FARADAY

Excited-state acidity of bifunctional compounds

Part 5† 5-(2-Hydroxyphenyl)-3-phenyl-1,2,4-oxadiazole and 3-(2-hydroxyphenyl)-5-phenyl-1,2,4-oxadiazole‡

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Fluorescence emission and excitation spectra and experimental dipole moments are presented for 5-(2-hydroxyphenyl)-3-phenyl-1,2,4-oxadiazole and 3-(2-hydroxyphenyl)-5-phenyl-1,2,4-oxadiazole. These data indicate that the long-wavelength emission of the former, in non-hydrogen bonding solvents, is due to a tautomeric PT structure. The latter exhibits only the 'normal' band. The striking difference in behavior between these two compounds of very similar structure is explained on the basis of coplanarity between the aryl ring in position 5 and the heterocycle ring, the aryl ring in the 3 position not being in the same plane.

Excited state intramolecular proton transfer (ESIPT) in bifunctional compounds dissolved in non-polar solvents has been a subject of intense interest for the last twenty years, or so. This interest stems not only from potential applications of this process to the lasing process,[2–4] as a solar energy filter[5] and as molecular size[6] computer memories, but also from a more fundamental interest in understanding the effect of excitation on electronic redistribution. It is the speed of the ESIPT process (normally 1 ps or less) which allows it to monitor this redistribution.

Compounds containing the heterocyclic ring 1,2,4-oxadiazole are important in their own right and three review articles,[7–9] have been devoted to them. Their main applications arise from their physiologic activities, compounds being utilized as antitussigens,[10,11] coronary vasodilators,[12] anticonvulsants,[13] hypocholesterics,[14] tranquilizers,[15] anorexigens,[16] anthelmintics,[17] antiesquistosoms[18] and antimicrobians.[19] However, they also have been used as pesticides,[20] herbicides,[21] fungicides[22] and acaracides[23] in agriculture and antistatic agents,[24] thermal stabilizers[25] and blue dyes[26] in the polymer industry.

Dual fluorescence from 5-(2-hydroxyphenyl)-3-phenyl-1,2,4-oxadiazole (5HPPO) in non-hydrogen-bonding solvents was initially explained[27] as arising from a 'normal, N, configuration (structure **1a** in Fig. 1, band at *ca.* 350 nm) and from a hydrogen-bonded structure (long wavelength, LW, band at *ca.* 500 nm.) The experimental evidence cited to argue against the LW band being due to a proton transfer (PT) structure (structure **1b** in Fig. 1) was the different excitation spectra for the two bands, indicating that both structures are already present in the ground state. These same experimental results were interpreted[28] by another research group as being consistent with the LW band being due to a PT structure, the proton from the hydroxy group being transferred to the oxygen atom of the heterocycle. This paper reports four different types of experimental results on 5HPPO, 3-(2-hydroxyphenyl)-5-phenyl-1,2,4-oxadiazole (3HPPO), 5-(2-methoxyphenyl)-3-phenyl-1,2,4-oxadiazole (5MPPO), 5-(2-hydroxyphenyl)-3-(2-methylphenyl)-1,2,4-oxadiazole (5HPTO) and the double phenolyl compound, 3,5-bis(2-hydroxyphenyl)-1,2,4-oxadiazole (DHPO) which were prepared recently. These results not only help to explain the ESIPT behavior of these compounds, but also help to rationalize this observed behavior in terms of molecular conformation.

Methods

3HPPO and 5HPPO were prepared as described[27] previously for the latter. As a basis for comparison, the previously unreported methoxy compound, 5MPPO, toluyl compound, 5HPTO and double phenolyl compound, DHPO were also prepared. 5MPPO was synthesized by dissolving 20 mg of 5HPPO in 2 ml of diethyl ether and allowing it to react with 6 mg of sodium ethoxide. An excess of methyl iodide was then added and the solution was stirred for 2 h at room temperature. When the solvent was extracted and the resulting solid recrystallized from *n*-hexane, 8 mg (38%) of the product was obtained; mp = 122–123 °C. 5HPTO was synthesized by slowly adding a solution of 52 mg of 2-hydroxybenzoyl chloride in 5 ml of dry pyridine to a previously prepared solution of 50 mg of 2-methylbenzamidoxime in 10 ml of the same solvent and refluxing for 24 h. The solvent was extracted and the solid recrystallized from *n*-hexane, yielding 21 mg (25%) of solid, in the form of needles; mp = 108–109 °C. DHPO was synthesized by adding a solution of 40 mg of 2-hydroxybenzoyl chloride in 5 ml of dry pyridine to a previously prepared solution of 50 mg of 2-

