Synthesis and spectral properties of 4-amino- and 4-acetylamino-*N*-arylnaphthalimides containing electron-donating groups in the *N*-aryl substituent

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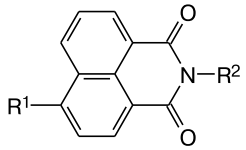
A method for the synthesis of *N*-aryl-substituted 4-amino- and 4-acetylaminonaphthalimide derivatives with mono- and dialkoxy groups or a 15-crown-5 moiety in the *N*-aryl substituent is described. The introduction of electron-donating alkoxy groups into the benzene ring of the *N*-aryl fragment results in fluorescence quenching of the naphthalimide chromophore, which is most pronounced in the spectra of *N*-acetyl derivatives. The photophysical properties of the synthesized 4-amino- and 4-acetylaminonaphthalimides depend on the solvent polarity and its specific solvating ability due to H-bonding. The crown-containing compounds are promising fluorescent chemosensors for metal cations.

Key words: naphthalimide, 15-crown-5, fluorescence, hydrogen bond, UV-Vis absorption spectra, fluorescent sensors, 4-nitronaphthalic anhydride, photoinduced charge transfer.

Organic luminophores on the base of naphthalimide are of the great practical significance. They are used as dyes for natural and synthetic fibers,[1] optical brighteners,[1] laser dyes,[2] fluorescent dichroic dyes,[3] reagents for luminescent defectoscopy.[1] Recently, on the base of naphthalimides, electroluminescent materials known as integral parts of the organic light-emitting diodes have been obtained.[4—6] It was also found that some naphthalimide derivatives possess antitumor activity due to their ability to cause the photochemical cleavage of nucleic acids.[7—10]

The photophysical properties of naphthalimide derivatives evoke strong interest of researchers not only due to a variety of practical applications. Electron-deficient properties of the naphthalimide ring in the excited state make these compounds appropriate models for studying the processes of photoinduced electron transfer widespread in nature.[8,11] Based on naphthalimide, the systems where electron excitation energy transfer can be realized were obtained and studied.[12—14] In most cases, naphthalimide derivatives possess solvatochromism, which allows studies of the effect of the solvent nature on spectral properties.

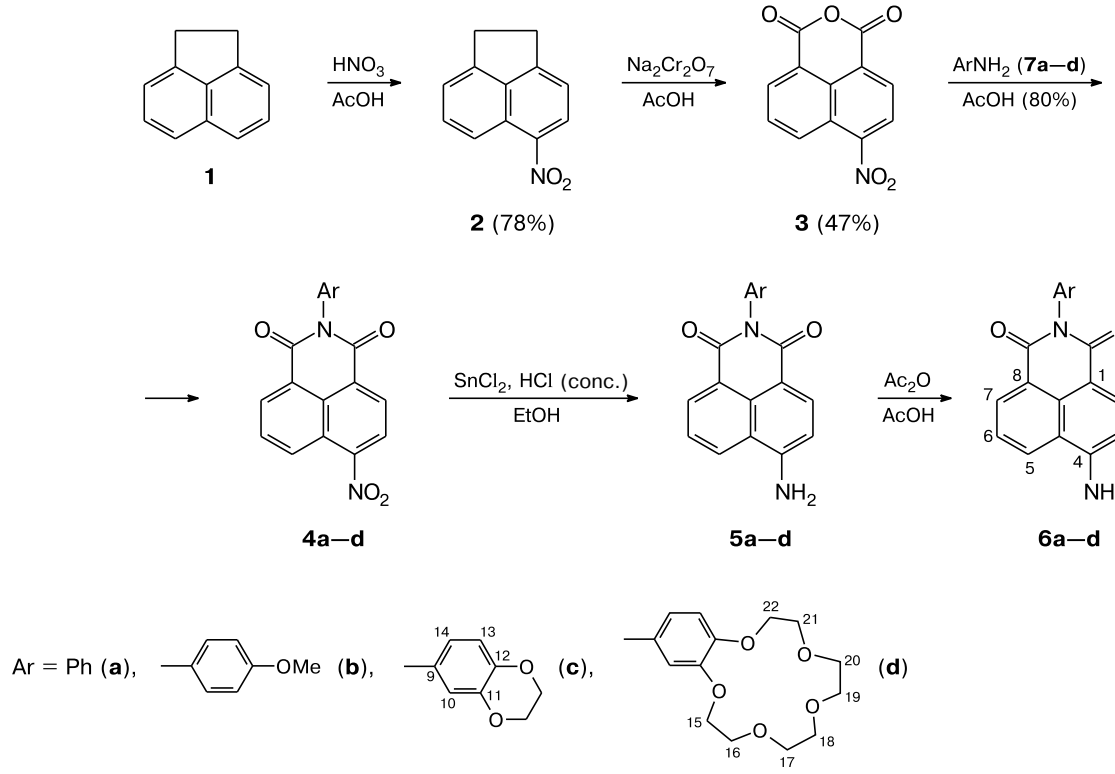
Owing to the fact that naphthalimide derivatives are efficient luminophores, it seems very attractive to use them as signaling elements for the construction of various types of molecular devices. Thus, examples of fluorescent sensors for cations and anions containing naphthalimide residue are documented.[15—33] Introduction of an ionophore into a naphthalimide derivative from the side of the electron-donating substituent R^1 located in the position 4 of the naphthalene ring is the common feature in the design of such sensors.



