

Full Length Research Paper

Effects of solvent on the UV-visible absorption spectra of acenaphtho(1,2-b) quinoxaline and acenaphtho(1,2-b)benzo(g)quinoxaline

S. A. Ahmed^{1*}, N. O. Obi-Egbedi², N. W. Odozi², I. Iweibo² and M. D. Adeoye³

¹Department of Chemistry, University of Agriculture, Abeokuta, Nigeria.

²Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

³Department of Chemical Sciences, Fountain University, Osogbo, Nigeria.

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The effects of solvent on the electronic absorption spectra has been used to investigate the structural and molecular properties of acenaphtho(1,2-b)quinoxaline and acenaphtho(1,2-b) benzo(g)quinoxaline. The structures of the compounds have been established by UV-visible spectrophotometer. The spectra behaviours in terms of dipole moments in the ground and excited states have been interpreted and related to the transition energies, intensities and the molecular structures of the compounds.

Key words: Solvent effects, dipole moments, solvent polarizability, transition energies.

INTRODUCTION

Various aspects on the spectra of some quinoxaline compounds have been studied previously by several authors, such as, electronic absorption bands of quinoxalines in cyclohexane by Mason (1962), of 2,3-diphenylquinoxalines by Bohlmann (1951), spectra properties of some derivatives of 6H-indolo{2,3-b}quinoxaline by Sarki and Al-Badri (1980), transient absorption fluorescence spectra in n-hexane by Greene et al. (1978), the fluorescence quantum yield of quinoxaline in iso-octane by Yamatoto et al. (1978), fluorescence decay of apparent $S_n \leftarrow S_i$ absorption in n-hexane by Halliday and Topp (1977), excited state absorption spectra of quinoxaline in benzene, iso-octane and cis-1,3-pentadiene by Anderson et al. (1979), the electronic transition dipole moments of charge transfer absorption and fluorescence of some quinoxaline derivatives by Czerwiec et al. (2000). However, no attempts have been made neither to report the absorption spectra nor assign the observed band for these quinoxaline derivatives.

In this work, besides the assignment of the spectra bands, the spectra behaviours in terms of dipole moments in the ground and excited states vis-à-vis the

transition energies and intensities are interpreted and related to the molecular structures of these two compounds.

MATERIALS AND METHODS

Spectroscopic grade of acenaphtho(1,2-b)quinoxaline and acenaphtho(1,2-b)benzo(g) quinoxaline were obtained from Tokyo Kasei (Japan). Methanol, ether and chloroform are products of British Drug House Ltd and were redistilled several times.

Electronic spectra of dilute solution of each compound in the concentration range of 10^{-5} to 10^{-6} M and 200 to 500 nm respectively, were determined with a computerized, double beam Shimadzu UV-1650 coupled with UV probe 2.3 version software.

Molar absorptivities and integrated absorption coefficient were determined by deconvolution of the spectra. A plot of molar extinction coefficient against wave number was used to determine the transition energy. The oscillator strength (f) in solution from states i to j was calculated using equation described in Iweibo et al. (1990) and given as Equation 1:

$$f = \frac{2.303m_e c^2 \epsilon_0}{N_o e^2 n} \int \epsilon_{(\tilde{\nu})} d\tilde{\nu} \quad (1)$$

where e is the electronic charge, m is mass of the electron, c is speed of light, ϵ vacuum permittivity, n the refractive index of solvent and $\epsilon_{(\tilde{\nu})}$ the molar absorptivity of the absorbing solute at the wave number $\tilde{\nu}$. The integral $\int \epsilon_{(\tilde{\nu})} d\tilde{\nu}$ was calculated using

*Corresponding author. E-mail: ahmedakinoye@yahoo.co.uk.