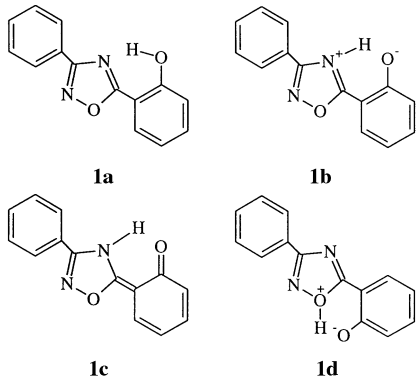

Fig. 1 Possible structures for 5HPPO; **1a** normal structure, **1b** zwitterionic PT structure, **1c** ketonic PT structure and **1d** PT structure (H transferred to oxygen)

† Part 4: ref. 1.

‡ Taken, in part, from the MS thesis of C. E. M. Carvelho, Universidade Federal do Rio de Janeiro, 1996.

hydroxybenzamidoxime in 10 ml of the same solvent and refluxing for 24 h. The solvent was extracted and the solid recrystallized from *n*-hexane, yielding 15 mg (18%) of product; mp = 169–171 °C. The ^{1}H, ^{13}C NMR, vibrational and mass spectra were all consistent with the assumed structures.

All of the solvents used for synthesis were reagent grade (P.A.) from either Merck/Brasil or Grupo Quimica/Brasil. The solvents used for spectroscopy were acetonitrile, benzene, chloroform, dichloromethane, *n*-hexane and *N*,*N*-dimethylformamide (Merck-UVASOL) and butan-2-ol, chloroform, *n*-hexane and propan-2-ol (Grupo Química-UV/HPLC). These were not purified further. The solvents used for the electro-optical dipole moment determinations were reagent grade cyclohexane and dioxane. These were purified, as described[29,30] elsewhere and thoroughly dried by refluxing in the presence of a Na–K liquid alloy.

Fluorescence spectra were taken using an Hitachi F-4500 fluorescence spectrophotometer. The electro-optical absorption measurements were made on an instrument described[30,31] previously.

Results and Discussion

Fluorescence spectra

The fluorescence maxima of 3HPPO, 5HPPO, DHPO, 5HPTO and 5MPPO in solvents of different polarity are listed in Table 1. For 3HPPO, only the N band is observed in both polar and non-polar solvents. 5HPPO is quite different, showing an N band in both polar and non-polar solvents as well as a broad LW band in the same non-polar solvents. 5MPPO, which cannot undergo proton transfer, is similar to 5HPPO, only without the LW band. DHPO and 5HPTO are also quite similar to 5HPPO, showing two fluorescence bands in a non-polar solvent, but only one band in a polar solvent, whose maxima appear at approximately the same wavelength as 5HPPO. For both DHPO and 5HPTO the interpretation that can be given is that neither the addition of a methyl group nor a hydroxy group in an *ortho* position on the ring in the 3-position has an appreciable effect on the emission spectrum of 5HPPO. In addition, for 5HPPO in non-polar solvents, the ratio of the intensities of the two emission peaks depends on excitation wavelength (in a non-linear fashion) and the extent to which the solvent has been dried by refluxing over Na (the drier the solvent the greater the contribution of the LW band).

The bathochromic shifts of 15 nm for the N band of 5HPPO and 6 nm for the same band of DHPO as the solvent polarity increases contrasts with the corresponding hypsochromic shift of 16 nm for the N band of 3HPPO. This not only suggests that the first excited singlet state (S_1) of the latter is an n–π* state while S_1 of 5HPPO and DHPO are π–π* states, but, more specifically, that the electronic distributions of the S_1 states are quite distinct in 3HPPO, as compared to the other two.

