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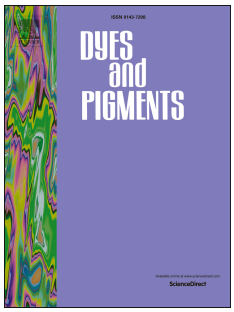

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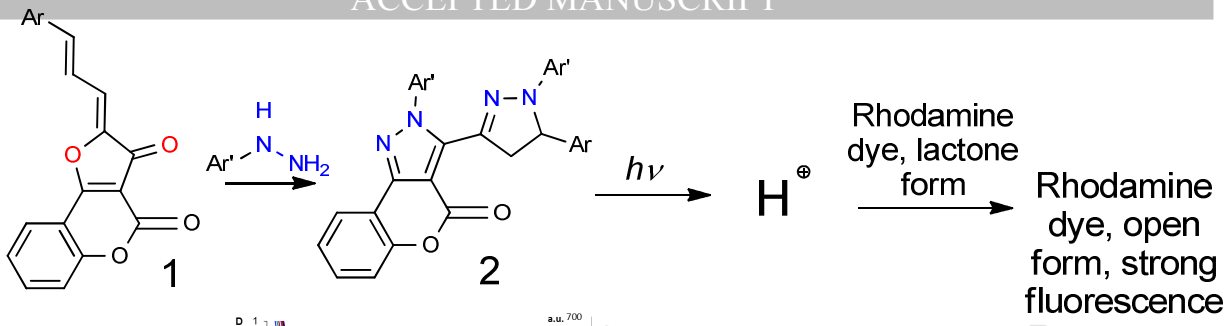
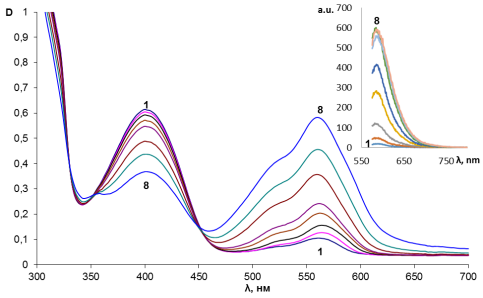
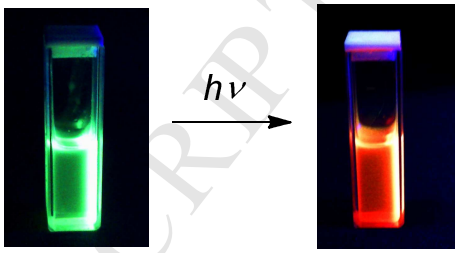


Absorption and emission spectra under illumination of 2





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

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Supporting Information

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.

Keywords:

One-pot synthesis

Aryl(hetaryl)pyrazolines

Michael addition

Photodehydrogenation

Fluorescence

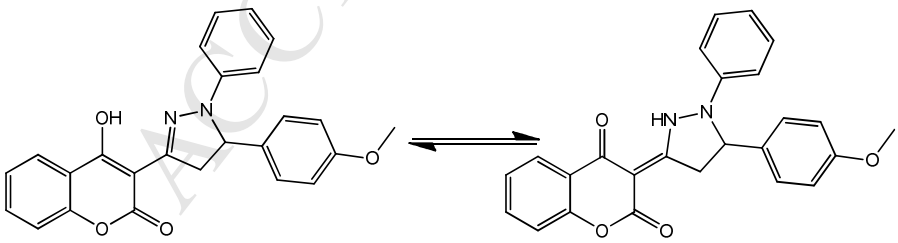
Optical memory

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 CCl_4 or C_2Cl_6 [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.



1a, hydroxy-form **1a**, keto-form

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-cinnamyliden)-2H-furo[3,2-c]coumarin-3-ones with 2 mols of arylhydrazines chlorohydrates provides a new one-pot regioselective route to 2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one derivatives. These derivatives possess photosensitivity, form nonfluorescent photoproducts, do not undergo tautomeric trnsformations in different medium and behave themselves as more effective photogenerators of Rhodamine dyes lactone opening.

