Quantum Electronics **46** (10) 873–876 (2016)

DOI: 10.1070/QEL16191

New efficient laser dyes for the red spectral range. Part 2. Pyrone derivatives

S.P. Belov, O.A. Burdukova, I.V. Komlev, V.A. Petukhov, V.A. Povedailo, O.V. Ponomareva, M.A. Tavrizova, M.A. Semenov

Abstract. **We report the generation characteristics of ethanol solutions of some dyes belonging to the derivatives of 2H- and 4H-pyrones, as well as of some structurally similar model fluorophores. The tuning curves of these dyes generating light in the orange and red spectral regions are measured, and the wavelength tuning ranges are determined. The dependences of the generated energy on the pump energy in a non-selective cavity are also measured. It is shown that some of the studied compounds possess better characteristics than those of widely used laser dyes in these spectral regions.**

Keywords: *dye laser, generation characteristics, derivatives of 2H- and 4H-pyrones, tuning range, energy efficiency.*

1. Introduction

In the first part of the present paper [1] we reported the measurement results of generation characteristics of newly synthesised dyes belonging to peri-indenones (benzanthrones and phenalemines). Some of them are interesting for practical applications since they have a wide region of wavelength tuning and a high energy efficiency.

The present paper is devoted to the study of lasing properties of fluorophores synthesised from 2H- and 4H-pyrones, as well as some model dyes with a similar structure. The general feature of pyrones is the presence of an oxygen atom in the hexagonal ring that opens the chromophore chain, which significantly reduces the probability of transition of dye molecules from singlet to triplet state and thus can improve the luminescence and generation characteristics according to the Drexhage's loop rule [2]. That is why among the pyrones many efficient laser dyes have been found, particularly, coumarins. However, most of the known coumarins emit only in the blue and green spectral regions. We know only solitary compounds of this class that luminesce in the red region. The synthesis of fluorophores for the red region is possible also on the basis of derivatives of 4-pyrones, which is interesting because in the red and near-IR regions there are still no dyes, comparable in efficiency with pyrromethenes and rhodamines, used in the yellow and orange spectral regions [3]. The aim of the present work was to synthesise and to study the generation characteristics of fluorophores based on 2H- and 4H-pyrones, as well as several model dyes with similar structures. The derivatives under study were synthesised using the schemes and conditions, close to those described previously [4–9].

S.P. Belov I.G. Petrovsky Bryansk State University, ul. Bezhitskaya 14, 241036 Bryansk, Russia;
O.A. Burdukova Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia;
I.V. Komlev, O.V. Ponomareva, M.A. Tavrizova SPF 'Deltarus' LLC, 5, Likhachevskii proezd, 141700 Dolgoprudnyi, Moscow region, Russia;
V.A. Petukhov P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia; e-mail: petukhov@sci.lebedev.ru;
V.A. Povedailo B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, prosp. Nezavisimosti 68, 220072 Minsk, Belarus;
M.A. Semenov P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia

Received 4 August 2016
Kvantovaya Elektronika **46** (10) 873–876 (2016)
Translated by V.L. Derbov

2. Experiment

The structural formulas of the molecules of all studied substances are presented in Fig. 1.

We measured the tuning curves, i.e., the dependences of the generation energy in a selective cavity on the chosen wavelength at a fixed pump energy. For the most efficient substances, we also measured the dependences of the generation energy on the pump energy in a broadband cavity in order to determine the differential efficiency and the threshold pump energy. For comparing the studied dyes with the known substances, we measured the generation characteristics of Rhodamine 6G, Rhodamine 101, DCM and pyridine-1 under the same conditions. The technique of measurements and the design of the measurement stands are thoroughly described in Ref. [1], so in this paper we restrict ourselves to a brief description of the experiment.

In measuring the dependence of the generation energy on the pump energy, the solutions of the studied dyes were poured into a cuvette with two parallel windows. One window was a plate of TF-1 glass and served as an exit mirror with a reflection coefficient of 6%, and the second window had an interference coating at the outer surface and played the role of a highly reflecting mirror with a refection coefficient of ~99%. The thickness of the dye layer was 8 mm, and the total length of the cavity was 2.4 cm. The quasi-longitudinal pumping was implemented via the exit window. The pump radiation was focused into a spot with the diameter 3 mm with sharp edges and the intensity distribution over the spot area close to uniform. For pumping, we used the second harmonic of the radiation from a pulsed Nd:YAG laser having a pulse duration of 25 ns. The slope efficiency was determined as a tangent of the curve slope angle at pump energies exceeding the threshold by two–three times. The threshold pump energy was determined by extrapolating the initial linear part of the dependences to the zero generation energy.