In the present work, a method for the synthesis of 4-amino- and 4-acetylaminonaphthalimide derivatives containing a crown-ether receptor in the *N*-aryl fragment R^2 is developed. The known compounds where R^2 is phenyl or 4-methoxyphenyl group as well as previously unknown benzodioxane derivatives (R^2 is the benzodioxane residue) were synthesized for comparative analysis of the influence of the electron-donating groups on the spectral parameters.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1199—1206, June, 2009.
1066-5285/09/5806-1233

Scheme 1



Yield of the products (%): 94 (**4a**), 88 (**4b**), 95 (**4c**), 67 (**4d**), 92 (**5a**), 87 (**5b**), 95 (**5c**), 94 (**5d**), 75 (**6a**), 86 (**6b**), 62 (**6c**), 74 (**6d**)

Synthesis. For the synthesis of naphthalimide derivatives, acenaphthene (**1**) produced in industrial scale from coal tar[34] was used as the starting compound. 4-Amino- and 4-acetylamino naphthalimide derivatives **5a—d** and **6a—d** were prepared according to Scheme 1.

Nitration of acenaphthene (**1**) and subsequent oxidation of 4-nitro derivative **2** with sodium bichromate in acetic acid resulted in 4-nitrophthalic anhydride **3**.[35—37] The next steps involved conventional acylation of primary aromatic amines **7a—d** with 4-nitrophthalic anhydride (**3**), reduction of the nitro group in 4-nitronaphthalimides **4a—d**, and acylation of amines **5a—d** with acetic anhydride according to common methods.[38—40]

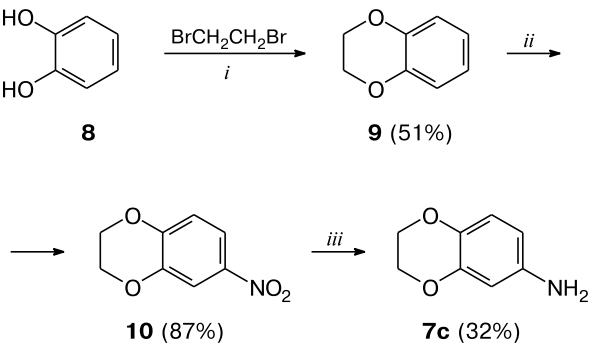
6-Amino-2,3-dihydrobenzo[*b*][1,4]-dioxin (**7c**) was prepared in three steps from catechol (**8**) using a known procedure[41] (Scheme 2).

Crown-containing amine **7d** in the form of hydrochloride is commercially available. Free amine **7d** was generated *in situ* in the acylation with anhydride **3** by addition of sodium acetate to the reaction mixture.

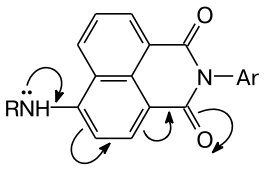
The structures of the compounds synthesized were established based on the data from ^{1}H NMR and UV spectroscopy and confirmed by the data from elemental analysis.

Study of spectral properties. Long-wavelength band in the absorption spectra of 4-amino- and 4-acetylamino-naphthalimides **5a—d** and **6a—d** is due to the charge transfer from the electron-donating amino or acylamino group to the carbonyl groups of the carboxymide fragment.[1]

Scheme 2



i. Na_2CO_3, glycerol, Δ; *ii*. HNO_3 (dilute), 60 °C; *iii*. N_2H_4, Ni, EtOH, Δ.



R = H, Ac

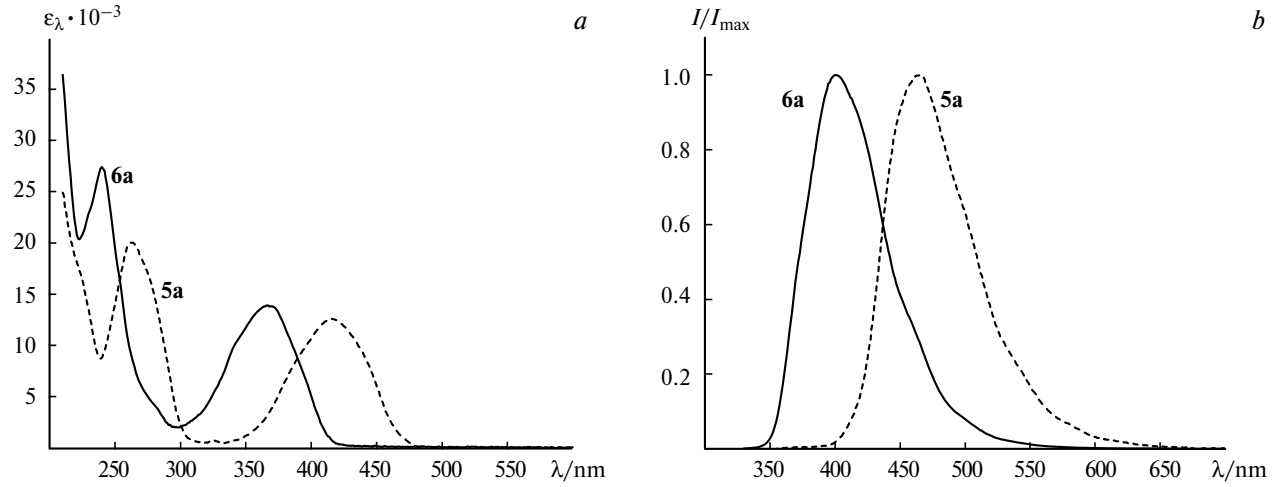


Fig. 1. Absorption spectra (*a*) and fluorescence emission spectra (*b*) of compounds **5a** and **6a** in acetonitrile; $C_{\mathbf{5a}} = 3.2 \cdot 10^{-5}$ mol · L^{-1}, $C_{\mathbf{6a}} = 1.8 \cdot 10^{-5}$ mol · L^{-1}, $\lambda_{ex} = 365$ nm.