2. Experimental

2.1. Materials

The deuterated solvent (CDCl3) for NMR spectroscopy was obtained from Merck. The lactone form of Rhodamine B was used as precursor of flurescent 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

^{1}H, ^{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 ^{1}H, ^{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,13C correlation via heteronuclear single quantum coherence and double inept transfer), edited-HSQC (HSQC with CH multiplicity editing), HMBC (2D 1H-detected 1H,13C 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), 15N-HMBC (1H,15N HMBC using natural abundance of 15N-isotope) and 15N-LR-HMBC (long range 1H,15N 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, 20x2.0 mm. Electronic absorption spectra were recorded on an APELPD_303UV spectrometer and fluorescent spectra – on Cary Eclipse (Varian) spectrofluorimeter. Photo-irradiation was carried out using an L 5283 xenon lamp (HAMAMATZU 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 (MoKα radiation, λ = 0.71073 Å, graphite monochromator, T = 120 K, 2θmax = 56.5°). 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**: $C_{33}H_{25}Cl_3N_4O_2$ (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, α = 76.790(2)°, β = 86.793(2)°, γ = 68.3190(10)°, V = 1470.55(19) $Å^3$, Z = 2, Dcalc = 1.391 g/cm^3, 16939 reflections measured (2.828° ≤ 2Θ ≤ 56.56°), 7312 unique (Rint = 0.0334, Rsigma = 0.0520) which were used in all calculations. The final R = 0.0584 (I > 2σ(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*

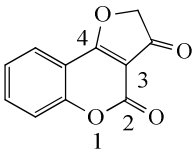
Powder pattern was measured with Huber G670 Guinier camera (Cu $K_{\alpha 1}$ radiation, λ = 1.54059 Å, transmission mode) in the 3 – 70° 2θ region. Orthorhombic unit-cell dimensions were determined using three indexing programs: TREOR90, ITO and

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 MRIA *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**: $C_{32}H_{24}N_4O_2$ (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) Å^3, Z = 8, D_{calc} = 1.297 g/cm^3, powder pattern was measured in 3 – 70^o 2θ region with 0.01^o step. The final R-factors are: R_p = 0.0231, R_{wp} = 0.0297, R_{exp} = 0.0177, χ^2 = 2.83. Crystal structure has been deposited with Cambridge Crystallographic Data Center (CCDC reference number 1443154).

3. Synthesis

We have found a novel way to synthesize pyrazolines of coumarin series. Interactions of coumarin α,β-unsaturated carbonyl derivatives with arylhydrazines is known to provide promising route to new heterocyclization reactions [15-21]. For example, interaction of 2,3-dihydrofuro[3,2-c]coumarin-3-one **2** and its benzilydene derivatives **3** with arylhydrazines has earlier been studied [22,23]. Compound **2** reacts with phenylhydrazine in acetic acid or in toluene with formation of hydrazinoimine **4** as the only product both at excess of phenylhydrazine and at reactants equimolar ratio [22].

Compounds **3** interact with phenylhydrazine in toluene with formation of ozazone **5** [23]. It should be noted, that furanone ring opening undergoes in both reactions without breaking of C(4, coumarin)-O(furanone) bond.



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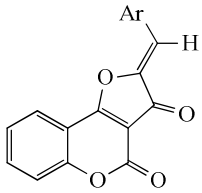

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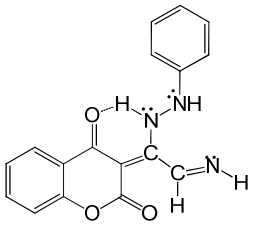

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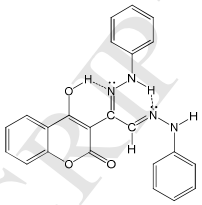
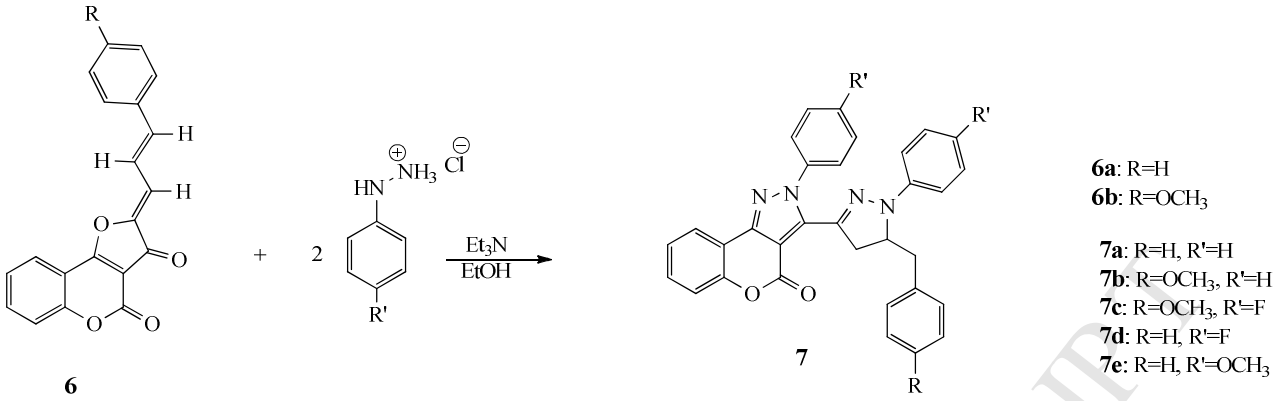


