

Optical properties of DCM dye and its derivatives at two-photon excitation

V.A. Svetlichnyi,¹ E.A. Vaitulevich,¹ A.P. Lugovskii,²
M.P. Samtsov,² and Yu.P. Meshalkin³

¹ Siberian Physical-Technical Institute at the Tomsk State University, Tomsk, Russia

² Seochenko Institute of Applied Physical Problems at the Belarus State University, Minsk, Belarus

³ Novosibirsk State Technical University, Novosibirsk, Russia

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Optical properties of four (dicyanomethylene)-pyran derivatives were investigated at two-photon excitation by nanosecond Nd–YAG laser radiation (12 ns, 1064 nm). The two-photon absorption (TPA) cross section of dyes in solutions and polymeric matrix were determined by the fluorescent method of two-quantum standard. Nonlinear transmission and lasing of dye solutions of (dicyanomethylene)-pyran two-photon excitation were investigated. A difference in TPA cross-sections determined by the fluorescent method and by the direct nonlinear transmission (NLT) method is discussed. The reduction in output laser energy to 36% of the initial pulse energy was obtained. The possibility of using the studied dyes for limiting the laser power is considered. Two-photon pumped lasing (TPPL) in the spectral range 648–663 nm for three studied dyes was obtained, and TPPL characteristics were investigated. The lasing efficiency higher than 1% was achieved.

Introduction

Two-photon absorption (TPA) in organic molecules and molecular systems based on organic molecules under pulsed laser irradiation is intensively studied now.¹ This is connected both with interesting basic problems (determination of the influence of the molecular structure and intermolecular interactions on nonlinear properties of organic compounds of different classes, investigation of changes in absorption properties of different molecules at different selection rules for one- and two-photon transitions) and with possible practical applications. Two-photon excitation is already used efficiently in some laser technologies, for example, in fluorescent spectroscopy,² confocal fluorescent microscopy of biological objects,^{3–5} photodynamic therapy and diagnostics,^{6–8} as well as in 3D microproduction (multiphoton photopolymerization).^{9–11} In some fields of practical usage of two-photon (multiphoton) absorption, intensive investigations are carried out, such as the construction of lasers with multiphoton pumping,^{12–15} the limiting of laser output power (optical limiting),^{12,16,17} development of 3D optical memory devices,^{18–20} etc.

To use successfully organic molecules and based on them molecular compositions, it is necessary to study thoroughly their optical characteristics. In addition to the high TPA cross section, other requirements, depending on potential applications, are imposed upon such systems, for example, a high (or, to the contrary, low) emittance, a particular spectral range, high solubility in certain fluids, compatibility with biological objects, etc. Therefore, the search for compounds with a high two-photon

absorption cross section, meeting other requirements, important for possible applications, still goes on.²¹ The correct determination of the TPA cross section remains urgent, because several nonlinear processes can take place simultaneously with TPA in a medium under high-power laser excitation, and it is a quite difficult problem to separate them. This problem is solved individually for any particular compound (or class of compounds).

(Dicyanomethylene)-pyran substitutes form a promising class of organic molecules.^{22–25} Studying the optical properties of the molecular series of (dicyanomethylene)-pyran substitutes under two-photon excitation by the Nd–YAG laser radiation of nanosecond duration (1064 nm) is the issue of this paper. This series consists of the DCM molecule (4-dicyanomethylene-2-methyl-6-(*n*-dimethylaminostyryl)-4(H)-pyran), which is a well-known laser dye, and three its derivatives.

Instrumentation, and objects of investigation

Objects of investigation

For investigations, we took a series of four compounds (including a well-known laser dye DCM):

1 – 4-dicyanomethylene-2-methyl-6-(*n*-dimethylaminostyryl)-4(H)-pyran (DCM),

2 – 4-dicyanomethylene-2-methyl-6-(*p*-dioctylaminostyryl)-4H-pyran,

3 – 4-dicyanomethylene-2-tert-butyl-6-(*n*-dimethylaminostyryl)-4(H)-pyran,

4 – 4-dicyanomethylene-2-phenyl-6-(*n*-dimethylaminostyryl)-4(H)-pyran.

The structural formulas of the studied molecules are shown in Fig. 1.

