ELECTRONIC STRUCTURE OF QUINOXALINE-2,3(1*H*,4*H*)DIONE AND ITS PROTOTROPIC SPECIES IN THE GROUND AND EXCITED SINGLET STATES

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(Received December 2, 1986)

Summary

The solvent-dependent electronic absorption and fluorescence spectra indicate that quinoxaline-2,3(1*H*,4*H*)dione exists in its keto form, even in non-polar solvents, but the deprotonation reaction is observed from its enol form. The protonation reaction in comparison with those of the parent quinoxaline and 1,4-dimethylquinoxaline-2,3-dione suggests that the cation is formed by the gain of a proton on one of the carbonyl groups of the molecule.

1. Introduction

Electronic absorption taken in conjunction with fluorescence spectra is known to be an important technique of studying the photophysical properties, chemical behaviour and electronic orientations of the substituents in organic molecules [1, 2]. For potentially tautomeric molecules, the change in the electronic spectral maxima with change in pH is sometimes due to a change in the chromophore as a result of tautomerism and sometimes to simple protonation and deprotonation reactions [3, 4]. From our recent studies on the absorption and fluorescence characteristics of indazolinone [5], we have concluded that in non-polar solvents the molecule is present in an enol form and in polar solvents as a keto form. However, all the proton transfer reactions take place from the enol form, irrespective of the nature of the solvents. By comparison, for benzimidazolone [6] the molecule is present in the keto form in all the solvents but its pH behaviour resembles that of indazolinone.

Quinoxaline-2,3(1*H*,4*H*)dione (QD), having two carbonyl groups with a labile hydrogen atom present on the adjacent nitrogen atom of each of the carbonyl groups, is known to exhibit keto–enol tautomerism, with the

0047-2670/87/$3.50

equilibrium more towards the keto form [7, 8]. Hence it will be interesting to study the keto–enol tautomerism and proton transfer reactions of QD to establish its electronic structure in both the S_0 and S_1 states. Our interest is thus focused on a study of the solvent and pH dependence of the electronic spectra of QD. The various species involved in the tautomeric and prototropic reactions are detected in the S_0 and S_1 states. The pK_a values have also been calculated in both states. The present investigation has been supplemented by a similar study on the parent quinoxaline and the *N,N*-dimethyl derivative of QD.

2. Experimental details

Quinoxaline was obtained from Aldrich Chemical Co. (U.S.A.); QD was prepared from 1,2-phenylenediamine by the procedure outlined by Mager and Berends [9] and 1,4-dimethylquinoxaline-2,3-dione (DQD) was prepared by methylation of QD [10]. All three compounds were recrystallized from alcohol. The purity of these compounds was checked by means of the melting point, the electronic spectra and by obtaining similar fluorescence spectra with excitation at different wavelengths. While spectrograde methanol was used as such, cyclohexane, ether and acetonitrile were purified for spectral purposes as reported in the literature [11]. Analytical grade H_2SO_4, H_3PO_4 and NaOH were used as such. Triply distilled water was used for making the aqueous solutions. The pH of the solutions was measured on a Toshniwal pH meter model CL 46, in the range from 1 to 13. The solutions were prepared by adding appropriate amounts of H_3PO_4 and NaOH. Solutions below pH 1 were prepared by following Jorgenson and Hartter's H_0 scale [12] for H_2O–H_2SO_4 mixtures and above pH 13 by Yagil's H_- scale [13] for H_2O–NaOH mixtures.

Absorption measurements were made on a Shimadzu UV-190 spectrophotometer, equipped with a U-135 chart recorder. The fluorescence spectra were recorded on a laboratory-made scanning spectrofluorimeter, the details of which have been reported elsewhere [14]. The fluorescence spectra at liquid nitrogen temperature were recorded using the Aminco–Bowman accessory to our spectrofluorimeter. The fluorescence quantum yields Φ_f were calculated by the corrected fluorescence method and using quinine sulphate in 0.05 M H_2SO_4 as standard [15]. For the fluorimetric titrations, the isosbestic wavelengths were used for the measurements of the relative fluorescence intensities at the analytical wavelengths as a function of H_0–pH. The concentration of the solutions was of the order of 10^{-5} M.