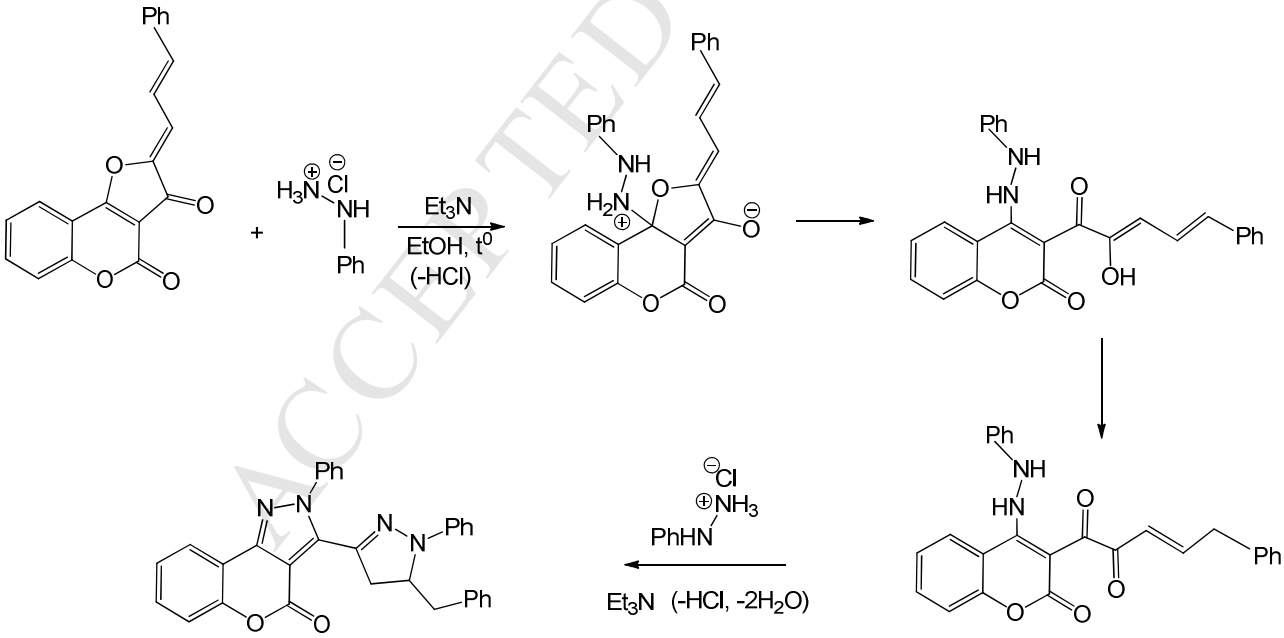
5

Another path of coumarin derivatives interaction with arylhydrazines is reported in this paper. Reaction of cinnamylidene derivatives **6** with arylhydrazine chlorohydrates undergoes with "substitution" of furanone ring in 2H-furo[3,2-c]coumarin-3-one fragment for pyrazole cycle. The C(4, coumarin)-O(furanone) bond and C-C(furanone) bond turned to be substituted for C=N and C-N bonds respectively along heating of compounds **6** with 2.5 mols arylhydrazine chlorohydrates in ethanol for 2 hours. 3-(5-Benzyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)-2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-ones **7** (**6**) have been found as predominant products of the reaction with yields up to 53% (Scheme 1).



Scheme 1. Synthesis of 3-(4,5-dihydro-1*H*-pyrazol-3-yl)-chromeno[4,3-*c*]pyrazol-4(2*H*)-ones **7**.

One can suggest that interaction of compounds **6** with arylhydrazines chlorohydrates undergoes by the Scheme 2.



Scheme 2. Proposed mechanism of 3-(4,5-dihydro-1*H*-pyrazol-3-yl)-chromeno[4,3-*c*]pyrazol-4(2*H*)-ones **7** formation.

On the first step 2H-furo[3,2-c]coumarin-3-one **6a** reacts with phenylhydrazine as a nucleophile at position 4 of coumarin fragment, since the coumarin 3-4 double bond is strongly activated to such Michael addition by two carbonyl functions that are conjugated with this bond. Michael addition is then followed by furanone cycle opening and intermediate enolate-ion formation. Subsequent intramolecular cyclization of phenylhydrazido-function to pyrazole ring leads to 3-cinnamoyl-2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one unit. Its tandem interaction with the second mol of arylhydrazine provides formation of the final compound **7a**.

