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7-Dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins: two-photon absorption in solution and in polymer film

Valerii F. Traven,*[a] Dmitrii A. Cheptsov,[a] Sergei M. Dolotov,[a] Ivan V. Ivanov,[a] Dmitrii V. Khudyakov[b] and Valerii A. Barachevsky[c]

[a] *D. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation. E-mail: valerii.traven@gmail.com*

[b] *Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

[c] *Photochemistry Centre, FSRC 'Crystallography and Photonics', Russian Academy of Sciences, 119421 Moscow, Russian Federation*

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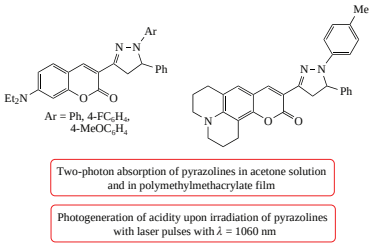
Cross section of the two-photon absorption in 7-dialkylamino-3-(3-pyrazolinyl)coumarins in acetone and polymethylmethacrylate films has been found to be dependent on the substrate and medium nature. 7-Dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins are shown to be effective in the photosensitive media with excitation at 1060 nm for optical recording of information.



Keywords: two-photon absorption, acid photogenerators, pyrazolines, rhodamine B lactone, fluorescent image, recording media.

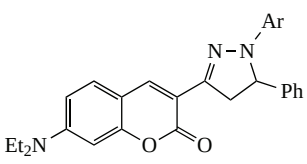
Two-photon absorption (TPA) effect provides great potential for application of organic dyes and their structural analogues in photonic and biomedical fields, such as two-photon excited fluorescence microscopy,[1] high-density optical data storage,[2] three-dimensional microfabrication,[3] and photodynamic therapy.[4]

One of the most promising directions in the development of modern information technologies is the creation of three-dimension (3D) optical memory with a super high information capacity, in particular optical disks, using light-sensitive recording media with fluorescent readout of recorded information.[5] The high information capacity is provided in these systems by the multilayered structure of the recording medium and two-photon excitation of light-sensitive compounds.[6]

Media based on the participation of acid photogenerators (PAG) provide formation of fluorescent photoproducts as well.[7,8] Light-sensitive recording media with PAG contain dye precursors (DP). The DP molecules are colourless and stable in neutral media. However, they become strongly coloured and fluorescing in the presence of acid produced by the light-sensitive PAG molecules under irradiation. Typical photogenerators of acidity proposed for the use in archival recording media are triarylsulfonium and triarylmethane salts of certain organic and inorganic acids, derivatives of sulfonic acids, nitrobenzaldehyde and nitronaphthaldehyde.[7,8] The disadvantage of these photogenerators is their short-wave absorption and, as a consequence, the need to use the UV light for their phototransformation. Ultraviolet radiation in some cases is too hard and causes degradation of the fluorescent DP. The use of the most developed lasers with radiation at a wavelength λ = 1060 nm for two-photon recording of information is currently the most practically acceptable trend.[9–11] Previously, we have found a new photodehydrogenation reaction of aryl(hetaryl)pyrazolines, when they were irradiated in the presence of CCl_4 or C_2Cl_6. That reaction was accompanied by the generation of acidity and had been applied to create new photofluorescent media for optical information recording.[12,13] Here, we report results of the study of TPA of 7-dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins **1a**–**c** and **2**.

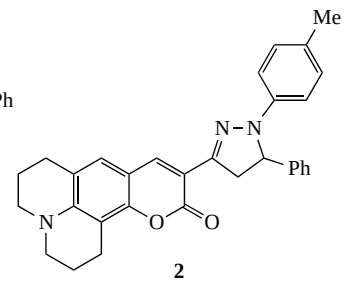
It was previously shown that such compounds have absorption in the longer wavelength region (up to 500 nm), and generate acidity when irradiated, in contrast to other compounds with similar photophysical properties.[14–17] Moreover, the generation of acidity by these compounds occurs 2–3 orders of magnitude faster than that of the previously described pyrazolines.[18,19] All compounds absorb in the same spectral region, except for compound **2**, whose absorption band is shifted to the long-wave spectral region. As expected, spatial fixation of the amino function in the coumarin derivative **2** provides the maximal effect on the absorption due to the best conditions for the conjugation of occupied p_z-orbital of nitrogen atom, coumarin π-system and vacant π*-orbital of pyrazoline C=N bond.

Measurements of the TPA of 7-dialkylamino-3-[1,5-diaryl-(3-pyrazolinyl)]coumarins **1a**–**c** and **2** at a wavelength of 1060 nm have been carried out in acetone. The values of the TPA



1a–c

a Ar = Ph
b Ar = 4-FC_6H_4
c Ar = 4-$MeOC_6H_4$



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coefficients at the positions of maxima absorption and at 530 nm were calculated with the use of the experimental transmittance changes during the motion of the sample along *Z*. The values of the cross section (δ) of the TPA of solutions were then determined in units GM (1 GM = 1×10^{-50} cm^4 s per photon). The experimental data and values of δ measured in acetone are given in Table 1.

As it can be seen in Table 1, compound **2** possesses maximal value of the cross section. The higher ability of compound **2** to TPA is not surprising since it has the maximum absorption coefficients in the electronic spectrum: ε = 39400 dm^3 mol^{-1} cm^{-1} (at the maximum of absorption band λ_{max}) and ε = 14200 (at λ = 530 nm).