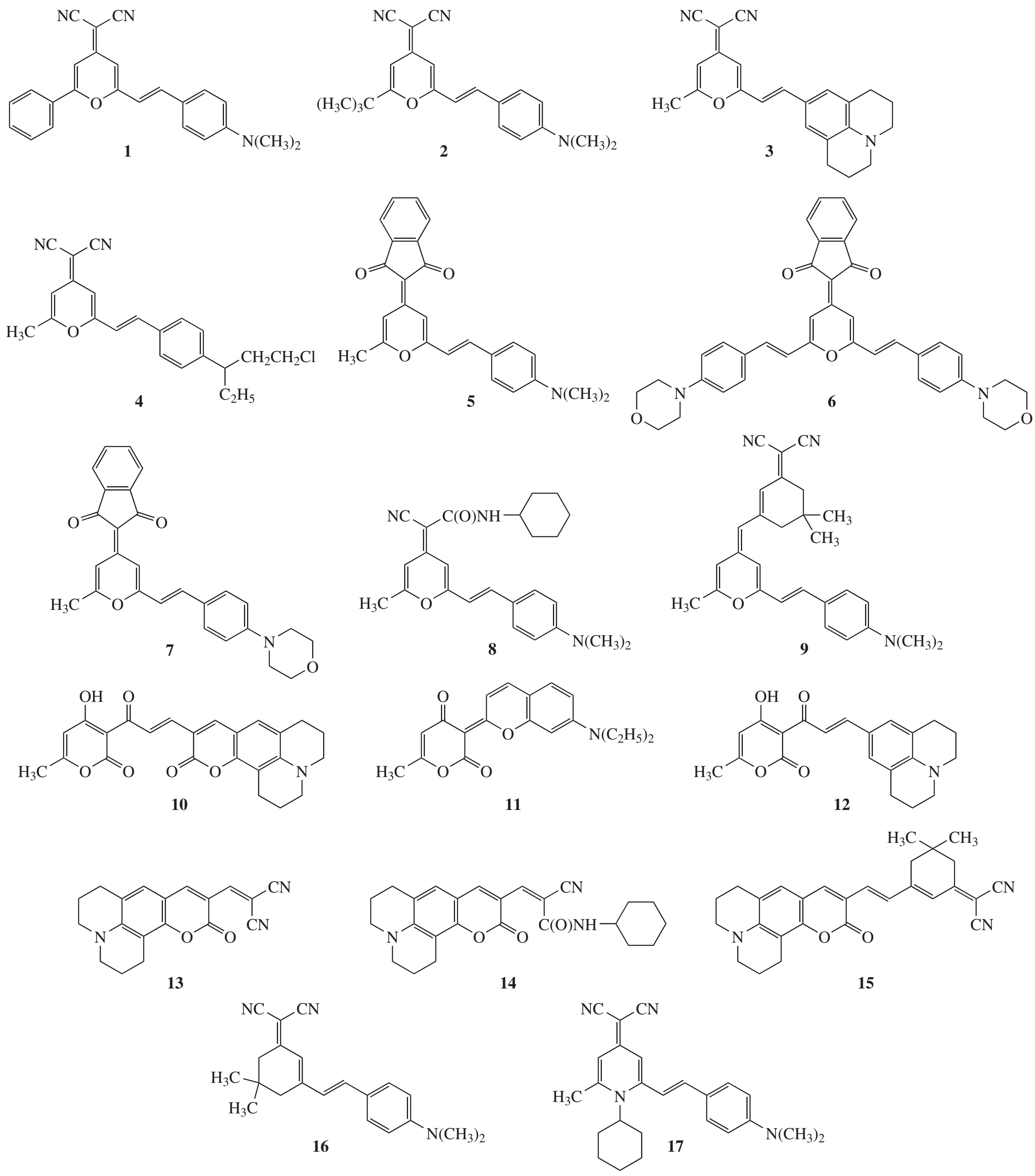

Figure 1. Structural formulae of the studied dyes. The dye numbers correspond to those in Table 1.