3. Results and discussion

3.1. Effect of solvents

The absorption maxima and molar absorptivity ($\log \epsilon_{max}$) values of quinoxaline, QD and DQD are compiled in Table 1. In the non-polar sol-

TABLE 1

Absorption maxima λ_a and log of molar absorptivity ϵ values in various solvents at 298 K

Solvent	λ_a (nm) (log ϵ(dm^3 mol^{-1} cm^{-1})) *for the following molecules*		
	Quinoxaline[a]	*QD*	*DQD*
Cyclohexane	366 (2.44)		
	360 (2.57)		
	353 (2.66)		
	346 (2.75)		
	315 (3.69)		
	310 (3.60)		
	303 (3.65)		
	297 (3.56)		
	291 (3.51)		
	236 (4.29)		
	232 (4.35)		
Ether	365 sh		
	360 (2.56)		
	351 (2.63)		
	346 (2.73)		
	314 (3.69)	339	340
	309 (3.58)	323	325
	302 (3.62)	305	308
	296 (3.53)	275	296
	290 sh	266	260
	234 sh	218	231
	231 (4.26)		226
Acetonitrile	314 (3.73)	339 sh	340 sh
	302 (3.68)	321 sh	322 (3.79)
	231 (4.35)	308 (3.91)	308 (3.86)
		298 sh	297 sh
		274 (3.46)	274 (3.42)
		261 (3.49)	262 (3.48)
		236 (3.74)	236 (3.75)
		230 (3.78)	230 (3.79)
Methanol	313 (3.73)	341 sh	343 sh
	302 sh	324 (3.90)	324 (3.84)
	223 (4.42)	309 (3.98)	310 (3.92)
		298 sh	299 sh
		274 (3.50)	275 (3.48)
		262 (3.49)	262 (3.47)
		236 (3.83)	236 (3.80)
		230 (3.87)	230 (3.84)
Water pH 6	313 (3.49)	342 sh	343 sh
	302 sh	326 (3.88)	327 (3.79)
	232 (4.07)	312 (3.89)	312 (3.86)
		299 sh	300 sh
		260 (3.49)	258 (3.44)
		236 (3.50)	235 (3.49)
		230 (3.81)	229 (3.76)

(continued)

TABLE 1 *(continued)*

Solvent	λ_a (nm) (log ϵ(dm^3 mol^{-1} cm^{-1})) *for the following molecules*		
	Quinoxaline[a]	*QD*	*DQD*
H_2SO_4 H_0 −7	355 (3.77)	359 sh	358 sh
	285 (3.36)	346 (3.83)	348 (3.84)
	250 (3.60)	263 (3.60)	261 (3.59)
	214 sh	257 (3.58)	256 (3.58)
		226 (3.87)	226 (3.82)
NaOH H_- 15	313 (3.49)	341 (3.95)	343 sh
	302 sh	327 (4.10)	327 (3.79)
	232 (3.96)	315 (3.98)	312 (3.86)
		302 sh	300 sh
		262 sh	258 (3.41)
		231 (4.44)	235 (3.44)
			229 (3.71)

sh, shoulder.
[a]At H_0 −2 quinoxaline exhibits 333 (3.63) and 240 (4.08) nm absorption bands.

vents, cyclohexane and ether, structured long wavelength absorption characteristics of the $n \rightarrow \pi^*$ transition of quinoxaline are observed. In the polar solvents, however, this band system is blue shifted and merged with the more intense $\pi \rightarrow \pi^*$ transition (291 - 316 nm). The spectral characteristics are in agreement with those reported by Hirt *et al.* [16]. The absorption band of quinoxaline in cyclohexane in the range 316 - 291 nm has a fine vibronic structure, with a vibrational frequency of about 700 cm^{-1}. With increasing solvent polarity, the structure of the above transition is lost, but little change is observed in the band maxima at about 315 and 303 nm. This could be due to the symmetric nature of the two nitrogen atoms in the molecule, as well as to the rigid geometry of the molecule.

QD and DQD are found to be insoluble in the non-polar solvent (cyclohexane) and the solubility in ether is so small that the absorption maxima only could be given in Table 1. However, on increasing the polarity or hydrogen bond formation tendency of the solvents, a small red shift is observed in most of the peaks of the absorption spectrum. The QD molecule can be envisaged in two ways. (i) If QD is considered to be a dihydroxyl derivative, a blue shift would be expected in the $n \rightarrow \pi^*$ transition and a red shift in the $\pi \rightarrow \pi^*$ transition of the parent molecule, *i.e.* quinoxaline. At the same time a blue shift in both transitions would be observed with the increase in the hydrogen bonding capacity of the solvent as the lone pair of the oxygen atom of the hydroxyl group would be blocked by the proton of the solvents and thus would not be able to perturb the π cloud of the parent molecule. Our results of Table 1 do not follow this trend and thus this model can be discarded. (ii) If QD is viewed as the dione, the two carbonyl groups, joined to a rigid structure, will be *cis* to each other. As well as $\pi \rightarrow \pi^*$ transitions, this kind of system can have four $n \rightarrow \pi^*$ transitions, two of them

