Reactions of aminals of conjugated ω-dimethylaminoaldehydes with coumarin derivatives

Zh. A. Krasnaya,[a] Yu. V. Smirnova,[a] A. S. Tatikolov,[b] V. S. Bogdanov,[a] E. V. Nikishova,[a] and V. L. Savel'ev[a]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328*

[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 938 2156*

The reactions of aminals of conjugated ω-dimethylaminoaldehydes with various derivatives of 4-methyl- or 3-acetyl coumarins produce ω-dimethylaminopolyenones containing coumarin fragments. Unlike the starting coumarins, these polyenones practically do not fluoresce. Dialkyl-substituted coumarins with hydroxyl groups in positions 5 or 7 react with β-dimethylaminoacrolein aminal to give salts consisting of 1 mole of doubly charged dimethylaminopropenylidenedimethylammonium cations and 2 moles of phenoxide ions (derived from the starting coumarins). The structure and the properties of the salts in solutions have been studied by absorption and fluorescence spectroscopy.

Key words: aminals of conjugated ω-dimethylamioaldehydes, coumarins, ω-dimethylaminopolyenones, trimethine salts, absorption spectra, fluorescence spectra, laser dyes.

Previously we have found that aminals of conjugated ω-dimethylaminoaldehydes readily undergo condensation with cyclic and acyclic ketones as well as with various β-dicarbonyl compounds.[1–3]

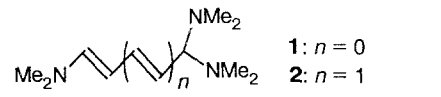
These reactions, the directions of which depend both on the structure of the starting reactants and on the conditions chosen, made it possible to obtain aminopolyenes possessing a number of specific properties (solvatochromy, thermochromy, fluorescence, generation of laser radiation) and trimethinoxanine salts, which can be used as the anionic component in the preparation of cationic-anionic dyes of a new type.[4–7]

It is also known that coumarin derivatives constitute an important group of organic luminophors and laser dyes, which efficiently generate radiation in the 400—560 nm region.[8–10] They are also used in medicine and biochemistry as fluorescent compounds.[11]

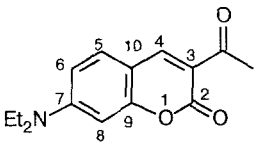
The spectral and luminescent characteristics of coumarins are substantially affected by substituents. Coumarin dyes with substituents in positions 4, 6, and 7 provide the most efficient generation.

The introduction in position 3 of a 7-substituted coumarin of substituents that extend the chain of conjugation results in a bathochromic shift in their absorption and luminescence spectra, and this expands the field of application of this type of coumarin.

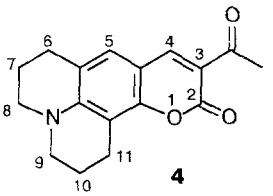
In the present work, in order to prepare novel derivatives of coumarins incorporating a ω-dimethylaminopolyene fragment as one of the substituents and to investigate their optical properties, we studied the reactions of aminals of conjugated ω-dimethylaminoaldehydes (**1**, **2**) with coumarins (**3**—**11**).



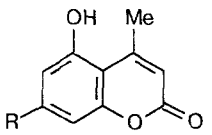
1: $n = 0$
2: $n = 1$



3

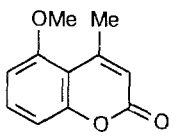


4

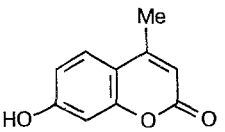


5—**8**

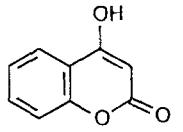
5: R = Me ;
6: R = C_5H_{11} ;
7: R = C_6H_{13} ;
8: R = C_7H_{15}



9



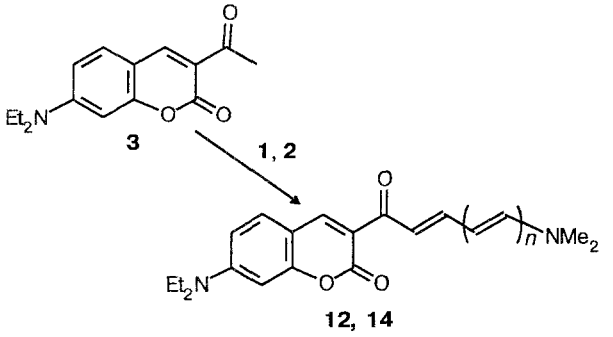
10

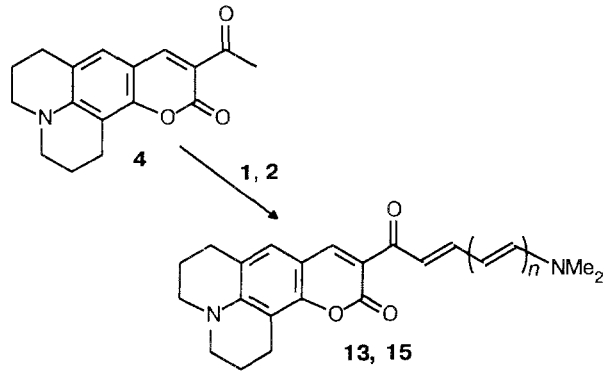


11

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 537—543, March, 1995.

