

Photochromism, anomalous multi-banded fluorescence and laser properties of some amino- and tosyl-amino derivatives of oxadiazole

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Abstract

The multi-banded fluorescence and laser properties of 11 new amino- and tosylamino derivatives of 2,5-di(phenyl)-1,3,4-oxadiazole and oxadiazole in various solvents at 293 K are reported. All the compounds investigated possess intra-molecular hydrogen quasi-bond (IHB) of 4.6–5.2 kcal mol⁻¹ in the ground state. In the excited state they can undergo protolytic dissociation or intra-molecular photon-initiated transfer of proton and reveal anomalous fluorescence which cannot be explained within the framework of the Kasha and Kasha–Vavilov rules. Depending upon the excitation wavelength, solvent, concentration and pH of the medium, the compounds studied show a single, double, triple or even a four-banded fluorescence, which has not been reported earlier. The nature of multi-banded fluorescence is explained in terms of the possible photochromic processes in excited states. Quantum yields and decay times of the different fluorescence bands are reported. Anomalous dependence of quantum yield upon concentration of the solution is observed. Laser properties of the compounds studied are carefully tested. Laser action based on the fluorescence of the so-called bi-radical molecules is reported. Various possible arrangements of singlet and triplet levels of compounds investigated are discussed.

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1. Introduction

A number of molecules containing donor (D) and acceptor (A) groups show multiple fluorescence. In dual fluorescent compounds where the D and A moieties are separated by a single bond, the two fluorescence bands often originate from a “locally excited” (LE) state and an intra-molecular charge transfer (CT) state. The most well known example is *p*-(dimethylamino)benzonitrile (DMABN) [1]. In this molecule, charge transfer leads to a configurational change, the nature of which has been the subject of much discussion in the literature [2–6]. DMABN displays two fluorescence emission bands, which are strongly dependent on both the polarity of the solvent and the temperature [1,7]. In non-polar solvents only the LE type band is observed while an additional longer wavelength band appears in polar solvents. Since the discovery of dual fluo-

rescence in DMABN, it has been found to be common in other flexible D–A type molecules. Several tertiary amino derivatives of DMABN display this phenomenon. Cyano-substituted *N*-phenylpyrroles show interesting changes in their dual fluorescence under different conditions. *N*-Phenylpyrrole itself shows dual fluorescence in the polar solvents ethanol and acetonitrile with the CT component increasing with decreasing temperature [8]. The presence of the electron-accepting cyano group at the 4-position leads to a strong increase of the CT component. In many cases while dual fluorescence is observed in *n*-hexane in polar solvents only the CT component is obtained [8–12]. Some compounds even exhibit triple fluorescence. *p*-(*N,N*-Dihexylamino)benzoate displays dual fluorescence in cetyl trimethylammonium micelles, with an excimer emission being dominant [13,14]. Upon aggregation in a water–dioxane mixture, this compound shows triple fluorescence. This phenomenon is also exhibited by *p*-(dialkylamino) salicylic acids and their esters. Here, an intra-molecular proton transfer is thought to be responsible for one of the emission bands [15–17]. A similar process is responsible for one of the bands in the double

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and triple fluorescence exhibited by molecules containing the tosylamino group with a chelated cycle in the S_0 state [18–20]. In molecules containing the tosylamino group in which an intramolecular proton transfer is possible, one fluorescence band is formed by the so-called bi-radical molecules, and the other one is due to protolytic dissociation [20]. The multi-band fluorescence of such molecules has nothing to do with either the fluorescence of excimers or exiplex molecules [20,21]. Firstly, the absorption spectra of such compounds do not depend on the concentration of solution either in inert or in polar solvents. Secondly, analogous multi-banded fluorescence is observed in inert and in polar solvents. Thus, there are many compounds that exhibit double or even triple fluorescence. However, in many cases, the quantum yields and fluorescence decay times of the various bands have not been measured and the possibility of laser action in these compounds has not been tested.

This paper presents a careful study of the multi-banded fluorescence and laser properties of amino- and tosylamino derivatives of 2,5-di(phenyl)-1,3,4-oxadiazole (PPD). The compounds studied are: (1) PPD, (2) 2-(*o*-aminophenyl)-5-phenyl-1,3,4-oxadiazole, (3) 2,5-di(*o*-aminophenyl)-1,3,4-oxadiazole, (4) 2-phenyl-5-(*o*-tosylaminophenyl)-1,3,4-oxadiazole, (5) 2,5-di(*o*-tosylaminophenyl)-1,3,4-oxadiazole, (6) 2-phenyl-5-[(2-tosylamino-5-bromine)-phenyl]-1,3,4-oxadiazole, (7) 2-(4-biphenyl)-5-(*o*-tosylaminophenyl)-1,3,4-oxadiazole, (8) 2-(α -naphthyl)-5-(*o*-tosylaminophenyl)-1,3,4-oxadiazole, (9) 2-(*p*-dimethylaminophenyl)-5-(*o*-tosylaminophenyl)-1,3,4-oxadiazole, (10) 1-phenyl-2-[2-phenyl-5-(2-tosylaminophenyl)-1,3,4-oxadiazolyl]-ethylene, (11) 1-(β -naphthyl)-2-[2-(2-tosylaminophenyl)-5-(4-phenylene)-1,3,4-oxadiazolyl]-ethylene, (12) 1-styrenyl-2-[2-(2-tosylaminophenyl)-5-(4-phenylene)-1,3,4-oxadiazolyl]-ethylene. The molecular structures of these compounds are shown schematically in Fig. 1.

