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Solvent Effects in NMR Spectroscopy.
The Geometry of Solute/Solvent Collision Complexes

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The specific shielding effect in NMR shown by aromatic solvents on polar solutes is experimentally well established. During the ten years since its discovery (1,2), many workers have investigated this effect and stereochemical aspects of it. (Papers containing many references: (3,4), more recent works: (5-24)). It is felt, however, that this effect and its potential applications by no means has attained the attention it deserves. One reason for this may be the lack of a generally accepted model for solute/solvent collision complexes. The effect is based on:

1) The presence of one or more polar sites in the solute molecules.
2) The diamagnetic anisotropy of an aromatic solvent.
3) A non-random mutual orientation of the polar solute and the aromatic solvent molecules.

Evidence for the formation of collision complexes between the polar solute and the aromatic solvent exists (7,21). They seem to be 1/1 complexes. The enthalpy and entropy of their formation have been found in the range -0.9 - -1.7 kcal/mole and -3.5 - -4.4 e.u., respectively.

For large solute molecules with more than one polar site, one aromatic solvent molecule may be associated to each site, provided they are not too closely located. So far, complete agreement may exist about the phenomenon. Concerning the general geometry of the collision complexes, however, widely differing models have been put forward by the various workers (25-30,2,7,14,21,23). The divergences in conclusions seem to have two main causes: 1) Too special types and/or too restricted numbers of solutes investigated in each case. 2) The use of different pairs of aromatic/non-aromatic reference solvents. Results obtained with polar solvents are *per se* very interesting and useful, but may cause undue complication and confusion. In order to obtain safe conclusions about the collision complex geometry, any degree of polarity should be restricted to the solutes investigated, which should include simple compounds of known and differing structures. The aromatic solvent used should preferably have all other properties except the diamagnetic anisotropy in common with the reference solvent. The solvent pair best fulfilling this ideal requirement seems to be benzene (or hexadeuterobenzene) and carbon tetrachloride, some physical constants of which are compared with those of toluene and chloroform in Table I below.

Table I

Solvent	Dipole moment (Debye)	Dielectric constant (c.g.s. e.s.u.)	Susceptibility ($\chi \cdot 10^6$)	Molar volume
Benzene	0.00	2.28	0.63	88.8
Carbontetrachloride	0.00	2.22	0.68	96.6
Chloroform	1.20	4.64	0.73	80.2
Toluene	0.37	2.38	0.63	106.3

Although solvent shifts $\Delta = (\delta CCl_4 - \delta C_6H_6)$ in many cases are nearly the same as the corresponding $(\delta CHCl_3 - \delta C_6H_6)$ shifts, great differences have also been observed (6,13).

It is important to keep all measuring conditions as constant as possible, and concentrations low enough to avoid dipole-dipole interactions between solute molecules. Special care should also be taken in the case of hydroxyl and other hydrogens having chemical shifts which markedly depend on concentration and temperature.

Conclusions should primarily be based on relative differences between the solvent shielding values of different hydrogens within the same molecule.

The purpose of the present investigation is to find a possible common model for the geometry of collision complexes and the main factors which seem to determine this geometry. Preliminary findings (5) gave only some indications in this respect. NMR measurements have been performed with 5% or weaker solutions in carbon tetrachloride and benzene as solvents with different types of solutes.* The solvent shifts found and the corresponding proposed geometry of the collision complexes are indicated below.

