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SPECTRAL AND LUMINESCENT PROPERTIES OF 9-ARYLAMINOACRIDINES

M. F. Budyka and R. M. Fatkulbayanov

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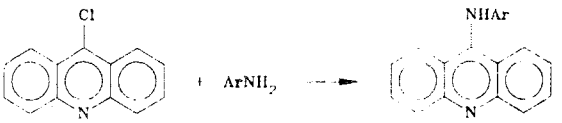
A study has been made of the influence of electronic and steric factors of the aromatic substituent in 9-arylaminoacridines on the behavior of these compounds when subjected to light quanta or electron impact. It has been shown that the introduction of donor substituents shifts the absorption and luminescence spectra toward longer wavelengths, with a simultaneous increase of the Stokes shift and a decrease of the quantum yield of luminescence; it has been established that the introduction of sterically hindered substituents has a similar effect. In the mass spectra, the introduction of substituents with stronger donor properties tends to increase the stability of the molecular ions.

Because of the spectral properties of aminoacridines, they are being investigated actively as generation media of lasers [1] and as luminescent labels in biology [2]. Among the isomeric compounds, 9-arylaminoacridines are distinguished by ready availability and the possibility of varying their properties over a broad range by changing the structure of the aromatic radical Ar. However, data that have been reported in the literature on the spectral and luminescent properties of these compounds are very limited, and often are only qualitative in nature.

We have synthesized a series of derivatives of 9-aminoacridine by a nucleophilic substitution reaction from 9-chloroacridine and the appropriate aromatic amine, and we have also investigated their spectral characteristics.



I–XII

We found that acceptor substituents in the aromatic amine retard the reaction, whereas donor substituents accelerate the reaction significantly (see Table 1). With excess amine, the 9-chloroacridine is converted almost quantitatively to the aminoacridine; variations in the preparative yield most likely reflect differences in the behavior of compounds I-XII in the course of purification by crystallization.

Spectral and luminescence characteristics of the arylaminoacridines have been determined (Table 2). For comparison, the quantum yields of luminescence of the compounds are referred to the quantum yield of the simplest representative of the series, 9-phenylaminoacridine (I). In the electronic spectrum of this compound we observe a broad absorption band at λ_{max} 397 nm; in the short-wave part, bands that are characteristic for absorption by the acridine ring are preserved (345 and 361 nm) [3]. In the long-wave part we observe a weak inflection that becomes more and more distinct when donor substituents are introduced into the *para* position of the phenyl ring; this absorption increases to give an additional maximum with λ_{max} 436 nm for the dimethylamino derivative V. At the same time, the intensity of the principal maximum drops off.

The luminescence spectra are affected to an even greater degree by the introduction of donor substituents into compound I. For the methoxy derivative III, the luminescence maximum is shifted "bathofluorically" by 105 nm, and the Stokes shift ($\Delta\nu$) increases to 9000 cm^{-1}. Because of the insolubility of the hydroxy derivative IV in toluene, we were unable to determine its spectral characteristics.

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TABLE 1. 9-Arylaminoacridines

Compound	Ar	mp, °C	Reaction time, min	Yield, %
I	C_6H_5	224 (224 [3])	30	80
II	4-CH_3O—C_6H_4	175 (174 [3])	5	68
III	4-CH_3—C_6H_4	151 (151 ([3])	2	70
IV	4-HO—C_6H_4	320 (decomp.)	120	77
V	4-$(CH_3)_2N$—C_6H_4	210	2	45
VI	4-Cl—C_6H_4	209 (sublimes)	60	83
VII	4-O_2N—C_6H_4	221 (221 [3])	240	79
VIII	2-C_6H_5—C_6H_4	177	120	82
IX	4-C_6H_5—C_6H_4	203	180	53
X	2,4-$(CH_3)_2C_6H_3$	190	30	72
XI	$C_{10}H_7$-1	195	180	58
XII	$C_{10}H_7$-2	200	120	64

