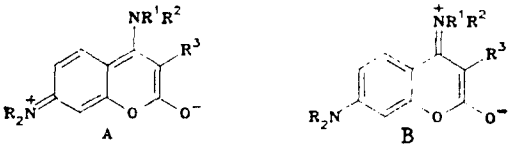
SPECTRAL-LUMINESCENCE AND ACID–BASE PROPERTIES OF 4,7-DIAMINOCOUMARINS

L. A. Karandashova, M. A. Kirpichënok, D. S. Yufit, Yu. T. Struchkov, and I. I. Grandberg

UDC 547.587.51.04:543.422:541.65

The absorption and luminescence spectra of a series of 4,7-diaminocoumarins have been investigated in ethanol and acetonitrile solution. The pk_a^I and pk_a^{II} values for several of the compounds have been measured. It has been found that the site of primary protonation is the nitrogen atom in the 7-position, and that the second protonation reaction occurs at the lactone oxygen atom. The effects of steric and electronic factors on the spectral-luminescence and acid–base characteristics of these compounds are discussed.

We have previously reported [1] the synthesis of 4,7-diaminocoumarins I-XIX from the corresponding 4-chloro derivatives. Interest in these compounds has been stimulated by several factors. First of all, many of these 4,7-diaminocoumarins I-XIX are efficient luminophores, and several of these compounds (for example compounds I, III-V) also fluoresce in a short-wavelength region (400-440 nm) which is relatively rare for 7-aminocoumarins. In addition, compounds with similar structures (such as coumarins VI-IX) may have sharply different luminescence quantum yields. Second, according to [2], the excited singlet state (S_1) for 7-aminocoumarins is a charge transfer state (CT state, formula A). For this reason it was not clear a priori what influence a strong electron-donating substituent in the 4-position would have on the π-electron density distribution in the ground and excited states. In the case of 4,7-diaminocoumarins we cannot exclude the possibility of a different CT state in which charge transfer occurs from the 4-amino group (formula B).



A B

Since many 4-aminocoumarins exhibit luminescence as well [3], the question arose which amino group would interact more efficiently with the lactone carbonyl group and, in general, on what factors do the spectral-luminescence properties of compounds I-XIX depend.

The absorption spectra of coumarins I-XIX in ethanol or acetonitrile solution contain, as expected, from three to five intense bands in the regions 245-260, 280-300, and 345-380 nm. The high oscillator strength values (f ~ 0.4-0.8), calculated according to [4] for long-wavelength absorption maxima in compounds I-XIX (Table 1), indicate that the corresponding electronic transitions are not forbidden. We assume that the absorption maximum in the 345-380 nm range in the spectra of coumarins I-XIX corresponds to a type A CT state; the same conclusion has been reached previously for close structural analogs of the coumarins in question, namely coumarin-1 (XX) and coumarin-102 (XXI) [2]. In our further discusisons we shall limit ourselves primarily to consideration of the long-wavelength absorption maximum since, as has been explained, this band provides the most information and also correlates with the luminescence properties of the compounds. It is apparent from the data in Table 1 that replacement of a 4-methyl group by an amino group in the transition from compounds XX and XXI to 4,7-diaminocoumarin derivatives with similar structures (I-IX, XVIII, XIX), is accompanied by a hypsochromic shift of the absorption bands by 10-15 nm, and by a hypsofluoric shift of the emission bands by approximately 20-30 nm. The

K. A. Timiryazev Agricultural Academy, Moscow.. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1610-1618, December, 1990. Original article submitted May 5, 1989; revision submitted September 27, 1989.

 0009-3122/90/2612-1338$12.50

greater sensitivity of the emission band to the effect of a substituent in the 4-position is not in conflict with our earlier-stated hypothesis concerning the existence of a type A CT state, in which the electron density in the lactone ring is enriched [5] and the lactone ring may also undergo strong perturbation as a result of interaction with the 4-amino group.