Absorption spectra and the cross sections of the TPA of 7-dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins **1a–c** and **2** have also been measured in the polymethylmethacrylate (PMMA) films under irradiation at λ = 1060 nm (see Table 1 and Online Supplementary Materials, Figure S4). Comparison of the obtained spectra in PMMA film with the absorption spectra of compounds **1a–c** and **2** in acetone (Figure S3) indicates minor changes. However, the values of the cross sections for TPA in PMMA film are 2–3 times higher than those in acetone. Two reasons for this fact can be suggested. Firstly, an increase in the concentration of pyrazolines in PMMA film should be mentioned. Secondly, a packing of pyrazoline molecules in the polymer matrix can increase due to their planar arrangement. As a consequence, planar structure improves conjugation of π-electrons in the molecule which leads in turn to increase in the cross section of two-photon absorption. As it was shown earlier, even a small change of the angle between two pyrazoline molecular planes to higher planarity can enhance the value of TPA cross section in several times.[10]

It is also important that the TPA cross sections of compounds **1a–c** and **2** in acetone and in PMMA film turned to be in good agreement. The cross section values both in acetone and in films gradually increase from samples **1a–c** to sample **2** (see Table 1).

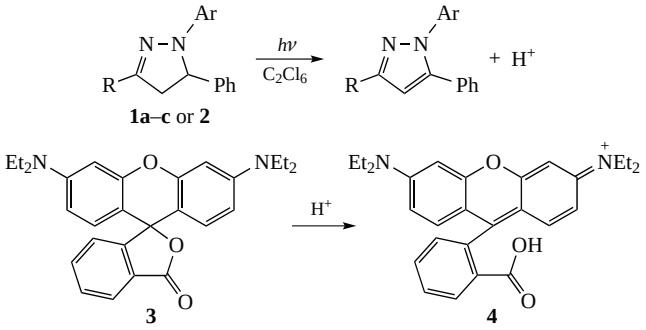
To demonstrate the generation of fluorescent signals in the PMMA film that contain pyrazoline (for example, compound **1b**), hexachloroethane and lactone form of Rhodamine B **3**, a sample of such a recording medium has been prepared. Formation of a fluorescent product is a result of the transformation of a DP into fluorescing Rhodamine B **4** due to acid photogeneration during irradiation of pyrazoline (Scheme 1).

The spectral characteristics and photochemical changes in the PMMA film are shown in Figure 1. It is seen that irradiation of the film by laser light with wavelength λ = 1060 nm provides formation of fluorescent dye Rhodamine B.

Table 1 Values of the TPA cross sections of 7-dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins **1a–c** and **2** in acetone and in polymethylmethacrylate films under excitation by irradiation with λ = 1060 nm.[a]

Compound	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}		$C \times 10^3$/M	δ/GM
		at λ_{max}	at λ = 530 nm		
in acetone					
1a	456	36600	6700	0.23	240
1b	452	34800	5700	0.22	240
1c	462	24800	8000	0.39	260
2	470	39400	14200	0.21	280
in polymethylmethacrylate films					
1a	458	22000	4980	4.6	420
1b	452	15600	3120	5.3	490
1c	462	24100	8320	4.3	570
2	470	38600	14200	4.2	650

[a] λ_{max} is the wavelength of the maximum absorption band, ε is the coefficient of molar extinction, *C* is the concentration of the compound in the solution, δ is the cross section of the two-photon absorption.



Scheme 1

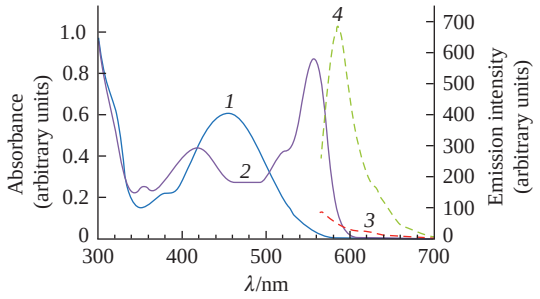


Figure 1 Electronic absorption (curves *1*, *2*) and emission (curves *3*, *4*) spectra of a PMMA film with dissolved compound **1b**, lactone form of Rhodamine B and C_2Cl_6 before (*1*, *3*) and after (*2*, *4*) irradiation.

As follows from Figure 2, the diameter of the photochemical transformations (~20 μm) is less than laser beam diameter of 52 μm. The reducing of area of transformation is associated with the fact that TPA is more effective in high intensity central zone of the laser beam profile.

In conclusion, 7-dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]-coumarins in acetone solution and in a PMMA film undergo photoexcitation upon irradiation with femtosecond laser pulses with λ = 1060 nm. The dependence of the TPA cross section on the structure of 3-(pyrazolinyl)coumarins has been revealed. Upon photoexcitation by laser pulses with λ = 1060 nm, these values in the polymer PMMA matrix are 2–3 times higher than those measured in the acetone. A real two-photon recording of a photoinduced fluorescent image by laser pulses with λ = 1060 nm has been demonstrated using a polymer sample of the recording medium. When this process is implemented in a film of PMMA in the presence of lactone Rhodamine B as a DP and hexachloroethane, a laser dye Rhodamine B is formed, that provides optical information recording with fluorescence readout. These results also open up the use of 7-dialkylamino-3-[1,5-diaryl(3-pyrazolinyl)]coumarins as acid photogenerators in biochemical studies.

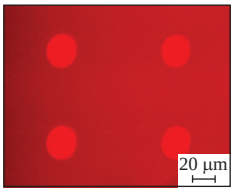


Figure 2 A sample of PMMA recording medium that contains compound **1b**, C_2Cl_6 and lactone form of Rhodamine B after two-photon excitation of photochemical transformation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.028.

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