We found that brief heating of equimolar amounts of aminal **1** or **2** with coumarin **3** or **4** affords δ-dimethylaminodienones (**12** and **13**) and ξ-dimethylaminotrienones (**14** and **15**) as crystalline solids with a color varying from dark-red to violet in good yields. Their yields and ^{1}H NMR and UV spectral data are listed in Table 1.

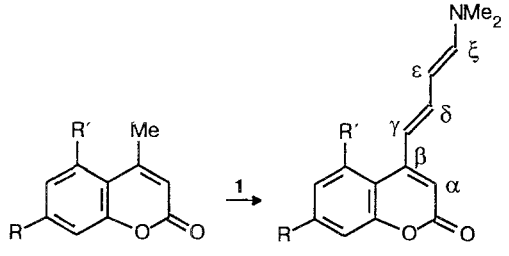




12,13: n = 1;
14,15: n = 2.

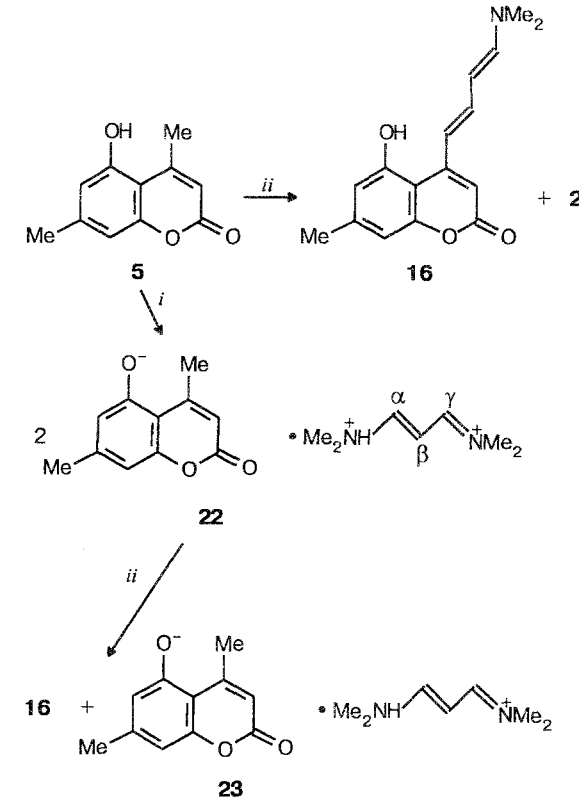
Previously[2] we showed that the reactivity of aminals **1** and **2** is so high that their condensation can involve not only the α-methyl group but also Me groups separated from the carbonyl group by one or two double bonds.

Therefore, one could expect that the reaction of aminal **1** with coumarins **5—10** would result in the corresponding ζ-dimethylaminopolyenones (**16—21**):



5, 16: R = Me, R′ = OH
6, 17: R = C_5H_{11}, R′ = OH
7, 18: R = C_6H_{13}, R′ = OH
8, 9: R = C_7H_{15}, R′ = OH
9, 20: R = Me, R′ = OMe
10, 21: R = OH, R′ = H

However, the interaction of aminal **1** with coumarin **5** (benzene, 20 °C) unexpectedly gave a crystalline solid in an 84 % yield, which, according to ^{1}H NMR, ^{13}C NMR, and UV spectra and elemental analysis, was a salt (**22**) consisting of one mole of the doubly charged trimethine cation and two moles of the anion derived from the starting coumarin.



i. **1**, 20 °C, benzene.
ii. **1**, 80 °C, benzene

Salt **22** decomposes when boiled in benzene, however, heating it in benzene in the presence of aminal **1** results in the formation of a crystalline product. According to the data of the ^{1}H NMR, UV, and mass spectra, this product is a mixture of trienone **16** and trimethine salt **23** (in a 1:2.5 ratio), which we were not able to separate.

Coumarins **6—8** and **10** containing OH groups in positions 5 or 7 react with aminal **1** in a similar way. In all cases, the reactions at 20 °C or with brief heating gave salts (**24—27**) incorporating doubly charged cations; their yields, physicochemical characteristics, and the data of their ^{1}H NMR and UV spectra are presented in Table 2.