forbidden and two of them allowed. One is at about 420 nm and the other is at the normal position, *i.e.* around 270 nm [17]. Further, the presence of the $-NH_2$ group in formamide lowers the $n \rightarrow \pi^*$ transition from 270 to 210 nm. QD in the dione form has one imino group adjacent to each carbonyl group and thus both the $n \rightarrow \pi^*$ bands will be blue shifted. Our study did not quantify the blue shift. Lastly the ϵ values of these two $n \rightarrow \pi^*$ transitions fall in the range 30 - 200 $dm^3\ mol^{-1}\ cm^{-1}$ [17]. The data of Table 1 show that the ϵ values of the long wavelength band as well as of other bands are more than $5 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$. This clearly indicates that the long wavelength band of QD is of $\pi \rightarrow \pi^*$ character and the $n \rightarrow \pi^*$ transitions which are substantially blue shifted are hidden under the strong $\pi \rightarrow \pi^*$ transitions. The spectral behaviour of DQD further confirms that the methyl group is attached to each nitrogen atom, thus forming a dione system, rather than forming the methoxyl derivatives of quinoxaline.

The fluorescence maxima and quantum yields of quinoxaline, QD and DQD are compiled in Table 2. While the fluorescence maxima of QD are hardly affected by the change in the polarity or the hydrogen bonding nature of the solvents, a small red shift is observed in the fluorescence spectra of quinoxaline and DQD under similar environments. The small change in the spectral shift indicates that there is not much change in the polarity of the molecules on excitation. This is due to the symmetrical nature of the carbonyl or imino groups present in QD or DQD [18] and the tertiary nitrogen atoms present in the quinoxaline molecule. A similar insensitivity of the fluorescence spectra towards solvents in benzimidazolinone [6] was also observed, thereby indicating that the carbonyl C=O and imino groups are

TABLE 2

Fluorescence maxima λ_f and fluorescence quantum efficiencies Φ_f in various solvents at 298 K

Solvent	λ_f (nm) (Φ_f) *for the following molecules*		
	Quinoxaline	*QD*	*DQD*
Cyclohexane	399 (0.01)	—	—
Ether	403 (0.01)	410 (0.02)	402 (0.03)
Acetonitrile	406 (0.02)	410 (0.03)	403 (0.05)
Methanol	412 (0.02) 401[a]	409 (0.08)	407 (0.09)
Water	403[a]	408 (0.03) 387[a], 370[a]	408 (0.04)
NaOH H_- 15	—	396, 359 377 (0.02) 394[a], 356[a] 377[a]	408 (0.04)
H_2SO_4 H_0 −3	—	439 (0.17) 409[a]	440 (0.20)

[a]Fluorescence maxima at 77 K.

present adjacent to each other. Further support to the dione structure of QD in the S_1 state is also obtained by the near-mirror-image relationship of the absorption and fluorescence spectra, as well as the similar behaviour of DQD. Although it cannot be said with certainty from the present results, the very low fluorescence quantum yield could lead to speculation of a mixing of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of all the molecules studied. Similar results were also observed as mentioned in earlier papers [19].

3.2. Effect of pH on the absorption and fluorescence spectra

3.2.1. Quinoxaline

The absorption maximum of quinoxaline in neutral solutions (313 nm) is shifted to 333 nm in solutions of H_0 0 and further red shifted to 355 nm in solutions of H_0 −5. These shifts are consistent with the formation of a monovalent cation V and a divalent cation VI obtained by the protonation of one of the tertiary nitrogen atoms (V) and both the tertiary nitrogen atoms (VI) respectively, as shown in Fig. 1. The pK_a values, calculated spectrophotometrically, for the reactions are found to be 0.7 (V) and −4.5 (VI). The pK_a value for the first protonation reaction is consistent with the value given in the literature (*i.e.* 0.6), whereas the second is a little higher than the reported value (−5.5) [20]. The pK_a value for the first protonation of quinoxaline is very low compared with that of the pyridine molecule (5.4), but is similar in base strength compared with pyrazine (−0.6) [21]. This is due to the presence of a second nitrogen atom at the

