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A STUDY OF THE NUCLEAR CONFORMATION AND THE PROTON TRANSFER REACTION OF 3,5-DIPHENYLPYRAZOLE IN THE EXCITED STATE

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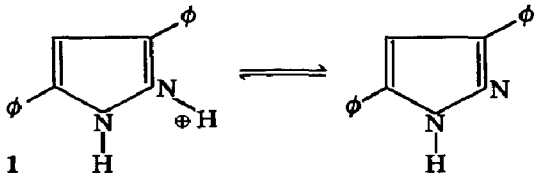
Summary

The effects of solvents and pH on the absorption and fluorescence spectra of 3,5-diphenylpyrazole were studied. The changes in the absorption spectra observed in polar solvents were explained on the basis of steric effects caused by solvent interaction. The absorption and fluorescence spectra in cyclohexane indicated a change in the nuclear conformation of the molecule upon excitation. The pK_a^* values for both the equilibria, *i.e.* the cation $\rightleftharpoons$ neutral $\rightleftharpoons$ anion forms, calculated using the Förster cycle method are analysed.

1. Introduction

The electron density changes significantly in a molecule when it is excited electronically. This change may cause a substantial alteration in the molecular geometry, the solvent cage and the acidity or basicity of the molecule. It has been suggested in the literature [1 - 4] that comparison of the absorption and fluorescence spectra in different solvents could provide a method of investigating these characteristics provided that the molecules fluoresce.

The present investigation was carried out to study changes in the nuclear conformation on excitation and the effect of solvents on the absorption and fluorescence spectra of 3,5-diphenylpyrazole (DPP). In addition to this the pK_a^* values for the proton transfer reactions



(I)

(II)

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in the S_0 and S_1 levels of DPP where **1** is the cation, **2** is the neutral molecule and **3** is the anion of DPP were calculated using Förster cycle methods and fluorometric titration.

2. Experimental details

DPP was prepared from dibenzoylmethane and hydrazine hydrate as described in the literature [5] and was purified by several recrystallizations. BDH spectroquality cyclohexane and methanol were used as received. Merck analytical grade acetonitrile was further purified [6]. The low and high pH solutions were prepared using BDH analytical grade H_2SO_4 and NaOH. Buffers of very low concentrations (about 10^{-3} M) were used to prepare solutions with medium pH. pHs between 1 and 13 were measured using a pH meter (Toshniwal model CL 44A). Hammett's acidity scale was used for pH < 1 [7] and the H_- scale [8] was used for pH > 13. The absorption spectra were recorded using a Cary 17D spectrophotometer and the fluorescence spectra were obtained using a scanning spectrofluorometer fabricated in our laboratory [9].

3. Results and discussion

The long wavelength absorption maxima of DPP in different solvents and under different pHs where each form exists alone are given in Table 1 and the spectra are shown in Fig. 1. There is a small blue shift in $\bar{\nu}_{max}$ as the solvent polarity increases whereas the $\bar{\nu}_{max}$ for DPP^+ and DPP^- are red shifted.

The longest wavelength transition observed in the pyrazoles [10 - 12] is π,π^* and the above behaviour is contrary to the normal red shift obtained with increasing solvent polarity. The dispersive interaction between the solute and the solvent is similar to the formation of a partial bond. Because of this the phenyl ring rotates around the single bond and the coplanarity of the phenyl ring and the pyrazole ring is destroyed. Therefore there is

TABLE 1

$\bar{\nu}_{max}$ of absorption and fluorescence spectra of 3,5-diphenylpyrazole in different solvents at 298 K

	$\bar{\nu}_{abs} \times 10^{-4}$ (cm^{-1})	$\bar{\nu}_{flu} \times 10^{-4}$ (cm^{-1})
Cyclohexane solvent	3.93	3.18
Methanol solvent	3.94	3.09
Acetonitrile solvent	3.94	3.05
Water solvent (pH 7)	3.95	2.95
DPP^+ (5 M H_2SO_4)	3.73	2.89
DPP^- (pH 14.95)	3.79	2.70