It is also interesting that substitution of a 4-monoalkylamino group by a 4-dialkylamino group, in the transition from compounds II-V, X, and XI to coumarins VI-IX, XII-XIV, is accompanied by a bathochromic shift of the long-wavelength absorption band by 7-19 nm, although the transition from 4-aminocoumarin I to 4-monoalkylcoumarins II-V does not produce any significant shift in this band. If we consider the normal increase in electron-donating properties of an amino group in the series NH_2 < NHAlk < $NAlk_2$, then we must conclude that this trend distorted in the case of 4,7-diaminocoumarins, in which a 4-dialkylamino group appears to act as a weaker electron-donating substituent than an NH_2 group. We feel that the factor responsible for this distortion is steric hindrance between the 4-dialkylamino group and the 5-H atom, which interferes with p-π conjugation in the $N–C_{(4)}=C_{(3)}–C–O$ system. This type of steric strain or hindrance also increases even when the alkyl groups are fixed in a ring, such as, for instance, in the transition from compounds VI and VII to coumarins VIII and IX; the difference in the positions of the absorption maxima in these compounds is approximately 10 nm. Introduction of an alkyl group in the 3-position exerts an analogous effect, leading to a bathochromic shift of the absorption band by 6-13 nm (compare compounds III, IV, IX, and X-XIV). We note, however, that in the 3,4-dialkyl-7-aminocoumarin series introduction of a 3-alkyl substituent is accompanied, in contrast, by a ~10 nm hypsochromic shift relative to 3-unsubstituted analogs [6]. Considering the similarity in the spectral characteristics of coumarin I and monoalkylaminocoumarins II-V, we conclude that the alkyl group in compounds II-V in their most favorable molecular conformations is spatially distant from the 5-H and in proximity to the 3-H atom. The $H–N–C_{(4)}$ fragment in coumarins I-V would therefore be expected to adopt similar structures. Supplementary confirmation of this conclusion is obtained from the PMR spectra of these compounds [1].

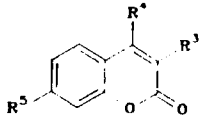
In the case of a substituent in the 7-position the steric factor is not expected to be significant, and so the 5-10 nm hypsochromic shift observed in the position of the long-wavelength absorption maximum in the transition from the 7-diethylaminocoumarins VI and IX to their 7-morpholino analogs XVI and XVII can be ascribed to the reduced electron-donating properties of the nitrogen atom in the 7-position [$N_{(1)}$]. Qualitative support for this conclusion concerning decreased electron-donating characteristics of a morpholino group relative to piperidino and diethylamino groups in the 7-position is provided by the basicity data for morpholine, piperidine, and diethylamine, whose pK_A values are 8.33, 11.12, and 11.09, respectively [7]. Securing or fixing the 7-dialkylamino group in a julolidine fragment as in compounds XVIII and XIX is accompanied by a bathochromic shift of the absorption band by 15-20 nm relative to the 7-diethylamino derivatives VI and IX. An analogous trend has also been shown to be valid for coumarins XX and XXI.

The general principles delineated above for the positions of the long-wavelength absorption bands in the spectra of compounds I-XIX are characteristic of their emission bands as well (Table 1). Coumarin II appears to be an exception to this rule; its fluorescence maximum is shifted approximately 30 nm toward longer wavelength compared to the fluorescence maxima in compounds III-V. This effect may be due to steric hindrance of strain arising in the S_1 state between the tert-butyl group and the 3-H (or 4-H) atom; the steric strain, in turn, reduces the degree of electron-donating interaction between the substituent in the 4-position and the 7-aminocoumarin fragment.

