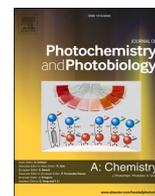




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Molecular photonics of dienones based on cycloalkanones and their derivatives

V.N. Gutrov^{a,*}, G.V. Zakharova^a, M.V. Fomina^a, V.N. Nuriev^{a,b}, S.P. Gromov^{a,b}, A.K. Chibisov^a^a Photochemistry Center of RAS, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Novatorov str. 7A-1, Moscow 119421, Russian Federation^b Faculty of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1, build. 3, 119991 Moscow, GSP-1, Russian Federation

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ABSTRACT

Spectroscopic, luminescent, and spectral kinetic properties of cycloalkanone-based dienones and their diethylamino, methylthio, methoxy, and dimethoxy derivatives were studied. The presence of electron-donating substituents results in a red shift of the absorption and fluorescence spectral maxima. A laser pulse causes dienones to undergo intersystem crossing to the underlying triplet state with a lifetime of 0.2–40 μs as well as results in the formation of stable photoproducts capable of photoinduced conversion to the initial dienones. It also gives rise to intermediate products resulting from redox photoreactions of 2,4-bis(4-diethylaminobenzylidene)cyclobutanone in methanol in the presence of electron donor (ascorbic acid) and acceptor (*para*-nitroacetophenone) compounds.

1. Introduction

Study of the photophysical and photochemical properties of cross-conjugated dienones, which are also known as ketocyanine dyes, was the subject of several publications [1–5]. It was shown that dienones exhibit solvatochromic properties, which are manifested as shifts of the absorption and fluorescence spectral maxima depending on the polarity of the medium as well as on the structure of the dye molecule. Therefore, dienones can be used to assess solvent polarity [6,7]. Dienones are also employed in their use as dye lasers, for information recording, and in organic synthesis [8,9]. Dienones containing an electron donor and acceptor functional groups are promising compounds for luminescence analysis of the cell membrane structures, evaluating the micro-environmental characteristics of biochemical and biological systems [10–12]. Of special note are dienones that contain crown ether moieties and form complexes with alkali and alkaline earth metal cations [13–16]. Research studies have also reported that dienones undergo rapid intersystem crossing to the underlying triplet state with a quantum yield of intersystem crossing ranging between 0.25 and 0.36 [17,18], and act as singlet oxygen sensitizers [19,20], making them applicable in photodynamic therapy [21,22]. The presence of carbon–carbon double bonds in dienone molecules gives rise to the existence of *E*- and *Z*-

isomers [23]. Upon photoexcitation, the equilibrium between the isomers shifts towards the less stable one [24]. One photochemical property of dienones is their ability to undergo [2 + 2] photocycloaddition reactions [25–27], which can be controlled by means of supramolecular pre-organization of the double bonds. Furthermore, dienones and the products of their heterocyclization are biologically active in that they exhibit antiviral [28], antimicrobial [29,30], and anti-inflammatory properties [31,32]. Dienones can also be used as anesthetics [33] and contraceptives [34]. It was proposed [35] to use pyridine-containing dienones as exodentate ligands, which react with metal ions to form coordination polymers.

Here we present the results of the effect of the structure of dienones and polarity media on the spectral luminescence and spectral kinetic properties of dienones. Dienones with various central cycles (cyclobutanone, cyclopentanone, and cyclohexanone) and different structure (donor–acceptor–donor or donor–acceptor–acceptor) as well as various electron-donating properties or 18-crown-6 and aza-18-crown-6 moieties were considered. The structures of the compounds are shown in Figure 1.

* Corresponding authors at: Photochemistry Center of RAS, FSRC "Crystallography and Photonics", Russian Academy of Sciences, Novatorov str. 7A-1, Moscow 119421, Russian Federation.

E-mail addresses: vngutrov@gmail.com (V.N. Gutrov), gvzakharova@gmail.com (G.V. Zakharova), mv_fomina@mail.ru (M.V. Fomina), nvn@org.chem.msu.ru (V.N. Nuriev), spgromov@mail.ru (S.P. Gromov), alexander.chibisov@gmail.com (A.K. Chibisov).

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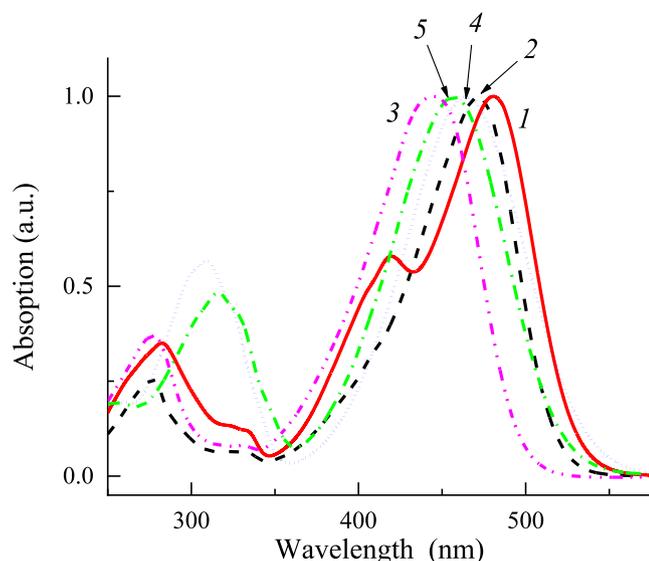


Fig. 2. Normalized absorption spectra of **1e** (**1**), **2e** (**2**), **3e** (**3**), **4e** (**4**), **5e** (**5**) in acetonitrile.

unsubstituted dienones (**1a**, **2a**, **3a**), the longer wavelength edge of the intense band has a weak shoulder corresponding to the $n \rightarrow \pi^*$ transition in the C=O group. The positions of the absorption maxima of dienones in acetonitrile are summarized in Table 1.

