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Synthesis and Optical Properties of 2-Alkylamino-4-amino-6-arylpyridine-3,5-dicarbonitriles

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Abstract—2-Alkylamino-4-amino-6-arylpyridine-3,5-dicarbonitriles were synthesized by the reaction of primary and secondary amines with 4-amino-6-aryl-2-chloropyridine-3,5-dicarbonitriles. The study of the spectral luminescent properties showed the presence of fluorescence in solutions with a maximum in the region of 399–471 nm and in the solid state with a maximum in the region of 393–502 nm.

Keywords: nicotinonitriles, nucleophilic substitution, fluorescence

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INTRODUCTION

Derivatives of 2-aminonicotinonitriles have a wide range of practically important properties, such as biological activity [1–4] or spectral-luminescent properties [5–11]. Examples include effective fluorophores [8, 10] and pH-stable heterocyclic azo dyes [5–7].

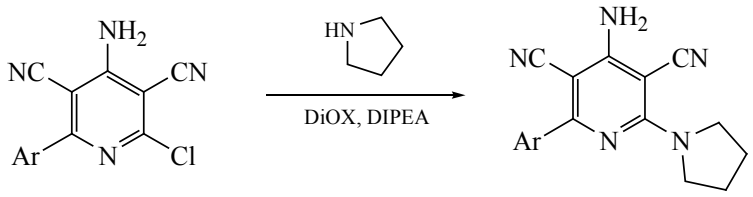
We earlier reported the synthesis of 4-amino-6-aryl-2-chloro(bromo)pyridine-3,5-dicarbonitriles **1** by the reaction of arylmethylidene derivatives of malononitrile dimer with hydrogen halides in the presence of oxidizing agents [12–14]. It was found that compounds **1** containing donor substituents in the benzene ring exhibits intense fluorescence in solutions and in the solid state, with the quantum yield reaching 92% [14]. In this work, we present the synthesis and spectral and luminescent properties of 2-alkylamino-4-amino-6-arylpyridine-3,5-dicarbonitriles **2** derived from compounds **1**.

RESULTS AND DISCUSSION

Derivatives of 2-aminonicotinonitriles can be obtained using multicomponent cascade transformations [3, 8, 15–17] and rearrangements [18], but the most common method is the substitution of a halogen substituent in the pyridine ring [1, 4, 12, 13, 19–21]. We substituted chlorine in compounds **1** under the action of primary and secondary amines. Pyrrolidine was chosen as the base amine to study the effect of substituents in the benzene ring on the optical properties of the synthesized compounds. In was found that the reaction proceeds best in 1,4-dioxane under heating at 70–80°C for 1 h in the presence of an excess of *N*,*N*-diisopropyl(ethyl)-amine (DIPEA). The final 2-alkylamino-4-amino-6-arylpyridine-3,5-dicarbonitriles **2a–2e** were obtained in yields of 63–94% (Scheme 1).

Chloropyridine **1b** was also reacted with various primary and secondary amines, including ciprofloxacin, a fluoroquinolone antimicrobial agent (Scheme 2).

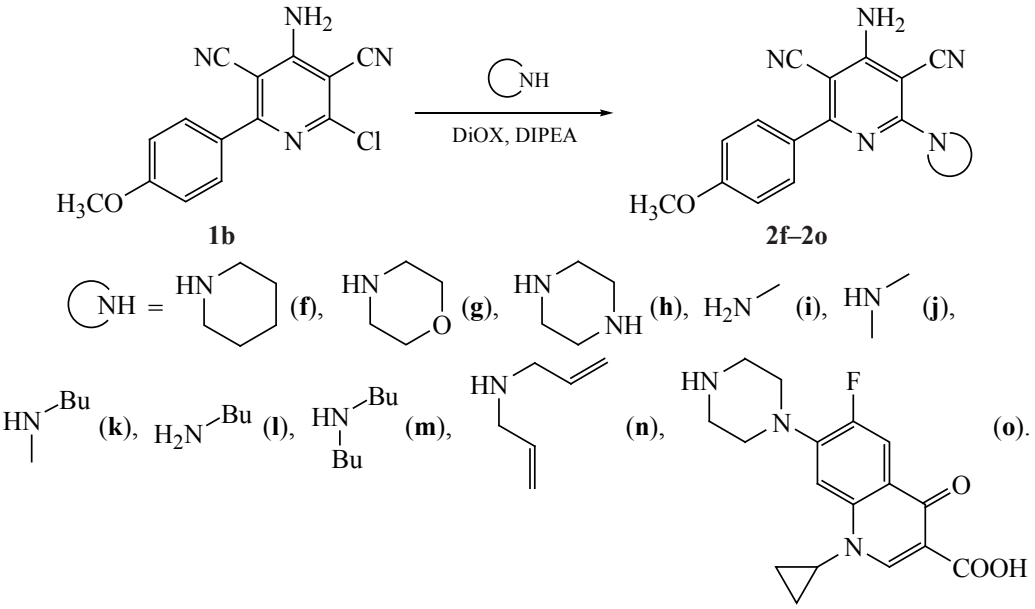
Scheme 1.



