3,3-Bis(hydroxymethyl)-2-butanone (VII). To a solution of 3.6 g (28 mmoles) of dioxane I in 50 ml of a 10:1 methanol–water mixture was added 0.1 ml of concentrated H_2SO_4. The reaction mixture was heated with distillation at 40-42°C for 15 h. Then the solvent was driven off, and the residue was chromatographed on SiO_2 (600 × 30-mm column, hexane–ethyl acetate eluent, 1:1, and R_f 0.13). We obtained 0.8 g (24%) of compound VII. IR spectrum: 1740 and 3290 cm^{-1}. PMR spectrum: 1.0 (3H, singlet, CH_3), 2.25 (3H, singlet, CH_3CO), 3.64-3.99 ppm (6H, multiplet, CH_2, OH).

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LUMINESCENCE-SPECTRAL AND ACID-BASE CHARACTERISTICS OF 3-ARYL-7-DIETHYLAMINOCOUMARINS

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The absorption and fluorescence spectra and the acid-base characteristics of 7-diethylaminocoumarins containing an aromatic substituent at position 3 and H, Cl, CH_3, CF_3, *and* $N(CH_2CH_2)_2O$ *at position 4 were studied. For the para-substituted derivatives a linear correlation was obtained between the* pK_a *values and the Hammett* σ_p *constants. On the basis of the obtained data, and also of an x-ray crystallographic investigation of 3-phenyl-4-methyl-7-diethylaminocoumarin it was concluded that there is weak π–π conjugation between the 3-aryl groups and the coumarin fragment.*

Earlier we reported the synthesis of a series of 3-aryl-7-diethylaminocumarins by means of photochemical substitution reactions [1, 2]. It is known that the 3-aryl derivatives of 7-aminocoumarins exhibit strong fluorescence and can be used as laser dyes [3].

In the present work we studied the luminescence-spectral and acid-base characteristics of 3-arylcoumarins (I-XIV) in order to investigate the following questions: The effectiveness of π–π conjugation between the aryl substituent and the aminocoumarin fragment; the spectral changes in the ground (S_0) and excited (S_1) states which occur with change in the electronic nature of the substituents in the phenyl ring; the effect of the substituent R at position 4 on the above-mentioned characteristics of 3-aryl-7-aminocoumarins.

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TABLE 1. Luminescence-Spectral Characteristics of 7-Aminocoumarins (I-XVI)