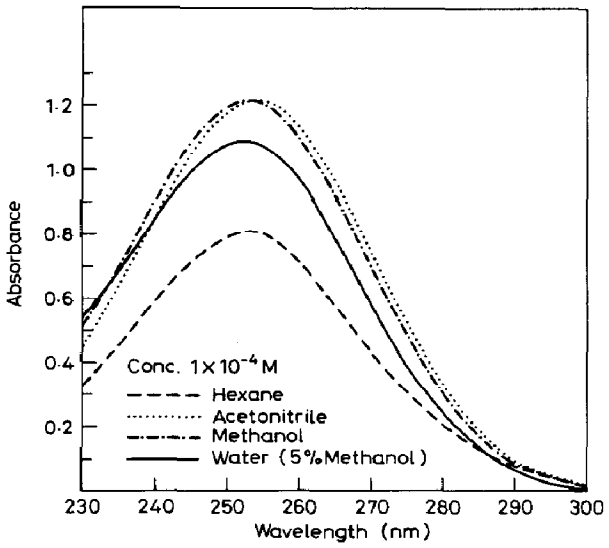

Fig. 1. Absorption spectra of DPP in different solvents.

a loss of conjugation and a blue shift in the absorption spectrum. This effect is more pronounced in the case of 1-phenyl-3,5-dimethylpyrazole and 1,3,5-triphenylpyrazole [9].

The fluorescence spectra of DPP in different solvents are shown in Fig. 2 and the values of $\bar{\nu}_{max}$ are listed in Table 1. Contrary to the behaviour of the absorption spectra, a significant red shift in the fluorescence occurs as the solvent polarity increases. This behaviour is quite consistent with the theoretical predictions for molecules where the dipole moment increases upon excitation. Further the fluorescence spectrum of cyclohexane is structured and this structure is lost with increasing solvent polarity.

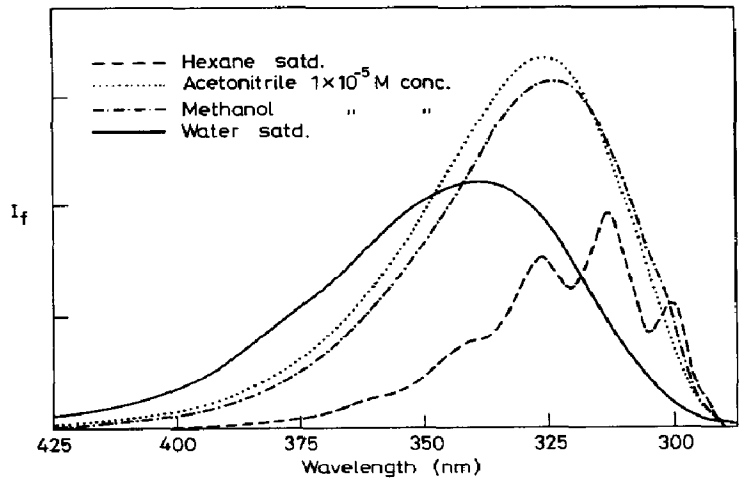

Fig. 2. Fluorescence spectra of DPP in different solvents.

On comparing the results in cyclohexane and water, it is found that the red shift is quite large and cannot be exclusively due to solvent relaxation. It may also be due to a change in the geometry of the molecule upon excitation. To study this the absorption spectrum is compared with the corrected fluorescence spectrum of DPP in cyclohexane in which the solvent interaction is small (Fig. 3). The longest wavelength absorption band is centred at 3.93×10^4 cm^{-1} and is broad whereas the fluorescence spectrum is highly structured and the Stokes shift is quite large (0.35×10^4 cm^{-1}). This and other parameters such as the blue shift in the absorption maxima and the red shift in the fluorescence maxima with increasing solvent polarity and the loss of symmetry between the absorption and fluorescence spectra indicate that the molecule is more planar in the S_1 state than in the S_0 state and according to Berlman's classification [1] is a class 3 molecule like diphenyl.