The absorption spectra of 4-amino- and 4-acetylamino-*N*-phenylnaphthalimides (**5a** and **6a**) in acetonitrile are shown in Fig. 1, *a* as an example.

The replacement of the amino group in **5a** by the acetylamino group in **6a** reduces the electron-donating properties of the nitrogen atom at the naphthalimide fragment resulting in a hypsochromic shift of the charge transfer band by 50 nm in the absorption spectrum. The fluorescence spectra are also shifted hypsochromically (Fig. 1, *b*). Thus, 4-amino-substituted compound **5a** has yellow-greenish fluorescence, while **6a** is a luminophore with bluish fluorescence.

In the series of compounds **5a—d** and **6a—d**, the effect of the nature of the *N*-aryl substituent on spectral-fluorescence properties was analyzed. The fluorescence quantum yields and maxima in the absorption and emission spectra (λ_{max}^{abs} and λ_{max}^{fl}) in acetonitrile are listed in Table 1. The introduction of the electron-donating groups in the benzene ring does not virtually change λ_{max}^{abs} and λ_{max}^{fl}. This observation allows assumption that in the ground state only very weak π-electron interaction exists between the *N*-aryl fragment and the naphthalimide moiety.

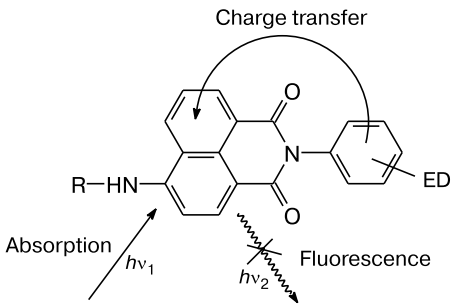
Table 1. Spectral properties of **5a—d** and **6a—d** in acetonitrile at 20 °C

Compound	λ_{max}^{abs} / nm	λ_{max}^{fl} / nm	φ^{fl}
5a	416	523	0.52
5b	416	515	0.43
5c	415	522	0.46
5d	413	521	0.43
6a	366	457	0.85
6b	370	455	0.030
6c	366	454	0.0048
6d	366	456	0.0030

The intensity of the fluorescence depends on the presence of the electron-donating group in the benzene ring. The introduction of one methoxy group into the phenyl ring decreases the quantum yield of 4-acetylamino-*N*-phenylnaphthalimide **6a** from 0.85 to 0.030, and the presence of two methoxy groups in compounds **6c,d** reduces the quantum yield to a few thousandths (Table 1). In the series of amino derivatives, the annulation of dioxane or crown-ether moieties with the benzene ring (compounds **5c,d**) does not lead to such significant changes, the quantum yield decreases only slightly.

Based on the analysis of the literature data,[15—33] the quenching of the fluorescence can probably be explained by assuming that in the excited state S_1 nonradiative deactivation due to the charge transfer from the *N*-aryl substituent to the naphthalimide chromophore competes with the fluorescence. The increase in the electron-donating properties of the *N*-aryl residue due to the pres-

Scheme 3



R = H, Ac

ED is an electron-donating group

ence of the alkoxy groups will increase the probability of the nonradiative deactivation of the excited state S_1 and as a result, the fluorescence quantum yield will decrease (Scheme 3).

Photophysical properties of the compounds synthesized depend considerably on the nature of the solvent. The absorption and emission fluorescence spectra of 4-amino- and 4-acetylaminonaphthalimides **5a,c,d** and **6a,c,d** were recorded in eleven different solvents, including five aprotic and six protic solvents. The Stokes shifts ($\Delta\nu$), fluorescence quantum yields (φ^{fl}), and lifetime of the excited states (τ_s) were also determined (Tables 2 and 3).

These data show that the increase in the solvent polarity resulted in the increase in the Stokes shifts. This suggests that the excited state S_1 has a higher dipole moment (compared with S_0) and results from charge transfer from the amino or acetylamino group in position 4 of the naphthalene moiety to the carbonyl groups of the imide residue.

The fluorescence spectra of all compounds mentioned in Tables 2 and 3 always shift bathochromically with the increase in the solvent polarity and its ability to form hydrogen bonds. In all cases, the longest-wavelength fluorescence band were observed in water (~560 nm for the 4-amino derivatives and ~480 nm for the 4-acetylamino derivatives). The shortest-wavelength fluorescence was observed in diethyl ether (~500 nm for the 4-amino derivatives and ~440 nm for the 4-acetylamino derivatives). It is also possible to assume that the excited state formed upon charge transfer is less polar in the case of acetylamines than for the amines, since in the latter the solvent change leads to larger changes in λ_{max}^{fl}.