A pair of Brewster prisms inside the cavity was used as a dispersion element to select the wavelength in the measurements of the tuning curves. The studied solutions were poured into a rectangular glass cuvette with the dye layer thickness of 5 mm. The cuvette was placed at the Brewster angle inside the cavity, formed by the Brewster roof prism and the stack of two glass plates, used as an exit mirror. The quasi-longitudinal pumping was provided by the second harmonic of the Nd : YAG laser at a small angle to the cavity axis. The pump beam was focused into a spot with a diameter of $\sim$0.8 mm. The pump energy was 7 mJ, and the pulse duration was 20 ns. The generated wavelength was recorded using a laser wavelength meter with an accuracy of 0.01 nm.

3. Results

The measured tuning curves are shown in Fig. 2, and the dependences of the generation energy on the pump energy are presented in Fig. 3. Table 1 summarises the results of measurements of the main characteristics, namely, the wavelength

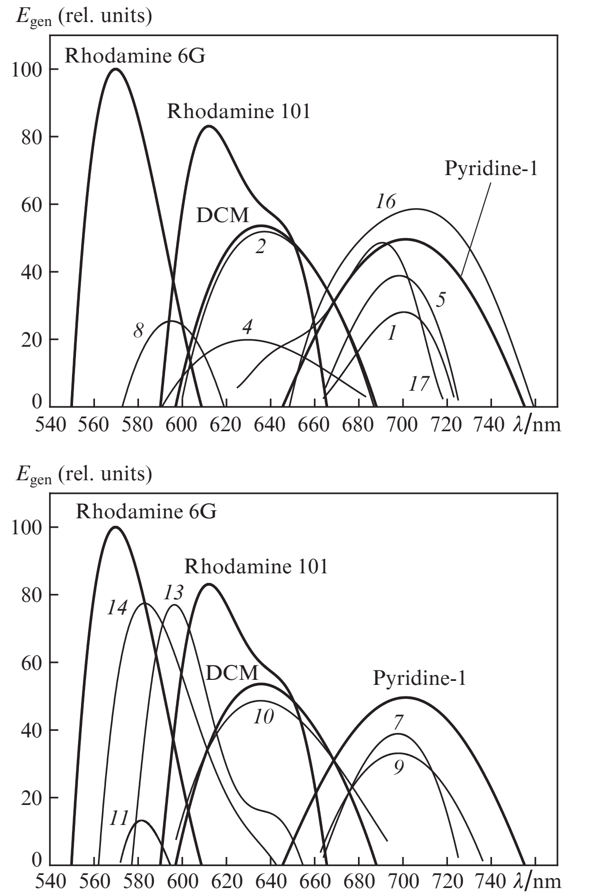

Figure 2. Dependences of the generation energy on the wavelength in a selective cavity at a fixed pump energy. Here and in Fig. 3 the numbers of the curves correspond to those of dyes in Table 1.

Table 1.

Substance	λ_{abs}^{max}/nm	Selective cavity		Broadband cavity	
		λ_{gen}^{max}/nm	$\Delta\lambda$/nm	η (%)	E_{pump}^{th}/mJ
1	491	698	665–722		
2	470	637	602–684	33.8	7.0
3	512	675		30.1*	11.4*
4	467	635	590–680	25.5	8.5
5	513	700	671–720	16.7	18.2
6	503			0*	
7	482	695	665–726	11.4	20.5
8	510	593	574–618	22.5	28
9	507	706	641–756	32.2	13.0
10	470	638	590–694	35.8	7.4
11	512	582	573–594	6.0	40
12	520			0	
13	550	595	579–648	40.6	8.3
14	507	584	563–635	40.7	9.7
15	540			15.5	12.9
16	510	711	650–755	28.6	12.4
17	475	690	624–725	24.4	9.82
Rhodamine 6G		570	550–618	50.9	4.9
Rhodamine 101		612	593–665	42.3	4.6
DCM		635	595–691	28.9	7.4
Pyridine-1		700	654–746	26.7	18.8

*Weak absorption at the pump wavelength, insufficient solubility.

of the absorption maximum, λ_{abs}^{max}; the wavelength of the generation maximum, λ_{gen}^{max}; the width of the tuning range, $\Delta\lambda$; the slope efficiency, η; and the threshold pump energy in a non-selective cavity, E_{pump}^{th}.

