# Activation of fluorescence of lactone forms of rhodamine dyes by photodehydrogenation of aryl(hetaryl)pyrazolines

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Aryl(hetaryl)pyrazolines are effective photogenerators of acid providing an irreversible photochemical activation of fluorescence of rhodamine group dyes. The effect of solvent on two consecutive reactions, photodehydrogenation of pyrazoline and lactone ring opening of the dye was studied. An increase in solvent polarity leads to an increase in the rate of both reactions by different degrees. The systems under study are believed to be promising for the formation of recording media for multilayer optical file type disks of ultrahigh data storage capacity with fluorescent readout.

**Key words:** pyrazoline, rhodamine lactone, fluorescence.

Rapid development of computer and information technologies requires higher performance data recording systems, capable of storage, readout and processing of huge amounts of data using organic light sensitive media of various types.[1—7] One of the most promising ways of increasing the amount of recorded information is the development of multilayer optical disks, which provide an increase in data capacity by several orders of magnitude compared to modern optical data carriers through the use of a two-photon process of data recording.

In particular, a promising direction is the development of recording media for multilayer optical file type disks, in which a single two-photon recording of data with laser radiation is carried out in the form of the so-called fluorescent pits of information. The pits are formed as a result of photochemical transformation of nonfluorescent organic precursors to compounds, which are characterized by strong fluorescence (a reverse process of fluorescence decay is also possible as part of a photochemical reaction).[8—12] The recorded fluorescent form of the material, which makes up the pits, must possess a high fluorescence quantum yield, whereas the precursor and the photoproduct must be thermally stable.[13—15] Coumarins, lactones, and lactams of xanthene rhodamine group dyes, thioindigoid dyes, stilbene derivatives, substituted anthracenes, anthraquinones, and other compounds were studied as fluorescent precursors suitable for use in systems of optical data recording.[16—19] Some of the precursors listed above are able to activate fluorescence in the absence of any additives merely upon influence of radiation. However, the UV radiation required for this is quite strong and may cause destruction of the dye.

Irradiation of the precursor in the presence of an acid photogenerator (APG) is less destructive. For this process, the role of the APG consists in the transformation of the fluorescent precursor molecule: elimination of a protecting group,[20,21] lactone/lactam ring opening in the leukobase,[17,22—24] protonation of the amino group for the purpose of deactivation of fluorescence or the shift of the emission maximum to the long wavelength region. A light sensitive thermally stable compound, which under excitation by light of an appropriate wavelength undergoes a photochemical transformation with the formation of an acid, is used as the APG. Typical acid photogenerators, which are suggested for use in systems of file type data recording, are triarylsulfonium and triaryliodonium salts of some organic and inorganic acids, sulfonic acid derivatives, as well as nitrobenzaldehydes and nitronaphthaldehydes.[14]

By studying new photoregistering media for file type data recording, we showed that the role of the APG can also be carried out by some halogen-containing compounds.[25] However, their photochemical properties require the use of short wavelength UV radiation ($\lambda = 254$ nm), which leads to partial photodestruction of the precursor. Therefore, a pressing concern is the search for new acid photogenerators, which are capable of activating the fluorescence of precursors under longer wavelength irradiation, which is consequently less destructive.

## Results and Discussion

Earlier we reported on the photodehydrogenation reaction of 5-(4-anisyl)-3-(4-hydroxycoumarin-3-yl)-1-

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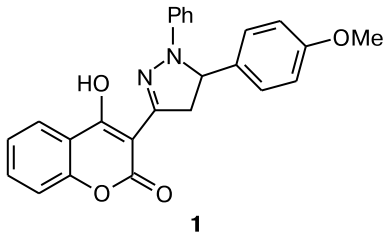
phenylpyrazoline (**1**) under irradiation treatment in the presence of carbon tetrachloride.[26—28] As it turns out, photodehydrogenation is not limited to this pyrazoline among derivatives of coumarin and its analogues. About 20 pyrazolines containing at positions 1, 3, and 5 fragments of coumarin, its analogs, and benzene derivatives underwent photodehydrogenation. A scheme for transformations occurring during the photodehydrogenation process is suggested (Scheme 1).[28]




