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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF AZOMETHINES IN THE COUMARIN SERIES

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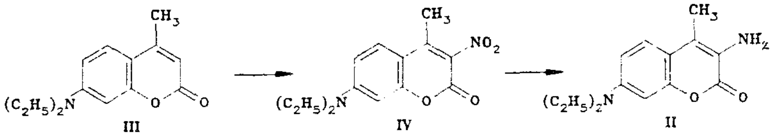
Nitration of 7-diethylamino-4-methylcoumarin and reduction of the resulting 3-nitro derivative gave 7-diethylamino-3-amino-4-methylcoumarin. A series of azomethines have been synthesized based on this material. The spectral-luminescence properties of the products have been investigated.

Substituted coumarins with electron-donating substituents in the 7-position are of interest as organic luminophores and as efficient laser dyes for the blue-green region of the spectrum [1, 2]. Introduction into the 3-position of 7-substituted coumarins of substituent groups which lengthen the conjugation chain leads to a bathochromic shift in their absorption and luminescence spectra; this makes it possible to expand the available selection of fluorescent coumarin dyes [3].

In the present paper we have synthesized and studied azomethines I (Table 1) derived from 7-diethylamino-3-amino-4-methylcoumarin, which was itself prepared by nitration of 7-diethylamino-4-coumarin followed by reduction of the intermediate nitro derivative IV with metallic iron in aqueous ethanol. Optimizing the nitration procedure made it possible to prepare the 3-nitrocoumarin (IV) in 54% yield, since in the nitration of 7-dimethylamino-4-methylcoumarin the 3-nitro derivative was formed in a mixture along with other isomers in equal amounts [4].

The presence of a nitro group in the 3-position in (IV) is indicated by the absence of the 3-H proton signal in the PMR spectrum of compound IV and by the absence of splitting of the 4-CH_3 group signal which is present in the spectrum of compound III due to spin-spin coupling with the 3-H proton.



III IV II

Scientific Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 321-323, March, 1990. Original article submitted August 9, 1988.

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TABLE 1. Properties of Azomethines I

Compound No.	Molecular formula	mp, °C*	Yield, %	Compound No.	Molecular formula	mp, °C*	Yield, %
Ia	$C_{21}H_{22}N_2O_2$	140...141	84	Ie	$C_{22}H_{22}N_2O_3$	201...202	20
Ib	$C_{21}H_{22}N_2O_3$	226...227	87	If	$C_{25}H_{24}N_2O_2$	182...183	47
Ic	$C_{23}H_{27}N_3O_2$	228...229	75	Ig	$C_{25}H_{24}N_2O_3$	243...244	90
Id	$C_{25}H_{31}N_3O_3$	205...206	95	Ih	$C_{29}H_{28}N_2O_2$	217...218	50

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*Compounds Ic, Ie, and Ig crystallize from DMF, the others from aqueous DMF.

TABLE 2. Spectral Characteristics of the Newly Synthesized Compounds*

Compound	IR spectrum, $\nu_{C=O}$, cm^{-1} (CCl_4)	Electronic spectrum, λ_{max}, nm (log ε)			
		absorption		luminescence	
		in benzene	in ethanol	in benzene	in ethanol
III	1710**	360 (4,34)	375 (4,38)	425 (0,64)	450 (0,54)
IV	1720**	406 (4,36)	418 (4,47)	—	—
II	1714	368 (4,32)	377 (4,43)	436 (0,55)	480 (0.64)
Ia	1723	424sh (4,72); 411 (4,73)	417 (4,68)	—	—
Ib	1722	441 (4,76); 419 (4,76)	440 (4,76)	545 (0,10)	545 (0,08)
Ic	1714	435 (4,70); 421 (4,77)	422 (4,73)	—	—
Id	1720	452 (4,77); 445 (4,82)	445 (4,77)	508 (0,06)	523 (0.31)
Ie	1708	456 (4,64); 438 (4,64)	444 (4,57)	—	—
If	1708	450 sh (4,58); 427 (4,65)	428 (4,65)	—	—
Ig	1715	505 sh (3,60); 466 (4,65); 439 (4,67)	505 sh (4,15); 467 (4,58); 445 (4,55)	490 530 (0,07)	553 (0,13)
Ih	1712	438 (4,51)	435 (4,53)	—	—

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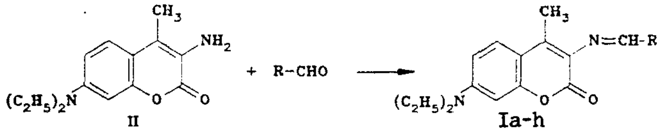
*PMR Spectrum (in C_6D_6), δ_{O-H}: for Ib 13.3; Id 14.3; Ig 15.6 ppm.