Excitation spectra

For 5HPPO, the three-dimensional excitation-emission contour diagram shown in Fig. 2 clearly differentiates between the excitation spectrum of the N band and that of the LW band, in a 1.17×10^{-4} M *n*-hexane solution. The longer wavelength excitation maximum for the N band is located at 300 ± 2 nm, while a second maximum appears at 270 ± 2 nm. The first excitation maximum for the LW band is located at 323 ± 2 nm, the second excitation maximum coinciding with that of the N band. The continuous diagonal lines represent Raman and elastic scattering, in the upper left-hand corner, and second-order scattering in the lower right-hand corner of the contour diagram. This suggests that the ground-state

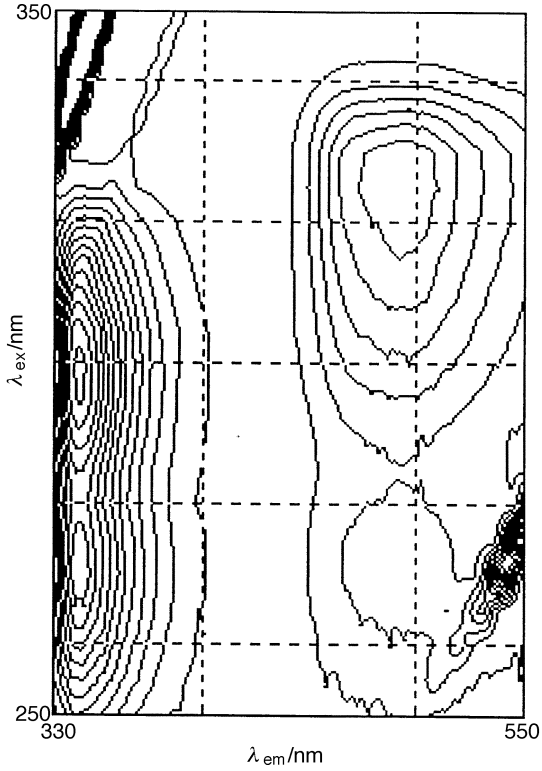

Fig. 2 Contour diagram of 5HPPO. λ_{ex} *vs.* λ_{em}

Table 1 Fluorescence emission maxima[a] (nm)

solvent	Δ*f*	3HPPO	5HPPO	DHPO	5MPPO	5HPTO
n-hexane	0.001		345	354	345	348
			498	500		500
benzene	0.0039		346			
			498			
chloroform	0.1408	350	350			
			498			
dichloromethane	0.2183	348				
dichloroethane	0.223		356			
			498			
butan-2-ol	0.2606		359			
propan-2-ol	0.2744	333		360	348	355
dimethylformamide	0.2755		366			
acetonitrile	0.3062		377			
			498			

[a] All values ± 0.5 nm.

structures responsible for the two bands are appreciably different, that our previous interpretation[27] is incorrect and that these experiments can be interpreted as confirming the assignment of the N band, favored by the presence of small quantities of water in non-polar solution and indicating that the LW band is due to a PT structure whose origin is a pre-existent hydrogen bond in the ground state (S_0).

This interpretation leads to the conclusion that 3HPPO does not exhibit an LW band, in part, because it does not establish a viable hydrogen bond in S_0. This conclusion is supported by the ^{1}H NMR spectra measured in $CDCl_3$. The hydroxy proton in 3HPPO exhibits a chemical shift of only δ 9.62, whereas the corresponding value for 5HPPO is δ 10.5, indicating the latter to be more acidic. The double phenolyl compound, DHPO, shows values of δ 8.65 and 10.3, consistent with its having one proton of each type. In addition, it is worthwhile to note that all of the ^{1}H NMR hydroxy peaks are extremely sharp, indicating the presence of only one conformer. This interpretation is also consistent with the pK_a values in aqueous solution, 9.03 ± 0.05 for 5HPPO compared to 9.8 ± 0.1 for 3HPPO. These values not only show the hydroxy group on the ring in the 5-position to be considerably more acidic than the hydroxy group on the ring in the 3-position, but also indicate that the heterocyclic ring has little effect on acid dissociation in 3HPPO, since the pK_a of 3HPPO is quite close to the corresponding value[32] for phenol, *i.e.*, 10.0 Combining the evidence of the emission spectra with that of the excitation spectra leads one to suggest that the aryl ring in the 5-position is coplanar with the heterocylic ring whereas the aryl ring in the 3-position is not. Thus, for 3HPPO, not only is there no pre-established hydrogen bond in the ground state (lower δ value) but also no ESIPT is observed because the hydroxyphenyl group in the 3-position is not involved in the excitation, being considerably out of the plane of the other two rings. It is worthwhile emphasizing that it is the presence of the aryl ring in the 5-position in 3HPPO that forces the hydroxyphenyl ring in the 3-position out of coplanarity. This is illustrated by the fact that 3-(2′-hydroxyphenyl)-5-methyl-1,2,4-oxadiazole, which can be considered to be 3HPPO with a methyl group substituted in the 5-position instead of a phenyl group, exhibits[33] dual fluorescence in non-polar solvents and therefore has coplanar aryl and heterocyclic rings.