2. Experimental methods

The compounds shown in Fig. 1 were re-crystallized, sublimed and purity-controlled using chromatography. Ultraviolet absorption spectra were recorded using a SPECORD M40 spectrophotometer with spectrograde heptane, toluene or ethanol as solvents. A Hitachi MPF-4 spectrofluorimeter was used to record the fluorescence spectra with the spectral band-pass of the excitation monochromator chosen to be not greater than 0.5 nm in each case. The emission slit-width was chosen depending on the fluorescence intensity, but was always sufficiently narrow to avoid distortion of the fluorescence spectrum. The quantum yields of fluorescence were measured using the method described [22] and explained previously [23]. A dilute solution of 9,10-diphenylanthracene in ethanol was used as the standard, with its quantum yield taken as 0.95 [24]. The standard refractive index correction was performed according to [24]. The decay times of fluorescence, τ_f , were measured using an SLM-4800S phase fluorimeter. The error limits were 10% for quantum yields of fluorescence and 5–10% for decay times.

Optical pumping during the testing of the laser properties was carried out using either a XeCl or a N_2 laser, whose frequencies are 32,466 and 29,679 cm^{-1} , respectively. In all cases,

transverse pumping was employed. A Bethune-cell with a bore of two millimetres in a prism was used [25]. A qualitative test for laser action was done in the broad-band mode [26]. A plane-parallel resonator without telescope or Fabry-Perot Etalon was used.

The tuning range was found with the help of a grating, instead of a blind mirror. The concentration of each solution was chosen to get the maximum laser effect and depended on the compound studies.

3. Results and discussion

PPD consists of the oxadiazole ring and two phenyl rings which are joined to the oxadiazole ring at positions 2 and 5. The PPD molecule is distorted slightly from planarity in the ground state. The $S_0 \rightarrow S$ transition is accompanied by π -electron density transfer from the oxadiazole ring to the phenyl rings and has an oscillator strength of 1.59. It displays normal single-banded molecular fluorescence (denoted in the following as M-fluorescence), with the quantum yield and the decay time in cyclohexane of 0.80 and 1.35 ns, respectively [27]. In heptane the quantum yield and decay time are the same as in cyclohexane, altering to 0.81 and 1.30 ns in ethanol. PPD shows laser activity in ethanol with $\lambda_{\text{las}}^{\text{max}}$ at 348 nm (see Table 1), obtained using the XeCl laser for pumping.

Compounds (2) and (3) are *ortho*-amino derivatives of PPD possessing chelated cycles in the ground state, due to the internal hydrogen bond (IHB). Pariser-Parr-Pople (PPP) [28,29] semi-empirical quantum chemical simulations show that in contrast to PPD, the $S_0 \rightarrow S^1$ transition (which is of $l \rightarrow a_\pi$ nature) of compounds (2) and (3) is accompanied by π -electron density transfer from the NH_2 group(s) and peripheral rings to the oxadiazole ring. During this transition the IHB strengthens. The second, $S_0 \rightarrow S^2$, transition in these molecules is of $^1A \rightarrow ^1L_b$ nature and hence forbidden. The third, $S_0 \rightarrow S^3$, transition is accompanied by π -electron density transfer from the oxadiazole ring to the peripheral rings and NH_2 group(s) leading to a weakening of the IHB. Hence, the $S_0 \rightarrow S^3$ transition in compounds (2) and (3) has the same nature as the $S_0 \rightarrow S^1$ transition in PPD. The absorption and fluorescence spectra of compound (2) is given in Fig. 2. The absorption spectra of these compounds are very structured, especially that of compound (3). This can be explained in terms of the geometry of molecules (2) and (3). These molecules are planar and rigid in the ground state, because of the chelated cycles. The absorption bands due to the $S_0 \rightarrow S^1$ and $S_0 \rightarrow S^3$ transitions are indicated in Fig. 2. They are clearly well separated and easily distinguishable. The $S_0 \rightarrow S^3$ absorption band of compound (2) resembles the $S_0 \rightarrow S^2$ absorption band of PPD and occurs over a very similar spectral range. The same can be said about compound (3), although in this case the intensity of the $S_0 \rightarrow S^3$ band is much lower. In fact, simulation predicts that the oscillator strength of the $S_0 \rightarrow S^3$ transition in compound (3) is merely 0.315. The decrease in the $S_0 \rightarrow S^3$ band intensity between compounds (2) and (3) and relative to the corresponding band of PPD is explained by π -electron charge shifting towards the NH_2 group(s) (which have donor nature) during the $S_0 \rightarrow S$ transition.