The position of the bands in the absorption spectra, apparently, depends on two factors: the polarity of the solvent and its capacity for hydrogen bonding. An increase in the polarity leads to bathochromic shift of the absorption band, but in contrast, the formation of the hydrogen bond resulted in a short wavelength shift due to

Table 2. Absorption and fluorescence spectral data for 4-aminonaphthalimides **5a—d** in different solvents at 20 °C

Compound	Solvent (ε)	λ_{max}^{abs} /nm ($lg\varepsilon_\lambda$)	λ_{max}^{fl} (λ_{exc}) /nm	$\Delta\nu$ /cm^{-1}	φ^{fl}	τ_s /ns
5a	Propylene carbonate (65.0)	421 (4.15)	531 (420)	4921	0.50	9.9
	Dimethyl sulfoxide (46.5)	437 (4.14)	539 (440)	4330	0.46	9.2
	Acetonitrile (36.0)	416 (4.03)	523 (415)	4918	0.52	9.5
	Dimethoxyethane (7.2)	419 (4.14)	516 (420)	4487	0.47	9.4
	Diethyl ether(4.2)	413 (4.12)	501 (415)	4253	0.50	9.8
	Water (78.4)	434 (4.13)	560 (430)	5184	0.091	2.8
	Methanol (32.6)	434 (4.19)	544 (430)	4659	0.30	4.0
	Ethanol (24.5)	437 (4.15)	538 (430)	4296	0.39	7.5
	n-Butanol (17.5)	439 (4.18)	537 (430)	4157	0.43	8.0
	n-Heptanol (11.1)	438 (4.23)	534 (410)	4104	0.50	8.6
	n-Decanol (7.2)	437 (4.18)	531 (410)	4051	0.52	8.9
5c	Propylene carbonate (65.0)	418 (4.22)	526 (420)	4912	0.52	9.6
	Dimethyl sulfoxide (46.5)	436 (4.19)	539 (430)	4383	0.52	9.0
	Acetonitrile (36.0)	415 (4.24)	522 (415)	4939	0.46	9.4
	Dimethoxyethane (7.2)	418 (4.19)	513 (420)	4430	0.49	9.1
	Diethyl ether (4.2)	411 (4.18)	500 (430)	4331	0.55	9.6
	Water (78.4)	433 (3.90)	558 (430)	5174	0.09	2.8
	Methanol (32.6)	433 (4.27)	542 (430)	4645	0.29	6.1
	Ethanol (24.5)	436 (4.22)	537 (430)	4314	0.40	7.4
	n-Butanol (17.5)	438 (4.23)	536 (430)	4174	0.44	7.8
	n-Heptanol (11.1)	437 (4.22)	532 (430)	4086	0.48	8.6
	n-Decanol (7.2)	435 (4.19)	529 (430)	4085	0.51	8.8
5d	Propylene carbonate (65.0)	418 (4.22)	525 (420)	4876	0.49	9.2
	Dimethyl sulfoxide (46.5)	436 (4.19)	539 (430)	4383	0.50	8.8
	Acetonitrile (36.0)	413 (4.23)	521 (415)	5019	0.43	9.0
	Dimethoxyethane (7.2)	417 (4.19)	512 (420)	4450	0.47	8.9
	Diethyl ether (4.2)	411 (3.65)	499 (420)	4291	0.54	9.7
	Water (78.4)	431 (4.22)	557 (430)	5249	0.089	2.7
	Methanol (32.6)	432 (4.24)	542 (430)	4698	0.28	6.0
	Ethanol (24.5)	435 (4.41)	537 (430)	4367	0.35	7.3
	n-Butanol (17.5)	438 (4.28)	536 (430)	4174	0.40	7.7
	n-Heptanol (11.1)	437 (4.20)	532 (420)	4086	0.46	8.4
	n-Decanol (7.2)	435 (4.21)	530 (420)	4121	0.47	8.8

Table 3. Absorption and fluorescence spectral data for 4-aminonaphthalimides **6a—d** in different solvents at 20 °C

