

Spectral, luminescent and lasing properties of pyran derivatives

T.N. Kopylova, V.A. Svetlichnyi, L.G. Samsonova, N.N. Svetlichnaya,
 A.V. Reznichenko, O.V. Ponomareva, I.V. Komlev

Abstract. The spectral, luminescent and lasing properties of eight organic molecules, substituted pyrans (DCM), are studied upon pumping by an exciplex XeCl laser at 308 nm and by the second harmonic from a Nd:YAG laser at 532 nm. These molecules exhibit lasing in the red spectral region between 600 and 780 nm with the efficiency of 45%. Lasing was also obtained in bis-substituted pyrans having the quantum yield of fluorescence equal to 0.01. The possibility of preparation of solid active media for tunable lasers based on polymer matrices doped with substituted pyrans is discussed.

Keywords: dye lasers, new active media, pyran derivatives.

1. Introduction

One of the most important fields of application of tunable dye lasers is medical biology, in particular, photodynamic therapy, which requires efficient narrow-band radiation sources emitting in the red spectral region, for example, at 630 nm [1]. The number of molecules emitting in this spectral region is limited, so that the search for new highly efficient and photostable organic molecules lasing in the red spectral region is still urgent. In the last years, much progress has been achieved in the development of solid active laser media based on organic molecules lasing in the red spectral region, whose parameters compare well with those in solutions [2]. Lasers based on such media can be made more compact, safe and convenient for applications in medicine.

It is known that pyrromethenes [3, 4], phenalemines [5, 6], xanthenes [7] and some other dyes [8] in solutions and solid matrices produce efficient and stable lasing in the red spectral region. Substituted pyrans are promising for the use as solid active laser media. So far only the study of one of the pyran derivatives – DCM [4-(decyanomethylene)-2-methyl-6-(para-dimethylaminostyryl)-4H-pyran] has been reported in the literature. DCM produces lasing that can be tuned within a broad band (up to 100 nm). This dye is

photostable, exhibits lasing upon flashlamp pump [9, 10], and produces efficient lasing in a solid matrix [11].

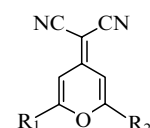
The aim of this paper is to develop the synthesis of substituted pyrans and to study the spectral and lasing properties of new compounds.

2. Synthesis of pyran derivatives and their properties

2.1 Synthesis

The structural formulas of substituted pyrans studied in the paper are shown in Fig. 1, where DCM-CH-90 is the known DCM dye [9, 10].

The DCM derivatives studied in the paper were synthesised from dicyanomethylene γ -pyran and the corresponding benzaldehyde. The compounds were purified by the method of column chromatography on silica gel, subjected to the elemental analysis, and their melting temperature was measured. The structure of the compounds was confirmed by their IR and NMR spectra.















	R ₁	R ₂
DCM-CH-90	CH ₃	CH=CH-  N(CH ₃) ₂
Bis-DCM-CH-90	CH=CH-  N(CH ₃) ₂	CH=CH-  N(C ₈ H ₁₇) ₂
DCM-doa	CH ₃	CH=CH-  N(C ₈ H ₁₇) ₂
Bis-DCM-doa	CH=CH-  N(C ₈ H ₁₇) ₂	CH=CH-  N(C ₈ H ₁₇) ₂
DCM morpholine	CH ₃	CH=CH- 
Bis-DCM morpholine	CH=CH- 	CH=CH- 
DCM julolidine	CH ₃	CH=CH- 
Bis-DCM julolidine	CH=CH- 	CH=CH- 

Figure 1. Structural formulas of dyes.

T.N. Kopylova, V.A. Svetlichnyi, L.G. Samsonova, N.N. Svetlichnaya
 V.D. Kuznetsov Siberian Physicotechnical Institute, Novo-Sobornaya pl.
 1, 634050 Tomsk, Russia; e-mail: kolylova@phys.tsu.ru;
 A.V. Reznichenko, O.V. Ponomareva, I.V. Komlev 'Alpha-Akonis'
 Research and Device Enterprise, Likhachevskii proezd 5, 141700 Dol-
 goprudnyi, Moscow region, Russia; e-mail: akonis@hotmail.com

Received 18 December 2002

Kvantovaya Elektronika 33 (9) 807–810 (2003)

Translated by M.N. Sapozhnikov

2.2 Spectral and luminescent properties

The absorption and luminescence spectra were recorded by a standard method using a Specord M-40 spectrophotometer and Hitachi-850 spectrofluorimeter.

