

PACS numbers: 42.70.Nq; 42.70.Jk
DOI: 10.1070/QE2003v033n11ABEH002532

Limitation of high-power optical radiation by organic molecules: I. Substituted pyranes and cyanine dyes

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Abstract. **Photophysical processes proceeding in polyatomic organic molecules (pyran derivatives and cyanines) excited by high-power laser radiation at 532 nm are studied. Some properties of their changes depending on the structure, solvent, and excitation conditions are determined. The effect of limitation of high-power exciting radiation by the organic molecules is found. The maximum limitation ($K_{max} = 15.0$ at the initial transmission equal to 70 %) was observed for the cyanine derivative and is comparable to this effect for fullerenes C_{60}, which are widely used as radiation limiters.**

Keywords: *organic molecules, nonlinear optical properties, high-power laser excitation, optical radiation limiters.*

1. Introduction

The study of nonlinear-optical properties of organic molecules is of obvious interest for obtaining new fundamental knowledge about photoprocesses proceeding in such molecules in high-power laser radiation fields and for fabricating new molecular materials for practical applications in lasers, organic photodiodes, optical amplifiers in telecommunication systems, etc. One of the important and promising applications of organic molecules is their use as optical radiation limiters.

The scope of organic molecules capable of limiting optical radiation is quite broad: these are first of all phthalocyanines and naphthalocyanines [1, 2], porphyrins [3–6], fullerenes [7, 8], biphenyles [9, 10], butadienes [11], indanthrones [12], stilbenes [13–15], and luminescing polymers [16, 17].

Materials based on organic molecules often combine successfully a high initial transparency and photophysical properties such as excited-state lifetimes, the relaxation rates of the electronic excitation (internal conversion and intersystem crossing), high excited-state absorption cross sections, which exceed at the excitation wavelength the ground-state absorption cross section, etc.

The mechanism of nonlinearity in organic molecules is most often related to inverse saturated absorption [18–22] or two-photon absorption of light [23, 24]. In the first case, a molecule has a stronger absorption from excited states (singlet or triplet states) than from the ground state, so that laser radiation is weakly absorbed in the region of the maximum sensitivity of photodetectors and a human eye. High-power irradiation produces a high concentration of molecules in the excited state, from which light is absorbed stronger than from the ground state. This results in a decrease in transmission (transparency), i.e., darkening. This mechanism takes place in phthalocyanines and naphthalocyanines, porphyrins, and some other organic molecules. The best results on the limitation of the laser pulse energy were obtained for indium, tin, and lead phthalocyanines. These molecules excited to the singlet state undergo a rapid transition to the triplet state, and for nanosecond pulses the darkening occurs due to triplet–triplet absorption. Upon excitation by picosecond pulses, the transition to the triplet state has no time to occur, and darkening is caused by induced absorption between singlet states.

An obvious advantage of two-photon absorption is the possibility of its realisation in a transparent medium. This mechanism is especially efficient upon excitation by picosecond and femtosecond pulses and it takes place in stilbene derivatives, polyphenyles, butadienes, organic luminescing polymers in solutions (for example, PPV in chloroform), etc. Recently, new multifunctional materials based on organic molecules were created [25].

Although many organic molecules have been already studied as possible materials for optical limiters, and organic chemistry has a great potential for the synthesis of molecules with prescribed properties for fabricating organic materials, further progress in this field requires the use of a complex approach combining the theoretical and experimental studies of photoprocesses proceeding in polyatomic organic molecules.

The quantum-chemical study of series of molecules with a similar structure will allow us to determine the dependence of photoprocesses proceeding in these molecules on their structure, to find the molecular structures that are promising for some or other applications, and to give recommendations for the purposeful synthesis of molecules with

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Received 18 December 2002; revision received 21 April 2003
Kvantovaya Elektronika **33** (11) 967–974 (2003)
Translated by M.N. Sapozhnikov

prescribed properties. The experimental study of photoprocesses in synthesised molecules makes it possible to find the optimal conditions for their use in devices being developed. The fruitfulness of such an approach has been demonstrated in Ref. [26], however, not all of its possibilities were used so far.

In this paper, we performed the combined theoretical and experimental study of photoprocesses in substituted pyranes and cyanine dyes. The structural formulas of these molecules are presented in Fig. 1.

2. Investigation methods

2.1 Quantum-chemical calculation

We performed quantum-chemical calculations of molecules by a standard method of incomplete neglect of differential overlap with spectroscopic parametrisation that is especially oriented to obtain correctly the excited electronic energy level diagram [27]. This method gives information on the energies of electronic states of organic molecules corresponding to the maxima of absorption or luminescence, the oscillator strengths of electronic transitions corresponding to spectral intensities, the polarisation of electronic transitions, as well as on the coefficients of expansion of the wave functions over configurations and of molecular orbitals over atomic orbitals, which characterise the nature of excited electronic states and permit the calculation of various intramolecular interactions (for example, spin–orbit interaction).

