SYNTHESIS, LUMINESCENCE, AND SPECTRAL CHARACTERISTICS OF 7-DIETHYLAMINO-3-(2-ARYLETHENYL)COUMARINS

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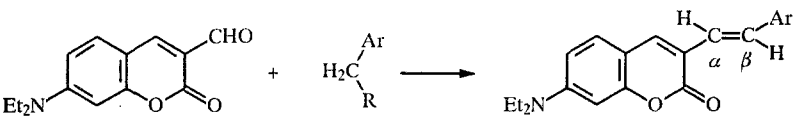
By condensation of 7-diethylamino-3-formylcoumarin with aromatic compounds containing an active methyl or methylene group, a number of previously unreported 7-diethylamino-3-(2-arylethenyl)coumarins have been obtained. The reaction conditions depend on the activity of the methyl (or methylene) component. The spectral and luminescent properties of the synthesized compounds have been investigated.

In the course of searching for new derivates of coumarin as effective organic luminophores and lasing compounds [1], we have continued our research on substituted styrylcoumarins (see previous communication [2]) and have investigated the influence of branching of the conjugation chain in position 3 of the coumarin on the spectral and luminescence properties.

3-Arylethenylcoumarins, unsubstituted in position 7, were obtained recently by Chodankar et al. [3] by the reaction of coumarin-3-acetic acid with aromatic aldehydes. Because of the poor accessibility of 7-dialkylaminocoumarin-3-acetic acids, these investigators obtained 7-diethylamino-3-(2-phenylethyl)coumarin only by a complex, multistage synthesis. The 4-methyl-substituted analog of the latter compound has also been obtained photochemically from the 3-iodo derivative [4,5].

In view of the fact that 3-formylcoumarins are readily condensed with compounds containing an active methylene grouping, such as derivatives of malonic acid [6,7], it was of interest to investigate the possibility of condensing the accessible 7-diethylamino-3-formylcoumarin (I) with aromatic and heterocyclic compounds containing an active methylene or methyl group. As a result, we obtained a series of 7-diethylamino-3-(2-arylethenyl)coumarins (IIIa-f).



I IIa-f IIIa-f

II, III a Ar = 2-quinolyl, R = H; b Ar = 2-pyridyl, R = H; c Ar = 4-pyridyl, R = H; d Ar = phenyl, R = COOH; e Ar = 4-ClC_6H_4, R = COOH; f Ar = 4-$NO_2C_6H_4$, R = COOH

The reaction conditions depend on the activity of the methyl or methylene component. Thus, when the aldehyde I is refluxed with quanaldine (IIa) in acetic anhydride, the coumarin IIIa is obtained with a 39% yield. Under these conditions, no reaction takes place with picolines (IIb, c) or *p*-nitrotoluene. The activity of the methyl group in picolines was enhanced by obtaining N-benzopicolinium salts *in situ* [8]; these salts react with the aldehyde I, giving the coumarins IIIb, c with 38 and 32% yields, respectively. In contrast to *p*-nitrotoluene, *p*-nitrophenylacetic acid (IIf) reacts with the coumarin I in pyridine in the presence of piperidine. For phenylacetic acid (IId) and *p*-chlorophenylacetic acid (IIe), more severe conditions are required. 7-Diethylamino-3-[2-(4-aminophenyl)ethenyl]coumarin (IIIg) was obtained by reduction of the nitro derivative (IIIf).

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The structures of the synthesized compounds were confirmed by elemental analyses and by PMR, IR, and mass spectrometry (Tables 1 and 2).

In the PMR spectra of the compounds III in $CDCl^3$ (Table 2), the signals of the protons of the coumarin system are located in the regions that are expected for such compounds [9]; the signals of the α and β protons at the ethylene double bond are located in the 7.0-7.8 ppm interval in the form of two doublets with SSCC $J_{\alpha,\beta} \sim 16$ Hz, providing evidence in favor of the *trans* configuration of these compounds.

The spectral and luminescent properties of the compounds are summarized in Table 1. It will be seen that the long-wave absorption maximum of each of the coumarins III undergoes a significant bathochromic shift in comparison with the 7-diethylaminocoumarin. In ethanol, the long-wave band has a single maximum; but in toluene, it has two maxima: The less intense maximum is manifested in the form of a shoulder that very nearly coincides with the absorption maximum in ethanol, while the more intense maximum is displaced hypsochromically relative to the other maximum by 10-15 nm. The compounds III exhibit intense fluorescence with a Stokes shift ~80 nm. For compound IIIg in ethanol, we observe an increase of the Stokes shift to 130 nm, with a sharp drop of the quantum yield.