The proposed mechanism (Scheme 2) of interaction 2H-furo[3,2-c]coumarin-3-one cinnamylidene derivatives with arylhydrazine chlorohydrates is in accordance with exclusive formation 2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one key fragment of the compounds **7** in the reaction. The reported route of 2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one derivatives syntheses is based on interaction 3-acetyl-4-hydroxycoumarin phenylhydrazone with phenylhydrazine chlorohydrate. It undergoes with formation of mixture of 2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one and 1- phenylchromeno[4,3-*c*]pyrazol-4(1*H*)-one derivatives [24, 25].

4. Structural aspects

The composition of the final products **7** was established by means of elementary analyses and HRMS. New pyrazolines of coumarin series possess very poor crystalization ability. Therefore, structures of all compounds were determined by ^{1}H, ^{13}C and ^{15}N NMR

spectroscopy using 1D and 2D HSQC and HMBC spectra. Structure of the compound **7a** was determined in much more detail with use of DEPT, COSY, TOCSY, NOESY, editing-HSQC, LR-HMBC, ^{15}N-HMBC and ^{15}N-LR-HMBC spectra (SI, p.8). Key cross-peaks and correlations in 2D NMR spectra are shown in Fig. 1 by color arrows. Looking for molecular structures of the final compounds, **7b** sample labelled by two ^{15}N-atoms (N11 and N22) has been obtained in the reaction of **6b** with of $^{15}NH_2$-NH-C_6H_5.HCl (SI, p.3).

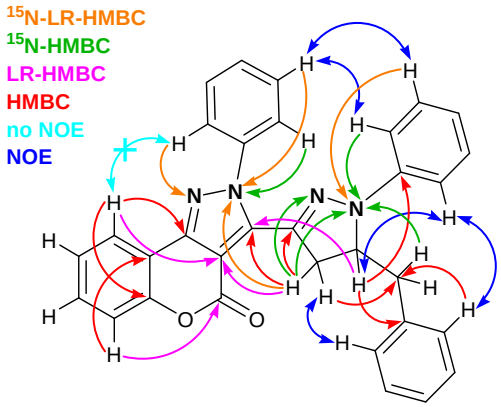


Fig. 1. Key cross-peaks and correlations in 2D NMR spectra for the **7a** structure assignments indicated by arrows (blue – NOE; light blue – absence of NOE; red – HMBC; pink – LR-HMBC; green – ^{15}N-HMBC; orange – ^{15}N-LR-HMBC).

Crystallization of the compounds **7** from different solvents has not provided crystals suitable for X-ray diffraction studies, since powder samples have only been isolated along the procedure. However, crystals suitable for X-ray diffraction studies have been obtained for compound **7a** chloroform solvate by slow concentration of its chloroform solution. The molecular structure of **7a** chloroform solvate is represented in Fig. 2

(structure **A**). Chromeno[4,3-c]pyrazol-4-one fragment is almost planar, it forms angles of 57° with the plane of the phenyl and of 31° with the plane of the C21–N22 double bond, which, in its turn, forms an angle of 8° with the plane of the neighboring phenyl. Molecule conformation is stabilized by intramolecular N22-pi(C13) stacking with N22-C13 distance being 2.93 Å and intramolecular hydrogen bond (C31–H…O2) with C…O distance being 3.106(2) Å and C–H…O angle being 140°. Analysis [26, 27] of calculated electron density (PBE0-D3/TZVP, see SI) estimates this CH…O interaction to be ~6 kcal/mol (see S4 for details), thus being a strong hydrogen bond [28]. The crystal structure of **7a** chloroform solvate is stabilized by C–H…N and C–Cl…N interactions of **7a** with chloroform, intermolecular C–H…O bonds and chromenone-phenyl π-stacking (SI, p. 4, 5).

