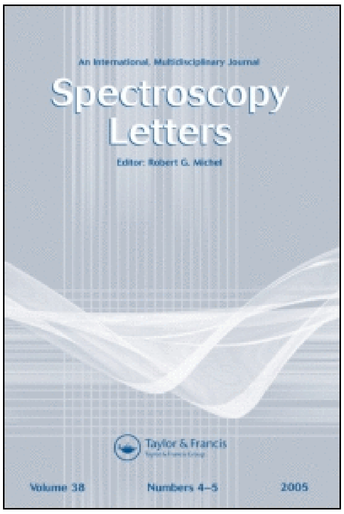

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Trends in the O-H... π Interaction between Proton Donors and Proton Acceptors

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Trends in the O-H...π Interaction Between Proton Donors and Proton Acceptors

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Abstract

The O-H...π interaction between proton donor systems phenol, substituted phenols, benzyl alcohol and cyclohexanol anc proton acceptor systems benzene, toluene, m- and p-xylenes, naphthalene and anthracene have been studied by infrared spectroscopy. It is found that the strength of the

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O-H...π hydrogen bonding decreases in the following order: phenol > benzyl alcohol > cyclohexanol, and phenol > cresol> 2,6-dimethyl phenol > 2,4,6-tri-tret-butyl phenol. The strength of the proton acceptors, on the other hand, decreases in the following order: xylene > toluene > benzene > chlorobenzene, and for polyaromatic bases the trend is benzene > naphthalene > anthracene.

Introduction

The O-H...π interaction has recieved considerable attention [1-10] by using IR spectroscopy. It was suggested using ^{1}H NMR data [11] that phenol form a O-H...π bond with benzene, where the OH proton is perpendicular to the aromatic ring. No data are available on the relative strength of O-H...π interaction between hydrogen bonding donor systems and hydrogen bonding acceptors.

The aim of this work is to present some qualitative relationship concerning these systems.

Experimental

Phenol, cresol, 2,6-dimethylphenol, 2,4,6-tri-tert-butylphenol, benzyl alcohol, cyclohexanol, benzene, toluene, m- and p-xylene, chlorobenzene,naphthalene and anthracene (all Fluka) were purified and dried before their use. The IR spectra were run on PYE UNICUM SP1100 Infrared Spectrophotometer using variable path length cell for the measurements.

The concentration of the hydrogen donors was kept constant while the hydrogen acceptor concentration was varied.

All systems were prepared in carbon tetrachloride solvent which was purified and dried over aluminum oxide for 24 hours.

Results and Discussion

Phenol and related hydrogen donor compounds exhibit two hydroxyl stretching vibration spectra in the region 3200-3700 cm^{-1} which belong to free and bonded OH bonds. In the presence of hydrogen acceptor aromatic base (π - rich group) the IR absorption spectra show new absorption band located between the free and bonded OH bands of the hydrogen donor compound, Fig. 1.

The different IR absorption of the donor-acceptor systems studied are shown in Table 1. This table shows three absorption bands; one for the free OH, the second for O-H...O bond and the third assigned to O-H...π bond. The strength and position of the new band relative to the free OH band depend on the type of interacting systems. On the basis of the recorded results one can draw the following comments: i) in phenol system the frequency of the new band changed by 40 cm^{-1} in going from xylene to anthracene, indicating that, the strength of O-H...π interaction in the phenol systems decrease in the following order: m- and p-xylene > toluene > benzene ≈ chlorobenzene > naphthalene ≈ anthracene, ii) fixing the concentration of the hydrogen