Electro-optical dipole moment determination

From the effect of an external electric field (E) on the absorption and fluorescence spectra of compounds in solution the dipole moments of the respective ground and excited states can be determined.[31] In addition, this method generates information about the homogeneity[34] of the bands observed. Although the fluorescence bands of 3HPPO and 5HPPO were too weak to apply this method, an analysis of the first absorption band was performed. This analysis is capable of determining the ground state and Franck–Condon excited singlet state dipole moments. In the case of DHPO it was not possible to perform the same analysis, apparently because the first band is not a pure transition.

The method generates a macroscopic quantity (L), first defined[35] by Liptay as

$$L(\lambda, \phi) \equiv \chi(\lambda, \phi)/\boldsymbol{E}^2 \quad (1)$$

where χ is the relative field induced change of the absorption coefficient and λ is wavelength. L can be related[30,31,34] to microscopic quantities by

$$L(\lambda, \phi) \equiv (E/30)s(\phi) + [Fr(\phi) + Gs(\phi)]t(\lambda) + [Hr(\phi) + Is(\phi)]u(\lambda) \quad (2)$$

where

$$s(\phi) \equiv 3\cos^2\phi - 1 \quad (3)$$

$$r(\phi) \equiv 2 - \cos^2\phi \quad (4)$$

$$t(\lambda) \equiv (-\lambda/5hc\kappa)[\delta(\kappa\lambda)/\delta\lambda] \quad (5)$$

$$u(\lambda) \equiv (\lambda^2/10h^2c^2\kappa)[\delta^2(\kappa\lambda)/\delta\lambda^2] \quad (6)$$

ϕ is the angle between the external field $\boldsymbol{E}$ and the electric field vector of the linearly polarized light used in the experiment (usually the values of $\phi = 0$ and 90 are used) $\kappa(\lambda, \phi)$ is the absorption coefficient, and $t(\lambda)$ and $u(\lambda)$ are related to the first and second derivatives of the absorption band with respect to wavelength, respectively, and can be determined[30,31,34] independently from the absorption spectrum.

The coefficients E through I in eqn. (2) are defined, in non-polar solvents, as follows

$$E \equiv \beta^2 f_e^2[3(\vec{m}\vec{\mu}_g)^2 - \vec{\mu}_g^2] \quad (7)$$

$$F \equiv \beta^2 f_e^2 \vec{\mu}_g \Delta\vec{\mu} \quad (8)$$

$$G \equiv \beta^2 f_e^2(\vec{m}\vec{\mu}_g)(\vec{m}\,\Delta\vec{\mu}) \quad (9)$$

$$H = f_e^2(\Delta\vec{\mu})^2 \quad (10)$$

$$I = f_e^2(\vec{m}\,\Delta\vec{\mu})^2 \quad (11)$$

$\beta \equiv (1/kT)$, $\vec{m}$ is a unit vector in the direction of the moment of the transition being considered, $\vec{\mu}_g$ is the total dipole moment of the ground state, $\vec{\mu}_e$ the total dipole moment of the Franck–Condon excited state and $\Delta\vec{\mu} \equiv (\vec{\mu}_e - \vec{\mu}_g)$ in the case of non-polar solvents. Total dipole moment here means that some amount of solvent induced moment (usually, around 10%) is included. The separation of permanent and induced moments can be done on the basis of the Onsager model (these details will not be discussed here), f_e is a field correction factor[29–31,34,35] whose value is 1.2 for non-polar solvents with relative permittivity *ca.* 2.

