Aromatic Solvent-induced Shift(ASIS). I. An Interpretation Based on the Dipole-Quadrupole Interaction[1]

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Two general theoretical ways of estimating aromatic solvent-induced shifts(ASIS), which are based on the dipole (solute)-induced diple(solvent) interaction [(μ-μ')interaction] or the dipole(solute)-quadrupole(solvent) interaction [(μ-Q) interaction], are proposed. Solvent shifts can occur by means of the magnetic anisotropy of solvent molecules, which take specific orientations due to those electro-static interactions. As an example, we calculate the ASIS of a hypothetical spherical molecule, a model for camphor, with a dipole near the center and covered with protons, immersed in benzene. The estimated ASIS based on (μ-μ') interaction is much too small to account for the shifts normally observed, while those based on (μ-Q) interaction agree well with the observed ASIS in respect to both its magnitude and angular dependency (*e.g.*, the carbonyl plane rule). More specifically, the theoretical and experimental ASIS for methyl protons of camphor are compared.

It is well known that large chemical-shift differences are often incurred by the proton resonance of organic molecules if the medium is changed from a solvent such as cyclohexane or carbon tetrachloride to an aromatic solvent like benzene. This phenomenon is frequently referred to as the aromatic solvent-induced shift (ASIS).[2–5]

Various explanations have been put forward to explain the ASIS. These have been based on a kind of hydrogen-bonding,[6] the 1 : 1 complex formation between the solute and the solvent, particularly of the specifically oriented one,[7–9] the dipole-induced dipole interaction,[10] the time-averaged 1 : *n* cluster formation,[5] *etc.* Several years ago one of the present authors suggested that the interaction between the permanent dipole of the solute and the permanent quadrupole of the aromatic solvent might cause ASIS.[12] The purpose of this paper is to give quantitative evidence for this interaction.

Theoretical

It is noteworthy that ASIS are observed for those molecules having a permanent dipole. Hence, whatever the origin of the ASIS, the permanent dipole of the solute should be responsible for the solute-solvent interaction which causes the ASIS. There are various possible modes of electrostatic interaction between the solute and the solvent, in which the solute permanent dipole plays an important role. These modes are the dipole(solute)-dipole(solvent) interaction, the dipole(solute)-induced dipole(solvent) interaction [hereafter specified as the (μ-μ') interaction], the dipole(solute)-quadrupole(solvent) interaction [hereafter specified as the (μ-Q) interaction], and interactions of higher orders. The first will not be considered here since a benzene molecule has no permanent dipole; also, the last need not be taken into consideration, as their magnitude must be very small. Now, these two (μ-μ') and (μ-Q) interactions will be compared.

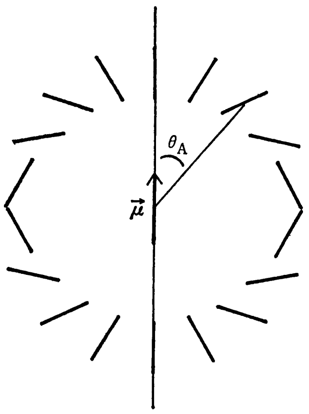

Fig. 1a. Orientation of benzene molecules in the least stable direction based on the (μ-μ') interaction. —— is a six-fold axis of symmetry of benzene.

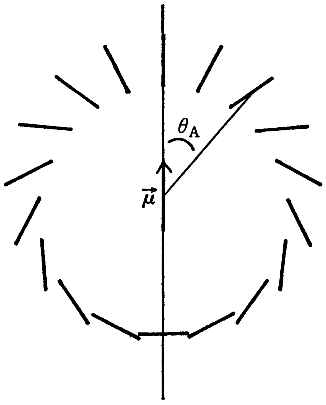

Fig. 1b. Orientation of benzene molecules in the most stable direction based on the (μ-Q) interaction.