1a–1e **2a–2e**

Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 3,4-di$MeOC_6H_3$ (**c**), 4-$Me_2NC_6H_4$ (**d**), 4-$NO_2C_6H_4$ (**e**).

Scheme 2.



The ^{1}H NMR spectra show proton signals of the aryl substituent and the free amino group (a singlet at 6.94–7.26 ppm) and other amine fragments. The IR spectra display absorption bands of the conjugated cyano groups at 2200–2214 cm^{-1}, as well as the amino groups in the region of 3245–3494 cm^{-1}. The mass spectra of all compounds contain molecular ion peaks.

Compounds **2a–2o** are white or yellow crystals. Using compound **2f** as an example, we studied the solvatochromic properties of the synthesized compounds. It was found that the nature of the solvent

Table 1. Optical properties of compound **2f** in different solvent

Solvent	λ_{abs}, nm	*A*	ε, M^{-1} cm^{-1}	log ε	λ_{em}, nm	Stokes shift, cm^{-1} (nm)	Φ, %
1,4-Dioxane	272 340[a]	0.395 0.101	39488 10077	4.60 4.00	434	6370 (94)	0.8
DMSO	274 340[a]	0.430 0.113	43040 11292	4.63 4.05	452	7288 (112)	0.7
Acetic acid	271 340[a]	0.436 0.109	43624 10920	4.64 4.04	438	6581 (98)	1.1
Benzene	290 345[a]	0.281 0.090	28140 9038	4.45 3.96	431	5784 (86)	2.0
Ethyl acetate	271 335[a]	0.404 0.104	40387 10378	4.61 4.02	442	7226 (107)	0.6
Dichloromethane	272 287 345[a]	0.413 0.331 0.097	41284 33146 9734	4.62 4.52 3.99	435	5997 (90)	1.8
Acetonitrile	271 340[a]	0.456 0.101	45629 10098	4.66 4.00	452	7288 (112)	0.7
Ethanol	271 335[a]	0.387 0.106	38728 10622	4.59 4.03	435	6862 (100)	0.6

[a] Estimated position of an overlapping maximum.