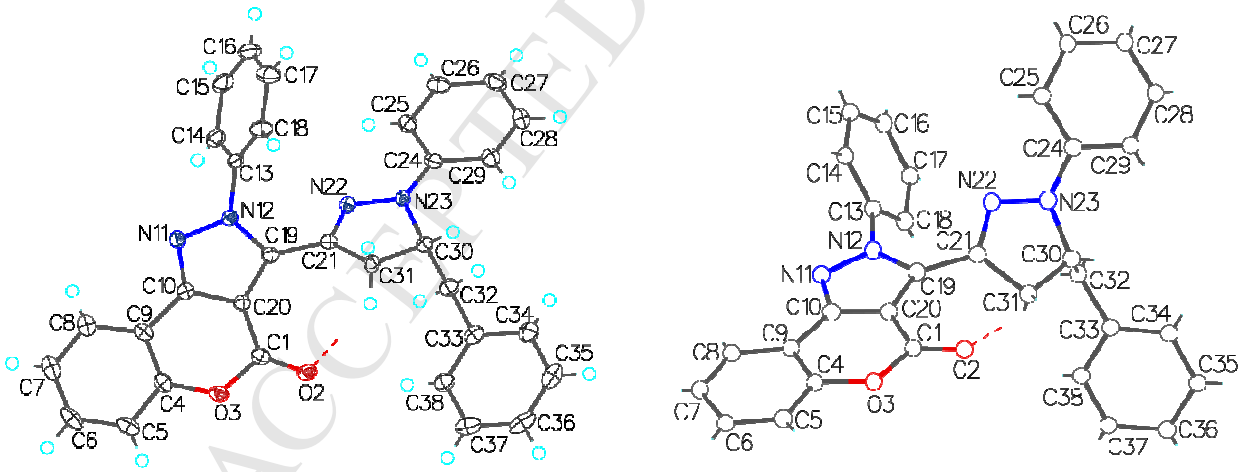


Fig. 2. A - General view of compound **7a** in its chloroform solvate given with atomic displacement ellipsoids at p=50%; **B** - Molecule conformation of **7a** in its pure form

(powder XRD study).

Molecule conformation of **7a** in its pure form has been found from powder XRD study following the procedure used by us earlier (Fig. 2, structure **B**) [29]. This conformation is quite different from that in the chloroform solvate (Fig. 2, structure **A**). The main change is the twist around C19-C21 bond. Although, conformation is again stabilized by similar N22-pi(C13) stacking and rather strong C31–H…O2 bond, however, involving a different hydrogen.

5. Compounds 7 as photogenerators of H^+-acidity

Compounds **7** possess photochemical activity and behave themselves as acid photogenerators (abbreviated in this paper as **PAGs**). As it is seen in Fig.3, they change both absorption and emission spectra in carbon tetrachloride or in toluene + C_2Cl_6 (2-5%) under illumination at the absorption maximum of compound **7**. Due to phototransformation of compound 7a emission of its solution (λ_{max} at 505 nm) is disappeared along illumination since photoproduct practically has no fluorescence (λ_{max} at 400 nm).

Being illuminated in the same solutions in the presence of acid-base indicators, Thymol Blue, for instance, compounds **7** provide coloring related to the increase of solution acidity. The compounds **7** activate also intensive fluorescence of laser

Rhodamine dyes, namely Rhodamine B, when illuminated in the presence of Rhodamine lactone forms. These forms are known to be easily converted into open forms in the presence of acids [30].

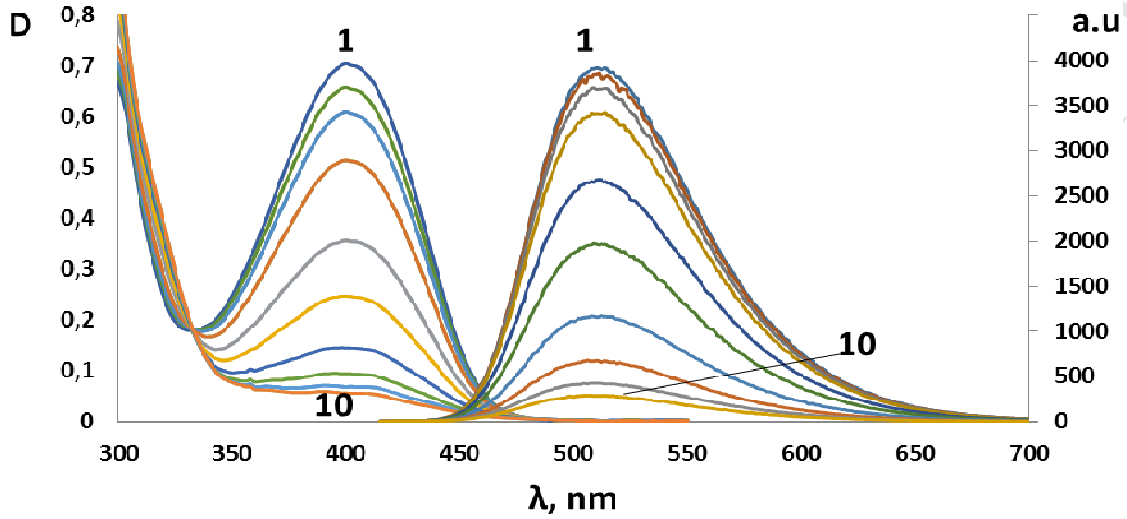


Fig. 3. Electronic absorption (left) and emission (right, excitation wavelengths = 305 and 400 nm) spectra of compound **7a** in toluene (+ C_2Cl_6) solution before (1) and after (2-10) irradiation at 420 nm