When molecules with a permanent dipole are dissolved in benzene, the orientation of benzene molecules surrounding a solute molecule is less random than that of pure benzene molecules; they take a specific orientation due to the electric field caused by the permanent dipole. The situation is best represented in Figs. 1a and 1b. As is indicated, the orientation is, as a whole, determined by the assumed interaction, (μ-μ') or (μ-Q), between the solute and the solvent. The ASIS should reflect the orientation involved. The calculation of the ASIS will be carried out in the following manners.

ASIS Caused by the Dipole-induced Dipole (μ-μ') Interaction. First, the energy of the (μ-μ') interac-

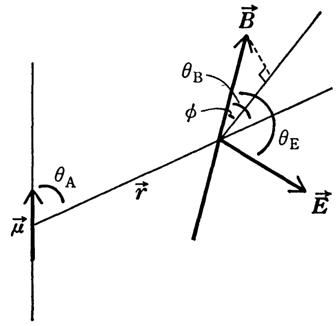

Fig. 2. A benzene molecule in a permanent dipole field of a solute molecule.

tion between one solute and one solvent is carried out. In Fig. 2 the parameters required for the calculation are defined: $\vec{\mu}$ is the permanent dipole of the solute located at the point of origin, $\vec{r}$ is the distance from the origin to the center of a solvent molecule, and θ_A is the angle between $\vec{\mu}$ and $\vec{r}$. The orientation of a benzene molecule is conveniently defined by the direction of its six-fold axis $\vec{B}$, rather than by its plane. θ_B is the angle between $\vec{B}$ and $\vec{r}$. ϕ is the dihedral angle between the plane containing $\vec{\mu}$ and $\vec{r}$ and that containing $\vec{r}$ and $\vec{B}$. $\vec{E}$ represents the electric-field vector at the benzene molecule caused by the $\vec{\mu}$ of the solute, and $|\vec{E}|$ is defined by Eq. (1):

$$E = |\vec{E}| = |\vec{\mu}|\sqrt{1+3\cos^2\theta_A}\cdot r^{-3} \tag{1}$$

θ_E is the angle between $\vec{B}$ and $\vec{E}$; it is related to θ_A, θ_B, and ϕ as is shown in Eq. (2):

$$\cos\theta_E = (\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi)/\sqrt{1+3\cos^2\theta_A} \tag{2}$$

An induced dipole, $\vec{\mu}'$, is caused in a benzene molecule when it is placed in the electric field, $\vec{E}$, as defined by Eq. (3):

$$\vec{\mu}' = \boldsymbol{\alpha}\cdot\vec{E} \tag{3}$$

where $\boldsymbol{\alpha}$ is the electric polarisability of a benzene molecule.

The energy of interaction between $\vec{\mu}$ and $\vec{\mu}'$ is given by Eq. (4):

$$\begin{aligned} U_{\mu\text{-}\mu'} &= -\vec{\mu}'\cdot\vec{E} \\ &= -(1/2)\{\alpha^{\parallel}(E\cdot\cos\theta_E)^2 + \alpha^{\perp}(E\cdot\sin\theta_E)^2\} \end{aligned} \tag{4}$$

By substituting Eqs. (1) and (2) in Eq. (4), Eq. (5) is obtained:

$$\begin{aligned} U_{\mu\text{-}\mu'} = &-\mu^2\{(\alpha^{\parallel}-\alpha^{\perp})(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi)^2 \\ &+ \alpha^{\perp}(1+3\cos^2\theta_A)\}.r^{-6} \end{aligned} \tag{5}$$

where $\alpha^{\parallel}$ and $\alpha^{\perp}$ are the parallel and perpendicular components of the electric polarisability of a benzene molecule in respect to its axis of symmetry.

As a result of this solute-solvent interaction, benzene molecules will be oriented around the solute with a decreased randomness of orientation.