**1**

($\lambda$ = 405 nm, toluene)

In contrast to authors of work,[29] discussing the photodehydrogenation mechanism of Hantzsch dihydropyridines under similar conditions, we do not assume a direct transfer of energy from the pyrazoline molecule to a $CCl_4$ molecule. During the first stage, pyrazoline apparently is transferred into an excited state, after which an electron is transferred from the excited pyrazoline molecule to the $CCl_4$. The $CCl_4^{\cdot -}$ radical anion is extremely unstable and consequently quickly dissociates into a trichloromethyl radical and a chloride ion. The formed pyrazoline radical cation splits off a proton and reacts with the trichloromethyl radical to form pyrazole. According to this scheme, the aryl(hetaryl)pyrazoline molecule acts as a destruction sensitizer of $CCl_4$ under the effect of radiation. Earlier it was shown that the $CCl_4$ molecule can act as an acceptor of electrons. Accepting an electron, this molecule forms an unstable radical anion, which very quickly dissociates liberating the chloride ion and forming a trichloromethyl radical, which can then abstract a hydrogen atom from the corresponding substrate; in turn, the chloride ion can act as a proton acceptor.[30,31]

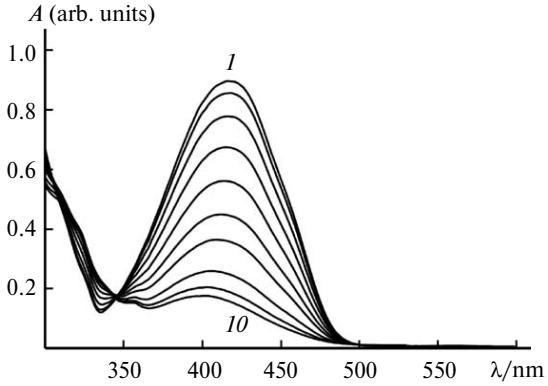
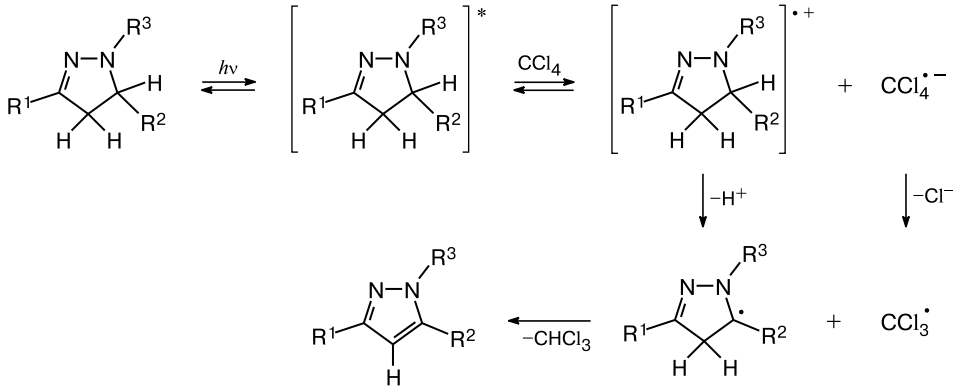


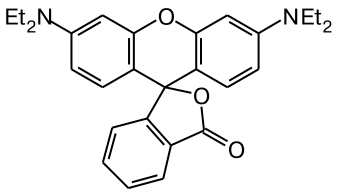

**Fig. 1.** Changes in the absorption spectrum of a solution of pyrazoline **1** ($c$ = 24 μmol $L^{-1}$) in toluene in the presence of hexachloroethane ($c$ = 8.2 mmol $L^{-1}$) before (*1*) and after (*2—10*) irradiation with UV light with a wavelength of 420 nm.