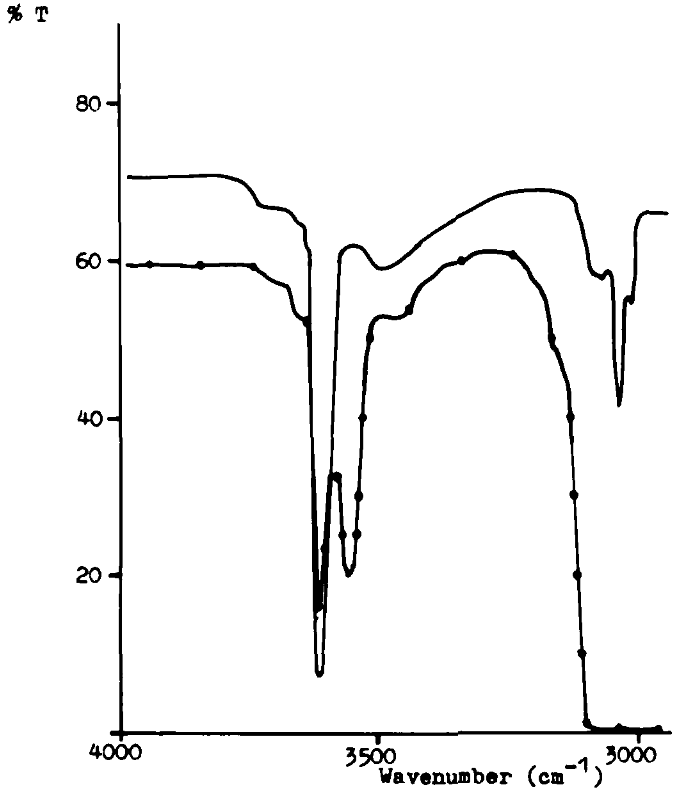

Fig.1. OH stretching spectra of phenol:(-)0.05M phenol; (●) in presence of 1.67M toluene.

acceptor the extent of O-H...π interaction decrease in the following order: phenol > cresol > cyclohexanol ≈ benzyl alcohol > 2,6-dimethylphenol > 2,4,6-tri-tert-butylphenol.

The force constant was calculated approximately from the wavenumber of the new band using the equation [12]:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Table 1 Absorption maxima, $\bar{\nu}$ in cm^{-1} and force constant, k in $N.m^{-1}$ for free and bonded OH groups.

System	Free O-H $\bar{\nu}$	Free O-H k	Bonded O-H...O $\bar{\nu}$	Bonded O-H...O k	Bonded O-H...π $\bar{\nu}$	Bonded O-H...π k
Phenol	3620	727.2	3485	674.0	-	-
= - m-Xylene	=	=	3460	664.4	3550	699.4
= - p-Xylene	=	=	3460	664.4	3550	699.4
= - Toluene	=	=	3460	664.4	3560	703.3
= - Benzene	=	=	3480	672.1	3580	711.2
= - Chlorobenzene	=	=	3480	672.1	3580	711.2
= - Naphthalene	=	=	3462	664.4	3580	711.2
= - Anthracene	=	=	3460	664.4	3590	715.2
Toluene-o-Cresol	3640	735.3	3500	679.8	3580 a	711.2
= -2,6-Dimethylphenol	3640	735.3	-	-	3610 b	723.2
= -2,4,6-tri-tert-Butyl phenol	3680	751.5	-	-	3620 b	727.2
= -Cyclohexanol	3660	743.4	3440	656.7	3600 a	719.2
= -Benzylalcohol	3660	743.4	3440	656.7	3600	719.2

a: weak
b: very weak

In a series of experiments to show the trend of the O-H...π ineraction, the phenol concentration was kept constant at 0.1 M and the hydrogen acceptor concentration is changed, Fig.2. This fiqure indicates the extent of interaction of phenol with the different hydrogen acceptors. The