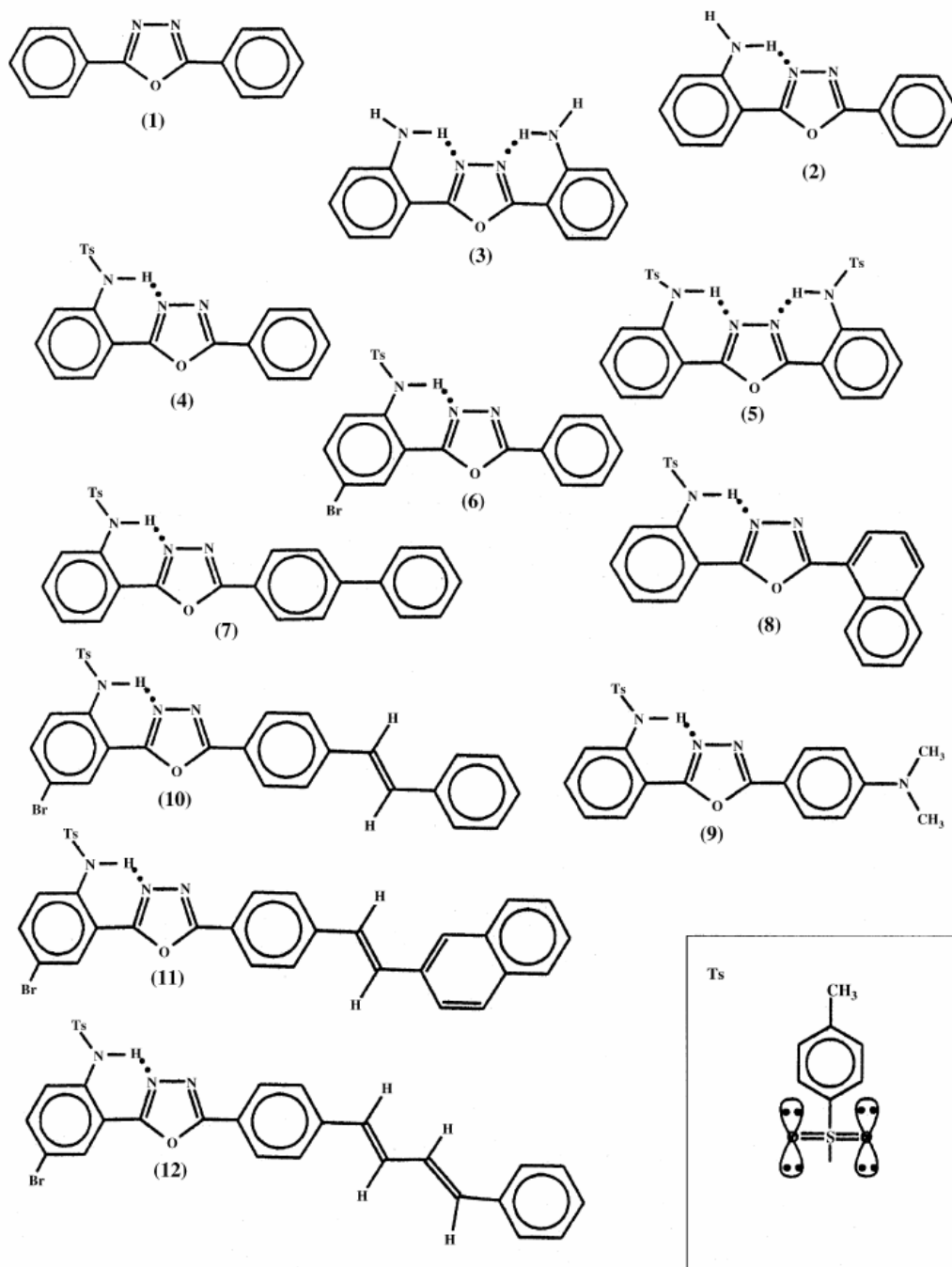


Fig. 1. Structural formulae of the compounds investigated.

Table 1
Experimental and calculated values of the main fluorescence and laser parameters of the investigated compounds

No.	Solvent	$S_0 \rightarrow S^1$		Fluorescence bands λ_{fl}^{max} (nm) (γ , τ_f)				λ_{las}^{max} (nm)	$\Delta\lambda_{las}$ (nm)
		λ_{abs}^{max} (nm)	f_0	M'	M	M^-	BR		
1	Heptane	284	1.590	–	345 (0.80, 1.35)	–	–	–	–
	Ethanol	282	1.600	–	344 (0.81, 1.30)	–	–	348	345–355
2	Heptane	350	0.464	330 (0.15, 0.80)	392 (0.26, 2.45)	–	–	–	–
	Ethanol	361	0.506	333 (0.25, 0.80)	430 (0.38, 4.60)	–	–	–	–
3	Heptane	355	0.920	Weak	400 (0.36, 1.80)	–	–	–	–
	Ethanol	365	1.008	Weak	408 (0.49, 2.50)	–	–	425	422–430
4	Toluene	320	0.530	Very weak	–	410 (0.01, 4.30)	514 (0.02, 0.80)	530	528–534
	Ethanol	313	0.480	328 (0.01, 0.70)	–	416 (0.04, 4.40)	500 (0.03, 0.90)	520	518–526
5	Toluene	333	0.738	Very weak	–	416 (0.04, 4.20)	520 (0.08, 1.20)	540	538–542
	Ethanol	316	0.573	Very weak	–	422 (0.03, 4.10)	515 (0.07, 1.10)	535	533–537
6	Toluene	334	0.450	Very weak	–	400 (0.01, 2.50)	534 (0.08, 1.50)	–	–
	Ethanol	329	0.340	Very weak	–	412 (0.01, 2.60)	518 (0.10, 1.30)	–	–
7	Toluene	326	1.440	Very weak	381 (0.08, 1.50)	400 (0.08, 2.30)	515 (0.13, 1.10)	543	540–545
	Ethanol	321	1.540	329 (0.01, 0.60)	376 (0.11, 1.60)	398 (0.10, 2.40)	510 (0.14, 1.00)	–	–
8	Toluene	333	0.760	–	378 (0.07, 2.35)	–	534 (0.15, 1.15)	–	–
	Ethanol	330	0.804	–	380 (0.16, 2.80)	–	515 (0.05, 1.10)	–	–
9	Toluene	348	1.450	–	458 (0.47, 1.40)	–	–	–	–
	Ethanol	358	1.500	–	478 (0.64, 1.60)	–	–	487	478–490
10	Toluene	346	1.270	–	396 (0.43, 1.50)	–	540 (0.05, 0.90)	410	406–424
	Ethanol	337	1.420	–	409 (0.53, 1.70)	–	–	430	405–445
11	Toluene	341	2.010	–	420 (0.70, 1.00)	–	–	435	428–448
	Ethanol	334	2.215	–	434 (0.52, 1.27)	–	–	440	425–475
12	Toluene	369	2.400	–	450 (0.59, 0.85)	–	–	460	445–480
	Ethanol	364	2.540	–	456 (0.65, 0.70)	–	–	465	450–490

Headings from left to right are: no. (compound number), λ_{abs}^{max} (maximum of the absorption band formed by the $S_0 \rightarrow S^1$ transition), f_0 (oscillator strength), λ_{fl}^{max} (maximum of the fluorescence band), γ (fluorescence quantum yield measured at $C=5 \times 10^{-5}$ mol/l), τ_f (decay time), M' (molecule with broken IHB), M (neutral molecule), M^- (anionic form), BR (bi-radical form), λ_{las}^{max} (maximum of laser action range), $\Delta\lambda_{las}$ (tuning range).