Continuing the study of the photodehydrogenation reaction of aryl(hetaryl)pyrazolines, we investigated their behavior as APG in various media. It was found that the indicated reaction can take place not only in carbon tetrachloride, but also in other solvents in the presence of substrates, which contain trihalomethyl fragments. As it turns out, this reaction proceeds smoothly, for example, in toluene in the presence of hexachloroethane. The change in the absorption spectrum of pyrazoline **1** upon of irradiation its solution in toluene is shown in Fig. 1.

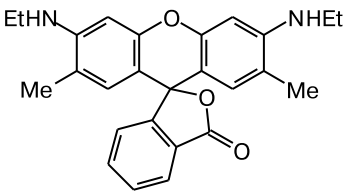
The particularity of the transformation (see Scheme 1) is the abstraction of a proton, *i.e.*, the generation of acidity during the process of irradiation of aryl(hetaryl)coumarin. We studied the possibility of using aryl(hetaryl)pyrazolines as APG for lactone form ring opening and activation of fluorescence of rhodamine dyes, using lactone forms of rhodamine B and rhodamine 19 as examples.

**Scheme 1**

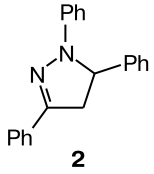




Rhodamine B
($\lambda_{max}^{fl}$ = 587 nm)

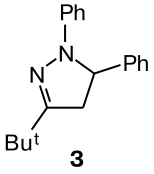


Rhodamine 19
($\lambda_{max}^{fl}$ = 560 nm)



**2**

($\lambda_{max}$ = 385 nm, toluene)



**3**

($\lambda_{max}^{fl}$ = 360 nm, toluene)

For the activation of fluorescence of the lactone forms of these dyes, pyrazolines **1**—**3** were used.

As it turns out, aryl(hetaryl)pyrazolines **1** and **2** are effective activators of fluorescence of rhodamine dyes under irradiation of the corresponding solutions in the pyrazoline absorption maxima in both carbon tetrachloride and toluene with the addition of 2—5% $CCl_4$ or hexachloroethane. For example, irradiation of a solution of pyrazoline **1** and the lactone form of rhodamine B in toluene in the presence of hexachloroethane with filtered light (light filter ZhS-10) leads to the solution changing its color to pink (absorption band with $\lambda_{max}$ = 560 nm) and

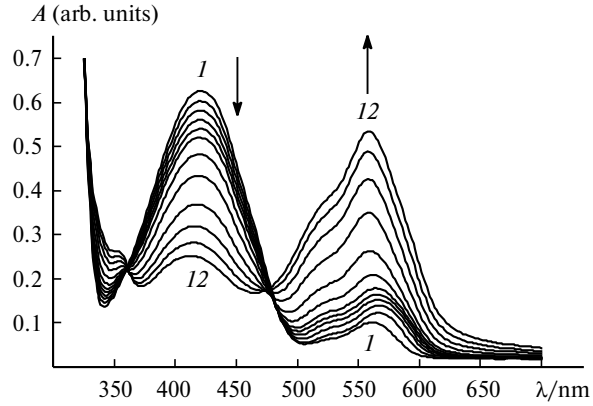



**Fig. 2.** Changes in the absorption spectrum of a solution of pyrazoline **1** ($c$ = 48 μmol $L^{-1}$) and rhodamine B ($c$ = 50 μmol $L^{-1}$) in toluene in the presence of hexachloroethane ($c$ = 840 мкмol $L^{-1}$) before (*1*) and after (*2—12*) irradiation with UV light with a wavelength of 420 nm.