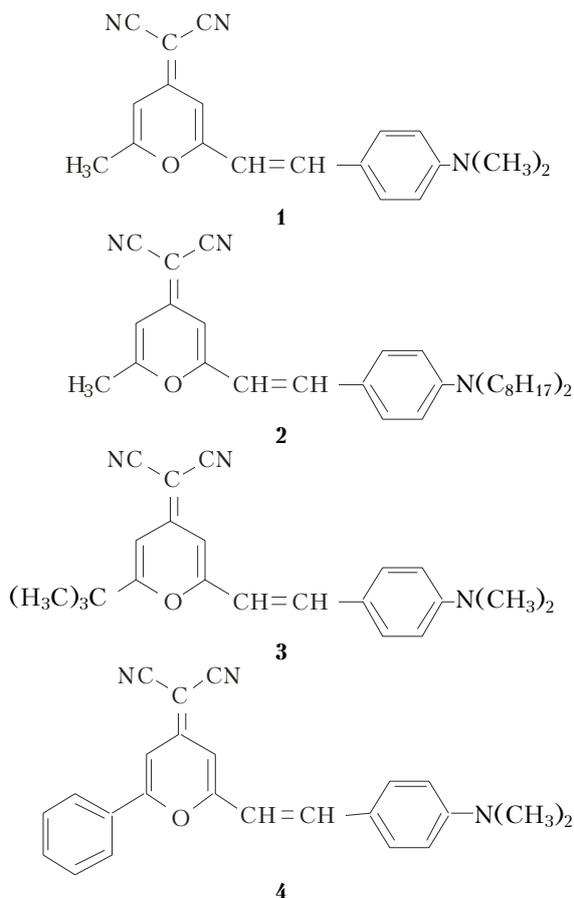


Fig. 1. Structural formulas of the studied molecules.

The dyes were investigated in three solvents [ethylacetate, ethanol, 1-methyl-2-pyrrolidone (MP)] and in polymer matrices. Ethylacetate and MP of high purity were used without additional purification; ethanol was additionally purified by standard techniques.²⁶ The dye concentration ranged from 10^{-5} M (when studying linear spectral-luminescent properties) to $5 \cdot 10^{-2}$ M (when studying nonlinear transmission at two-photon excitation).

Polymethylmetacrilate (PMMA) was taken as a material of the polymer matrix, since it has good optical characteristics, well developed production technology, and satisfactory operating ability. A dye and an initiator of polymerization were solved in the initial monomer (methylmetacrilate or MMA) purified from a stabilizer.²⁷ Then the solutions were filtered and hardened through block radical polymerization.²⁸ Dinitrile of azobisisobutyric acid was used as a thermal initiator. To avoid the inhibitory action of air, the solutions were placed in glass vessels and blown by argon; then the vessels were carefully closed. Polymerization proceeded in dark in a thermostat. As a result, transparent homogeneous blocks were obtained, which were then subjected to hand processing.

In addition to PMMA samples with the studied dyes, polymer samples based on PMMA, modified by a low-molecular addition (10% MP), were produced. In this case, a dye was previously solved in MP, and then MP was mixed with MMA. The further technological process of sample production corresponded to the process described above for nonmodified PMMA.

Rectangular blocks of 10×10 mm cross section and 20 mm height were cut from the polymer samples. The block surfaces were abraded and polished manually.

Experimental technique

Linear absorption and fluorescence spectra of the dyes were studied on the SM2203 spectrofluorimeter (Solar, Minsk). The first harmonic radiation of a Q-switched Nd–YAG laser (1064 nm, 12 ns, 1–100 mJ) was used for two-photon excitation. The laser radiation intensity was attenuated by calibrated neutral filters. The intensity, spectra, and temporal characteristics of two-photon excited fluorescence and lasing were recorded with the S100-1024 spectrometer (Solar LS) with a fiber input and rapid DET210 PIN photodiodes (Thorlabs) with a Tektronix TDC224 oscilloscope (100 MHz). The laser energy was determined with the IMO-2N calorimeter, KTP-2 microcalorimeter, and the ED100-A-uv pyroelectric detector (Gentec).

Determination of two-photon absorption cross section

To determine the TPA cross section of the studied dyes, we used the fluorescent method of two-quantum standard which is based on the comparison of the intensity of two-photon excited fluorescence (TPEF) of a standard, having the known TPA cross section, with that of a studied object under identical conditions of excitation and TPEF recording.²⁹ The TPA cross section in this case is determined as

$$\delta_x = \frac{\delta_{st} \eta_{st} C_{st} I_x^{TPEF}}{\eta_x C_x I_{st}^{TPEF}}, \quad (1)$$

where δ_{st} is the TPA cross section of the standard; η_{st} , η_x are the quantum yields of fluorescence of the standard and the studied object, respectively; C_{st} , C_x are the concentrations of the standard and the studied substance, respectively; I_{st}^{TPEF} , I_x^{TPEF} are the TPEF intensities of the standard and the studied substance, respectively.