It follows from the spectral data presented in Table 1 that for the donor–acceptor–donor (D–A–D) ketocyanine dyes (groups of dienones **1**, **2**, and **3**), a decrease in the size of the central ring results in a red shift of the long wavelength absorption maximum. This is caused by increasing planarity of the molecule and, as a consequence, increasing degree of π -electron delocalization. Therefore, the most pronounced spectral shifts among the whole set of compounds are observed for cyclobutanone-based dienones. In the case of donor–acceptor–acceptor (D–A–A) dyes

Table 1
Luminescence properties of dienones **1–5** in acetonitrile.

Dienone	λ_{Abs} , nm	λ_{Fl} , nm	Stokes shift $\Delta\lambda$, nm
1a	340	–	–
1b	384	470	86
1c	398	507	109
1d	402	522	120
1e	481	576	95
1f	476	577	101
2a	345	–	–
2b	379	458	86
2c	395	500	105
2d	396	511	115
2e	472	560	88
2f	466	562	96
2g	397	500	103
3a	327	–	–
3b	355	–	–
3d	369	–	–
3e	446	562	116
3f	446	564	118
4a	344	–	–
4b	<u>371</u> ^a , 308	498	127
4c	386, 307	546	160
4d	384, 307	540	156
4e	465, 308	627	162
5a	343	–	–
5b	369, 316	480	111
5c	382, 329	520	143
5d	380, 317	523	138
5e	457, 317	605	148

^a – position of the principal absorption maximum is underlined.

(dienones **4**, **5**), the short wavelength absorption band is red shifted relative to that of **2** as a result of interaction of the lone pair of the heteroatom with the aromatic π -system. Conversely, the long wavelength absorption band is blue shifted. The longest wavelength absorption maximum of **4e** attests to increasing the degree of π -conjugation of the nitrogen atom in the *para*-position of the pyridine ring.

Since the long wavelength band is due to the charge transfer from the electron-donating substituent to the carbonyl group, the red shift with respect to the unsubstituted dienone increases with the increasing of the electron donating strength of the *para*-substituent.

The strong shift of the absorption maximum was observed for diethyl amino dienone derivatives. This is due to the fact that shifting of the electron density from the amine nitrogen atom requires less energy than that from oxygen and sulfur atoms. Therefore, the shift of electron density from electron-donating groups to the carbonyl group on passing to the excited state is higher for the amino derivative than for oxo- and thio- derivatives. The 426 nm band of **1e** (Fig. 2) refers to the $S_0 \rightarrow S_2$ transition [19].

The shift of the principal absorption band increases with increasing polarity of the solvent, which is due to dipole–dipole interactions of the diarylidencycloalkanone with the polar solvent. Excitation results in increasing the dipole moment of the molecules, which induces a red shift of the absorption band, and the value of the shift depends on the difference between the interaction energies of the molecule dipoles in the excited and ground states with respect to solvent dipoles. In protic solvents, a part from the dipole–dipole interactions, cycloalkanone-based dienones can undergo specific interactions with the solvent to form hydrogen bonds with the carbonyl oxygen atom. The π -electron structure of dienones can be described using two resonance structure, nonpolar (**A**) and charge separated bipolarones (**B**) [43–45], as depicted in Fig. 3. The degree of contribution of structure **A** and **B** to the structures of dienone depends on the solvent properties, determining both general and specific interactions, and on the dienone ability to form hydrogen bonds.

Both general and specific interactions with solvent molecules result in an increase in the energy of the $n\text{-}\pi^*$ and a decrease in the energy of the $\pi\text{-}\pi^*$ singlet and triplet states and thereby change the arrangement of electron states in the molecules [46–48]. If the $n\text{-}\pi^*$ singlet and triplet state energy exceeds the energy of the lower $\pi\text{-}\pi^*$ singlet state, rapid ($\sim 10^{11} \text{ s}^{-1}$) singlet–triplet intersystem crossing becomes impossible, which results in efficient fluorescence.

Fig. 4 shows the normalized fluorescence spectra of **1b–e** in acetonitrile. The emission spectra exhibit a single band, which is red shifted as the electron-donating ability of *para*-substituent increases. The positions of fluorescence maxima of the dienones are summarized in Table 1.

It is noteworthy that unsubstituted dienones **1a–5a** do not fluoresce, since the lower excited singlet state energy level is $n\pi^*$. The appearance of fluorescence upon the introduction of electron donating substituents at the *para*-positions of the aromatic ring is due to inversion in the order of the $n\pi^*$ and $\pi\pi^*$ state energy levels in the dienone molecule, resulting in the $n\pi^*$ level positioned above $\pi\pi^*$. The fluorescence measurements for dienones **3b**, **3d**, and **3e** in acetonitrile, dimethyl sulfoxide, and methanol showed the emission only for **3e**. The relative fluorescence efficiency virtually does not change on passing from acetonitrile to dimethyl sulfoxide and decreases 7-fold in methanol (see Fig. 5). The decrease in the fluorescence efficiency of **3e** in methanol is attributed to specific interactions with methanol involving hydrogen bonding with the carbonyl oxygen atom. This results in efficient radiationless decay of the excitation energy, which competes with fluorescence [49]. In the series of symmetric dienones, more strong Stokes shifts (see Table 1) were inherent in dienones based on cyclohexanone **3e**, indicating that the molecular geometry change upon transition to the excited state is greater for **3e** than for **1e** or **2e**.

