ANIONIC AND ZWITTERIONIC PHOTOPHYSICAL EFFECTS IN SOME PYRIDINIUM OXAZOLE LASER DYES

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Kauffman and Bentley [*Laser Chem.* 8, 49–59 (1988)] have reported increased laser output by changing the anion of certain pyridinium oxazole dyes from the tosylate to the mesylate salt. Likewise, zwitterion variants of these dyes are also reported to have a significantly improved laser output. We find anion changes to be modest and, with one exception, all zwitterions tested were no better or not as good as the tosylate salt with respect to lasing output. However, both the mesylate salt and the zwitterion variants have greatly improved lifetimes if there is no fluorine auxochrome in the basic dye. These authors also report observation of bifurcated lasing output curves. We see no such phenomena.

1. INTRODUCTION

1-methyl-4-[5-(4-methoxyphenyl)-2-oxazolyl]pyridinium *p*-toluenesulfonate (called Ox 2) was the first very long-lived, moderate output dye observed in our laboratory.¹ Recently Kauffman and Bentley² (K-B) found that in methanol the mesylate salt of Ox 2 has about twice the output of the tosylate salt and a sulfopropyl zwitterion form has about 2.5 times the output of the tosylate salt. Because the pyridinium oxazole dyes are salts, the solvent plays an important part in the photophysical properties of the dye. Certainly, the possibility exists that different anions and solvent interaction could also change the photophysical properties of the dye. In the past we have not observed any strong effects due to changing the anion between perchlorate and tosylate.³

2. EXPERIMENTAL

Our dye laser system is a flashlamp-pumped Phase-R DL 10Y laser head in a triaxial configuration. The cavity has an approximate 100% reflector wideband rear mirror

† Deceased.

and we use output couplers with 20 to 90% reflectivity. The flashlamp cooling jacket contains a 0.1% caffeine/water solution which cuts off UV radiation for wavelengths shorter than 295 nm. For many of the dyes we have tested, an output coupler of 50% reflectivity is near the peak of the output curve at our usual operational temperature of 27.3°C. Temperature of coolant and dye solutions can be controlled separately to 0.01°C.⁴ The laser beam is wavelength analyzed in a 3/4 meter Spex model 1702 spectrometer. Quantum yield measurements were made using a Spex F222 fluo-

Table 1 The pyridinium oxazole dyes discussed in this paper

Dye	A	B	C	2	4
Ox 2 ^a	tosylate	methyl	methoxy	H	H
Ox 2A	mesylate	methyl	methoxy	H	H
Ox 2Z3	sulfopropyl zwitterion ^b		methoxy	H	H
Ox 12 ^a	tosylate	methyl	methoxy	ethylene bridge	
Ox 13 ^a	tosylate	methyl	H	H	H
Ox 13A ^a	perchlorate	methyl	H	H	H
Ox 15 ^a	tosylate	methyl	H	vinylene bridge	
Ox 16 ^a	perchlorate	methyl	F	ethylene bridge	
Ox 16Z3	sulfopropyl zwitterion ^b		F	ethylene bridge	
Ox 17 ^a	perchlorate	methyl	H	H	phenyl
Ox 17A	tosylate	methyl	H	2,2' bridge phenyl	phenyl ^c
Ox 17AA	mesylate	methyl	H	2,2' bridge phenyl	phenyl ^c
Ox 17AZ3	sulfopropyl zwitterion ^b		H	2,2' bridge phenyl	phenyl ^c
Ox 20 ^a	tosylate	methyl	H	H	methyl
Ox 20Z3	sulfopropyl zwitterion ^b		H	H	methyl
Ox 21 ^a	tosylate	methyl	F	H	methyl
Ox 21Z3	sulfopropyl zwitterion ^b		F	H	methyl
Ox 27A	mesylate	methyl	n-butoxy	H	H
Ox 27Z3	sulfopropyl zwitterion ^b		n-butoxy	H	H

^aDyes reported in Ref. 3.

^bThis means the structure $\text{N}^+ - (\text{CH}_2)_3\text{SO}_3^-$

^cThis means the structure

rometer with quinine sulfate as the comparison standard. For the latter measurements, the dye concentrations were in the 10^{-7} M range with peak absorbances ≤ 0.014 . For the laser tests, concentrations were 2.0×10^{-4} M unless otherwise noted.