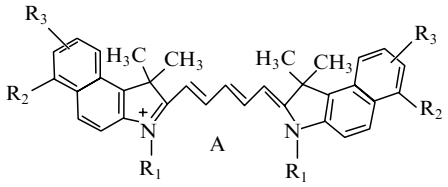
The method for numerical estimates of the relaxation rates of excited electronic states developed in Refs [28, 29] and realised in our papers was used to determine the properties of photophysical processes proceeding in polyatomic organic molecules of different classes [30–34]. For example, the rate constants of radiative decay (k_r) and singlet–triplet conversion (k_{st}) were estimated for many benzoxazoles and their $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_m$ absorption spectra were calculated. These calculations made it possible to establish the principles for obtaining lasing in benzoxazoles and to determine the influence of their molecular structure on lasing parameters [30].

2.2 Calculation of transmission of exciting radiation

We calculated transmission using the generalised energy level diagram of an organic molecule (Fig. 2).

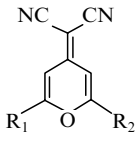
Laser radiation is absorbed by dye molecules in the S_0 state with the absorption cross section $\sigma_{01}(\sigma_{0n})$ and the molecules undergo a transition to the $S_1(S_n)$ state. Then, the molecules relax during the time $\sim 10^{-12}$ s to the lower vibrational level of the S_1 state. We took into account in the calculation the following processes upon transitions from the S_1 state: the reabsorption of exciting radiation with the cross section σ_{1n}, the $S_1 \rightarrow S_0$ radiative transition with the rate $1/\tau_{iz}$, and the $S_1 \rightarrow T_1$ intersystem crossing with the rate k_{st} followed by the $T_1 \rightarrow S_0$ relaxation with the rate $1/\tau_{ts}$ and the $T_1 \rightarrow T_n$ absorption with the cross section σ_{tt}.

The system of differential equations describing processes proceeding in molecules excited by laser radiation has the form



Molecule	A	R_1	R_2	R_3
1	$Na^{\oplus}$	C_4H_9	SO_3	–
2	$Et_3NH_4^{\ominus}$	C_4H_9	SO_3	–
3	$Bu_3NH_4^{\oplus}$	C_4H_9	SO_3	–
4	$3Na^{\oplus}$	C_4H_9	SO_3	SO_3
5, 5*	$ClO_4^{\ominus}$	C_4H_9	–	–
6	CH_3–C$_6$H$_4$–$SO_3^{\ominus}$	C_4H_9	–	–
7	$ClO_4^{\ominus}$	CH_3	–	–

a



Molecule	R_1	R_2
I	CH_3	CH=CH–(benzoquinolyl)
II	CH=CH–(benzoquinolyl)	CH=CH–(benzoquinolyl)
III	CH_3	CH=CH–C$_6$H$_4$–$N(CH_3)_2$
IV	CH=CH–C$_6$H$_4$–$N(CH_3)_2$	CH=CH–C$_6$H$_4$–$N(CH_3)_2$
V	CH_3	CH=CH–(morpholinyl)
VI	CH=CH–(morpholinyl)	CH=CH–(morpholinyl)
VII	CH_3	CH=CH–C$_6$H$_4$–$N(C_8H_{17})_2$
VIII	CH=CH–C$_6$H$_4$–$N(C_8H_{17})_2$	CH=CH–C$_6$H$_4$–$N(C_8H_{17})_2$

b

Figure 1. Structural formulas of cyanine dyes (a) and substituted pyranes (b) (denoted by Arabian and Roman numbers, respectively).

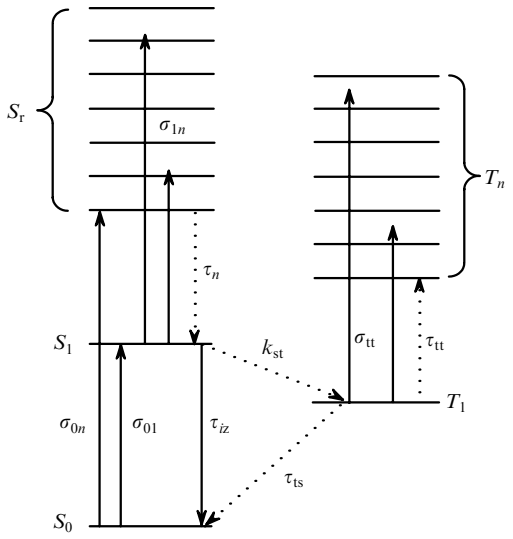


Figure 2. Generalised energy level diagram and electronic transitions in a polyatomic organic molecule.