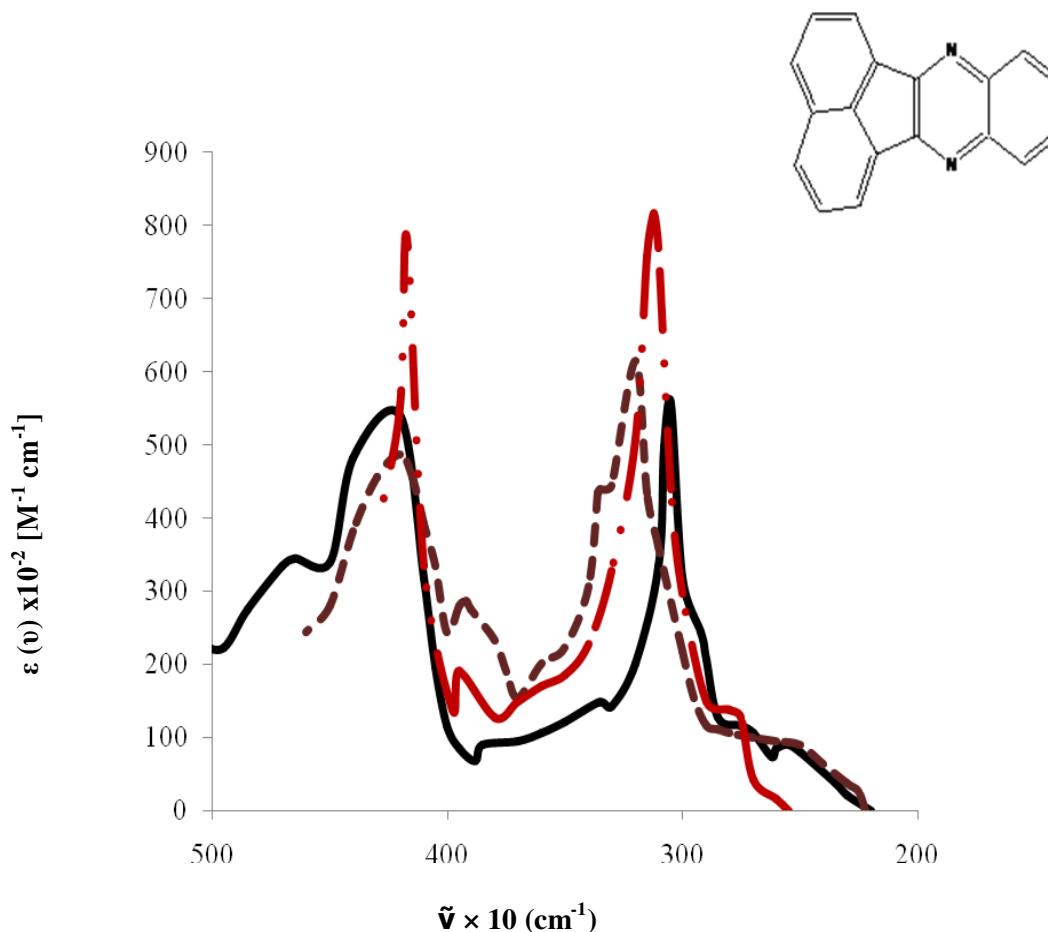


Figure 1. Electronic absorption spectra of acenaphtho(1,2-b)quinoxaline in methanol (—), ether (---) and chloroform (- · - · -).

assumptions of symmetrical bands or conformity with Gaussian distributions as described by Iweibo et al. (1982).

RESULTS AND DISCUSSION

Presented in Figures 1 and 2 are the electronic absorption spectra of acenaphtho(1,2-b) quinoxaline and acenaphtho(1,2-b)benzo(g)quinoxaline respectively in the representative solvents (methanol, ether and chloroform). Also, detailed assignment of the spectra properties in few solvents have been displayed for each compound in Table 1 to avoid overcrowding of symbols and masking of salient spectra features.

Acenaphtho(1,2-b) quinoxaline

The absorption spectra of acenaphtho(1,2-b)quinoxaline showed four distinct bands which were designated as

$S_o \rightarrow S_1$, $S_o \rightarrow S_2$, $S_o \rightarrow S_3$ and $S_o \rightarrow S_4$ in order of increasing energy.

The $S_o \rightarrow S_1$ transition is a broad band with low intensity in the three representative solvents. The bands show shoulders towards red at $26,074 \text{ cm}^{-1}$ in methanol, at $27,454 \text{ cm}^{-1}$ in chloroform. Because of their low intensities, the bands are assigned as 1L_b band (using Platt's notations) which implies that they are both quantum mechanically and overlap forbidden (that is, totally forbidden).

The $S_o \rightarrow S_2$ transition was of concentrated intensities in the three solvents, they are characterized with shoulders towards blue at $31,738 \text{ cm}^{-1}$ in methanol, $32,972 \text{ cm}^{-1}$ in ether, and $32,509 \text{ cm}^{-1}$ in chloroform.