Tables 1–5 (discussed below) list the dyes studied and the properties measured under various conditions. However, because we wish to compare our data with previous results, the data in Table 3, which contains the lasing parameters for the dyes tested, were determined under the same conditions as in Ref. 3 (and references cited therein). Thus, the cavity parameters, including the output coupler, were the same.

3. RESULTS

The basic dye molecule is shown in Table 1 with substitutions germane to our discussion. The short form nomenclature is as in Ref. 3. Based on the results of K-B,

Table 2 Energy output of laser dyes related to the basic pyridinium oxazole dye. The cover gas is argon

Dye	Solvent	Energy		Dye	Solvent	Energy	
		In, J	Out, mJ			In, J	Out, mJ
Ox 2	EtOH	50	34.7	Ox 17	EtOH	60	19.1
Ox 2A	EtOH	60	86.5	Ox 17A	EtOH/H ₂ O	60	33.1
Ox 2	EtOH/H ₂ O	40	36.4	Ox 20	EtOH	55	37.4
Ox 2A	EtOH/H ₂ O	60	76.9	Ox 20Z3	EtOH	60	24.7
Ox 2Z3	EtOH/H ₂ O	60	106.3		EtOH/H ₂ O	60	37.8
					H ₂ O	60	30.7
Ox 12	EtOH	35	41.0	Ox 21	EtOH	55	42.2
				Ox 21Z3	EtOH	60	40.3
					EtOH/H ₂ O	60	65.8
					H ₂ O	60	30.0
Ox 13	EtOH	45	37.5	Ox 27A	EtOH	60	76.9
Ox 13A	EtOH	45	44.9	Ox 27Z3	EtOH	60	58.3
					EtOH/H ₂ O	60	83.1
Ox 16	EtOH	60	30.7				
Ox 16Z3	EtOH	60	60.7				
	EtOH/H ₂ O	60	80.5				
	H ₂ O	60	31.2				

Table 3 Comparison of lasing parameters for dyes in this study with prior work. The cover gas is argon. *K* is the slope efficiency, *t* is lasing threshold, 1/*C* the lifetime, and FOM the figure of merit

Dye	Solvent	10 ³ <i>K</i>	<i>t</i> , J	1/ <i>C</i> MJ/ℓ	FOM kJ/ℓ
Ox 2 ^a	EtOH	1.53	22.1	10,000	15,300
Ox 2A	EtOH	2.05	18.9	>>10,000	---
Ox 2Z3	EtOH	1.55	32.9	>>10,000	---
Ox 2 ^a	EtOH/H ₂ O	2.63	26.2	438	1,152
Ox 2A	EtOH/H ₂ O	2.29	26.7	>>10,000	---
Ox 2Z3	EtOH/H ₂ O	2.57	18.7	>>10,000	---
Ox 2Z3	H ₂ O	1.59	33.9	---	---
Ox 12 ^a	EtOH	3.00	21.8	188	564
Ox 12 ^a	EtOH/H ₂ O	3.60	21.5	219	788
Ox 13 ^a	EtOH	1.64	22.5	3.2	5.2
Ox 13A ^a	EtOH	1.84	22.1	1.7	3.1
Ox 15 ^a	EtOH	1.29	25.8	10,000	12,900
Ox 16	EtOH	0.85	26.8	61.0	52.0
Ox 16Z3	EtOH	1.77	22.2	25.2	44.6
Ox 17 ^a	EtOH	0.64	29.1	18.0	12.0
Ox 17A	EtOH/H ₂ O	0.89	21.4	0.005	0.004
Ox 20 ^a	EtOH	1.57	26.8	704	1,106
Ox 20Z3	EtOH	0.71	23.9	>>10,000	---
Ox 21 ^a	EtOH	1.63	26.0	10,000	16,300
Ox 21Z3	EtOH	1.13	21.0	1,493	1,687
RHO 6G TFB ^b	EtOH	3.35	15.9	345	1,200

^aTaken from Ref. 3.^bTaken from Ref. 7.