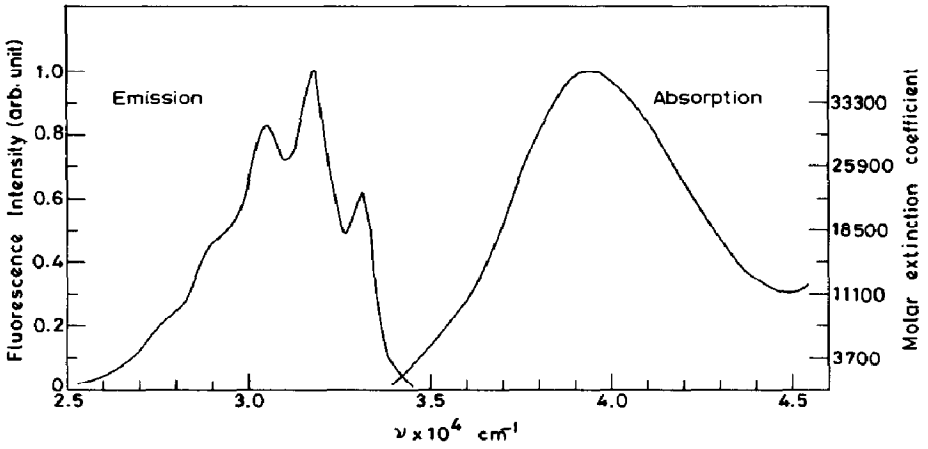

Fig. 3. Absorption spectra and corrected fluorescence spectra of DPP in cyclohexane.

3.1. Proton transfer reactions

The ground state pK_a values for both the equilibria were determined spectrophotometrically and given in Table 2. The values obtained agree well with the theory that the basicity and acidity of the molecule are increased by electron-donating groups like methyl and decreased by electron-withdrawing groups like phenyl [13]. The pK_a(I) and pK_a(II) values for pyrazole [14] are 2.48 and 14.21 respectively.

TABLE 2

pK_a and pK_a^* of 3,5-diphenylpyrazole

Equilibrium	pK_a	pK_a^*		
		Absorption	*Fluorescence*	*Titration*
I	1.43	6.10	2.71	1.70
II	12.94	9.48	7.75	12.64

The excited state pK_a values pK_a^* at 298 K were calculated from the results of fluorometric titration and using methods based on the Förster cycle:

$$pK_a - pK_a^* = 2.1 \times 10^{-3}(\bar{\nu}_{HA} - \bar{\nu}_A) \quad (1)$$

where $\bar{\nu}_{HA}$ and $\bar{\nu}_A$ are the band maxima in reciprocal centimetres of the acid HA and the conjugate base A respectively. The values obtained are listed in Table 2. The Förster cycle calculations are based on the assumptions that (i) the vibrations are equally spaced, (ii) the solvent relaxations are similar and (iii) there is no geometrical change between the S_0 and S_1 states of the species involved in the equilibrium. The large difference between the pK_a^*(I) values calculated using the absorption and fluorescence data is due to the different solvent relaxations and geometries of the species in the S_0 and S_1 states, whereas the small difference in the pK_a^*(II) values is due to the violation of assumption (ii).

The data in Table 2 also indicate that the pK_a^* values obtained from fluorometric titration are very similar to the ground state pK_a values. Similar behaviour has also been observed for most of the heterocyclic systems whose pK_a values fall in the medium pH region (3 - 11) [15 - 21]. This is due to the fact that the concentration of the protons is very small and that, even though the second-order rate constant is large, the rate of proton transfer will be slower than the other deactivation processes of the excited species. However, if under such circumstances the compound is sparingly soluble in water (about 10^{-6} M), the pK_a determined by fluorometric titration using an aqueous solution is more accurate and meaningful than the pK_a determined by absorptiometric titration using a mixed solvent solution [22].

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