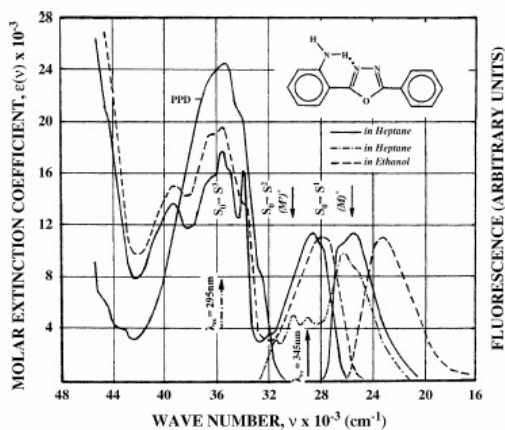


Fig. 2. Absorption and fluorescence spectra of compound (2) in heptane and ethanol. Excitation wavelengths are indicated by the upward arrows. The emission bands lie to the red of the corresponding excitation. The absorption spectrum of PPD is shown for reference.

Depending on the excitation wavelength, compound (2) can exhibit either normal single-banded fluorescence (the long-wavelength band) or dual fluorescence. Normal M-fluorescence is exhibited if the excitation occurs within the range of the long wavelength absorption band. For example, when the excitation wavelength is 345 nm the heptane solution of compound (2) reveals normal M-fluorescence (shown by the longest wavelength solid line in Fig. 2). However, if the excitation wavelength is situated in the range of the $S_0 \rightarrow S^3$ absorption band then dual fluorescence is produced (Fig. 2, dash-dot curve). The position and form of the short wavelength fluorescence band (hereafter referred to as M' fluorescence) of compound (2) resembles the fluorescence of PPD itself. Due to the aforementioned shift of the π -electron density to the NH_2 group, during the $S_0 \rightarrow S^3$ transition, when the NH_2 group loses its donor properties, the chelated ring can be broken by inter-molecular collisions. As a consequence, the conjugation between the NH_2 group and the rest of the molecule is also broken. Hence, the short wavelength M' -band of the dual fluorescence of compound (2) originates from molecules with broken IHB. Compound (3) can also display single and dual fluorescence, depending on the excitation wavelength, in the same manner as compound (2). Furthermore, compound (3) shows laser activity when dissolved in ethanol.

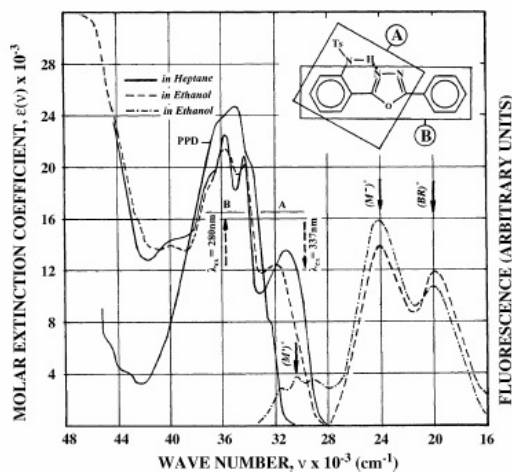


Fig. 3. Absorption and fluorescence spectra of compound (4) in ethanol and heptane. The range of excitations corresponding to transitions localized as indicated by A and B are shown with horizontal bars. Otherwise details as in Fig. 2.

Compounds (4)–(6) may be regarded as derivatives of PPD. Compounds (4) and (5) are *ortho*-tosylamino derivatives of PPD. Investigation shows that these compounds possess an IHB of 4.6–5.2 kcal mol⁻¹ in the S₀ state. The tosylamino group is a donor, but is much weaker than the NH₂ group. Absorption and fluorescence spectra of compound (4) are given in Fig. 3.

It is clearly seen that the absorption spectrum of this compound consists of two bands. The long wavelength absorption band is situated in the range 28,000–33,000 cm⁻¹. PPP calculation reveals that this band belongs to excitation localized on the chromophore labelled A in Fig. 3, and is formed by the S₀ → S¹ transition. During this transition the π-electron density is transferred from the tosylamino group to the oxadiazole ring. The short wavelength absorption band is situated in the range 33,000–38,000 cm⁻¹, with the maximum situated at approximately 35,500 cm⁻¹. This band originates on chromophore B, and results from the S₀ → S³ transition, during which π-electron density is transferred from the oxadiazole ring to the peripheral rings and onto the tosylamino group. The fluorescence properties of this compound are very complicated. Depending on the conditions, it can display single, dual or even triple fluorescence. The shape of the fluorescence bands and the fluorescence parameters are strongly dependent upon the solvent, concentration and excitation wavelength (Fig. 4). For example, in ethanol with an excitation wavelength of 337 nm, compound (4) displays dual fluorescence with the band maxima at 24,000 and 20,000 cm⁻¹ (see Fig. 3).