Compound	Solvent	Absorption λ_{max}, nm (log ε)	Fluorescence	
			λ_{max}, nm	φ_f*
I	C_2H_5OH	243 (3,98), 269 (4,24), 312 (3,46), 326 (3,54), 401 (4,62)	484	0,92
	CH_3CN	241 (3,90), 268 (4,12), 312 (3,36), 328 (3,52), 397 (4,53)	480	0,73
II	C_2H_5OH	257 (4,19), 306 (3,53), 318 (3,61), 383 (4,49)	475	0,86
	CH_3CN	244 (4,18), 256 (4,22), 306 (3,61), 318 (3,74), 377 (4,57)	468	0,61
III	C_2H_5OH	247 (4,15), 259 (4,19), 284 (4,47), 308 (3,63), 318 (3,69), 284 (4,47)	468	0,75
	CH_3CN	246 (4,12), 258 (4,12), 310 (3,67), 320 (3,74), 377 (4,48)	465	0,30
IV	C_2H_5OH	248 (4,18), 257 (4,19), 308 (3,67), 319 (3,72), 383 (4,46)	454	1,00
	CH_3CN	246 (4,14), 255 (4,15), 308 (3,68), 319 (3,76), 376 (4,45)	455	0,73
V	C_2H_5OH	240 (4,25), 254 (4,21), 318 (3,66), 385 (4,48)	464	0,95
	CH_3CN	242 (4,19), 256 (4,12), 320 (3,70), 380 (4,44)	460	0,63
VI	C_2H_5OH	254 (4,30), 309 (3,76), 319 (3,79), 388 (4,63)	472	0,53
	CH_3CN	248 (4,17), 310 (3,71), 320 (3,85), 380 (4,50)	470	0,58
VII	C_2H_5OH	252 (4,29), 308 (3,67), 319 (3,73), 385 (4,57)	462	0,92
	CH_3CN	250 (4,20), 308 (3,61), 320 (3,73), 380 (4,52)	454	0,89
VIII	C_2H_5OH	255 (4,21), 306 (3,67), 319 (3,70), 386 (4,48)	465	0,97
	CH_3CN	250 (4,11), 308 (3,58), 320 (3,66), 378 (4,44)	474	0,57
IX	C_2H_5OH	248 (4,31), 256 (4,32), 308 (3,71), 318 (3,76), 384 (4,64)	475	0,78
	CH_3CN	256 (4,22), 308 (3,64), 318 (3,76), 380 (4,54)	457	0,83
X	C_2H_5OH	253 (4,17), 280 (3,60), 322 (3,50), 394 (4,48)	485	0,70
	CH_3CN	252 (4,27), 280 (3,75), 324 (3,86), 386 (4,59)	486	0,45
XI	C_2H_5OH	252 (4,26), 282 (3,68), 320 (3,55), 393 (4,55)	475	0,66
	CH_3CN	246 (4,20), 282 (3,67), 320 (3,63), 388 (4,49)	475	0,60
XII	C_2H_5OH	260 (4,23), 314 (4,03), 382 (4,50)	470	<0,10
	CH_3CN	260 (4,17), 314 (4,04), 375 (4,46)	470	<0,10
XIII	C_2H_5OH	250 (4,14), 261 (4,18), 308 (3,59), 397 (4,50)	490	<0,10
	CH_3CN	249 (4,13), 260 (4,16), 308 (3,53), 320 (3,58), 393 (4,52)	465	<0,10
XIV	C_2H_5OH	263 (4,07), 415 (4,23)	545	<0,10
	CH_3CN	264 (4,28), 408 (4,46)	545	<0,10
XV	C_2H_5OH	244 (4,10), 254 (4,10), 282 (3,31), 310 (3,53), 322 (3,67), 380 (4,48)	462	0,29
	CH_3CN	242 (4,10), 254 (4,08), 308 (3,55), 324 (3,75)	450	0,34
XVI	C_2H_5OH	244 (4,24), 250 (4,22), 280 (3,31), 306 (3,55), 317 (3,65), 377 (4,46)	455	0,68
	CH_3CN	243 (4,14), 250 (4,22), 281 (3,27), 306 (3,57), 319 (3,71), 370 (4,41)	439	0,75

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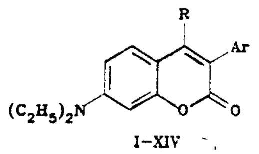
*φ_f is the quantum yield of fluorescence.



I-XIV

I R=H, II—XI R=CH_3, XII R=$N(CH_2CH_2)_2O$, XIII R=Cl, XIV R=CF_3; I, II, XII—XIV Ar=C_6H_5, III Ar=p-$CH_3C_6H_4$, IV Ar=o-$CH_3C_6H_4$, V Ar=p-$C_6H_5OC_6H_4$, VI Ar==p-ClC_6H_4, VII Ar=o-ClC_6H_4, VIII Ar=p-FC_6H_4, IX Ar=o-FC_6H_4, X Ar=p-CNC_6H_4, XI Ar=o-CNC_6H_4