The changes in the electronic absorption and emission spectra of toluene (+C_2Cl_6) solution, containing compound **7a** and Rhodamine B lactone form are shown in Fig. 4: the increase in intensity of the absorption band at 560 nm and of the emission band at 590 nm is due to an increase in the concentration of the Rhodamine B open form. It is important that similar irradiation of Rhodamine B lactone form in toluene containing C_2Cl_6 without compound **7a** does not result in any spectral changes. It should be noted that electronic absorption of compound **7a** photoproduct is shifted into the shorter

wavelengths (as it is seen in Fig. 3) and do not intersect emission band of Rhodamine B open form. These results provide good perspectives for new pyrazolines to be used in archival optical recording media as acid photogenerators. As we have shown, compounds 7 effectively activate Rhodamine B fluorescence in polymer films as well.

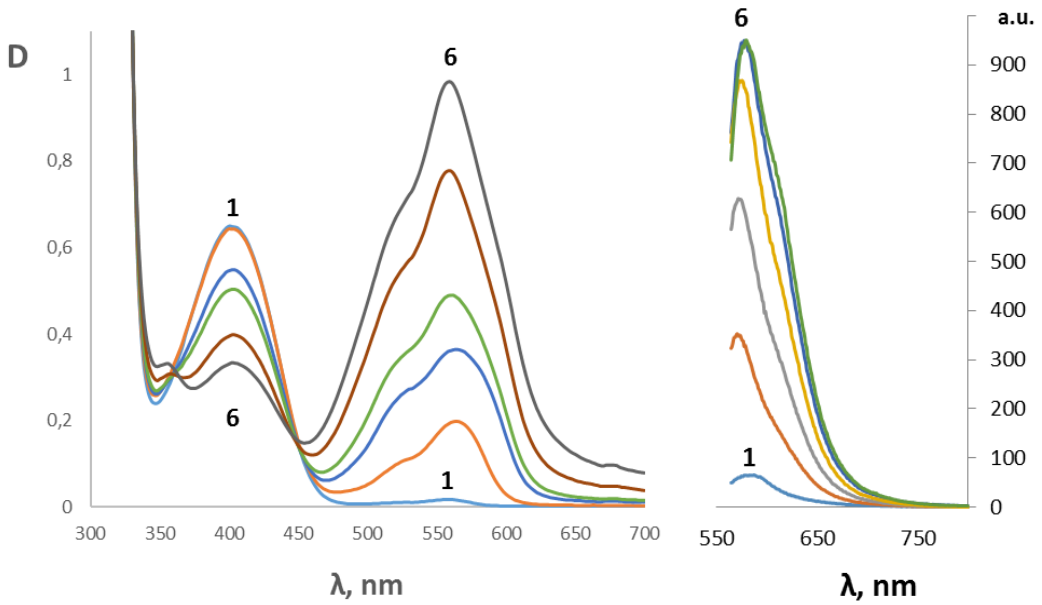


Fig. 4. Electronic absorption (left) and emission (right, excitation wavelength = 560 nm) spectra of toluene (+C_2Cl_6) solution, containing compound **7a** and Rhodamine B lactone form before (1) and after (2-6) irradiation at 420 nm

Irradiation of both polymethylmethacrylate (PMMA) and polystyrene films containing compound **7a**, hexachloroethane and Rhodamine B lactone form at 360 nm provides coloring and fluorescence activation of the polymer films. Absorption and emission spectra of the PMMA film along illumination are shown in Fig. 5.