One can see from Fig. 2 that dye 16 exceeds the widely used pyridine-1 in efficiency due to a lower threshold, providing a similar range of tuning, so that it can be recommended for application. Dyes 13 and 14, belonging to coumarins, provide efficient lasing in a region of 590 nm between the regions of generation of Rhodamine 6G and Rhodamine 101, with an efficiency insignificantly smaller than that of Rhodamine 101. Commonly in this region the Rhodamine B dye is used, which also has an efficiency comparable with that of Rhodamine 101, but is characterised by a small width of the tuning range (~45 nm), considerably smaller than that of dyes 13 and 14. One more coumarin dye 10 generates radiation with an even longer wavelength at 640 nm. Note that usually coumarins generate in the region of smaller wavelengths, e.g., in the well-known handbook on laser dyes issued by Lambda Physics [3] the substance of this class with a maximal wavelength of radiation is coumarin 540A (coumarin 153) with a maximum generation wavelength of 540 nm. We have no data on coumarin dyes with greater generation wavelengths. Dye 10 has an acceptable efficiency, not high threshold, and efficiently absorbs radiation of high-power semiconductor lasers, operating at a wavelength of 445 nm due to a large Stokes shift. Therefore, this substance is promising for diode-pumped dye lasers.

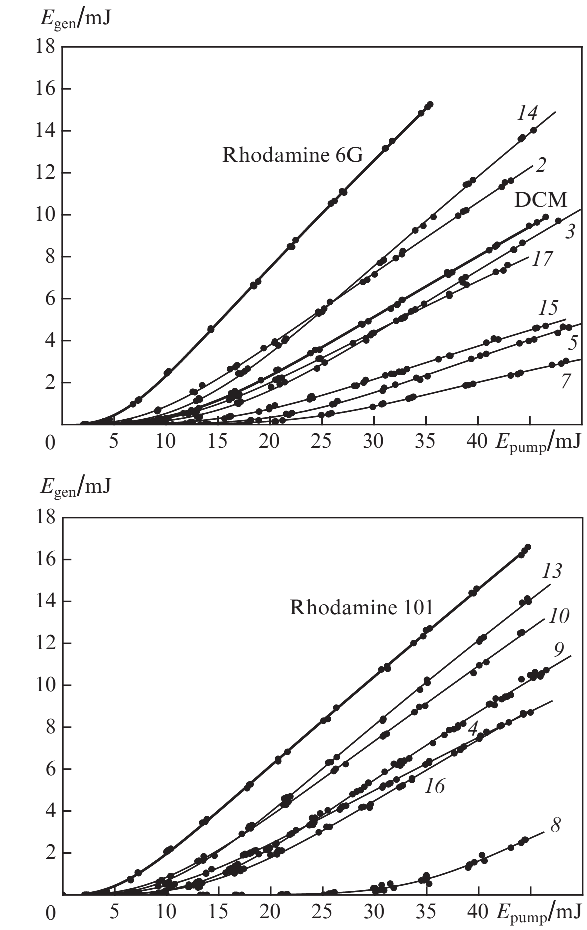

Figure 3. Dependence of the generation energy on the pump energy in a non-selective cavity.

4. Conclusions

For the solutions of 17 new dyes, we have measured the generation characteristics in a selective cavity and broadband cavities. The studied dyes generate the radiation in the red and orange spectral regions. We have measured the tuning curves and the dependences of the generation energy on the pump energy in a non-selective cavity. The ranges of tuning and slope efficiencies have been determined. With respect to the energy efficiency, the best of the studied substances do not yield the widely used dyes.

Acknowledgements. This work was supported by the Presidium of Russian Academy of Sciences ['Fundamental and Applied Problems of Photonics and Physics of New Optical Materials' Programme (1.25P)] and by the LPI Educational-Scientific Complex, Russian Academy of Sciences.

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