EXPERIMENTAL

PMR spectra of saturated solutions of compounds III in $CDCl_3$ were registered in a Bruker WP-200 SY instrument with TMS as an internal standard. Electronic absorption spectra were recorded in a Specord UV-Vis instrument, luminescence spectra in a type SDL-1 unit with a DKSSh-1000 lamp as the excitation source, and with a correction for the sensitivity of the unit. The quantum yield of fluorescence (η) was measured relative to a standard, 3-aminophthalimide ($\eta = 0.60$) [10]. Mass spectra were measured in a MKh-1320 instrument, with an ionizing voltage of 50 eV. IR spectra were registered in a UR-20 instrument in KBr tablets.

The elemental analyses of compounds III for C, H, N, and Cl were in agreement with the calculated data. Characteristics of the synthesized compounds are listed in Tables 1 and 2.

7-Diethylamino-3-formylcoumarin (I) was obtained by a procedure given in [11], from 7-ethylaminocoumarin.

7-Diethylamino-3-[2-(2-quinolyl)ethenyl]coumarin (IIIa). A solution of 0.74 g (3 mmoles) of the formylcoumarin I and 0.43 g (3 mmoles) of quinaldine IIa was refluxed in 10 ml of acetic anhydride for 4 h. The acetic anhydride was partly driven off (~5 ml); the residue was neutralized with a sodium carbonate solution and extracted with methylene chloride (3 × 25 ml). The extract was dried over $CaCl_2$ and evaporated down to a minimum volume; the product was separated chromatographically in a column (Al_2O_3, methylene chloride). By crystallization from heptane, 0.43 g of the compound IIIa was obtained.

7-Diethylamino-3-[2](2-pyridyl)ethenyl]coumarin (IIIb) and 7-Diethylamino-3-]2-(4-pyridyl)ethenyl]coumarin (IIIc). A mixture of 0.37 g (4 mmoles) of the picoline IIb or IIc and 0.56 g (4 mmoles) of benzoyl chloride was dissolved in 6 ml of DMF and stirred for 10 min. Then 0.74 g (3 mmoles) of the 3-formylcoumarin I was added, and the mixture was refluxed 4 h. After cooling, 2 ml of concentrated hydrochloric acid was added, and the mixture was stirred for 6 h at room temperature. The reaction mass was poured into 50 ml of water, and 6 ml of 20% NaOH solution was added. The resulting precipitate was filtered off, dried, purified chromatographically (Al_2O_3, benzene-ethyl acetate), and crystallized from octane.

7-Diethylamino-3-(2-phenylethenyl)coumarin (IIId) and 7-Diethylamino-3-[2-(4-chlorophenyl)ethenyl]coumarin (IIIe). A mixture of 1.48 g (6 mmoles) of the 3-formylcoumarin I, 8 mmoles of arylacetic acid (IId,e), and 1 ml of tributylamine was heated in an oil bath at 220-230°C for 40 min. The oily products, after cooling, were dissolved in benzene. The product was separated chromatographically (silica gel, benzene) and crystallized with heptane with the addition of activated carbon.

7-Diethylamino-3-[2-(4-nitrophenyl)ethenyl]coumarin (IIIf). To a solution of 0.74 g (3 mmoles) of the 3-formylcoumarin I and 0.68 g (3.75 mmoles) of the acid IIf in 10 ml of pyridine, 1 ml of piperidine was added, and the mixture was refluxed 6 h. The mixture was then poured into 70 ml of water and extracted with methylene chloride (4 × 25 ml). The extract was dried over $CaCl_2$ and evaporated down to minimum volume. The product was separated chromatographically (silica gel, methylene chloride) and crystallized from toluene. Obtained 0.34 g of the substance IIIf.

7-Diethylamino-3-[2-(4-aminophenyl)ethenyl]coumarin (IIIg). To a solution of 0.73 g (2 mmoles) of the coumarin IIIf in a mixture of 30 ml of methanol and 4 ml of water, 0.6 g of iron powder, previously etched in hydrochloric acid, was added. The mixture was refluxed 3 h and filtered to remove sludge; the sludge was washed with 10 ml of hot ethanol. The