However, in the case of unsymmetrical dienones, the Stokes shifts increase to 162 nm for **4e**. This is due to the fact that the electron-withdrawing pyridine residue depletes the carbon atom of the central

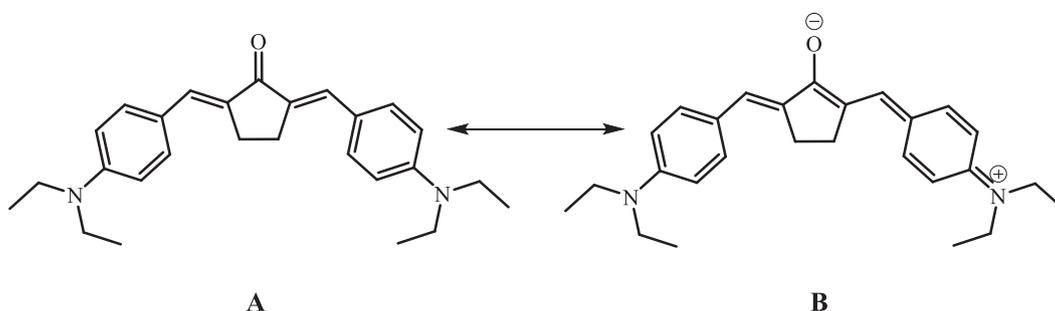


Fig. 3. Nonpolar (A) and bipolarones (B) resonance structures of dienone **1e**.

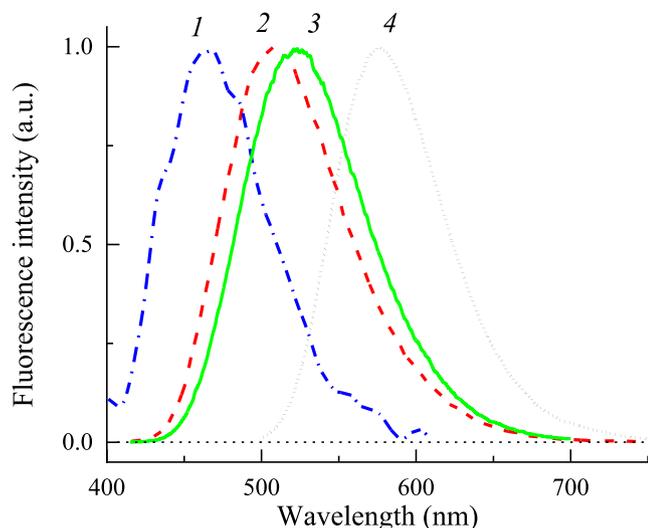


Fig. 4. Normalized fluorescence spectra of dienones **1b** (1), **1c** (2), **1d** (3), and **1e** (4) in acetonitrile.

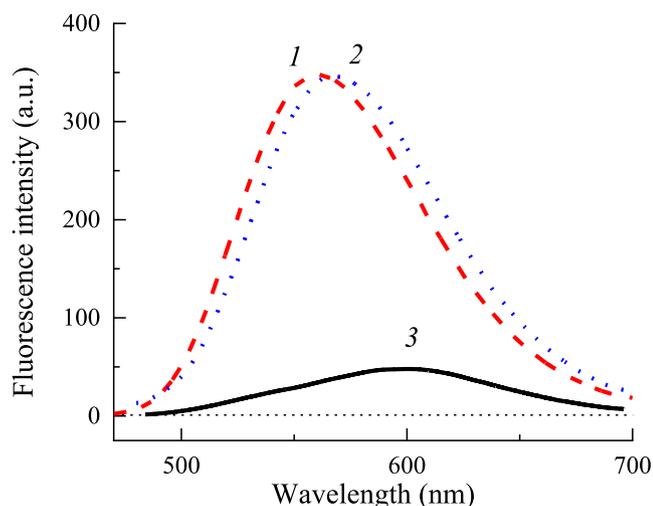


Fig. 5. Fluorescence spectra **3e** ($C_{3e} = 5 \times 10^{-6}$ M) in acetonitrile (1), dimethyl sulfoxide (2), and methanol (3).

ring of electrons, thereby facilitating the charge transfer from the electron-donating substituent to the carbonyl oxygen atom. As a result, the molecule in the excited state a zwitterion type bipolar structure with separated charges. Symmetrical dyes (groups 1–3) are characterized by strong stabilization in the ground state, whereas in the excited state, the interaction of chromophores becomes more difficult due to the presence

of the potential barrier. This assumption is supported by the increase in the Stokes shift for **2e** in methanol ($\Delta\lambda = 127$ nm) owing to the higher solvation of the carbonyl group.

Phosphorescence spectra of dienones **1a**, **1b**, **1c**, and **1e** were measured in acetonitrile at 77 K (Fig. 6). The phosphorescence spectra exhibit two bands. In the spectrum of **1a–c**, a weak band is located in the long wavelength region, whereas in the spectrum of **1e**, the band at 575 nm refers to the delayed fluorescence of the dye and its maximum coincides with the maximum of rapid fluorescence. Apparently, the absence of delayed fluorescence of **1d** and **1c** is caused by the greater energy gap between the T_1 and S_1 levels, which were 4090 cm^{-1} for **1d** and 3440 cm^{-1} for **1c** versus 2742 cm^{-1} for **1e** [50].

