



One-pot synthesis of new acid photogenerators for Rhodamine laser dyes fluorescence activation



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ARTICLE INFO

Article history:

Received 22 June 2016

Received in revised form

6 September 2016

Accepted 7 September 2016

Available online 12 September 2016

Keywords:

One-pot synthesis

Aryl(hetaryl)pyrazolines

Michael addition

Photodehydrogenation

Fluorescence

Optical memory

ABSTRACT

New aryl(hetaryl)pyrazolines fitted for fluorescence activation of Rhodamine laser dyes have been obtained via one-pot tandem Michael addition of two arylhydrazine molecules with 2-(4'-R-cinnamyliden)-2H-furo[3,2-c]coumarin-3-ones. These aryl(hetaryl)pyrazolines do not undergo tautomeric transformations both in organic solvents and in polymer films and behave themselves as effective acid photogenerators of Rhodamine dyes fluorescence activation. New aryl(hetaryl)pyrazolines can be used in the fabrication of two-photon volumetric optical memory materials.

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1. Introduction

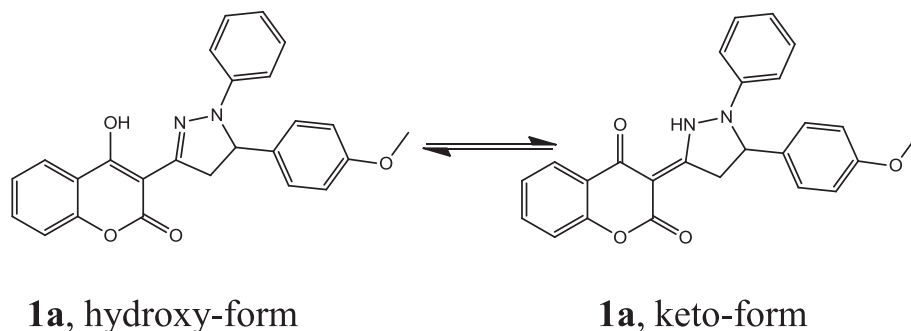
Optical disks (ODs) are widely used for archival information storage of WORM type (Write Once Read Many), which ensure multiple readouts of the recorded optical data. Increasing the information capacity of ODs is an urgent problem. It is related to the design of multilayer light-sensitive recording media. The media based on photochemical transformations of organic compounds are intended as the recording layers for such ODs, since light-sensitive photofluorescent materials appear to be the most promising for the design of the WORM OD recording media for 3D bitwise archive optical memory. They are based on heterocyclic organic compounds that have no luminescence in their initial form but form fluorescent photoproducts. Reverse fluorescence behavior of recording media is also applicable. Moreover, organic photosensitive media have, in principle, a higher resolution than the currently used temperature-sensitive materials. The most perspective type of

WORM materials recording media is composed of two components: a photogenerator of acidity (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 [1–10].

4-Hydroxy-3-pyrazolinylcoumarins **1** have been earlier found to undergo quantitative photodehydrogenation to 4-hydroxy-3-pyrazolylcoumarins in the presence of CCl₄ or C₂Cl₆ [11]. Due to the reaction they behave themselves as photogenerators of H⁺-acidity that are able to generate highly fluorescent Rhodamine dye from its lactone form under UV light irradiation both in organic solvents and in polymer films. However, 4-hydroxycoumarin derivatives **1**, depending on the media composition, have been found to undergo hydroxy-keto tautomeric transformations. For example, 4-hydroxy-3-pyrazolinylcoumarin **1a** shown below exist in hydroxy-form in toluene and in keto-form in dimethylformamide. Meanwhile, as we have earlier shown, substrates **1** can effectively operate as acid photogenerators being only in hydroxy-form [11c]. Therefore, search of new acid photogenerators for archival recording process is in a obvious demand.

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In this paper we report a new way to synthesize effective acid photogenerators. “Substitution” of a furanone ring for a pyrazole one in 2H-furo[3,2-c]coumarin-3-one derivatives via tandem interaction of 2-(4'-R-cinnamylidene)-2H-furo[3,2-c]coumarin-3-ones with 2 mol of arylhydrazines chlorohydrates provides a new one-pot regioselective route to 2-phenylchromeno[4,3-c]pyrazol-4(2H)-one derivatives. These derivatives possess photosensitivity, form nonfluorescent photoproducts, do not undergo tautomeric transformations in different medium and behave themselves as more effective photogenerators of Rhodamine dyes lactone opening.

2. Experimental

2.1. Materials

The deuterated solvent (CDCl_3) for NMR spectroscopy was obtained from Merck.

The lactone form of Rhodamine B was used as precursor of fluorescent laser dye (high purity grade, Aldrich). Hexachloroethane was used as an halogen-containing additive (high purity grade, Aldrich). The other chemicals were Aldrich HPLC or spectral grade and were used without further purification.

