Tetrahedron Letters No. 24, pp 2037 - 2040, 1976. Pergamon Press. Printed in Great Britain.

THE EFFECTS OF SOLVENTS ON THE INTRAMOLECULAR OH...π BONDED SYSTEM

Shinichi Ueji*

Institute of Chemistry, College of General Education, Kobe University,
Tsurukabuto, Nada, Kobe 657, Japan

and

Toshio Kinugasa

Department of Chemistry, Faculty of Science, Kobe University,
Rokkodai, Nada, Kobe 657, Japan

(Received in Japan 10 April 1976; received in UK for publication 4 May 1976)

In contrast to the extensive investigation of solvent effects on the intermolecular hydrogen bonded system, much less attention has been paid to the effects of solvents on the intramolecular hydrogen bonded system. In former case Yoshida *et al.* showed that solvent dependence of the bonded OH frequency shifts was mainly due to the dipolar association between lone pair dipole of the H-bonded system and bond dipole of the solvent.[1] On the basis of the dipolar association theory, we report the solvent effects on the intramolecular hydrogen bonded system in which π-electrons are participated as proton acceptor base.

The frequencies of the intramolecular OH...π bonded bands, νOH...π, in 2-arylphenols (I)-(VI) are found to be fairly sensitive to the change of solvent (Table 1). These frequency shifts as a function of solvent follow the Bellamy - Hallam - Williams (BHW) plot[2] (Figure 1). In this plot, it is known that the reciprocal slope of the BHW function (1/S) becomes a direct measure of the solvent sensitivity.[3]

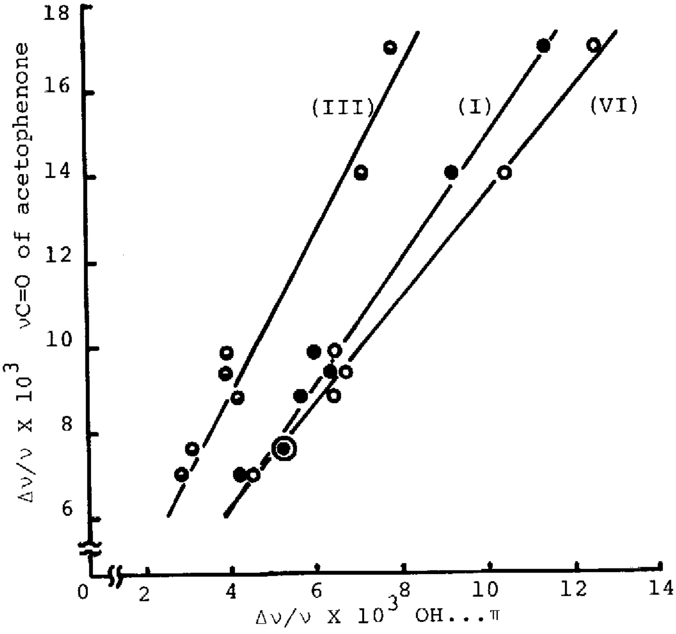
For the intermolecular H-bonded system, Yoshida *et al.* reported the parallelism between the 1/S value and the strength of H-bond.[1] This fact is consistent with the dipolar association theory, because lone pair dipole of the

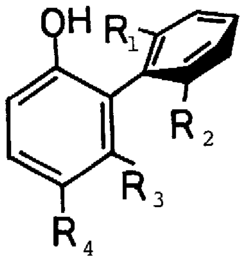
H-bonded system increase with the strength of the H-bond.

Table 1. The intramolecular OH...π bonded frequencies in a range of solvents[a)]

	ν(OH...π) cm^{-1}					
	(I)	(II)	(III)	(IV)	(V)	(VI)
(Vapour)	3588	3580	3567	3570	3553	3566
Hexane	3573	3566	3557	3559	3545	3550
Cyclohexane	3569	3565	3556	3558	3544	3547
Decaline	3568	3563	3552	3554	3542	3543
Tetrachloroethylene	3565	3560	3553	3553	3542	3542
Carbon tetrachloride	3567	3562	3553	3556	3543	3543
Dichloromethane	3555	3551	3542	3544	3533	3526
Bromoform	3547	3544	3539	3541	3532	3519

a) The frequency calibration was the same in our previous paper[4] and the frequencies in the vapour phase was obtained by the method as described in Ref. 1





(I) $R_1=R_2=R_3=R_4=$ H

(II) $R_1=R_2=R_4=$ H, $R_3=$ CH_3

(III) $R_1=R_4=$ H, $R_2=R_3=$ CH_3

(IV) $R_1=R_3=R_4=$ H, $R_2=$ OH

(V) $R_4=$ H, $R_1=R_3=$ CH_3, R_2=OH

(VI) $R_1=R_2=R_3=$ H, $R_4=$ NO_2

Fig. 1. BHW plots of νOH..π *vs.* νC=O(acetophenone).