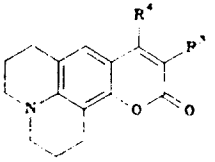
In order to understand the factors responsible for the wide variation in fluorescence quantum yields among the coumarins studied herein we have also investigated the low-temperature luminescence spectra of cumarins I, III, VI, IX, and XII. It was found that the fluorescence quantum yields for compounds I, III, VI, and XII under these conditions were substantially enhanced (φ_f = 0.8-0.9), and exhibited a leveling-off effect. In contrast, however, the fluorescence quantum yield for coumarin IX was found to be largely unchanged at 77 K (φ_f = 0.56). We conclude, therefore, that the fluorescence quenching effect observed for compounds VI, VII, and others at room temperature must be associated not with any electronic influence of the 4-dialkylamino group, but rather with vibrational loss. In this vein, a diethylamino group possesses greater vibrational degrees of freedom than does a morpholino group, for instance, which increases the probability of energy degradation or loss via radiationless transition channels from the S_1 state. This factor also explains the increased fluorescence quantum yields observed in the absence of one of the N-alkyl groups (cf. compounds II-V and VI, VII). Fixing the dialkylamino group in a ring, as in the transition from compounds VI and IX, for example, to coumarins XVIII and XIX also leads to enhanced fluorescence (Table 1).

In order to settle any remaining questions or controversy concerning the nature and degree of electronic influence of the amino groups in 4,7-dialkylaminocoumarins we have measured the pK_a values of the conjugate acids of compounds I, III, IV, VI, IX, XII, XIII, XVI, XVII, and XIX (Table 2). Acidification of aqueous ethanol solutions of these coumarins is accompanied by a decrease in the position of and finally, by complete disappearance of their long-wavelength absorption maxima at

TABLE 1. Spectral-Luminescence Characteristics of 7-Aminocoumarins I-XXII



I–XVII, XX, XXII



XVIII, XIX, XXI

Compound	R^3	R^4	R^5	Solvent	Absorption, λ_{max}, nm (Log ε)	Fluorescence λ_{max}, nm	
						λ_{max}, nm	φ_f*
I	H	NH_2	$N(C_2H_5)_2$	C_2H_5OH	245 (4,14), 258 (4,13), 276 (4,15), 303 (3,81), 350 (4,44)	410	0,58
				CH_3CN	245 (4,18), 258 (4,13), 275 (4,02), 282 (3,99), 307 (3,88), 352 (4,45)	400	0,64
II	H	NH—*t*-C_4H_9	$N(C_2H_5)_2$	C_2H_5OH	247 (4,16), 263 (4,11), 282 (4,32), 302 (3,92), 349 (4,45)	445	0,62
				CH_3CN	242 (4,23), 261 (4,13), 282 (4,27), 290 (4,23), 304 (3,96), 348 (4,48)	430	0,48
III	H	*cyclo*-$C_6H_{11}NH$	$N(C_2H_5)_2$	C_2H_5OH	246 (4,15), 263 (4,08), 285 (4,35), 294 (4,19), 349 (4,45)	414	0,67
				CH_3CN	242 (4,19), 262 (4,07), 283 (4,27), 292 (4,22), 348 (4,45)	400	0,52
IV	H	$NHCH_2C_6H_5$	$N(C_2H_5)_2$	C_2H_5OH	249 (3,99), 282 (4,09), 306 (3,65), 340 (4,15), 350 (4,22)	410	0,68
				CH_3CN	249 (4,05), 261 (4,00), 282 (4,05), 288 (4,02), 306 (3,76), 340 (4,19), 350 (4,26)	404	0,58
V	H	$NHCH_2CH_2OH$	$N(C_2H_5)_2$	C_2H_5OH	248 (4,14), 263 (4,08), 283 (4,26), 302 (3,90), 349 (4,42)	412	0,63
				CH_3CN	244 (4,19), 261 (4,10), 290 (4,18), 306 (3,95), 348 (4,46)	402	0,62
VI	H	$N(C_2H_5)_2$	$N(C_2H_5)_2$	C_2H_5OH	246 (4,42), 292 (4,34), 356 (4,50)	440	<0,10
				CH_3CN	250 (4,18), 296 (4,20), 356 (4,41)	435	<0,10
VII	H	$N(C_4H_9)_2$	$N(C_2H_5)_2$	C_2H_5OH	252 (4,23), 297 (4,27), 358 (4,50)	440	0,15
				CH_3CN	250 (4,14), 298 (4,17), 356 (4,43)	440	<0,10
VIII	H	$N(CH_2)_5$	$N(C_2H_5)_2$	C_2H_5OH	254 (4,17), 299 (4,16), 365 (4,39)	447	0,36
				CH_3CN	251 (4,16), 299 (4,13), 360 (4,38)	434	0,31
IX	H	$N(CH_2CH_2)_2O$	$N(C_2H_5)_2$	C_2H_5OH	253 (4,24), 295 (4,17), 365 (4,45)	445	0,70
				CH_3CN	252 (4,19), 295 (4,10), 360 (4,44)	434	0,54
X	*cyclo*-C_6H_{11}	*cyclo*-$C_6H_{11}NH$	$N(C_2H_5)_2$	C_2H_5OH	254 (4,19), 295 (4,11), 363 (4,39)	440	0,33
				CH_3CN	252 (4,25), 295 (4,16), 360 (4,48)	430	0,10
XI	$CH_2C_6H_5$	$NHCH_2C_6H_5$	$N(C_2H_5)_2$	C_2H_5OH	254 (3,99), 290 (3,95), 356 (4,46)	435	0,31
				CH_3CN	252 (3,93), 290 (3,85), 356 (4,42)	435	0,12

