

Full Length Research Paper

Effect of solvents on the electronic absorption spectra of 9,14 dibenzo (a, c) phenazine and tribenzo (a, c, i) phenazine

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9,14-dibenzo (a, c) phenazine and tribenzo (a, c, i,) phenazine, were synthesized and solvent effect on the electronic absorption spectra of the compounds were studied. In some aspects of the spectra, the features of anthracene were carried into the spectrum of these synthesized phenazine derivatives with a change in symmetry. The absorption spectra of the two compounds were red-shifted compared with that of phenazine. Polar solvents shift the wavelength of absorption to the red relative to non-polar solvents, thus revealing that the observed bands have more charged excited state. This suggests that the transition is $\pi \rightarrow \pi^*$ transition.

Key words: 9,14-dibenzo (a, c) phenazine, tribenzo (a, c, i,) phenazine, electronic absorption spectra, solvent effect.

INTRODUCTION

Phenazine and its derivatives phenazine dyes (were of great commercial importance in the 1920's and 1930's, however they are still used in some staining experiments) are members of a series of heterocyclic hydrocarbon whose fluorescence, phosphorescence and other spectroscopic properties are strongly dependent on solvent concentration and pH. Through experimental and theoretical investigations on a number of organic molecules, it has been observed that, the shape, position and intensity of electronic absorption bands are affected by changes in solvent properties like polarity, dielectric constant, polarizability, acidity and the nature of solute solvent interactions (Reichardt, 2004). Statistical theories have interpreted these changes in spectra shift to unequal perturbation of light absorber between the ground and excited state of the molecules (Iweibo, 1992). Identification of the nature of such interactions and the measurement of the extent of perturbations are used in the elucidation of molecular

and the structure of molecules.

The effects of solvents, including polymeric substrates, and substituents on the absorption spectra of substituted and unsubstituted azo dyes had been studied. The position of the intense, visible charge-transfer band was dependent on the dielectric properties of the solvent; a linear relationship was found between observed and calculated frequency shifts (Gether, 1972). Spectral behavior obtained for the dyes in polymeric solvents was consistent with that obtained for the dyes in nonpolymeric solvents. Shifts in absorption maxima with substitution in positions insulated from the conjugated chromophoric system were consistent with Taft polar-substituent constants; the effects of such substituents were, therefore, primarily inductive in nature (Gether, 1972).

Qing et al. (2002) have studied the solvent effect on infrared spectroscopy of 5-methyl-7-methoxy-iso-flavone in 20 different pure organic solvents to investigate the solvent-solute interactions and to correlate solvent properties such as the Kirkwood-Bauer-Magat (KBM) equation, the solvent acceptor number (AN) and the linear solvation energy relationships (LSER), respectively, with the infrared band shift. Little linear relation between dielectric

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constants and the frequencies showed that the KBM relationship was unsuitable for the complicated molecules. Józefówich et al. (2002) also confirmed that the wave number difference of absorption and excitation spectra are solvents dependent and that bathochromic shift is larger in non-polar solvent than in polar solvent. Earlier we have shown the relationship between the absorption spectra shift and polarity of solvent (Adeogun et al., 2007, 2008), in this study, approach to the synthesis of the 9,14-dibenzo (a, c) phenazine and tribenzo (a, c, i) phenazine was developed coupled with the effect of solvent polarity on UV - visible electronic absorption spectra of the synthesized compounds. The effect of solvent media on transition energies, oscillator strength and other absorption parameter are also presented. Based on the shifts, the transitions are assigned and the band shapes were explained according to the Frank Condon Principle.

MATERIAL AND METHODS

The solvents used were all analytical grades and are products of British Drug House Limited London. Phenanthrenequinone, 0-phenylenediamine and 2,3-diaminonaphthelene were all products of sigma chemicals. The solvents were distilled several times to spectroquality grade, while the solutes were used without further purification. All weighing were carried out on Mettler H18 chemical balance.

Synthesis of 9,14-dibenzo (a, c) phenazine

0.100 g of phenanthrenequinone powder was quantitatively transferred into a 12 ml Erlenmeyer flask and dissolved in ethanol. An orange yellow solution obtained was warmed for 8 min for complete dissolution of the powder. 0.055 g 0-phenylenediamine was also dissolved in 8 ml of ethanol solution, warmed for 2 min for complete dissolution of the powder. The two solutions were mixed together, refluxed over water bath for 6 min for the reaction to complete.

The golden yellow solution formed was allowed to cool, the yellow crystals of 9,14-dibenzo (a, c) phenazine formed were filtered under pressure from the solution. These were then thoroughly washed with ethanol solution to remove unreacted solutes and recrystallised with hexane to obtain pure product. Melting point was determined using standard method (Nasta et al., 2006) and was found to be between 222 - 224°C.