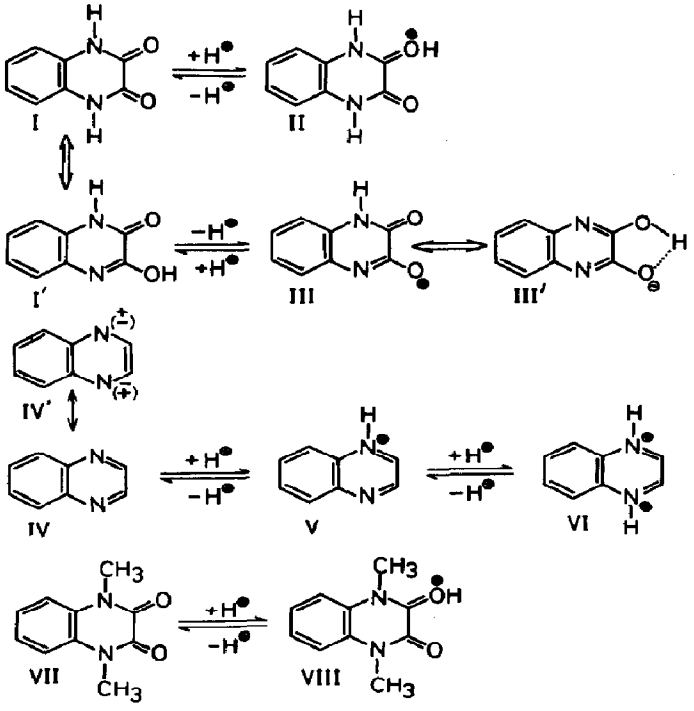

Fig. 1. Prototropic equilibria of QD I, quinoxaline IV and DQD VII.

para position of the quinoxaline molecule, which will lead to the formation of an exactly equivalent dipolar structure (IV′) in the non-ionized molecule and this may strengthen the resonance of these species at the expense of the ion. These molecules (quinoxaline, phenazine and pyrazine) are analogues of azobenzene, which is a very weak base for a similar reason [22].

No fluorescence could be obtained for quinoxaline in the entire acidity range studied at 298 K. However, the fluorescence maximum of 403 nm in water at 77 K, relative to 401 nm in methanol at 77 K, supports the proton-accepting behaviour of quinoxaline with hydrogen bonding solvents. Monocation V and dication VI species are found to be non-fluorescent even at 77 K. The pK_a^* values of both reactions are calculated, using the Förster cycle method [23, 24] and absorption data. These values clearly indicate that both tertiary nitrogen atoms become basic on excitation and this behaviour is consistent with the earlier views [14].

3.2.2. Quinoxaline-2,3(1H,4H)dione and 1,4-dimethylquinoxaline-2,3-dione

The absorption and fluorescence spectra of QD and DQD have been studied in the H_0–pH–H_- range from −10 to 16. The relevant data are recorded in Tables 1 and 2. The absorption and fluorescence spectra of the various prototropic species of QD are shown in Figs. 2 and 3 respectively. The absorption maximum of QD is red shifted on increasing the acidity to H_0 −6 and no further change is observed even up to H_0 −10. A similar behaviour is also observed for DQD, indicating that the cationic species formed in these cases are the same. The pK_a values, calculated spectrophotometrically, are −5.1 for QD and −6.1 for DQD. The protonation reactions in QD and DQD are thought to be different from that of the parent quinoxaline and the monocations are formed by the protonation of one of the car-

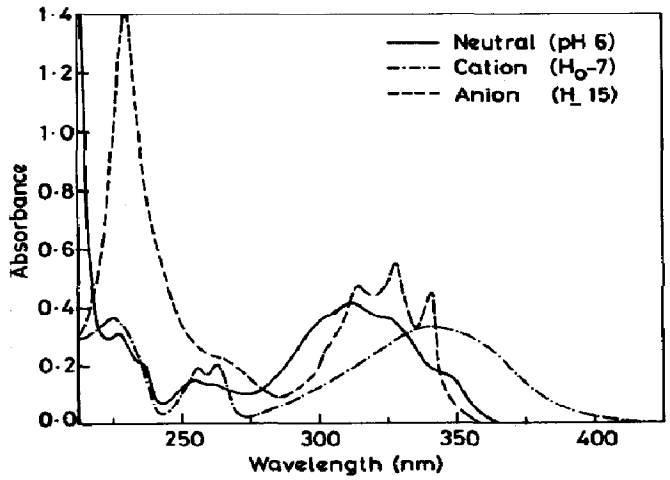

Fig. 2. Absorption spectra of the prototropic species of QD at 298 K: ——, neutral (pH 6); — · —, cation (H_0 −7); — — —, anion (H_- 15).