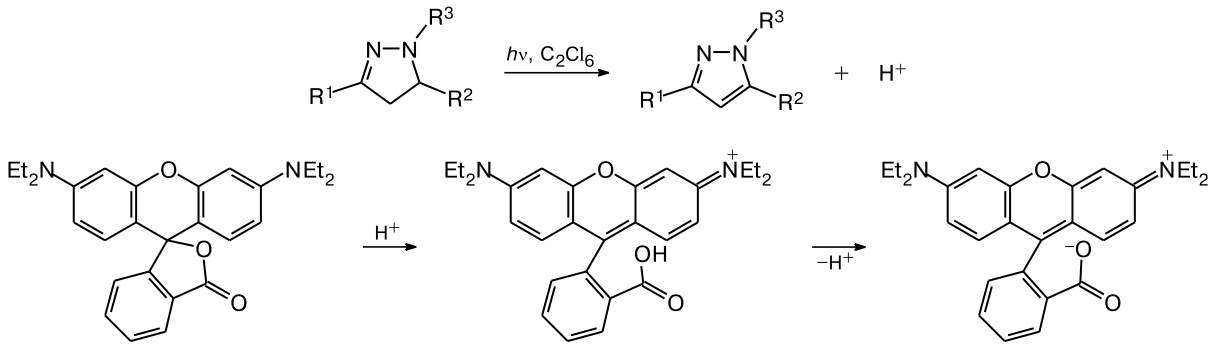
an appearance of a fluorescence band with a maximum at 587 nm that indicates the accumulation of the open form of rhodamine B in the solution (Fig. 2). The irradiation of a solution of the lactone form of rhodamine B not containing pyrazoline **1** under the same conditions does not result in any spectral changes.

The appearance of color of rhodamine B under the indicated conditions is caused by two following reactions occurring in the solution (Scheme 2): the photodehydrogenation of pyrazoline with the proton abstraction and the dye lactone ring opening upon treatment with this proton.

We measured the rates of the indicated reactions in various solvents. First of all, it was determined that the presence of the lactone form of the rhodamine dye in the solution does not significantly affect the rate of pyrazoline photodehydrogenation. The pseudo-first order reaction rate constants in the absence and in the presence of the lactone form of the dye were equal to 0.0402 and 0.0391 mol $L^{-1}$ $s^{-1}$, respectively.

Using the change of the absorption band intensity of pyrazoline **1** (420 nm) and rhodamine B (560 nm) during

**Scheme 2**



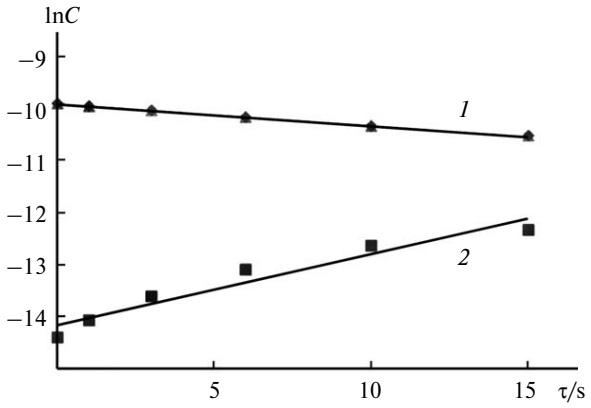


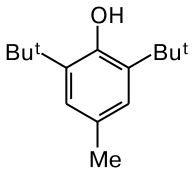

**Fig. 3.** Semilogarithmic plots of the dependence of the substrate concentration (*C*) on the duration of irradiation with UV light with a wavelength of 420 nm for the photodehydrogenation of pyrazoline **1** (*1*) and opening the lactone form of rhodamine B (*2*).

irradiation of the solution, we calculated the rate constants of the reaction of dehydrogenation of pyrazoline **1** and $H^+$-catalyzed opening of the lactone form of rhodamine B. As it can be determined from the linear dependencies $\ln C/\tau$, where $\tau$ is the duration of irradiation, both reaction adhere to first order kinetics (Fig. 3). At that, the photodehydrogenation reaction occurs somewhat slower than lactone ring opening: the rate constants are equal to $0.039\pm0.001$ and $0.122\pm0.006$ mol $L^{-1}$ $s^{-1}$, respectively.