Kauffman⁵ suggested that we make the zwitterion dye form for Ox 2 by quaternizing the pyridyl nitrogen with the propane sultone. He also suggested synthesis and testing of the mesylate salts. *Table 2* lists the observed energy output for the dyes we used, as well as some comparison data.³ Because of the coating on the cavity rear mirror, it was not always possible to input 60 J when the output was expected to exceed approximately 50 mJ. In the discussion we have used the measured slope efficiency and threshold to estimate the output at 60 J input using the relationship⁶

$$\varphi = k(I - t) \text{ [J]} \quad (1)$$

φ is the output in joules, k the slope efficiency, I the input in joules, and t the threshold for lasing in joules. *Table 2* shows that the zwitterions, with the exception of Ox 2Z3 and Ox 16Z3, do not perform any better than or as well as the tosylate salt.

Ox 2Z3 had the highest output of any dye we have observed. Under the same conditions, rhodamine 590 chloride output was 100.2 mJ.

Table 3 lists the calculated lasing parameters in ethanol and/or ethanol:water (50:50 by volume). Rhodamine 6G tetrafluoroborate is included for comparison;⁷ these data would indicate a large output at 60 J input in ethanol. That measurement has not been made.

We find in ethanol, which should be similar to methanol, that the mesylate salt has about 1.5 times the output of the tosylate, but the sulfopropyl zwitterion only has

Table 4 Lasing bands for dyes we have studied

Dye	Solvent	Band, nm
Ox 2A	EtOH - Air	554-579
	EtOH - Argon	553-587
Ox 2A	EtOH/H ₂ O - Air	565-592
	EtOH/H ₂ O - Argon	559-592
Ox 2Z3	EtOH/H ₂ O - Air	562-591
	EtOH/H ₂ O - Argon	562-591
Ox 16Z3	EtOH/H ₂ O - Air	525-545
	EtOH/H ₂ O - Argon	525-544
Ox 16Z3	H ₂ O - Air	526-553
	H ₂ O - Argon	525-553
Ox 20Z3	EtOH - Air	501-519
	EtOH - Argon	501-520
Ox 20Z3	EtOH/H ₂ O - Air	502-521
	EtOH/H ₂ O - Argon	503-522
Ox 20Z3	H ₂ O - Air	501-524
Ox 21Z3	EtOH - Air	500-519
	EtOH - Argon	500-520
Ox 21Z3	EtOH/H ₂ O - Air	503-523
	EtOH/H ₂ O - Argon	503-524
Ox 21Z3	H ₂ O - Air	504-526
	H ₂ O - Argon	504-526
Ox 27A	EtOH - Air	556-585
	EtOH - Argon	564-592
Ox 27Z3	EtOH/H ₂ O - Air	566-592
	EtOH/H ₂ O - Argon	569-593

Table 5 Absorption and emission wavelength maxima and fluorescence quantum yields for selected pyridinium oxazole dyes in ethanol under air. Ox 17AZ3 is in ethanol/water 50/50 by volume

Dye	Abs. peak, nm	Em. peak, nm	FQY
Ox 2	410	567	0.73
Ox 2A	411.2	565	0.76
Ox 2Z3	409.7	563	0.92
Ox 16Z3	417.7	520	0.86
Ox 20Z3	389.7	491	1.03
Ox 21Z3	387.0	495	1.01
Ox 27	411.2	571	0.83
Ox 27Z3	411.8	567	0.91
Ox 17A	410.6	534	0.99
Ox 17AA	412.2	532	0.85
Ox 17AZ3	412.2	533	1.02
Ox 12	452.2	584	0.65

approximately the same output as the tosylate salt. However, both of these variations of Ox 2 exhibit even longer life times than Ox 2. By changing solvent to ethanol:water (50:50 by volume), we find that the tosylate salt has the largest slope efficiency of the three variants. Were it not for a large decrease in the threshold for lasing of the sulfopropyl zwitterion, the ordering by output would be tosylate > zwitterion > mesylate. Instead we observe zwitterion > tosylate > mesylate. However, the difference between the tosylate and mesylate salts is only about 16%. This difference in output is about the same order of magnitude we have found between perchlorate and tosylate anions with perchlorate being the larger. These observations lead us to our original conclusion that, in general, no strong effects on output are noticed by changing the dye anion among those tested on the pyridinium oxazole dyes in the polar solvents we have been using.

However, we also note that in changing solvents from ethanol to ethanol:water the lifetimes of the mesylate and zwitterion variants of Ox 2 remain large while Ox 2 itself drops by a factor of almost 25. Peculiar to the zwitterion variant of Ox 2 among the zwitterion dye variants in this study is its high output, actually exceeding that of rhodamine 590 chloride.