As a standard, we used the ethanol solution of the well-known laser dye Rhodamine 6G.^{30,31} Concentrations of solutions and solid-state polymer samples with the dyes under study and the standard were $2 \cdot 10^{-5} - 2 \cdot 10^{-4}$ M. The pump laser radiation was focused by a long-focus lens ($F = 350$ mm). The cell with the studied solution or a solid-state sample

with an optical path length of 10 mm was placed in the path of the convergent beam at a distance of 300–320 mm from the lens. The scheme of recording of spectra and TPEF intensity is shown in Fig. 2*a*.

To determine correctly the TPA cross section by this method, the particular attention was paid to observance of the square dependence of the TPEF intensity on the excitation intensity in order to avoid the influence of other nonlinear processes on the measured cross section.³² The most measurements of the TPA cross sections were carried out at the excitation power not exceeding 50 MW/cm².

Investigation of nonlinear transmission

Nonlinear transmission of the dyes was studied on the same setup as the TPEF. The dye concentration in this case was $2 \cdot 10^{-2}$ M, and the optical path length in the cell was 20 mm. The area of the beam cross section at the sample length varied by no more than 10%. The intensity of the exciting radiation was changed with the use of calibrated neutral filters.

Using the method of direct nonlinear transmission (NLT method), it is possible to determine the two-photon absorption cross section from the dependence of transmission on the exciting radiation intensity.¹⁷ On the assumption that the change in transmission of the studied medium is caused only by the two-photon absorption, the TPA cross section can be determined as

$$\delta = \frac{h\nu\beta}{CN_A}, \quad (2)$$

where $h\nu$ is the energy of a quantum of the exciting radiation; C is the molar concentration of the studied dye; N_A is the Avogadro number; β is the two-photon absorption coefficient related to nonlinear transmission as¹⁷:

$$T(I_0) = \frac{I(L)}{I_0} = \frac{\ln(1 + I_0 L \beta)}{I_0 L \beta}, \quad (3)$$

where I_0 is the exciting radiation intensity, L is the effective length of the medium (in the case of absent linear absorption, the optical path length in the medium).