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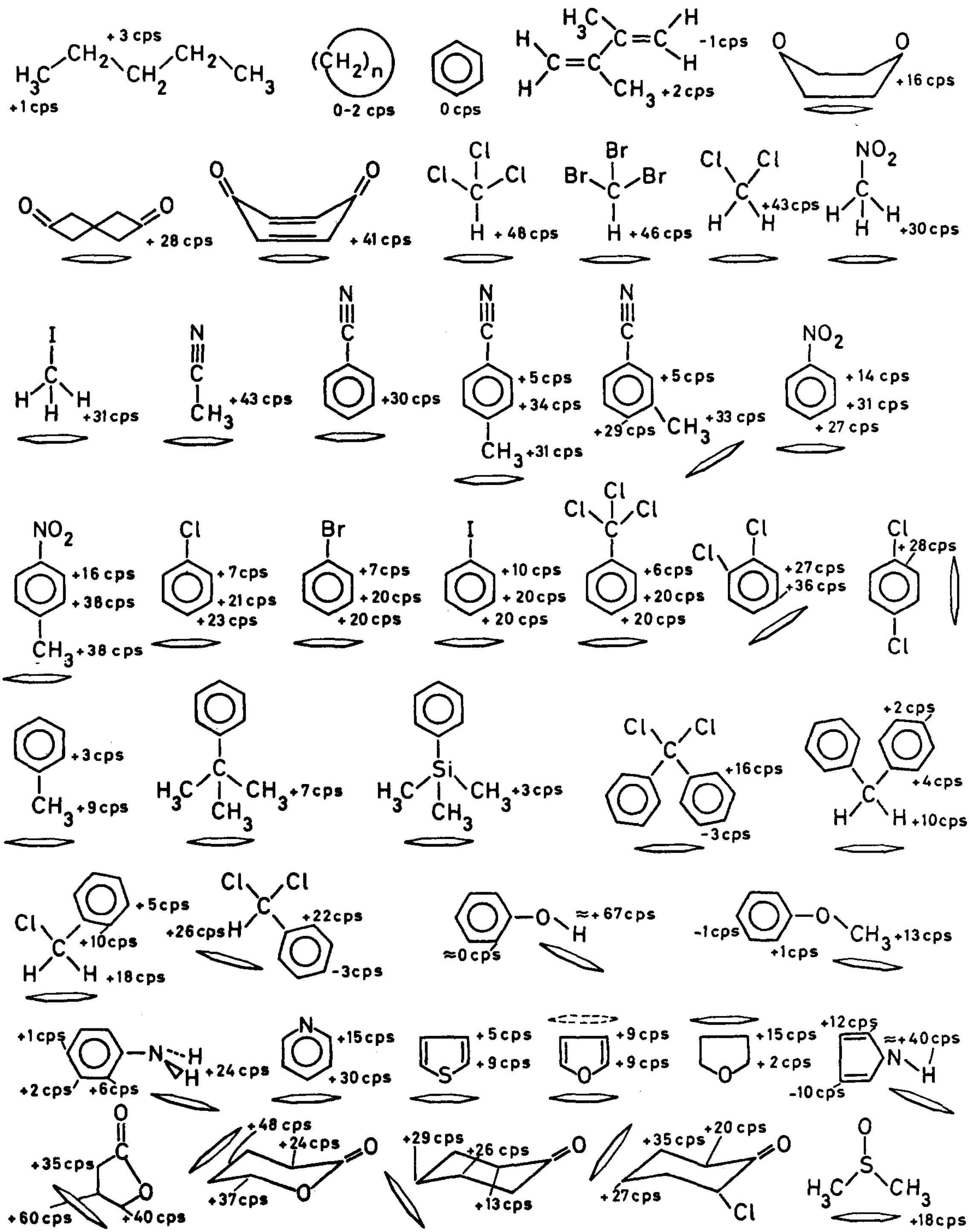
*Measured with an A60A spectrometer at 37°C with TMS as an internal standard.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+43 cps
+30 cps
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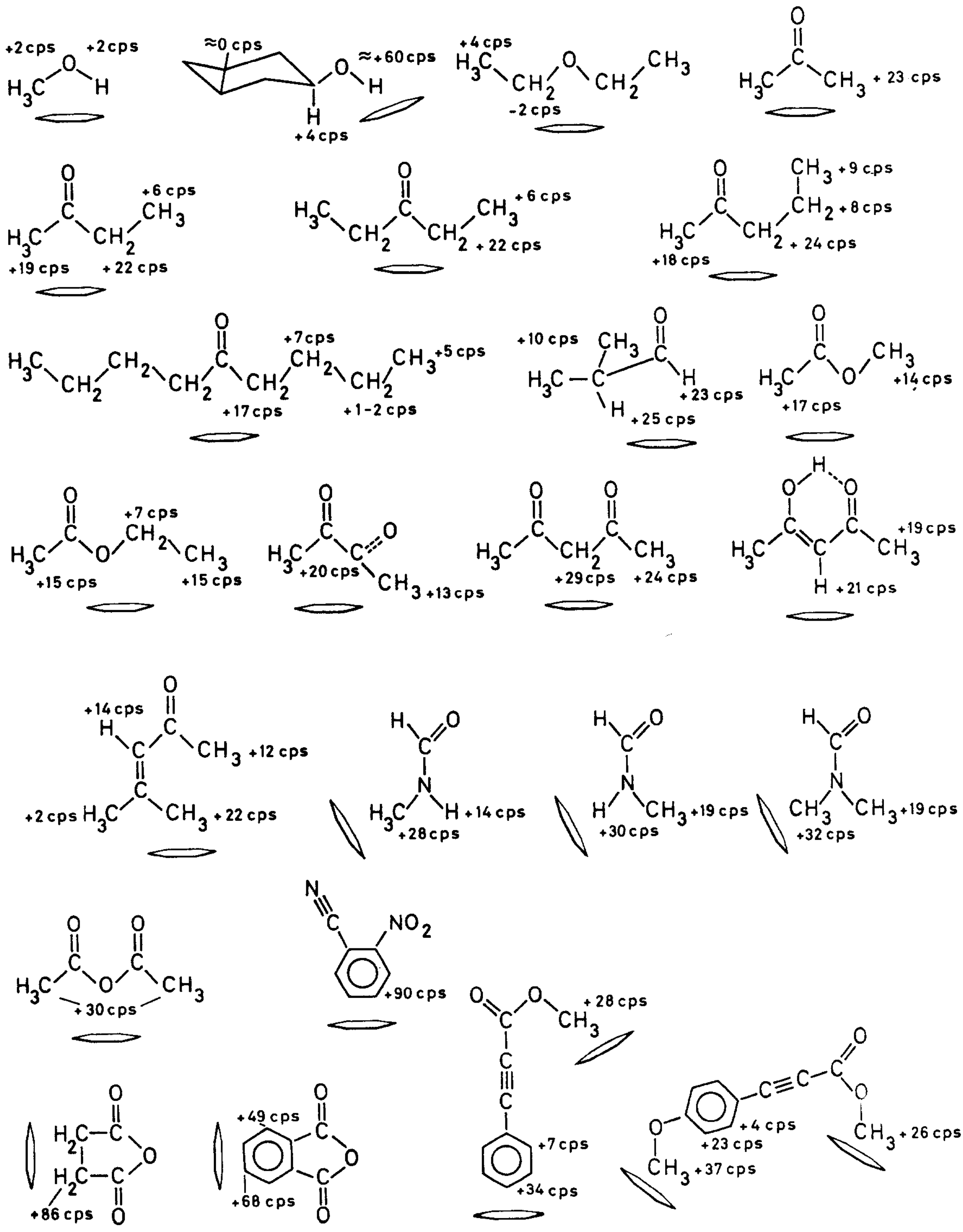
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O H
H +4 cps
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O
H3C C CH3 + 23 cps
+6 cps
H3C C CH2 CH3
+19 cps +22 cps
+6 cps
H3C CH2 C CH2 CH3
+ 22 cps
CH3 +9 cps
CH2 +8 cps
H3C C CH2 + 24 cps
+18 cps
+7 cps
+5 cps
H3C CH2 CH2 CH2 C CH2 CH2 CH2 CH3
+17 cps +1-2 cps
+10 cps
CH3
H3C — C C H
H +25 cps
+23 cps
H3C C O CH3
+17 cps +14 cps
+7 cps
H3C C O CH2 CH3
+15 cps +15 cps
H3C C C O
+20 cps
CH3 +13 cps
H3C C CH2 C CH3
+29 cps +24 cps
H O O
H3C C C C CH3
+19 cps
H +21 cps
+14 cps
H C C CH3 +12 cps
+2 cps H3C C CH3 + 22 cps
H C O N H3C H +14 cps
+28 cps
H C O N H CH3 +19 cps
+30 cps
H C O N CH3 CH3 +19 cps
+32 cps
H3C C O C CH3
+30 cps
N C NO2
+90 cps
O C O CH3
+ 28 cps
C C C
+7 cps
+34 cps
H2C — C O
H2C — C O
+86 cps
+49 cps
+68 cps
O C C C C O O
CH3 +37 cps
+23 cps +4 cps
CH3 + 26 cps

