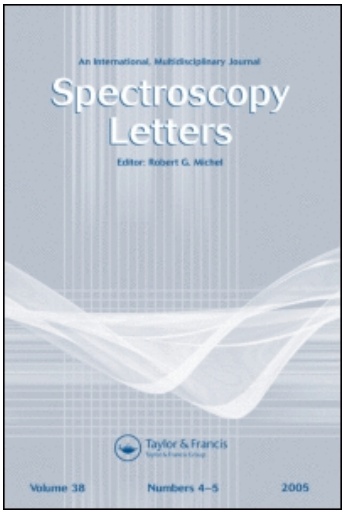

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Spectral Studies On Some Phenol Derivatives

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Abstract:

The electronic absorption spectra of 2-nitrophenol, salicylic acid, 2-aminophenol, catechol, pyrogallol and gallic acid, have been measured in different solvents. The solvent effects on the spectra have been discussed and the solvent induced spectral shifts have been analyzed as a function of different solvent polarity parameters. Moleculer orbital calculations of the different singlet-singlet and triplet-triplet transitions in these systems have been done using the PPP method.

1. Introduction

The solvent effects in the electronic and infrared absorption spectra of some substituted phenols using different solvent mixtures have been investigated[1,2]. The electronic spectra of various substituted phenols have been also calculated using different MO methods.

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The PPP method has been found to successfully describe the electronic spectra of O-, m- and p-benzenediols[3,4]. Structural parameters and electronic properties of monosubstituted phenols calculated by CNDO and INDO methods were found[5-7] to be consistent with experimental results. Ab initio calculations of orbital energies and substituent interactions have been also performed[8-10].

The present study reports the electronic absorption spectra of 2-nitrophenol, salicylic acid, 2-aminophenol, catechol, pyrogallol and gallic acid in different solvents and the results of regression analysis for solvent effects on peak locations. The PPP calculated singlet-singlet and triplet-triplet $\pi \longrightarrow \pi^*$ transitions for these compounds are also reported.

2. Experimental

The electronic absorption spectra were obtained using a Pye-Unicam SP-1800 spectrophotometer. All chemicals were of analytical reagent grade and the solvents used were spectroquality.

3. Method of Calculations

a) The Regression Analysis:

In the regression analysis the observed peak location is considered as the dependent variable while the independent variables have been selected to be the solvent interaction mechanisms E, M and N. The parameter

E is an empirical solvent polarity parameter sensitive to both solvent-solute hydrogen bond and dipolar interactions, and the parameters M and N are defined as follows[11,12].

$$M = \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

$$N = \frac{d - 1}{d + 1} - \frac{n^2 - 1}{n^2 + 2} \qquad (2)$$

A Fortran IV program[13] which utilizes the Gauss elimination method to solve the sets of multilinear equations by standard matrix methods has been used in the present calculations.

b) MO Calculations

The PPP method[14,15] has been used to calculate the different singlet-singlet and triplet-triplet $\pi \longrightarrow \pi^*$ transitions for the substituted phenols studied here. Full configuration interaction calculations including only singly excited configurations have been performed. The resonance integrals, VSIP's and one-center electron repulsion integrals have been assigned their well known values[16,17]. The two-center electron repulsion integrals have been calculated using the Mataga-Nishimoto approximation[18]. A Fortran IV program [19] for the PPP method has been used in our calculations and the molecules have been assigned their experimental geometries[20]. The calculations have been performed on a PDP 11/70 computer.

4. Results and Discussion

a) Analysis for the Solvent Effects:

The electronic absorption spectra of 2-nitrophenol in n-hexane as the solvent exhibit three bands with peak locations at 226 nm, 270 nm and 345 nm. Since the nitro group is being one of the strongest acceptor substituents and the hydroxyl group being a strong donor the third band can be assigned as an intramolecular charge transfer band. This band is shifted to longer wavelengths on going to more polar solvents (Table 1) due to the more stabilization of the excited state than that of the ground state. A consistent red shift has been also observed for the second band while the first band appeared only as a shoulder at 230 nm in cyclohexane.

In case of salicylic acid, the first band appeared in hexane and ethanol with λ_{max} located at 239 nm and 236 nm respectively, while the second band appeared at 278 nm, 277 nm and 260 nm in cyclohexane, methanol and water respectively. More systematic changes have been observed for the intramolecular CT band where it appeared at 309 nm, 330 nm, 306 nm, 310 nm and 305 nm in hexane, acetone, DMF, acetic acid and ethanol respectively. The possible ionization of the -COOH group results in a blue shift of the intramolecular CT band and may explain its disappearence in solvents such as water.