Compound	Solvent (ε)	λ_{max}^{abs} /nm (lgε$_\lambda$)	λ_{max}^{fl} (λ_{exc}) /nm	Δν /cm^{-1}	φ^{fl}	τ_s*
6a	Propylene carbonate (65.0)	369 (4.32)	460 (330)	5361	0.75	6.3
	Dimethyl sulfoxide (46.5)	371 (4.32)	460 (330)	5215	0.69	3.6
	Acetonitrile (36.0)	366 (4.27)	457 (330)	5441	0.85	6.5
	Dimethoxyethane (7.2)	369 (4.34)	449 (330)	4829	0.69	5.9
	Diethyl ether (4.2)	368 (4.32)	440 (330)	4447	0.67	6.1
	Water (78.4)	356 (4.35)	482 (320)	7343	0.73	6.8
	Methanol (32.6)	364 (4.33)	473 (320)	6331	0.77	7.0
	Ethanol (24.5)	366 (4.37)	467 (320)	5909	0.66	6.7
	n-Butanol (17.5)	369 (4.41)	465 (320)	5595	0.81	6.3
	n-Heptanol (11.1)	371 (4.37)	462 (320)	5309	0.75	6.2
	n-Decanol (7.2)	372 (4.33)	460 (320)	5143	0.76	6.2
6c	Propylene carbonate (65.0)	368 (4.20)	456 (370)	5244	0.012	90
	Dimethyl sulfoxide (46.5)	371 (4.21)	465 (370)	5449	0.0072	78
	Acetonitrile (36.0)	366 (4.23)	454 (360)	5296	0.0048	61
	Dimethoxyethane(7.2)	369 (4.25)	446 (370)	4679	0.0020	35
	Diethyl ether (4.2)	368 (4.23)	439 (370)	4395	0.0018	35
	Water (78.4)	356 (4.19)	480 (360)	7257	0.0030	52
	Methanol (32.6)	363 (4.22)	470 (360)	6272	0.0032	65
	Ethanol (24.5)	366 (4.23)	461 (360)	5630	0.0026	75
	n-Butanol (17.5)	368 (4.29)	458 (360)	5340	0.0030	40
	n-Heptanol (11.1)	371 (4.19)	454 (370)	4928	0.0049	54
	n-Decanol (7.2)	371 (4.19)	453 (370)	4879	0.0085	100
6d	Propylene carbonate (65.0)	368 (4.20)	457 (370)	5292	0.0096	48
	Dimethyl sulfoxide (46.5)	371 (4.18)	464 (370)	5402	0.0041	65
	Acetonitrile (36.0)	366 (4.24)	456 (365)	5393	0.0030	27
	Dimethoxyethane (7.2)	369 (4.24)	448 (370)	4779	0.0013	19
	Diethyl ether (4.2)	368 (3.72)	441 (370)	4498	0.0016	19
	Water (78.4)	356 (4.26)	481 (360)	7300	0.0017	30
	Methanol (32.6)	363 (4.16)	469 (360)	6226	0.0025	32
	Ethanol (24.5)	366 (4.17)	462 (365)	5677	0.0023	27
	n-Butanol (17.5)	369 (4.21)	460 (370)	5361	0.0057	21
	n-Heptanol (11.1)	370 (4.20)	456 (370)	5097	0.0099	27
	n-Decanol (7.2)	371 (4.21)	455 (370)	4976	0.0075	30

* For compound **6a** lifetime value τ_s is given in ns, for compound **6c,d** — in ps.

specific solvation of the polar ground state. Thus in the series of aprotic solvents, diethyl ether (ε = 4.2) — dimethoxyethane (ε = 7.2) — acetonitrile (ε = 36.0) — propylene carbonate (ε = 65.0), long-wavelength bands in the absorption spectra of the 4-amino- and the 4-acetylamino derivatives undergo a bathochromic shift. The different pattern is observed in protic solvents. In the case of the 4-amino derivatives, λ_{max}^{abs} shifts bathochromically on going from decanol to butanol (the solvent polarity is the critical factor). On going from butanol to methanol, λ_{max}^{abs} undergoes hypsochromic shifts (the ability of the solvent to form hydrogen bonds begins dominate). The absorption spectrum of the amino derivatives in water is almost in the same position as in methanol. The latter is likely due to the fact that on going from methanol to water not only polarity of the solvent, but also its ability to specific solvation increase dramatically.

No initial increase in λ_{max}^{abs} of 4-acetylamines in the series of solvents from decanol to water is observed with the increase in the solvent polarity, instead λ_{max}^{abs} shifts hypsochromically. Apparently, the solvent polarity is of less importance for the acetylamino derivatives as their molecules possess smaller dipole moments.

It should be noted that in DMSO, unlike other aprotic solvents, the absorption spectra of amines and acetylamines are observed in an abnormally long-wavelength region. Apparently, this could be explained by specific solvation due to hydrogen bonding between the hydrogen atoms of the amino or acetylamino groups and the oxygen atoms of the DMSO molecules bearing relatively high partial negative charge.

Determination of the fluorescence quantum yields in the aprotic solvents shows that the change in the solvent influences the quantum yield of the compounds, but no clear pattern could be established. In the protic solvents, a tendency was noted for decreasing the fluorescence quantum yield and lifetime of the excited state of 4-aminonaphthalimides with increasing the ability of the solvent

for hydrogen bonding. This regularity is not observed in the series of 4-*N*-acyl derivatives (Tables 2 and 3).

Thus, we synthesized naphthalimide derivatives containing monoalkoxy and dialkoxy groups and a 15-crown-5 moiety in the *N*-aryl substituent. It was found that the introduction of an electron-donating substituent into the *N*-phenyl ring leads to quenching of fluorescence in the series of 4-amino and 4-acetylaminonaphthalimides caused by redistribution of the charge in the excited state between the naphthalimide chromophore (acceptor) and the *N*-aryl moiety (donor). It was also found that the substituents in the benzene ring do not affect the position of the long-wavelength band in the absorption spectra, which suggests certain independence of the π-systems of the naphthalimide residue and the *N*-aryl moiety in the ground state. The influence of the nature of the solvent on spectral properties of the series of the synthesized compounds was analyzed.

The observed effect of the fluorescence quenching caused by the introduction of the crown-ether moiety into the *N*-phenyl ring of 4-amino and 4-acetylaminonaphthalimides suggests the existence of sensor properties of the corresponding crown ether derivatives with respect to metal cations. For this type of compounds, one should expect the fluorescence enhancement upon cation binding by the crown-ether moiety since the complex formation decreases electron-donating properties of the oxygen atoms at the benzene rings. Study of the complexation in the series of crown ether-containing naphthalimide derivatives will be the subject of our further research.