The quantum yield of fluorescence was measured by a standard method [12] by comparing it with a standard solution of Rhodamine C in ethanol with the quantum yield of fluorescence $\eta_{fl} = 0.65$ [13].

Ethanol, ethyl acetate, and dimethyl sulfoxide (DMSO) were used as solvents. Ethyl acetate was used to study the possibility of preparing solid laser active elements based on pyran.

2.3 Lasing properties

The lasing properties of pyran derivatives were studied upon transverse pumping in a nonselective plane-parallel resonator. An aluminium mirror was used as the highly reflecting mirror in the resonator, and a face of a rectangular cell with the dye solution under study served as the output mirror. The dyes were pumped by 15-ns, 40-mJ pulses from an exciplex XeCl* laser at 308 nm or by 6-ns, 15-mJ second-harmonic pulses from a Nd:YAG laser at 532 nm.

The energy parameters of pump radiation and lasing were detected with IMO-2H and KTP-2 power meters, and the lasing spectrum was recorded per pulse with a Real laser spectrometer.

2.4 Photostability

We measured the quantum yields

$$\gamma = \frac{N_{ph}}{N^*} \quad (1)$$

of phototransformation of pyran derivatives, which characterise their photostability. Here, N^* is the number of excited molecules, which is assumed equal to the number of photons absorbed in the medium; N_{ph} is the number of phototransformed molecules (N_{ph} was estimated from a change in the optical density in the long-wavelength absorption band). We also estimated the operating life of active media (lasing photostability) defined as the energy input to the active-medium unit volume before the reduction of the lasing efficiency by 20% ($P_{0.8}$).

3. Discussion of results

Table 1 presents the spectral and luminescent parameters of pyran derivatives. We found that the long-wavelength absorption of pyran derivatives depends on a solvent. The long-wavelength absorption band of all pyran derivatives studied in the paper shifts to the blue by 15–20 nm with decreasing polarity of a solvent (on passing from DMSO and ethanol to ethyl acetate). The extinction coefficient in the long-wavelength absorption bands of the dyes is rather high: 40000–50000 L mol⁻¹ cm⁻¹.

The absorption and fluorescence bands of bis-structures are shifted to the red, indicating the increase in the conjugation chain in these molecules. Note that the dyes of this class have a large Stokes shift (4000–6000 cm⁻¹) and broad fluorescence bands (75–115 nm), which means that the geometry of these molecules strongly changes in the excited state. The emission intensity of pyran derivatives depends on their structure and solvent. For example, while the quantum yield of fluorescence for the first group of dyes (DCM-CH-90, DCM-doa, and DCM morpholine) is $\eta_{fl} = 0.4 - 0.6$ and decreases down to 0.1 in their bis-structures, $\eta_{fl} = 0.10 - 0.12$ for DCM julolidine and its bis-structure. The emission intensity of the first group of dyes strongly depends on a solvent, the quantum yield of fluorescence decreasing by an order of magnitude with increasing solvent polarity (ethyl acetate and DMSO). For example, $\eta_{fl} = 0.10$ for bis-DCM-CH-90 in ethyl acetate, whereas $\eta_{fl} = 0.01$ in DMSO. The fluorescence intensity of DCM julolidine and its bis-structure did not almost change with changing solvent. Thus, $\eta_{fl} = 0.10$ for DCM julolidine and its bis-structure in ethyl acetate and $\eta_{fl} = 0.12$ and 0.11 in DMSO, respectively.

The lasing parameters of pyran derivatives are presented in Table 2. One can see that all the dyes produce lasing in the red spectral region upon pump by a XeCl laser or the second harmonic of a Nd:YAG laser, the lasing efficiency being 24% and 45%, respectively.

Note that the lasing efficiency of pyran derivatives in acetyl acetate is high, which is, as mentioned above, very important for predicting the lasing efficiency of the dyes in a polymethyl methacrylate (PMMA) matrix. Pyran derivatives produce lasing in this solvent in the spectral range from 600 to 650 nm, and their bis-structures exhibit lasing

Table 1. Spectral and luminescent characteristics of pyran derivatives.