$$\frac{dN_0}{dt} = -N_0\sigma_{01}I_p + \frac{N_1}{\tau_{iz}} + \frac{N_3}{\tau_{ts}},$$

$$\frac{dN_1}{dt} = N_0\sigma_{01}I_p - N_1\sigma_{1n}I_p + \frac{N_2}{\tau_n} - \frac{N_1}{\tau_{iz}} - N_1k_{st},$$

$$\frac{dN_2}{dt} = N_1\sigma_{1n}I_p - \frac{N_2}{\tau_n}, \qquad (1)$$

$$\frac{dN_3}{dt} = N_1k_{st} + \frac{N_4}{\tau_{tt}} - N_3\sigma_{tt}I_p - \frac{N_3}{\tau_{ts}},$$

$$\frac{dN_4}{dt} = N_3\sigma_{tt}I_p - \frac{N_4}{\tau_{tt}},$$

where N_0, N_1, N_2, N_3, and N_4 are the relative populations of the S_0, S_1, S_n, T_1, and T_2 levels; τ_n, τ_{iz}, τ_{tt}, and τ_{ts} are the lifetimes of the S_2, S_1, T_2, and T_1; σ_{01}, σ_{1n}, and σ_{tt} are the absorption cross sections for the $S_0 \rightarrow S_1$, $S_1 \rightarrow S_n$, and $T_1 \rightarrow T_2$ transitions; k_{st} is the rate of intersystem crossing; and I_p is the incident radiation intensity.

We solved system of equations (1) by the Runge–Kutta method of the fourth degree with respect to the energy level population and then calculated the transmission of laser radiation by a dye.

2.3 Experimental methods

We studied spectral and luminescent properties of molecules using standard methods and equipment (Specord M40 spectrophotometer and Hitachi 850 spectrofluorimeter).

Stimulated emission spectra and laser-induced fluorescence spectra were studied using a setup described in detail in Ref. [35]. Fluorescence was excited by excimer XeCl lasers with different parameters of the exciting pulse (the pulse energy was $E_p = 10 - 500$ mJ, the pulse duration was $\tau = 10 - 50$ ns, and the pulse repetition rate was $f_0 = 1 - 5$ Hz). Laser-induced fluorescence spectra and stimulated emission spectra were recorded per pulse with a Real spectrometer. The time characteristics of the emission were recorded with a Tektronix TDS224 oscilloscope.

We studied the photostability $\gamma = N_{fot}/N^*$, of the molecules, where N^* is the number of phototransformed molecules, which was estimated by a change in the optical density in the long-wavelength absorption band).

We studied induced triplet–triplet absorption using a setup for laser flash photolysis, which is described in Ref. [36]. Excitation was performed by a high-power XeCl laser ($E_p = 500$ mJ, $\tau = 40$ ns, $f_0 = 0.5$ Hz). Absorption was probed by radiation from a laser spark in xenon having a continuous spectrum in the visible region. Absorption spectra were recorded with a DFS-452 spectrograph equipped with a broadband photomultiplier and a Tektronix TDS224 oscilloscope and computer-processed.

We studied the nonlinear-optical properties of the molecules by investigating the dependence of the transmission of their solutions on the exciting radiation power density. Excitation was performed by a XeCl excimer laser at 308 nm ($\tau_{1/2} = 15$ ns, $E_p = 50$ mJ) and a single-mode doubled frequency Nd : YAG laser at 532 nm ($\tau_1/2 = 6$ ns, $E_p = 20$ mJ). The excitation schemes are shown in Fig. 3.

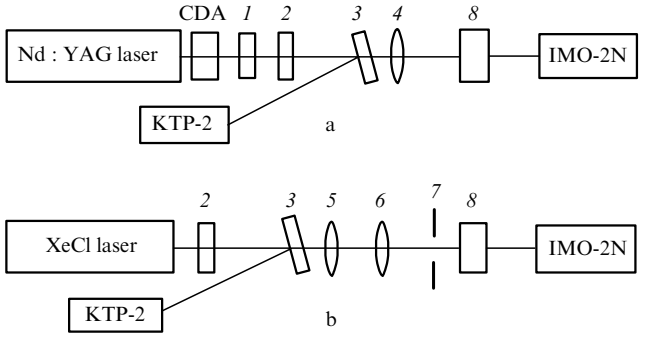


Figure 3. Schemes of experimental setups for studying the nonlinear absorption of solutions of organic molecules excited by a Nd:YAG (a) and XeCl (b) lasers: (*1*) optical filter rejecting the fundamental 1064-nm harmonic of a Nd : YAG laser; (*2*) neutral optical filters; (*3*) beam-splitter; (*4*) spherical lens with $F = 200$ mm; (*5, 6*) cylindrical lenses; (*7*) 1-mm aperture; (*8*) cell with a solution; (CDA) SHG (532 nm) nonlinear crystal; (KTP-2 and IMO-2N) calorimeters for measuring laser radiation power.

An exciting beam was focused by long-focus lenses (two crossed cylindrical lenses with $F_5 = 500$ mm and $F_6 = -250$ mm upon excitation by a XeCl laser and a spherical lens with $F = 200$ mm upon excitation by a Nd : YAG laser) to the centre of quartz cell (*8*) with a solution under study. The 5-mm thick cell (*8*) was placed in a converging laser beam of diameter 1 mm, which changed no more than by 10 % over the cell length (the beam cross section was ~ 0.8 mm^2). To improve the homogeneity of the incident radiation, the laser beam was diaphragmed, and its transverse profile was bell-shaped. The initial transmission of the molecular solutions was 70 %.