Polymeric films were fabricated using the pouring method. A solution containing poly(methyl methacrylate), the lactone form of Rhodamine B, pyrazoline **7a**, as well as an 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.

2.2. General equipment

^1H , ^{13}C and ^{15}N NMR spectra were recorded on « Bruker AMX-III 400 » and 300 — « Bruker AVANCE-II 300 » spectrometers in CDCl_3 containing 0.05% Me_4Si as the internal standard. Determinations of structures and stereochemistry of obtained compounds and assignments of ^1H , ^{13}C and ^{15}N signals were made with the aid of COSY (2D ^1H , ^1H homonuclear shift correlation spectroscopy), TOCSY (2D ^1H , ^1H homonuclear total shift correlation spectroscopy), NOESY (Nuclear Overhauser Effect (NOE) based 2D ^1H , ^1H homonuclear shift correlation spectroscopy), HSQC (2D ^1H -detected ^1H , ^{13}C correlation via heteronuclear single quantum coherence and double inept transfer), edited-HSQC (HSQC with CH multiplicity editing), HMBC (2D ^1H -detected ^1H , ^{13}C multiple bond correlation via heteronuclear zero and double quantum coherence optimized on long range couplings), LR-HMBC (long range HMBC optimized on very small couplings), ^{15}N -HMBC (^1H , ^{15}N HMBC using natural abundance of ^{15}N - isotope) and ^{15}N -LR-HMBC (long range ^1H , ^{15}N HMBC optimized on very small couplings) spectra.

Mass-spectra were recorded on Kratos MS-30, ionizing energy equal to 70 eV. Chromato-mass spectra have been obtained on spectrometer PE SCIEX API165 (ELSD UV254), column Synergi 2u Hydro-RP Mercury, 20×2.0 mm. Electronic absorption spectra were recorded on an APELDPD_303UV spectrometer and fluorescent spectra — on Cary Eclipse (Varian) spectrofluorimeter. Photo-irradiation was carried out using an L 5283 xenon lamp (HAMA-MATZU lamp) through a light filter to select light in UV region at 360 nm and in the visible region at 420 nm with corresponding glass filters. Analytical thin layer chromatography was performed on silica gel plates (Merck, Kieselgel 60, 0.25 thickness) with F254 indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70–200 or 230–400 mesh).

2.3. Single crystal X-ray analysis

The X-ray crystal structure analysis was made on a Bruker SMART APEX2 CCD ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, $T = 120$ K, $2\theta_{\text{max}} = 56.5^\circ$). The structure was solved in Olex2 [12] with the ShelXT [13] structure solution program using Direct Methods and refined with the ShelXL [14] refinement package using Least Squares minimization. Non-hydrogen atoms were refined anisotropically. Crystal data for **7a**: $\text{C}_{33}\text{H}_{25}\text{Cl}_3\text{N}_4\text{O}_2$ ($M = 615.92$ g/mol): triclinic, space group P-1 (no. 2), $a = 10.2992(7)$ Å, $b = 10.6702(8)$ Å, $c = 14.7989(11)$ Å, $\alpha = 76.790(2)^\circ$, $\beta = 86.793(2)^\circ$, $\gamma = 68.3190(10)^\circ$, $V = 1470.55(19)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.391$ g/cm³, 16939 reflections measured ($2.828^\circ \leq 2\theta \leq 56.56^\circ$), 7312 unique ($R_{\text{int}} = 0.0334$, $R_{\text{sigma}} = 0.0520$) which were used in all calculations. The final $R = 0.0584$ ($I > 2\sigma(I)$) and $wR2 = 0.1183$ (all data). Crystal structure has been deposited with Cambridge Crystallographic Data Center (CCDC reference number 1454727).

2.4. Powder diffraction study

Powder pattern was measured with Huber G670 Guinier camera ($\text{Cu K}\alpha_1$ radiation, $\lambda = 1.54059$ Å, transmission mode) in the $3\text{--}70^\circ$ 2θ region. Orthorhombic unit-cell dimensions were determined using three indexing programs: TREOR90, ITO and AUTOX. Space group $Pbca$ was assigned taking into account the systematic extinctions. The crystal structure was solved with the use of simulated annealing technique and molecular model taken from the single-crystal structure of solvated form. The solution found was refined with the program MR1A via a bond-restrained Rietveld refinement (see Fig. 2B in SI) in the same way as was reported earlier. Crystal data for solvent free **7a**: $\text{C}_{32}\text{H}_{24}\text{N}_4\text{O}_2$ ($M_r = 496.55$ g/mol): orthorhombic, space group $Pbca$ (no. 61), $a = 48.703(4)$ Å, $b = 14.5829(19)$ Å, $c = 7.1614(11)$ Å, $V = 5086.2(11)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.297$ g/cm³, powder pattern was measured in $3\text{--}70^\circ$ 2θ region with 0.01° step. The final R-factors are: $R_p = 0.0231$,

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