Experimental

^{1}H NMR spectra were recorded on a Varian-XR-400 spectrometer (400 MHz) in deuteriated chloroform, pyridine, DMSO, and acetonitrile. Chemical shifts were determined relative to hexamethyldisiloxane with accuracy of 0.01 ppm, the coupling constants with accuracy of 0.1 Hz. The assignment of the proton signals H(2), H(3), H(5), and H(7) for compounds **4c,d**, **5c,d**, and **6b—d** is based on theoretical calculations that were made using ACD/Labs 6.0 program package.

Melting points were determined in open capillaries and are uncorrected.

Elemental analysis was carried out at the Laboratory of physicochemical methods of analysis of the Department of Chemistry, the M.V. Lomonosov Moscow State University.

Thin-layer chromatography was performed on precoated plates Sorbfil UV-254 in benzene—ethanol or chloroform solvent systems. Silica gel 60 (Fluka) was used for column chromatography.

The absorption spectra were measured on a Varian-Cary spectrophotometer. The fluorescence spectra were measured on a FluoroMax-3 spectrofluorimeter. The observed fluorescence was recorded at a right angle to the excitation beam. All measured fluorescence spectra were corrected for the non-uniformity of detector spectral sensitivity. The fluorescence quantum yields were determined in aerated solutions at 20±1 °C using quinine sulfate in 1 *N* sulfuric acid ($\varphi^{fl} = 0.55$)[42] and Rodamine 6G in ethanol ($\varphi^{fl} = 0.95$)[43] as standards. The fluorescence quantum yields were calculated by Equation (1)[44]

$$\varphi_i^{fl} = \varphi_0^{fl} \cdot \frac{(1-10^{-D_0}) \cdot S_i \cdot n_0^2}{(1-10^{-D_i}) \cdot S_0 \cdot n_i^2}, \qquad (1)$$

where φ_i^{fl} and φ_0^{fl} are quantum yields of analytical and standard samples, respectively, D_i and D_0 are absorbance of the analytical and standard samples, respectively, S_i and S_0 are areas under the curves of the fluorescence spectra for analytical and standard samples, respectively, n_i and n_0 are refractive indices for analytical and standard samples, respectively.

The solvents of the spectrophotometric grade (Aldrich, Acros) were used for the spectroscopic studies as purchased.

The time-resolved fluorescence spectra were measured on a Chromex 250 spectrograph coupled to a streak camera Hamamatsu 5680 equipped with a fast sweep unit M5676 with temporal resolution of 2 ps. Excitation pulses were generated by optical parametric generator pumped by fundamental beam derived from a femtosecond laser Ti-sapphire Femtopower Compact Pro. All excited state lifetimes were obtained using a depolarized excitation light. The highest pulse energy of fluorescence excitation did not exceed 100 nJ, average power of an excitation beam was 0.1 mW at a pulse repetition rate of 1 kHz focused into a spot with a diameter 0.1 mm in the 10 mm long fused quartz cell. The fluorescence kinetics were later fitted by the Levenberg-Marquardt least-square curve-fitting method using a solutions of the differential equations describing the evolution in time of a single excited state and neglecting depopulation of the ground state:

$$dI/dt = Gauss(t_0,\Delta t,A) - I(t)/\tau,$$

where $I(t)$ is fluorescence intensity, τ is lifetime of the excited state, *Gauss* is the Gauss profile of the excitation pulse, t_0 is time position of its maximum, Δt is the pulse width, A is the pulse amplitude. Initial conditions: $I(-\infty) = 0$. Typically, the fit shows a χ^2 value better than 10^{-4} and a correlation coefficient $R > 0.999$. The uncertainty of the lifetime was better than 1%. Routinely, the fluorescence accumulation time in our measurements did not exceed 90 s.

Compounds **2**[36], **3**[37], **4a**[38], **4b**[38], **5a**[39], **5b**[39], **6a**[40], **7c**[41], **8**[41], **9**[41] were synthesized according to the known methods. The structures of the compounds were confirmed by coincidence of the melting points with the literature data.

Acylation of amines 7a—d with 4-nitronaphthalic anhydride. (general procedure).[38] To a suspension of 4-nitronaphthalic anhydride (**3**) (6.00 g, 25.0 mmol) in glacial acetic acid (75 mL), the corresponding amine (50.0 mmol) was added and the mixture was refluxed for 1.5 h. The crystalline product was filtered off, washed on a filter with 5% hydrochloric acid, hot 10% aqueous Na_2CO_3, distilled water, and ethanol. The product was dried at 80 °C.

2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-6-nitro-2,3-dihydrobenzo[*d*,*e*]isoquinoline-1,3(1*H*)-dione (4c). Compound **4c** were prepared using the general procedure from **3** (1.60 g) and 6-amino-2,3-dihydrobenzo[*b*][1,4]dioxin **7c** (2.00 g) in glacial acetic acid (15 mL) in a yield of 2.36 g (95%), m.p. 300—302 °C. ^{1}H NMR (DMSO-d_6), δ: 4.28 (br.s, 4 H, $-CH_2-CH_2-$); 6.82 (dd, 1 H, H(14), J = 8.3 Hz, J = 2.2 Hz); 6.93 (d, 1 H, H(10), J = 2.2 Hz); 6.96 (d, 1 H, H(13), J = 8.3 Hz); 8.06—8.12 (m, 1 H, H(6)); 8.52—8.59 (m, 2 H, H(2), H(3)); 8.60 (d, 1 H, H(7), J = 7.3 Hz); 8.72 (d, 1 H, H(5),

J = 8.6 Hz). Found (%): C, 63.73; H, 3.05; N, 7.44. $C_{20}H_{12}N_2O_6$. Calculated (%): C, 63.83; H, 3.21; N, 7.44.

