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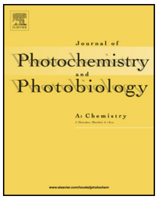

Aryl(hetaryl)pyrazolines as new photoacid generators for optical information recording

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ABSTRACT

Photodehydrogenation of aryl(hetaryl)pyrazolines in the presence of organohalogen compounds has been used for fluorescence activation of Rhodamine laser dyes both in organic solvents and in polymer films. The ability of aryl(hetaryl)pyrazolines as photoacids to generate a highly fluorescent Rhodamine dye can be used for optical information recording.

1. Introduction

The progress in information technologies calls for an increase in the information capacity of recording media, and the rate of information processing demands an extension of their functional capabilities [1–7]. Analysis of the state-of-the-art research into the design of recording media shows that the limiting information capacity of magnetic disks can be increased to 20 GB. The data processing rate may be equal to 1 GB/s.

Apart from magnetic disks, optical disks (ODs) are used for archival information storage of CD type (I), which ensure multiple readouts of the optical data recorded in a recording studio, as well as WORM (write once read many) (II), which ensure a single data recording and multiple data readout directly in a personal computer.

Optical data recording on the majority of the known ODs is based on thermo-induced transformation of compounds. The information capacity of these ODs is about 4.7 GB when a semiconductor laser with a radiation wavelength of 650 nm is used for data readout. Modern ODs developed by the Blu-ray Disc Association possess a record information capacity equal to 25 GB for one-sided and 50 GB for two-sided data media. This is attained by the use of a semiconductor laser with a shorter wavelength (405 nm), an optical system with a digital aperture of 0.7/0.8, and a 0.1-mm thick light-sensitive layer.

The prospects for increasing the information capacity of ODs are related to the design of multilayer light-sensitive recording media for bitwise data recording by 2-photon excitation and thick (more than 2 mm thick) light-sensitive layers for holographic data recording. These ODs can provide a 3D- optical memory of more than 1 TB by data recording and display in different layers of the recording medium in the case of bitwise optical memory, or under different incidence angles of the activating and restoring laser radiation in the case of holographic optical memory. Light-sensitive organic recording media based on photochemical transformations of organic compounds are intended as the recording layers for such ODs. These media have, in principle, a higher resolution than the currently used temperature-sensitive materials.

Light-sensitive photo fluorescent materials appear to be the most promising for the design of the WORM OD recording media for 3D bitwise archive optical memory. The development of these media is based on heterocyclic organic compounds that have no luminescence in their initial form but form fluorescent photoproducts [8–12]. Unfortunately, the development of recording media of this type has not received adequate attention, despite the high demand for WORM ODs. The few studies along this line are represented by the development of organic photoluminescent layers [13–15]. Irreversible light-sensitive recording media with photoinduced fluorescence have been developed, based on

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irreversible photochemical reactions of aromatic azides, diarylamine and tetrabromomethane, as well as haloacridine and naphthacenequinone derivatives [16–19].

Yet another type of WORM materials recording media is composed of two components: a photoacid generator (PAG) and a dye precursor (DP). The DP molecules are colorless and stable in neutral media, however they become strongly colored and fluorescing in the presence of an acid produced by the light-sensitive PAG molecules when they are exposed to light [20,21]. Rhodamine dyes in their passive forms are often used as dye precursors [17,22–24]. For example, lactone forms of these dyes have no fluorescence in neutral media, but easily undergo into strong fluorescent open forms in the presence of acid. Different compounds were tested as photosensitive acid generators: diaryliodonium and triarylsulfonium cations, nitro-aldehydes etc. They are differed in two-photon absorption cross section at the writing wavelength, efficiency of the photoreaction and thermal stability [14]. Despite of intensive studies, use of DP–PAG compositions for optical information recording has still unsolved questions. New PAGs are of interest to diminish subside processes of dye destruction along irradiation and therefore to increase resolution and information capacity of the WORM materials.

In our study, aryl(hetaryl)pyrazolines were found to be photosensitive acid generator compounds which are capable of generating highly fluorescent Rhodamine dye from its lactone form under UV light irradiation both in organic solvents and in polymer films.

2. Experimental

Aryl(hetaryl)pyrazolines have been prepared as it was earlier reported [25]. Copolymer of methylmethacrylate and 2,2,2-trichloroethylmethacrylate has been prepared as it was reported in [26]. The other chemicals were Aldrich HPLC or spectral grade and were used without further purification.