TABLE 2. Spectral and Luminescent Properties of 9-Arylaminoacridines

Compound	λ_{max}^{abs}, nm (and $\varepsilon \cdot 10^{-3}$, M cm^{-1})		λ_{rel}^{lum}, nm*	η_{max}^{lum}, nm*	$\Delta\nu^{lum}$, cm^{-1}*
	in ethanol	in toluene			
I	343 (2,0), 412 (8,2), 435 sh. (5,9)	345 sh. (2,0), 361 (4,1) 397 (6,8)	505	1**	5400
II	343 (2,8), 358 (3,0), 413 (8,0), 438 sh. (6,4)	345 (3,4), 362 (4,0), 397 (6,2)	555	0,51	7180
III	343 (1,9), 358 (2,8); 415 (8,4), 435 sh. (7,6)	362 sh. (2,8), 394 (5,0), 417 sh. (4,8)	610	0,04	9000
IV	392 sh. (4,9), 417 (7,8), 436 (8,7)	—	—	—	—
V	343 (2,4), 360 (2,2), 417 sh. (4,8), 438 (5,2)	362 (4,5), 391 (5,2), 436 (5,8)	—	$<10^{-3}$	—
VI	—	362 sh. (5,2), 397 (9,4)	488 533	1,07	4700
VII	344 (11,6), 360 (12,6), 417 (18,6)	336 (9,2), 470 (11,3)	—	$<10^{-3}$	—
VIII	392 sh. (6,1), 420 (10,5), 436 (10,6)	363 sh. (3,8), 394 (7,5), 427 sh. (4,5)	505	0,77	5550
IX	343 (4,8), 358 (6,5), 397 (5,0)	344 (6,6), 360 (8,2), 385 (6,9)	480	0,99	5200
X	394 sh. (9,0), 408 (9,7), 435sh. (4,8)	360 sh. (4,2), 392 (8,6), 429 sh. (3,6)	555	0,22	7480
XI	357 sh. (4,5), 396 sh. (10,9), 405 (11,4)	377 sh. (6,8), 394 (8,8)	560	0,09	7490
XII	343 (4,3), 360 (4,7), 415 (10,0), 447 (7,4)	345 sh. (4,1), 362 (5,1), 397 (8,2), 427 sh. (6,0)	535	0,49	6500

*In toluene.

**Quantum yield relative to rhodamine B $\eta = 0.12$.

One of the components of the Stokes shift is the energy difference (ΔE) between the Frank—Condon state and the emitting excited state. In the present case, stabilization of the excited state is evidently related to intramolecular electron transfer from the arylamine fragment to the acridine nucleus; therefore, a strengthening of the electron-donor properties of the substituent will lead to an increase in ΔE and a linear relationship between $\Delta\nu$ and the Hammett σ^+ constant (see Fig. 1):

$$\Delta\nu\ (cm^{-1}) = (5400 \pm 650) - (4800 \pm 1540)\,\sigma^+ \quad (r = 0.994),$$

which corresponds to the electron transfer model, since these particular constants characterize the capability of substituents for electron transfer to a reaction center [4].

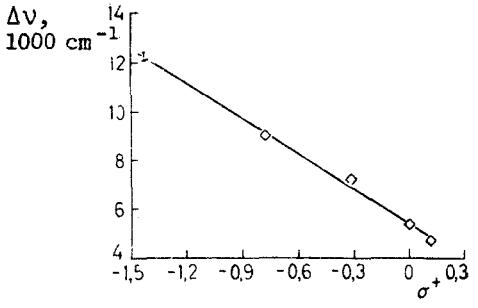


Fig. 1

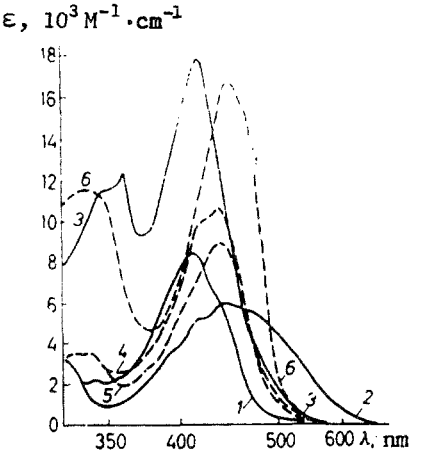


Fig. 2

Fig. 1. Stokes shift as a function of resonance constants of substituents for 9-arylaminoacridines.

Fig. 2. Differences in alignment in spectral absorption bands of 9-arylaminoacrylidene in ethanol (1-3) and by acidified solutions (4-6): 1, 4) compound I; 2, 5) compound II; 3, 6) compound V.