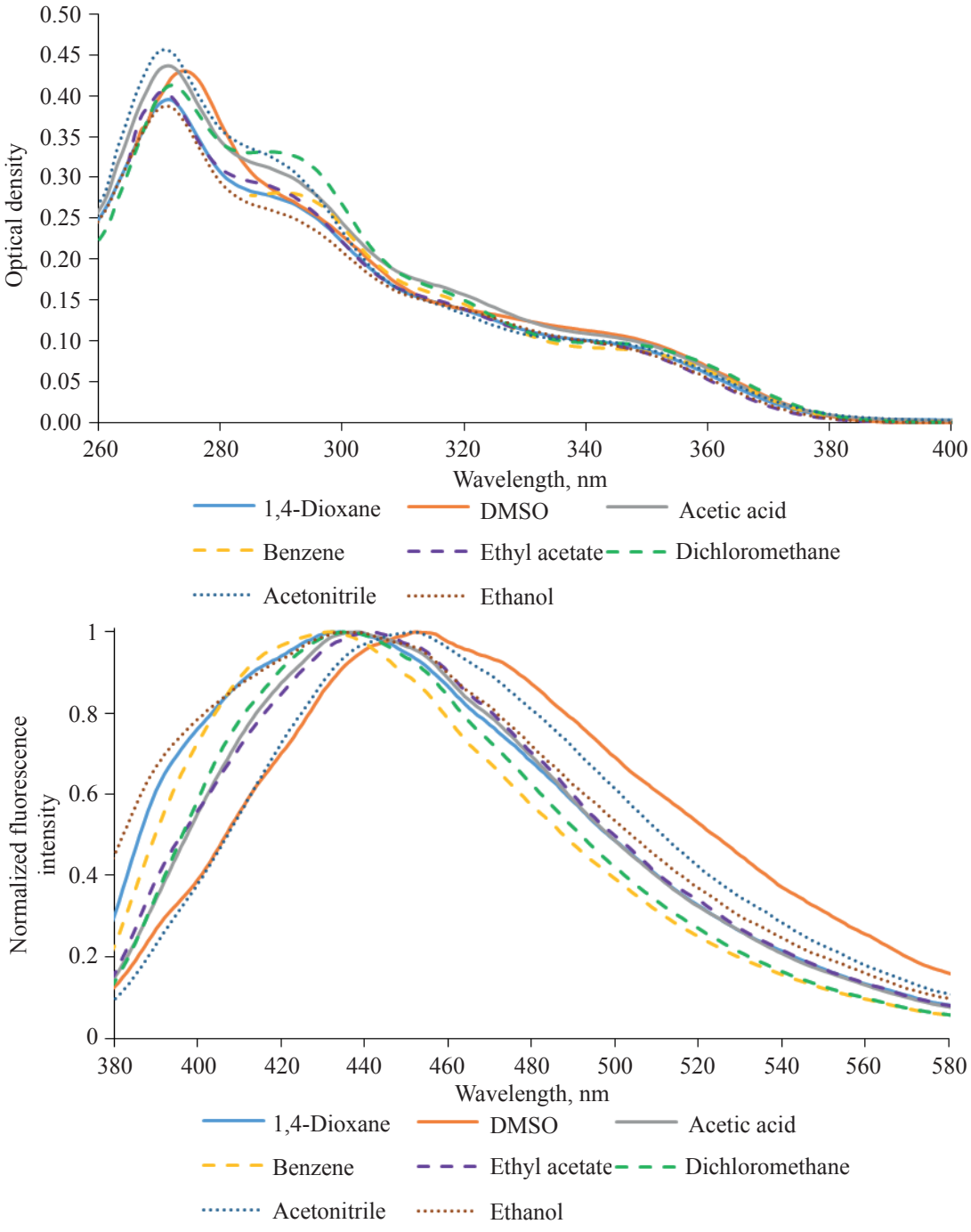


Fig. 1. Absorption and fluorescence spectra of compound **2f** in different solvents.

has practically no effect on the position of the short-wavelength maximum in the absorption spectra at 271–274 nm (Table 1). The absorption spectrum itself is a superposition of different maxima, the longest wavelength of which should be in the region of 350 nm (Table 1, Fig. 1), corresponding to the optimal excitation wavelength. The position of the fluorescence maximum changes insignificantly, but it correlates well with the dipole moments of the solvents: the shortest wavelength is the maximum in benzene and the long-wavelength maxima are in DMSO and acetonitrile. The highest quantum yields were observed in dichloromethane and benzene.

Further on we studied the spectral-luminescent properties of compounds **2a–2e** in dichloromethane.

Table 2. Optical properties of compounds **2a–2e**

Comp. no.	λ_{abs}, nm	A	ε, M^{-1} cm^{-1}	log ε	λ_{em}, nm	Stokes shift, cm^{-1} (nm)	Φ, %	$\lambda_{em.sol.}$, nm[a]	I_{rel}, arb. units[b]
2a	269 345	0.633 0.088	63291 8803	4.80 3.94	437	6102 (92)	2.7	432	1566
2b	270 344	0.445 0.097	44526 9653	4.65 3.98	435	6081 (91)	2.1	414	825
2c	270 322	0.257 0.112	25727 11185	4.41 4.05	435	8067 (113)	3.4	469	191
2d	270 292 341	0.248 0.123 0.233	24796 12335 23340	4.39 4.09 4.37	407	4755 (66)	7.9	428	96
2e	275 329	0.483 0.138	48331 13770	4.68 4.14	399	5332 (70)	0.9	502	310

[a] Solid-state fluorescence maximum.
[b] Relative intensity of the solid-state fluorescence maximum.

The nature of the substituents in the benzene ring has practically no effect on the position of the absorption maxima of compounds **2a–2e**, while the short-wavelength maximum is attenuated in the presence of donor substituents (Table 2, Fig. 2). The methoxyl substituents have almost no effect on the position of the fluorescence maxima, while both the nitro and dimethylamino substituents shift the maximum to the short-wavelength region. Donor substituents in the benzene ring generally increase the fluorescence quantum yield.

The study of the spectral and luminescent properties of compounds **2c**, **2f–2o**, obtained from various primary and secondary amines, showed that the short-wavelength absorption maximum shifted hypsochromically in the case of compounds **2i** and **2l** derived from the primary methyl- and butylamine (Table 3, Fig. 3). The nature of the amine has practically no effect on the position of the fluorescence maximum, except for compounds **2i** and **2n**, whose maxima appear in a shorter wavelength region, and compound **2o** derived from ciprofloxacin, whose absorption spectrum does not fit into the general series because of the inherent absorption of the

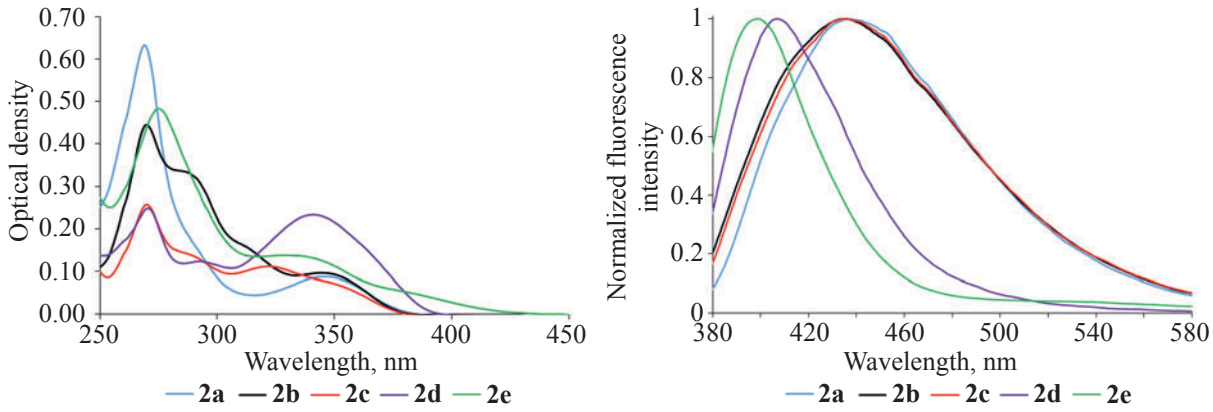


Fig. 2. Absorption and fluorescence spectra of compounds **2a–2e**.