XII	C_2H_5	$N(CH_2CH_2)_2O$	$N(C_2H_5)_2$	C_2H_5OH	257 (4,37), 312 (4,15), 375 (4,58)	465	0,39
				CH_3CN	254 (4,19), 314 (4,04), 368 (4,44)	450	0,20
XIII	*cyclo*-C_6H_{11}	$N(CH_2CH_2)_2O$	$N(C_2H_5)_2$	C_2H_5OH	256 (4,29), 310 (3,93), 320 (3,97), 376 (4,53)	464	0,76
				CH_3CN	248 (4,08), 260 (4,05), 310 (3,81), 320 (3,88), 370 (4,35)	454	0,45
XIV	$CH_2C_6H_5$	$N(CH_2CH_2)_2O$	$N(C_2H_5)_2$	C_2H_5OH	268 (4,28), 315 (4,06), 378 (4,50)	466	0,65
				CH_3CN	256 (4,27), 315 (4,08), 374 (4,53)	452	0,24
XV	H	$N(CH_2CH_2)_2O$	$N(CH_2)_5$	C_2H_5OH	252 (4,18), 298 (4,12), 360 (4,31)	455	0,49
				CH_3CN	251 (4,09), 298 (4,11), 355 (4,27)	440	0,59
XVI	H	$N(C_2H_5)_2$	$N(CH_2CH_2)_2O$	C_2H_5OH	244 (4,19), 295 (4,21), 314 (4,24), 344 (4,35)	440	<0,10
				CH_3CN	250 (3,92), 277 (3,92), 294 (4,24), 335 (4,29)	435	<0,10
XVII	H	$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$	C_2H_5OH	246 (4,16), 296 (4,13), 350 (4,30)	450	0,31
				CH_3CN	245 (4,15), 296 (4,12), 346 (4,32)	435	0,27
XVIII	H	$N(C_2H_5)_2$	—	C_2H_5OH	280 (4,10), 302 (4,19), 372 (4,38)	467	0,89
				CH_3CN	254 (4,09), 277 (4,11), 303 (4,18), 368 (4,41)	455	0,41
XIX	H	$N(CH_2CH_2)_2O$	—	C_2H_5OH	270 (4,11), 279 (4,14), 300 (4,06), 382 (4,36)	466	1,00
				CH_3CN	264 (4,07), 270 (4,14), 298 (3,99), 370 (4,36)	450	0,89
XX	H	CH_3	$N(C_2H_5)_2$	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 (3,28), 306 (3,57), 319 (3,71), 370 (4,41)	439	0,75
XXI	H	CH_3	—	C_2H_5OH	250 (4,05), 312 (3,51), 324 (3,67), 394 (4,37)	474	0,86
				CH_3CN	247 (4,04), 286 (3,44), 310 (3,44), 324 (3,56), 385 (4,38)	455	0,78
XXII	H	H	$N(C_2H_5)_2$	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), 375 (4,49)	450	0,34