TABLE 1. Characteristics of Synthesized Compounds

Compound	Empirical formula	Mass spectrum, M^+	mp, °C	IR spectrum, ν, cm^{-1}, in KBr		Spectral and luminescent properties: a) in ethanol; b) in toluene			Yield, %
				lactone C=O	other	λ_{max}^{abs}, nm (log ε)	λ_{max}^{lum}, nm	quantum yield η	
	$C_{13}H_{15}NO_2$	—	90...90,5	1712	1615	a) 247 (4,12), 380 (4,38) b) 363 (4,46), 376 (4,49)	465 425	0,55 0,94	—
I	$C_{14}H_{15}NO_3$	—	160...161	1720	1680 1628	a) 215 (4,23), 240 (3,88), 269 (3,90), 451 (4,66) b) 425 (4,59), 443 (4,73)	495 465	0,06 0,75	65
IIIa	$C_{24}H_{22}N_2O_2$	370	142...143*	1712	1614 1592	a) 238 (4,49), 286 (4,22), 323 (4,08), 447 (4,72) b) 320 (4,04), 435 (4,73), 450 (4,69	535 510, 535	0,62 0,70	39
IIIb	$C_{20}H_{20}N_2O_2$	320	156...157	1702	1622 1592	a) 250 (4,08), 310 (4,08), 432 (4,73) b) 310 (4,06), 421 (4,70), 437 (4,60)	515 492, 515	0,80 0,75	38
IIIc	$C_{20}H_{20}N_2O_2$	320	163...164	1713	1618 1591	a) 235 (4,28), 307 (4,06), 439 (4,68) b) 301 (4,04), 422 (4,65), 435 (4,63)	515 490, 515	0,70 0,70	32
IIId	$C_{21}H_{21}NO_2$	319	194...195	1710	1623 1600	a) 243 (4,22), 297 (4,26), 425 (4,70) b) 295 (4,17), 416 (4,65), 427 (4,62)	510 485, 510	0,75 0,80	30
IIIe	$C_{21}H_{20}ClNO_2$	353	172...173	1710	1616 1600	a) 247 (4,22), 300 (4,27), 428 (4,72) b) 300 (4,19), 420 (4,71), 432 (4,67)	510 490, 515	0,75 0,80	33
IIIf	$C_{21}H_{20}N_2O_4$	364	262...262,5	1706	1622 1590	a) 255 (4,23), 325 (4,00), 460 (4,77) b) 320 (3,96), 450 (4,66), 460 (4,64)	— 540	— 0,60	31
IIIg	$C_{21}H_{22}N_2O_2$	334	206...207	1694	1611 1590 3455 3360	a) 252 (4,03), 305 (4,23), 435 (4,70) b) 305 (4,15), 425 (4,64), 437 (4,61)	565 505, 525	0,15 0,65	70

*Literature mp 133°C [3].

TABLE 2. PMR Spectra of 7-Diethylamino-3-(2-arylethenyl)coumarins III in $CDCl_3$

Compound	Chemical shift δ, ppm								SSCC (J), Hz		
	$N(CH_2—CH_3)_2$	4-H	5-H	6-H	8-H	α-H	β-H	H_{Ar} (and number of protons)	J_{56}	J_{68}	$J_{\alpha,\beta}$
IIIa	1,23 (t); 3,44 (q)	7,86	7,1...7,8	6,61	6,52	7,1...7,8		7,1...7,8 (4H); 8,06 (1H); 8,11 (1H)	8,8	2,5	—
IIIb	1,21 (t); 3,42 (q)	7,0...7,8	7,0...7,8	6,58	6,50	7,0...7,8		7,0...7,8 (3H); 8,58 (1H)	9,0	2,2	—
IIIc	1,23 (t); 3,44 (q)	7,71	7,31	6,61	6,51	7,46	7,22	7,34 (2H); 8,55 (2H)	9,0	2,5	16,4
IIId	1,21 (t); 3,41 (q)	7,66	7,2...7,6	6,58	6,50	7,45	7,08	7,2...7,6 (5H)	8,8	2,2	16,4
IIIe	1,22 (t); 3,43 (q)	7,66	7,29	6,59	6,51	7,44	7,04	7,29 (2H); 7,44 (2H)	8,8	2,4	16,3
IIIf	1,23 (t); 3,44 (q)	7,72	7,31	6,67	6,50	7,59	7,19	7,61 (2H); 8,19 (2H)	9,0	2,3	16,4
IIIg	1,21 (t); 3,41 (q)	7,61	7,27	6,57	6,49	7,34	6,92	3,75 (H_2); 6,66 (2H); 7,35 (2H)	9,0	2,4	16,5

ethanol filtrate was poured into 100 ml of water; the residue was filtered off; dried, and crystallized from toluene. Obtained 0.47 g of the coumarin IIIg.

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