When aminal **1** and coumarins **6—8** and **10** are heated in benzene for a long period, ξ-dimethylaminotrienones are formed. However, only from coumarin **10** were we able to obtain individual trienone **21**; compounds **17—19** were produced as mixtures with the corresponding trimethine salts similar to **23** (the contents of trienones were ~30 %).

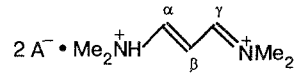
Table 1. Yields, physicochemical characteristics, and spectral data for compounds **12—15**, **20**, and **21**

Compound	The starting reactants		T/°C[a] (τ/h)	Yield (%)	M.p. /°C	M^+ (m/z)	λ_{max}/nm(ε)		^{1}H NMR[b]			
									δ			J/Hz
	Aminal	Coumarin					in EtOH	in $CHCl_3$	NMe_2	Olefinic protons	The other protons	
12	**1**	**3**	80 (0.1)	77	175—177[c]	340	490 (64000) 420 sh	480	2.95	7.19 (α) 7.70 (β) 5.40 (γ) 6.82 (δ)	8.5 (1 H, H-4) 7.38 (1 H, H-5) 6.58 (1 H, H-6) 6.47 (1 H, H-8) 3.44 (4 H, CH_2) 1.22 (6 H, CH_3)	14.5 (α,β) 12.5 (β,γ) and (γ,δ)
13	**1**	**4**	80 (0.15)	78	> 220	364	510 (60000)	490	2.93	7.21 (α) 7.68 (β) 5.39 (γ) 6.80 (δ)	8.40 (1 H, H-4) 6.96 (1 H, H-5) 1.96 (4 H, H-7, H-10) 2.88 (2 H, H-6[d]) 2.75 (2 H, H-11[d]) 3.32 (4 H, H-8, H-9)	14.5 (α,β) 12.5 (β,γ) (γ,δ)
14	**2**	**3**	20 (24) 40—65 (0.4)	60	174—177[c]	366	440 (13000) 535 (36000)	515 440 sh	2.88	7.29 (α) 7.63 (β) 6.18 (γ) 6.73 (δ) 5.18 (ε) 5.75 (ξ)	8.5 (1 H, H-4) 7.40 (1 H, H-5) 6.6 (1 H, H-6) 6.48 (1 H, H-8) 3.45 (4 H, CH_2) 1.22 (6 H, CH_3)	14.6 (α,β) 11.6 (β,γ) 14.3 (γ,δ) 11.0 (δ,ε) 13.0 (ε,ξ) 9.0 (H-5, H-6) 2.5 (H-6, H-8)
15	**2**	**4**	80 (0.75)	41.5	196—199[e]	390	550 (45000)	520	2.90	7.33 (α) 7.62 (β) 6.20 (γ) 6.70 (δ) 5.18 (ε) 6.57 (ξ)	8.40 (1 H, H-4) 6.98 (1 H, H-5) 1.97 (4 H, H-7, H-10) 2.77 (4 H, H-6, H-11) 3.33 (4 H, H-8, H-9)	15.0 (α,β) 11.5 (β,γ) 14.5 (γ,δ) 11.5 (δ,ε) 13.0 (ε,ξ)
20[f]	**1**	**9**	60—65[g] (0.5)	39	162—166[c]	285	460 (33500)	440	2.87	6.12 (α) 7.00 (γ) 7.25 (δ) 5.30 (ε) 6.94 (ξ)	6.75 (1 H, H-6) 6.73 (1 H, H-8) 3.88 (3 H, OCH_3) 2.35 (3 H, CH_3)	15.0 (δ,γ) 11.4 (δ,ε) 12.0 (ε,ξ)
21[f]	**1**	**10**	80—90 (0.5)	24	186—187	257	455 (35000)	–	2.89	6.07 (α) 6.32 (γ) 7.39 (δ) 5.35 (ε) 7.00 (ξ)	7.78 (1 H, H-5) 6.74 (1 H, H-6) 6.64 (1 H, H-8)	15.0 (γ,δ) 13.0 (δ,ε) 12.5 (ε,ξ) 8.5 (H-5, H-6)

[a] T is the temperature; τ is the reaction time. Compounds **14**, **20**, and **21** were prepared without a solvent; compounds **12**, **13**, and **15** were prepared in benzene (2 mL of benzene per 1 mmol of compound **3** or **4**). [b] For compounds **12—15**, in $CDCl_3$, for **20** and **21**, in DMSO-d_6. [c] From MeOH. [d] The signals were arbitrarily assigned to H-6 and H-11. [e] From EtOH. [f] Mass spectra of trienones **20** and **21** also exhibit intense peaks associated with the corresponding products of 1,6-cyclodeamination. [g] The yield decreases somewhat in benzene.