Using this equation, we calculated the Stokes shift for the dimethylamino derivative V, which proved to be 12,300 cm^{-1} (vertical segment shown in Fig. 1). On the basis of this value, the calculated luminescence maximum for compound V occurs at 940 nm. However, since an increase in donor strength of the substituent entails not only a "bathofluoric" shift of the band, but also a drop in the quantum yield of luminescence, compound V does not luminesce in toluene solutions.

It is known that a disruption of coplanarity of a molecule, for example the introduction of o,o′-substituents into derivatives of biphenyl, leads to a "hypsofluoric" shift and a sharp decrease in luminescence intensity [5, p. 19]. For the amine II, the introduction of a methyl into the *ortho* position of the phenyl ring (compound X) does not affect the position of the maximum but does lower the quantum yield of luminescence. At the same time, a comparison of properties of the pairs of isomeric compounds VIII, IX and XI,XII shows that the more sterically hindered amines with o-biphenyl and α-naphthyl substituents VIII and XI luminesce at longer wavelengths and have greater Stokes shifts than the less sterically hindered p-biphenyl and β-naphthyl analogs IX and XII. By analogy with diarylethylenes [5, p. 22], we can assume that the more sterically hindered compounds in the excited state have a structure much more nearly planar than they have in the ground state, and hence differences in the spatial structure of the ground and excited states of the isomeric compounds are less distinct. Thus, the introduction of steric hindrance into the molecule of an arylaminoacridine has the same sort of effect as the introduction of donor substituents — a "bathofluoric" shift of the spectrum with a simultaneous increase of the Stokes shift and a decrease of the quantum yield of luminescence.

The nitro derivative VII differs in its spectral properties in the presence of an intense long-wave absorption band with λ_{max} 470 nm, and also by the absence of luminescence, since the lowest excited state of this compound corresponds to a local n, π transition with the participation of electrons of the nitro group.

Passage of dry HCl into the toluene solutions gives a bathochromic shift of the absorption maximum and a decrease in luminescence of most of the arylaminoacridines; in contrast, weak luminescence ($\eta_{rel} \sim 10^{-3}$) in the 620 nm region is observed for the dimethylamino and nitro derivatives V and VII.

In neutral alcohol solutions, the differences in absorption spectra of the amines I-XII are less prominent than in toluene solutions (see Table 2), and the differences very nearly disappear when the alcohol solutions are acidified: The cations of all of the arylaminoacridines in this group have intense absorption bands ($\varepsilon \cdot 10^4$) in the 430-440 nm region (see Fig. 2). This particular property has served as the basis of an analytical procedure for selective determination of primary aromatic amines by means of 9-chloroacridine according to the absorbance of the 9-arylaminoacridine product at a wavelength of 435 nm [6], since the products of chloroacridine interaction with aliphatic or secondary aromatic amines generally do not absorb at this wavelength.

TABLE 3. Mass Spectra of 9-Arylaminoacridines

Amine	m/z (I/I_{max})	W_M
I	271 (20,0), 270 (100), 269 (82,7), 268 (28,1), 267 (6,3), 179 (2,1), 178 (2,3)	16,9
II	285 (21,2), 284 (100), 283 (55,4), 282 (11,0), 281 (4,0), 269 (13,6), 268 (13,8), 179 (1,6), 178 (1,7)	33,4
III	301 (22,5), 300 (100), 299 (7,3), 286 (14,1), 285 (63,2), 284 (3,7), 257 (8,2), 256 (11,8), 255 (8,4), 179 (4,6), 178 (3,3)	29,1
IV	287 (20,2), 286 (100), 285 (62,8), 284 (16,7), 269 (4,2), 268 (4,0), 256 (4,7), 255 (5,6), 179 (2,6), 178 (2,4)	20,3
V	314 (23,3), 313 (100), 312 (10,4), 299 (4,1), 298 (16,4), 297 (2,8), 296 (3,6)	52,2
VI	307 (6,3), 306 (32,4), 305 (37,5), 304 (100), 303 (59,2), 302 (9,0), 269 (11,7), 268 (28,2), 267 (12,9), 266 (6,3), 179 (2,6), 178 (3,7)	18,7
VII	316 (21,5), 315 (100), 314 (19,8), 286 (6,7), 285 (33,3), 284 (28,2), 283 (81,8), 282 (24,4), 281 (9,3), 269 (21,4), 268 (42,5), 267 (21,6), 256 (11,9), 255 (20,4), 179 (6,9), 178 (4,2)	18,6
VIII	347 (25,5), 346 (100), 345 (65,9), 344 (7,4), 343 (4,2), 269 (8,4), 195 (8,5), 180 (6,9), 179 (20,6), 178 (2,77)	30,6
IX	347 (27,0), 346 (100), 345 (10,2), 344 (2,6), 255 (3,1), 254 (15,0), 253 (8,4)	43,2
X	299 (22,2), 298 (100), 297 (55,3), 296 (7,3), 283 (18,9), 282 (12,7), 281 (6,7), 268 (4,5), 179 (4,2), 178 (1,4)	34,5
XI	321 (23,8), 320 (100), 319 (65,0), 318 (22,9), 317 (6,0)	40,5
XII	321 (23,7), 320 (100), 319 (65,5), 318 (17,5), 317 (3,3), 179 (1,6)	41,7