Table 3. Optical properties of compounds **2**

Comp. no.	λ_{abs}, nm	*A*	ε, $M^{-1}\cdot cm^{-1}$	log ε	λ_{em}, nm	Stokes shift, cm^{-1} (nm)	QY, %	$\lambda_{em.sol.}$, nm[a]	I_{rel}, arb.units[b]
2c	270 344	0.445 0.097	44526 9653	4.65 3.98	435	6081 (91)	2.1	414	826
2f	272 287 345[c]	0.413 0.331 0.097	41284 33146 9734	4.62 4.52 3.99	435	5997 (90)	1.8	420	556
2g	272 290 345[c]	0.359 0.295 0.101	35929 29490 10085	4.56 4.47 4.00	453	6910 (108)	0.9	454	143
2h	270 291 340[c]	0.382 0.286 0.118	38202 28642 11803	4.58 4.46 4.07	434	6370 (94)	1.7	400	844
2i	260 310 335[c]	0.308 0.143 0.112	30847 14291 11171	4.49 4.16 4.05	399	4788 (64)	3.0	393	321
2j	269 345[c]	0.409 0.100	40892 9965	4.61 4.00	438	6154 (93)	1.0	407	599
2k	270 344	0.391 0.090	39111 8986	4.59 3.95	436	6134 (92)	1.4	413	594
2l	260 310 337	0.398 0.170 0.120	39758 16959 12033	4.60 4.23 4.08	436	6738 (99)	0.8	399	2466
2m	271 347	0.438 0.096	43771 9598	4.64 3.98	438	5987 (91)	2.3	414	820
2n	268 345[c]	0.375 0.100	37529 10002	4.57 4.00	401	4048 (56)	11.3	405	384
2o	285 335[c]	0.867 0.376	86746 37590	4.94 4.58	471	8619 (136)	12.3	430	250

[a] Solid-state emission maximum.
[b] Relative intensity of the solid-state fluorescence.
[c] Estimated position of an overlapping maximum.

ciprofloxacin residue. The fluorescence quantum yield, too, is almost insensitive to the nature of the amine, except for compound **2n**, whose quantum yield was 11.3%.

The solid-state emission of compounds **2a–2o** is weak, and donor substituents generally shift the emission maximum to short-wavelength region, which acceptor substituent, to the long-wavelength region.