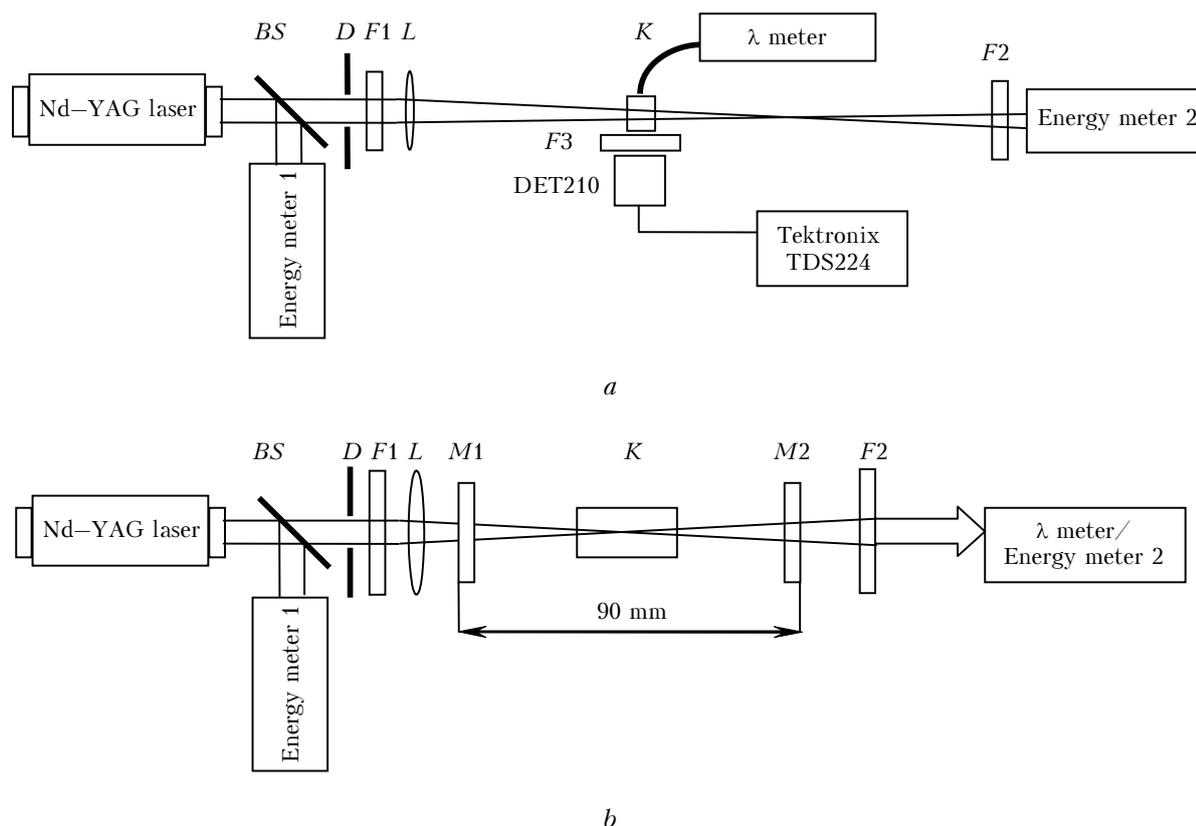


Fig. 2. Block diagrams of experimental setups for investigation of spectra, TPEF intensity, nonlinear transmission (*a*), and lasing characteristics (*b*) of organic dyes under two-photon excitation: beam splitter *BS*; diaphragm *D*; calibrated neutral filters *F1* for attenuation of radiation with a wavelength of 1064 nm; selective filters *F2* and *F3* cutting off radiation with a wavelength of 1064 nm; spherical lens *L* with $F = 120$ mm (*a*) and 350 mm (*b*); totally reflecting mirror *M1* with $R = 99\%$ for wavelengths of 600–700 nm and $T = 98\%$ for a wavelength of 1064 nm, exit mirror *M2* with $R = 70\%$ for wavelength of 600–700 nm and $T = 90\%$ for a wavelength of 1064 nm; Energy meters 1, 2 are ED100A-uv pyroelectric energy meters; λ -meter is a spectrometer with fiber input; DET210 are fast PIN photodiodes; TDS224 is the oscilloscope.

Investigation of lasing characteristics at two-photon excitation

Since the TPA cross section even at power densities of tens MW/cm² is much lower as compared to linear absorption of organic dyes, the main problem in obtaining stimulated radiation at two-photon excitation is to achieve population inversion and the necessary gain.³³ Toward this end, high excitation power densities, a longitudinal pumping scheme, a higher-Q cavity, and high dye concentrations (compared to one-photon excitation) are commonly used.³⁴

The lasing under two-photon excitation was studied at longitudinal excitation in two versions:

1. In the absence of the cavity. A 10-mm cell with the dye solution under study was placed at the lens focus $F = 45$ mm. In one case, the cell sides were slant relative to the optical axis to prevent the positive feedback. Then the single-pass gain scheme (superluminescence) was realized. In another case, the cell with the active medium was located strictly normally to the cavity axis and the cell side (reflection of about 4%), thus providing the feedback.

2. In the presence of the cavity, formed by two plane-parallel dichroic mirrors. The scheme for investigation of lasing in a cavity under two-photon excitation is shown in Fig. 2*b*. The similar scheme was used in Refs. 34 and 35. The pump laser radiation was focused by a spherical lens with $F = 120$ mm, and the cell was filled with the active medium. The dye concentration was $2 \cdot 10^{-2}$ M, and the lengths of the cell with the active medium were 10, 20, and 50 mm.

The pumping was carried out through the mirror $M1$ (98% transmission at a pump wavelength of 1064 nm and 99% reflection in the lasing range of the studied dyes (600–700 nm)). The cavity length was determined by the optical resistance of the dielectric coating mirrors and was equal to 90 mm (the decrease in the cavity base length by installing mirrors closer to the focal plane of the focusing lens resulted in the coating damage). The pump radiation, passed through the medium and the cavity mirrors, was filtered by the selective filter $F2$. The cavity was aligned with the aid of a He–Ne laser.

Results and discussion

TPA cross section

The TPA cross sections of the studied dyes measured by the method of standard are summarized in Table 1. For dyes **1–3**, as the polarity of the solvent (ethylacetate – MP) increases, a significant increase in the TPA cross section is observed, which can be explained by the bathochromic shift of the dye absorption bands and, correspondingly, by more efficient excitation of the dyes, since the doubled frequency of the first harmonic of the Nd–YAG laser

falls on the long-wavelength edge of the absorption band.