Alcohol solutions of these compounds give essentially no luminescence, probably because of proton transfer in the excited state from the alcohol molecule to the aminoarylacridine molecule in a complex with a hydrogen bond. This will be favored by the sharp increase in basicity of the acridine ring, in view of transfer of electron density to the endocyclic nitrogen atom [7].

In recent work using laser photolysis, we have registered an analogous sequence of processes in photochemical reactions of 9-chloroacridine with arylamines, with the difference that the initial phototransfer of an electron from the amine to the acridine was intermolecular with the formation of the anion radical of chloroacridine which, upon subsequent transfer of a proton from the alcohol molecules, was converted to a neutral radical; all of the intermediate products were registered spectrometrically [8].

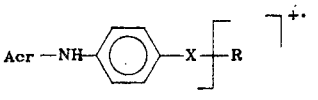
Kurapov et al. [9] attributed the lack of any luminescence of derivatives of 9-(4-aminophenyl)acridine (XIII), in alcohol solutions at room temperature, to the very limited conjugation of the acridine and phenyl nuclei, owing to the large dihedral angles between these nuclei. Upon lowering the temperature to 77 K, the quantum yield of luminescence was much higher; this was explained in [8] by stabilization of the more planar conformers and a consequent increase in conjugation between the nuclei. On the basis of our data, when we consider the analogy between the properties of compounds I and XIII, we can conclude tentatively that the quenching of luminescence in this case is not related to the lack of coplanarity of the system, but rather to proton transfer from an alcohol molecule to an excited molecule of compound XIII and the formation of weakly luminescing salts. And, in fact, in a toluene solution N,N-dimethylaminophenylacridines luminesce with λ_{max} 523 nm and $\eta = 0.6$; passage of dry HCl into the solution eliminates the luminescence.

At the same time, the general concept of an increase in luminescence strength with increasing coplanarity of individual fragments of the molecule, favoring π-electron interaction of these fragments, as was shown above, is supported in the example of the properties of pairs of isomeric compounds in toluene solutions.

The electronic and steric effects of substituents are also manifested in the behavior of compounds I-XII when subjected to electron impact. For all of the compounds investigated, the maximum peak in the mass spectra is the peak of the molecular ion M^+; the introduction of donor substituents into the phenyl ring of compound I gives a significant increase in the stability of M^+ (increase in W_M; see Table 3). The largest value of W_M is observed for the dimethylamino derivative V, obviously reflecting stabilization of W_M through intramolecular charge transfer. An exception is compound IV with a hydroxyl group; also, the introduction of acceptor substituents has little effect on the stability of M^+.

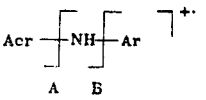
The most characteristic path for the decomposition of the molecular ion of the arylaminoacridines, the same as symmetric diarylamines [10], is successive elimination of up to three hydrogen atoms, with the most intense process, the elimination of the first H, proceeding mainly from the *para* position of the benzene ring; when

substituents are introduced into this position, the intensity of the peak of the $[M - H]^+$ ion decreases sharply (compounds III, V, IX). An alternate path of decomposition appears — elimination of a radical R from the substituent:



X=CH_2, O, NCH_3; R=H, CH_3

With X = O, detachment of the radical R is equally probable for R = CH_3 (amine III) and R = H (amine IV); the resulting peak for the ion 285* is equally intense in the two cases (63%) — explained by stabilization of the cation that is formed because of the *para*-quinoid structure of the monoquinonimium. Elimination of a methyl group is also observed for the tolyl and dimethylaminophenyl derivatives II and V; for the xylyl derivative X, this process takes place twice. For the unsubstituted compound I we observe a low-intensity decomposition through path A with rupture of the acridyl—N bond and localization of charge on the acridine fragment (ion 178):