The exciting radiation power density was varied from 2–5 to 250–400 MW cm^{-2} using neutral optical filters. Upon UV excitation, we took into account the possible change in the transmission of a solution in high-power light fields. The emission energy was measured with an IMO-2H calorimeter and a KTP-2 microcalorimeter. The error of transmission measurements did not exceed 10 %.

The nonlinear absorption of molecules was determined from the attenuation coefficient $K_1 = T_0/T_W$, where T_0 is

Table 1. Spectral, luminescent, and lasing properties of substituted pyranes.

Molecule	λ_{abs}/nm			λ_{fl}/nm			$\Delta\lambda$/nm			η			λ_{las}/nm			Lasing efficiency (%)		
	Ethanol	DMSO	Ethyl acetate	Ethanol	DMSO	Ethyl acetate	Ethanol	DMSO	Ethyl acetate	Ethanol	DMSO	Ethyl acetate	Ethanol	DMSO	Ethyl acetate	Ethanol	DMSO	Ethyl acetate
I	512	515	490	649	667	600	74	83	100	0.12	0.12	0.10	675	694	635	0.5	10	19
II	512	515	500	646	667	600	85	108	101	0.10	0.10	0.10	675	693	638	1.0	16	15
III	472	476	455	618	636	580	82	85	83	0.50	0.50	0.50	631	655	604	18	19	17
IV	485	487	476	620	650	624	85	99	100	0.10	0.01	0.10	–	745	666 672	–	0.5	7.6
V	440	455	435	615	634	585	75	95	84	0.50	0.60	0.40	635	657	607	10	10	5.2
VI	454	472	453	617	650	624	86	95	102	0.04	0.01	0.10	–	748	673 679	–	1.2	6.3
VII	490	492	476	620	636	585	81	88	80	0.60	0.60	0.50	635	656	606	24	6.0	19
VIII	495	500	490	650	660	625	115	88	93	0.04	0.01	0.20	–	–	657	–	–	10

Note: λ_{abs} and λ_{fl} are the wavelengths of the absorption and fluorescence maxima, respectively; $\Delta\lambda$ is the absorption band shift; η is the quantum yield of fluorescence; λ_{las} is the lasing wavelength.

the initial transmission of the solution and T_W is the transmission of the solution for the exciting radiation power density equal to W. We used in our calculations the value of K_1 at $W = 100$ MW cm^{-2} and the maximum attenuation K_{max} for the solution under study.

3. Results and discussion

3.1 Substituted pyranes

The spectral, luminescent, and lasing properties of substituted pyranes are presented in Table 1. We studied solutions of pyranes in ethanol, dimethyl sulfoxide (DMSO), and ethyl acetate (the latter is of interest for studying the possibility of doping solid matrices with substituted pyranes).

One can see from Table 1 that the absorption of substituted pyranes depends on their structure. The absorption bands of the bis-structures are shifted to the red by 10–15 nm; however, in ethyl acetate, their absorption bands are shifted to the blue. The fluorescence spectra of substituted pyranes exhibit a large Stokes shift, up to 150 nm (4000–6000 cm^{-1}), indicating to a strong change in the geometry of molecules in the excited state.

The quantum yield of fluorescence decreases in passing to bis-structures (for example, from 0.50 down to 0.04 in passing from DCM morpholine to bis-DCM morpholine in ethanol).

The quantum-chemical calculations of substituted pyranes agree with the experimental data that we obtained (Fig. 4). For example, the maximum of the long-wavelength absorption band of DCM morpholine in ethanol and ethyl acetate is observed at 440 and 434 nm, respectively, while its calculated value is 441 nm. The maximum of the fluorescence band in toluene is observed at 540 nm, while the calculated maximum lies at 530 nm. Figure 5 shows the energy level diagrams of DCM morpholine and bis-DCM morpholine (fluorescing from the S_1 state). We estimated the rate constants of photophysical processes proceeding in these molecules and found that the rate of the radiative transition from the S_1 state for DCM morpholine was $k_r = 1.61 \times 10^8$ s^{-1}, while the rate of the internal conversion was $k_{ic} = 2.39 \times 10^7$ s^{-1}. The energy level diagram changes in passing to the bis-structure. A new lower S_1 state appears, whose radiative decay rate is $k_r = 1.8 \times 10^7$ s^{-1} and the internal conversion rate increases to 2.77×10^8 s^{-1}, which probably causes a decrease in the quantum yield of fluorescence, in accordance with experimental data. The rate constant k_{st} of intersystem crossing for DCM morpholine and its bis-structure are 5.28×10^8 and 2.08×10^9 s^{-1}, respectively.