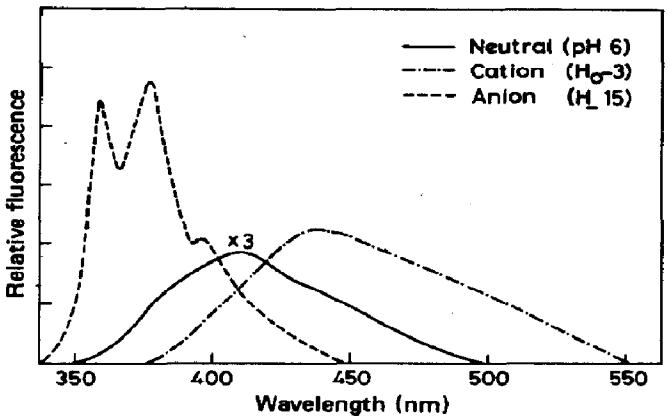

Fig. 3. Fluorescence spectra of the prototropic species of QD at 298 K: ——, neutral (pH 6); — · —, cation (H_0 —3); — — —, anion (H_- 15).

bonyl groups of QD or DQD. These conclusions are based on the following reasons. (i) If it is considered that QD and DQD contain the hydroxyl or methoxyl groups respectively, the pK_a values for the formation of the monocations would have been more than those for the parent molecule, because both these groups are electron donating. (ii) Two prototropic reactions, similar to those for quinoxaline, should have been observed. (iii) If the protonation had occurred at the imino group, the pK_a values would have been expected to be close to —2 because the pK_a values for the similar reactions in benzamide [25] and salicylamide [26] are found to be —2.0 and —2.6 respectively. (iv) The pK_a values obtained for the protonation reactions of the carbonyl group fall in this range [18].

With increasing pH, although the absorption maxima (Fig. 2) of neutral QD are little affected, there is a change in the ϵ values. However, no change is observed for DQD. The change in QD is attributed to the formation of a monoanion. The pK_a associated with this change is found to be 9.7. The monoanion is thought to be formed by deprotonation of the hydroxyl group rather than the imino group. This is because (i) the pK_a values observed for phenols [18] and aromatic hydroxyl compounds [5, 27] are found to be in this range and (ii) the pK_a value for the imino deprotonation reactions are generally greater than 12 [5, 6, 14] and the presence of an electron-withdrawing group (carbonyl) cannot lower the basicity to that extent. Thus it is thought that QD is first converted to the enol or semienol form and then the hydroxyl group is deprotonated. This is supported by a similar pK_a value observed for 3-indazolinone [5] and 3-substituted 2-hydroxyquinoxaline [28]. No further change is observed in the absorption spectra with a further increase in the basicity of the solution. Since DQD does not contain labile protons, similar reactions are not observed for it.

On increasing the acidity to H_0 —3, a red shift is observed in the fluorescence spectra of QD and DQD. This trend is similar to that observed in the absorption spectra and thus a monocation is formed by protonation of

the carbonyl group in the S_1 state, similar to that in the S_0 state. With a further increase in the hydrogen ion concentration, the fluorescence intensity decreased to a minimum at H_0 −6. This may be due either to the proton-induced fluorescence quenching of the monocation [29, 30] or to the formation of a dication. However, the fluorescence intensity at 77 K of the monocation remains the same even up to H_0 −10. This suggests that the fluorescence quenching is proton induced and is dynamic in nature.

The fluorescence intensity of neutral QD starts to decrease around pH 9, without the appearance of any other new band. Only at pH > 11 does a blue-shifted structured band appear and its intensity continues to increase even up to H_ 16, as shown in Fig. 4. The monoanion starts to form in the S_0 state at pH 9, and the same is also expected in the S_1 state at the same pH or lower than that in the S_0 state if the former is fluorescent.