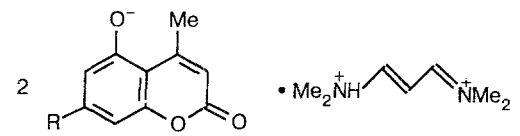
It should be noted that trimethine salts containing one doubly charged cation and two anions have not been known before. It is likely that the presence of the hydroxyl groups in coumarins **5—8** and **10** is favorable for the formation of rather stable salts **22**, **24—27**. In the case of coumarin **9** (the product of methylation of

Table 2. Conditions of the syntheses, yields, and physicochemical characteristics for salts **22**, **24**—**27**

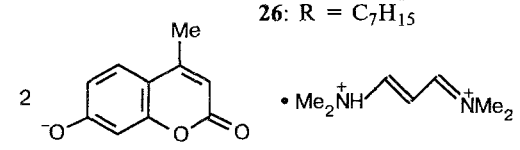


Salt	T/°C[a] (τ/h)	Aminal: coumarin mol/mol	Yield (%)	M.p. °C	λ_{max}/nm(ε), EtOH	^{1}H NMR ($CDCl_3$) Anion δ (*J*/Hz)	Cation δ	Cation *J*/Hz
22[b]	20 (0.5)	1:1	84	150—153	256 (26500) 312 (110000)	5.77 (2 H, H-3) 6.60 (2 H, H-6) 6.25 (2 H, H-8) 2.69 (6 H, Me) 2.18 (6 H, Me)	3.19 (6 H, NMe_2) 2.96 (6 H, NMe_2) 12.25 (1 H, NH) 7.35 (2 H, α,γ) 4.87 (1 H, β)	12.0 (α,β) and (β,γ)
24	55—60 (1)	1:2	61	74—76	312 (92400) 256 (23000)	5.84 (2 H, H-3) 6.66 (2 H, H-6) 6.38 (2 H, H-8) 2.70 (6 H, Me) 1.52 (4 H, CH_2) 1.26 (8 H, $(CH_2)_2$) 2.44 (4 H, CH_2) 0.85 (6 H, Me)	3.00 (6 H, NMe_2) 3.23 (6 H, NMe_2) 7.47 (2 H, α, γ) 4.87 (1 H, β)	12.0 (α,β) and (β,γ)
25	55—70 (1)	1:2	50	Oil	256 (22000) 312 (79000)	5.81 (2 H, H-3) 6.67 (2 H, H-6) 6.33 (2 H, H-8) 2.70 (6 H, Me) 1.50 (4 H, CH_2) 1.23 (12 H, $(CH_2)_3$) 2.42 (4 H, CH_2) 0.85 (6 H, Me)	3.00 (6 H, NMe_2) 3.23 (6 H, NMe_2) 7.43 (2 H, α, γ) 4.91 (1 H, β) 9.70 (1 H, NH)	11.5 (α,β) and (β,γ)
26	20 (1)	1:2	41	Oil	256 (22000) 312 (83000)	5.84 (2 H, H-3) 6.67 (2 H, H-6) 6.39 (2 H, H-8) 2.67 (6 H, Me) 1.51 (4 H, CH_2) 1.23 (16 H, $(CH_2)_4$) 2.43 (4 H, CH_2) 0.85 (6 H, Me)	3.01 (6 H, NMe_2) 3.29 (6 H, NMe_2) 7.74 (2 H, α, γ) 4.93 (1 H, β) 8.40 (1 H, NH)	11.3 (α,β) and (β,γ)
27	20 (0.75)	1:2	25	153—160	312 (69000)	5.84 (2 H, H-3) 7.34 (2 H, H-5, ^3J = 9.0) 6.81 (2 H, H-6, ^4J = 2.4) 6.62 (2 H, H-8) 2.33 (2 H, CH_3)	3.04 (6 H, NMe_2) 3.28 (6 H, NMe_2) 7.80 (2 H, α, γ) 5.0 (1 H, β)	12.0 (α,β) and (β,γ)

[a] *T* is the temperature; τ is the reaction time. Benzene was used as the solvent, 3 mL per 1 mmols of coumarin.
[b] Found (%): C; 68.75; H, 6.87, N, 5.07. $C_{29}H_{34}O_6N_2$. Calculated (%): C; 68.7; H, 6.72, N, 5.53.



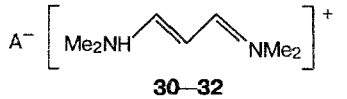
24: R = C_5H_{11}
25: R = C_6H_{13}
26: R = C_7H_{15}



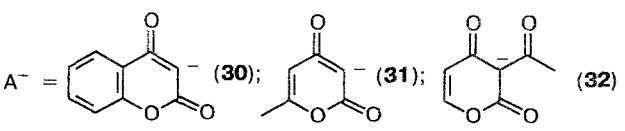
27

compound **5**), only trienone **20** was obtained. The yields, physicochemical properties, and the data of the ^{1}H NMR and UV spectra of trienones **20** and **21** are presented in Table 1.

