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Synthesis of New Efficient Laser Dyes of Red Spectral Range, the DCM Analogs, Based on 2-Aryl-6-methyl-4*H*-pyrone

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Abstract—A new method was developed for the synthesis of 2-aryl-6-methyl-4*H*-pyrones by the condensation of arylmethylketones with the acetoacetic ester ethylene ketal in the presence of sodium alkoxylate. New laser merocyanine dyes, the analogues of 4-dicyanomethylene-2-methyl-6-[(4-dimethylamino)styryl]-4*H*-pyran (DCM), were obtained based on the synthesized 2-aryl-4-pyrones. The dyes are characterized by high generation efficiency in the red spectral range.

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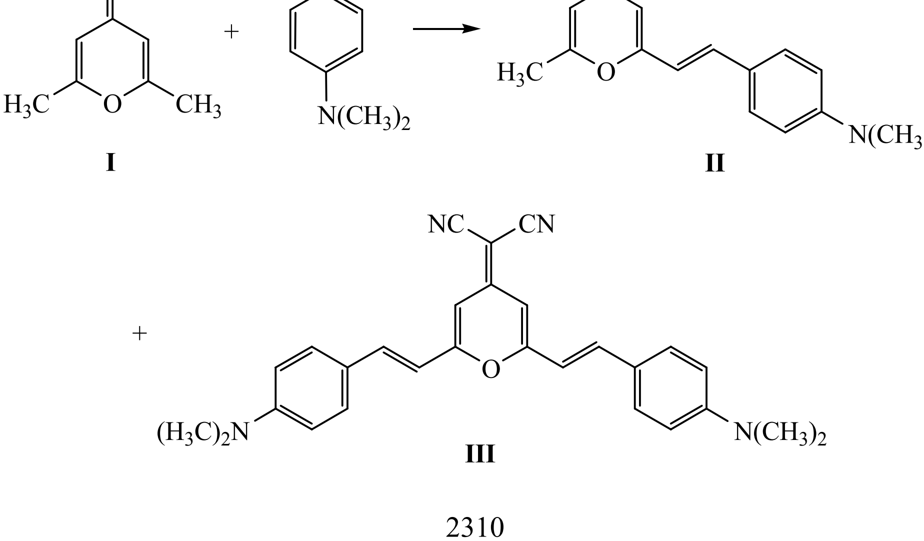
DCM (4-dicyanomethylene-2-methyl-6-[(4-dimethylamino)styryl]-4*H*-pyran) and its derivatives are highly efficient laser dyes for the red spectral range [1]. Their implementation as working substances in electroluminescent devices [2], using a two-photon technologies [3] and solar concentrators [4] has been reported. The synthesis of new derivatives of these dye merocyanines, development and improvement of methods for obtaining the fluorophores of this type is very relevant.

Usually, the synthesis of DCM **II**, the basic dye of this series, is performed by condensation of 4-dimethylaminobenzaldehyde with the synthetically accessible 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran (**I**).



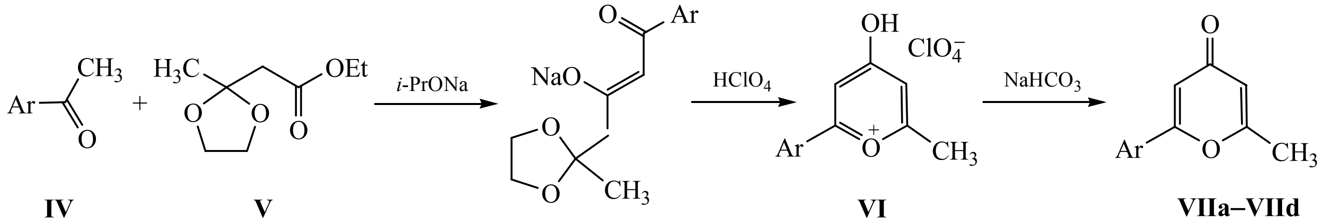
However, preparation of the desired laser dye of spectral purity is complicated considerably by the necessity to remove a deeply colored product **III** of condensation the aldehyde at the second methyl group identical in terms of reactivity with the first methyl group of the pyran fragment, which is formed even at the stoichiometric ratio of initial reagents. The purification increases the product cost.

