The Mechanism of Benzene-induced Solvent Shifts of Proton Resonances in N.m.r. Spectra

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SOLVENT shifts (Δ) of proton resonances induced by benzene are usually defined by $\Delta = \delta' - \delta_{C_6H_6}$ p.p.m., where δ' is the chemical shift of a proton in an "inert" solvent (carbon tetrachloride, chloroform, cyclohexane) or in the pure liquid, and $\delta_{C_6H_6}$ is the chemical shift for that proton in benzene solution. The large range of Δ-values (approximately $-0{\cdot}5$ to $+1{\cdot}5$ p.p.m.) observed for protons attached to carbon atoms in organic molecules has been widely interpreted[1] in terms of stereospecific solvation by benzene of aromatic or aliphatic solute molecules with shifts then arising due to the anisotropy of benzene. Such an interpretation seems reasonable in the light of widely differing Δ-values observed for protons in the same solute molecule.

To account for the signs of Δ-values observed in a wide range of organic compounds, we formulate the following generalizations, some of which incorporate previously published ideas, but some of which modify existing ideas or are new.

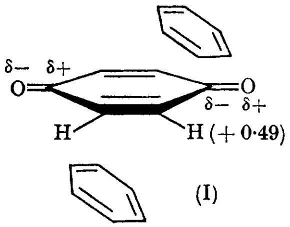
(i) Benzene will interact at electron-deficient sites in the solute molecule.[1c]

(ii) Dilution curves suggest that benzene–solute interactions may occur in a transient 1 : 1 collision complex, but it is felt that phase independent 1 : 1 associations may occur at *each* electron-deficient site in the solute molecule.

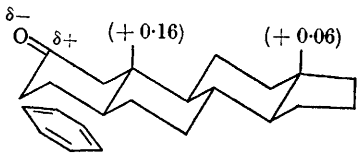
(iii) The orientation of benzene molecules is caused by *local dipole*-induced dipole interactions (it may be adequate in some cases for purposes of prediction to consider only the solute molecular dipole).

(iv) A benzene solvent molecule interacting with the partial positive charge of a local dipole will probably be orientated in a *nonplanar* collision complex so that the benzene ring lies as far as possible from the negative end of the dipole.[2]

Our generalizations mainly modify existing suggestions by considering the possible non-planarity of collision complexes, the importance of local dipoles, the occurrence of a number of independent 1 : 1 associations, and also in applying the principles to solutes in general. To support the suggestions Δ-values ($\delta' - \delta_{C_6H_6}$ p.p.m.) are given with a number of schematic illustrations (I—VI) and formulae (VII—XII) for a variety of organic compounds; δ' is measured using dilute solutions ($< 2\%$ w/w) in cyclohexane (I, V, VI),[1a] deuterochloroform (II—IV), or carbon tetrachloride (VII—XII). The suggestions account for the large positive Δ-values observed for the protons of *p*-benzoquinone (I), which has no molecular dipole.[1a] Different mechanisms for benzene–aromatic solute and benzene–aliphatic solute interactions would seem unlikely since the carbonyl function induces shifts of similar sign and magnitude in both aliphatic[1d] and aromatic[3] carbonyl compounds. The importance of local dipoles in transient orientation of solvent is also established by the additivity of solvent shifts[1d] [for example, the angular methyl shifts in (IV) are the sum of those found in (II) and (III), indicating independent association at each carbonyl group]. The generalizations rationalize the Δ-values observed for *NN*-dimethylaniline (V) and



(I)



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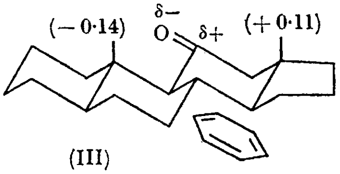

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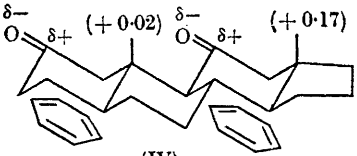

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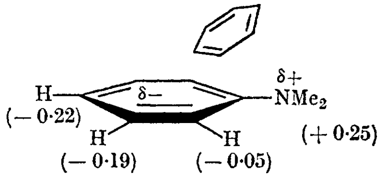
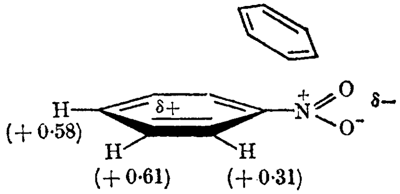
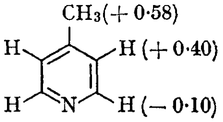


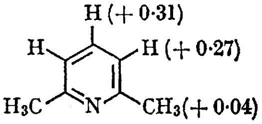
(V)



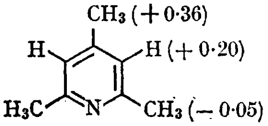
(VI)



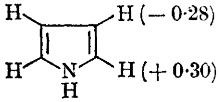
(VII)



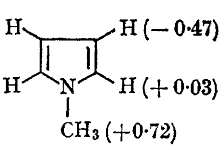
(VIII)



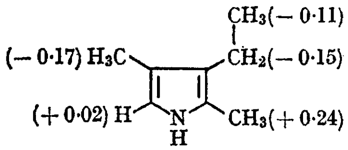
(IX)



(X)



(XI)



(XII)

nitrobenzene (VI),[1a] and allowed us to predict small or negative Δ-values for 2–H or 2–CH_3 resonances in an alkylpyridine, but larger positive values for 4–CH_3 resonances (see VII—IX). Since the positive end of the pyrrole dipole is at the nitrogen atom, negative Δ-values may be anticipated for the β-hydrogens of (X) and (XI) and for the 3- and 4-alkyl substituents of (XII), exactly as observed.[4]

Benzene solvent shifts would therefore seem to have potential for indicating the direction of local or molecular dipoles, as well as great utility in structure elucidation.* The detailed ramifications of the proposals will be considered in a subsequent full paper, but it is noteworthy that the present suggestions are consistent with the results available for ketones,[1d] $\alpha\beta$-unsaturated ketones,[5] amides,[1b,6] and various substituted cyclopropanes.[7,8]

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* It is of course necessary to use hexadeuterobenzene when the benzene resonance would obscure solute resonances of interest [as in (VII—XII)].

[1] See, for example, (a) W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653; (b) J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, **5**, 139; (c) R. E. Klinck and J. B. Stothers, *Canad. J. Chem.*, 1962, **40**, 2329; (d) D. H. Williams and N. S. Bhacca, *Tetrahedron*, 1965, **21**, 2021.

[2] Such a generalization has previously been made considering molecular (rather than local) polarizations for planar collision complexes (ref. 1b).

[3] J. H. Bowie, D. W. Cameron, P. E. Schütz, and D. H. Williams, *Tetrahedron*, 1966, **22**, 1771.

[4] The spectra of 4-methylpyridine (VII) and pyrrole (X) have previously been compared in hexane and benzene solutions (T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1224). Our results (measured relative to internal Me_4Si) using either carbon tetrachloride *or hexane* (*at the same solute concentrations*) as reference solvent establish that the reported values (measured relative to external chloroform) differ from ours by amounts varying from 0·3 to 1·2 p.p.m.

[5] C. J. Timmons, *Chem. Comm.*, 1965, 576.

[6] A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, 1966, **22**, 1825, and references cited therein.

[7] P. S. Wharton and T. I. Blair, *J. Org. Chem.*, 1965, **30**, 1681.

[8] J. Seyden-Penne, T. Strzalko, and M. Plat, *Tetrahedron Letters*, 1965, 4597; 1966, 3611.