In the absorption spectra of the coumarins (I-XIV) (Table 1) in acetonitrile or ethanol there is a group of strong bands in the regions of 245-260, 280-320, and 375-415 nm. The position of the maximum of the long-wave absorption band corresponding to the CT state [4] depends quite weakly on the nature of the substituent in the phenyl ring in the series of closely related coumarins (II-XI). It should only be noted that there is a small (≤10 nm) bathochromic shift of the given band in the transition from electron-donating (CH_3, OC_6H_5) to electron-withdrawing groups (F, Cl, CN). This indicates weak π–π conjugation between the aromatic and heteroaromatic fragments. This relationship does not contradict the published analogs [5, 6], according to which the increase in the electron-withdrawing capacity of the substituents in the pyran ring of 7-aminocoumarins is accompanied by a shift of the CT band into the red region. For compounds (III, IV) and (VI, XI) it is also possible to trace a weak tendency for a bathochromic shift of the longwave maxima in the transition from the ortho to the para derivatives. This relationship is evidently explained by an increase in the steric hindrances for the ortho derivatives, which leads to an additional decrease of the π–π conjugation in the system.

The similarity of the characteristics of the 3-phenyl derivatives (I, II) and of the related 7-diethylaminocoumarin (XV) and 4-methyl-7-diethylaminocoumarin (XVI) not having an aryl group at position 3 can serve as independent evidence for the weak electronic interactions between the 3-aryl group and the heterocyclic part of the molecule (Table 1).

The position of the absorption maximum is affected more appreciably by the substituent at position 4. Thus, for 3-phenylcoumarins (I, II, XII-XIV) the absorption maximum is shifted toward the longwave region as a whole by more than 30 nm with increase in the electron-withdrawing characteristics of the substituent at the $C_{(4)}$ atom and also with decrease in the steric hindrances [for the coumarin (I)] in the order $N(CH_2CH_2)_2O \leq CH_3 < Cl < H < CF_3$. The fluorescence spectra of the investigated compounds are significantly more sensitive to the effect of the substituents. In ethanol or acetonitrile the coumarins (I-XIV) fluoresce in the region of 460-545 nm (Table 1). Compounds (I-XI) give particularly strong fluorescence ($\varphi_f > 0.5$). The effect of the substituents on the position of the emission band in the coumarins (I-XIV) is similar in principle to the effect on the CT band but is more clearly defined. Thus, for example, in the coumarins (VI-XI) the bathofloric shift of the fluorescence maximum in the transition from the ortho to the para derivatives amounts to 10-15 nm and the overall range of the shifts of the spectral maxima of the aryl derivatives (II-XI) exceeds 20 nm. In contrast to compounds (I-XI), the coumarins (XII-XIV) exhibit weak fluorescence ($\varphi_f < 0.1$). The low capacity of the coumarin (XIII) for fluorescence is also typical of other 4-chlorocoumarins [7], but the small φ_f value for the coumarin (XII) is fairly unusual, since the familiar 4-morpholino-7-aminocoumarins are effective luminophores [8]. The marked quenching of the fluorescence in the coumarin (XII) may be due to steric hindrances which arise between the substituents at positions 3 and 4 [9] and lead to transformation of the CT state into the nonfluorescent TICT state [10] with rotation of the 4-morpholino group. The insignificant quantum yield of fluorescence for the coumarin (XIV) in polar solvents is confirmed by the analogous relationships in the series of other 4-trifluoromethyl derivatives, explained in [6] by an increase in the specific solvation due to increase in the polarity of such molecules.

The small capacity of the 3-aryl substituents for π–π conjugation with the coumarin fragment also follows from the ^{13}C NMR spectrum of the coumarin (II) (see Experimental). The assignment of the signals was made by means of an additive scheme on the basis of data for 3-phenyl-4-methyl-7-methoxycoumarin [11]. The discrepancy in the values of the calculated and experimental chemical shifts here does not exceed 1 ppm. Comparison of the ^{13}C NMR spectra of (II) and of the 3-unsubstituted analog (XVI) shows agreement in the majority of the signals except for the signals of the $C_{(3)}$ and $C_{(4)}$ atoms. Thus, in the ground state the electronic influence of the 3-phenyl group in the coumarin (II) does in fact extend only to the $C_{(3)}$ and $C_{(4)}$ atoms of the pyrone ring.