The reactions of aminal **1** with 4-hydroxycoumarin **11**, with 6-methyl-2,4-pyranedione (**28**), or with 3-acetyl-2,3(3*H*)-dihydropyrane-2,4-dione (**29**) yield only trimethine salts (**30**—**32**):



30—**32**



Type **23** trimethine salts, **30—32**, are intermediate products in the formation of δ-aminodienones from aminals and CH acids, and in some cases, the reaction is arrested at the step of salt formation.[12]

It follows from the data of the ^{1}H NMR spectra (Table 1) that dienones **12**, **13** and trienones **14**, **15**, **20**, and **21** have *trans*-configurations and exist as *s-trans*-conformers (J = 11—15 Hz).

A comparison of the data of the electron absorption spectra of ω-aminopolyenones **12—15**, **20**, and **21** (Table 1) with the corresponding data for the starting coumarins (Table 3) indicates that the introduction of the ω-aminopolyenone moiety results in a substantial bathochromic shift of λ_{max}, which amounts to 40—80 nm. ω-Aminopolyenones **12—15**, **20**, and **21** exhibit positive solvatochromy, since on going from $CHCl_3$ to EtOH, their λ_{max} shifts bathochromically by 10—30 nm.

Unlike the starting coumarins, which have intense fluorescence, the corresponding ω-aminopolyenones **12—15**, **20**, and **21** virtually do not fluoresce. Thus, the addition of a ω-aminopolyenone moiety to a coumarin leads to quenching of the fluorescence of the latter, possibly due to active participation of the flexible polyene chain in the nonradiating deactivation of the excitation energy (fluorescence of the corresponding ω-aminopolyenones is also very weak).

The compositions of salts **22** and **27** were studied in detail by spectral fluorescence methods. The absorption spectrum of salt **22** ($1.8 \cdot 10^{-7}$—$6.5 \cdot 10^{-3}$ mol L^{-1} in 2-propanol) exhibits two bands with λ_{max} = 310 and 400 nm and extinction coefficients ε ~ 90000 and 8800 mol^{-1} L cm^{-1}, respectively. The former band results from superposition of absorption bands of coumarin **5** (λ_{max} = 305 nm, ε = 13600 mol^{-1} L cm^{-1}) and the Me_2N—CH=CH—CH=N^+Me_2 cation (λ_{max} = 312 nm) and the latter band is due to the absorption of the phenoxide anion of coumarin **5** (λ_{max} = 400 nm, ε = 8100 mol^{-1} L cm^{-1}). The ratio between the bands corresponding to coumarin and its phenoxide anion in a solution of salt **22** can be varied by adding an acid or a base. The fluorescence spectrum of salt **22** (Fig. 1, curves *1* and *2*) also exhibits two bands (λ_{max} = 447 and 454 nm), which were assigned to fluorescence of coumarin **5** and its phenoxide anion by a comparison of the fluorescence and excitation spectra (curves *3* and *4*). In short-wave excitation (300 nm), fluorescence is mostly due to coumarin **5** with a small contribution from the phenoxide anion in the long-wave region (curve *1*), while in the case of long-wave excitation (400 nm), the fluorescence of the phenoxide anion prevails (curve *2*) and the Me_2N—CH=CH—CH=N^+Me_2 cation practically does not fluoresce. Similar bands are observed in the absorption spectrum of salt **27** (λ_{max} = 314 and 381 nm in isopropanol) and in its fluorescence spectrum (Fig. 2, curves *1* and *2* with λ_{max} = 388 and 448 nm, respectively). On the short-wave excitation (300 nm), fluorescence is mostly due to coumarin **10** (the long-wave fluorescence of its phenoxide anion makes a certain contribution to it), and in the case of the long-wave excitation (380 nm), it is mostly due to the phenoxide anion. It should be noted that the quantum yield of the fluorescence of coumarin **10** is much higher than that of coumarin **5** and its phenoxide anion.

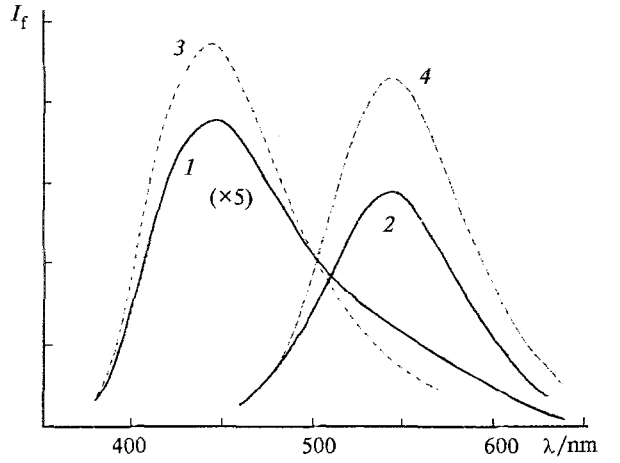


Fig. 1. Fluorescence spectra of salt **22** in 2-propanol at excitations λ_{ex} = 300 (*1*) and 400 nm (*2*), coumarin **5** at λ_{ex} = 300 nm (*3*), and its phenoxide anion at λ_{ex} = 420 nm (*4*).