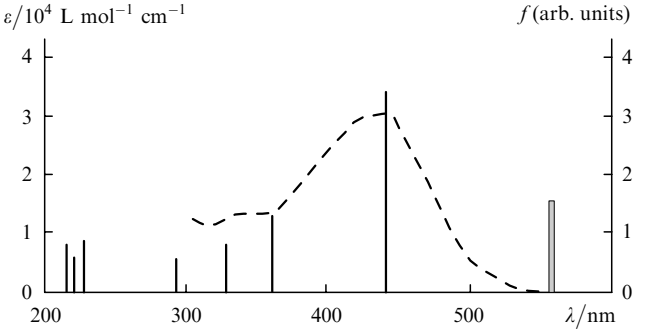


Figure 4. Absorption spectra and oscillator strengths for molecule V: the experimental absorption spectrum in ethyl acetate at room temperature (dashed curve) and its calculated maxima (vertical bars); the shaded vertical bar is absorption from the S_1 state.

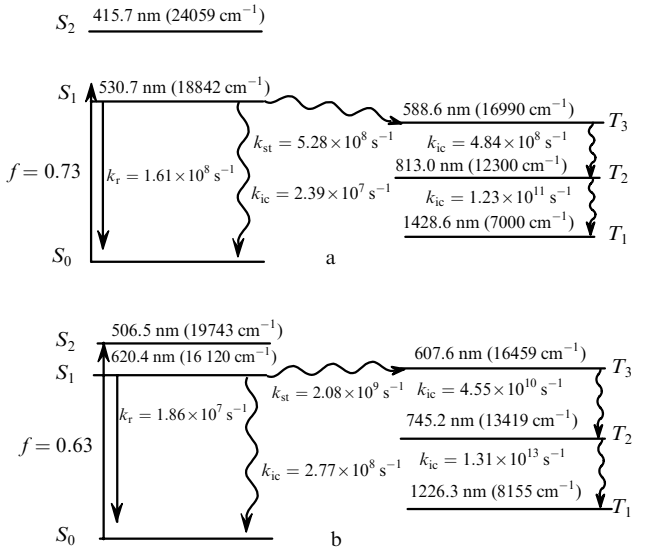


Figure 5. Energy level diagram for DCM morpholine (molecule V) (a) and bis-DCM morpholine (molecule VI) (b).

We studied the lasing properties of substituted pyranes in ethyl acetate and DMSO pumped by a XeCl laser or the second harmonic from a Nd : YAG laser. A transversely pumped plane–parallel resonator of length 1.5 cm was formed by a highly reflecting aluminium mirror and the wall of a cell containing the solution under study. The stimulated emission spectrum of the solution was detected per pulse.

Note that all the molecules studied produced lasing upon pump both at 308 and 532 nm. The lasing thresholds were $\sim 1-40$ MW cm^{-2}, and the lasing efficiency was $\sim 24\,\%$ upon pump at 308 nm (Table 1) and 45 % upon pump at 532 nm. The stimulated emission band of these molecules lies at 607 and 672 nm, respectively.

Note that we obtained lasing in bis-structures with the quantum yield of fluorescence as low as 0.1–0.01. Although lasing of organic molecules with such low quantum yields of fluorescence was earlier reported in the literature [37], these cases are very rare and their interpretation requires further studies.

Note that pyran derivatives have a high photostability: the quantum yield $0.1-0.01$ of photochemical transformations of DCM morpholine in DMCO excited at 532 nm was $(1.3\pm0.23)\times10^{-5}$ and $(1.2\pm0.3)\times10^{-3}$ upon excitation at 308 nm.

The nonlinear-optical properties of substituted pyranes are presented in Tables 2–4. Table 2 shows that DCM morpholine and bis-DCM morpholine have the best nonlinear-optical properties, both in ethanol and ethyl acetate. Figure 6 presents the dependences of the transmission of DCM morpholine and bis-DCM morpholine on the exciting radiation power density at 532 nm. The initial transmission T_0 of the solutions was 70 %. One can see that nonlinear absorption begins at power densities $W < 1$ MW cm^{-2}. The attenuation coefficient K_1 for $W = 100$ MW cm^{-2} achieved 4.0 for DCM morpholine in ethanol and 2.4 in ethyl acetate. The maximum attenuation coefficient K_{max} for the power density $200-400$ MW cm^{-2} was 6.5 and 4.0, respectively. For bis-DCM morpholine in ethanol and ethyl acetate, $K_1 = 4.2$ and 4.5, and $K_{max} = 6.3$ and 7.0, respectively.

Table 2. Nonlinear-optical properties of substituted pyranes ($T_0 = 70\,\%$, $\lambda_p = 532$ nm).