Measurement of the fluorescence quantum yields shows a strong effect of making the zwitterions of these dyes. *Table 5* lists the measured quantum yields along with their absorption and emission maxima. For one of the two cases where all dye variants (mesylate, tosylate, zwitterion) were made, there is essentially no difference in quantum yield between Ox 2 and Ox 2A. However, the zwitterionic dyes have high fluorescence quantum yields, even if the tosylate salt does not. For the Ox 17A series, the mesylate salt (Ox 17AA) appears to have a somewhat lower fluorescence quantum yield than the tosylate. However, the zwitterion (Ox 17AZ3) again has the apparent characteristically high quantum yield.

Figures 1–3 show some of the spectrometer films taken for determination of the dye tuning range. In order to measure the upper and lower wave length extremities, 6 to 10 shots were fired because of the small fraction of light diverted to the spectrometer. The pictures are thus, in a sense, composites. However, it is clear that there is no null in the lasing bands for the same dyes studied by K-B nor in any of the other new dyes. Figure 4 shows a series of single shots over a range of 35 to 60 J input energies for the dye Ox 16Z3 as typical for these dyes. In Figure 1a the dye is Ox 2 in methanol (under argon), the same solvent as used by K-B. Figures 1b–e are for the mesylate salt of Ox 2. These photographs show the effect of the removal of oxygen on the lasing band. Under argon the lasing band increases, sometimes markedly, and there is generally improved performance. With the zwitterionic dye forms the lasing band does not change under air or argon as exemplified in Figures 1f and g. Figures 2 and 3 show the lasing bands for the remainder of the zwitterions studied. For these latter figures, the output coupler was 55% reflective instead of 80% as in Fig. 1. Independent of output, the lasing band is broader the greater the reflectivity of the output coupler. *Table 4* tabulates the lasing bands for the dyes.

4. DISCUSSION

We have found that solvent and auxochrome substitution on the pyridinium oxazole to be of larger effect on the photophysical properties of the dyes than changes in the anion. We feel that in the dyes without fluorine in position C, the zwitterionic dye form (using the propane sultone to make the zwitterion) results in an improved dye having a very long lifetime and, at least for Ox 2Z3, performing even better in aqueous ethanol than in pure ethanol. Considering the Ox 2 dye series, we see essentially a reversal of the threshold energies between the mesylate and zwitterionic variants in changing between ethanol and ethanol:water whereas there is little change in the tosylate salt. The mesylate variant does have a somewhat greater output in ethanol than the tosylate, but in ethanol:water this result is reversed in the more polar solvent. In part the explanation of these observations is based on the assumption that the zwitterion forms a dimer, and in the high dielectric medium of ethanol:water, the dimer formation is greatly reduced. In ethanol there is a strong secondary absorption band for Ox 2Z3 at 261 nm constituting over 35% by area of the $S_1 \leftarrow S_0$ band. In ethanol:water this same band is only about 16% by area of the principal absorption band and in pure water 15.5%. We also note the extreme stability of both the mesylate salt and the sulfopropyl zwitterion in both ethanol and ethanol:water under argon. In neither case did we detect any degradation under the test conditions which varied between 1.5 and 4.5 million shots at 10 J input at 25 Hz. The tosylate salt has a significantly reduced lifetime in ethanol:water leading one to suspect the tosylate anion to be more easily subject to photochemical degradation than the mesylate anion or the zwitterion.

The structural effects of auxochromes directly attached to the oxazole ring are seen in the series Ox 12, 15, 17,³ and Ox 17A. In this group the phenyl ring has been rigidized either in plane or out of plane with respect to the oxazole ring. Generally

Figure 1 The dye Ox 2 and variants. The mercury lines are at 546.07 and 579.07 nm. The doublet is not always visible.

Figure 2 The dyes Ox 16Z3 and 20Z3 in various solvents. In a–d the mercury lines are at 507.3 and 546.07 nm, in e–i the one line is at 507.3 nm.

Figure 3 The dyes Ox 21Z3, 27A and 27Z3 in various solvents. In a-f the mercury line is at 507.3 nm, in g-j the two visible lines are at 546.07 and 576.96 nm.