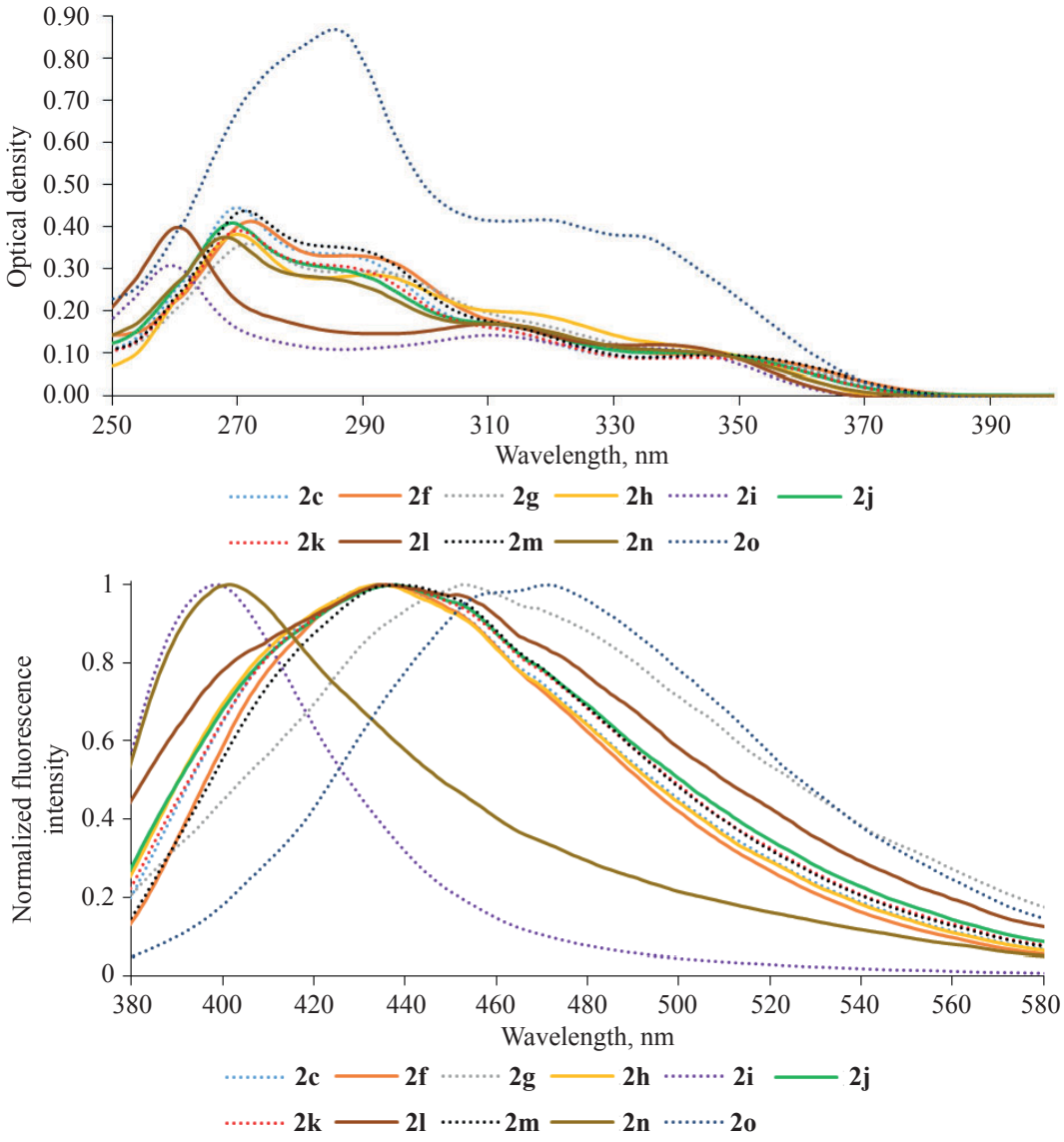


Fig. 3. Absorption and fluorescence spectra of compounds **2c** and **2f–2o**.

The nature of the amine only slightly affects the solid-state emission, except that compounds **2i** and **2l**, derived from primary amines, emit at shorter wavelengths.

EXPERIMENTAL

The IR spectra were recorded on an FSM-1202 Fourier spectrometer for thin films (suspensions in mineral oil). The ^{1}H and ^{13}C NMR spectra were obiained on a Bruker DRX-400 spectrometer in DMSO-d_6, internal standard TMS. The mass spectra were measured on a Shimadzu GCMS-QP2020 instrument (EI, 70 eV). The elemental analyses were obtained on an Elementar vario MICRO cube CHN analyzer. The absorption spectra were recorded on a Cary 60 spectrophotometer. The fluorescence spectra were run on a Cary Eclipse instrument. The melting points were determined on an OptiMelt MPA100 automatic melting point apparatus. The reaction progress and the purity of the synthesized compounds were monitored by TLC on Sorbfil PTSKh-AF-A-UV plates, eluent EtOAc, visualization by exposure to UV light, iodine vapor, and high temperature. Compounds **1** were synthesized as described in [14]. Primary and secondary amines, DIPEA, and 1,4-dioxane are commercial products.

4-Amino-2-(pyrrolidin-1-yl)-6-phenyl-3,5-dicarbonitrile (2a). Pyrrolidine (1.1 mmol) and DIPEA (1.1 mmol) were added to a suspension of 0.255 g

(1 mmol) of 4-amino-2-chloro-6-phenylpyridine-3,5-dicarbonitrile (**1a**) in 5 mL of 1,4-dioxane. The reaction mixture was stirred for 1 h at 70–80°C. After completion of the reaction (TLC monitoring), the mixture was cooled, and the precipitate that formed was filtered off and washed with cold distilled water and *i*-PrOH. When necessary, the product was recrystallized from 1,4-dioxane. Yield 0.263 g (91%), mp 208–209°C. IR spectrum, ν, cm^{-1}: 3476, 3367 (NH_2), 2206 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.83–1.98 m (4H, CH_2), 3.69–3.78 m [4H, $N(CH_2)_2$], 7.07 s (2H, NH_2), 7.38–7.61 m (3H, C_6H_5), 7.72–7.89 m (2H, C_6H_5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.5, 49.7, 71.7, 81.0, 117.4, 117.6, 128.8, 129.1, 130.9, 138.4, 157.4, 161.1, 163.6. Mass spectrum, *m/z* (I_{rel}, %): 289 (49), 260 (100). Found, %: C 70.68; H 5.17; N 24.15. $C_{17}H_{15}N_5$. Calculated, %: C 70.57; H 5.23; N 24.20. *M* 289.34.

Compounds **2b–2o** were prepared in the same way.

4-Amino-2-(4-methoxyphenyl)-6-(pyrrolidin-1-yl)pyridine-3,5-dicarbonitrile (2b). Yield 0.262 g (82%), mp 208–209°C. IR spectrum, ν, cm^{-1}: 3432, 3371 (NH_2), 2214 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.82–2.05 m (4H, CH_2), 3.65–3.78 m [4H, $N(CH_2)_2$], 3.83 s (3H, OCH_3), 6.99 s (2H, NH_2), 7.01–7.12 m (2H, C_6H_4), 7.76–7.81 m (2H, C_6H_4). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.5, 49.6, 56.0, 71.3, 80.2, 114.2, 117.5, 117.9, 130.6, 130.8, 157.3, 161.2, 161.6, 162.8. Mass spectrum, *m/z* (I_{rel}, %): 319 (55), 290 (100). Found, %: C 67.80; H 5.32; N 22.01. $C_{18}H_{17}N_5O$. Calculated, %: C 67.70; H 5.37; N 21.93. *M* 319.37.