Synthesis of tribenzo (a, c, i) phenazine

0.104 g phenanthrenequinone was dissolved in 18 ml of ethanol, warmed for 20 min until a clear orange coloured solution was obtained. 0.0794 g of 2,3-diaminonaphthelene (5×10^{-4} M) solution was also made by dissolving the powdered compound in 8 ml of ethanol and warmed slightly for 5 min. The two solutions were mixed together, refluxed under water bath with intermittent shaking for 10 min. On cooling, the orange crystals of tribenzo (a, c, i) phenazine formed were filtered from the solution and thoroughly washed with cold ethanol. Melting point was also determined, and was found to be between 297 and 298°C.

Absorption spectra analysis of 9,14-dibenzo (a, c) phenazine and tribenzo (a, c, i) phenazine

The spectrophotometric analysis of the dilute solution of the synthesized compounds was done in each of the solvents, in the

concentration range of ($10^{-5} - 10^{-6}$) M using Perkins-Elmer Lambda 3D double beam UV - visible spectrophotometer. One of the pair of matched quartz cuvettes contained in the reference compartment of the spectrophotometer and the other in the sample compartment contained dilute solution of known concentration. The optical excitation was done with deuterium lamp as light source in the UV region and tungsten lamp in the visible region. The spectra were scanned at 25°C in the range of 220 - 500 nm for both the solution and the solvent whose absorption serve as blanks or base lines for the solution absorption bands. The data obtained from the chart recorder were used in the calculation of molar absorptivity, according to the relations below:

$$\text{Absorptivity} = \mathcal{E}_{(v)} = \log \frac{I_o}{I} = \frac{A}{C \times l}$$

Where $\mathcal{E}_{(v)}$ is the absorptivity, A is the absorbance, C is the concentration of the solute in mol dm^{-3} (M) and l is the path length of the light. The plots of $\mathcal{E}_{(v)}$ in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ against ν (wave number) in cm^{-1} were made for each spectrum.

RESULTS AND DISCUSSION

Presented in Figure 1 and 2 are the representative spectra of 9,14-dibenzo (a, c) phenazine and tribenzo (a, c, i) phenazine in dichloromethane and ether. Table 1 and 2 are the summary of the properties of maximum absorptivity band peaks, that is, oscillator strength, halve numbers (both at full and halve band width), and molar absorptivities of the different transitions for the two compounds in the solvents of choice.

(a) For 9,14-dibenzo (a,c) phenazine

The spectra 9,14-dibenzo (a,c) phenazine (Figure 1) shows four vibronic bands both in dichloromethane and ether. These bands are designated as bands I, II, III and IV in order of increasing energies. The intensities (area under the curves) follow the order. When compared with anthracene, band II is likely to be $A \rightarrow {}^1L_b$ while band I is $A \rightarrow {}^1L_a$ transition. The band 1 or $A \rightarrow {}^1L_a$ has molar absorptivity of $21450 \text{ M}^{-1} \text{ cm}^{-1}$ in dichloromethane. This band may also be assigned $S_0 \rightarrow S_1$ transition. It is red-shifted in less polar ether relative to polar dichloro-methane. Band II ($S_0 \rightarrow S_2$) transitions is of little intensity and exhibits the vibrational fine structures. The transitions at 32308 cm^{-1} ($\epsilon = 14026 \text{ M}^{-1} \text{ cm}^{-1}$) in dichloromethane and 32220 cm^{-1} ($\epsilon = 34211 \text{ M}^{-1} \text{ cm}^{-1}$) in ether show a blue shift in dichloro-methane relative to less polar ether. Band III ($S_0 \rightarrow S_3$) is assigned $A \rightarrow {}^1B_b$ transitions which occurs at 35251 cm^{-1} ($\epsilon = 42904 \text{ M}^{-1} \text{ cm}^{-1}$) in dichloro-methane overlaps with a more intense band IV which appears at 38925 cm^{-1} ($\epsilon = 67657 \text{ M}^{-1} \text{ cm}^{-1}$). Band III can also be assigned as short-axis polarised 1B_b , while band IV with ($A \rightarrow {}^1B_a$) designation is mechanically an intense long axis polarized band, with the largest areas under the graph in accordance with the selection rule, that is, it is both a symmetry and quantum mechanically allowed transition.