Table 1. Spectral-luminescent properties and TPA cross sections of the molecules under study

Dye	Matrix/solvent	λ_{abs} , nm	λ_{fl} , nm	ϕ_{fl}^*	δ , GM
1 (DCM)	ethylacetate	452	585	0.45	3 ± 1
	PMMA	458	575	0.74	7 ± 1
	PMMA:MP(9:1)	466	594	0.95	9.1 ± 1.2
	MP	478	630	0.87	12 ± 1.5 (1500)**
2	ethylacetate	476	595	0.56	8 ± 2
	PMMA	476	590	0.78	18 ± 2
	MP	494	630	0.95	20 ± 3 (5400)**
3	ethylacetate	454	585	0.45	3 ± 1
	PMMA	462	575	0.76	7.4 ± 1.1
	PMMA:MP(9:1)	470	594	0.97	9.5 ± 1.5
	MP	480	630	0.87	15 ± 2 (2300)**
4	ethylacetate	478	630	0.41	8.0 ± 1.5
	PMMA	482	600	0.82	21 ± 3
	PMMA:MP(9:1)	485	630	0.87	14 ± 2
	MP	500	700	0.02	10 ± 5 (700)**

* Measured relative to Rhodamine 6G and Rhodamine S; error in determination of the quantum yield of fluorescence is 10%.

** Measured by the NLT method

For dye **4**, such an increase is not observed: the TPA cross section in ethylacetate and MP are close. This may be connected with a significant drop of the dye **4** emittance in polar solvents. Possible causes for such a drop in the quantum yield of fluorescence for some (dicyanomethylene)-pyran substitutes have been discussed in Refs. 36 and 37.

All the studied dyes have a rather high TPA cross section in the polymer matrix (PMMA) as compared to the ethylacetate, which in its structure and properties is close to MMA. The linear spectral-luminescent characteristics of dyes **1–4** in these media are close. The determined TPA cross section of dye **1** in MMA before polymerization is 3 GM, which corresponds to the data in ethylacetate (see Table 1). The increase in the TPA cross section of the studied dyes in PMMA can be connected with a change in the properties of the dyes in rigid (as compared to solution) matrix, with existence of dye conformers³⁸ with the different TPA cross sections in PMMA, or with the effective participation of the polymer matrix vibrational states in the process of two-photon absorption.³⁹

Note that as (dicyanomethylene)-pyrans are excited by shorter-wavelength radiation (~ 800 nm), the TPA cross section, measured by the fluorescent method, increases, depending on the structure, by more than an order of magnitude and ranges from several hundreds GM for nonsymmetrically substituted (dicyanomethylene)-pyrans^{25,37,40} to several thousands for symmetric substitutes.²⁵

In addition to measurements by the two-quantum standard method, the TPA cross section for

dyes **1–4** in MP was determined by the NLT method from transmission curves as functions of the pump power density by the above described technique [Eq. (2)]. The results of measurement of the TPA cross section have shown that the experimental TPA cross sections obtained for the same objects differ by more than an order of magnitude. Thus, if the TPA cross sections measured by the fluorescent method are equal to 10–20 GM, then the corresponding TPA cross sections of the same dyes determined by the NLT method are equal to 700–5400 GM (see Table 1). The similar results were obtained by us earlier for (dicyanomethylene)-pyrans excited by the femtosecond 790 nm radiation: the TPA cross section determined by the fluorescent method of standard was more than an order of magnitude smaller than that obtained by the *z*-scanning method.⁴⁰

The difference in the TPA cross sections determined by different methods is characteristic not only for (dicyanomethylene)-pyrans. The same method can give both overestimated and underestimated values of the TPA cross section for different dyes and different exciting radiation parameters. Therefore, direct methods based on immediate measurement of absorption (transmission) should be used with caution.

The main reason for different experimental values of the TPA cross section is that different nonlinear processes (absorption from excited states, fluorescence quenching in the strong light field, stimulated emission at a pump wavelength, nonlinear absorption of a solvent, etc) can simultaneously take place in a medium under high-power laser excitation, and these processes exert different influence on results of TPA cross section measurements by different methods.

The results of measurements can also depend on the fact that it is not always possible to repeat identical experimental conditions for different measurement methods. For example, concentrations *C* of molecules in the studied media vary from 10^{-5} – 10^{-4} M at fluorescent methods to $5 \cdot 10^{-2}$ M at direct measurement methods. The difference in the concentrations is connected with the different sensitivity of methods. The high concentration of molecules in the medium can lead, for example, to formation of complexes and aggregates having quite different nonlinear properties as compared to a single molecule.

Despite the existent problem, only few papers, devoted to the comparison and analysis of measurements of the TPA cross sections by different methods, are available.^{41,42} On the one hand, this is connected with experimental difficulties arising in such measurements, because they require not only up-to-date instrumentation, but also the selection of close excitation conditions and parameters of the active medium, which can not be achieved successfully for all organic compounds. On the other hand, to obtain the actual values of the TPA cross section of a molecule, it is often necessary to develop the corresponding theoretical model describing the whole set of photoprocesses proceeding in the

medium under the high-power laser excitation and contributing to the measured parameters.