The molecular process responsible for the fluorescence bands of compound (4) are as follows. During the S₀ → S¹ transition, the π-electron density is transferred from the tosylamino group to the oxadiazole ring. As a result of this process a proton can be transferred along the IHB from the amino group to the N-atom of the oxadiazole group so that a bi-radical (BR) molecule is produced. This bi-radical molecule is responsible for the long wavelength fluorescence band. The process can be expressed as

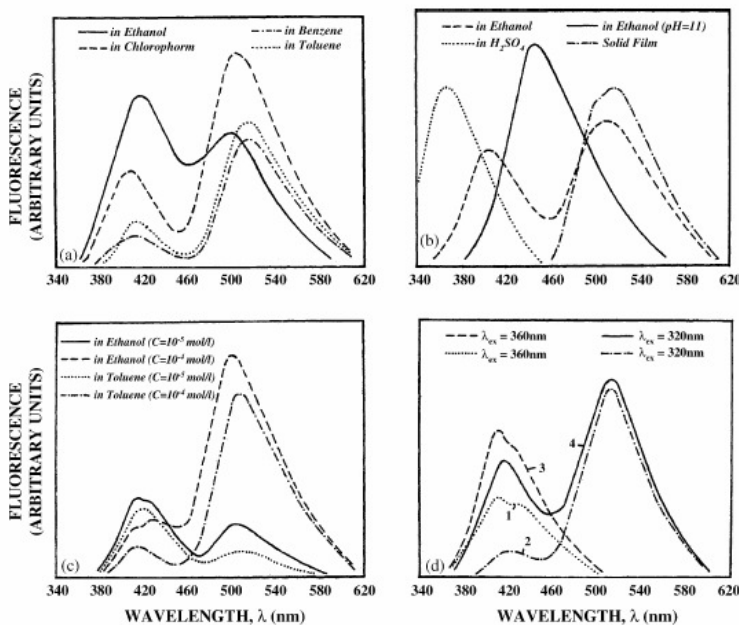
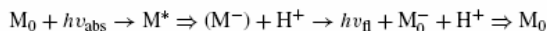


Fig. 4. Fluorescence spectra of compound (4) recorded under different conditions: (a) and (b) in different solvents ($C = 5 \times 10^{-5}$ mol/l, $\lambda_{\text{ex}} = 337$ nm), (c) at different concentrations ($\lambda_{\text{ex}} = 337$ nm), (d) at different excitation wavelengths, fresh and old ethanol solutions, (1) and (2) fresh solutions; (3) and (4) after 5 min of illumination.

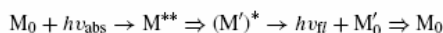
follows:



or, as a result of inter-molecular collisions the following process can occur (protolytic dissociation).



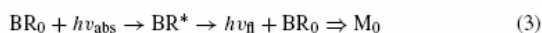
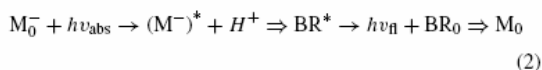
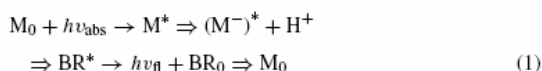
Hence, one of the two bands of fluorescence results from the formation of excited BR^* molecules. In other words, the longest wavelength fluorescence band is formed due to the intra-molecular proton transfer (IPT) process. The other fluorescence band is caused by the excited $(M^-)^*$ molecules, formed by protolytic dissociation. At an excitation wavelength of 280 nm, compound (4) exhibits triple fluorescence in ethanol solution (pH 7). The shortest fluorescence band belongs to excited molecules with a broken IHB, M' -fluorescence, as described earlier. This process can be represented by the following scheme:



At low temperature (77 K) compound (4) exhibits only one fluorescence band, which is attributed to intra-molecular proton transfer (BR^* fluorescence). At low temperature protolytic dissociation becomes almost impossible and only intra-molecular proton transfer can occur.

In Fig. 4(a) and (b), the shorter wavelength band is attributed to excited anion, and the longer wavelength band is formed by the emission from excited bi-radical. At $\text{pH} \geq 11$ only one fluorescence band arises, formed by excited $(M^-)^*$ molecules (due to protolytic dissociation). This is to be expected, since the protolytic dissociation is likely to be the predominant mechanism in basic solutions. In solid film only the BR fluorescence band is exhibited since intra-molecular proton transfer is the preferred process. Only one fluorescence band is seen in H_2SO_4 solution, although the nature of this band is not clear. It possibly arises due to some complex molecule formation, perhaps between molecules of H_2SO_4 and compound (4).

The quantum yield of the $(BR)^*$ fluorescence band anomalously depends on the concentration of the solution (see Fig. 4(c)). Increasing the concentration of the solution from $C = 1 \times 10^{-5}$ mol/l to $C = 1 \times 10^{-4}$ mol/l results in an eight-fold increase in the $(BR)^*$ fluorescence quantum yield, while the quantum yield of $(M^-)^*$ fluorescence is slightly decreased. Such behaviour can be explained as follows. With the increase of concentration the following three processes can contribute to the $(BR)^*$ fluorescence.



In the first process, an excited neutral molecule initially loses a proton, becoming an excited anion which then gains a proton from the medium onto the oxadiazole ring, forming the excited bi-radical. The second process is initiated through ground state anion absorption before following a similar path to the first. The third possibility involves a ground state bi-radical as the starting point. All these three processes become more probable with increasing concentration.