As an aromatic solvent has an anisotropy of magnetic susceptibility, the shift $\delta(\mu\text{-}\mu')$ observed for a proton of the solute due to one benzene molecule at the one position is given by:

$$\delta(\mu\text{-}\mu') = \frac{\int_{\theta_B}\int_{\phi}\Delta\chi(1-3\cos^2\xi)(3R^3)^{-1}\exp(-U_{\mu\text{-}\mu'}/kT)\sin\theta_B d\theta_B d\phi}{\int_{\theta_B}\int_{\phi}\exp(-U_{\mu\text{-}\mu'}/kT)\sin\theta_B\, d\theta_B\, d\phi} \tag{6}$$

where $\Delta\chi(=\chi^{\parallel}-\chi^{\perp}=\chi^{\perp}-\chi^{\perp *})$ is the diamagnetic anisotropy of benzene, ξ is an angle between the axis $\vec{B}$ and $\vec{R}$, and $\vec{R}$ is the distance from the center of benzene to the proton in question (see Fig. 3).

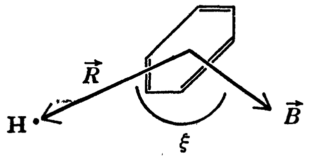

Fig. 3. Relationship between a benzene molecule and a proton in question.

By difinition, the ASIS, $\sigma(\mu\text{-}\mu')$, is the sum of the effect of all the benzene molecules around the solute; thus,

$$\sigma(\mu\text{-}\mu') = \int\rho\delta(\mu\text{-}\mu')\,d\tau \tag{7}$$

where ρ is the specific density of benzene. The integration is carried out throughout the space except for the excluded volume of the solute (as $\rho=0$). The excluded volume was defined as the region surrounding a solute molecule into which the center of a solvent molecule cannot enter.

ASIS Caused by the Dipole-Quadrupole(μ-Q) Interaction. The calculation of the ASIS caused by the interaction between the permanent electric dipole moment of a solute molecule and the permanent electric quadrupole moment of a benzene molecule was performed in the following manner. The molecular quadrupole moment along a principal axis is defined by:[13)]

$$Q_{\alpha\alpha} = \frac{|e|}{2}\sum_n Z_n(3\alpha_n^2 - r_n^2) - \frac{|e|}{2}\langle 0|3\alpha_i^2 - r_i^2|0\rangle \tag{8}$$

$$\alpha = x,\ y,\ z$$

where e is the unit electric charge, Z_n is the atomic number of the n-th nucleus, α_n and α_i are the nuclear and the electric coordinates, and the summation is over the n nuclei and i electrons. $\langle 0|\ \ |0\rangle$ indicates the electric ground-state average value. A quadrupole tensor of a benzene molecule, calculated from the magnetic anisotropy, is given by:[13)]

$$\boldsymbol{Q} = \begin{vmatrix} 2.8\pm1.4 & 0 & 0 \\ 0 & 2.8\pm1.4 & 0 \\ 0 & 0 & -5.6\pm2.8 \end{vmatrix} \times 10^{-26}\ \text{esu} \tag{9}$$

The electrostatic energy of a molecular quadrupole at the position of r from the dipole is given by:

$$U_{\mu\text{-}Q} = qq'\left(\frac{2}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} - \frac{2}{r_4} + \frac{1}{r_5} + \frac{1}{r_6}\right) \tag{10}$$

where q is the electric charge of the bar-dipole (solute) with the length of $2a$, where q' is the electric charge of a bar-quadrupole (solvent) with the length of $2b$, and where r_1^{-1}, r_2^{-1}, r_3^{-1}, *etc.* are given by:

$$\begin{aligned} r_1^{-1} &= r^{-1}(1-2\cos\theta_A\cdot ar^{-1}+a^2r^{-2})^{-1/2} \\ &= r^{-1}\{1+\cos\theta_A\cdot ar^{-1}+(1/2)(3\cos^2\theta_A-1)\cdot a^2r^{-2} \\ &\quad+(1/2)(5\cos^3\theta_A-3\cos\theta_A)\cdot a^3r^{-3}+\cdots\cdots\} \end{aligned} \tag{11}$$