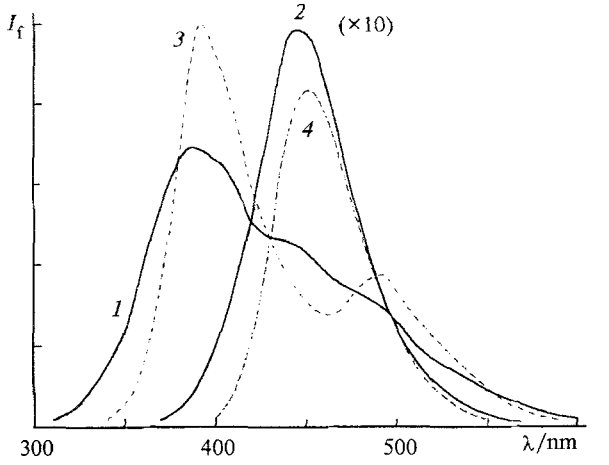


Fig. 2. Fluorescence spectra of salt **27** in 2-propanol at excitations λ_{ex} = 300 (*1*) and 380 nm (*2*), coumarin **10** at λ_{ex} = 320 nm (*3*), and its phenoxide anion at λ_{ex} = 390 nm (*4*).

Thus, the results obtained in the present work allow one to conclude that salts **22** and **24—27** occur in solutions as the following equilibrium

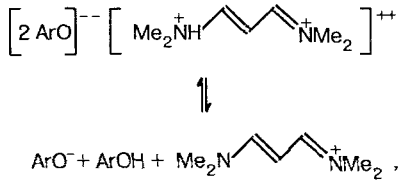


Table 3. UV and ^{1}H NMR spectra of coumarins **3**—**6**, **9**, and **10**

Compound	λ_{max}/nm (EtOH)	^{1}H NMR δ, *J*/Hz	Solvent
3	445	8.44 (1 H, H-4), 7.40 (1 H, H-5), ^3J = 9, 6.62 (1 H, H-6), ^4J = 2.5, 6.48 (2 H, H-8), 2.69 (3 H, COMe), 3.45 (4 H, $(CH_2)_2$), 1.27 (6 H, Me_2),	$CDCl_3$
4	470	8.36 (1 H, H-4), 6.98 (1 H, H-5), 2.87[a] (2 H, H-11), 2.9[a] (2 H, H-6), 3.34 (4 H, H-8, H-9), 1.98 (4 H, H-7, H-10), 2.69 (3 H, COMe)	$CDCl_3$
5	213 256 306	5.98 (1 H, H-3), ^4J = 1.3, 6.63 (2 H, H-6, H-8), 2.59 (3 H, Me). 9.5 (1 H, OH), R at C_7: 2.31 (3 H, Me).	$(CD_3)_2CO$
6	212 258 308	6.03 (1 H, H-3), 6.65 (1 H, H-6), 6.59 (1 H, H-8), 2.64 (2 H, Me), R at C_7: 1.66 (2 H, (CH_2), 1.38 (4 H, $(CH_2)_2$), 2.60 (2 H, (CH_2), 0.93 (3 H, Me).	CD_3OD
9	210 248 306	6.03 (1 H, H-3), ^4J = 1.2, 6.74 (1 H, H-6), 6.52 (1 H, H-8), 2.48 (3 H, Me), 3.87 (3 H, OMe), R at C_7: 2.39 (3 H, Me).	$CDCl_3$
10	206 220 320	6.12 (1 H, H-3), ^4J = 1.5, 7.62 (1 H, H-5), 6.85 (1 H, H-6), ^4J = 2.4, 6.78 (1 H, H-8), 2.45 (3 H, Me).	CD_3OD

[a] Assignment of the signals to H-6 and H-11 is tentative.

where ArOH is the corresponding coumarin, and ArO^- is the phenoxide anion. In dilute solutions, this equilibrium is shifted toward dissociation of the salt to give coumarin, the phenoxide anion, and the polymethine cation, while in concentrated solutions, it is shifted in the direction of association of these components to give the salt. Since the spectral data indicate that both ArO^- and ArOH are present in the system, this equilibrium is shifted to the right, at least to some extent at concentrations of the salt up to $6.5 \cdot 10^{-3}$ mol L^{-1}. Figure 3 indicates that the concentration of ArO^- is approximately equal to the initial concentration of the salt up to $6.5 \cdot 10^{-3}$ mol L^{-1}, therefore, salt **22** dissociates almost entirely into its components. Similar results were obtained for salts **24**—**27**. At the same time, at the higher concentrations that were used for recording the NMR spectra (on the order of $4 \cdot 10^{-2}$ mol L^{-1}) and in the solid state salts **22** and **24**—**27** are almost entirely associated.