Replacing one methyl group by a substituent not containing active methylene component allows to avoid the formation of the condensation by-product. Such a substituent may be an aryl group.

A method for producing 2-aryl-6-methyl-4-pyrones by the condensation of arylacethylenecarboxylic esters with acetone in 48–50% yield has been described [5]. Its drawback is inaccessibility of the arylacethylenecarboxylic esters, particularly those containing different substituents in the aryl ring.

More accessible method for the synthesis of the 4-pyrone 2-aryl derivatives that has been tested by us [6] is the condensation of acetylacetone dianion with carboxylic acid esters followed by the cyclization of obtained 1,3,5-triketones [7]. This method, however, involves the use of unsafe and expensive sodium hydride. In addition, the yield of the desired product does not exceed 20%.

In this paper we propose a method for the synthesis of 2-aryl-4-pyrone based on the condensation of arylmethylketones **IV** with the acetoacetic ester ethylene ketal **V**. The ethylene ketal protector of the acetoacetic ester carbonyl group prevents enolization of the latter by blocking sterically the α-methylene center for nucleophilic reactions. This allows the use of ethylene ketal **V** as the ester component in the condensation with ketones **IV**.

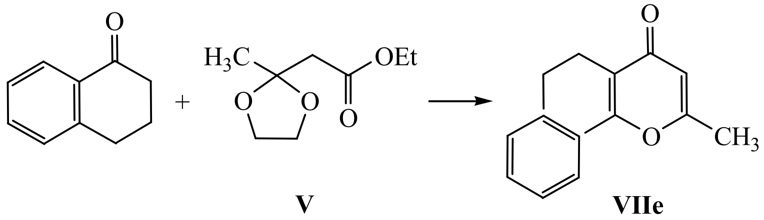


R = Ph (**a**), 4-EtO-C_6H_4 (**b**), 1-$C_{10}H_7$ (**c**), 2-$C_{10}H_7$ (**d**).

Condensation reaction was carried out in toluene as a solvent, in the presence of sodium ethoxide or isopropoxide. The optimum molar ratio of reactants (ketone–ethylene ketal–alkoxylate) was found equal to 1:1.5:1. Dibenzo-18-crown-6 added to the reaction mixture in an amount of 0.5–1 mol % increases the final product yield (Table 1). Replacement of sodium isopropoxide by sodium ethoxide had no effect on the pyrone yield.

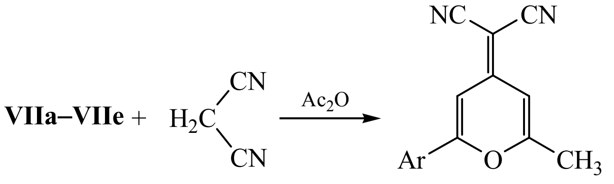
A similar situation observed at the use of sodium hydride in monoglime or toluene. 4-Etoxyacetophenone and 2-naphthylmethylketone give higher yield of respective arylpyrones.

It should be noted that application of this method to α-tetralone resulted in the arylpyrone **VIIe** with annelated hydroaromatic fragment, not synthesised previously.



Cyclization with simultaneous removal of the ketal protection requires two equivalents of perchloric acid: one equivalent is consumed for the formation of sodium perchlorate, and the second serves to the formation of 4-hydroxypyrilium perchlorate **VI.** The latter is soluble in hot water phase and crystallizes at cooling the solution. Separation of the desired product from resinous by-products was carried out by treatment of the filtered off salt **VI** with a sodium hydrocarbonate solution.

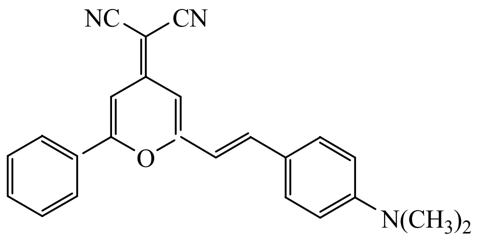
Malononitrile derivatives **VIII** were prepared using a procedure similar to that given in [8, 9]: by boiling 2-arylpyrones **VIIa–VIIe** in acetic anhydride with equimolar amount of malonic dinitrile.