4-Amino-2-(3,4-dimethoxyphenyl)-6-(pyrrolidin-1-yl)pyridine-3,5-dicarbonitrile (2c). Yield 0.255 g (73%), mp 195–196°C. IR spectrum, ν, cm^{-1}: 3494, 3397 (NH_2), 2208 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.86–2.01 m (4H, CH_2), 3.70–3.77 m [4H, $N(CH_2)_2$], 3.80 s (3H, OCH_3), 3.83 s (3H, OCH_3), 6.98 s (2H, NH_2), 7.06 d (1H, C_6H_3, *J* 8.3 Hz), 7.41–4.46 m (1H, C_6H_3), 7.47 d (1H, C_6H_3, *J* 2.1 Hz). Mass spectrum, *m/z* (I_{rel}, %): 349 (78), 320 (100). Found, %: C 65.41; H 5.42; N 19.96. $C_{19}H_{19}N_5O_2$. Calculated, %: C 65.32; H 5.48; N 20.04. *M* 349.39.

4-Amino-6-(4-dimethylaminophenyl)-2-(pyrrolidin-1-yl)pyridine-3,5-dicarbonitrile (11d). Yield 0.219 g (66%), mp 183–184°C. IR spectrum, ν, cm^{-1}: 3450, 3342 (NH_2), 2210 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.79–2.04 m (4H, CH_2), 2.84 s [6H, $N(CH_3)_2$], 3.69–3.77 m [4H, $N(CH_2)_2$], 6.69 d (2H, C_6H_4, *J* 8.7 Hz), 6.94 s (2H, NH_2), 7.78–7.83 m (2H, C_6H_4). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.5, 49.6, 56.0, 71.3, 80.2, 114.2, 117.5, 117.9, 130.6, 130.8, 157.3, 161.2, 161.6, 162.8. Mass spectrum, *m/z* (I_{rel}, %): 332 (19). Found, %: C 68.58; H 6.10; N 25.32. $C_{19}H_{20}N_6$. Calculated, %: C 68.65; H 6.06; N 25.28. *M* 332.41.

4-Amino-2-(4-nitrophenyl)-6-(pyrrolidin-1-yl)pyridine-3,5-dicarbonitrile (2e). Yield 0.267 g (80%), mp 236–237°C. IR spectrum, ν, cm^{-1}: 3422, 3346 (NH_2), 2204 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.88–2.00 m (4H, CH_2), 3.71–3.79 m [4H, $N(CH_2)_2$], 7.24 s (2H, NH_2), 7.88–8.17 m (2H, C_6H_4), 8.35 d (2H, C_6H_4, *J* 8.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 25.5, 49.7, 72.2, 81.5, 117.0, 117.1, 124.0, 130.5, 144.2, 148.9, 157.3, 160.9, 161.5. Mass spectrum, *m/z* (I_{rel}, %): 334 (64) $[M]^+$. Found, %: C 61.17; H 4.15; N 25.05. $C_{17}H_{14}N_6O_2$. Calculated, %: C 61.07; H 4.22; N 25.14. *M* 334.34.

4-Amino-2-(4-methoxyphenyl)-6-(piperidin-1-yl)-pyridine-3,5-dicarbonitrile (2f). Yield 0.293 g (88%), mp 201–202°C. IR spectrum, ν, cm^{-1}: 3462, 3330 (NH_2), 2208 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.58–1.70 m (6H, CH_2), 3.74–3.79 m [4H, $N(CH_2)_2$], 3.83 s (3H, OCH_3), 7.06 d (2H, C_6H_4, *J* 8.9 Hz), 7.16 s (2H, NH_2), 7.80 d (2H, C_6H_4, *J* 8.9 Hz). Mass spectrum, *m/z* (I_{rel}, %): 333 (100) $[M]^+$. Found, %: C 68.52; H 5.69; N 20.94. $C_{19}H_{19}N_5O$. Calculated, %: C 68.45; H 5.74; N 21.01. *M* 333.40.

4-Amino-2-(4-methoxyphenyl)-6-(piperazin-1-yl)pyridine-3,5-dicarbonitrile (2g). Yield 0.217 g (65%), mp 191–192°C. IR spectrum, ν, cm^{-1}: 3394, 3326, 3244 (NH_2, NH), 2209 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.77–2.82 m [4H, $HN(C\underline{H}_2)_2$], 3.70–3.75 m [4H, $N(CH_2)_2$], 3.83 s (3H, OCH_3), 7.06 d (2H, C_6H_4, *J* 8.8 Hz), 7.19 s (2H, NH_2), 7.80 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 46.1, 49.2, 55.8, 73.0, 81.4, 114.1, 116.9, 117.4, 130.3, 130.8, 160.8, 161.3, 161.6, 162.4. Mass spectrum, *m/z* (I_{rel}, %): 334 (5), 266 (100). Found, %: C 64.75; H 5.49; N 25.07. $C_{18}H_{18}N_6O$. Calculated, %: C 64.66; H 5.43; N 25.13. *M* 334.38.