Compound (4) shows very interesting laser properties. Laser oscillation of this compound is based on the BR^* fluorescence band. Such laser oscillation becomes possible at $C > 10^{-3}$ mol/l. To the best of the authors' knowledge, this is the first report of laser activity in a compound capable of showing multi-banded fluorescence. The absorption and fluorescence of compound (5) are shown in Fig. 5. The fluorescence properties of this compound are very similar to those of compound (4). Depending on the excitation wavelength it can also show dual or triple fluorescence and shows laser activity based on the BR^* fluorescence band. The intensity of the BR^* fluorescence band is greater than in compound (4). For both compounds (4) and (5), the Stokes shift of the fluorescence bands is large: 10,000–12,000 cm^{-1} for BR^* band and 6000–8000 cm^{-1} for the $(M^-)^*$ band.

It is also interesting to note that the fluorescence properties of newly prepared solutions of compounds (4) and (5) differ slightly from those that have been kept under illumination for some time. Older solutions show more intense $(M^-)^*$ and BR^* fluorescence (see Fig. 4(d)). This phenomenon is difficult to explain. It may be that following the illumination of solutions of compounds (4) and (5), the relative concentrations of the ground state anionic and bi-radical forms of the molecules increase. Excitation spectra for the fluorescence bands are different and very complicated. This is due to the presence of small quantities of ground state M_0^- and BR_0 molecules. The excitation spectra of the (M^-) -band (fluorescence of the molecule with broken chelated ring) look very much like the absorption spectra of PPD.

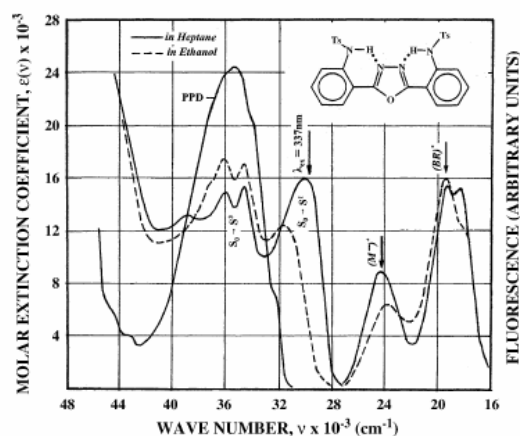


Fig. 5. Absorption and fluorescence spectra of compound (5) in ethanol and heptane. Details as in Fig. 3.

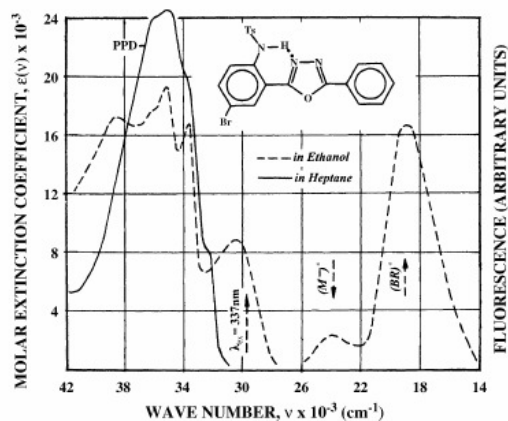


Fig. 6. Absorption and fluorescence spectra of compound (6).

Absorption and fluorescence spectra of compound (6) are given in (Fig. 6). Fluorescence properties of compound (6) are very similar to compound (4). It can also reveal double or triple fluorescence; only the M' fluorescence is very weak and BR-fluorescence is more intense. The increase in the intensity of BR-fluorescence is explained by the fact that BR^* state is very similar to the triplet state.

Absorption and fluorescence spectra of compound (7) are given in (Fig. 7). Depending on the excitation wavelength it can reveal double-banded or triple-banded or even four-banded fluorescence. Besides M' -fluorescence, (M^-)-fluorescence and BR-fluorescence it can also show neutral M-fluorescence. For example, if $\lambda_{ext} = 320$ nm then ethanol solution of compound (7) shows double fluorescence (M-fluorescence and BR-fluorescence). If $\lambda_{ext} = 345$ nm then it again shows double fluorescence, but of a different nature (M^- -fluorescence and BR-fluorescence), and if $\lambda_{ext} = 300$ nm then compound (7) reveals four-banded fluorescence.

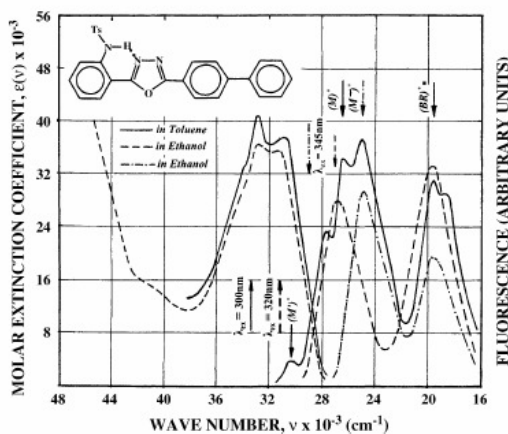


Fig. 7. Absorption and fluorescence spectra of compound (7). Details as in Fig. 3.

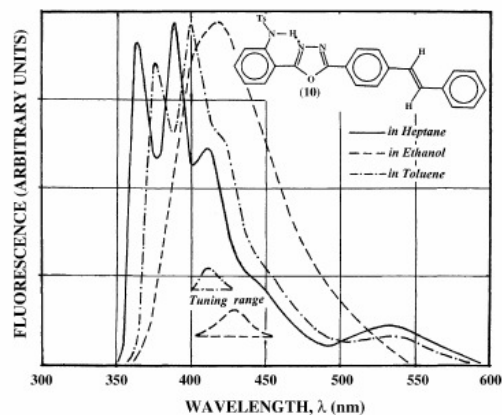


Fig. 8. Fluorescence spectra of compound (10).