*φ_f, quantum yield.

TABLE 2. Characteristics of Mono- and Diprotonated Forms of 7-Aminocoumarins

Compound	Absorption, λ_{max}, nm			pK_a^{I*}	pK_a^{II**}	pK_a^{**}
	neutral molecule	mono-cation	di-cation			
I	356	315	310	2,12	−2,50	−5,71
III	354	315	315	2,12	−1,47	−5,37
IV	354	312	308	2,08	−1,25	−6,05
VI	360	304	318	1,84	−2,48	−9,09
IX	373	309	315	1,86	−3,69	−10,01
XII	378	313	318	2,39	−3,50	−9,36
XIII	383	311	322	2,47	−3,13	−10,45
XVI	340	315	315	−0,31	−3,34	−5,32
XVII	350	313	314	−0,32	−3,99	−7,55
XIX	388	314	324	0,04	−3,13	−12,97
XX	384	310	303	1,97	−7,40	−11,34
XXI	400	320	300	0,20	−7,12	−13,20

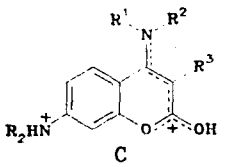
*In ethanol–water (1:1) solution.

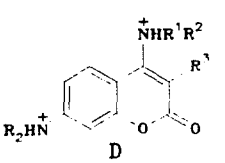
**In water–sulfuric acid solution.

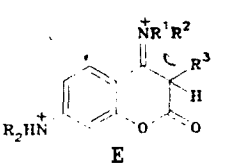
350-380 nm, and a concomitant increase in the absorption maximum at 310-320 nm, with isobestic points in the 320-350 nm range. Coumarins XX and XXI were selected as models for comparison. The low basicity of coumarins XX and XXI (2-4 orders of magnitude lower than β-naphthylamine [7]) indicates that the 7-dialkylamino group in these compounds is in effective conjugation with the lactone fragment. Since the pK_a^I values for coumarins I, III, IV, IX, XII, XIII, XVI, XVII, and XIX are similar to those found for the model compounds XX and XXI, we assume that the first protonation site in these compounds is also at the 7-dialkylamino group. This is supported by the observed loss of fluorescence upon protonation. Apparently, immobilization of the unshared electron pair on the nitrogen atom in the 7-position [$N_{(1)}$] renders charge transfer along pathway A impossible.

Comparison of the pK_a^I values for these compounds reveals an interesting effect, namely the pronounced decrease in the basicity of the julolidine (compounds XIX and XXI) and 7-morpholino (coumarins XVI and XVII) derivatives. In the case of coumarins XIX and XXI this effect can be explained in terms of the unfavorable tetrahedral configuration arising upon protonation of the $N_{(1)}$ atom, which is flattened by the six-membered ring structure. The diminished basicity of coumarins XVI and XVII, on the other hand, is probably due to the electron-withdrawing influence of the γ-oxygen atom, and not to the conformation of the saturated ring. The basicity of the $N_{(1)}$ site is substantially increased, in contrast, upon introduction of an alkyl group in the 3-position, such as in compounds XII and XIII, compared to coumarin IX. The effect of a substituent in the 4-position on the magnitude of pK_a^I, in contrast, is significantly lower. For example, for the 7-diethylaminocoumarin derivatives I, III, IV, VI, and IX their pK_a^I values are in the range 1.8-2.1. Furthermore, the pK_a^I value for the methyl derivative XX is also in this range. We conclude, therefore, that the electronic effect of the 4-amino group in compounds I-XIX on the (basicity of the) $N_{(1)}$ atom is not large.