Dye	Ethyl acetate				Ethanol				Dimethyl sulfoxide			
	λ_{abs}/nm	λ_{fl}/nm	$\Delta\lambda_{fl}/nm$	η_{fl}	λ_{abs}/nm	λ_{fl}/nm	$\Delta\lambda_{fl}/nm$	η_{fl}	λ_{abs}/nm	λ_{fl}/nm	$\Delta\lambda_{fl}/nm$	η_{fl}
DCM-CH-90	455	585	83	0.5 ± 0.1	472	615	82	0.5 ± 0.1	476	635	85	0.5 ± 0.1
Bis-DCM-doa	476	625	100	0.10 ± 0.05	481	620	85	0.10 ± 0.03	488	650	99	0.010 ± 0.005
DCM-doa	476	585	80	0.5 ± 0.1	488	620	81	0.6 ± 0.1	493	635	88	0.6 ± 0.1
Bis-DCM-doa	490	625	93	0.2 ± 0.1	498	650	115	0.04 ± 0.02	500	660	88	0.013 ± 0.005
DCM morpholine	435	580	84	0.4 ± 0.1	441	615	75	0.5 ± 0.1	455	630	95	0.6 ± 0.1
Bis-DCM morpholine	453	630	102	0.10 ± 0.05	455	620	86	0.04 ± 0.02	472	650	95	0.011 ± 0.005
DCM julolidine	490	585	100	0.10 ± 0.02	512	650	74	0.12 ± 0.02	515	665	83	0.12 ± 0.02
Bis-DCM julolidine	500	585	101	0.10 ± 0.02	512	650	85	0.10 ± 0.02	515	665	108	0.11 ± 0.02

Notes: λ_{abs} and λ_{fl} are the positions of the maxima of absorption and fluorescence bands; $\Delta\lambda_{fl}$ is the FWHM of the fluorescence band; η_{fl} is the quantum yield of fluorescence upon excitation into the long-wavelength absorption band.

Table 2. Lasing characteristics of pyran derivatives.

Dye	$\lambda_p = 532$ nm						$\lambda_p = 308$ nm					
	Ethyl acetate		Ethanol		Dimethyl sulfoxide		Ethyl acetate		Ethanol		Dimethyl sulfoxide	
	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)	$\lambda_{\text{las}}/\text{nm}$	Efficiency (%)
DCM-CH-90	607	35.2	635	39.5	658	44	604	16.5	631	18	655	18
Bis-DCM-CH-90	682	28.5	insoluble		755	12	672	7.6	insoluble		745	0.5
DCM-doa	611	34.3	635	45.0	656	45	606	18.5	635	24	656	6
Bis-DCM-doa	670	13.5	insoluble		insoluble		657	9.6	insoluble		insoluble	
DCM morpholine	no lasing		639	13.7	654	36	607	5.2	635	10	654	11.5
Bis-DCM morpholineñ	684	6	insoluble		755	7	675	6.3	insoluble		748	1.2
DCM julolidine	635	44.5	675	9	695	43.5	635	19.2	675	0.5	694	10
Bis-DCM julolidine	635	43.5	675	16	695	43.0	635	14.4	675	1.0	693	15

between 620 and 690 nm. The lasing efficiency of DCM julolidine at 635 nm pumped at 532 nm is 44.5 %, while that of its bis-structures is 43.5 %. No lasing was observed in DCM morpholine in ethyl acetate pumped at 532 nm because this dye does not absorb in this region.

The lasing efficiency of pyran derivatives in ethyl acetate pumped by a XeCl laser was 16 %–19 %. The lasing efficiency of their bis-structures was 6 %–9 %.

We found that the lasing band of some pyran derivatives pumped by a XeCl laser shifted to the blue compared to the band observed upon pumping by the second harmonic from a Nd:YAG laser. This can be explained by the fact that, upon excitation to the high-lying state by the 308-nm line, vibrational relaxation related to a change in the molecule geometry has no time to occur, and lasing is observed from higher vibrational levels of the S_1 state than upon excitation at 532 nm. However, this assumption should be additionally verified.

The solubility of some pyran derivatives in ethanol (DCM morpholine and DCM julolidine) and their bis-structures is much worse than in ethyl acetate, which impairs their lasing parameters. Upon pumping at 532 nm, the best results in ethanol were obtained for DCM-CH-90 (lasing efficiency at 635 nm was 39.5 %) and DCM-doa (lasing efficiency at 635 nm was 45 %). Upon pumping at 308 nm, the lasing efficiency of DCM-CH-90 and DCM-doa was 18 % and 24 % at 631 and 635 nm, respectively, which is comparable with the lasing efficiency of Rhodamine 6G (25 %) for the same pump.

The use of DMSO as a solvent makes it possible to advance to the long-wavelength spectral region (655–755 nm). Upon pumping at 532 nm, the maximum lasing efficiency was observed in this spectral range for DCM julolidine and its bis-structure at 695 nm (43.5 % and 43 %, respectively). Bis-DCM-CH-90 and bis-DCM morpholine produce lasing at the longest wavelength of 755 nm, with lasing efficiencies 12 % and 7 %, respectively.