Fig. 3 shows a plot of experimental L values *vs.* λ, between 304 and 340 nm for 5HPPO. A multilinear regression analysis according to eqn. (2) (using $\phi = 0$ and 90° and λ at 4 nm intervals) yields the coefficients E–I. These results are shown in Table 2 for both 5HPPO and 3HPPO; for the former the regression coefficient r was 0.991 whereas for 3HPPO the corresponding value was 0.992, *i.e.* both are considered to be

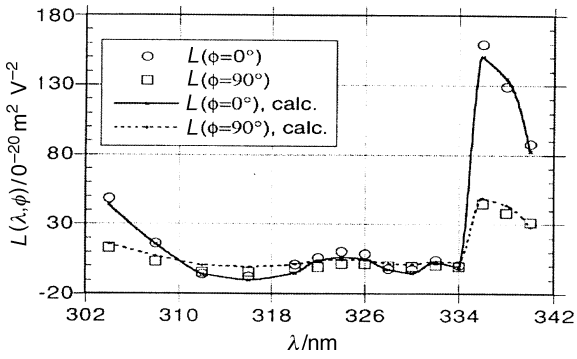

Fig. 3 *L vs.* λ for 5HPPO

Table 2 Regression coefficients and electro-optical dipole moment determination

coefficient [eqn. (6)]	5HPPO	3HPPO
$E/10^{-20}$ m^2 V^{-2}	56 ± 8	1630 ± 70
$F/10^{-40}$ C V^{-1} m^2	38 ± 3	-500 ± 30
$G/10^{-40}$ C V^{-1} m^2	44 ± 3	-590 ± 30
$H/10^{-30}$ C^2 m^2	145 ± 9	310 ± 70
$I/10^{-30}$ C^2 m^2	144 ± 9	(310)

excellent fits. This confirms the hypothesis that only one conformational species is absorbing over the entire wavelength range studied in both compounds.

For both 3HPPO and 5HPPO, the results show that $F \approx G$ and $H \approx I$, to a good approximation. This means that $\vec{m}$ is parallel to $\vec{\mu}_g$ and to $\Delta\vec{\mu}$, within experimental error. Starting from this observation, eqn. (7)–(11) can be used to derive values for $\vec{\mu}_g$, $\vec{\mu}_g\Delta\vec{\mu}$ and $\vec{\mu}_e$ and results are shown in Table 3. This allows the calculation of $\vec{\mu}_e$, which turns out to be parallel to $\vec{\mu}_g$ for 5HPPO but antiparallel for 3HPPO, as shown in Table 3. It is worth noting that $|\mu_e| > |\mu_g|$ for 5HPPO, whereas $|\mu_g| > |\mu_e|$ for 3HPPO, consistent with the spectroscopic results and most likely indicating that S_1 for 5HPPO is a π–π^* state whereas it is an n–π^* state for 3HPPO. It is also worthwhile to point out the good agreement of μ_g, independent of the variables used to obtain results for both compounds.

Solvatochromic dipole moment determination

Utilizing the maxima of the absorption and emission bands as a function of solvent polarity, Lippert derived[36,37]

$$(\mu_e - \mu_g)^2 = \Delta\mu^2 = hc\alpha^3\Delta\bar{\nu}/2\,\Delta f \qquad (12)$$

where

$$\Delta f \equiv (D-1)/(2D+1) - (n^2-1)/(2n^2+1) \qquad (13)$$

Δf is a measure of solvent polarity, D is the relative permittivity and n is the refractive index of the solvent, $\Delta\nu$ is the average of the maxima of the absorption and emission bands (in cm^{-1}), and α is the 'effective' spherical radius of one solute molecule, which is taken as

$$\alpha \cong \{3M/4\pi\rho N\}^{1/3} \qquad (14)$$

where M is the molecular weight and ρ is the density of the solute, N is Avogadro's number, h is Planck's constant and c, the velocity of light. A plot of $\Delta\nu$ *vs.* Δf should yield a straight line of slope $= 2\Delta\mu^2/hc\alpha^3$, which yields μ_e, if μ_g is known.