An independent assessment of the electronic effect of the 3-aryl substituent on the 7-aminocoumarin system was also made as a result of measurement of the pK_a values of the conjugate acids of the coumarins (I-XIV) in 50% ethanol. Protonation of the 7-aminocoumarins takes place at the $N_{(7)}$ atom and is accompanied by loss of the luminescent characteristics [8].

The basicity of the 7-aminocoumarins (II-XI) decreases regularly, although not very substantially, with increase in the electron-withdrawing characteristics of the substituents in the 3-aryl group. Moreover, a good linear correlation (r = 0.97) between the pK_a values and the Hammett σ_p constants was obtained for the para-phenyl-substituted derivatives (III, V, VI, VIII, X) and for the coumarin (II):

$$pK_a = 1{,}88 - 0{,}46\sigma_p$$

The increase in the effectiveness of π–π conjugation between the aromatic systems in the transition from the ortho to the para derivatives is also confirmed by the lower basicity of the coumarins (VII, IX, XI) compared with the coumarins (VI, VIII, X) ($\Delta pK_a = 0.06$-0.11) in the case of electron-withdrawing substituents (Cl, F, CN). On the other hand, the basicity of the p-tolyl-substituted coumarin (III) is somewhat higher than that of the ortho derivative (IV).

The dependence of the pK_a values on the substituents at position 4 is much more significant. In the series of coumarins (I, II, XII-XIV) the range of variation in the basicity exceeds an order of magnitude. It can be concluded from the data in Table 2 that the basicity of compounds (XV) and (XVI) practically coincides with the basicity of the corresponding 3-phenyl-

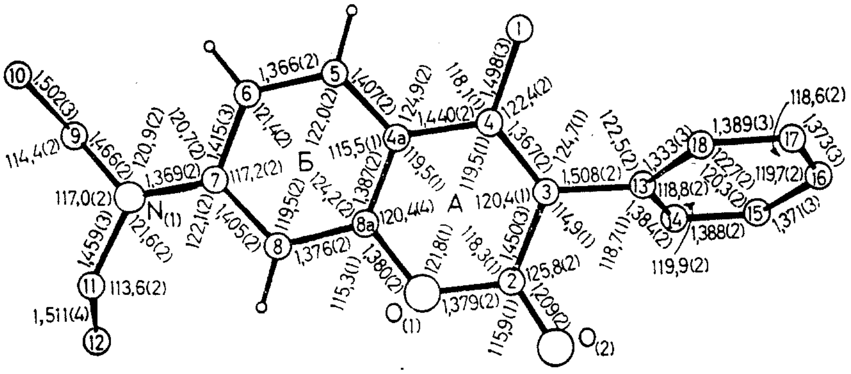


Fig. 1. General appearance of the molecule of (II); bond lengths, Å; bond angles, deg.

TABLE 2. Acid-Base Characteristics of 7-Aminocoumarins (I-XVI) in 50% Aqueous Ethanol

Compound	Absorption, λ_{max}, nm		$pK_a \pm 0{,}04$	$pK^*_a \pm 0{,}10$	Compound	Absorption λ_{max}, nm		$pK_a \pm 0{,}04$	$pK^*_a \pm 0{,}10$
	NM*	cation				NM*	cation		
I	408	323	1,78	−12,02	IX	393	315	1,84	−11,64
II	392	314	1,92	−11,65	X	399	315	1,59	−12,73
III	390	317	1,98	−10,67	XI	399	316	1,68	−12,42
IV	390	314	1,95	−11,34	XII	380	341	1,97	−10,23
V	392	315	2,93	−11,33	XIII	406	318	0,96	−13,64
VI	395	316	1,76	−12,34	XIV	423	314	0,72	−16,85
VII	392	314	1,87	−11,70	XV	390	311	1,79	−12,14
VIII	394	314	1,78	−12,07	XVI	385	310	1,97	−11,49

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*NM) neutral molecules.

coumarins (I) and (II). In relation to the coumarin (XVI) compounds (III-V), containing electron-donating substituents in the phenyl group, are somewhat stronger bases while the coumarins (VI-XI), containing electron-withdrawing substituents, are weaker bases.