As mentioned above, pyran derivatives have broad fluorescence bands – up to 100 nm. The FWHM of the lasing band in a nonselective resonator amounts to 20 nm (100 nm at the band base), which provides a broad tuning of the laser line (up to 100 nm) [8].

We estimated the quantum yield of phototransformation of pyran derivatives. The quantum yield for DCM morpholine, DCM-doa, and DCM-CH-90 pumped at 308 and

532 nm was $(1.2 \pm 0.2) \times 10^{-3}$ and $(1.3 \pm 0.2) \times 10^{-5}$, respectively. These values are comparable with the quantum yield of phototransformation of the known xanthene dye, Rhodamine 6G at the same excitation. The study of the absorption spectra of solutions of substituted DCM showed that photoproducts produced upon laser irradiation do not absorb in the lasing region of these compounds, and a decrease in the lasing efficiency of the active medium upon photodegradation of the dye is caused only by a decrease in the concentration of active molecules. Because organic dyes produce efficient lasing, as a rule, in a rather broad range of concentrations, a small decrease in the concentration caused by photodissociation will not reduce the lasing efficiency, providing a long service life of the active medium. The lasing photostability $P_{0.8}$ of DCM morpholine, DCM-doa, and DCM-CH-90 at the concentration $C_0 = 10^{-3}$ M pumped by a XeCl laser was estimated as 150–200 J cm $^{-3}$, which is several times higher than that of Rhodamine 6G and Phenalemine 512 lasing in the red spectral region. The lasing photostability of DCM julolidine was somewhat lower ($P_{0.8} = 50$ J cm $^{-3}$).

4. Conclusions

Our study of the lasing efficiency of pyran derivatives has shown that these dyes are efficient active laser media emitting in the spectral range between 600 and 780 nm with the high lasing efficiency (up to 45 %). Lasing of pyran derivatives in ethyl acetate makes them promising for doping a PMMA matrix.

Because we have observed lasing in pyran derivatives with the quantum yield of fluorescence $\eta_{\text{fl}} = 0.01$ (for example, in bis-DCM-CH-90 and bis-DCM morpholine in DMSO), it is necessary to continue studies combining the quantum-chemical analysis of these structures, the estimates of the rate constants of electronic-energy deactivation processes in them, and the investigation of induced absorption spectra in the singlet and triplet channels. The fundamental knowledge acquired in these studies will make it possible to understand better the phenomenon of lasing in organic molecules, the relation between the lasing efficiency and the molecular structure, and to prepare active media based on pyran derivatives.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 02-02-08104).

References

1. Gvishi R., Reifeld R. *J. Phys. (Colloques C7)*, **1**, 199 (1993).
2. Costela A., Garcia-Moreno I., Figuera J.M., et al. *Appl. Phys.*, **80** (6), 3167 (1996).
3. Costela A., Garcia-Moreno I., Carrascoso M.L., Sastre R. *Opt. Commun.*, **201**, 437 (2002).
4. Aldeg G.R., Dolotov S.M., Koldunov M.F., et al. *Kvantovaya Elektron.*, **30**, 1055 (2000) [*Quantum Electron.*, **30**, 1055 (2000)].
5. Kuznetsova R.T., Kopylova T.N., Tel'minov E.N., Reznichenko A.V. *Opt. Atmos. Okeana*, **6** (3), 274 (1993).
6. Dolotov S.M., Koldunov M.F., Kravchenko Ya.V., et al. *Kvantovaya Elektron.*, **32**, 669 (2002) [*Quantum Electron.*, **32**, 669 (2002)].
7. Maslyukov A., Sokolov S., Kailova M., et al. *Appl. Opt.*, **34** (9), 1516 (1995).
8. Kopylova T.N., Maier G.V., Reznichenko A.V., et al. *Kvantovaya Elektron.*, **30**, 887 (2000) [*Quantum Electron.*, **30**, 887 (2000)].
9. *Lambda Physik AG Laser Dyes Catalog* (Göttingen, 2000) p. 184ss.
10. *Kodak Laboratory Chemicals Catalog*, (54), 255 (1990).
11. Hu W., Ye H., Li C., Jiang Z., Zhou F. *Appl. Opt.*, **36** (3), 579 (1997).
12. Parker C. *Photoluminescence of Solutions* (Amsterdam: Elsevier, 1968; Moscow: Mir, 1972).
13. Kubin R.F., Fletcher A.N. *J. Luminescence*, **27**, 455 (1982).