CHEMISTRY LETTERS, pp. 1239-1242, 1972. Published by the Chemical Society of Japan

AROMATIC SOLVENT-INDUCED SHIFT (ASIS). A NOVEL APPROACH

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The aromatic solvent-induced shift (ASIS) has been explained in terms of the dipole-induced dipole interaction. It can hardly account for the experimental results. The dipole-quadrupole interaction seems better to explain ASIS. A preliminary calculation has been carried out for acetone in benzene.

Although considerable attention has been focused on the aromatic solvent-induced shift (ASIS) in proton nmr spectra, the problem is not yet completely settled.[1,2] As for the origin of ASIS, according to the most widely accepted interpretation, a solute and a solvent (benzene) form a 1:1 complex in which the benzene molecule has a specific orientation. It is, however, very unlikely that only ONE benzene molecule is responsible for the observed ASIS. Indeed, it is often pointed out that the 1:1 complex is hypothetical rather than a real existence. What is most likely is that all the solvent molecules suffer from an interaction with the solute in a way or other. This interaction will cause a less random arrangement of solvent molecules around the solute. The observed ASIS should be the sum of the effect of these oriented solvent molecules.

Laszlo et al.[3], for instance, ascribed ASIS to the effect of solvent molecules clustering around polar sites of a solute. As the origin of this interaction, Schneider[4] suggested the dipole-induced dipole interaction by the Debye force. If so, the energy of orientation of benzene is given by

$$U(\text{dipole}) = (\alpha'' \cos\phi + \alpha^{\perp} \sin\phi) \cdot \mu^2 \cdot (1+3\cos^2\theta) / r^6 \qquad (1)$$

where α'' and $\alpha^{\perp}$ are, respectively, parallel and perpendicular values of the electric polarizability of a benzene molecule in respect of the six fold axis ($\vec{B}$) of that molecule, $\vec{\mu}$ is the dipole moment of the solute, $\vec{r}$ is the distance from the dipole to benzene, ϕ is the angle between $\vec{B}$ and $\vec{E}$, which

is the electric field at benzene due to the dipole, and θ is the angle between $\vec{\mu}$ and $\vec{r}$.

ASIS $\Delta\delta$(dipole) by ONE benzene molecule at the distance $\vec{R}$ from the proton in question is given by

$$\Delta\delta(\text{dipole}) = \Delta\chi\cdot(1-3\cos^2\psi)\cdot[\exp\{-\Delta U(\text{dipole})/kT\}-1]/3R^3\cdot[2+\exp\{-\Delta U(\text{dipole})/kT\}] \quad (2)$$

where $\Delta\chi$ is the diamagnetic anisotropy of a benzene molecule, ψ is the angle between $\vec{R}$ and the axis $\vec{B}$. ΔU(dipole) is the difference of the energy of orientation of benzene molecules perpendicular to the direction of the electric field due to the dipole of the solute ($\phi=90^0$), and of these parallel to it ($\phi=0^0$), and is equal to $\Delta\alpha\cdot\mu^2\cdot(1+3\cos^2\theta)/r^6$, where $\Delta\alpha=\alpha''-\alpha^{\perp}$.

The observed ASIS, $\Sigma\Delta\delta$(dipole) is the sum of the effects of all benzene molecules, and is given by

$$\Sigma\Delta\delta(\text{dipole}) = \int_v \Delta\delta(\text{dipole})\cdot\rho d\tau \quad (3)$$

where ρ is the specific density of benzene, $d\tau$ is a volume element, and suffix v means that the integration is carried out throughout the space except the excluded volume of the solute.

The situation can be represented by Fig. 1, where the solute (the dipole is indicated by a small arrow placed at the center) is surrounded by benzene molecules with specific orientation. As a result of such an orientation $\Sigma\Delta\delta$(dipole) as well as $\Delta\delta$(dipole) are negative for most protons. Thus, for protons, located at a, b, d, e and f positions in Fig. 1 are associated with negative $\Delta\delta$ values. Protons at the c position or near exceptionally show positive $\Delta\delta$ values. Such predictions are contrary to the observations.

Several years ago, one of us[5] suggested that the solute-aromatic solvent interaction should be of dipole- quadrupole rather than of dipole-induced dipole. Recently an accurate quadrupole moment (Q) of benzene and other compounds were reported[6], which promoted us to refine our original proposal.

The orientation energy of the quadrupole (Q) of benzene at the position of r from the dipole (μ), is given by

$$U(\text{quadrupole}) = (3\mu Q_{BB}/4r^4)\cdot[\,2\sin2\phi\cdot\sin\theta\cdot\cos^2\chi + \{\,3(\cos2\phi+1)\cdot\cos^2\chi - 2\,\}\cos\theta\,] \quad (4)$$

where ϕ is the angle between $\vec{r}$ and $\vec{B}'$, which is a projection the six fold axis ($\vec{B}$) of benzene to the meridian plane of the dipole field, χ is the angle between $\vec{B}'$ and $\vec{B}$, θ is the angle between $\vec{\mu}$ and $\vec{r}$, and Q_{BB} is the principal value of quadrupole in $\vec{B}$ direction, which has negative sign.