Molecule		$K_1(W = 100\,\mathrm{MW\,cm^{-2}})$		$K_{max}(W = 250\,\mathrm{MW\,cm^{-2}})$	
		Ethanol	Ethyl acetate	Ethanol	Ethyl acetate
I	DCM julolidine	0.95	1.0	0.9	1.0
II	Bis-DCM julolidine	0.95	1.3	0.9	1.4
III	CH-90	1.5	2.8	1.6	5.0
IV	Bis-CH-90	1.1	1.8	1.1	2.5
V	DCM morpholine	4.0	2.4	6.5	4.0
VI	Bis-DCM morpholine	4.2	4.5	6.3	7.0
VII	DCM-doa	1.1	1.6	1.1	2.2
VIII	Bis-DCM-doa	1.1	1.0	1.1	1.2

Tables 3 and 4 present the values of K_1 for these two molecules depending on the solvent and initial transmission. One can see that K_{max} for DCM morpholine increased up to 8.8 with decreasing T_0 down to 53 %.

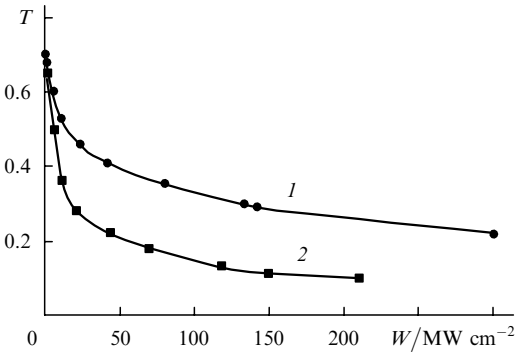


Figure 6. Dependences of the transmission T of substituted pyranes, bis-DCM morpholine (*1*) and DCM morpholine (*2*), in acetyl acetate on the 532-nm second-harmonic power density W.

Table 3. Effect of a solvent on the nonlinear-optical properties of DCM morpholine and bis-DCM morpholine.

Molecule		Ethyl acetate		Toluene		DMCO		Ethanol	
		K_1	K_{max}	K_1	K_{max}	K_1	K_{max}	K_1	K_{max}
V	DCM morpholine	2.2	3.5	1.3	2.6	3.0	4.4	4.0	6.5
VI	Bis-DCM morpholine	4.5	7.0	2.5	4.1	1.1	1.2	4.2	6.3

Table 4. Effect of the initial transmission on the nonlinear-optical properties of DCM morpholine.

Molecule		T_0(%)	K_1	K_{max}
V	DCM morpholine	85	1.7	1.8
		75	3.0	4.4
		53	5.3	8.8

We studied theoretically the dependence of the transmission of substituted pyranes on the exciting radiation power density by the method described above using the experimental results and quantum-chemical calculations. We found that good agreement between the theoretical and experimental dependences was observed in the case when molecules did not undergo rapid $S_1 - T_1$ transitions and, hence, the $T - T$ absorption was not observed, and also if the lifetime of the S_1 state was $\tau_{S_1} = 10^{-9}$ s and $\tau_{S_n} = 10^{-12}$ s, these values being somewhat smaller than those obtained in quantum-chemical calculations. In addition, good agreement between the theoretical and experimental dependences of the transmission of bis-DCM morpholine on the exciting radiation power density was achieved when the value of σ_{1n} was doubled compared to the calculated value. We considered above photophysical processes in molecules by neglecting their triplet states; however, the possible effect of these states on the nonlinear-optical properties of molecules requires further studies.

Therefore, the limitation of laser radiation by substituted pyranes is probably caused by inverse singlet–singlet absorption saturation.

3.2 Cyanine dyes

The second class of molecules studied in the paper is cyanine dyes (Fig. 1), which are known in the literature as cardiogreenes.

The nonlinear-optical properties of molecules of this class and the possibility of their use as radiation limiters

Table 5. Spectral, luminescent, and lasing properties of cyanine dyes.

Molecule	Ethanol							DMCO					
	λ_{abs}/nm	$\varepsilon/10^5$ L ×mol^{-1} cm^{-1}	λ_{fl}/nm	η	λ_{gen}/nm*	Efficiency (%)*	Efficiency (%)**	λ_{abs}/nm	$\varepsilon/10^5$ L ×mol^{-1} cm^{-1}	λ_{fl}/nm	λ_{gen}/nm*	Efficiency (%)*	Efficiency (%)**
1	685	1.0	761	0.19	783	3.4	1.6	692	1.5	735	794	5.6	3.5
2	685	2.1	756	–	787	3.8	2	–	–	–	–	–	–
3	680	2.1	770	0.17	790	3.7	–	694	1.3	742	799	0.1	–
4	–	–	712	0.22	–	–	–	694	1.4	731	795	1.0	<1
5	683	1.8	743	0.15	779	4.7	3.6	690	1.9	740	785	10	3.2
5*	683	2.0	753	0.17	781	7.5	3.7	678	2.2	740	787	11	4.4
6	680	2.1	760	0.16	777	7.5	3.6	678	1.9	735	785	11	4
7	678	1.2	727	0.14	773	7.3	1.6	682	2.3	736	780	11	3.5

*$\lambda_p = 308$ nm, **$\lambda_p = 532$ nm.

were studied in a number of papers, for example, in Ref. [38]. The authors of paper [38] showed that the ground-state absorption cross section of carbothiacyanine derivatives decreased with increasing the number of units in a bridge (from zero to three), whereas the excited-state absorption cross section increased. As a result, the ratio (σ_{ex}/σ_{gr}) of these cross sections increased from 0.3 to 5.29, which probably caused the limitation of laser radiation at 532 nm.