3.2. Kinetic spectroscopy

Pulsed laser irradiation of solutions of dienones **1–5** resulted in the production of the triplet state and the formation of a short-lived intermediate (0.2–40 μs) (**Pr1**) as well as a long-lived product (**Pr2**) with the lifetime greater than 1 s. In the case of cross-conjugated dienones, the laser pulse was found to produce a variety of intermediates, the properties of which depend on both the dienone structure and the solvent nature [17].

It was shown [50–52] that the laser excitation of unsubstituted dienones **2a** and **3a** in acetonitrile produces the short-lived product **Pr1**. Fig. 7 shows the time-resolved difference spectra of a deoxygenated solution of **3a** in acetonitrile. The absorption maximum at 450 nm is due to the formation of **Pr1** with a lifetime of 40 μs . The inset shows the kinetic decay of **Pr1**.

The lifetime of the intermediate does not depend on the presence of dissolved oxygen. Apparently, the **Pr1** should be a result of steric and/or

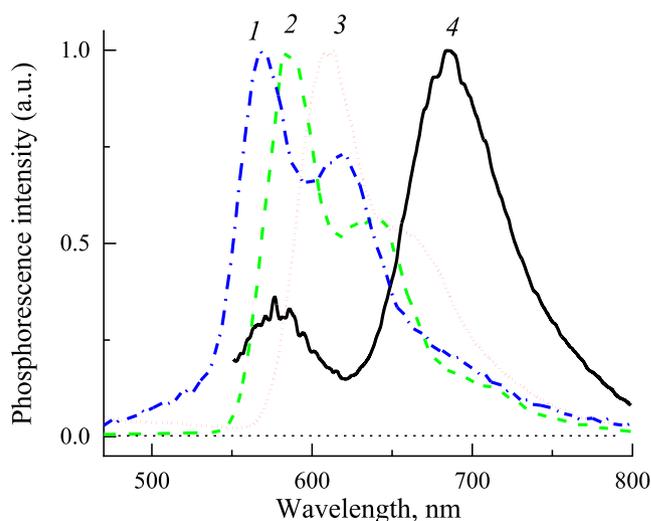


Fig. 6. Normalized phosphorescence spectra of **1a** (1), **1b** (2), **1c** (3), and **1e** (4) in acetonitrile at 77 K.

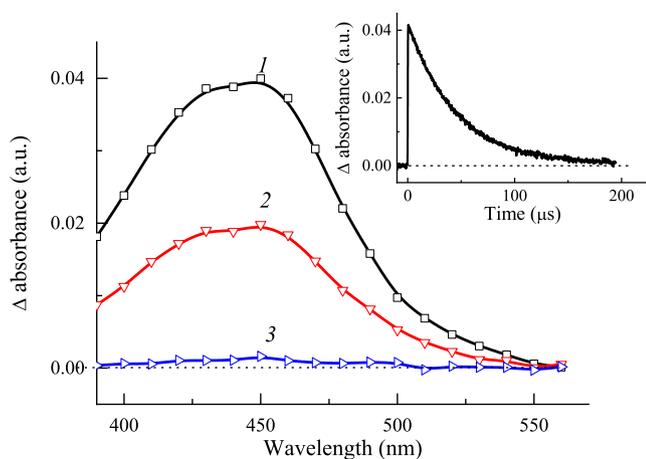


Fig. 7. Time-resolved difference absorption spectra of **3a** in deoxygenated acetonitrile measured at 2 (**1**), 35 (**2**), and 200 (**3**) μs after the laser pulse ($\lambda_{\text{ex}} = 354 \text{ nm}$). Inset: decay kinetics of **Pr1**.

conformational changes of the dye structure. The lifetimes of **Pr1** are summarized in Table 2. It can be seen that the decrease in the size of the central ring of group 1–3 dienones gives rise to shorter lifetimes of **Pr1**.

The lifetime of **Pr1** derived from cyclopentanone dienone **2a** is 0.7 μs . In the case of cyclobutanone dienone **1a**, which has flatter structure than **2a**, no intermediate product **Pr1** was detected. Perhaps, the lifetime of **Pr1** is markedly shorter than the laser pulse duration, which precludes the possibility of recording of the difference absorption spectrum. The introduction of electron-donating substituents does not significantly affect the lifetime of **Pr1** derived from dienones **1** and **2**, while for cyclohexanone-based dienones (**3**), the introduction of methoxy and methylthio groups decreases the lifetime of **Pr1** from 40 μs (**3a**) to 10 μs for **3b** and 20 μs for **3d**. It is noteworthy that a change in the polarity of the medium has no marked effect either on the product yield or on the product half-life.

Apart from the short-lived **Pr1**, the formation of long-lived intermediate product **Pr2** was detected upon laser irradiation. Fig. 8 shows the difference absorption spectra of **2c** measured at a different time after the laser pulse. Spectrum **1** with a wavelength maximum between 460 and 465 nm is an overall spectrum caused by the absorption of both the short-lived product **Pr1** and the long-lived product **Pr2**, whereas spectrum **2** characterizes the absorption of only **Pr2**. The inset shows the kinetic curve for the formation and decay of **Pr1** over $\sim 0.7 \mu\text{s}$. In the case of methylthio, methoxy, and dimethoxy derivatives **2b-d** and 18-crown-6-containing dienone **2g**, the pulsed radiation gives rise to similar spectral changes. Note that the life time of stable product **Pr2** is more than several hours for any of the dienones.