Using Forster's method [13], we also estimated the basicity of the coumarins (I-XVI) in the excited state (Table 2). A common feature of the 7-aminocoumarins is the marked decrease of the basicity during excitation [5]. The pK_a^* values of the investigated compounds confirm this fact – the observed decrease in basicity exceeds 12 orders of magnitude. As expected, the smallest pK_a^* values are observed in the coumarins having the most electron-withdrawing substituents at position 4 or in the 3-aryl group. On the whole, the changes in the basicity of the coumarins (I-XVI) in the excited state are similar to the changes in the basicity of the unexcited molecules. However, it can be concluded for the case of the coumarins (II-XI) that the pK_a^* values are approximately four times more sensitive than the pK_a values to the nature of the substituent (σ_p) in the phenyl ring.

For a more rigorous and sounder conclusion about the effectiveness of the π–π conjugation between the aryl and heteroaryl fragments in the 7-aminocoumarins (I-XIV), we undertook an x-ray crystallographic investigation of compound (II).

Earlier [14, 15] we conducted x-ray crystallographic investigations into the coumarin (XV), 4-morpholino-7-ethylaminocoumarin (XVII), and 4-methyl-3-(β-methoxycarbonylvinyl)-7-diethylaminocoumarin (XVIII). The results from analysis of the distribution of the bond lengths in the 7-aminobenzopyran systems and their conformational characteristics, and also a comparison of these data with the ^{13}C NMR spectra of the compounds studied in [14], confirmed the significant contribution from the forms with charge separation to the observed geometry of the molecules.

In contrast to the coumarin (XVII), where the conjugation with the 4-morpholino group leads to loss of the planarity of the heterocycle A, in the molecule of (II) (Fig. 1), as also in the molecules of (XV) and (XVIII), the conformation of both rings A and B of the coumarin nucleus is planar [within the limits of 0.015(2) Å]. The dihedral angle between the planes of rings A and B amounts to 3.4°, while the dihedral angle between the mean-square plane of the bicyclic system and the phenyl substituent is 67.8°, i.e., the π systems of the phenyl group and the coumarin fragment are largely isolated. Evidence for this can also be obtained from the elongation of the $C_{(3)}$–$C_{(13)}$ bond to 1.508(2) Å compared with the standard $C_{(sp^2)}$–C(Ar) length of 1.483 Å [16]. At the same time some decrease in the endocyclic bond angle at the $C_{(3)}$ atom to 120.4(1)° [122.5° in the molecule of (XV), 122.4° in (XVII)], similar to the decrease observed in aromatic systems with electron-donating substituents, may result from weak π–π interaction between the phenyl group and the $C_{(3)}$–$C_{(4)}$ double bond. The increase in the length of the $C_{(3)}$–$C_{(13)}$ bond, and also the significant rotation of the benzene ring are evidently due to steric repulsion between the substituents at the $C_{(3)}$ and $C_{(4)}$ atoms, leading to substantial inequality in the exocyclic bond angles at the $C_{(3)}$ atom and, to a lesser degree, at the $C_{(4)}$ atom.

We note that, as a result of the less-effective electron-donating effect of the methyl group compared with the morpholino group at position 4, some increase in the length of the $C_{(2)}$–$C_{(3)}$ bond and decrease in the lengths of the $C_{(4)}$–$C_{(4a)}$ and $C_{(3)}$–$C_{(4)}$ bonds should be expected in the molecule of (II) compared with (XVII). In fact, the $C_{(2)}$–$C_{(3)}$ bond in the molecule of (II) is elongated to 1.450(3) Å [1.428 Å in the coumarin (XVII)], while the $C_{(4)}$–$C_{(4a)}$ bond is shortened a little to 1.440(2) Å [1.449 Å in the coumarin (XVII)]. At the same time the $C_{(3)}$–$C_{(4)}$ bond [1.367(2) Å] is even a little longer than that found in the molecule of (XVII) (1.362 Å) on account, evidently, both of the steric hindrances (as mentioned above) and of the different electronic nature of the substituents in the molecules of (II) and (XVII). Both these factors probably have an effect, since the $C_{(3)}$–$C_{(4)}$ bond in the molecule of (II) is one of the longest of those obtained in the structurally investigated derivatives of coumarin (XV) and coincides with the maximum in the molecules of 7-diethylamino-2-alkylidenebenzopyrans [17].