When (dicyanomethylene)-pyrans are excited by the first harmonic radiation of the Nd–YAG laser, the high TPA cross sections obtained by the NLT method are likely caused by absorption from excited states. It has been shown experimentally that intense singlet–singlet^{43,44} and triplet–triplet absorption⁴³ is observed in the DCM molecule, and $S_1 \rightarrow S_n$ absorption has a narrow peak in the spectral range 460–480 nm and overlaps the spectrum of $S_0 \rightarrow S_1$ absorption.⁴⁴ In the red spectral range, $S_1 \rightarrow S_n$ absorption does not show itself.⁴³ Triplet–triplet absorption is observed nearly in the whole visible region (one peak lies near 520 nm), and its intensity increases in the near-IR region. At a wavelength of 790 nm, the molar extinction coefficient of $T_1 \rightarrow T_n$ absorption of DCM in methanol is about $20000 \text{ L} \cdot \text{M}^{-1} \cdot \text{cm}^{-1}$ at a triplet quantum yield of $\sim 3 \cdot 10^{-3}$ [Ref. 43].

Thus, at the femtosecond excitation by pulses with a wavelength of 790 nm and a pulse repetition frequency of 80 MHz, which was used by us for substituted (dicyanomethylene)-pyrans in Ref. 40, not only TPA, but also $T_1 \rightarrow T_n$ absorption should contribute significantly to the total nonlinear absorption of the medium. At a megahertz repetition frequency of pump pulses, when the interval between pulses is only a few nanoseconds, molecules have not enough time to relax from the T_1 state and, therefore, they are additionally accumulated in triplets until the establishment of quasistationary equilibrium.

The results of experimental investigation of the induced absorption⁴⁰ and quantum-chemical calculations³⁶ demonstrate that intense induced absorption at a wavelength of 1064 nm is possible in (dicyanomethylene)-pyrans as well. This is also supported by our tentative investigations of nonlinear absorption of dyes **1–4** in MP at a nanosecond pulsed flash-photolysis setup.⁴⁵ The solution was excited by the Nd–YAG laser second harmonic (532 nm), while the attenuated first harmonic of the same laser (1064 nm) served as a probing signal.

Thus, we can state that when the TPA cross section of (dicyanomethylene)-pyrans is measured in the near-IR region, the direct methods (NLT and *z*-scanning) overestimate the results due to the significant influence of the induced triplet–triplet absorption. Note that the triplet–triplet absorption almost does not affect the results of measurement of the TPA cross section by the fluorescent methods, because the fraction of excited molecules at the used power densities does not exceed fractions of percent, and the triplet yield is low. In the future, we plan to estimate numerically the intensity of the induced absorption at a wavelength of the Nd–YAG (1064 nm) and Ti:Sapphire (790 nm) lasers and its influence on the total nonlinear absorption of (dicyanomethylene)-pyrans under the IR excitation.

In addition to the induced triplet–triplet absorption for molecule **2**, aggregation of molecules

at high concentrations used in experiments can exert an additional influence on results of measurements of the TPA cross section by the NLT method, which is confirmed indirectly by a significant decrease in emittance of the concentrated dye solution **2** as compared to **1** and **3** [Ref. 46].

Lasing characteristics

To study the stimulated emission under two-photon excitation, we have selected three dyes (**1–3**) with the best emission characteristics in MP. Dye **4** in MP fluoresces very weakly ($\phi_{fl} = 0.02$), and, therefore, the lasing threshold for this molecule cannot be achieved at the two-photon excitation. The concentration of dye molecules in a solution was $2 \cdot 10^{-2}$ M when studying the lasing properties. The results are summarized in Table 2 and Fig. 3.

Table 2. TPPL characteristics of (dicyanomethylene)-pyrans

Compound	L , cm	λ_{las} , nm	$\Delta\lambda_{las}$, nm	E_{thr} , mJ	efficiency _{las} , %
1 (DCM)	1*	645*	31*	Not achieved	—
	1	648	6	4.6	0.39
	2	652	6	2.7	0.69
	5	660	6	2.7	1.00
2	1*	657*	2*	17.6*	0.04*
	1	658	5	3.8	0.27
	2	663	5	2.7	0.25
3	1*	649*	4*	17.6*	0.05*
	1	650	6	3.8	0.47
	2	651	6	2.4	0.72
	5	658	6	2.7	0.97

* Scheme without cavity.