Table 1. Electronics properties of (a,c) phenazine in Ether and Dichloromethane

Solvent	Band I				Band II				Band III				Band IV			
	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f
Ether	25, 523	26,625	55, 921	0.06	32, 220	31,750	34, 211	0.05	35, 390	37,250	100, 329	0.2	38, 950	39,363	157, 895	0.3
Dichloromethane	25, 641	26,250	21, 452	0.02	32, 308	32,125	14, 026	0.02	35, 251	36,125	42, 904	0.07	38, 935	38,874	67, 657	0.11

Table 2. Electronics properties of Tribenzo (a, c, i) phenazine in Ether and Dichloromethane

Solvent	Band I				Band II				Band III			
	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f	ν_{\max} (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	$\epsilon_{(v)\max}$ (M ⁻¹ cm ⁻¹)	f
Ether	23,833	24,500	18,000	0.02	31,613	31,875	94,563	0.13	40,193	40,000	52,000	0.09
Dichloromethane	23,762	27,300	20,095	0.02	31,498	32,125	92,000	0.13	40,019	40,063	60,520	0.1

Band III and IV are red shifted in dichloro – methane relative to ether due to an increase in dipole movement on excitation of the electron which make the band to interact more electrostatically. This leads to a change in charge distribution and increased delocalization of electrons. Thus, both the ground and the excited $n \rightarrow \pi^*$ transition does not occur in the molecule as the lone pair of electron on nitrogen atom can not be forced to overlap maximally due to the rigidity of the ring system of the molecule.

(b) Tribenzo (a,c,i) phenazine

Figure 2 as well as Table 2, summarizes the spectra features of tribenzo (a,c,i) phenazine in term of vibrational fine structures, band shapes and relative intensities. Three bands were observed for tribenzo (a,c,i) phenazine in both polar and non polar solvent, and they are designated as band I, II and III.

The intensities bands follow the order $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$, $S_0 \rightarrow S_2$, while the transitions in order of increasing energies follow the order, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$. The $S_0 \rightarrow S_2$ transition, that is, band I, is a mixture of $A \rightarrow {}^1L_b$ and $A \rightarrow {}^1L_a$ with the former submerged under the latter. $S_0 \rightarrow S_3$ transition is largely $A \rightarrow {}^1B_b$ transition, which has borrowed its intensities band from the symmetry allowed $A \rightarrow {}^1B_a$ transition. The borrowing appears to be very efficient as the areas under the $A \rightarrow {}^1B_b$ and $A \rightarrow {}^1B_a$ transition are comparable.

A slight red shift in absorption maximum is observed in the spectra of tribenzo (a, c, i) phenazine in dichloromethane relative to ether (a less polar as solvent) for bands II and III. This is due to the stabilization of the ground state and the excited state owing to the higher dipole moment for the solvent. The red shift in absorption spectrum of tribenzo (a, c, i) phenazine relative to dibenzo (a,c) phenazine is due to the condensation of additional benzene ring to dibenzo (a, c) phenazine at position (i) leading to the expansion of the

radius of the n -electron system of the ring, in conformity with the free electron molecular orbital theory (FEMO)

Comparison of the spectra of phenazine with 9,14-dibenzo (a,c) phenazine and tribenzo (a,c,i) phenazine.

Comparison of the absorption bands obtained from molecular orbital calculation of phenazine using a variable β -approximation according to Zimmermann (1970) with those of dibenzo (a,c) and tribenzo (a,c,i) phenazine, four symmetry allowed transition at 44800, 41300, 28000 and 25300 cm⁻¹ were obtained. These show that the spectra features of phenazine are retained but with slight red shift occurring in both 9,14-dibenzo (a,c) and tribenzo (a,c,i) phenazine respectively owing to the expansion of electron ring system as mentioned above. The absorption spectra of phenazine