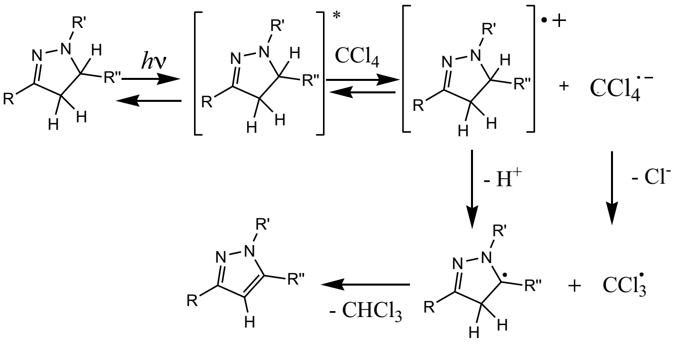
Electronic absorption spectra were recorded on an APELPD-303UV spectrometer in polar (ethanol, DMF) and nonpolar (CCl_4, chloroform) solvents. ^{1}H NMR spectra were measured on a Bruker WP 200-SY spectrometer (200 MHz) in chloroform-d_1, DMSO-d_6, and CCl_4 (in the latter case, a sealed capillary with acetone-d_6 was drawn down into a tube with the sample for lock tuning) using $SiMe_4$ as the internal standard. Photo-irradiation was carried out using an L 5283 xenon lamp (HAMAMATZU lamp) through a light filters to select light in UV region at 360 nm and in the visible region at 420 nm with corresponding glass filters.

Relative rates of the pyrazolines photodehydrogenation and Rhodamine dyes lactone ring opening reactions have been measured by intensity of absorption bands at 420 nm (pyrazoline **1**), 532 nm (Rhodamine B) and 560 nm (Rhodamine 19) both in solvents (CCl_4, toluene and ethyl acetate) and in polymer films (polymethylmethacrylate and its copolymers) in the 0.2–0.7 range of optical density. Rate constants of the first order reactions have been calculated, based on the measured data for 5 runs. Concentrations of the components have been changed as follows: pyrazoline **1** – 12–400 μM, C_2C1_6 – 80–85 mM and Rhodamine lactone form – 10–60 μM. The corresponding values are given in the figures legends and in the Supplementary data.

3. Results and discussion

Previously, we reported the photodehydrogenation of aryl (hetaryl)pyrazolines (**1**) under irradiation in the presence of carbon tetrachloride [27,28]. The following scheme of the aryl(hetaryl) pyrazolines transformation has been proposed (Scheme 1) [28].

In the first step, pyrazoline is transformed, most likely, into the excited state. In the excited state it behaves itself as electron donor.



Scheme 1. The proposed mechanism of aryl(hetaryl)pyrazolines transformation in CCl4 under irradiation at 360 nm.

An electron is transferring from the excited pyrazoline molecule to CCl_4. The determining step in the mechanism is the very fast dechlorination of the radical anion of CCl_4. It has been reported that alkyl and aryl halides undergo reductive dissociation upon accepting an electron either electrochemically or photochemically [30]. For example, the lifetime of the radical anion of CCl_4 was reported to be extremely short (less than 10 ps) [31]. This radical anion dissociates rapidly to the trichloromethyl radical and chloride ion [30]. The formed pyrazoline radical cation releases a proton and transforms into pyrazole upon the interaction with the trichloromethyl radical. An aryl(hetaryl)pyrazoline molecule plays, according to this scheme, a role of the sensitizer of CCl_4 destruction under irradiation.

Photoaromatization of dihydropyridines to pyridines was also reported. It undergoes with CCl_4 destruction followed by proton generation as well [29]. There are also other reports on carbon tetrachloride photodegradation, which occurs *via* the electron transfer to a CCl_4 molecule from the fluorescent dye serving as both the sensitizer and electron source. These reactions are initiated by the visible light irradiation [32,33].

In accordance with Scheme 1, the photodehydrogenation of pyrazolines accompanies by an increase in the acidity of the medium [28]. In continuation of our study on phototransformation of aryl(hetaryl)pyrazolines, we evaluated their function as photoacids with use of both various solvents (CCl_4, toluene, ethyl acetate) and polymer films. We found this reaction to occur not only in carbon tetrachloride but also in other solvents in the presence of organic compounds having trihalomethyl functions. Fig. 1 shows that the photoinduced changes in the electronic absorption spectra of pyrazoline **1** can be seen when its solution in toluene is irradiated in the presence of hexachloroethane: the pyrazoline **1** band at 420 nm decreases while the formed pyrazole absorption in the region 320–360 nm increases along irradiation. The pyrazoline **1** photodehydrogenation undergoes in these conditions as the first-order reaction with the rate constant equal to 0.032 ± 0.001 mol/(l × s) that is much slower than that of pyrazoline **1** photodehydrogenation in carbon tetrachloride, equal to 0.50 ± 0.02 mol/(l × s).

Despite of the lower rate of photodehydrogenation, aryl (hetaryl)pyrazolines can be successfully used for fluorescence activation of Rhodamine dyes lactone forms, namely, Rhodamine B and Rhodamine 19.

Lactone forms of Rhodamine dyes are converted into open forms in the presence of acids. The Rhodamine dyes open forms are characterized by strong fluorescence [34]. We have found fluorescence activation of Rhodamine dye lactone forms to occur when their solutions are irradiated in the presence of aryl(hetaryl) pyrazolines. Pyrazolines **1** and **2** were used in this study as photoacids.