$$\begin{aligned} r_2^{-1} &= r_1^{-1}\{1+(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\cdot 2br_1^{-1}+b^2r_1^{-2}\}^{-1/2} \\ &= r_1^{-1}[1-(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\cdot br_1^{-1}+ \\ &\quad(1/2)\{3(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)^2-1\}\cdot b^2r_1^{-2}- \\ &\quad(1/2)\{5(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)^3- \\ &\quad3(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\}b^3r_1^{-3}+\cdots\cdots] \end{aligned} \tag{12}$$

$$\begin{aligned} r_3^{-1} &= r_1^{-1}\{1-(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\cdot 2br_1^{-1}+b^2r_1^{-2}\}^{-1/2} \\ &= r_1^{-1}[1+(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\cdot br_1^{-1}+ \\ &\quad(1/2)\{3(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)^2-1\}\cdot b^2r_1^{-2}+ \\ &\quad(1/2)\{5(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)^3- \\ &\quad3(\cos\theta_B\cos\delta-\sin\theta_B\sin\delta\cos\phi)\}\cdot b^3r_1^{-3}+\cdots\cdots] \end{aligned} \tag{13}$$

etc., where δ is the angle between $\vec{r}$ and $\vec{r}_1$; then $\sin\delta=a\cdot\sin\theta_A/r_1$ (see Fig. 4).

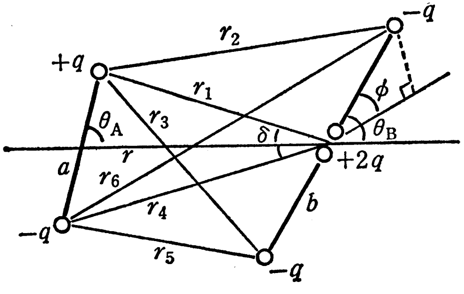

Fig. 4. Electrostatic interaction between bar-dipole and bar-quadrupole. q is the electric charge of the dipole. q' is the electric charge of the quadrupole.

The substitution of Eqs. (11), (12), (13), *etc.* into Eq. (10) and the use of the point-dipole and -quadrupole approximations, ($r\gg a$, $r\gg b$ and $\delta=0$), will give the orientation energy by means of:

$$\begin{aligned} U_{\mu\text{-}Q} &= -6qq'ab^2r^{-4}\{\cos\theta_A(1-3\cos^2\theta_B) \\ &\qquad+2\cos\theta_B\sin\theta_B\sin\theta_A\cos\phi\} \\ &= -(3/2)\mu Q_{zz}r^{-4}\{\cos\theta_A(1-3\cos^2\theta_B) \\ &\qquad+2\cos\theta_B\sin\theta_B\sin\theta_A\cos\phi\} \end{aligned} \tag{14}$$

where Q_{zz} is the principal value of the quadrupole moment on the six-fold axis of a benzene molecule.

Thus, the shift, $\delta(\mu\text{-}Q)$, observed for a proton of a solute molecule caused by one solvent molecule at one position is given by:

$$\delta(\mu\text{-}Q) = \frac{\int_{\theta_B}\int_{\phi}\Delta\chi(1-3\cos^2\xi)(3R^3)^{-1}\exp(-U_{\mu\text{-}Q}/kT)\sin\theta_B d\theta_B d\phi}{\int_{\theta_B}\int_{\phi}\exp(-U_{\mu\text{-}Q}/kT)\sin\theta_B d\theta_B d\phi} \tag{15}$$

The $\sigma(\mu\text{-}Q)$ ASIS can be estimated in the manner described in the previous section.

Calculation

Point-dipole (-quadrupole) approximations are employed for calculating the electrostatic interaction between the solute and the solvent. Thus, both the electric polarization of a solute molecule and the induced polarization of a benzene molecule are approximated as a point dipole, whereas the electric distribution in a benzene molecule (molecular quadrupole) was approximated as a point quadrupole at the center of the molecule. Unless the solvent molecule is in contact with the solute molecule, the dielectric constant of the medium should be considered. In our calculation, however, it was assumed to be unity for all the distances.