When comparing the results above with the other published values of (δCCl_4 - δC_6H_6) one arrives at the following conclusion: All these solvent shifts can be reasonably accounted for on the assumption that one and the same type of collision complexes exists in all cases. This common model has the dipole axis of the solute molecule located along the sixfold symmetry axis of a benzene nucleus with the positive end of the dipole nearest, and the negative end farthest away from it. This partly coincides with the generalisations of Ronayne and Williams (14). For simple dipole solutes the solvent shift of the different hydrogens then depends on their location relative to the positive end of the dipole, being a maximum when coinciding with this. For solutes of similar types the solvent shifts for correspondingly located hydrogens seem to parallel the dipole moment values of the solutes. The explanation of this is probably that the larger dipole moments are associated with the more stable collision complexes having the longer life times. The factors determining the collision complex geometry seem to be the attraction between the electrophilic positive end of the local solute dipole and the nucleophilic π-electron system of the benzene nucleus. The strong mutual repulsion between this electron system and the negative end of the solute dipole results in the fixed orientation. Complicating factors may be special steric, electronic and anisotropic effects in the solutes. However, as all such effects are at work in the reference solvent as well, and what one really observes, is the net solvent shift effect, such complications may not be too serious. When dealing with conformationally unstable solutes the possibility of course exists that the conformation may be different in carbon tetrachloride and benzene. For solutes without strongly anisotropic groups this may cause little trouble, as the chemical shifts with carbon tetrachloride as solvent then may be nearly independent of conformational changes. In such cases one only gets information about the solute conformation as it exists in the benzene collision complex. With solutes containing phenyl- and other anisotropic groups the interpretation of solvent shift values may be more difficult. However, such groups can also be useful, as they can influence solvent shifts in a way which clearly indicates the existence of one specific conformation in carbon tetrachloride and another in benzene solution.

Among the rather few and not very satisfying methods available for structural and conformational investigations in the liquid phase, NMR solvent shift seems at present to be the more promising. However, in order to bring the method from the present - rather qualitative - to a more quantitative basis, further investigations are needed.

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