The excitation of the selected dyes in the noncavity scheme (cell length of 10 mm) has shown that if the positive feedback is absent, then the stimulated emission is virtually not formed. Only insignificant narrowing of the dye fluorescence band to 45–50 nm was observed. If the cell was aligned with the aid of the He–Ne laser for its front face to be perpendicular to the optical axis of the pump radiation (in this case, the cell sides served as mirrors of a low-Q cavity with a reflection coefficient of $\sim 4\%$), then we observed an additional narrowing of the emission line for two of the studied dyes (**2** and **3**) to 2–4 nm and the appearance of radiation, directed along the optical axis.

The superluminescence wavelength was 645–649 nm for dyes **1** and **3** and 657 nm for dye **2**. The efficiency of conversion (only radiation in the forward direction was recorded^[32]) in the noncavity scheme was as low as 0.04–0.05% (see Table 2).

Then the stimulated emission under two-photon excitation was studied with the use of a two-mirror plane-parallel cavity. The lasing wavelength λ_{las} of the active medium in the cavity was several nanometers longer than that in the free-of-cavity scheme. The

spectral width of the lasing line $\Delta\lambda_{las}$ was 5–6 nm. The lasing threshold E_{thr} at the length of the active medium $L = 10$ mm was 3.8–4.6 mJ depending on the dye. As L increased up to 20 mm, the threshold decreased down to 2.4–2.7 mJ. The further increase of the active medium length did not lead to the decrease of the lasing threshold.

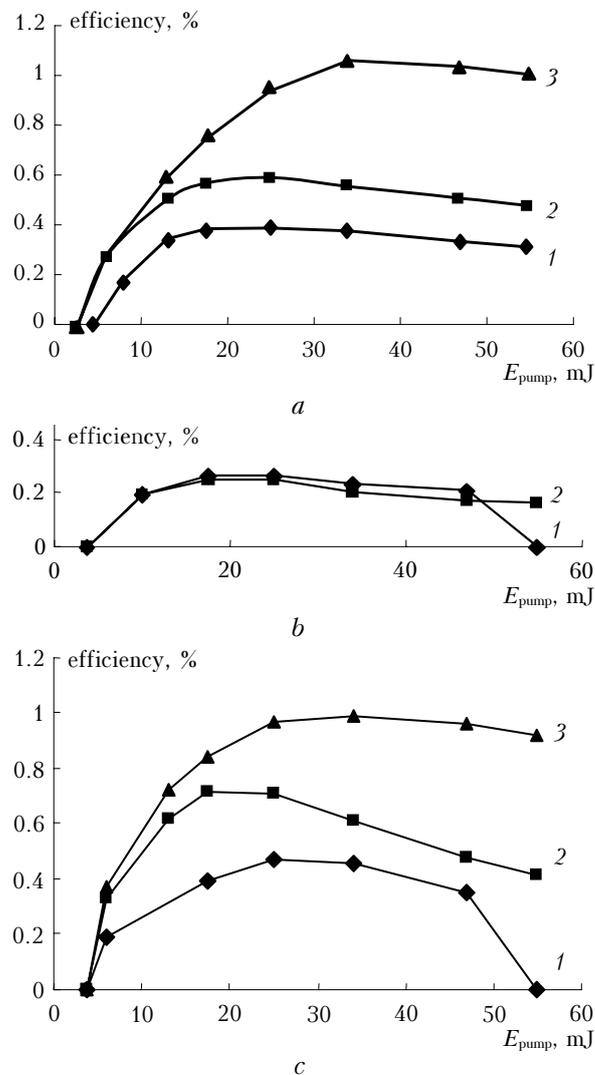


Fig. 3. TPPL efficiency of solutions of (dicyanomethylene)-pyrans **1** (a), **2** (b), and **3** (c) in MP ($C = 2 \cdot 10^{-2}$ M) as a function of the exciting pulse energy; the length of the active medium $l = 10$ (1), 20 (2), and 50 mm (3).

Figure 3 shows the lasing efficiency as a function of the pump energy for dyes **1–3** at different lengths of the active medium. Depending on the dye and lasing wavelength of the active medium, the maximal lasing efficiency was achieved at the energy of the pump pulse ranging within 18–35 mJ. At a further increase of the pump energy, we observed the decrease in the lasing efficiency and even suppression of lasing for dyes **2** and **3** at a 10 mm length of the active medium. This was likely connected with radiation defocusing in a medium at high-power

excitation and formation of a lens leading to the break of the medium optical homogeneity and, as a consequence, to suppression of lasing. For dye **2**, the situation was aggravated by the drop in emittance at a high concentration,⁴⁵ while the absorption of the medium with this dye was the highest among all media under study (see Fig. 3). Therefore, for dye **2**, despite the highest value of the TPA cross section among all studied molecules (20 GM; see Table 1), the lowest efficiency was obtained (only 0.3%), whereas for dyes **1** and **3** the efficiency achieved 1%.