TABLE 3. Coordinates (× 10^4) of the Nonhydrogen Atoms in the Molecule of (II)

Atom	x	y	z
$O_{(1)}$	7413(1)	1083(1)	4157(1)
$O_{(2)}$	8019(1)	772(2)	5683(1)
$N_{(1)}$	6399(1)	1859(2)	885(1)
$C_{(1)}$	4712(1)	3336(2)	4103(1)
$C_{(2)}$	7323(1)	1284(2)	4995(1)
$C_{(3)}$	6414(1)	2051(2)	4981(1)
$C_{(4)}$	5668(1)	2553(2)	4154(1)
$C_{(4a)}$	5807(1)	2368(2)	3299(1)
$C_{(5)}$	5130(1)	2940(2)	2415(1)
$C_{(6)}$	5327(1)	2788(2)	1636(1)
$C_{(7)}$	6218(1)	2018(2)	1675(1)
$C_{(8)}$	6894(1)	1418(2)	2549(1)
$C_{(8a)}$	6680(1)	1633(2)	3321(1)
$C_{(9)}$	5848(1)	2864(2)	52(1)
$C_{(10)}$	4939(2)	2032(2)	−671(1)
$C_{(11)}$	7228(2)	853(2)	875(1)
$C_{(12)}$	8201(2)	1799(3)	1129(2)
$C_{(13)}$	6390(1)	2266(2)	5930(1)
$C_{(14)}$	7079(1)	3325(2)	6567(1)
$C_{(15)}$	7063(1)	3565(2)	7439(1)
$C_{(16)}$	6383(1)	2730(3)	7681(1)
$C_{(17)}$	5711(2)	1661(3)	7053(1)
$C_{(18)}$	5734(1)	1470(2)	6179(1)

TABLE 4. Coordinates (× 10^3) of the Hydrogen Atoms in the Molecule of (II).

Atom	x	y	z
$H_{(1.1)}$	470(1)	338(2)	471(1)
$H_{(1.2)}$	416(1)	273(2)	373(1)
$H_{(1.3)}$	464(2)	444(3)	385(1)
$H_{(5)}$	450(1)	345(2)	234(1)
$H_{(6)}$	485(1)	318(2)	107(1)
$H_{(8)}$	753(1)	90(2)	265(1)
$H_{(9.1)}$	563(1)	400(2)	25(1)
$H_{(9.2)}$	636(1)	316(2)	−20(1)
$H_{(10.1)}$	439(1)	170(3)	−44(1)
$H_{(10.2)}$	464(1)	272(2)	−119(1)
$H_{(10.3)}$	514(2)	96(3)	−82(2)
$H_{(11.1)}$	701(1)	37(2)	20(1)
$H_{(11.2)}$	734(1)	−17(2)	131(1)
$H_{(12.1)}$	874(2)	99(3)	111(2)
$H_{(12.2)}$	807(2)	266(3)	61(1)
$H_{(12.3)}$	837(2)	240(4)	171(2)
$H_{(14)}$	758(1)	388(2)	640(1)
$H_{(15)}$	754(1)	437(2)	785(1)
$H_{(16)}$	639(1)	292(2)	833(1)
$H_{(17)}$	522(1)	99(2)	724(1)
$H_{(18)}$	528(1)	81(2)	576(1)

The larger relative contribution from the "quinonoid" form with charge separation in the molecule of (II) compared with the molecule of (XVII) shows up in an appreciable reduction in the lengths of the $C_{(5)}$–$C_{(6)}$ and $C_{(8)}$–$C_{(8a)}$ bonds, and the last of them remains somewhat larger than the first. This confirms the greater effectiveness of π–π conjugation in the system involving the participation of the $C_{(8)}$–$C_{(8a)}$ bond, which we mentioned earlier [14, 15, 17].