4-Amino-2-(4-methoxyphenyl)-6-morpholino-pyridine-3,5-dicarbonitrile (2h). Yield 0.308 g (92%), mp 205–206°C. IR spectrum, ν, cm^{-1}: 3397, 3337 (NH_2), 2200 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.69–3.72 m [4H, $O(CH_2)_2$], 3.77–3.80 m [4H,

$N(CH_2)_2$], 3.83 s (3H, OCH_3), 7.06 d (2H, C_6H_4, *J* 8.9 Hz), 7.26 s (2H, NH_2), 7.82 d (2H, C_6H_4, *J* 8.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 48.2, 55.8, 66.4, 73.6, 82.1, 114.1, 116.7, 117.3, 130.1, 130.8, 160.9, 161.2, 161.6, 162.5. Mass spectrum, *m/z* (I_{rel}, %): 335 (78), 278 (100). Found, %: C 64.57; H 5.05; N 20.81. $C_{18}H_{17}N_5O_2$. Calculated, %: C 64.47; H 5.11; N 20.88. *M* 335.37.

4-Amino-6-(4-methoxyphenyl)-2-(methylamino)-pyridine-3,5-dicarbonitrile (2i). Methylamine hydrochloride (1.1 mmol) and DIPEA (2.5 mmol) were used in the synthesis. Yield 0.218 g (78%), mp 232–233°C. IR spectrum, ν, cm^{-1}: 3432, 3351, 3250 (NH_2, NH), 2208 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.92 d (3H, $C\underline{H}_3NH$, *J* 4.5 Hz), 3.83 s (3H, OCH_3), 7.05 d (2H, C_6H_4, *J* 8.9 Hz), 7.09 s (2H, NH_2), 7.43 q (1H, $CH_3N\underline{H}$, *J* 4.4 Hz), 7.81 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 28.8, 56.0, 71.4, 81.0, 114.2, 115.8, 117.8, 130.8, 130.9, 159.4, 160.2, 161.6, 164.2. Mass spectrum, *m/z* (I_{rel}, %): 279 (100) $[M]^+$. Found, %: C 64.44; H 4.74; N 25.13. $C_{15}H_{13}N_5O$. Calculated, %: C 64.51; H 4.69; N 25.07. *M* 279.30.

4-Amino-6-(4-methoxyphenyl)-2-(dimethylamino)pyridine-3,5-dicarbonitrile (2j). Dimethylamine hydrochloride (1.1 mmol) and DIPEA (2.5 mmol) were used in the synthesis. Yield 0.217 g (74%), mp 214–215°C. IR spectrum, ν, cm^{-1}: 3393, 3340 (NH_2), 2210 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.27 s [6H, $(CH_3)_2N$], 3.83 s (3H, OCH_3), 7.05 d (2H, C_6H_4, *J* 8.9 Hz), 7.09 s (2H, NH_2), 7.81 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 40.7, 56.0, 71.5, 80.7, 114.2, 117.4, 117.8, 130.5, 130.9, 160.1, 161.5, 161.7, 162.3. Mass spectrum, *m/z* (I_{rel}, %): 293 (59), 264 (100). Found, %: C 65.60; H 5.19; N 23.80. $C_{16}H_{15}N_5O$. Calculated, %: C 65.52; H 5.15; N 23.88. *M* 293.33.

4-Amino-2-[butyl(methyl)amino]-6-(4-methoxyphenyl)pyridine-3,5-dicarbonitrile (2k). Yield 0.285 g (85%), mp 143–144°C. IR spectrum, ν, cm^{-1}: 3420, 3332 (NH_2), 2201 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.91 t (3H, CH_3, *J* 7.4 Hz), 1.27–1.32 m (2H, CH_2), 1.59–1.65 m (2H, CH_2), 3.27 s (3H, CH_3N), 3.59–3.75 m (2H, CH_2N), 3.83 s (3H, OCH_3), 6.92–7.13 m (4H, NH_2, C_6H_4), 7.81 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.3, 20.0, 29.9, 39.0, 51.6, 56.0, 71.1, 80.5, 114.2, 117.4, 117.8, 130.5, 130.8, 159.4, 161.6, 161.7, 162.3. Mass spectrum, *m/z* (I_{rel}, %): 335 (14), 293 (100). Found, %: C 67.95; H 6.25; N 20.97. $C_{19}H_{21}N_5O$. Calculated, %: C 68.04; H 6.31; N 20.88. *M* 335.41.