The energies of the dipole-induced dipole interaction and the dipole-quadrupole interaction are given by Eqs. (5) and (14) respectively. The maximum and the minimum energy of the two interactions are plotted against the distance, r, in Fig. 5. As in our calculation, the difference between the maximum and the minimum energy due to the (μ-Q) interaction at the one position at any value of r larger than 4.45 Å, the closest possible distance between the solute and benzene, was about 14 times as large as that due to the (μ-μ') interaction. This indicates that the (μ-Q) interaction is almost exclusively responsible for the orientation of the benzene molecules around the solute.

In order to obtain a general perspective as the magnitude of the ASIS caused by two interactions, a spherical-model molecule, with a diameter of 2.9 Å and a permanent dipole of 3.1 D which is located 1.5 Å

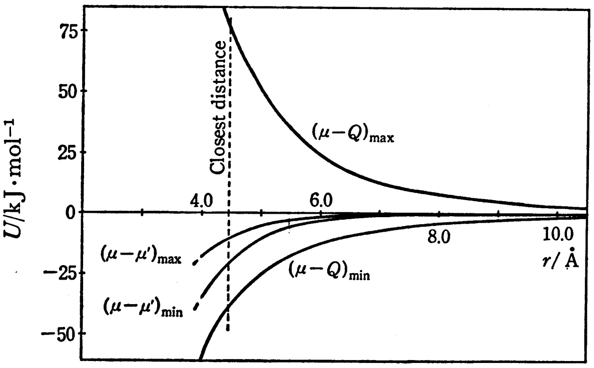

Fig. 5. The maximum energy and the minimum energy of the dipole-induced dipole interaction and the dipole-quadrupole interaction.

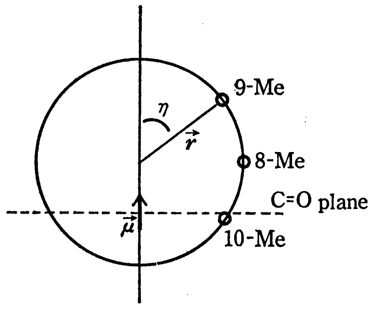

Fig. 6. A spherical "model" molecule. ↑ is the dipole, and ○ is a center of a "methyl" group on the sphere.

apart from, and pointed toward, the center of the sphere (Fig. 6), was introduced. The "average" position (proton point) of the three protons of each methyl group of camphor was on the surface of the sphere, when the dipole of camphor is superimposed on the dipole of the model. For the benzene molecule we assumed a sphere with a van der Waals radius of 1.85 Å. The values used for the calculation were as follows:

$\Delta\alpha$ (benzene): -60×10^{-25} esu
$\Delta\chi$ (benzene): -0.9×10^{-28} esu
Q_{zz} (benzene): -5.6×10^{-26} esu
ρ (benzene): 0.00679 molecule/Å^3
van der Waals radius of H: 1.2 Å.

In the computation of $\delta(\mu\text{-}\mu')$ and $\delta(\mu\text{-}Q)$, the $\int_{\theta_B}\int_{\phi} f(\theta_B, \phi)d\theta_B d\phi$ integration is approximated by a double summation:

$$\sum_{\theta_B=0}^{180^\circ}\sum_{\phi=0}^{360^\circ} f(\theta_B, \phi)\Delta\theta\Delta\phi$$

with $\Delta\theta_B=10^\circ$ and $\Delta\phi=10^\circ$.[**]

In a similar manner, $\int\rho\delta(\mu\text{-}\mu')d\tau$ and $\int\rho\delta(\mu\text{-}Q)d\tau$ are approximated by the triple summation:

$$\sum_{\theta_A=0}^{180^\circ}\sum_{\phi=0}^{360^\circ}\sum_{r=4.45\text{Å}}^{10.5\text{Å}} f(\theta_A, \phi, r)\Delta\theta_A\Delta\phi\Delta r$$

where $\Delta\theta_A$ and $\Delta\phi$ are taken as 10°[†] and Δr as $0.1r$. θ_A and ϕ varied from 0° to 180° and from 0° to 360° respectively, whereas r varied from 4.45 Å, which corresponds to the smallest possible distance between a benzene molecule and a solute molecule (closest distance), to 10.5 Å.[††]

The calculated ASIS for the model molecules based on $(\mu\text{-}\mu')$ or $(\mu\text{-}Q)$ interactions are plotted against an angle in the model molecule (see Fig. 6) in Fig. 7.

