CHEMISTRY LETTERS, pp.479-482, 1972. Published by the Chemical Society of Japan

INFRARED ABSORPTION INTENSITIES OF OUT-OF-PLANE CH BENDING VIBRATION BANDS OF SUBSTITUTED BENZENES. V. SOLVENT EFFECT ON THE INTENSITIES OF THE BANDS OF DIPHENYL SULFIDE AND DIPHENYL SULFOXIDE

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The band intensities of out-of-plane CH bending and ring out-of-plane deformation vibrations of Ph_2S and Ph_2SO were measured in ten solvents. The results were analyzed in terms of solvent-dependences of C-H bond moment and the angle of rotation θ of benzene rings. Different behaviours of θ were observed between the two molecules.

It was pointed out in the preceding paper[1] that, in case of Ph_nX type molecules, the characteristic vibrations of each benzene ring are interdependent and their phases and relative amplitudes have definite relationships governed by the symmetry of the whole molecule. When the intensities of out-of-plane CH bending and ring out-of-plane deformation modes belonging to the same symmetry species are summed up, such intensity sums can be expressed approximately by the product of two terms. One is the group characteristic intensity A_0, which is attributable to one benzene ring and corresponds to the group vibrational coordinate similar to out-of-plane CH bending vibration of benzene. The other is the term dependent on the symmetry of normal vibrations and including the valence angle φ and the angle of rotation θ of benzene ring. It was demonstrated that there are some cases where the values of not only A_0 but also θ can be obtained from the observed intensity data. In the present study, therefore, we have examined the solvent effect on the spectra of Ph_2S and Ph_2SO on the basis of the discussions in the previous paper. The purpose of this note is to discuss the changes in the observed band intensities of the above two compounds in different solvents in terms of the two main factors, i.e. the solvent-dependences of A_0 (therefore, C-H bond moment) and those of θ.

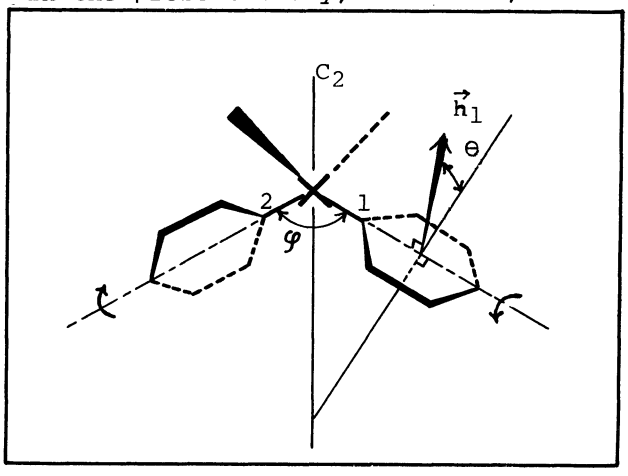

Fig.1 Model of Ph_2X type molecule. $\vec{h}$:unit vector of polarization

(1) The expressions for the intensities.

When Ph_2X type molecules are assumed to belong to the point group C_2, the following expressions for the intensity sums can be derived through Gribov's theory[2].

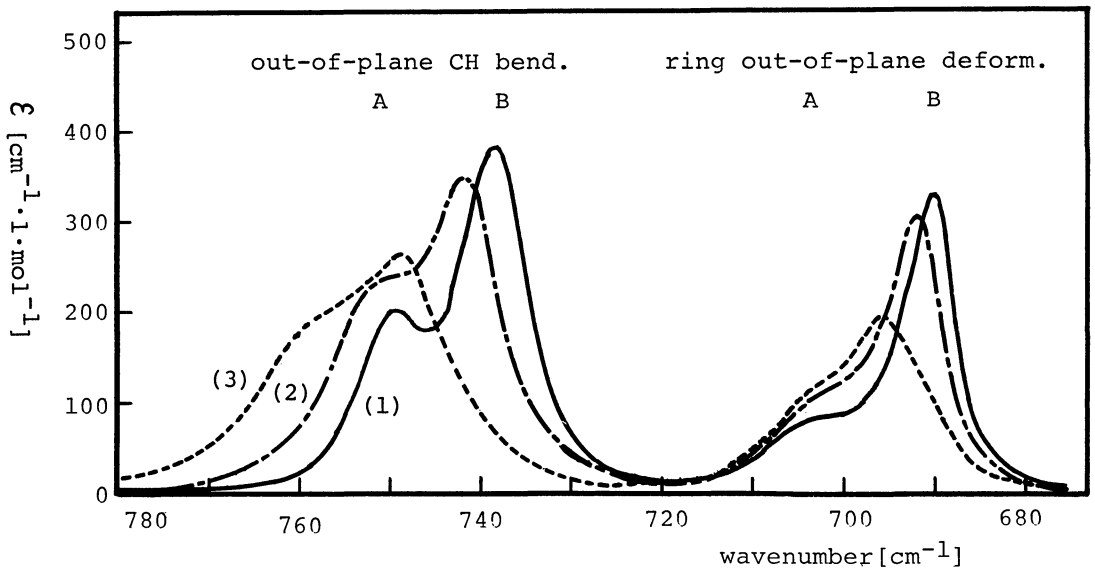

Fig.2 Changes of spectra of Ph_2S according to solvents, (1)in cyclohexane, (2)in acetone, (3)in N,N-dimethyl formamide.