Compounds (8)–(12) have very simple absorption spectra but show different fluorescence properties. In most cases compound (8) shows double fluorescence: M-fluorescence and BR-fluorescence. Compound (10) in heptane and in toluene shows double fluorescence: M-fluorescence and BR-fluorescence, but in ethanol it shows only M-fluorescence (see Fig. 8). Despite the presence of the tosylamino group, compounds (9) and (11)–(12) show only ordinary single-handed fluorescence, that is M-fluorescence. Laser action of compounds (9)–(12) is based on M-fluorescence, while laser action of compounds (4)–(5) and compound (7) is based on BR-fluorescence (see Table 1). The multi-form fluorescence properties of tosylamino derivatives of PPD and oxadiazole can only be explained by the mutual arrangements of different singlet and triplet levels. The position of $S_{n\pi}^1$ state, formed by the transition of n -electron from the oxygen of SO_2 group to π^* -orbitals of a molecule is extremely important, because due to such transitions oxygen becomes positively charged and pulls electron density from the $-NH$ group creating the possibility of protolytic dissociation and intra-molecular proton transfer. There could be several types of level arrangements. The most probable four of them are shown in Fig. 9. In the arrangement shown in Fig. 9(a), the lowest singlet level is formed by the electronic density transfer from a donor groups other than the tosylamino group, and $S_{n\pi}^1(O)$ and $T_{n\pi}^1(O)$ levels are situated higher than $S_{n\pi}^1(O)$ state. For example, in compound (9) the lowest singlet state is formed by the transfer of electron density from the dimethylamino group to the oxadiazole ring and onto the tosylamino group. In this case the protolytic dissociation and intra-molecular proton transfer are impossible. As a result of this only ordinary M-fluorescence is possible, because the $S_{\pi/\pi}^1 \approx T_{\pi/\pi}^1$ degradation process is the most preferable. In another possible arrangement (Fig. 9(b)), the lowest singlet state is formed by the electronic density transfer from tosylamino group to the oxadiazole ring, but the amount of electronic density transferred is not enough to create an opportunity for easy protolytic dissociation or for intra-molecular proton transfer. $S_{n\pi}^1(O)$ and $T_{n\pi}^1(O)$ levels are again higher than $S_{n\pi}^1$.

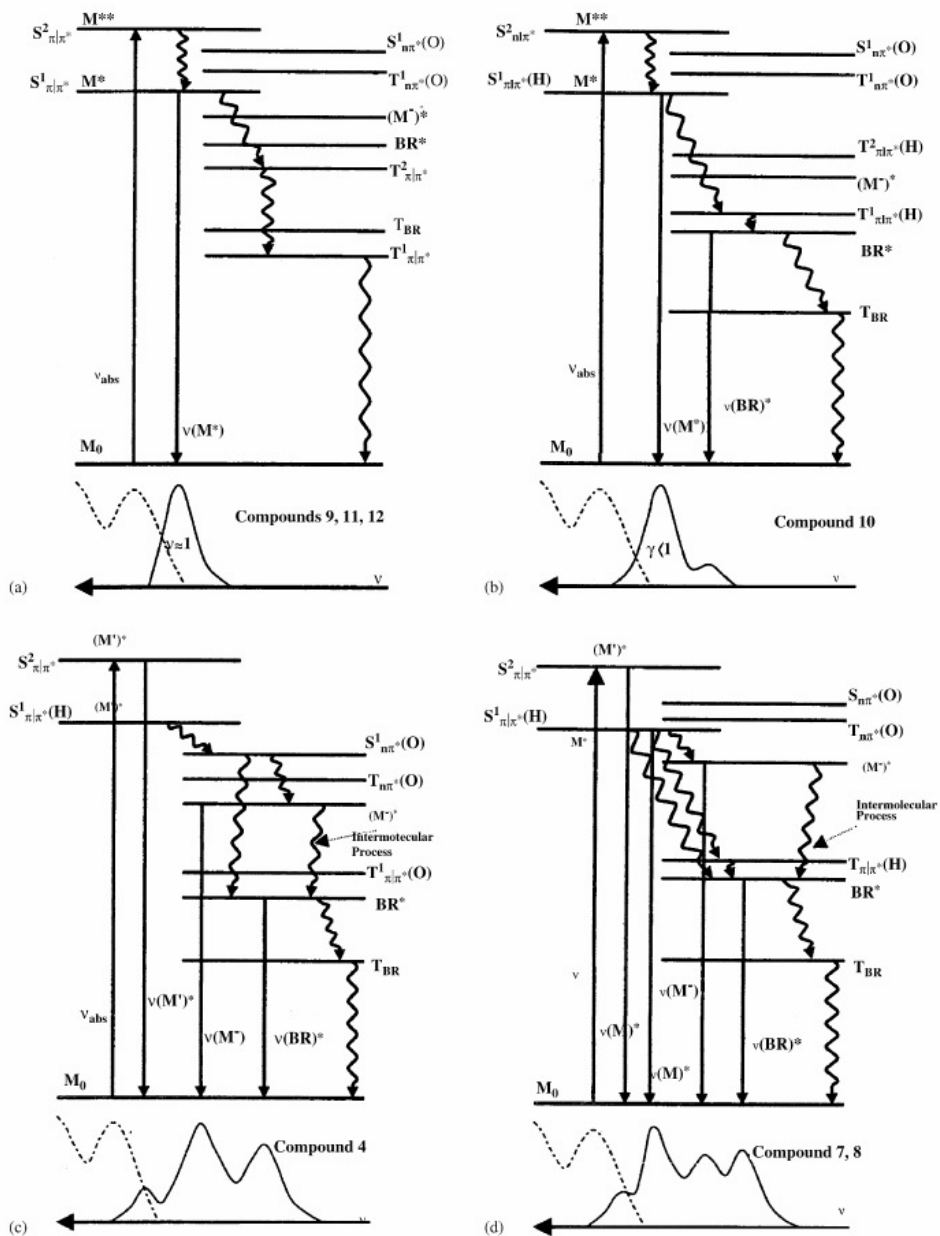


Fig. 9. Four types of relative arrangement of singlet and triplet levels of tosylamino derivatives of oxadiazole. $S_{1n\pi^*}(O)$ and $T_{1n\pi^*}(O)$ are singlet and triplet states which are formed by $n \rightarrow \pi^*$ transition from the SO_2 group. $S^1_{\pi|\pi^*}(H)$ and $T^1_{\pi|\pi^*}(H)$ are singlet and triplet states formed by the electron density transfer from tosylamino group to the oxadiazole ring.