Optical limiting

Figure 4 shows the transmission of solutions of the studied dyes as a function of the power density of the pump radiation (relative to the cell with the solvent MP). It is seen that at the low-intensity (linear) excitation the solutions are transparent, at higher densities the transmission decreases, and at a power density of 400 MW/cm² the transmission decreases down to 90% for dye **4** and to 36% for dye **2**.

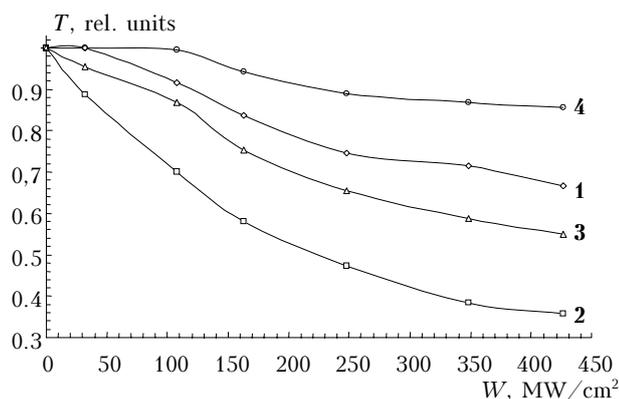


Fig. 4. Transmission of solutions of studied dyes 1–4 in MP ($C = 2 \cdot 10^{-2}$ M) as a function of the power density of the pump radiation.

If to estimate the nonlinear absorption in the studied media, caused by only two-photon transitions by Eqs. (2) and (3) using the TPA cross sections obtained by the fluorescent method, then even at a pump power density of 400 MW/cm² its value is much smaller than 1%. It has been shown above that the intense triplet–triplet absorption exists in the studied dyes in the near-IR region. Thus, two mechanisms take part in the process of limiting of optical power of the pump radiation:

1. Primary mechanism, i.e., two-photon absorption, which creates some population of the excited state.

2. Secondary mechanism, i.e., absorption from excited states (triplet–triplet absorption), whose probability at the used pump power densities many orders of magnitude exceeds that of two-photon absorption from the ground state.

The experimental results obtained allow the conclusion that dye **2** is promising for creation of

multicomponent limiters of laser radiation power as an active medium in combination, for example, with a dye operating only by the mechanism of reversible saturated absorption, for example, in the channel of singlet states.

Conclusions

As a result of investigation of nonlinear optical properties of four (dicyanomethylene)-pyran substitutes under the excitation by the Nd–YAG laser radiation (1064 nm) of nanosecond duration, the following results have been obtained:

1. The TPA cross section in solutions and polymer matrices is obtained by the fluorescent method of two-quantum standard. It is found that the TPA cross section of (dicyanomethylene)-pyrans in polymer matrices increases, and possible causes for this increase are discussed.

2. The TPA cross sections obtained by the fluorescent and NLT methods were compared. It is shown that the TPA cross sections of (dicyanomethylene)-pyran substitutes are strongly affected by the induced absorption in the channel of triplet states, due to which the cross sections are overestimated. The analysis of our experimental data and the literature data suggests that for the correct determination of the TPA cross section, depending on peculiarities of photoprocesses in the molecule under high-power laser excitation, the methods for determination of TPA cross sections and the corresponding mathematical model should be specially selected. For different molecular classes and excitation conditions, the ignoring of the above peculiarities is possible to result in both underestimated and overestimated values of the TPA cross sections.

3. The characteristics of stimulated emission of (dicyanomethylene)-pyran solutions under two-photon excitation in the mode of superfluorescence and lasing in a two-mirror cavity are studied. The excitation and lasing conditions are optimized. The efficiency of conversion at the nanosecond excitation up to 1% of the pump energy was achieved.

4. Nonlinear absorption of Nd–YAG laser radiation by concentrated solutions of (dicyanomethylene)-pyrans has been investigated. Two mechanisms take part in attenuation of the laser power by the studied media: the primary mechanism – two-photon absorption, and the secondary mechanism – absorption in the channel of triplet states. Thus, materials having not only the high TPA cross sections, but also the intense induced absorption at a wavelength of the pump radiation can be promising limiters of the laser radiation intensity.

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