4-Amino-2-(butylamino)-6-(4-methoxyphenyl)-pyridine-3,5-dicarbonitrile (2l). Yield 0.218 g (68%), mp 204–205°C. IR spectrum, ν, cm^{-1}: 3474, 3351, 3245 (NH_2, NH), 2212 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.89 t (3H, CH_3, *J* 7.4 Hz), 1.26–1.32 m (2H, CH_2), 1.45–1.68 m (2H, CH_2), 3.42–3.47 m (2H, $C\underline{H}_2NH$), 3.83 s (3H, OCH_3), 6.97–7.15 m (4H, NH_2, C_6H_4), 7.47 t (1H, $CH_2N\underline{H}$, *J* 5.7 Hz), 7.81 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.4, 20.1, 31.9, 41.0, 56.0, 71.2, 80.8, 114.2, 115.8, 117.8, 130.8, 159.6, 159.8, 161.6, 164.0, 164.3. Mass spectrum, *m/z* (I_{rel}, %): 321 (39), 279 (100). Found, %: C 67.38; H 6.02; N 21.71. $C_{18}H_{19}N_5O$. Calculated, %: C 67.27; H 5.96; N 21.79. *M* 321.38.

4-Amino-2-(dibutylamino)-6-(4-methoxyphenyl)-pyridine-3,5-dicarbonitrile (2m). Yield 0.286 g (76%), mp 119–120°C. IR spectrum, ν, cm^{-1}: 3418, 3346 (NH_2), 2206 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.90 t (6H, $2CH_3$, *J* 7.4 Hz), 1.27–1.35 m (4H, $2CH_2$), 1.52–1.75 m (4H, $2CH_2$), 3.54–3.71 m [4H, $(CH_2)_2N$], 3.83 s (3H, OCH_3), 6.96 s (2H, NH_2), 7.04 d (2H, C_6H_4, *J* 8.9 Hz), 7.80 d (2H, C_6H_4, *J* 8.8 Hz). Mass spectrum, *m/z* (I_{rel}, %): 377 (12), 335 (100). Found, %: C 69.89; H 7.26; N 18.61. $C_{22}H_{27}N_5O$. Calculated, %: C 70.00; H 7.21; N 18.55. *M* 377.49.

4-Amino-2-(diallylamino)-6-(4-methoxyphenyl)-pyridine-3,5-dicarbonitrile (2n). Yield 0.217 g (63%), mp 114–115°C. IR spectrum, ν, cm^{-1}: 3462, 3342 (NH_2), 2203 (C≡N). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.35 d [4H, $(C\underline{H}_2)_2N$, *J* 1.4 Hz], 3.82 s (3H, OCH_3), 5.15–5.28 m (4H, $=CH_2$), 5.86–6.00 m (2H, =CH), 7.06 d (2H, C_6H_4, *J* 8.8 Hz), 7.11 s (2H, NH_2), 7.81 d (2H, C_6H_4, *J* 8.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 52.1, 56.1, 71.9, 81.3, 114.4, 117.2, 117.6, 118.1, 130.4, 130.9, 134.3, 159.2, 161.6, 161.8, 162.5. Mass spectrum, *m/z* (I_{rel}, %): 345 (33). Found, %: C 69.63; H 5.49; N 20.23. $C_{20}H_{19}N_5O$. Calculated, %: C 69.55; H 5.54; N 20.28. *M* 345.41.

7-{4-[4-Amino-3,5-dicyano-6-(4-methoxyphenyl)-pyridine-2-yl]piperazin-1-yl}-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (2o). Yield 0.544 g (94%), mp 275–276°C (decomp.). IR spectrum, ν, cm^{-1}: 3430, 3325 (NH_2), 2210 (C≡N), 1662 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm:

1.15–1.22 m (2H, CH_2), 1.31–1.37 m (2H, CH_2), 3.50–3.62 m (4H, CH_2N), 3.85 s (3H, OCH_3), 4.02–4.10 m (4H, CH_2N), 7.07 d (2H, C_6H_4, *J* 8.0 Hz), 7.24 s (2H, NH_2), 7.57 s (2H, C_6H_2), 7.79–7.96 m (3H, C_6H_2, C_6H_4), 8.65 s (1H, =CH), 14.97 br.s (1H, COOH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 8.2, 26.1, 31.3, 36.5, 47.5, 49.6, 56.0, 67.0, 73.9, 82.4, 106.9, 107.4, 111.6, 111.8, 114.4, 116.9, 117.4, 119.3, 130.3, 131.0, 139.8, 145.4, 148.7, 161.1, 161.3, 161.8, 162.7, 166.6, 177.0. Mass spectrum, *m/z* (I_{rel}, %): 579 (7) $[M]^+$. Found, %: C 64.36; H 4.58; N 16.82. $C_{31}H_{26}FN_7O_4$. Calculated, %: C 64.24; H 4.52; N 16.92. *M* 579.59.

CONCLUSIONS

2-Alkylamino-4-amino-6-arylpyridine-3,5-dicarbonitriles **2** were synthesized and their spectral-luminescent properties were studied. Compounds **2** fluoresce in solutions with a maximum in the range of 399–471 nm and a quantum yield of up to 12.3%; they scarcely fluoresce in the solid state. The replacement of the chlorine atom in compounds **1** by an amine significantly reduces the luminescence quantum yield. It was found that donor substituents in the benzene ring generally cause a bathochromic shift of the fluorescence maximum. The absorption and solid-state fluorescence maxima of compounds **2** derived from primary amines are shifted to a shorter wavelength region.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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