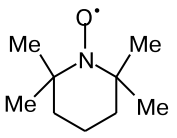
The noted ratio of the two reaction rates was observed in other solvents as well, and, with an increase of solvent polarity, the rate of lactone ring opening increases to a greater degree than the rate of the photodehydrogenation reaction.

Using the results of irradiation of solutions in different solvents and with different concentration ratios of pyrazoline **1** and rhodamine B, we plotted linear dependencies of the concentration as a function of the duration of irradiation ($\ln C/\tau$), which were used to calculate the rate constants of the photodehydrogenation reaction of pyrazoline **1** and lactone ring opening in rhodamine B (Table 1).

A greater sensitivity of lactone ring opening to the solvent polarity is probably explained by the ionic character of this $H^+$-catalyzed reaction. The reaction of photodehydrogenation of pyrazoline is less sensitive to solvent polarity due apparently to a radical character of some of its steps (see Scheme 1). The results of experiments carried out in the presence of inhibitors of radical reactions such as trialkylphenol **4**, nitroxyl radical **5**, acetophenone, and benzophenone, indicate that the character of this reaction is at least partially radical (Table 2).




**4**




**5**

All studied inhibitors decrease the rate of photodehydrogenation reaction of pyrazoline **1**, and the most effective inhibitor turned out to be the nitroxyl radical **5**. A comparably low inhibition effect is probably explained by fact that the step of the pyrazolinyl radical formation (see Scheme 1) is not rate-limiting. Similar changes were also observed in absorption spectra of pyrazolines **2** and **3** upon irradiation of their solutions under the conditions described above in the presence of the lactone form of rhodamine dyes.

At the same time, the changes in the absorption spectra under irradiation of solutions of pyrazoline **1** and lactone form of rhodamine dye in DMF (Fig. 4) is noticeably different from the results, obtained in toluene (see Fig. 2). The absorption maximum of pyrazoline **1** in DMF is located at 380 nm, however, under irradiation it rapidly shifts to a longer wavelength region to 420 nm, further changes being similar to those shown in Fig. 2. We suggest that the spectral changes in the initial stage of phototransformation (see Fig. 4) are caused by tautomeric transformations of pyrazoline **1**. This suggestion is in agreement with the changes in the absorption spectrum of compound **1**, which were observed upon the change of the solvent composition on going from toluene to DMF (Fig. 5) as a result of the transformation of a keto form of pyrazoline **1** to a hydroxy form (Scheme 3).

**Table 1.** Rate constants (*k*) of the photodehydrogenation reaction of pyrazoline **1** (I) and lactone ring opening of rhodamine B (II) in solvents of various polarity

| Solvent | $k$/mol $L^{-1}$ $s^{-1}$ | |
|---|---|---|
| | I | II |
| Toluene | –0.0391 | 0.1057 |
| Ethyl acetate | –0.0625 | 0.1333 |
| Acetone | –0.0931 | 0.9966 |
| MeCN | –0.0589 | 1.0894 |
| DMF | –0.1670 | 1.5407 |

**Table 2.** Rate constants (*k*) of the photodehydrogenation reaction of pyrazoline **1** in toluene with hexachloroethane in the presence of some radical inhibitors

| Inhibitor | $-k$/mol $L^{-1}$ $s^{-1}$ |
|---|---|
| Without inhibitor | 0.0931 |
| Compound **4** | 0.0394 |
| Compound **5** | 0.0227 |
| Acetophenone | 0.0409 |
| Benzophenone | 0.0363 |