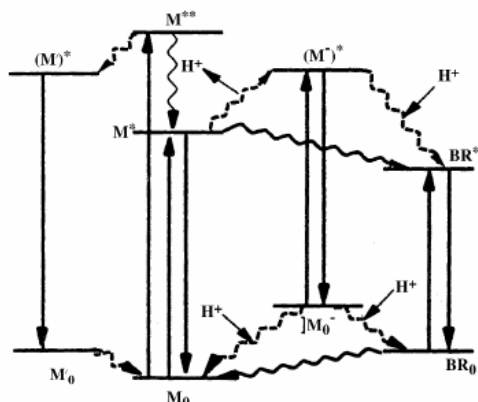


Fig. 10. Photochromic processes possible in the tosylamino derivatives of oxadiazole.

In this case, M-fluorescence and Br-fluorescence of low intensity are the only ones possible. In the levels arrangement shown in Fig. 9(c), the lowest singlet excited state is formed by the transfer of electronic density from tosylamino group to the oxadiazole ring. Here $S_{\pi/\pi^*}^1(O)$ and $T_{\pi/\pi^*}^1(O)$ levels are situated below $S_{\pi/\pi^*}^1(H)$ state. According to luminescence-laser classification of hetero-aromatic compounds [30] such molecules belong to class-III and do not display $\pi\pi^*$ - or π/π^* -fluorescence. On being excited to $S_{\pi/\pi^*}^1(H)$ state they are degraded in 10^{-11} s to $S_{\pi/\pi^*}^1(O)$ state, from which they degrade to $(M^-)^*$ or BR^* states. That is why such molecules reveal either double- or triple-fluorescence depending on the excitation wavelength. In the last type of level arrangement (shown in Fig. 9(d)), the lowest singlet state is $S_{\pi/\pi^*}^1(H)$, which is formed by a large transfer of electronic density from the tosylamino group to the oxadiazole ring, so that protolytic dissociation and intra-molecular proton transfer processes become possible. Such molecules, as with molecules of cases (a) and (b) belong to class-V as do molecules in case (a) and (b), and show π/π^* -fluorescence. $S_{\pi/\pi^*}^1(O)$ and $T_{\pi/\pi^*}^1(O)$ states, like in cases (a) and (b) do not play any role in energy degradation from the $S_{\pi/\pi^*}^1(H)$ state. The dominant non-radiative processes in this case are $S_{\pi/\pi^*}^1(H) \rightarrow (M^-)^*$, $S_{\pi/\pi^*}^1(H) \rightarrow BR^*$ or $S_{\pi/\pi^*}^1(H) \rightarrow T_{\pi/\pi^*}^1(H)$. Such molecules can reveal even four-banded fluorescence: M' , $-M$, $-(M^-)$ and BR -fluorescence. Hence, tosylamino derivatives of oxadiazole can reveal normal single banded (π/π^*) fluorescence or double-banded (M^- and BR) fluorescence or triple-banded (M' , (M^-) , BR) fluorescence or even four-banded (M' , M , (M^-) , BR) fluorescence. Schematically, these possibilities are shown in Fig. 10.

4. Conclusions

Amino- and tosylamino-derivatives of PPD and oxadiazole may display single, dual, triple or even four-banded fluorescence. From the fluorescence and laser data presented and discussed in this paper, the following conclusion may be drawn. Amino- and tosylamino-derivatives of PPD display

multi-banded fluorescence when the ground S_0 state structure includes a chelated cycle. The intensity of these bands and the quantum yield of the corresponding fluorescence depends upon the experimental conditions such as excitation wavelength, solvent, solution concentration and pH. In the case of the tosylamino derivatives, excitation within the absorption band formed by the $S_0 \rightarrow S^1$ transition gives rise to the possibility of two fluorescence bands (which may be observed simultaneously under certain conditions). One of these bands is due to the anionic form of the molecules (resulting from protolytic dissociation) and the other one is due to emission from the so-called bi-radical molecules (resulting from an intra-molecular proton transfer process). Excitation of the tosylamino derivatives via the absorption band formed by the $S_0 \rightarrow S^3$ transition (during which the π -electron density is transferred from the oxadiazole ring to the amino or tosylamino group) results in the observation of a third fluorescence band. This latter band is due to emission from molecules with a broken chelate cycle. Such emission is also possible when the *o*-amino derivatives are excited via the $S_0 \rightarrow S^3$ transition. To the best of the authors' knowledge this type of fluorescence has not been reported earlier. The *o*-amino derivatives also display a second fluorescence band which arises from the S^1 excited state which contains an unbroken chelated cycle. If excitation of the *o*-amino derivatives occurs within the $S_0 \rightarrow S^1$ band then this is the only fluorescence band observed. Investigation of laser properties of the compounds studied shows that *ortho*-tosylamino derivatives of PPD exhibit unusual laser oscillations. This results from the fluorescence of bi-radical molecules produced by the intra-molecular proton transfer process. This type of laser action is also observed for the first time.

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