Replacement of a 4-monoalkylamino group (compounds II and III) by a dialkylamino group (compounds VI and IX) under otherwise equivalent conditions leads to a sharp decrease in basicity. This is consistent with the general principles outlined for their absorption and fluorescence spectra, and is indicative of the reduced electron-donating effect of a 4-$N(Alk)_2$ group relative to a 4-NHAlk group due to steric factors.


C


D


E

The pK_a^{II} values for the 4,7-diaminocoumarins and 7-aminocoumarins in this study were also determined (Table 2). During the course of the second titration of these compounds in aqueous H_2SO_4 solution their absorption bands in the 290-310 nm range disappeared and were replaced by the appearance of longer wavelength absorption at 310-330 nm. Compounds III

TABLE 3. PMR Spectra of Coumarins IV and IX and Their Monoprotonated Forms IVa-c and IXa

Compound	Solvent*1	Chemical shift, δ, ppm (SSCC, Hz)							
		3-H, s	5-H (d, J=9,0)	6-H (d.d J=9,0; 2,5)	8-H (d, J=2,5)	7-NCH_2, m	7-NH_2CH_3 (t, J=7,0)	4-NCH_2, br.s	other protons
IV	$CDCl_3$	5,19	7,35	6,60	6,52	3,39*2	1,19	4,42*3	5,40 (1H, s, NH); 7,30...7,40 (5H, m, C_6H_5)
IVa	CF_3COOH	5,21	7,68	7,05	7,15	3,27	0,65	4,05	6,70 (5H, m, C_6H_5)
	D_2SO_4/D_2O	—	8,13	7,52	7,60	3,45; 3,60	0,99	4,49	6,90...7,20 (5H, m, C_6H_5)
IV b	D_2SO_4/D_2O	—	7,98	7,43	7,52	3,35; 3,49	0,85	4,47	7,05 (5H, m, C_6H_5)
IV c	D_2SO_4/D_2O	—	8,05	7,43	7,52	3,35; 3,49	0,85	4,47	7,05 (5H, m, C_6H_5)
IX	$CDCl_3$	5,42	7,39	6,55	6,47	3,40*2	1,20	3,21*4	3,90 (4H, t, J=5,0; $(CH_2)_2O$)
IXa	CF_3COOH	5,59	7,50	7,02	7,18	3,22	0,69	3,05*4	3,60 (4H, t, J=5,0; $(CH_2)_2O$)
	D_2SO_4/D_2O	—	7,95	7,32	7,40	3,47	0,92	3,11*4	3,78 (4H, t, J=5,0; $(CH_2)_2O$)

*1IVa, D_2SO_4/D_2O = 10:90; IVb, c, D_2SO_4/D_2O = 35:65; IXa, D_2SO_4/D_2O = 25:75.

*2Quartet, J = 7.0 Hz.

*3Doublet, J = 5.0 Hz.

*4Triplet, J = 5.0 Hz.

and IV were found to be 1-2 orders of magnitude more basic than the 4-dialkylamino derivatives VI, IX, XII, XIII, XVI, XVII, and XIX. This anomaly in our view can be rationalized in terms of steric factors. There are three theoretically possible sites available for secondary protonation to occur (structures C-E) (see scheme above).

In the O-protonated form C the positive charge would be expected to be localized to a large extent on the $O_{(1)}C_{(2)}O$ triad [8], thus retaining the susceptibility of the molecule to charge transfer upon excitation; this would explain the appearance of a new, longer-wavelength absorption band upon protonation. We propose, therefore, that in these 4,7-diaminocoumarin derivatives, as well as in the 7-aminocoumarins XX and XXI (secondary) protonation occurs at the lactone oxygen atom. Introduction of a second alkyl group at the $N_{(2)}$ atom in the transition from coumarin I to compounds III and IV is accompanied uniformly by an order of magnitude increase in basicity (Table 2).