6-Nitro-2-(1,4,7,10,13-pentaoxa-2,3,5,6,8,9,11,12-octahydrobenzo[*b*]cyclopentadecyn-15-yl)-2,3-dihydrobenzo[*d*,*e*]isoquinoline-1,3(1*H*)-dione (4d). Nitro derivative **4d** was prepared according to the general procedure form 4-nitronaphtalic anhydride **3** (0.38 g), amine hydrochloride **7d** (1.00 g) and sodium acetate (0.28 g) in glacial acetic acid (15 mL) in a yield of 0.53 g (67%), m.p. 258—261 °C. ^{1}H NMR(Py-d_5), δ: 4.77—4.93 (m, 12 H, C(16)H_2, C(17)H_2, C(18)H_2, C(19)H_2, C(20)H_2, C(21)H_2); 5.17—5.21 (m 4 H, C(15)H_2, C(22)H_2); 8.16 (d, 1 H, H(13), J = 8.3 Hz); 8.28 (dd, 1 H, H(14), J = 2.3 Hz, J = 8.3 Hz); 8.39 (d, 1 H, H(10), J = 2.3 Hz); 8.96 (dd, 1 H, H(6), J = 7.3 Hz, J = 8.6 Hz); 9.54 (d, 1 H, H(3), J = 8.1 Hz); 9.79 (d, 1 H, H(2), J = 8.1 Hz); 9.82 (d, 1 H, H(7), J = 8.6 Hz); 9.83 (d, 1 H, H(5), J = 8.6 Hz). Found (%): C, 61.47; H, 4.72; N, 5.41. $C_{26}H_{24}N_2O_9$. Calculated (%): C, 61.41; H, 4.76; N, 5.51.

Reduction of 4-nitronaphtalimide derivatives (general procedure).[39] To a suspension of a 4-nitronaphthaliminde derivative (4.0 mmol) in ethanol (20 mL) a solution of $SnCl_2 \cdot 2H_2O$ (6.45 g) in concentrated HCl (5 mL, ρ 1.18 g • mL^{-1}) was added dropwise with stirring at 50 °C. The mixture was refluxed for 1.5 h. The reaction mixture was poured into water (50 mL), the precipitate that formed was filtered off, washed with water, 1% aqueous NaOH (for the removal of tin), then with water and ethanol. The product was dried at 80 °C.

6-Amino-2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,3-dihydrobenzo[*d*,*e*]isoquinoline-1,3(1*H*)-dione (5c) was prepared according to the general procedure from nitro derivative **4c** (2.36 g) and $SnCl_2 \cdot 2H_2O$ (10.16 g) in concentrated HCl (7.5 mL) to give compound **5c** in the yield of 2.07 g (95%), m.p. 350—352 °C. ^{1}H NMR (DMSO-d_6), δ: 4.30 (br.s, 4 H, $-CH_2-CH_2-$); 6.73 (dd, 1 H, H(14), J = 8.3 Hz, J = 2.3 Hz); 6.82 (d, 1 H, H(10), J = 2.3 Hz); 6.87 (d, 1 H, H(13), J = 8.3 Hz); 6.94 (d, 1 H, H(3), J = 8.6 Hz); 7.43 (br.s, 2 H, NH_2); 7.63—7.71 (m, 1 H, H(6)); 8.18 (d, 1 H, H(2), J = 8.6 Hz); 8.42 (d, 1 H, H(7), J = 7.3 Hz); 8.65 (d, 1 H, H(5), J = 8.3 Hz). Found (%): C, 69.32; H, 3.92; N, 8.09. $C_{20}H_{14}N_2O_4$. Calculated (%): C, 69.36; H, 4.07; N, 8.09.

6-Amino-2-(1,4,7,10,13)-pentaoxa-2,3,5,6,8,9,11,12-octahydrobenzo[*b*]cyclopentadecyn-15-yl)-2,3-dihydrobenzo[*d*,*e*]isoquinoline-1,3(1*H*)-dione (5d). Compound **5d** was obtained according to the general procedure from nitro derivative **4d** (0.53 g) and $SnCl_2 \cdot 2H_2O$ (1.68 g) in concentrated HCl (1.2 mL) in a yield of 0.47 g (94%), m.p. 308—311 °C. ^{1}H NMR (DMSO-d_6), δ: 3.61—3.71 (m, 8 H, C(17)H_2, C(18)H_2, C(19)H_2, C(20)H_2); 3.75—3.81 (m, 2 H, C(16)H_2); 3.81—3.86 (m, 2 H, C(21)H_2); 4.02—4.08 (m, 2 H, C(15)H_2); 4.12—4.18 (m, 2 H, C(22)H_2); 6.81 (dd, 1 H, H(14), J = 8.3 Hz, J = 2.3 Hz); 6.90 (d, 1 H, H(3), J = 8.6 Hz); 6.92 (d, 1 H, H(10), J = 2.3 Hz); 7.04 (d, 1 H, H(13), J = 8.3 Hz); 7.32 (br.s, 2 H, NH_2); 7.65—7.71 (m, 1 H, H(6)); 8.20 (d, 1 H, H(2), J = 8.6 Hz); 8.44 (d, 1 H, H(7), J = 7.3 Hz); 8.65 (d, 1 H, H(5), J = 8.3 Hz). Found (%): C, 65.39; H, 5.34; N, 5.85. $C_{26}H_{26}N_2O_7$. Calculated (%): C, 65.26; H, 5.48; N, 5.85.