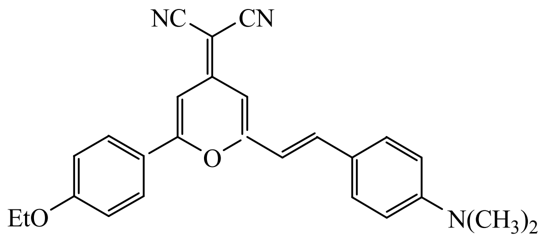
VIIIa–VIIIe

The presence of one reaction center has allowed to carry out the condensation of dicyanomethylenepyrans **VIIIa–VIIIe** with 4-dimethylaminobenzaldehyde in the pyridine–piperidine system by a single route. The DCM derivatives of high purity crystallized from the reaction medium after cooling.

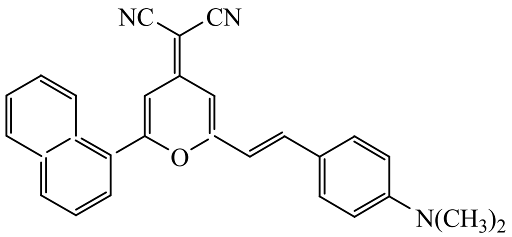
Structures of the DCM aryl analogues **IXa–IXe** thus obtained are shown below, yields and main physicochemical characteristics of the new merocyanine dyes and their intermediates are listed in Tables 1–3.



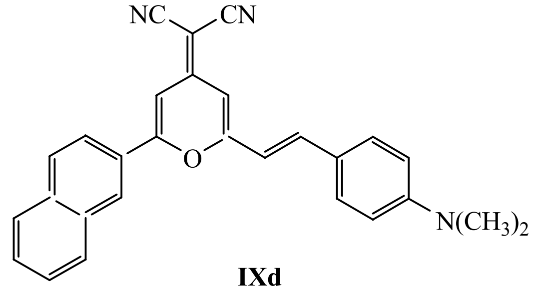
IXa



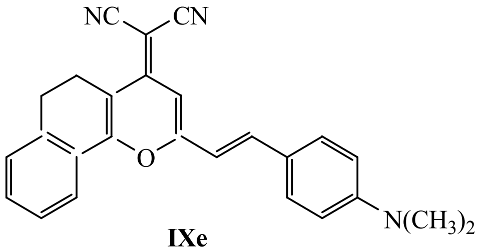
IXb



IXc



IXd



IXe

Replacement of the methyl group in DCM by phenyl (compound **IXa**) containing conjugated π-electron system, practically did not change the band position and shape in the electron absorption spectra. The synthesized merocyanine dyes **IXa–IXe** are characterized by a slight solvatochromism, like DCM (Table 2).

Stronger difference is seen in the luminescence spectra. For the 2-aryl compounds is typical a higher value of the Stokes shift and lower value of fluorescence quantum yield (φ_f) in polar solvents, associated apparently with the rotational-vibrational relaxation of the energy of the 2-phenyl substituent excited state. The higher value of the Stokes shift for the analyzed compounds is due, in our opinion, to the high content of the pyrilium tautomeric forms.

Two cyano groups withdraw strongly the electron density from the 4-methylene substituent, thus contributing to increased negative charge. At the same time the energetically favorable pyrilium structure

Table 1. Physicochemical characteristics of 2-aryl-6-methyl-4*H*-pyrones, 4-dicyanomethylene merocyanine derivatives and dyes based on them

