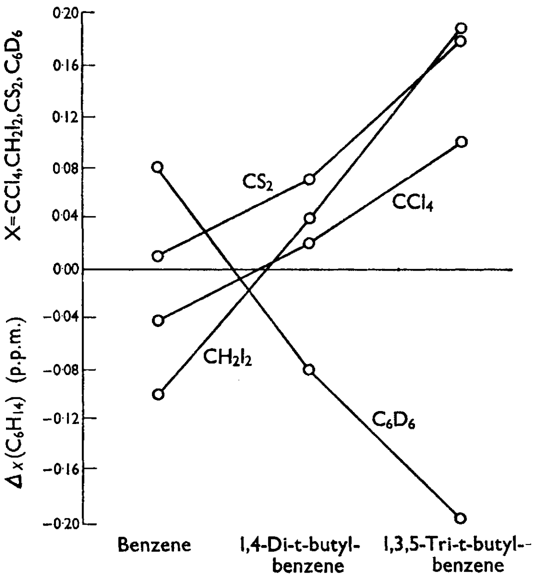


FIGURE 2

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† All measurements were made in 2% w/v solutions at normal probe temperatures.

All the measurements accord perfectly with the predictions as indicated in Figure 1. [Solvent shift $= \Delta_X(C_6H_{14}) = \delta(C_6H_{14}) - \delta_X$ p.p.m.]. When the steric effects are made more severe by the introduction of t-butyl groups (rather than methyl groups) into the benzene ring, then the changes in solvent shifts for the aromatic protons are much more marked (Figure 2). For example, the marked "downfield shift" (0·20 p.p.m.) of the aromatic proton of 1,3,5-tri-t-butylbenzene in [$^2H_6$]benzene solution relative to hexane solution, in conjunction with the correspondingly marked "upfield shifts" observed in methylene iodide and carbon disulphide solutions (Figure 2), reflect (in the absence of chemical solvent–solute associations) the crowded steric environment of this proton.

Obviously, in the correlation of benzene-induced solvent shifts with structure, the steric effect must be considered in conjunction with the polar effects.[2] In addition, the study emphasises that carbon tetrachloride (and also deuterochloroform[3]) is not an ideal solvent for the experimental determination of functional-group anisotropies if the introduction of the functional group modifies the steric environment of neighbouring protons.

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[2] J. Ronayne and D. H. Williams, *J. Chem. Soc.* (*B*), 1967, 540.

[3] P. Laszlo, *Bull. Soc. chim. France*, 1964, 2658.