On the other hand, the compounds studied here suggest that the 1/S value is inversely proportional to the strength of the OH...π bond (Table 2). However, it seems that our observation can be reconciled with the dipolar association theory by considering the difference between the inter- and intramolecular H-bonded systems. For the intramolecular OH...π bonded system, the steric factors on the dipolar association play a larger part than the electronic factors, because the OH...π bonded system is fixed in the same molecule by the spatial configuration. In other words, the dipolar association is strongly affected by the steric factors, and this effects are so great that the electronic effects are masked. In fact, for the compounds (I) and (VI) with the similar stereo-chemical environment around the OH...π bonded systems, the increasing order of the 1/S value agrees with the strength of the OH...π bond (see Table 2), supporting the dipolar association theory.

From these reasons, the 1/S values are compared with structural changes over a group of compounds (I) - (V).

Table 2. The numerical data for discussion

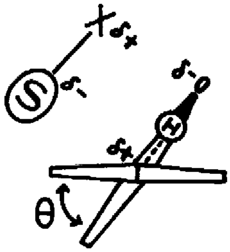
	1/S values	$\Delta\nu^{a)}$	$A_i/A_f{}^{b)}$	Dihedral angle $(\theta)^{c)}$	K-band$^{d)}$
(I)	0.71	41	6.1	50°$^{e)}$	245.5
(II)	0.63	47	9.7	60°	245.5
(III)	0.54	56	15.6	70°$^{e)}$	240.0
(IV)	0.50	45	8.5	70°	238.0
(V)	0.42	61	39.0	70° - 90°	Submerged
(VI)	0.90	48	8.6		

a) νOH(free) - νOH(OH...π) in CCl_4. b) Integrated intensity ratios in CCl_4; A_i(OH...π)/A_f(free). Both Δν and A_i/A_f can indicate the strength of the OH...π interaction (G. C. Pimentel and A. L.McClellan. "Hydrogen Bond, " W. H. Freeman and Co., San Francisco, Calif., 1960, PP 82 - 102). c) The angle was estimated from the K-band maximum in the u.v. spectrum (H. Suzuki, Bull. Chem. Soc. Japan, 33, 109 (1960). d) λ_{max} in Heptane. e) see Ref. 5.

As can be seen from Table 2, the 1/S value appears to decrease with increase of a dihedral angle made by two benzene rings. This means that solvent sensitivity can be strongly affected by the steric factors caused by the change of the dihedral angle.

From the angular dependence of the solvent sensitivity, we propose a simplified model for the dipolar association between lone pair dipole of the intramolecular OH...π bonded system and bond dipole of the solvent (Scheme). The assumed model indicate that the approach of solvent molecule to the OH...π bonded system is made difficult by the larger dihedral angle, because the steric repulsion between the solvent and the proton acceptor ring becomes an important factor. In addition to the dihedral angular effects, the presence of the substituent in proton acceptor ring also hinders the solvent molecule from approaching to the OH...π bonded system, again supporting the assumed model. These consideration may be justified, because the interdipolar distance greatly affects the dipolar association energy according to the Keesom equation.[6]

Scheme



S-X; bond dipole of the solvent

θ ; dihedral angle

References and note

1) a) E. Ōsawa and Z. Yoshida, Spectrochim. Acta 23A, 2029 (1967).

b) Z. Yoshida and E. Ōsawa, Nippon Kōgiyō Kagaku Zasshi, 69, 23 (1966).

The assumed model was represented by

$\overset{\delta-}{\mathrm{O}}\mathrm{H}\ldots\overset{\delta+}{\mathrm{B}}$

$\underset{\delta+}{\mathrm{H}}-\underset{\delta-}{\mathrm{X}}$ where B and H-X denote the base and the solvent respectively.

2) L. J. Bellamy and R. L. Williams, Trans. Fraday Soc. 55, 14 (1959).

The relative solvent shifts Δν/ν in the BHW plot mean [ν(vap) - ν(soln)]/ν(vap).

3) E. A. Cutmore and H. E. Hallam, Trans. Fraday Soc. 58, 40 (1962).

4) S. Ueji, N. Ueda and T. Kinugasa, J. C. S. Perkin II, 178 (1976).

5) M. Ōki and H. Iwamura, J. Amer. Chem. Soc., 89, 576 (1967).

6) W. H. Keesom, Z. Physik. 22, 129 (1921).