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
VIIa	53	82–83	77.13	5.27		$C_{12}H_{10}O_2$	77.40	5.41	
	52[a]								
	50[b]								
VIIb	58	78–79	72.81	6.05		$C_{14}H_{14}O_3$	73.03	6.13	
VIIc	44	87–88	80.63	5.01		$C_{16}H_{12}O_2$	81.34	5.12	
VIId	59	91–92	80.58	5.03		$C_{16}H_{12}O_2$	81.34	5.12	
VIIe	49	101–102	77.57	5.41		$C_{14}H_{12}O_2$	77.76	5.59	
VIIIa	60	184–186	75.98	4.11	11.83	$C_{15}H_{10}N_2O$	76.91	4.30	11.96
VIIIb	62	169–170	73.25	5.03	9.94	$C_{17}H_{14}N_2O_2$	73.37	5.07	10.06
VIIIc	59	171–172	80.06	4.11	9.46	$C_{19}H_{12}N_2O$	80.27	4.25	9.85
VIIId	62	175–176	79.87	4.03	9.51	$C_{19}H_{12}N_2O$	80.27	4.25	9.85
VIIIe	67	191–192	78.21	4.27	10.70	$C_{17}H_{12}N_2O$	78.45	4.64	10.76
IXa	91	274–275	78.81	5.07	11.31	$C_{24}H_{19}N_3O$	78.88	5.24	11.50
IXb	88	233–234	74.98	5.60	9.94	$C_{26}H_{23}N_3O_2$	75.26	5.66	10.26
IXc	87	229–230	80.78	5.03	10.01	$C_{28}H_{21}N_3O$	80.94	5.09	10.11
IXd	90	232–233	80.69	5.02	10.02	$C_{28}H_{21}N_3O$	80.94	5.09	10.11
IXe	90	276–277	79.21	5.20	10.03	$C_{26}H_{21}N_3O$	79.77	5.41	10.73

[a] The catalyst is sodium hydride in toluene (*method b*). [b] The catalyst is sodium hydride in monoglime (*method b*).

Table 2. Comparative spectral-luminescent and geberation characteristics of compounds **IXa–IXe** and the DCM dye

Dye	Sovent	λ^{absorb}_{max}, nm	λ^{fluor}_{max}, nm	φ_f	η_{gener}, %	$\Delta\lambda_{gener}$, nm
DCM	Dioxane	466	560	0.01	–	–
	Toluene	462	563	0.01	–	–
	Dichloromethane	472	582	0.02	–	–
	Acetone	488	628	0.14	–	–
	Ethanol	475	638	0.308	25	605–672
	DMF	481	640	0.45	28	607–690
	DMSO	482	660	0.59	27	611–712
IXa	Dioxane	480	582	0.45	47	–
	Toluene	472	565	0.04	47	–
	Dichloromethane	487	595	0.55	40	607–674
	Acetone	485	673	0.14	47	–
	Ethanol	480	676	0.05	47	–
	DMF	495	700	0.02	43	647–735
	DMSO	500	711	0.02	42	675–810
IXb	DMSO	497	693	0.05	38	620–800
IXc	DMSO	500	690	–	–	–
IXd	DMSO	500	730	–	–	–
IXe	DMSO	503	736	0.06	42	670–850

contributes to appearance of a positive charge on the oxygen. An increase in the solvent polarity also contributes to the shift of the equilibrium toward the more polar pyrilium form. Interaction of π-electron system of the aryl substituent with the π-electron system of the pyrane ring results in a bathochromic shift in the fluorescence spectra. The introduction of donor substituents in the phenyl ring reduces this effect

Table 3. ^{1}H NMR spectral characteristics of the synthesized intermediates **VII, VIII** and **IX** of merotsianinovyh dyes