The monoanion of QD (III) is thought to be non-fluorescent, similar to other phenolate and aromatic hydroxylate anions [5, 18, 31]. However, the fluorescence observed at pH > 11 is associated with fine vibronic structure with a vibrational frequency of about 1300 cm^{-1}. This suggests that the monoanion may undergo structural reorganization. The conversion of the anion from its semienol form (III) to the enol form (III′) seems to be probable in the excited state. With increasing basicity of the solvent medium, the structural reorganization may be facilitated and anion III′ may be stabilized by a probable hydrogen bonding between the oxygen atom of the deprotonated hydroxyl group and the hydroxyl group. This may also lead to rigidity of the molecule to account for the observed fine structure. The increase in the fluorescence intensity of the 400 nm band could be due to the competition between the deprotonation of the second hydroxyl group and the removal of the intramolecular hydrogen bonding, as observed similarly for the proton transfer reactions of 2-(2-hydroxyphenyl)benzoxazole [27] in the S_1 state.

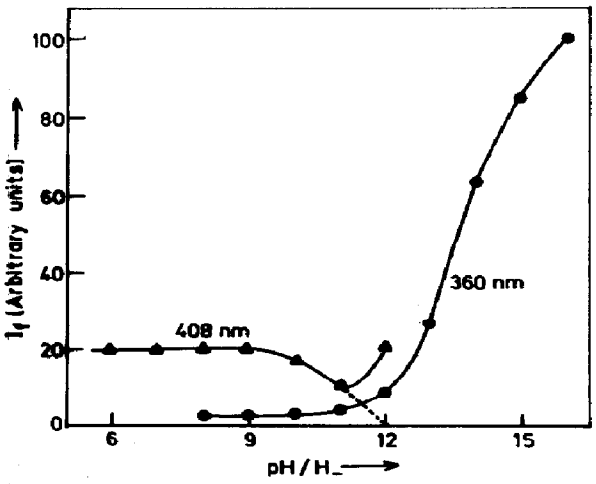

Fig. 4. Plot of the fluorescence intensities of neutral QD (▲——▲) and the anion of QD (●——●) *vs.* pH–H_.

TABLE 3

pK_a values[a] in the ground and excited singlet states

Equilibrium	$pK_a(S_0)^s$	$pK_a(S_1)^a$	$pK_a(S_1)^f$	$pK_a(S_1)^t$
Quinoxaline				
Cation ⇌ neutral	0.7	4.7	—	—
Dication ⇌ cation	−4.5	−0.6	—	—
QD				
Neutral ⇌ anion	9.7	—	—	—
Cation ⇌ neutral	−5.1	−1.4	−1.5	−0.6
DQD				
Cation ⇌ neutral	−6.1	−2.4	−2.4	−0.9

[a] $pK_a(S_0)^s$, obtained spectrophotometrically; $pK_a(S_1)^a$, obtained by the Förster cycle method using absorption; $pK_a(S_1)^f$, obtained by the Förster cycle method using fluorescence maxima; $pK_a(S_1)^t$, obtained by fluorimetric titration.

The various prototropic reactions of quinoxaline, QD and DQD are shown in Fig. 1. The absorption and fluorescence spectra of the various prototropic species of QD are shown in Figs. 2 and 3 respectively. The ground state pK_a values are calculated spectrophotometrically and the values are compiled in Table 3. Wherever possible, the pK_a values in the excited state are calculated with the help of fluorimetric titrations. These values have also been obtained with the help of the Förster cycle method, using absorption and fluorescence maxima, and are compiled in Table 3. It is clear, and consistent with the earlier views, that the tertiary nitrogen atom and the carbonyl group become more basic on excitation. The agreement between the pK_a^* values obtained by the absorption and fluorescence data is good, indicating that the solvent relaxation for the conjugate species involved in the equilibrium is similar in both the S_0 and S_1 states. Further, the pK_a^* values obtained from the fluorimetric titrations are not very different from those obtained by the Förster cycle method. The pK_a^* value for the equilibrium between the neutral species and the anion cannot be calculated by the Förster cycle method, as structural changes are taking place on deprotonation. In the fluorimetric titrations also the intensity of the conjugate species does not attain a constant value.

4. Conclusions

QD exists in its keto form in organic solvents and neutral aqueous solutions. The deprotonation reaction is found to be by the dissociation of the hydroxyl group of the semienol form of the molecule. The anion in the excited singlet state is thought to be stabilized by the structural reorganization to the enol form and probable hydrogen bonding. The protonation reactions show that the carbonyl oxygen of the diones becomes basic on excitation.

Acknowledgment

We are grateful to the Department of Science and Technology, Government of India, for financial support to the project "Proton transfer reactions in the excited states".

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