Figure 4 A series of single shots at 35, 40, 50 and 60 J input energies for the dye Ox 16Z3.

increasing the planarity of the π electron system should improve the dye. This series shows mixed results with large variations in the photophysical properties. Ox 12 with an ethylene bridge between the phenyl and oxazole rings, and therefore not planar, has the largest slope efficiency of any dye we have measured. Its lifetime is short and its fluorescence quantum yield is quite low. Ox 15 forces planarity with a vinylene bridge between the phenyl and oxazole rings. This dye is one of those exhibiting a very long lifetime like Ox 2 but with somewhat reduced slope efficiency. Ox 17 has two phenyl groups attached at the 4 and 5 positions on the oxazole ring. These are certainly not planar with themselves nor with the oxazole ring. The dye has a low slope efficiency and the lifetime is not useful. Forcing planarity in this enlarged π electron system by a 2,2' bond between the phenyl rings in Ox 17A produced a dye with a high fluorescence quantum yield but with low slope efficiency and extremely short lifetime. This extended system appears subject to rapid photochemical decomposition. Because of this observation only the quantum fluorescence yields of Ox 17AA and Ox 17AZ3 were measured.

Expanding the number of dyes considered to more than just the Ox 2 series used by K-B, we find mixed results compared to the relative dye output ordering in their work. In *Table 1* of Ref. 3, the first entry for Ox 13 is for the perchlorate salt, all remaining Ox 13 results are for the tosylate salt. The ratio of the slope efficiencies shows the perchlorate to have a little over 12% greater slope.⁸ A similar result is given in Ref. 1 with respect to differences between perchlorate and tosylate slope efficiencies. In *Table 3* the difference in slope efficiencies between Ox 17 and 17A is somewhat larger but we have solvent effects entering. Here the tosylate salt (Ox 17A) has poor photochemical stability in ethanol:water. Thus, in the polar solvents we are using, we have found only relatively small differences in output between tosylate and perchlorate salts of the pyridinium oxazole dyes. If we are comparing the energy output, we would now add mesylate salts as having only small differences from the former two.

Of the four other zwitterionic dye variants tested (*Table 2*), only one had a higher output than its tosylate analog. Ox 16Z3 has an output twice Ox 16 but its lifetime is reduced to a low level. Comparison with Ox 21Z3 and Ox 21, where the ethylene bridge has been replaced by a methyl group on the oxazole ring 4 position, shows a moderate output dye with a greatly improved lifetime for Ox 21Z3 over Ox 16Z3 though Ox 21 is still the better dye.

Again, in the dye Ox 20Z3 we see increased output in changing solvents from ethanol to ethanol:water. This dye also showed the extreme photostability of Ox 22Z3. The lasing parameters of Ox 27A and Ox 27Z3 were not measured. This *n*-butoxy substitution in position C was originally made to try to increase solubility; again, the zwitterion variant had less output than the mesylate salt. We have found that for most of the dyes studied, ethanol:water under argon gives the maximum output (*Table 3*). The removal of oxygen has been shown to greatly improve the performance of some dyes.⁹ However, we note that the zwitterionic dye variants we have tried in water also lase well under air or argon though with shortened lifetimes and reduced output. From Figures 2 and 3, the lasing bands of Ox 16Z3, 20Z3 and 21Z3 in water are seen to be as broad as in more favorable solvents.

K-B also report that their laser output curves are bifurcated. We find no such effects in any of the dyes we have studied, not even when we have used the same solvent as K-B. They postulate the possibility of absorption by a higher excited triplet state. Perhaps an even more unlikely explanation for the apparent null in their spectra is absorption by a higher excited singlet state, which they also postulated. We do not believe it to be lasing at two different wavelengths, i.e., dual lasing, which has been reported for some dyes.

We note that several old pictures in our library did indicate an apparent null in the lasing bands of some dyes. At the start of this work this null appeared again. Comparison with our earlier work showed the null was located at the same wavelength irrespective of the dye and, therefore, was not associated with the dye. Replacement of the rear mirror with another wideband mirror having different coatings completely eliminated the null.

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8. The second entry for Ox 13 in Table 1 of reference 3 is partly in error. The slope should be 1.64, threshold 22.5 J, lifetime 3.2 MJ/l, and FOM 5.2 kJ/l. Other parts of this entry are correct.
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