Comp. no.	δ, ppm
VIIa	2.06 s (3H, CH$_3$), 5.83, 6.22 s (2H, –CH=), 6.98, 7.37 m (5H, H$_{\mathrm{phenyl}}$)
VIIb	1.35 t (3H, CH$_3$), 2.06 s (3H, CH$_3$), 4.12 q (2H, CH$_2$), 5.82, 6.22 s (2H, –CH=), 6.87, 7.37 m (4H, H$_{\mathrm{phenyl}}$)
VIIc	2.05 s (3H, CH$_3$), 5.83, 6.24 s (2H, –CH=), 7.15, 8.17 m (7H, H$_{\mathrm{naphtyl}}$)
VIId	2.04 s (3H, CH$_3$), 5.83, 6.24 s (2H, –CH=), 7.12, 7.86 m (7H, H$_{\mathrm{naphtyl}}$)
VIIe	2.09 s (3H, CH$_3$), 2.94, 3.23 m (4H, CH$_2$), 5.43 s (1H, 3H$_{\mathrm{pyran}}$), 7.22, 7.45 m (4H, H$_{\mathrm{phenyl}}$)
VIIIa	2.13 s (3H, CH$_3$), 6.5, 7.02 s (2H, –CH=), 7.02, 7.51 m (5H, H$_{\mathrm{phenyl}}$)
VIIIb	1.35 t (3H, CH$_3$), 2.06 s (3H, CH$_3$), 4.13 q (2H, CH$_2$), 6.62, 7.11 s (2H, –CH=), 6.99, 7.47 m (4H, H$_{\mathrm{phenyl}}$)
VIIIc	2.14 s (3H, CH$_3$), 6.51, 7.12 s (2H, –CH=), 7.15, 8.17 m (7H, H$_{\mathrm{naphtyl}}$)
VIIId	2.14 s (3H, CH$_3$), 6.51, 7.12 s (2H, –CH=), 7.15, 8.17 m (7H, H$_{\mathrm{naphtyl}}$)
VIIIe	2.15 s (3H, CH$_3$), 2.86, 3.20 m (4H, CH$_2$), 5.91 s (1H, 3H$_{\mathrm{pyran}}$), 7.25, 7.44 m (4H, H$_{\mathrm{phenyl}}$)
IXa	3.07 s (6H, CH$_3$), 6.55, 7.46 d (2H, –CH=, *J* 16 Hz), 6.66 s (1H, 5H$_{\mathrm{pyran}}$), 7.06 s (1H, 3H$_{\mathrm{pyran}}$), 6.73, 7.87 d (4H, H$_{\mathrm{phenylene}}$), 7.05, 7.57 m (5H, H$_{\mathrm{phenyl}}$)
IXb	1.35 t (3H, CH$_3$), 3.07 s (6H, CH$_3$), 4.12 q (2H, CH$_2$), 6.54, 7.42 d (2H, –CH=, *J* 16 Hz), 6.68 s (1H, 5H$_{\mathrm{pyran}}$), 7.07 s (1H, 3H$_{\mathrm{pyran}}$), 6.73, 7.87 d (4H, H$_{\mathrm{phenylene}}$), 7.05, 7.57 m (4H, 6H$_{\mathrm{phenylene}}$)
IXc	3.07 s (6H, CH$_3$), 6.56, 7.48 d (2H, –CH=, *J* 16 Hz), 6.66 s (1H, 5H$_{\mathrm{pyran}}$), 7.06 s (1H, 3H$_{\mathrm{pyran}}$), 6.72, 7.86 d (4H, H$_{\mathrm{phenylene}}$), 7.15, 8.17 m (7H, H$_{\mathrm{naphtyl}}$)
IXd	3.07 s (6H, CH$_3$), 6.56, 7.48 d (2H, –CH=, *J* 16 Hz), 6.66 s (1H, 5H$_{\mathrm{pyran}}$), 7.06 s (1H, 3H$_{\mathrm{pyran}}$), 6.73, 7.87 d (4H, H$_{\mathrm{phenylene}}$), 7.15, 8.17 m (7H, H$_{\mathrm{naphtyl}}$)
IXe	2.96, 3.25 m (4H, CH$_2$), 3.07 s (6H, CH$_3$), 6.53, 7.44 d (2H, –CH=, *J* 16 Hz), 6.71 s (1H, 5H$_{\mathrm{pyran}}$), 6.71, 7.87 d (4H, H$_{\mathrm{phenylene}}$), 7.25, 7.39 m (4H, H$_{\mathrm{phenyl}}$)

(compound **IXb**). This is evidenced additionally by the comparison of the spectra of α- and β-naphthyl derivatives **IXc** and **IXd**, in which the electron density of the pyran ring is increased or decreased, respectively, and this effect is reflected by their luminescence spectra (Table 2).