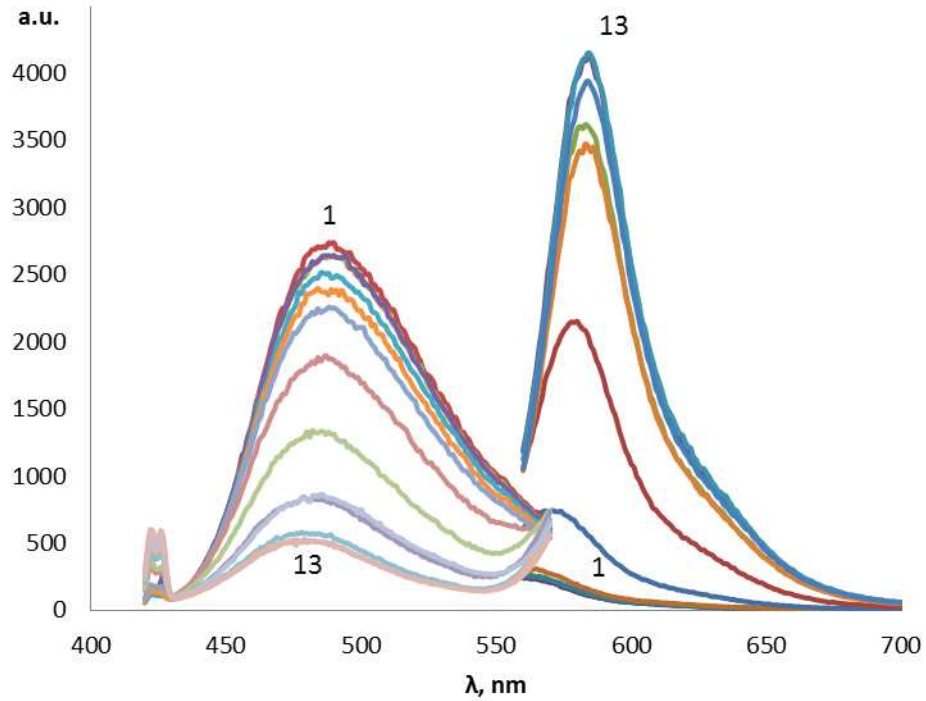
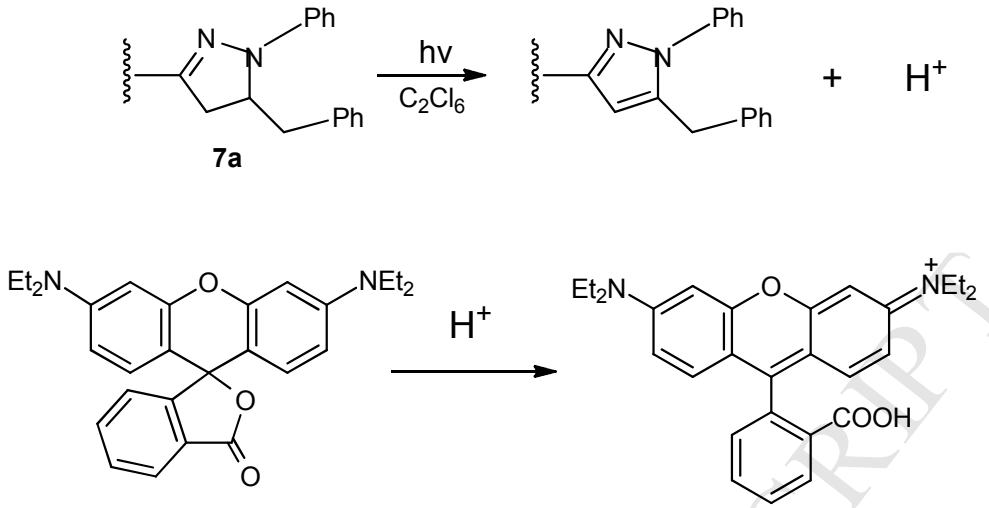


Fig. 5. Emission (right) spectra of PMMA film, containing compound **7a**, Rhodamine B lactone form and C_2Cl_6 before (1) and after (2-13) irradiation at 420 nm (excitation wavelengths = 400 and 560 nm)

Two organic reactions which initiate the coloring of a PMMA film, namely photodehydrogenation of pyrazoline derivative **7a** and Rhodamine B lactone ring opening, occur in a polymer matrix (Scheme 3).



Scheme 3. Acid photogeneration by new coumarinylpyrazolines for Rhodamine laser dye fluorescence activation

PAGs are widely used for a vast range of practical applications including optical information recording, microlithographic imaging with photoresists, photodynamic therapy and photocontrol of enzymatic activity [31]. For instance, arylsulfonium salts provide acid generation under illumination and efficiently initiate Rhodamine fluorescence activation in optical information recording materials. Photochromic bis(thiazolyl)benzothiophene derivatives have been found as effective photoinitiators for the cationic polymerization of cyclohexene oxide. However, the reported **PAGs** absorb light in the near UV-region which is not fitted for some (e.g. biochemical) applications. In opposite, compounds **7** are photosensitive at 360-420 nm, have no tautomeric transformation, form nonfluorescent photoproduct and look therefore as rather perspective **PAGs**.

Moreover, new coumarinylpyrazolines 7 can be useful in optical information

recording not only as acid photogenerators. In opposite to 4-hydroxy-3-pyrazolinylcoumarins **1** that form fluorescent products under illumination, compounds 7 are dehydrogenated with complete disappearing of intensive fluorescence as it is seen in Fig. 3. This property provides application of coumarinylpyrazolines 7 in optical information recording without use of Rhodamine lactone form or any other additional source of fluorescence.