The N–$C_{(7)}$ bond lengths in the molecules of (II, XV, XVII) are in fact identical (1.367-1.371 Å), i.e., the change in the degree of charge transfer does not have an appreciable effect on this value. It is necessary to note the equalization of the $O_{(1)}$–C bond lengths in the coumarin (II) similar to that observed in the molecule of (XV) and also the arrangement of the terminal methyl groups $C_{(10)}$ and $C_{(12)}$ on different sides of the plane of the bicyclic system.

In contrast to the structure of (XV), where the molecules form centrosymmetric dimers linked by dipole–dipole interactions, the molecules in the crystal of the coumarin (II) [as also in the crystal of (XVII)] are only linked by van der Waals forces. The reason for such a difference in the stacking of the molecules of (II), (XV), and (XVII) is the presence in (II) and

(XVII) of bulky cyclic systems not lying in the plane of the benzopyran system and hindering the formation of associates similar to those found in the structure of (XV).

EXPERIMENTAL

The UV spectra and the fluorescence spectra were recorded on a Hitachi EPS-3T spectrophotometer with a G-3 luminescence attachment. The relative quantum yields of fluorescence were determined with reference to 3-aminophthalimide [13]. The ^{13}C NMR spectrum of the coumarin (II) was obtained on a Bruker WM-250 instrument in deuterochloroform.

The pK_a values of the investigated 7-aminocoumarins were determined by a spectrophotometric method in 50% ethanol on a universal ÉV-74 ionometer with a glass and calomel electrodes. Hydrochloric acid was used as oxonium ion donor.

^{13}C NMR spectrum of coumarin (II), δ ($J_{^{13}C-^{1}H}$ Hz): 162.1 (s, $C_{(2)}$), 1.55.2 (dd, J = 9.3; J = 5.8, $C_{(8a)}$); 150.3 (m, $C_{(7)}$), 148.3 (m, $C_{(4)}$), 130.5 (ddd, J = 160.0, J = 7.0; J = 7.0, $C_{(13)}$ and $C_{(15)}$), 128.2 (dd, J = 160.7; J = 8.0, $C_{(12)}$ and $C_{(16)}$), 127.6 (ddd, J = 160.6; J = 7.4; J = 7.4, $C_{(14)}$), 126.1 (d, J = 158.4, $C_{(5)}$), 121.1 (m, $C_{(13)}$), 109.6 (m, $C_{(4a)}$); 108.6 (dd, J = 160.0, J = 5.7, $C_{(6)}$), 97.5 (dd, J = 160.0, 5.2, $C_{(8)}$), 44.8 (tq, J = 131.0, J = 4.2, $C_{(10)}$), 16.3 (q, J = 128.2, $C_{(9)}$), 12.5 ppm (q, J = 126.7, $C_{(11)}$).

X-ray Crystallographic Investigation of Coumarin (II) (Tables 3 and 4). The crystals of compound (II) ($C_{20}H_{21}NO_2$) were monoclinic. At 20°C, a = 14.509(2), b = 8.105(1), c = 15.638(2) Å, β = 114.06(10°, Z = 4, d_{calc} 1.22 g/cm^3, space group $P2_1/n$. The unit cell parameters and the intensities of 3446 reflections, 2541 of which with $I \geq 2\sigma(I)$ were used in the interpretation and refinement of the structure, were measured on a Syntex $P2_1$ four-circle diffractometer (λ_{MoK_α}, graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 27°$). The structure was interpreted by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation for all the nonhydrogen atoms. All the hydrogen atoms, revealed from the difference series, were refined isotropically. The final divergence factors were R = 0.049 and R_w = 0.049. All the calculations were conducted on an Eclipse S/200 computer using the INEXTL programs [18].

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