Using the average of the maxima of the absorption and emission (taken from Table 1) of the N band of 5HPPO as a function of solvent polarity, in *n*-hexane, benzene, chloroform, dichloroethane, butan-2-ol, *N*,*N*-dimethylformamide and acetonitrile yielded $\mu_e = (19 \pm 3) \times 10^{-30}$ C m (see Fig. 4, multiple $r = 0.909$) for the N state, in fair agreement with the μ_e value of 11.8×10^{-30} C m for the Franck–Condon state determined by the electro-optical absorption method. This suggests that there is no large change in structure, nor electronic distribution, upon relaxation of the structure responsible for the N emission, which is not surprising for what is expected to be a fairly rigid, monomeric, molecular structure. When applied to the LW emission of 5HPPO, the solvatochromic results obtained with the same solvents, with the exception of butan-2-ol and *N*,*N*-dimethylformamide, yielded $\Delta\mu \approx 0$, as can be seen from inspection of Table 1. Although the value for $\Delta\mu$ in the case of the N band is sensitive to the effective spherical Onsager radius chosen, the latter value, of course, is not. (A value of 3.85 Å was used for this radius, based on the assumptions of a density of 1.0 g cm^{-3} and efficient packing. However, 5HPPO is not expected to be spherical, therefore the Onsager treatment is only a rough approximation for this compound.) This small difference between the dipole moment values for the fluorescent state and the ground state of the tautomer suggest that the PT structure is not very polar and point to a structure which is considerably closer to the ketonic structure **1c** than to the zwitterionic structure **1b** (Fig. 1), as being responsible for the LW band. These values also weigh strongly against structure **1d**, which was previously suggested,[28] because no reasonable, strictly covalent, structure can be drawn for it.

Table 3 Electro-optical dipole moments for the N structure

dipole moment	5HPPO	3HPPO	variables used
$\lvert\Delta\mu\rvert/10^{-30}$ C m	10.0 ± 0.4	14.7 ± 1.5	*H*, *I*
$\mu_g\Delta\mu/10^{-60}$ C^2 m^2	11.8 ± 1.6	-156 ± 20	*F*, *G*
$\lvert\mu_g\rvert/10^{-30}$ C m	1.8 ± 0.2	9.8 ± 0.2	*E*
$\lvert\mu_g\rvert/10^{30}$ C m	1.2 ± 0.2	10.6 ± 1.7	*F*, *G*, *H*, *I*
$\lvert\mu_e\rvert/10^{-30}$ C m	11.8 ± 0.5	4.9 ± 1.5	*E*, *H*, *I*
	$\mu_e\uparrow\uparrow\mu_g$	$\mu_e\uparrow\downarrow\mu_g$	

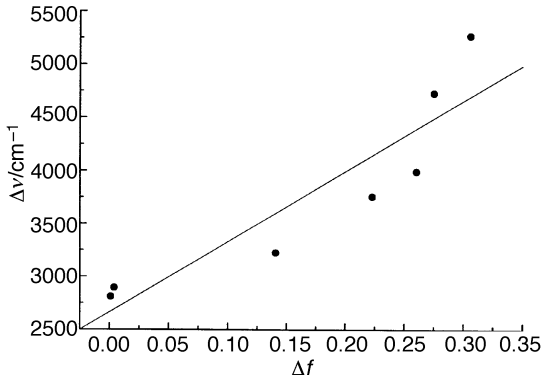

Fig. 4 Solvatochromic plot for 5HPPO

Conclusions

It is suggested that the LW emission observed for 5HPPO is from the covalent, ketonic, PT structure (**1c** in Fig. 1). It is further suggested that the difference in excitation spectra of the two structures in 5HPPO is due to the presence of moisture in the non-polar solvent, which favors the N emission. The LW band is not observed for 3HPPO, which is attributed to the aryl ring in the 3-position being considerably out of the plane shared by the other two rings.

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