Discussion

It is surprising that no quantitative calculation has ever been attempted to assess the ASIS caused by the $(\mu\text{-}\mu')$ interaction, although most, if not all, of the proposed interpretations have been based on this interaction.

Our calculations indicate that the energy of the $(\mu\text{-}\mu')$ interaction is so small that no appreciable orientation is incurred in benzene molecules. Hence, the ASIS caused by this interaction is negligibly small. On the contrary, the $(\mu\text{-}Q)$ interaction seems to cause a noticeable orientation; hence, the ASIS caused is at least hundred times as large. For example, the observed ASIS for three methyl groups of camphor are plotted in Fig. 7. The locations of the proton points were estimated from the geometry of the camphor, as determined by the HGS molecular model. The agreement between the calculated and observed values proves that our assumption is qualitatively correct. In our preliminary paper,[1] we took only three possible orientations of benzene molecules into consideration, for the sake of simplicity, instead of all the possible ones as we have done in this paper. The estimated ASIS under that approximation was twice as large as the present estimation.

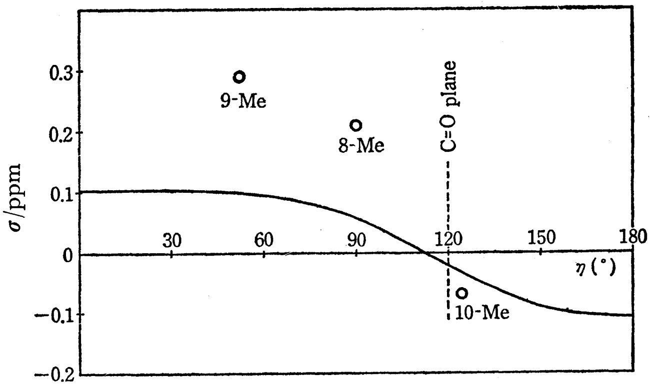

Fig. 7. The angular dependency of ASIS. η is an angle between $\vec{\mu}$ and $\vec{r}$ (a distance of a proton from the center of the sphere). A solid line represents calculated values, $\sigma(\mu\text{-}Q)$, and ○ represent observed values of ASIS of methyl groups of camphor.

Far more important in predicting the ASIS is its sense (its upfield or downfield shift, as compared with the chemical shifts in a neutral solvent). This is particularly the case with carbonyl compounds where the observed ASIS is quite dependent on the relative geometry of the proton(s) in question and on the carbonyl dipole, as summarised by the so-called carbonyl plane rule.[11] According to this rule, protons lying in front of (or behind) the carbonyl plane (a plane perpendicular to $\vec{\mu}$ and through the carbonyl carbon) exhibit a positive (negative) ASIS, while protons on the plane show virtually no ASIS. This empirical rule is in good agreement with our calculated results.

Thus, for a polar solute molecule the dipole-quadrupole interaction model is a much better approximation of the ASIS than the dipole-induced dipole interaction model in estimating its magnitude and "sense." This electrostatic interaction model is now being used in our laboratories to study the solvent shifts caused by other solvents, including hexafluorobenzene and carbon disulfide.

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[**] Much the same results were obtained with $\Delta\theta_B$ and $\Delta\phi=5^\circ$.

[†] Calculations were also carried out with $\Delta\theta_A$ and $\Delta\phi=5^\circ$; these results were much the same as those, given in the text.

[††] At this distance, δ is almost 1/4000 of that at the closest distance.

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