The most stable (S) and the most unstable (U) directions in orientation of the quadrupole of benzene are both in a meridian plane of the dipole field, and then ϕ_S or ϕ_U is given by

$$\cos 2\phi_{S,U} = \pm 3\cos\theta \;/\; \sqrt{4 + 5\cos^2\theta} \qquad (5)$$

where the positive one in (±) sign corresponds to S, while the negative one to U.

Then, the orientation energy is given by

$$U_{S,U} = (3\mu Q_{BB} / 4 r^4)\cdot(\pm \sqrt{4 + 5\cos^2\theta} + \cos\theta). \qquad (6)$$

Another direction in orientation of the quadrupole of benzene is M, which is perpendicular to that meridian plane, and the orientation energy (U_M) is equal to $-3\mu Q_{BB}\cos\theta/2r^4$.

The population of benzene, P, in each direction is a Boltzmann function and easily calculated.

$$P_S = \exp(-\Delta U_S /kT) \;/\; \{ 1 + \exp(-\Delta U_S /kT) + \exp(-\Delta U_U /kT) \}$$

$$P_M = 1 \;/\; \{ 1 + \exp(-\Delta U_S /kT) + \exp(-\Delta U_U /kT) \} \qquad (7)$$

$$P_U = \exp(-\Delta U_U /kT) \;/\; \{ 1 + \exp(-\Delta U_S /kT) + \exp(-\Delta U_U /kT) \}$$

where $\Delta U_S = U_S - U_M$ and $\Delta U_U = U_U - U_M$.

Thus, ASIS, $\Delta\delta$(quadrupole), due to the dipole-quadrupole interaction by ONE benzene molecule is given by

$$\Delta\delta(\text{quadrupole}) = \Delta\chi \{ 1 - 3 (\cos^2\psi_S\cdot P_S + \cos^2\psi_U\cdot P_U + \cos^2\psi_M\cdot P_M) \} / 3 R^3 \qquad (8)$$

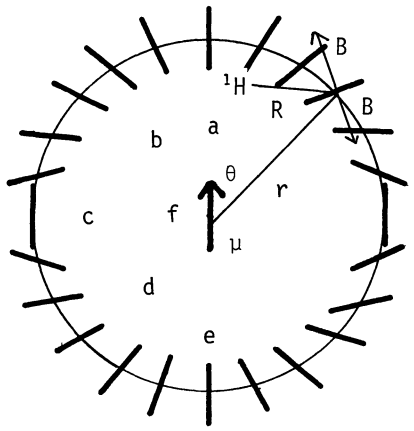

Fig.1 Orientation of solvent benzene molecules around a solute due to the dipole-induced dipole interaction. ——— represents the benzene plane.

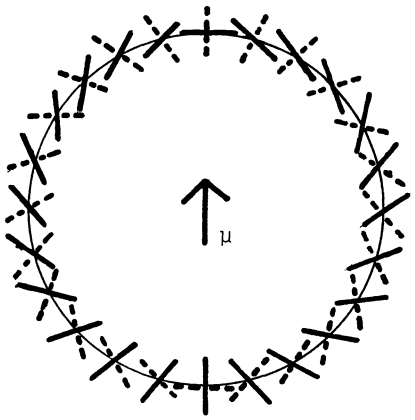

Fig.2 Orientation of solvent benzene molecules around a solute due to the dipole-quadrupole interaction. ——— represents the stable benzene plane and - - - - represents the unstable benzene plane.

where ψ_S, ψ_M, and ψ_U are the angle ψ between $\vec{R}$ and $\vec{S}$, $\vec{M}$, and $\vec{U}$, respectively. The observed ASIS, $\Sigma\Delta\delta$(quadrupole) can then be estimated by an equation similar to Eq.(3).

A preliminary calculation indicates that an upfield shift is expected for protons lying in front of the carbonyl plane[7], while a downfield shift is predicted for protons below the plane, which is in accordance with experimental results. As an example, $\Sigma\Delta\delta$(dipole) and $\Sigma\Delta\delta$(quadrupole) were calculated for the proton resonance of acetone in benzene. The former was estimated as -0.002 ppm while the latter was +0.068 ppm[8]. The observed ASIS[9], $\delta_{benzene} - \delta_{cyclohexane}$, is +0.435 ppm, which supports our interpretation in a qualitative manner. Details of this treatment as well as additional examples will be given in forthcoming papers.

References and Notes

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8) The values used for the calculation are : μ(acetone) = 2.85×10^{-18}esu, Q_{BB}(benzene) = -5.6×10^{-26}esu[6], $\Delta\alpha$(benzene) = -2.0×10^{-23} esu, $\Delta\chi$(benzene) = -9.0×10^{-29}esu, ρ(specific density of benzene) = 0.00679 molecule/A^3, and $\Delta\tau$(a volume element) = $(0.5\ A)^3$. Calculations were performed with a computer , OKITK 5090, in the Univ. Electro-Communications.

9) The spectra were determined with JEOL NH-100 spectrometer using 1 mole % solutions. The chemical shifts were calibrated with the aid of frequency counter.

(Received October 7, 1972)