The presence of the peak of the acridine molecular ion 179 in the spectrum indicates migration of the hydrogen atom in the acridine nucleus upon elimination of the arylamino group. (For 9-phenylacridine, H transfer has been observed previously, but without elimination of the phenyl group [11].) The introduction of substituents into the ortho position of the phenyl ring makes it more difficult to achieve a coplanar structure, thus leading to reinforcement of this path of decomposition and an increase of the M^+ peak of acridine to 21% for the most sterically hindered o-biphenyl derivative VIII. Steric hindrance leads simultaneously to a decrease in the stability of the molecular ion of this compound in comparison with W_M of the p-biphenyl derivative IX.

We did not observe alternative decomposition through the aryl—N bond (path B) in any of the compounds that have been studied.

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EXPERIMENTAL

Absorption spectra were measured in Specord UV-Vis and M40 instruments; the luminescence spectra were measured in an Élyumin-2 instrument, with correction of the spectra. The mass spectra were taken in a Hitachi M80A instrument with an MOOZ data processing system, ionizing electron energy 20 eV, emission current 100 μA, and ionization chamber temperature 200°C. The thin-layer chromatography was performed on Silufol plates in a methanol—chloroform system (1:3).

9-Arylaminoacridines. A solution of 0.5 mmole of chloroacridine and 1 mmole of the amine in 3 ml of solvent (toluene or DMFA) was heated in an ampul at a temperature of 110-130°C. Upon completion of the reaction, the mixture was cooled, and 2 ml of ethanol, 5 ml of benzene, and 5 ml of a saturated sodium carbonate solution were added. The mixture was shaken, the organic layer was taken off, the water layer was extracted with benzene, and the combined extract was washed with water and dried with potassium carbonate. The benzene was driven off, and the residue was recrystallized from alcohol or hexane.

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BROMINE-SUBSTITUTED 1,2,3,4-TETRAHYDRO-4-METHYLSPIRO[QUINOLINE-2-CYCLOHEXANES]

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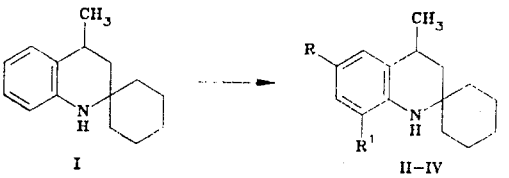
UDC 547.831.3.547.642

The bromination of 1,2,3,4-tetrahydro-4-methylspiro[quinoline-2-cyclohexane] has been carried out under various conditions. Dibromo and monobromo derivatives have been obtained; the monobromo derivatives were synthesized by cyclization of 1-allyl-1-bromophenylaminocyclohexanes.

A preparative method has been developed in our laboratory for the synthesis of 1,2,3,4-tetrahydro-4-methylspiro[quinoline-2-cycloalkanes] (I) [1, 2]. In the present communication we are describing the synthesis of bromine derivatives of compound I. In [3, 4], monobromo derivatives of tetrahydroquinoline were used as starting substances in syntheses of biologically active compounds.

It had been established previously that the main product of electrophilic bromination of compound I by N-bromosuccinimide in an acetic acid/methylene chloride system is 1,2,3,4-tetrahydro-6,8-dibromo-4-methylspiro[quinoline-2-cyclohexane] (II), which was obtained in a 40% yield. The total yield of 1,2,3,4-tetrahydro-4-methyl-6-bromo[quinoline-2-cyclohexane] and the corresponding 8-bromo derivative (III and IV) was 4% [2].

It could be assumed that protonation of the tetrahydroquinoline fragment of compound I by a strong acid would lead to deactivation of the aromatic ring, and this should favor the formation of monobromo derivatives. However, in the bromination of the spiro compound I by N-bromosuccinimide in a system consisting of 80% sulfuric acid and methylene chloride, we found that the dibromo derivative II is obtained in practically the same yield as in the system containing acetic acid. It may be that the free base of compound I is subjected to bromination, analogous to what takes place in the diazotization of primary aromatic amines.



I II–IV

II $R=R^1=Br$; III $R=Br$; $R^1=H$; IV $R=H$, $R^1=Br$

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