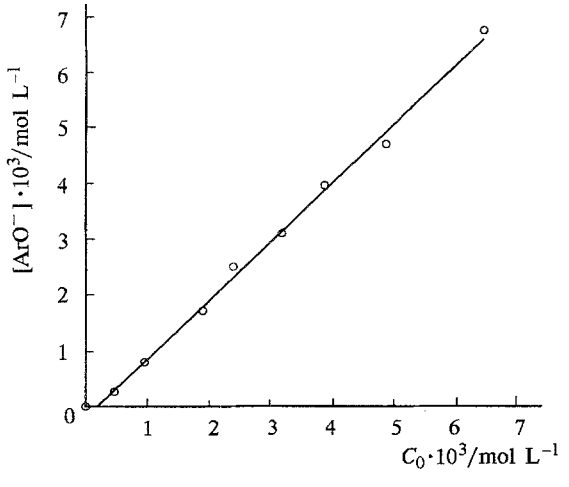


Fig. 3. The dependence of the concentration of ArO^- (the phenoxide anion derived from coumarin) on the concentration of salt **22** in 2-propanol (the ArO^- concentration was determined from its extinction coefficient ε = 8100 mol^{-1} cm^{-1} at λ_{max} = 400 nm).

Thus, the polymethine cation favors acid dissociation of coumarin by abstracting a proton from it to give salts of the type of **22** and **24**—**27**. This property can be used for increasing the efficiency of the generation of laser radiation, since the coumarin anion is known to possess more efficient generation than the starting coumarin.[9]

Experimental

UV spectra were recorded on a Specord UV VIS spectrophotometer, and fluorescence spectra were obtained on an Aminco-Bowman spectral fluorimeter with an R136 photomultiplier. The fluorescence spectra were not corrected. ^{1}H NMR spectra were obtained on a Bruker WM-250 instrument (250 MHz for ^{1}H) with respect to TMS and the ^{13}C NMR spectrum was measured on a Bruker AM-300 spectrometer (75.432 MHz).

Coumarins **5** and **6** were prepared by the procedure reported by Adams *et al.*,[13] **7** and **8** were obtained in a similar way, and coumarin **10** was prepared by the known procedure.[14] UV and ^{1}H NMR spectra of the coumarins are given in Table 3. All of the operations were carried out in anhydrous solvents.

The reaction conditions, yields, and characteristics of compounds **12**—**15**, **20**, and **21** are summarized in Table 1; those for salts **22**, **24**—**27** are in Table 2.

To isolate compound **12**, benzene was evaporated, and the precipitate that formed was recrystallized from MeOH. Compounds **13** and **14** were isolated by adding ether to the residue after evaporation and recrystallizing the precipitate from MeOH. In the case of compound **15**, the residue after evaporation was dissolved in MeOH and cooled to −70 °C, and the precipitate was separated and recrystallized from MeOH. To isolate aminopolyenone **20**, the residue was washed with ether and recrystallized from MeOH. In the case of compound **21**, the residue obtained after evaporation was washed with ether, dissolved in acetone, and cooled to −70 °C. The precipitate was separated by decantation, the residue was washed with ether, MeOH was added, and the precipitate was separated. Salts **22** and **27** were isolated by washing the residue with ether, dissolving it in EtOH, and precipitating the target compound with ether. To isolate compound **24**, the residue after evaporation was triturated with ether at −70 °C, and the precipitate was separated and washed with ether. In the case of compounds **25** and **26**, the residue after evaporation was washed with ether.

Compound **22** ^{13}C NMR ($CDCl_3$), δ: 162.8 (C_α, C_γ, J = 169 Hz); 89.4 (C_β, J = 162 Hz); 30.0 (NMe_2, J = 142 Hz); 46.3 (NMe_2, J = 142 Hz); 164.9 (C-2), 108.9 (C-3, J = 168 Hz); 158.1 (C-4, J = 6 Hz); 155.8 (C-5); 103.0 (C-6, J = 163 Hz); 142.6 (C-7, J = 6 Hz); 114.8 (C-8); 162.4 (C-9); 108.4 (C-10); 24.3 (C(4)-Me, J = 128 Hz); 21.7 (C(7)-Me, J = 128 Hz).