The basicity of 4-dialkylaminocoumarins VI, IX, XII, XIII, XVI, XVII, and XIX is substantially reduced due to steric hindrance between the 5-H (8-H in the case of coumarin XIX) atom and one of the alkyl groups (R^1) in the flattened imine fragment in structure C. As a consequence, diprotonation of 4-dialkylaminocoumarins takes place only in more acidic media. In the case of coumarins I, III, and IV steric strain in the dicationic structure C is apparently insignificant, due to the existence of a conformation in which the R^1 position is occupied by a hydrogen atom.

Analysis of these pK_a^{II} values reveals the extent of efficient p–π conjugation between the 4-amino group and the carbonyl fragment. This is further confirmed by the observation that the basicity of coumarins XX and XXI under secondary protonation conditions is 3-6 orders of magnitude lower than in the other compounds examined. Just as in the case of monoprotonation, conversion of the 4-diethylamino derivatives VI and XVI to 4-morpholino-substituted coumarins IX, XII, XVII, and XIX leads to a pronounced reduction in basicity. Coumarin XIII appears to be an exception to this trend, in that it is 0.5-1.0 orders of magnitude more basic than the other 4-morpholino derivatives. This can probably be attributed to the influence of the 3-cyclohexyl substituent, which partially interferes with conjugation of the unshared electron pair on the $N_{(2)}$ atom as a result of steric hindrance [1].

In order to define more accurately the basicity sites in these 4,7-diaminocoumarin derivatives we have also examined the PMR spectra of compounds IV and IX in D_2SO_4/D_2O solutions at pH (H_o) from –0.5 to 1.2 (Table 3); we have established that the monoprotonated forms IVa and IXa consist of quaternary diethylhetarylammonium salts. Protonation at the $N_{(1)}$ atom is verified by the nonequivalence of the α–methylene proton signals, as well as by the observed downfield shift of the 6-H and 8-H ortho aromatic proton signals relative to the coumarin starting materials. In the spectra of compounds IVa and IXa in D_2SO_4/D_2O the 3-H proton signal is absent due to rapid deuterium exchange. The position of the 3-H proton signal in these monoprotonated forms was ascertained, therefore, by recording the PMR spectra of coumarins IV and IX in CF_3COOH (pK_a 0.23). The fact that the chemical shifts for the 3-H protons in these compounds are largely unchanged relative to the spectra obtained in deuterochloroform solution (Table 3) is also consistent with protonation at the N(1) atom and further excludes from consideration different monocationic forms.

Using compound IV as an example, we were able in more concentrated solution of D_2SO_4 in D_2O ($H_o \sim -2$) to identify the presence of two conformers IVb and IVc in a 3:2 ratio. We assume that these conformers represent dicationic forms in which the lactone oxygen atom serves as the site of secondary protonation (structure C); rotation about the $C_{(4)}$–N bond in this structure should be hindered or retarded due to its increase in "double bonded" character. The predominant conformer IVb is assigned the structure of the E-isomer. In the less stable Z-isomer the signal for the 5-H proton is shifted downfield as a result of the deshielding influence of the N-benzyl substituent.