$S_o \rightarrow S_2$ peak in methanol is exceptionally sharp and submerges the $S_o \rightarrow S_3$ peaks. Two likely causes of this observation from theoretical explanation are:

- The possibility of fusion of two bands, the solvent has little or no effect on their separation or decomposition,
- The formation of charge transfer due to

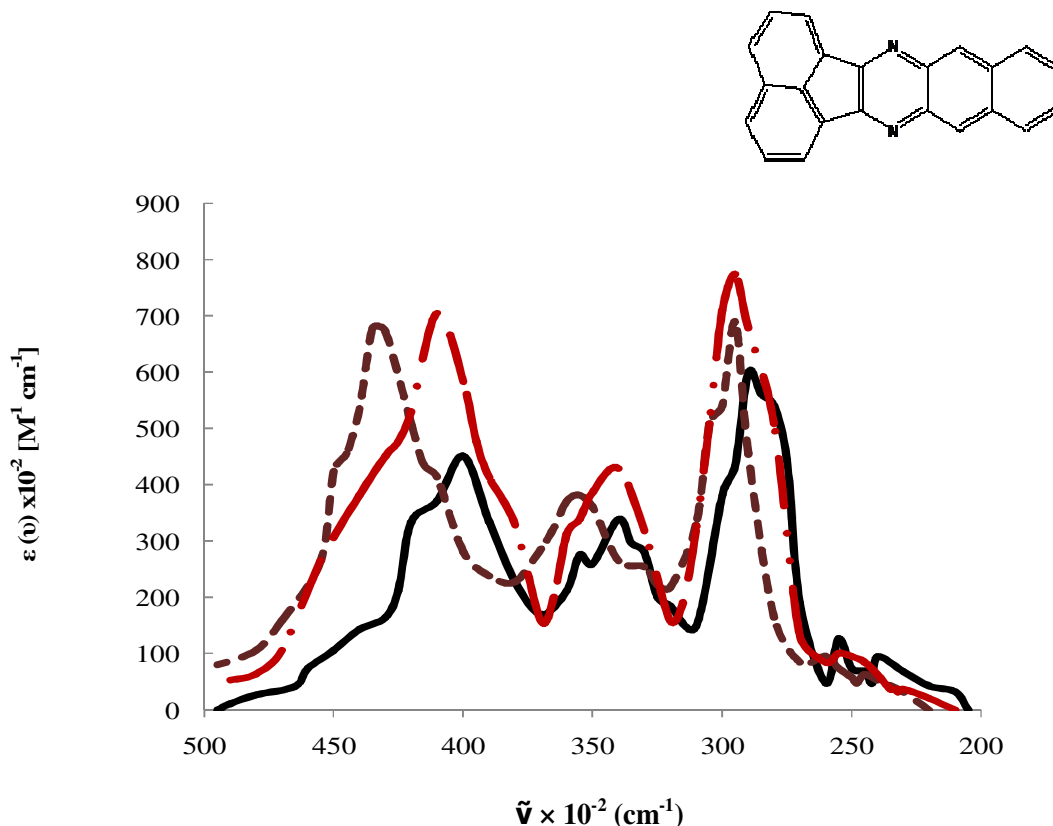


Figure 2. Electronic absorption spectra of acenaphtho(1,2-b)benzo(g)quinoxaline in methanol (—), ether (---) and chloroform (-·-·-).

donor–acceptor interaction as suggested by Czerwierniee et al. (2000).

The $S_0 \rightarrow S_3$ transition had broad bands in all the solvents, it is overlapping with the $S_0 \rightarrow S_2$ bands and can be assigned as 1B_b which implies that they are both quantum mechanically and overlap forbidden. The $S_0 \rightarrow S_4$ transitions in the three solvents had intense bands and are assigned as 1B_a bands which mean that they are both quantum mechanically and overlap allowed.

Generally, it was observed that the vibrational fine structure in all the transitions were completely lost in the solvents (much more pronounced in methanol). This suggests a specific solute interaction.

Acenaphtho(1,2-b)benzo(g)quinoxaline

Acenaphtho(1,2-b) benzo(g) quinoxaline shows five absorption band peaks in methanol, ether and four in chloroform. The fifth band peak suggests that the additional ring in acenaphtho(1,2-b)benzo(g)quinoxaline extends the radius of the π -electron of the ring. This is

in line with free electron molecular orbital {FEMO} theory, leading to relative red shift of the transition energies. The obscurity of the fifth band in chloroform agrees with the fact that chlorinated hydrocarbon suffer the disadvantage of non-transparency in the near UV region (where the transition occurred). $S_0 \rightarrow S_1$ transition was a broad band in the representative solvents. The bands were of low intensities but considerable distortion due to instrumental response was recorded for the peak in chloroform. These bands are labeled as 1L_a band indicating that the transition is totally forbidden.

$S_0 \rightarrow S_2$ transition in ether and methanol is broad, red-shifted and of low intensity with little distortion owing to instrumental response. However, the band in chloroform is intense and the transition is both quantum mechanically allowed and overlap allowed.