***N*-Acylation of 4-naphthalimide derivatives (general procedure).**[40] To a suspension of 4-aminonaphthalimide derivative (4.0 mmol) in glacial acetic acid (9.0 mL), acetic anhydride (0.053 mmol, 5.0 mL) was added dropwise with stirring at 80 °C, and the mixture was refluxed for 1.5 h. The precipitate that formed was filtered off, washed with water and ethanol, and dried at 80 °C.

***N*-(2-(4-Methoxyphenyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*d*,*e*]isoquinolin-6-yl)acetamide (6b).** Compound **6b** was prepared according to the general procedure from 4-amino-*N*-(4-methoxyphenyl)naphthalimide (**5b**) (1.26 g) and acetic anhydride (5.0 mL) in a yield of 1.23 g (86%), m.p. 334—337 °C. ^{1}H NMR (Py-d_5) δ: 3.49 (s, 3 H, CH_3CO-); 4.72 (s, 3 H, $-OCH_3$); 8.15—8.19 (m, 2 H, H(11), H(13)); 8.57—8.61 (m, 2 H, H(10), H(14)); 8.70 (dd, 1 H, H(6), J = 7.3 Hz, J = 8.6 Hz); 9.65 (d, 1 H, H(3), J = 8.1 Hz); 9.72 (dd, 1 H, H(7), J = 1.0 Hz, J = 7.3 Hz); 9.78 (d, 1 H, H(2), J = 8.1 Hz); 9.83 (dd, 1 H, H(5), J = 1.0 Hz, J = 8.6 Hz); 12.11 (br.s, 1 H, —NH—CO—). UV (MeCN), λ_{max}/nm (log ε): 365 (4.60). Found (%): C, 69.96; H, 4.42; N, 7.84. $C_{21}H_{16}N_2O_4$. Calculated (%): C, 69.99; H, 4.48; N, 7.77.

***N*-[2-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*d*,*e*]isoquinolin-6-yl]acetamide (6c)** was prepared according to the general procedure from 4-aminonaphthalimide **5c** (0.50 g) and acetic anhydride (1.8 mL) in a yield of 0.35 g (62 %), m.p. 310—313 °C. ^{1}H NMR (DMSO-d_6) δ: 2.30 (s, 3 H, CH_3CO-); 4.32 (br.s, 4 H, $-CH_2-CH_2-$); 6.81 (dd, 1 H, H(14), J = 2.3 Hz, J = 8.3 Hz); 6.90 (d, 1 H, H(10), J = 2.3 Hz); 6.96 (d, 1 H, H(13), J = 8.3 Hz); 7.91 (dd, 1 H, H(6), J = 7.3 Hz, J = 8.6 Hz); 8.33 (d, 1 H, H(3), J = 8.3 Hz); 8.48 (d, 1 H, H(2), J = 8.3 Hz); 8.53 (dd, 1 H, H(7), J = 0.8 Hz, J = 7.3 Hz); 8.74 (dd, 1 H, H(5), J = 0.8 Hz, J = 8.6 Hz); 10.32 (br.s, 1 H, —NH—CO—). Found (%): C, 68.11; H, 4.10; N, 7.46. $C_{22}H_{16}N_2O_5$. Calculated (%): C, 68.04; H, 4.15; N, 7.21.

***N*-[2-(1,4,7,10,13-Pentaoxa-2,3,5,6,8,9,11,12-octahydrobenzo[*b*]cyclopentadecyn-15-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*d*,*e*]isoquinolin-6-yl]acetamide (6d).** Compound **6d** was prepared by the general procedure from 4-aminonaphthalimide **5d** (0.15 g) and acetic anhydride (0.5 mL) in a yield of 0.12 g (74 %), m.p. 308—311 °C. ^{1}H NMR (DMSO-d_6) δ: 2.31 (s, 3 H, CH_3CO-); 3.61—3.71 (m, 8 H, C(17)H_2, C(18)H_2, C(19)H_2, C(20)H_2); 3.75—3.81 (m, 2 H, C(16)H_2); 3.81—3.87 (m, 2 H, C(21)H_2); 4.01—4.09 (m, 2 H, C(15)H_2); 4.12—4.19 (m, 2 H, C(22)H_2); 6.89 (dd, 1 H, H(14), J = 2.3 Hz, J = 8.3 Hz); 7.00 (d, 1 H, H(10), J = 2.3 Hz); 7.07 (d, 1 H, H(13), J = 8.3 Hz); 7.88—7.95 (m, 1 H, H(6)); 8.33 (d, 1 H, H(3), J = 8.3 Hz); 8.49 (d, 1 H, H(2), J = 8.3 Hz); 8.54 (d, 1 H, H(7), J = 7.3 Hz); 8.75 (d, 1 H, H(5), J = 8.6 Hz); 10.33 (br.s, 1 H, —NH—CO—). Found (%): C, 64.61; H, 5.27; N, 5.42. $C_{28}H_{28}N_2O_8$. Calculated (%): C, 64.61; H, 5.42; N, 5.38.

This work was financially supported by the Russian Foundation for Basic Research (Project 09-03-93116) and National Center for Scientific Research (CNRS program PICS 3904).

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Received November 27, 2008