The S_1 excited state basicity of 4,7-diaminocoumarins I, III, IV, VI, IX, XII, XIII, XVI, XVII, and XIX, as well as of coumarins XX and XXI, was determined using the Ferster method [9]. The sharp decrease in basicity of 4,7-diaminocoumarins upon excitation provides additional evidence for substantial charge transfer from the $N_{(1)}$ atom to the carbonyl group oxygen atom [2, 6]. The pK_a^* values for the 4-monoalkylamino-7-diethylaminocoumarins I, III, and IV are approximately seven orders of magnitude higher than for compounds XIX and XXI, and three to five orders of magnitude higher than for the 4-dialkylamino-7-diethylaminocoumarins VI, IX, XII, and XIII; this is in accord with the stereoelectronic factors discussed earlier with respect to the pK_a^I and pK_a^{II} properties of these compounds. The 7-morpholino derivatives XVI and XVII in their S_1 states are 2-4 orders of magnitude stronger acids than the analogous 7-diethylaminocoumarins VI and IX. This can be rationalized in terms of a greater degree of localization of electron density in the morpholine ring in the ground state, and the resulting concomitant greater facility of electron donation in the polar (excited) charge transfer state.

EXPERIMENTAL

4,7-Diaminocoumarins I-XIX were synthesized according to published procedures [1, 10]. PMR spectra were obtained on a Bruker WM spectrometer (250 MHz) versus HMDS as internal standard.

Spectral luminescence studies at 293 K were performed on a Hitachi EPS-3T spectrophotometer, which was equipped with a G-3 fluorescence accessory. Fluorescence was achieved upon irradiative excitation of the long-wavelength absorption band of the corresponding coumarin. Relative fluorescence quantum yields were determined according to [9] using 3-aminophthalimide (φ_f 0.60) as a reference standard. Low-temperature (77 K) spectra were recorded using a special procedure for such, and the reference standard for φ_f measurements at this temperature 77 K was a solution of anthracene in ethanol–diethyl ether (2:1) (φ_f 0.27 [9]).

pK_a^I Values were determined according to [11] using a spectrophotometric method in 50% ethanol solution (with hydrochloric acid serving as the source of oxonium ions) with an ÉV-74 universal Ph meter equipped with glass and calomel electrodes. pK_a^{II} Values were determined using the same method in sulfuric acid solutions having known acidity function values. The errors in these measurements are $pK_a^I \pm 0.04$, $pK_a^{II} \pm 0.10$. Twice-distilled water was used to prepare all solutions.

LITERATURE CITED

1. M. A. Kirpichënok, S. K. Gorozhankin, and I. I. Grandberg, *Khim. Geterotsikl. Soedin.*, No. 6, 836 (1990).
2. G. Jones, W. R. Jackson, Ch.-yoo Choi, and W. R. Bergmark, *J. Phys. Chem.*, **89**, 294 (1985).
3. S. D. Joshi, V. R. Sakhardande, and S. Seshadri, *Ind. J. Chem.*, **23B**, 206 (1984).
4. B. N. Matoo, *Trans. Faraday Soc.*, **52**, 1184 (1956).
5. H. A.-E. Rafie and A. H. E.-T. Bahgat, *Can. J. Chem.*, **63**, 1173 (1985).
6. L. A. Karandashova, N. S. Patalakha, P. B. Kurapov, M. A. Kirpichënok, S. K. Gorozhankin, I. I. Grandberg, and L. K. Denisov, *Izv. Timir. Sel'sko-khoz. Akad.*, No. 1, 188 (1988).
7. J. Barltrop and J. Coyle, *Excited States in Organic Chemistry* [Russian translation], Mir, Moscow (1978), p. 69.
8. M. A. Kirpichënok, S. K. Gorozhankin, and I. I. Grandberg, *Khim. Geterotsikl. Soedin.*, No. 7, 888 (1989).
9. S. Parker, *Photoluminescence of Solutions* [Russian translation], Mir, Moscow (1972).
10. S. K. Gorozhankin, M. A. Kirpichënok, N. A. Klyuev, and I. I. Grandberg, *Izv. Timir. Sel'sko-khoz. Akad.*, No. 4, 151 (1986).
11. I. Ya. Bernstein and Yu. L. Kaminskii, *Spectrophotometric Analysis in Organic Chemistry* [in Russian], Khimiya, Leningrad (1986), p. 200.