**KBr pellets.

Azomethines I were prepared by condensation of aminocoumarin II with aromatic aldehydes in ethanol in the presence of piperidine.



I a R=C_6H_5; b R=C_6H_4OH; c R=4-$C_6H_4NMe_2$; d R=2-OH-4-$NEt_2C_6H_3$; e R=4-C_6H_4CHO; f R=1-naphthyl; g R = 2-hydroxynaphthyl-1; h R = 9 anthryl

The purity of the resulting products was assessed based on TLC in systems of different polarities.

In the IR spectra of azomethines I incorporating the hydroxyaryl derivatives Ib, d, g, the $\nu_{C=O}$ frequencies are similar (Table 2). Compounds Ib, d, g do not contain any absorption in the 2000-3600 cm^{-1} region due to NH group vibrations. In their PMR spectra (Table 2) the chemical shift values for the hydroxyl protons are found downfield and do not change upon dilution of the solutions. Based on these data we propose that compounds Ib, d, g exist in the O-hydroxyaryl form with intramolecular hydrogen bonding between the hydroxyl group proton and the imine nitrogen [5, 6].

It is clear from the data in Table 2 that introduction of an amino group in the 3-position of compound III has practically no effect on the position of the long-wavelength absorption maximum relative to the electronic spectrum of compound III. We have carried out quantum mechanical calculations, which showed that introduction of an amino group does increase the energy of the HOMO in compound II relative to the HOMO energy level in compound III, but at the same time also simultaneously increases the energy of the LUMO; these two effects combined explain the absence of spectral changes accompanying substitution.

The long-wavelength absorption band in the electronic spectrum of compound II, as in compound III, has π,π^*-character. These compounds belong to the Group V spectral-luminescence type [7] and exhibit intense fluorescence. Elongation of the π-system in the transition to azomethines I induces a bathochromic shift in the long-wavelength π,π^* absorption band. The n,π^* band cannot be shifted substantially due to the absence of splitting of the singlet and triplet states of the n,π^*-type. Azomethines thus belong to the Group V spectral-luminescence type of molecules, and the absence of luminescence in compounds Ia, c, e, f, h cannot be attributed to intense intercombination conversion (intersystem crossing) of the $S_{\pi,\pi^*} \sim\rightarrow T_{n,\pi^*}$-type or to $s_{\pi,\pi^*} \sim\rightarrow s_{n,\pi^*}$-type internal conversion. The absence of luminescence in compounds Ia, c, e, f, h is apparently due to their noncoplanar structure (quenching effect associated with the presence of twisting vibrations). The appearance of luminescence in compounds Ib, d, g, featuring an ortho-oriented hydroxy group (relative to the azomethine bridge), can apparently be attributed to weakening of these twisting vibrations [8].

EXPERIMENTAL

PMR spectra were measured on a Bruker WP-80 spectrometer in $CDCl_3$ or acetone-D_6 vs. TMS as internal standard. IR spectra were recorded on a UR-20 spectrophotometer using CCl_4 solutions or KBr pellets. Electronic spectra were measured on a Specord UV-Vis spectrophotometer, fluorescence spectra on an SDL-1 instrument using a DKSSh-1000 lamp as the excitation source. Spectra were corrected to take into account the sensitivity of the instrument. Luminescence quantum yields (η) were measured relative to a standard, 3-aminophthalimide (η = 0.60 [9]). Quantum mechanical calculations were performed using the LCAO MO method with a PPO approximation [10, 11].

The results of C, H, N elemental analysis of compounds Ia-h, II, IV agreed with calculations.

7-Diethylamino-4-methylcoumarin (III). PMR spectrum (acetone-D_6): 2.34 (CH_3, d, $J_{CH_3,3\text{-}H}$ = 1 Hz); 5.86 (3-H, q, $J_{3\text{-}H,CH}$ = 1 Hz); 6.47 (8-H, d, $J_{8\text{-}H,6\text{-}H}$ = 2.5 Hz); 6.70 (6-H, d.d, $J_{6\text{-}H,8\text{-}H}$ = 2.5 Hz, $J_{6\text{-}H,5\text{-}H}$ = 9 Hz); 7.50 ppm (5-H, d, $J_{5\text{-}H,6\text{-}H}$ = 9 Hz).