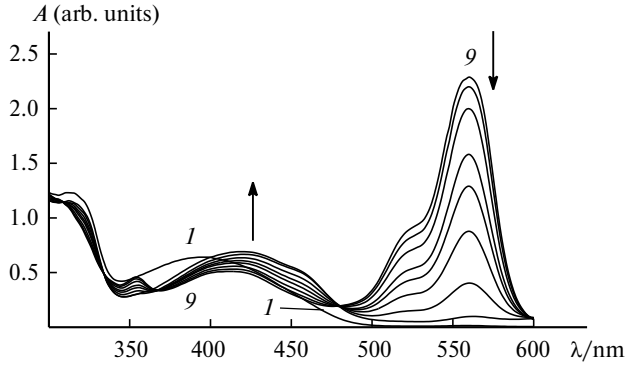



**Fig. 4.** Changes in the absorption spectrum of a solution of pyrazoline **1** ($c$ = 46 μmol $L^{-1}$) and lactone form of rhodamine B ($c$ = 50 μmol $L^{-1}$) in the presence of hexachloroethane in DMF. Duration of irradiation is 2.2 s.

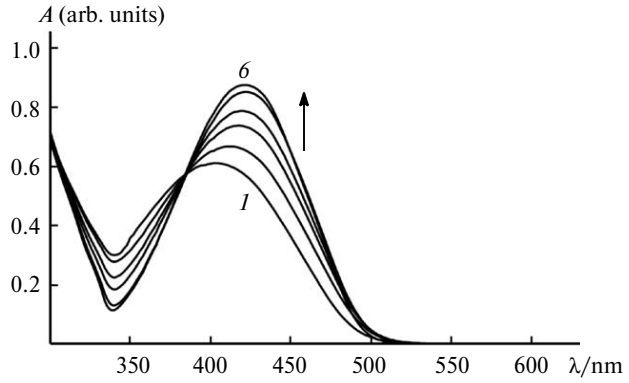



**Fig. 5.** Electron absorption spectra of pyrazoline **1** in DMF (*1*), in the mixtures of DMF—toluene in ratios 8 : 2 (*2*), 6 : 4 (*3*), 4 : 6 (*4*), 2 : 8 (*5*) and in toluene (*6*).

To sum up, under irradiation of a solution of pyrazoline **1** and the lactone form of rhodamine B in the presence of hexachloroethane, initially a tautomeric transition of pyrazoline **1** to a hydroxy form was observed that led to a shift of the absorption maximum of pyrazoline to a longer wavelength region. Further irradiation leads to a gradual photodehydrogenation of pyrazoline **1** and opening of the lactone form of rhodamine B. The following facts are in agreement with the suggested explanation:

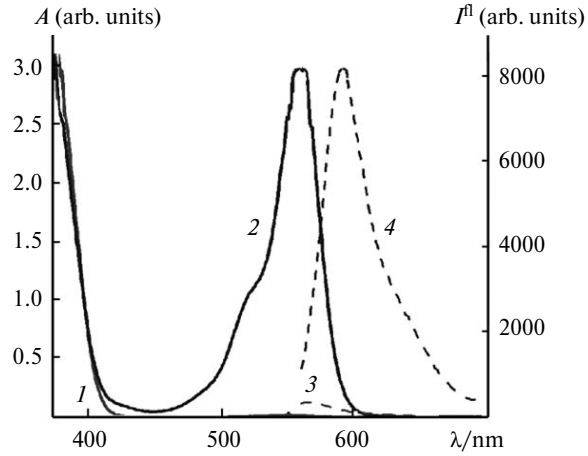
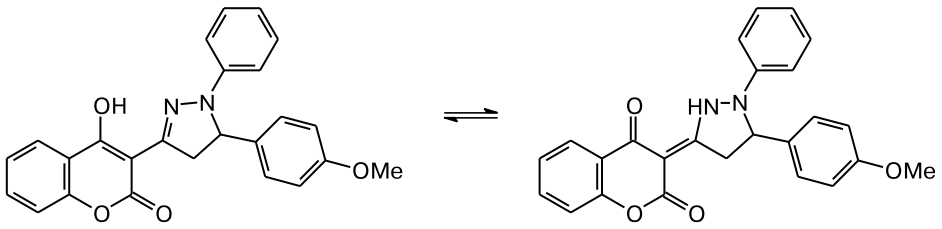