6. Synthetic procedures

2H-Furo[3,2-c]chromene-3,4-dione **2** has been obtained as reported in [22]. Below synthetic protocols are given for compounds **6a** and **7a**. Synthesis of other compounds is described in SI.

*6.1. Synthesis of compound **6a***

Cinnamaldehyde (2 mmols) in 3 ml acetic acid has been added by dropwise to solution of 2H-furo[3,2-c]chromene-3,4-dione **2** (1.5 mmol) in 15 ml acetic acid. The mixture has been boiled for 1 h. The formed precipitate was filtered off and recrystallized from acetic acid.

2-[3-phenylprop-2-en-1-ylidene]-4H-furo[3,2-c]chromene-3,4(2H)-dione **6a:** Yield 30% (AcOH), m.p. 229-230 ^{o}C. ^{1}H NMR (200 MHz, $CDCl_3$): 7.01 (dd, 1H, H(α), $^{3}J_{H(\alpha),\ H(\beta)}$ =11.6, $^{4}J_{C\alpha H,\ C\gamma H}$=0.6), 7.17 (d, 1H, H(γ), $^{3}J_{H(\beta),H(\gamma)}$=15.8),7.34 (dd, 1H, H(β), $^{3}J_{H\alpha,\ H\beta}$=11.6, $^{3}J_{H(\beta),\ H(\gamma)}$=15.8), 7.38-7.65 (m, 7H, H(2′), H(3′), H(4′), H(5′), H(6′), H(6), H(8)), 7.82 (m, 1H, H(7)), 8.09 (dd, 1H, H(5), $^{3}J_{H(5),H(6)}$=8.0, $^{4}J_{H(3),\ H(7)}$=2.0). MS, m/z: 316 ([M], 70), 317 ([M+1] 20). Found(%): C, 76.01; H, 3.80. Calc. for $C_{20}H_{12}O_4$(%): C, 75.94; H,

3.82.

*6.1. Synthesis of compound **7a***

Compound **6a** (1 mmol) and arylhydrazine chlorohydrate (2.5 mmol) have been boiled for 2 h in 20 ml of ethanol in the presence of 1 ml of triethylamine. The formed precipitate has been filtered off and recrystallized from ethanol.

3-(5-benzyl-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-2-phenylchromeno[4,3-c]pyrazol-4(2H)-one **7a:** Yield 53%(EtOH), m.p. 155-156^{o}C. ^{1}H NMR (200 MHz, $CDCl_3$+DMSO-d_6): 2.70 (dd, 1H, Ha(13), $^{2}J_{H(a),H(b)}$=14.0, $^{3}J_{H(b),CH}$=2.0), 2.93 (dd, 1H, H_b (13), $^{2}J_{H(a),H(b)}$=14.0, $^{3}J_{H(a),CH}$=8.0), 3.58 (narrow m, 2H, CH_2(11)), 4.64 (m, 1H, H(12)), 6.64(d, 2H, H(2‴), H(6‴), $^{3}J_{H,H}$=8.0), 6.77 (t, 1H, H(4‴), $^{3}J_{H,H}$=8.0), 7.05-7.55(m, 15H, H(3‴), H(5‴), H(2″), H(6″), H(3″), H(5″), H(4″), H(2′), H(3′), H(4′), H(5′), H(6′), H(6), H(7), H(8)), 8.04 (dd, 1H, H(5) ,$^{3}J_{5,6}$=8.0, $^{4}J_{5,7}$=2.0). MS, m/z: 497,5 (100) [M+1]. Found (%): C, 77.31; H, 4.86; N, 11.30. Calc. for $C_{32}H_{24}N_4O_2$(%): C, 77.40; H, 4.87; N, 11.28.

7. Conclusions

In conclusion, we report “substitution” of a furanone ring for a pyrazole one in 2H-furo[3,2-c]coumarin-3-one derivatives via one-pot tandem reaction of 2-(4’-R-cinnamyliden)-2H-furo[3,2-c]coumarin-3-ones with 2 mols of arylhydrazines chlorohydrates. The reaction provides new regioselective route to 2-phenylchromeno[4,3-*c*]pyrazol-4(2*H*)-one derivatives. These aryl(hetaryl)pyrazolines do not undergo

tautomeric transformations both in organic solvents and in polymer films and behave themselves as effective acidity photogenerators of Rhodamine dyes fluorescence activation. In this sense the new aryl(hetaryl)pyrazolines look to be more effective in the fabrication of two-photon volumetric optical memory materials when compared with 4-hydroxy-3-pyrazolinylcoumarins **1**.

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Notes

The authors declare no competing financial interest.

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