It was shown that the laser excitation of unsymmetrical dienones **4** and **5** produces the products similar to that resulting from pulsed excitation of dienones **2** [53,54]. The introduction of electron-donating substituents does not have a significant effect on the lifetime of product **Pr1** (see Table 2), but favors the formation of long-lived product **Pr2**. The change in the position of the nitrogen atom in the pyridine residue from *para*- (**4**) to *meta*-position (**5**) results in a decrease of the lifetime of

Table 2
Lifetimes of **Pr1** for dienones 1–5 in acetonitrile.

Dienone	Lifetime of Pr1 , μs				
	1	2	3	4	5
a	–	0.7	40	0.7	0.3
b	0.2	0.5	10	0.9	0.2
c	0.2	0.7	–	2	0.2
d	0.3	0.5	20	1	0.5
g		0.5			

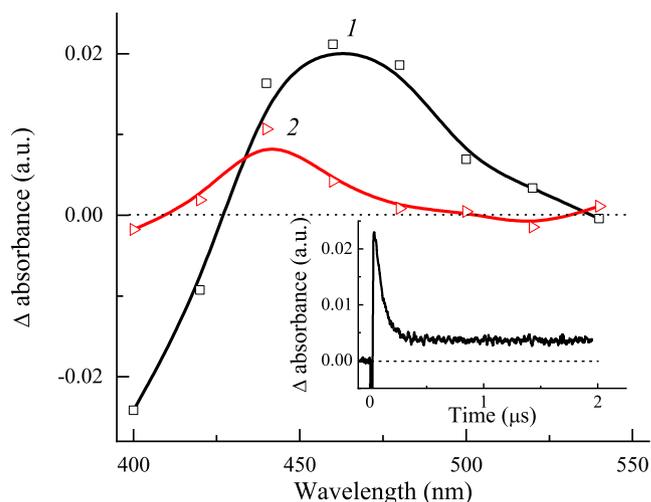


Fig. 8. Difference absorption spectra of **2c** in deoxygenated acetonitrile measured at 0.3 (**1**) and 10 (**2**) μs after the laser pulse ($\lambda_{\text{ex}} = 354 \text{ nm}$). Inset: kinetic curve measured at 460 nm.

product **Pr1**, which is probably due to the lower degree of conjugation of the nitrogen atom located in the *meta*-position of the pyridine ring.

Using pulsed laser photolysis, it was shown that diethylamino dienones **1e**, **2e**, and **3e** are capable of intersystem crossing of undergoing the corresponding triplet state [18,55]. Fig. 9 shows the difference absorption spectra of **1e** measured at different times after the laser pulse. The short-lived transient absorbing at 720 nm refers to the triplet–triplet (T-T) absorption, whereas the band at 520 nm corresponds to the absorption of stable photoproduct **Pr2**. The inset shows the kinetic curve for decay of the triplet state of **1e** in acetonitrile. The triplet state lifetime (τ_T) for **1e** was measured to be 3.5 μs .

The assignment of the 720 nm band to the T-T absorption is confirmed by disappearance of the band in the presence of air oxygen, which quenches the triplet state [56,57]. In addition, the lifetime of the triplet state of **1e** decreases in the presence of naphthalene as a triplet energy acceptor ($E_T = 10250 \text{ cm}^{-1}$ [58]). The T-T energy transfer between dienone **1e** and naphthalene is confirmed by the appearance of T-T absorption of naphthalene at 460 nm.

The triplet state lifetimes of dienones **1e-5e** in various solvents are summarized in Table 3. An increase in the size of the central ring leads to a decrease of the triplet state lifetime of the dienone. In acetonitrile, $\tau_T \approx 0.5 \mu\text{s}$ for dienone **2e**, while $\tau_T < 0.1 \mu\text{s}$ for dienone **3e**. This is due to

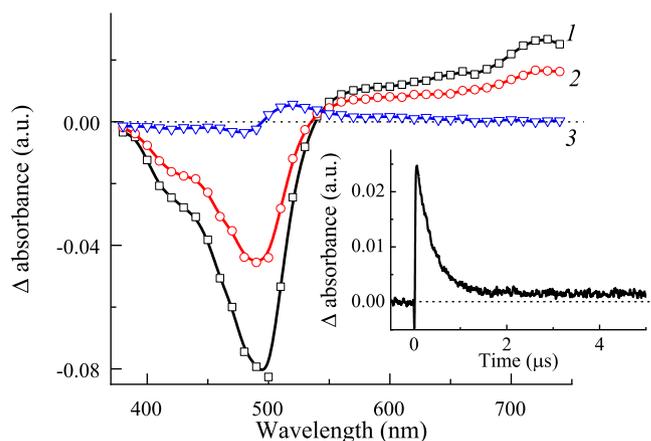


Fig. 9. Difference absorption spectra of the photoinduced absorption of a deoxygenated solution of **1e** ($C_{1e} = 5 \times 10^{-5} \text{ M}$) in acetonitrile measured at 2 (**1**), 5 (**2**), and 50 (**3**) μs after the laser pulse ($\lambda_{\text{ex}} = 354 \text{ nm}$). Inset: decay kinetics of the triplet state at 720 nm.

Table 3Triplet state lifetimes (τ_T) for dienones **1-5e** in solvents.