**Fig. 6.** Absorption (*1*, *2*) and fluorescence (*3*, *4*) spectra of pyrazoline **2** (21 mmol $L^{-1}$)—rhodamine B (2 mmol $L^{-1}$)—hexachloroethane (0.18 mol $L^{-1}$) system in a poly(methyl methacrylate) film before (*1*, *3*) and after (*2*, *4*) irradiation with UV light through a light filter UFS-1 (radiation in the 330—400 nm wavelength region).

(i) the irradiation of a solution of the lactone form of rhodamine B in the presence of hexachloroethane in DMF does not lead to noticeable changes in the absorption spectrum; (ii) the irradiation of the solution of pyrazolines **2** and **3** together with the lactone form of rhodamine B in the presence of hexachloroethane in DMF is not accompanied by the changes similar to those observed for pyrazoline **1**, since pyrazolines **2** and **3** cannot undergo tautomeric transformations.

The irradiation of aryl(hetaryl)pyrazolines in polymeric films in the presence of hexachloroethane and the lactone form of rhodamine dyes is also accompanied by activation of fluorescence of the dyes. Figure 6 gives the changes in the absorption and fluorescence spectra of poly(methyl methacrylate) film containing pyrazoline **2**, hexachloroethane, and lactone of rhodamine B upon their irradiation with light with a wavelength of 360 nm (see Fig. 6). The obtained results indicate that the studied media are promising candidates for file type data recording with fluorescent readout.[32,33] Similar to solutions, the irradiation of the lactone form of rhodamine B in a poly(methyl acryl-

**Scheme 3**




Hydroxy form (in toluene) Keto form (in DMF)

ate) film in the absence of pyrazoline does not lead to any spectral changes.

Aryl(hetaryl)pyrazolines are effective photogenerators of acid, providing an irreversible photochemical activation of fluorescence of dyes in the rhodamine group at the irradiation of the corresponding solution in the presence of $CCl_4$ or $C_2Cl_6$. An increase of the polarity of the solvent leads to an increase in both the rates of pyrazoline photodehydrogenation and the dye lactone form opening. Both reactions proceed smoothly in polymeric films, which is interesting for the development of new media for optical data recording with fluorescent readout.

## Experimental

Irradiation was accomplished with a HAMAMATZU lamp (xenon lamp L 5283) with light filter UFS-1 (spectral transmission region 300—400 nm) and ZhS-10 (spectral transmission region >380 nm). Absorption spectra were recorded on a Cary 50 spectrophotometer, and fluorescence spectra were recorded on a Varian Cary Eclipse spectrofluorimeter.

The synthesis and identification of pyrazolines **1** and **2** were described earlier;[28] pyrazoline **3** is a commercially available compound (high purity grade, Aldrich). As precursors of fluorescent dyes, the lactone form of rhodamine B and rhodamine 19 were used (high purity grade, Aldrich). Hexachloroethane was used as a halogen-containing additive (high purity grade, Aldrich).

Polymeric films were prepared using the pouring method. A solution containing poly(methyl methacrylate), the lactone form of rhodamine B or rhodamine 19, pyrazolines **1** or **2**, as well as a halogen derivative in a mixture of toluene—ethyl acetate (1 : 1), was poured onto a horizontally placed Petri dish, afterwards the solvent was evaporated. The films were removed from the substrate before undergoing irradiation. Films of methyl methacrylate copolymer with 2,2,2-trichloroethyl methacrylate containing the lactone form of rhodamine B or rhodamine 19 were prepared in a similar manner. The thickness of the film was 90—100 μm.

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