3-Nitro-7-diethylamino-4-methylcoumarin (IV, $C_{14}H_{16}N_2O_4$). To a solution of 4.62 g (20 mmoles) compound III in 25 ml 81% H_2SO_4 was added 0.83 ml (20 mmoles) fuming nitric acid at 2-4°C. The mixture was stirred at this temperature for 1 h, then the temperature was raised slowly to 25°C and the mixture stirred an additional 1 h. The reaction mixture was poured into 150 ml water and the precipitate was removed by filtration, washed with water, 5% NaOH solution, and water again, and dried. After recrystallization from ethyl acetate the yield was 2.98 g (54%) of nitro compound IV, mp 159-159.5°C. PMR spectrum (acetone-D_6): 2.46 (CH_3, s) 6.58 (8-H, d, $J_{8\text{-}H,6\text{-}H}$ = 2.5 Hz); 6.89 (6-H, d.d, $J_{6\text{-}H,8\text{-}H}$ = 2.5 Hz, $J_{6\text{-}H,5\text{-}H}$ = 9.3 Hz); 7.72 ppm (5-H, d, $J_{5\text{-}H,6\text{-}H}$ = 9.3 Hz).

7-Diethylamino-3-amino-4-methylcoumarin (II, $C_{14}H_{18}N_2O_2$). To a suspension of 0.95 g (3.5 mmoles) nitrocoumarin IV in 30 ml 80% ethanol was added 2.0 g iron powder which had been previously treated (soaked) in hydrochloric acid, and the mixture was refluxed for 40 min. The reaction mixture was filtered hot to remove the sludge, and the sludge was rinsed with 15 ml hot ethanol. The filtrate was diluted with 70 ml water and the resulting precipitate was filtered and washed with 25% ethanol followed by water. After drying the yield was 0.77 g (90%) of amine (II), mp 101.5-102°C (from 45% aqueous ethanol).

3-N-Benzylideneamino-7-diethylamino-4-methylcoumarin (Ia). To a solution of 2.46 g (10 mmoles) 3-aminocoumarin II in 50 ml ethanol was added 1 ml piperidine and 2 ml (20 mmoles) benzaldehyde, and the mixture was refluxed for 8 h. The mixture was cooled and the precipitate filtered and washed with 10 ml ethanol. Yield 2.82 g (84%) compound Ia.

Azomethines Ib-h were prepared in an analogous manner.

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REACTION OF 2-CHLORO-5-METHYLBENZOQUINONE WITH β-AMINOCROTONIC ESTER DERIVATIVES

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The reaction of 2-chloro-5-methylbenzoquinone with β-aminocrotonic ester derivatives was studied by PMR spectroscopy in CD_3COOD. The spectra indicate the formation of intermediate hydroquinone and quinone derivatives, which subsequently transform into the corresponding indoles. It was shown that the indolization proceeds unequivocally at the 3-position of the initial benzoquinone, and the rate of formation of the indole derivatives decreases with increase in the size of the substituent at the nitrogen atom of the β-aminocrotonic ester. The starting, intermediate compounds and the end products observed in the PMR spectra were identified by comparison with specially synthesized compounds.

The Nenitzescu reaction — the reaction of substituted benzoquinones with enamines — serves as the most convenient method of synthesis of 5-hydroxyindole derivatives [1]. It is known that the direction of the primary process — the addition of the enamine to quinone according to Michael is often determined by the size of the substituent at the enamine nitrogen atom [1-3]. In continuation of the study of the Nenitzescu reaction, we investigated in the present work the reaction of 2-chloro-5-methyl-benzoquinone (I) with β-aminocrotonic ester (IIa) and its N-methyl-, N-ethyl-, and N-benzyl derivatives (IIb-d). It was unexpectedly found that when the reaction was carried out under the usual conditions (CH_3COOH, 50-55°C), compounds of two types were isolated according to the structure of the starting enamine: in the case of esters IIa,b, 2-methyl-3-ethoxycarbonyl-4-chloro-5-hydroxy-7-methylindole (IIIa) and its N-methyl derivative IIIb were isolated in low yield, while when N-ethyl- and N-benzylaminocrotonic esters (IIc, d) were used, 2-chloro-3-(β-ethylamino- and -(β-benzylamino-β-methyl-α-ethoxycarbonyl)vinyl-5-methylhydroquinones (IVc, d) were obtained in satisfactory yields. The Michael addition takes place only at the 3-position of benzoquinone I, as unequivocally indicated by the PMR spectra: in the spectra of the isolated compounds, a splitting of the proton signals at the 6-position is observed due to the SSI [spin-spin interaction] with the methyl group of the benzene ring with $J \approx 0.7$ Hz. On the basis of the similarity of structures of the starting compounds and since the first stage of the Nenitzescu reaction is of the same type in the reactions studied (at the 3-position of the starting quinone), we concluded that the observed difference in the

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