Dienone	τ_T , μs		
	Toluene 0.099 ^a	Acetonitrile 0.460	Methanol 0.762
1e	0.5	3.5	15.0
2e	<0.1	0.5	10.0
3e	<0.1	<0.1	0.7
4e	<0.1	3.0	7.0
5e	<0.1	1.0	2.0

^a E_T^N value characterizing the solvent polarity [59].

the increase of the efficiency of decay of the triplet state via intersystem crossing. The introduction of aza-18-crown-6 ether residues into the dienone molecule increases the triplet state lifetime, which is 20 μs for **3f**. The crown ether residues in **3f** create steric hindrance to photoisomerization, which influences the probability ratio between the radiative and non-radiative degradation of excitation energy. The introduction of aza-18-crown-6 ether residues into cyclobutanone- (**1f**) and cyclopentanone- (**2f**) based dienone molecules decreases the efficiency of intersystem crossing to the triplet state in comparison with the efficiency of **3f** conversion to the triplet state. The pulsed laser irradiation of deoxygenated solutions of diethylamino dienones **4e** and **5e** induced the intersystem crossing to the triplet state with the lifetimes of 3 μs and 1 μs , respectively. The change in the pyridine nitrogen atom position from *para* to *meta* results in a shorter triplet state lifetime of dienone **5e** in comparison with **4e**. In the case of **4e** and **5e**, no long-lived photoproduct **Pr2** was observed in acetonitrile, but it was detected in non-polar solvents.

As noted above, a change in the solvent affects the formation and properties of the intermediate products resulting from pulsed excitation. Table 3 presents the lifetimes of the triplet states of diethylamino dienone derivatives **1-5** in toluene, acetonitrile, and methanol. As it follows from Table 3, the triplet state lifetimes of molecules **1e-5e** increase with respect to an increase in solvent polarity. The longest triplet state lifetime (15 μs) is inherent in dienone **1e** in methanol.

A decrease in the solvent polarity results in an increase in the yield of the stable photoproduct **Pr2**. However, the formation of **Pr2** was not detected in methanol. This fact attests to specific interaction of dienones with methanol caused by hydrogen bonding with the carbonyl oxygen atom, which produces a dienone structure that fails to form stable photoproduct **Pr2**.

It was noted [60] that steady state irradiation of dienone solutions in acetonitrile induced changes in the absorption spectrum. The changes in the absorption spectrum of the dye were accompanied by a decrease in the relative fluorescence efficiency, as a result of conversion of dienone **2e** to non-fluorescent product **Pr2**. The observed spectral changes are irreversible. However, the subsequent steady state irradiations of solutions through OS-11 + SZS-21 ($\lambda_{tr} = 530$ nm) light filters, which isolate the absorption range of **Pr2**, results in the restoration of both the absorption band and fluorescence intensity of **2e**, which is indicative of photoinduced transition of **Pr2** to **2e**.

Fig. 10 shows the difference absorption spectrum of an deoxygenated solution of **2e** upon laser excitation at the long wavelength absorption maximum of the dye ($\lambda_{ex} = 472$ nm). Spectrum 1 corresponds to the triplet-triplet absorption of **2e**, while spectrum 2 with a maximum at 510 nm characterizes the absorption of long-lived product **Pr2**, which is also observed upon steady state irradiation.

The subsequent laser excitation of an deoxygenated solution in the **Pr2** absorption range ($\lambda_{ex} = 550$ nm) gives rise to absorption at 460 nm and bleaching of the band at 510 nm (negative maximum) (Fig. 10, inset). The negative maximum in the absorption spectrum is due to the depletion of the ground state level of **Pr2**, owing to its photoinduced transition to the initial dienone **2e**, which absorbs at 460 nm (see Table 1). It is also noteworthy that saturation of the solution with air oxygen does not affect the yield of **Pr2**, which excluded the participation

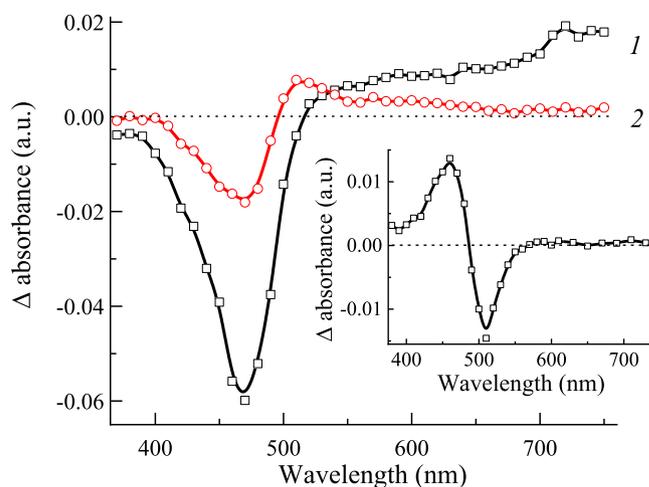


Fig. 10. Difference absorption spectra of **2e** ($C_{2e} = 5 \times 10^{-5}$ M) in deoxygenated acetonitrile measured at 1 (**1**) and 3 (**2**) μs after the laser pulse ($\lambda_{ex} = 472$ nm). Inset: difference absorption spectrum of **2e** in deoxygenated acetonitrile measured at 1 μs after the laser pulse ($\lambda_{ex} = 550$ nm).