The $S_0 \rightarrow S_3$ transition was intense in all the solvents and the transition is allowed. However, it was observed that the $S_0 \rightarrow S_3$ transition in chloroform derived its intensity from the more intense $S_0 \rightarrow S_2$ transition. This phenomenon is known as intensity borrowing. The

Table 1. Summary of observed absorption bands of compounds in different solvents.

Compounds and transitions	Methanol			Ether			Chloroform		
	$\bar{\nu}_{\max} (cm^{-1})$	$\epsilon_{\max} (M^{-1} cm^{-1})$	f	$\bar{\nu}_{\max} (cm^{-1})$	$\epsilon_{\max} (M^{-1} cm^{-1})$	f	$\bar{\nu}_{\max} (cm^{-1})$	$\epsilon_{\max} (M^{-1} cm^{-1})$	f
Acenaphtho(1,2-b)quinoxaline									
$S_0 \rightarrow S_1$	27693	11483	0.28	28992	17287	0.18	28867	17841	0.22
$S_0 \rightarrow S_2$	30157	56926	0.91	31481	59230	0.84	31196	85463	0.87
$S_0 \rightarrow S_3$	40545	8978	0.37	39415	26258	0.21	39082	14097	0.13
$S_0 \rightarrow S_4$	42582	55216	0.89	42043	54923	0.76	41675	77093	0.59
Acenaphtho(1,2-b)benzo(g)quinoxaline									
$S_0 \rightarrow S_1$	24050	4286	0.03	24518	3712	0.04	25530	8197	0.07
$S_0 \rightarrow S_2$	25437	6388	0.05	25936	5568	0.05	29546	75956	0.73
$S_0 \rightarrow S_3$	28960	62120	0.52	29501	69142	0.61	35746	30055	0.40
$S_0 \rightarrow S_4$	33892	24562	0.26	35781	23666	0.34	42024	59290	0.52
$S_0 \rightarrow S_5$	41760	68084	0.57	43495	71928	0.76	-	-	-

$S_0 \rightarrow S_4$ transition was of low intensity in methanol and ether and was submerged under the intensity of the $S_0 \rightarrow S_3$ transition, it is designated as 1B_b (that is, quantum mechanically allowed but symmetry forbidden). $S_0 \rightarrow S_4$ band peaks in chloroform was intense with a shoulder at $41,162cm^{-1}$ and is designated as 1B_a band (that is, both quantum mechanically and overlap allowed).

Band intensity

The transition intensities recorded in the form of oscillator strengths (f), in different solvents as shown in Table 1 reveal that the trend of the

oscillator strength is $f(S_0 \rightarrow S_1) < f(S_0 \rightarrow S_3) < f(S_0 \rightarrow S_2) < f(S_0 \rightarrow S_4)$ for the transitions in acenaphtho(1,2-b)quinoxaline.

For acenaphtho(1,2-b)benzo(g)quinoxaline, the oscillator strength follow the trend $f(S_0 \rightarrow S_1) < f(S_0 \rightarrow S_2) < f(S_0 \rightarrow S_4) < f(S_0 \rightarrow S_3) < f(S_0 \rightarrow S_5)$ for methanol and ether. However, in chloroform, the trend is $f(S_0 \rightarrow S_1) < f(S_0 \rightarrow S_3) < f(S_0 \rightarrow S_2) < f(S_0 \rightarrow S_4)$. Table 1 shows that the $S_0 \rightarrow S_2$ transition is far more sensitive to solvent perturbation than $S_0 \rightarrow S_1$ or $S_0 \rightarrow S_3$ in terms of changes in intensity and energy of the transition.

Conclusion

From the structure and symmetry of the acenaphtho(1,2-b)quinoxaline and acenaphtho(1,2-b)benzo(g)quinoxaline (both having C_{2v} symmetry); it is obvious that the molecules possess permanent dipole μ (nitrogen being more electronegative than carbon) in the ground state.

The blue shift observed in the most intense bands in polar solvents relative to non-polar solvents implies that the dipole moment in the ground state is greater than those in the excited states of acenaphtho(1,2-b)quinoxaline and acenaphtho(1,2-b)benzo(g)quinoxaline.

The earlier suggestion of the existence of $n \rightarrow \pi^*$ transition in acenaphtho(1,2-b)quinoxaline and acenaphtho(1,2-b)benzo(g)quinoxaline is not likely because the non-bonding, lone-pair

electrons on the N-atom are orthogonal to the π -electron system which gives rise to the observed absorption in the compounds.

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