4,7-Dimethyl-5-methoxycoumarin (9). A mixture of coumarin **5** (3.1 g, 0.015 mol), dimethyl sulfate (3.8 g, 0.03 mol), and dry K_2CO_3 (6 g) in 100 mL of acetone was boiled for 7 h. The acetone was evaporated *in vacuo*, the residue was treated with 2*N* NaOH, and the precipitate was filtered off, washed with water, dried in air, and recrystallized from benzene to give 2.97 g (97%) of coumarin **9**, m.p. 150—151 °C. Found (%): C, 70.72; H, 6.1. $C_{12}H_{12}O_3$. Calculated (%): C, 70.6; H, 5.9.

The reaction of aminal 1 with coumarins 5—8 with heating. Aminal **1** (0.25 mL, 0.0013 mol) was added at 50°C to a suspension of coumarin **5** (0.24 g, 0.0013 mol) in 2 mL of benzene. The mixture was heated for 2 h at 75—80 °C. After cooling, the precipitate was filtered off, washed with hot benzene, dissolved in MeOH, and precipitated with ether to give 0.14 g of a red precipitate, m.p. 154—157 °C, which was a mixture of trienone **16** and salt **23**. UV (EtOH), λ_{max}/nm: 312 (ε 40300), 465 (ε 13000). ^1H NMR (CD_3OD), δ, **23**: 7.58 (d, 2 H, C_α, C_γ); 5.33 (t, 1 H, C_β), 3.29 (s, 6 H, NMe_2); 3.11 (s, 6 H, NMe_2); 2.22 (s, 3 H, C(7)-Me); 2.37 (s, 6 H, C(4)-Me); 6.16 (s, 1 H, H-3); 6.37 (s, 1 H, H-8); 7.28 (s, 1 H, H-6); **16**: 2.42 (s, 3 H, Me); 2.90 (s, 6 H, NMe_2); 6.0—6.8 (m, 7 H, Ph, olefinic protons). MS, *m/z*: 271 [M^+].

The reactions of **1** with **6**, **7**, and **8** were carried out in a similar way.

The authors are grateful to I. V. Komlev for providing coumarins **3** and **4**.

References

1. Zh. A. Krasnaya, T. S. Stytsenko, E. P. Prokof'ev, V. A. Petukhov, and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 595 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25**, No. 3 (Engl. Transl.)].
2. Zh. A. Krasnaya, T. S. Stytsenko, E. P. Prokof'ev, and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 116; 1980, 1362 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1980, **29**, 980 (Engl. Transl.)].
3. Zh. A. Krasnaya, E. V. Grechkina, and V. S. Bogdanov, *Izv. Akad. Nauk, Ser. khim.*, 1994, 285 [*Russ. Chem. Bull.*, 1994, **43**, 264 (Engl. Transl.)].
4. L. A. Shvedova, A. S. Tatikolov, A. P. Darmanyan, V. A. Kuz'min, and Zh. A. Krasnaya, *Dokl. Akad. Nauk SSSR*, 1984, **276**, 164 [*Dokl. Chem.*, 1984, **276** (Engl. Transl.)].
5. L. A. Shvedova, A. S. Tatikolov, V. A. Kuz'min, Zh. A. Krasnaya, and A. R. Bekker, *Dokl. Akad. Nauk SSSR*, 1984, **276**, 654 [*Dokl. Chem.*, 1984, **276** (Engl. Transl.)].
6. Zh. A. Krasnaya, T. S. Stytsenko, D. G. Gusev, and E. P. Prokof'ev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1596 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1446 (Engl. Transl.)].
7. M. I. Demchuk, A. A. Ischenko, Zh. A. Krasnaya, and V. P. Mikhailov, *Chem. Phys. Lett.*, **167**, 170.
8. L. K. Denisov, and B. M. Uzhinov, *Khim. Geterotsikl. Soed.*, 1980, 723 [*Chem. Heterocycl. Comp.*, 1980 (Engl. Transl.)].
9. V. I. Alekseeva, V. K. Shalaev, and E. A. Luk'yanets, *Khim. Promst* [*Chemical Industry*], 1981, 597 (in Russian).
10. B. M. Krasovitskii, and G. M. Boloshin, *Organicheskie lyuminofory* [*Organic Luminophors*] Khimiya, Moscow, 1984, 145 (in Russian).
11. S. Yudenfel'd, *Fluorestsentnyi analiz v biologii i meditsine* [*Fluorescent Analysis in Biology and Medicine*] Mir, Moscow, 1965, 304 (Russ. Transl.).
12. Zh. A. Krasnaya, and T. S. Stytsenko, *Izv. Akad. Nauk SSSR, Ser Khim.*, 1987, 821 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 748 (Engl. Transl.)].
13. R. Adams, C. K. Cain, and S. Joewe, *J. Am. Chem. Soc.*, 1941, **63**,1977.
14. *Organic Syntheses*, Collective Vol. 3, New York, John Wiley and Sons, 1955, 281.

Received July 20, 1994