At the testsing the laser activity of the synthesized merocyanine dyes we found (Table 2) that they are effectively generating compounds for the red spectral region (generating efficiency is up to 47%) with wide tuning range, and can be recommended for practical use as components of active medium in liquid and polymer lasers.

EXPERIMENTAL

^{1}H NMR spectra were taken from 5% solutions of compounds on a Bruker AW 200 spectrometer at the operating frequency 200 MHz, internal reference TMS. The absorption spectra were recorded using a Solar PV-1251 spectrophotometer, fluorescence spectra using Spex Fluorolog fluorimeter.

At the measuring the generation parameters of dye solutions, their concentrations were optimized to maximize the energy generation. For pumping was used the second harmonic of the Q-switched yttrium–aluminum garnet laser with the following parameters: single pulse energy $E = 0.1$ J, $\tau = 20$ ns, $\lambda = 532$ nm. The spectral tuning range was determined from the level of 0.5 E_{max} of the generation in a selective resonator.

The DCM dye was synthesized by us earlier [10], the acetoacetic ester ethylene ketal **V** was prepared as described in [11] using a 60% dispersion of sodium hydride in mineral oil from Aldrich.

Synthesis of aryl derivatives of 4*H*-pyrone (VIIa–VIIe). *a*. In a three-necked 0.5 l flask equipped with mechanical stirrer, reflux condenser, dropping funnel and inert gas inlet was placed 200 ml of water-free toluene and 11.5 g (0.5 mol) of sodium metal. Solution was heated to boil, and while vigorously stirring strived the sodium pulverization. Then while stirring and maintaining the temperature in the flask 30–40°C was added dropwise 30 ml (0.5 mol) of isopropyl alcohol. After dissolution of sodium, 1.5 g (2.8 mmol) of dibenzo-18-crown-6 was added, the reaction mixture was heated to 100–105°C and a mixture of 0.5 mol of aromatic ketone and 133.5 g (0.75 mol) of acetoacetic ester ethylene ketal **V** was added dropwise, while the mixture of ethyl and isopropyl alcohols evolved in the reaction course was distilled off. Then the cooled reaction mixture was treated with 150 ml of 57% perchloric acid and 150 ml of water. The organic layer was distilled off with steam, the hot water fraction was cooled to room temperature. The precipitated perchlorate **VI** was filtered off and washed with diethyl ether. After treatment with 5% aqueous solution of sodium hydrocarbonate the precipitate was filtered off, washed with water, and dried in a vacuum. The isolated 2-aryl-6-methyl-4*H*-pyrones were of sufficiently high purity and could be used without further recrystallization in the following steps.

b. Similar to the *a*, but instead of sodium isopropoxide was used 0.1 mol of 60% sodium hydride in mineral oil.

c. The flask was charged with 24 g (0.6 M) of 60% sodium hydride in oil and 200 ml of monoglyme, and while stirring and boiling was added dropwise 0.5 mol of aromatic ketone for 2 h. Then to the boiling mixture was added 133.5 g (0.75 mol) of the ethylene ketal **V** and the mixture was refluxed for 2 h. Further processing is analogous to the *method a*.

4-Dicyanomethylene-2-aryl-6-methyl-4*H*-pyran (VIII). A mixture of 0.1 mol of pyrone **VII**, 7.26 g (0.11 mol) of malonodinitrile and 80 ml of acetic anhydride was refluxed for 3 h. After cooling to 5–8°C the precipitate was filtered off and washed with diethyl ether. A sample for the analysis was additionally crystallized from alcohol.

4-Dicyanomethylene-2-aryl-6-[(4-dimethylamino)-styryl)-4*H*-pyrans IXa–IXe. A mixture of 0.1 mol of 4-dicyanomethylene-2-aryl-6-methyl-4*H*-pyran **VIII**, 16.39 g (0.11 mol) of 4-dimethylaminobenzaldehyde, 80 ml of pyridine and 8 ml of piperidine was refluxed for 1.5–2 h. After cooling, the precipitated crystals were separated and washed sequentially with ethyl acetate (2×20 ml), 5% aqueous HCl (2×20 ml), and hot water. After drying, the compounds were further crystallized from cyclohexane.

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