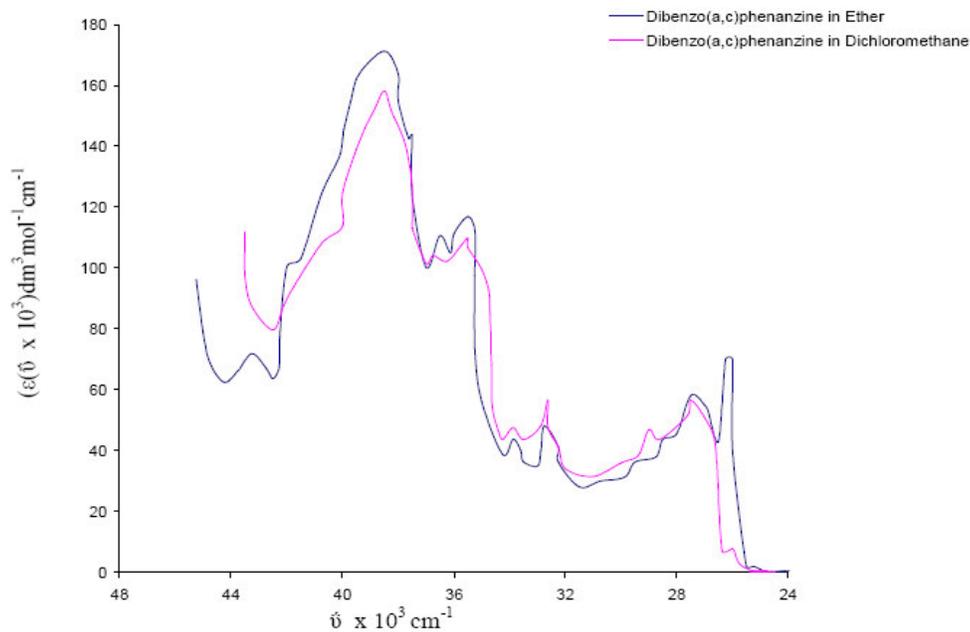


Figure 1. Absorption spectra of dibenzo (a,c) phenazine in ether and dichloromethane.

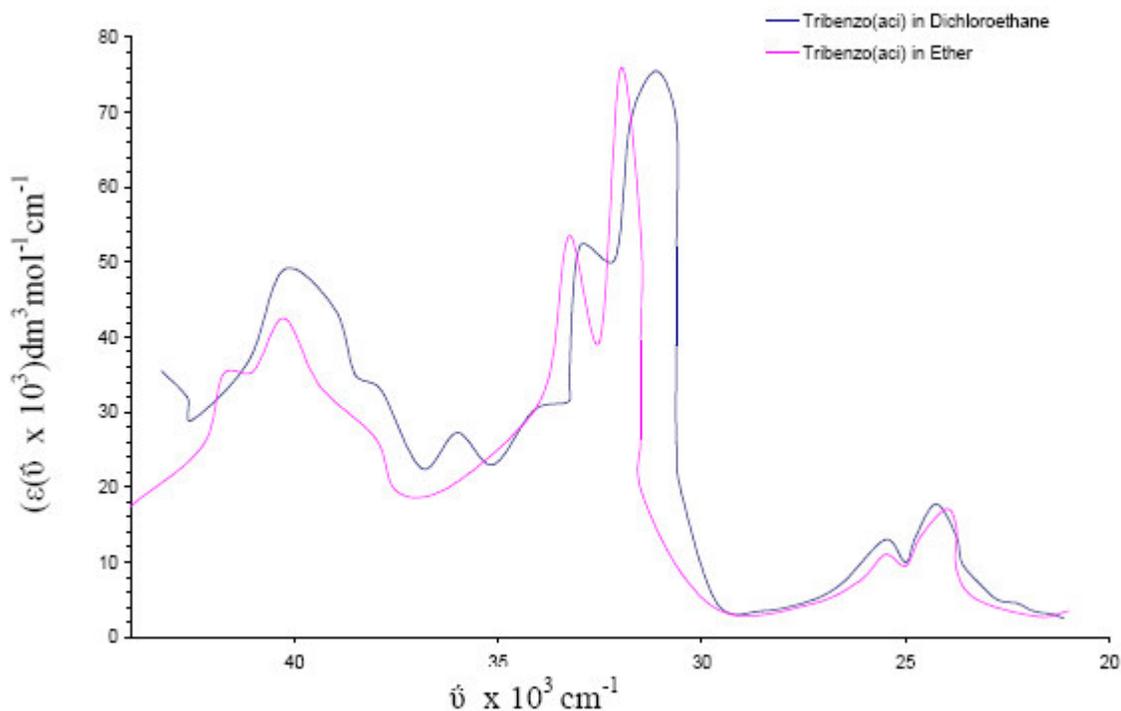


Figure 2. Absorption spectra of Tribenzo (a, c, i) phenazine in ether and dichloromethane.

nazine and anthracene is characterized into long axis and short axis polarized transition by comparison of the spectra obtained with the result obtained from those of the Parriser-pear-pople calculation involving β approximation (Inoue, 1971).

Conclusions

Properties of molecular interactions based on the absorption spectra of 9,14-dibenzo (a,c) phenazine and tribenzo (a,c,i) phenazine have been studied. Assignments of the

electronic transitions involved are suggested on the basis of absorption spectra and solvent effects. From the results, we note that the molecule emission state in non-polar solvents is of $\pi \rightarrow \pi^*$ nature, having a charge transfer character. Moreover, we have considered a possible inversion of the first two electronic levels in the polar medium involving a stabilization of the $\pi \rightarrow \pi^*$ state compared with the $n \rightarrow \pi^*$ state.

The total energy of interactions of the two solutes in dichloromethane is controlled by hydrogen bond and polarity effects. This means that the hydrogen bond and the dipolar interactions play an equivalent role in stabilization of the first singlet electronic level of the molecules. These results can therefore be exploited to envisage an energy diagram involving a principal photo physical process of solute molecules in different media.

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