of the triplet state of **2e** in the formation of **Pr1**. Previous studies have found that ketocyanine dyes undergo photoisomerization [24]. Product **Pr2** should most likely be identified as a dye photoisomer. The formation of long-lived photoisomer **Pr2** was observed upon steady state irradiation of dienones in toluene. The yield of **Pr2** is higher in toluene than in acetonitrile. Fig. 11 shows the absorption spectra of **1e** in toluene measured before (spectrum 1) and after (spectrum 2) the steady state irradiation with the KGM filament lamp through set of glass light filters ZHS-12 + SS-15 ($\lambda_{tr} = 460$ nm). The irradiation resulted in a decrease in the absorbance at 468 nm and the appearance of long wavelength absorption at $\lambda = 500$ nm (the isobestic point at 475 nm). Fig. 11 (inset) shows the spectrum which was subtracted of spectrum 2 from 1. The difference spectrum with maximum at 493 nm refers to absorption of the photoisomer. The subsequent steady state irradiations of solutions through combination of glass filters ZHS-17 + SzS-20 ($\lambda_{tr} = 520$ nm), which isolate the absorption range of **Pr2**, results in the restoration of the absorption band of **1e** (spectrum 3), which is indicative of photo-induced transition of **Pr2** to **1e**.

To summarize, pulsed and steady-state excitations resulted in the formation of a stable photoisomer, capable of undergoing a reversible

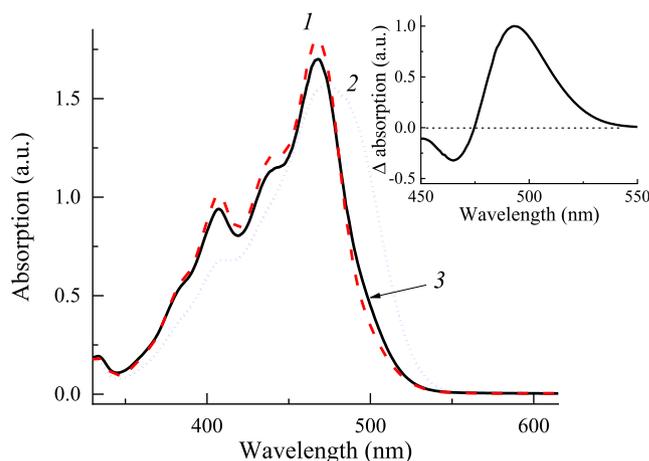


Fig. 11. Absorption spectra of **1e** ($C_{1e} = 5 \times 10^{-5}$ M) in toluene before steady state irradiation (**1**), after irradiation through the ZHS-12 + SS-15 combination of glass filters for 2 min (**2**), and after the subsequent irradiation through ZHS-17 + SzS-20 glass filters (**3**). Inset: the difference spectrum between curves 2 and 1.

photoinduced transition to the initial dienone. The formation of photoisomers was observed for dienones of groups 1–5 both in polar and in nonpolar solvents. Furthermore, it was found that photoisomerization occurs most efficiently in nonpolar solvents.

3.3. Products of redox photoreactions of dienones

In this study, we found the ability of dienones **1e** and **2e** in the triplet state to undergo redox photoreactions. The photoreduction of dienone **1e** with ascorbic acid (AA) and photooxidation with methyl viologen and *para*-nitroacetophenone (*p*-NAP) in methanol have been studied [61].

Fig. 12 shows the difference absorption spectra of a deoxygenated solution of **1e** measured in the presence of AA at different time after the laser pulse. Spectrum 1 was measured after 3 μ s; the addition of AA in a concentration of 5×10^{-4} mol/L has virtually no effect on the change in the absorbance ΔA in comparison with a pure solution of **1e**. The admission of air into the cell leads to virtually complete disappearance of the spectrum of 1, which attests to the triplet state as the intermediate formed upon laser excitation. Thus, the difference absorption spectrum of 1 at $\lambda > 740$ nm is due to the T-T absorption of **1e**.

The difference absorption spectrum measured after 30 μ s (spectrum 2) refers to the absorption of the semireduced form (anion radical) of the dye ($\lambda_{\max} = 460$ nm). Kinetic curves 1 and 2 for triplet state decay shown in the inset indicate a decrease in the triplet state lifetime for **1e** caused by quenching of the triplet state by AA to give the dye anion radical with a lifetime of 3×10^{-4} s (inset, curve 3). The rate constant for quenching was found to be 1.5×10^8 L mol $^{-1}$ s $^{-1}$.

The difference absorption spectrum recorded upon pulsed excitation of an deoxygenated solution of **1e** in the presence of methyl viologen as an electron acceptor in methanol exhibited the absorption caused by conversion of **1e** to the triplet state and absorption of products with maximum at 390 and 610 nm, corresponding to both dienone cation radical and methyl viologen cation radical (MV $^{+ \cdot}$) [62] with a lifetime of 70 μ s. The addition of methyl viologen results in a decrease in the triplet state lifetime, which indicates that the electron reaction takes place. The rate constant for quenching was found to be 3×10^9 L mol $^{-1}$ s $^{-1}$.

Fig. 13 shows the difference absorption spectra of a deoxygenated solution of **1e** in the presence of *p*-NAP as an electron acceptor in methanol. The addition of *p*-NAP in a concentration of 2×10^{-5} mol/L results in complete quenching of the triplet state of **1e** via electron