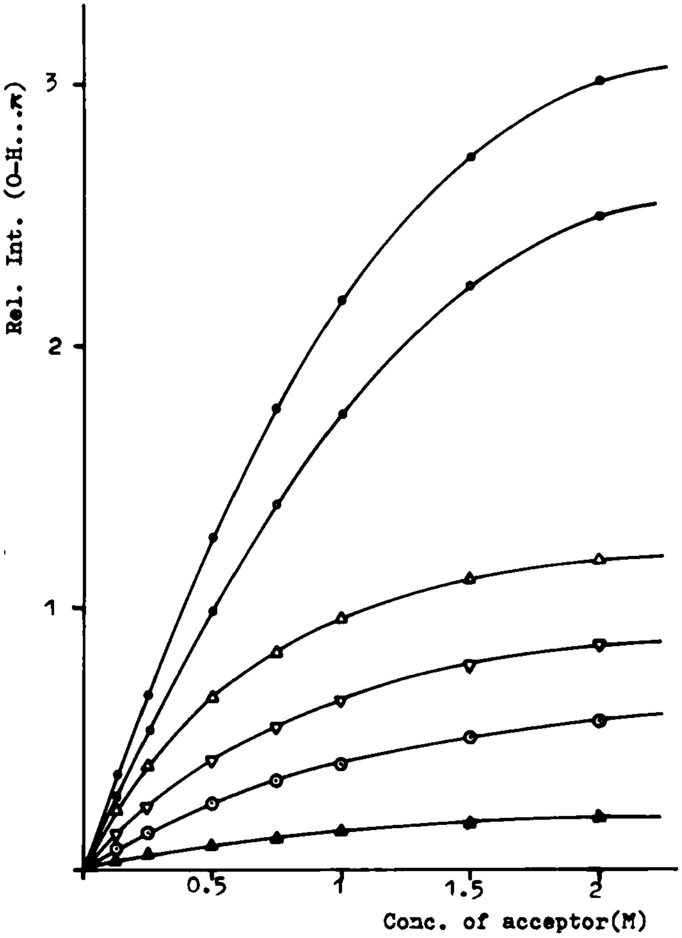

Fig.2. Relationship between the concentration of hydrogen acceptors added to 0.05M phenol and relative intensity of O-H...π band: (•) xylene; (o) toluene; (△) benzene; (▼) chlorobenzene; (◉) naphthalene; (▲) anthracene.

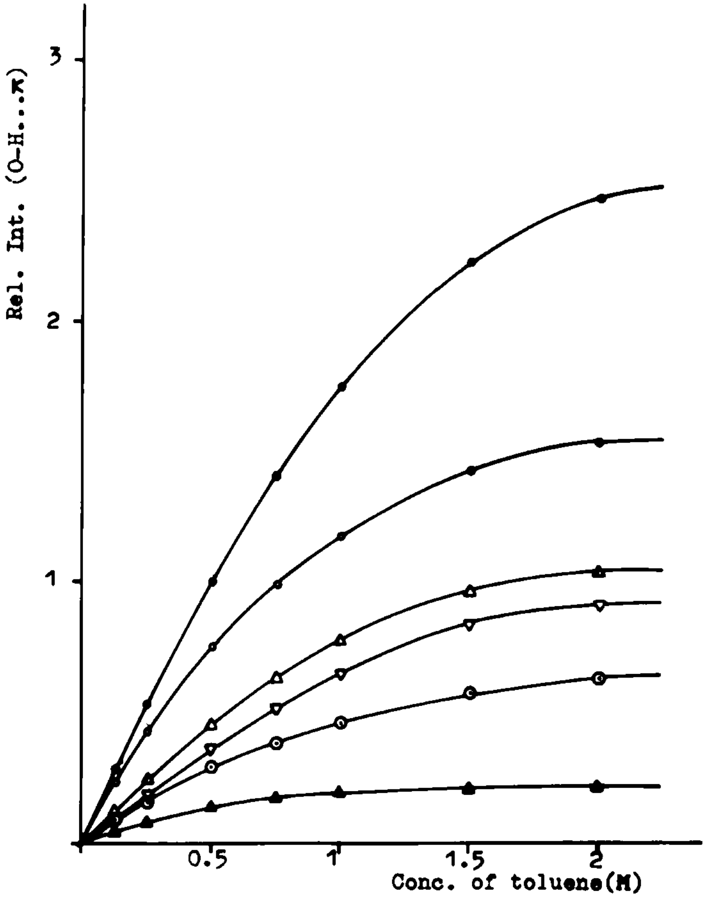

Fig.3. Relationship between the concentration of toluene added to 0.05M of hydrogen donors and relativ intensity of O-H...π band:(●) phenol;(o) o-cresol;(Δ) 2,6-dimethylphenol;(▽) benzylalcohol;(⊙) 2,4,6-tri-tert-butylphenol;(▲) cyclohexanol.

interaction of the different hydrogen donors with toluene as a hydrogen acceptor is shown in Fig.3. This figure shows the trend of O-H...π interaction in these systems.

The strength of the O-H...π bond depends on the proton of the phenol compounds which decrease on alkyl substituent of the ring, and the π charge on the benzene ring which increases on alkyl substituent in the ring and decreases on chloro or multiring substituent as in naphthalene and anthracene in which the π charge spreads over a wide area.

In conclusion the relationships shown in figures 2 and 3 indicates that the O-H...π hydrogen bonding decrease in the following order: phenol > cresol > benzyl alcohol > cyclohexanol > 2,6-dimethylphenol > 2,4,6-tri-tert-butyl phenol, and the hydrogen acceptor ability to form O-H...π hydrogen bonding decreases in the following order: m- xylene ≈ p-xylene > toluene > benzene ≈ chlorobenzene > naphthalene > anthracene.

Thus measured $\Delta\nu_{OH}$ with the change of the intensity of the band could be used to give the relative extent of O-H...π interaction.

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