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IR SPECTROSCOPIC MANIFESTATIONS OF H-BONDING INTERACTION

SPECTROSCOPIC techniques provide powerful tools for investigating the nature of H-bonding. Infrared and Raman spectra reveal the characteristic frequencies of molecular vibrations. Such frequencies are fixed by the masses of the vibrating atoms, the molecular geometry and the restoring forces holding the atoms in their equilibrium positions in the molecule. Because of molecular interactions, frequencies of normal vibrational modes of a molecule are shifted to higher or lower values and the integrated intensity of the characteristic vibrational band is also modified. In general, the integrated intensity is increased and the stretching mode and its harmonics are shifted to lower frequencies by H-bond formation. In many systems the shift is 10% of normal mode of vibration. This effect is due to the weakening of the force constant for the A-H stretching mode caused by the formation of the H-bond. The shifted absorption bands due to the H-bonded A-H stretching vibrations are much broader than the corresponding bands of the

non-H-bonded A-H group. These spectral variations correlate very well with important chemical and physical properties of H-bonding systems. The correlation is based mainly on the fact that the formation of H-bond restricts certain rotational and translational degrees of freedom and forms an equal number of new vibrational degrees of freedom¹.

It is observed that there is a slight decrease in integrated intensity of the corresponding overtones. This can be explained on the basis that the intensity of absorption due to ir active vibrations is directly proportional to the rate of change of the electrostatic dipole moment ($d\mu/dr$) with internuclear distance. An estimation of the magnitude of $\vec{\Delta}\mu$, the H-bond interaction moment is possible from ($d\mu/dr$) calculation with ir spectra. In the present study an attempt is made to evaluate $\vec{\Delta}\mu$ by considering the interaction of phenol + carbonyl systems.

The integrated intensity (A) of the complexed C=O can be obtained from the relation derived by Freeman². Using the integrated intensity values and assuming that the carbonyl vibration is a pure stretching mode, the change in bond moment on stretching can be calculated from the relation³,

$$\left(\frac{d\mu}{dr}\right) = \left[\frac{1}{m_c} + \frac{1}{m_o}\right]^{-1/2} \frac{d\mu}{db}$$

and

$$\frac{d\mu}{db} = \pm \left(\frac{3C}{\pi} A\right)^{1/2}$$

where C is the velocity of light and m_c and m_o are the masses of carbon and oxygen atoms. The mean dipole moment derivatives of the C=O bond characteristic of the 1:1 and 1:2 complexes in various phenol + carbonyl systems and their frequency shift along with the fundamental⁴ are reported in Table I.

TABLE I

Complexing system	Frequencies (cm ⁻¹)			$(d\mu/dr)_{\text{mean}}$ 1:1	$(d\mu/dr)_{\text{mean}}$ 1:2
	$\nu_{\text{C=O}}$ free	1:1	1:2		
Phenol + methyl acetate	1757	1735	1713	8.865	6.503
Phenol + ethyl acetate	1749	1731	1714	5.447	4.063
Phenol + isobutyl acetate	1753	1726	1715	7.677	1.781
Phenol + <i>n</i> -amyl acetate	1750	1728	1718	7.706	4.518
Phenol + benzyl acetate	1756	1731	1720	8.013	4.199
Phenol + phenyl acetate	1778	1754	1748	8.395	5.913

$(d\mu/dr)$ for the O-H bonds should naturally be higher. In the present work, it is not possible to calculate the exact values from the O-H band intensities, because of the overlapping bands arising from self-association effects and that of two other symmetrical bands resulting from H-bond isomerism as explained by Fritzsche⁵. However, the magnitude of $\Delta\mu$, the interaction moment along the O-H...O bond, can be estimated from the $(d\mu/dr)$ value for the C=O bonds reported here for the 1:1 complexes.

The value of $(d\mu/dr)$ for 1:1 complexes of the carbonyl systems considered here varies from about 5×10^{-10} esu cm⁻¹ to 8×10^{-10} esu cm⁻¹. If one of the oxygen sp²-hybrid orbitals is almost collinear with the O-H...O axis, it will be in a most favourable position for maximum interaction between the O-H bond and the lone pair forming an atomic dipole. Using minimized distances of 1.03 Å and 1.04 Å for free and H-bonded O-H⁶⁻⁸, and a maximum displacement of 0.025 Å⁹, along the O...O distance, one obtains a $\Delta\mu$ of about 0.10-0.15 D, owing to the polarization of the C=O bond. A similar or slightly higher value would also be expected for the induced moment for the O-H bond. So a total $\Delta\mu$ of about 0.3-0.4 D may be explained by considering the vibrations of the lone pair of electrons together with the vibrations of the O-H bond. The estimation of $\Delta\mu$ from the dielectric polarization method confirms this order of interaction moment¹⁰. In the present study, only a weak H-bonding interaction is considered. In many complexes such as triethylamine + hydrobromic acid, the H-bonding interaction is much stronger and is due to proton-transfer effect. Ratajczak *et al.*¹¹ found that $\Delta\mu$ in triethylamine + phenol complexes in nonpolar solvents changes continuously within a wide range from 0.30 to about 10.00 D. To account such high polarity they suggested the possibility of partial proton-transfer species. In weak H-bonded complexes, the partial proton transfer is hindered due to the existence of resonance structure of type O⁻...H-O⁺.

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SYNTHETIC STUDIES IN 2-ARYLBENZOFURANS

AMONG the methods employed for the synthesis of 2-arylbenzofurans, the method of Whally and Lloyd¹ using Pd-C in mild acetic acid medium has greater applicability on account of its simplicity and easy availability of the intermediate desoxybenzoins. These workers¹ have, however, reported that the cyclization does not proceed well in a few cases. Dann *et al.*² have extended the method more successfully for the cyclization of many desoxybenzoins to 2-arylbenzofurans using the demethylation mixture of aluminium bromide and benzene.

As can be seen, this method has two variables namely:

- (a) The demethylation agent,
- (b) The solvent.

With a view to develop a convenient procedure and appropriate conditions for the synthesis of 2-arylbenzofurans from desoxybenzoins, a comparative study of these two variables has been made using a few demethylation agents in different solvents. The following reagents in the chronological order have been studied: (A) AlCl₃-CH₃CN, (B) HBr-AcOH, (C) HI-Ac₂O, (D) AlCl₃-C₆H₅NO₂ and (E) AlCl₃-C₆H₆. Using these reagents the following 2-arylbenzofurans (i) 6-methoxy-2 (2', 4'-dimethoxyphenyl)-benzofuran I (methyl ether of naturally occurring vignafuran³, II), (ii) 6-methoxy-2- (2', 3', 4'-trimethoxyphenyl)-benzofuran III (dimethyl ether of naturally occurring pterofuran^{4,5} IV) and (iii) 6-methoxy-2 (2', 4', 6'-trimethoxyphenyl)-benzofuran V, have been prepared from the desoxybenzoins (i) 2-hydroxy-4-methoxyphenyl-2', 4'-dimethoxybenzyl ketone⁶ VI, (ii) 2-hydroxy-3, 4-dimethoxyphenyl-2', 4'-dimethoxybenzyl ketone⁷ VII and 2-hydroxy-4, 6-dimethoxyphenyl-2', 4'-dimethoxybenzyl ketone⁸ VIII.

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