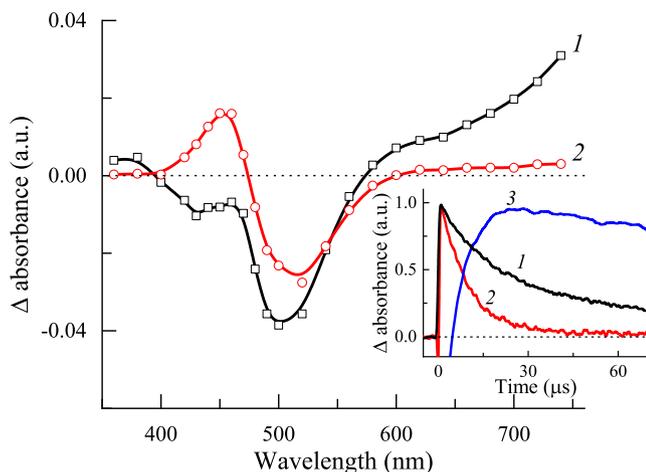


Fig. 12. Difference absorption spectra of deoxygenated solution of **1e** ($C_{1e} = 1 \times 10^{-4}$ M) in methanol in the presence of AA ($C_{AA} = 5 \times 10^{-4}$ M) measured after 3 (1) and 30 μ s (2). The inset shows the normalized kinetic curves at $\lambda = 740$ nm in the absence (1) and in presence (2) of AA and at $\lambda = 460$ nm (3) in the presence of AA ($C_{AA} = 5 \times 10^{-4}$ M).

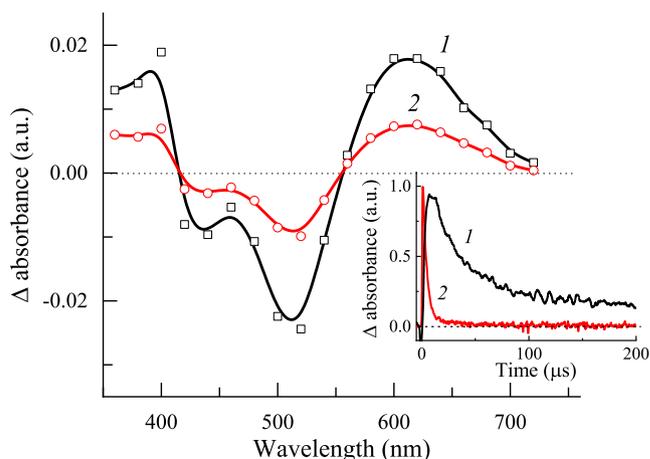
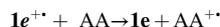


Fig. 13. Difference absorption spectra of a deoxygenated solution of **1e** ($C_{1e} = 1 \times 10^{-4}$ M) in methanol measured after 5 (1) and 40 (2) μ s in the presence of *p*-NAP (2) ($C_{p-NAP} = 2 \times 10^{-5}$ M). Inset: normalized kinetic curves for the decay of **1e $^{+ \cdot}$ at 620 nm measured in the absence (1) and in presence of AA ($C_{AA} = 5 \times 10^{-5}$ M) (2).**

transfer to give the dienone cation radical (**1e $^{+ \cdot}$).**

In the difference absorption spectra, the maximum at 615 nm refers to the dye cation radical (**1e $^{+ \cdot}$), resulting from oxidation of **1e**. The lifetime of **1e $^{+ \cdot}$ is 20 μ s. The formation of dienone cation radicals was noted previously [63]. The difference absorption spectrum of dienone **2e**, obtained by pulsed irradiation of an deoxygenated solution in methanol in the presence of *p*-NAP ($C_{p-NAP} = 2 \times 10^{-5}$ M), also demonstrates the formation of dienone cation radical **2e** with the lifetime of 50 μ s. The absorption maximum of cation radical **2e** is located at 600 nm. The difference spectra of both **2e** and **1e** show absorption at a wavelength shorter than 400 nm, which apparently is due to the product of one-electron reduction of *p*-NAP [64].****

The ability of **1e** to act as a photosensitizer in the reduction of *p*-NAP with AA was studied. When the concentration of *p*-NAP is 1×10^{-6} mol/L and the concentration of AA is 5×10^{-5} mol/L, the primary step of the photoreaction was the one-electron oxidation of triplet state **1e** to give a solvent-separated radical ion pair **1e $^{+ \cdot}$...*p*-NAP $^{\cdot -}$. This step was then followed by dissociation into ion radical **1e $^{+ \cdot}$ and *p*-NAP $^{\cdot -}$. The second step of the photosensitized redox reaction was the thermal reduction of **1e $^{+ \cdot}$ with AA, resulting in recover of **1e**.******



The decrease in the lifetime of the dienone cation radical in the presence of AA (inset, Fig. 13) attests to the occurrence of photosensitized redox reaction.

4. Conclusion

The photophysical and photochemical properties of certain dienones (ketocyanine dyes) and their derivatives were studied. The dienone structure (the size of the central ring, the presence of electron-donating substituents) influences the spectral and luminescence properties, which were manifested as the shifts of the maxima in the absorption and fluorescence spectra. The spectral luminescence properties of dienones and the products of pulsed laser excitation are influenced by the nature of the solvent. In the case of laser and steady state excitation, the stable photoproduct (photoisomer) is formed, capable of undergoing photoinduced conversion to the initial dienone. The diethylamino dienone derivatives can be converted to the triplet state. In the presence of exogenic electron donors and acceptors, photosensitized redox reaction can occur to give semi-oxidized and semi-reduced dye. The properties of dienones (ketocyanine dyes) can be utilized for the design of a new types of photoactive supramolecular systems.

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CRedit authorship contribution statement

V.N. Gutrov: Investigation, Writing – original draft, Writing – review & editing. **G.V. Zakharova:** Investigation, Methodology. **M.V. Fomina:** Investigation, Visualization. **V.N. Nuriev:** Methodology, Investigation. **S.P. Gromov:** Conceptualization, Methodology, Funding acquisition, Writing – review & editing. **A.K. Chibisov:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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