We studied the spectral, luminescent, and lasing properties of cyanine dyes in different solvents [water, ethanol, DMSO, and proylene glycol carbonate (PGC)]. The nonlinear-optical properties of the dyes were studied upon laser excitation at 532 nm. The results are presented in Tables 5 and 6 and in Figs 7 and 8.

Table 6. Nonlinear-optical properties of cyanine dyes ($T_0 = 70$ %).

Molecule	Ethanol		PGC	
	K_1	K_{max}	K_1	K_{max}
1	2.0	2.9	3.5	4.7
2	7.2	12	7.0	12
3	3.2	6.9	7.0	13
4	0.75	0.75	1.5	1.5
5	8.1	14	10	15
5*	7.7	14	7.6	12
6	7.2	13	7.0	12
7	7.0	11	5.5	8.0

Note: $W = 100$ MW cm^{-2} for K_1 and 400 MW cm^{-2} for K_{max}.

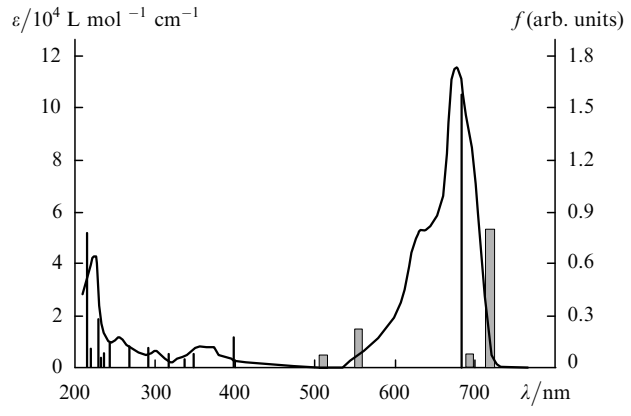


Figure 7. Absorption spectra and oscillator strengths for molecule 7: the experimental absorption spectrum in ethanol at room temperature (solid curve) and its calculated maxima (vertical bars); the shaded vertical bars are absorption from the S_1 state.

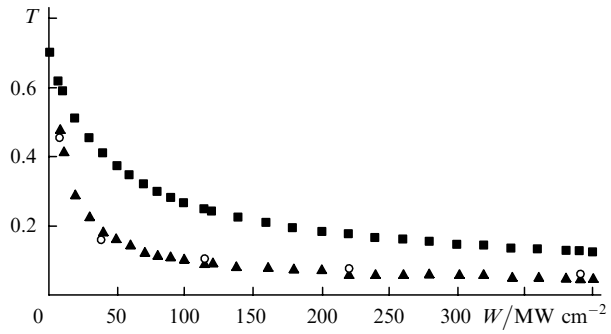


Figure 8. Experimental (○) and theoretical (calculated for $\tau_{iz} = 9$ ns) (▲) dependences of transmission on the pump power density for molecule 7; (■) is a quantum-chemical calculation for $\tau_{iz} = 1.27$ ns.

The cyanine dyes studied in the paper can be divided into several groups depending on their structure. The molecules of the first group (2, 3, 4) have the same structure (being disulfo-substituents) and differ from each other only by counter ions (Fig. 1). The spectral and luminescent properties of these molecules in ethanol are similar, their long-wavelength absorption band lies at 685 nm and has a high intensity ($\varepsilon \lesssim 2 \times 10^5$ L mol^{-1} cm^{-1}), and the fluorescence band lies at ~ 760 nm.

The introduction of new sulfo groups (molecule 4) reduces the solubility of the molecule in ethanol. The positions of the long-wavelength absorption band and the fluorescence band in DMSO almost do not change.

The third group includes molecules without sulfo groups (the C_4H_9 group is attached to the nitrogen atom in the five-membered ring), which differ from each other only by counter ions (Fig. 1). Molecules 5 and 5* have the same structure and differ only by the method of synthesis. One can see that the counter ion and the method of synthesis only weakly affect the spectral and luminescent properties. The same concerns sulfo groups: their introduction into molecules weakly change the spectral and luminescent properties of the latter. The introduction of $-CH_3-$ instead of $-C_4H_9-$ leads to the same result.

We studied the lasing properties of molecules pumped by a XeCl laser at 308 nm and the second harmonic of a Nd : YAG laser at 532 nm by the method described above. We found that all the molecules studied produced lasing in the region from 700 to 800 nm. The lasing efficiency upon pump by a XeCl laser achieved 11 % and the photostability of molecules was rather high ($\gamma = 1.5 \times 10^{-5}$ and 1.2×10^{-3} upon pump at 532 and 308 nm, respectively). These mole-

cules are of interest because their produce lasing in a poorly utilised spectral range and their lasing efficiency can be enhanced by optimising the resonator. In addition, the study of various photophysical processes proceeding in molecules, including stimulated emission, is necessary to elucidate their influence on the nonlinear-optical properties of molecules.