$$A(A) = A_0 \cdot (\nu/\nu_0)^2 \cdot (1 - \cos\varphi) \cdot \cos^2\theta \quad (1)$$

$$A(B) = A_0 \cdot (\nu/\nu_0)^2 \cdot [(1 + \cos\varphi) + (1 - \cos\varphi) \cdot \sin^2\theta] \quad (2)$$

where A(A) and A(B) are the intensity sums of the two vibrational modes belonging to the same symmetry species, i.e. A(symmetric) and B(asymmetric), respectively. The definition of φ and θ is given in Fig.1.

(2) The measurements of intensities. A JASCO Model DS-403G Infrared Spectrophotometer was used for the measurements of intensities. Spectra were recorded in absorbance with the frequency scale in cm^{-1}, and integrated areas were obtained directly from the instrumental charts. The solvents used are as follows. 1.cyclohexane, 2.dioxane, 3.carbon disulfide, 4.ethyl ether, 5.dimethyl disulfide, 6.ethyl acetate, 7.methyl iodide, 8.acetone, 9.nitromethane, 10.N,N-dimethyl formamide. As shown in Fig.2, two bands overlap for each of out-of-plane CH bending and ring out-of-plane deformation vibrations, and it becomes necessary to divide these overlapping bands into each component. In this study, such operation was made by use of a Du Pont 310 Curve Resolver, assuming the Lorentzian band contours for each component.

(3) The solvent effect on A(A) and A(B). In Fig.2 are shown the typical examples of the changes of spectra of Ph_2S according to alterations of solvents. It can be seen from this figure that the difference of solvents causes remarkable changes in wavenumbers, peak intensities and band shapes. From these spectra, the intensities of each of the normal vibrations have been determined for each solute-solvent system. The assignment of the bands has been proposed in the previous study[1]. Among the various factors determining the values of A(A) and A(B), the one which corresponds to the forms of group vibrations are considered to be approximately common between the two different species. In such situation, as shown by the formula (1) and (2), A(A) and A(B) are determined by the products of the group characteristic intensity A_0, the factor common between A and B types of vibrations, and the terms dependent on the vibrational symmetries and involving φ and θ. Therefore, the changes in A(A) and A(B) can be discussed in terms of the two main factors A_0 and θ, since the valence

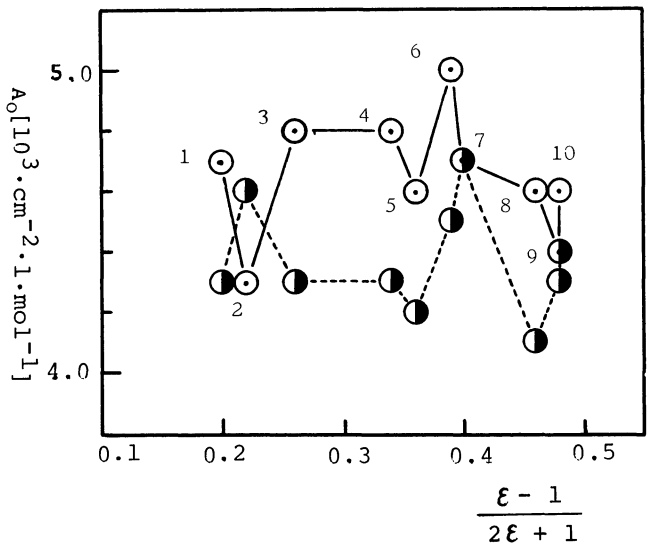

Fig.3 A_o vs. polarity of solvents
⊙:Ph_2S, ◑:Ph_2SO,
the numbers indicate the solvents.

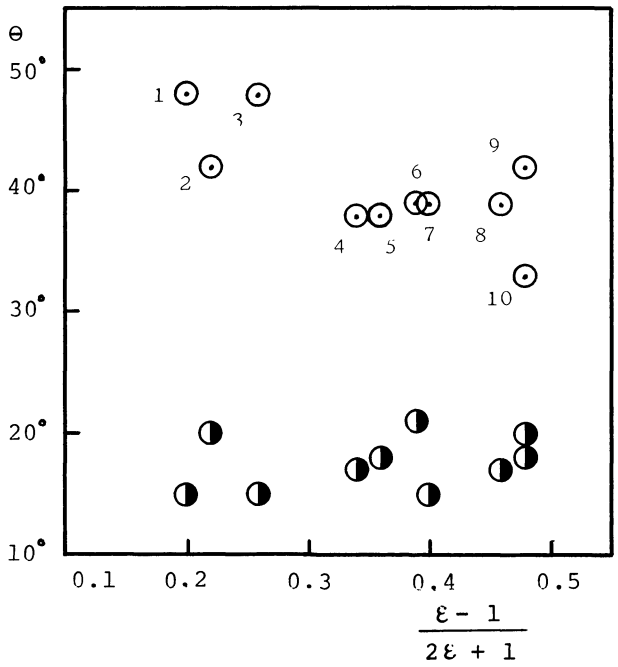

Fig.4 Θ vs. polarity of solvents,
⊙:Ph_2S, ◑:Ph_2SO.