Table 1: Electronic absorption spectra of substituted phenolo in different solvents.

Solvent	Observed peak locations (nm)					
	I	II	III	IV	V	VI
Hexane	226,270,345	239,309	234,286	279	230,265	274
Cyclohexano	213,230,272,345	216,278	216,234,286	214,240,310	218,265	-
Carbontetrachloride	275,350	-	-	-	-	-
Acatone	350	330	-	-	-	325
Dimethylformamide	270,345	306	294	282	270	276
Acetic acid	274,350	310	278	269	270	276
Ethanol	275,350	236,305	-	290	266	273,302
Methanol	273,345	220,277	233,285	236,304	222,267	222,274
Water	280,354	212,260	224,277	230,283	226,270	232,296

For 2-aminophenol where the two substituents introduced into the benzene ring are strong donor groups such an intramolecular CT band has disappeared and both the first and second bands have shown more n ——π^* character. The peak locations of the first band were 234 nm, 233 nm and 225 nm in hexane, methanol and water respectively, while of the second band were at 286 nm, 278 nm, 285 nm and 277 nm in hexane, acetic acid, methanol and water respectively. This shows a blue shift as the polarity of the solvent increases indicating the n ——π^* character of both bands.

Similar solvent effects have been observed for catechol. The peak locations of the first band are 240 nm, 236 nm and 230 nm in cyclohexane, methanol and water respectively and those for the second band are 279 nm, 282 nm, 269 nm, 290 nm and 283 nm in hexane, DMF, acetic acid, ethanol and water respectively. It is worthmentioning that MO claculations on catechol[6] using the CNDO/2 method showed that only one rotational isomer with interamolecular hydrogen bond can exist (Fig. 1). This hydrogen bonding may somewhat hinder the n —— π^* transition in this molecule. Similar hydrogen bonded structures are expected for 2-nitro-, 2-carboxy and 2-aminophenols as shown in Fig. 1.

For pyrogallol only the first and second bands are observed. The solvent effects on peak locations are more