Table 5 presents the results of the study of the nonlinear-optical properties of cyanine dyes.

Note that all the cyanine dyes (except molecule 1) in ethanol exhibit nonlinear-optical properties, and the maximum attenuation coefficient of laser radiation at 532 nm achieves 15 for $T = 70\,\%$, which considerably exceeds the values of K_{max} obtained for substituted pyranes (Table 2).

The results depend on the molecular structure and the counter ion type. For example, the role of the 'heavy' ClO_4^- counter ion is obvious (for molecules 5, 5*, and 6 in ethanol, $K_{max} = 14$, 14, and 13, respectively). The substitution of the C_4H_9 group by the CH_3 group results in a weak decrease in K_{max} (for molecules 5 and 7 in ethanol, $K_{max} = 14$ and 11, respectively).

To understand the mechanism of laser radiation limitation, we performed quantum-mechanical calculations of molecule 7. One can see that the theoretical and experimental ground-state absorption spectra are in good agreement (Fig. 7). The intense induced absorption from the S_1 state lies in the region between 500 and 720 nm, the oscillator strength achieves 0.78, and no intense reabsorption from this state at 308 nm was observed. The rate of radiative decay of the excited state is $k_r = 1.79 \times 10^8$ s^{-1} and the internal conversion rate is $k_{ic} = 6.13 \times 10^8$ s^{-1}. We estimated the quantum yield of fluorescence as 0.23. Our calculations showed that the $S_1 - T_1$ intersystem conversion rate did not exceed 10^3 s^{-1}. We did not observe the induced $T - T$ absorption, which probably suggests that the role of triplet states in the limitation of optical radiation is insignificant.

We found that the agreement between the theoretical and experimental dependences of the transmission on the exciting power density was achieved for molecule 7 when the lifetime of the excited S_1 state was increased compared to the quantum-chemical value (from 1.27×10^{-9} up to 9.00×10^{-9} s).

The results presented above suggest that the limitation of optical radiation by substituted cyanine dyes can be also explained by absorption saturation, when the cross section for absorption from excited singlet states greatly exceeds the ground-state absorption cross section.

Figure 9 shows the dependences of the normalised transmission of solutions of cyanine dye 5 and DCM morpholine on the distance between the cell and the focal plane of a lens with the focal distance equal to 10 cm (the *z*-scan method with an open aperture). Because experiments were performed for the solutions of cyanine dye 5 and DCM morpholine under the same conditions, we can claim that the nonlinear absorption coefficient of the cyanine dye is greater than that of DCM morpholine. The transmission of the solution of cyanine dye in the lens focus decreases by a factor of 67 with respect to linear transmission.

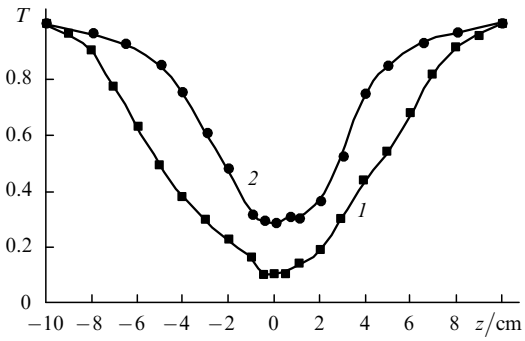


Figure 9. Normalised transmission of the second harmonic of a Nd : YAG laser by solutions of organic molecules as a function of the distance to the focal plane of a lens for the pulse energy of 12 mJ, $\tau_{1/2} = 6$ ns, and the initial transmission $T_0 = 70\,\%$ for cyanine dye 5 in PGC (*1*) and DCM morpholine in DMSO (*2*).

4. Conclusions

Our study of photophysical processes proceeding in substituted pyranes and cyanine dyes excited by lasers has shown that these molecules are capable of limiting high-power laser radiation at 532 nm. Cyanine dyes have the greater attenuation coefficient. The maximum attenuation coefficient ($K_{max} = 15$ and 13) was obtained for cyanine dyes 5 and 7 at the initial transmission equal to 70 %. This value is comparable to the attenuation coefficient for fullerenes ($K_{max} \approx 10$), which are widely used at present for the development of optical radiation limiters [7]. The results obtained in the paper show that cyanine dyes are promising for this purpose. Our theoretical and experimental study of the induced absorption in these molecules has shown that the limitation of optical radiation by these molecules is caused by inverse saturated singlet-singlet absorption.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant Nos 01-02-16901 and 02-02-08104) and the Interindustry Scientific and Technology Program of Collaboration between the Ministry of Education and the Defence Ministry of the Russian Federation (Grant No. 04.01.051).

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