angle φ can not be expected to change so much by differences in the environment surrounding the molecules in question. Thus, the values of A_o and Θ for each solute-solvent system have been calculated from the obtained values of A(A) and A(B). In those calculations, the valence angle φ was assumed to be the tetrahedral angle for Ph_2S[3] and 97°19' for Ph_2SO[4]. In Fig.3, the obtained data for A_o are plotted against the corresponding "reaction field constant" $(\varepsilon - 1)/(2\varepsilon + 1)$, which is used in this study as a quantitative measure of the polarity of solvents. It is seen that there is no great change in the values of A_o according to the solvents used here, for both Ph_2S and Ph_2SO. This result agrees with the fact that the intensity sums of the two modes of the monosubstituted benzenes of usual PhX type are little influenced by the polarity of solvents[5]. When some marked changes are observed in A_o, they can be attributed to the changes in C-H bond moment according to the molecular systems in question. Thus, the results demonstrated in Fig.3 suggest that the changes of the spectra according to the solvents are not attributable to the alterations in C-H bond moment. On the other hand, the correlations between the obtained data for Θ and the polarity of solvents are demonstrated in Fig.4. The values of Θ seem, as a rough tendency, to decrease with the polarity of solvents in case of Ph_2S, while they seem to be independent of solvents in case of Ph_2SO. The values of Θ are determined from the ratio A(A)/A(B) and the above results correspond to the fact that, in Ph_2S, such ratios change considerably according to the solvents, i.e. from 0.43 to 0.89, while they are held between 0.96 and 1.12, approximately constant, in Ph_2SO. From the above-mentioned experimental results, the following conclusions can be drawn. The dependences of A(A) and A(B) on the solvents are pronounced in case of Ph_2S, and they are reduced through the formula (1) and (2) to the changes in Θ rather than in A_o. On the other hand, no marked change in A(A) and A(B) are observed in case of Ph_2SO, leading to the conclusion that in this case, not only C-H bond moment but also Θ is

independent of the solvents used.

(4) Some discussions on the obtained values of Θ. We will make some comments on the validity of the values of Θ obtained here. LeFèvre et al. reported the value 44° as Θ of Ph_2S in CCl_4 solvent in one of their papers[3] and, 48° in the other[6], both of which were derived through the analysis of the molar Kerr constant of this molecule. The values of Θ obtained in our study for nonpolar solvents agree well with those quoted above. As for Ph_2SO, Abrahams[4] obtained the value 8°3' by the X-ray diffraction method. Since this value was obtained for the sample in crystal phase, it may not be appropriate to compare it directly with those derived in our study. However, it can be said that the value 8°3' suggests the validity of considerably small magnitudes of Θ obtained in our work. As for the behaviours of Θ, it is rather difficult to make decisive discussions at present. Nevertheless, the following qualitative discussions may be possible, by analogy with the analysis of Θ of biphenyl molecule according to Fischer-Hjalmars[7]. In Ph_2X type molecules, the possibility of π-X-π conjugation is considered to become maximum when both phenyl groups are coplanar with C_{ar}-X-C_{ar} plane, i.e. Θ = 90°. In this case, however, the effect of repulsion between nonbonded atoms is also to become large. On the other hand, when both phenyl groups are perpendicular with C_{ar}-X-C_{ar} plane, i.e. Θ = 0°, both the possibility of the conjugation and the effect of repulsion become smaller. It is considered probable that the magnitude of Θ is brought to a certain value between 0° and 90° according to the degree of contributions of the above two effects acting in the opposite directions. Qualitative understanding of the remarkable differences of Θ between Ph_2S and Ph_2SO is possible in terms of the wavelengths of the benzenoid bands in UV spectra. That is, in case of Ph_2S, λ_{max} is 280 nm (solvent:n-hexane)[8], suggesting that the considerable degree of conjugation occurs, while the shorter wavelength of Ph_2SO, i.e. 267 nm (solvent:cyclohexane)[8], shows that there is little effect of the resonance. The greater degree of the conjugation in Ph_2S is in accord with the greater magnitude of Θ in this case, while, in Ph_2SO, the energy of the stabilization due to the resonance is almost lacking and the effect of repulsion is relatively pronounced, resulting in the much smaller values of Θ. Moreover, the smaller valence angle φ of Ph_2SO may also be one of the reasons for which the effect of repulsion acts the principal role. On the basis of this consideration, the differences in the solvent-dependences of Θ between Ph_2S and Ph_2SO may be interpreted to be due to the differences in the main factors determining Θ. In the present situation, however, we think that the further discussions would only be speculation. Further experimental investigations in relation to the above-mentioned considerations are now required.

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(Received March 7, 1972)