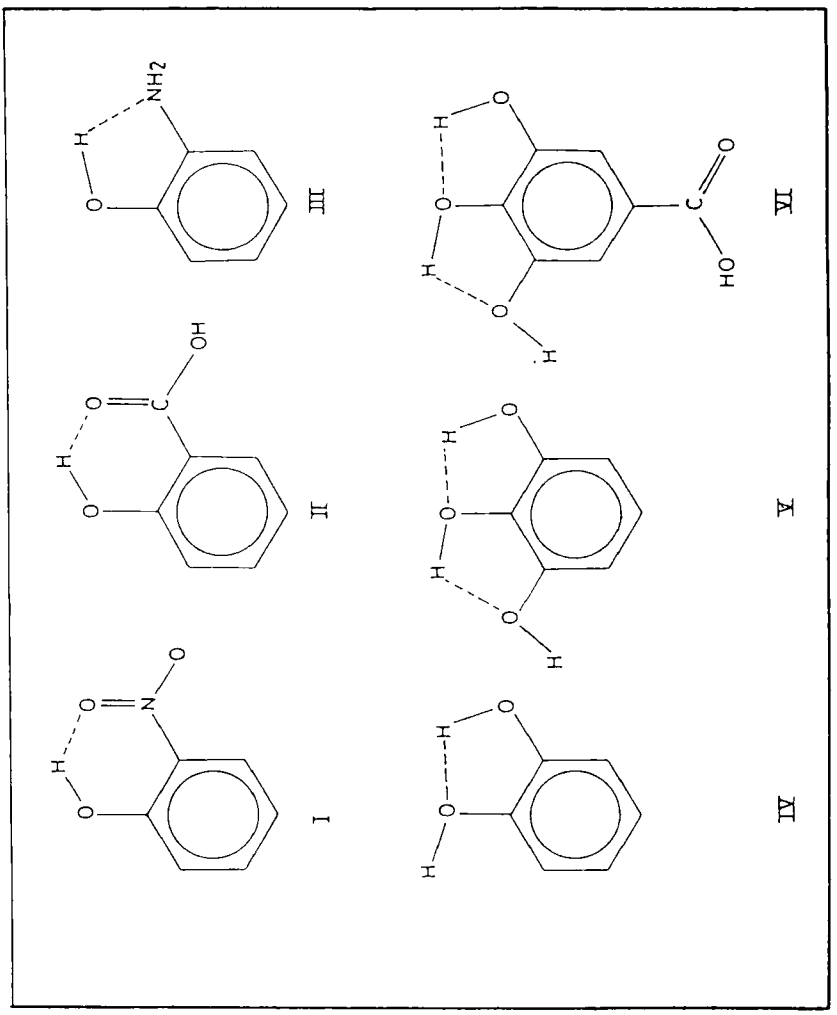

Fig 1-Possible intramolecular hydrogen bonds in substituted phenols

clear for the second band where it appeared at 265 nm, 266 nm, 267 nm and 270 nm in cyclohexane, ethanol, methanol and water respectively. Introducing a carboxylic group into pyrogallol to give gallic acid caused the appearence of the intramolecular CT band with peak locations at 325 nm, 302 nm and 296 nm in acetone, ethanol and water respectively. The second band appeared at 274 nm, 276 nm 273 nm and 274 in hexane, DMF, ethanol and methanol respectively.

A multiple linear regression analysis for the solvent effects on the spectra of these substituted phenols has been done and the results are reported in Table 2. As an indication of the fit the sum of the squared residuals has been calculated for each. In a test for significance referring to a one-tail test the level of significance has been found to be above 90% corresponding to the value of the multiple correlation coefficient. This may indicate that the shift in peak location in different solvents can be reasonably expressed in terms of the solvent polarity parameters E, M and N.

b) MO Calculations:

The calculated singlet-singlet and triplet-triplet $\pi \longrightarrow \pi^*$ transitions using the PPP method are given in Table 3. The agreement between calculated and observed transitions is reasonable. In Table 3 the calculated moleculer ionization potentials are also given together with the only available experimental value for catechol

Table 2: Results of the regression analysis

System	Band	regression coefficients a_0	a_1	a_2	a_3	MCC[a]
I	^1L_b	230.8077	0.5664	115.9703	-12.4689	0.8635
II	CT	479.9697	-1.1093	-715.3577	31.3132	0.7931
III	^1L_b	359.7670	-1.4493	-150.9686	43.7441	0.9337
IV	^1L_b	274.4448	-0.0404	12.1021	15.3173	0.7939
V	^1L_b	244.4797	0.1068	141.1507	-0.9686	0.7113

a : Multiple correlation coefficient.

which shows a good agreement. Although the effects of substituents on acidity are largely determined by effects in the phenoxide anion and only to a slight extent by those in the corresponding neutral phenol[21], a reasonable correlation between the calculated positive charge on the phenolic group oxygen and the available experimental acidities has been obtained as shown in Table 3.

Table 3: Calculated and experimental ionization potentials and transition energies in eV:

System	IP Caled.[a]	IP Exptl.[b]	Acidity pK[c]	Acidity q[d]	Singlet states Calcd.	Singlet states Exptl[e]	a_o^f	Triplet states
I	11.330	-	7.33	+0.037	4.903 5.457 6.377	3.583 4.591 5.485	- 5.371	3.037 4.342 4.442
II	12.310	-	-	+0.054	5.381 5.908 6.712	3.999 4.459[g] 5.187	2.583	3.774 4.880 5.913
III	8.381	-	10.45	+0.014	3.185 5.210 6.571	4.334 5.298	3.445	2.295 4.031 5.810
IV	8.162	8.56[b]	10.05	+0.015	3.182 5.258 6.522	3.998[g] 4.443 5.165	— 4.518	2.315 4.003 5.746
V	11.130	-	-	+0.028	6.137 6.475 6.742	4.660 5.390	—	3.613 4.902 4.983
VI	7.353	-	-	+0.030	3.503 3.814 6.053	4.188[h] 4.524 5.343	— 5.070	3.475 3.657 3.770

a) Applying Koopman's theorem b) Reference 9.

c) Reference 21; for the ionization of the hydroxyl group in 20% dioxane-water solvent at 30°C.

d) The calculated atomic charge on the hydroxyl oxygen.

e) In hexane as solvent. f) Regression intercept (eV)

g) In cyclchexane as solvent h) In water as solvent.

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