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4-Amino-3-nitro naphthalimides—Structures and spectral properties

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ABSTRACT

4-Aryl(alkyl)amino-3-nitro-1,8-naphthalimides show substituent and solvent dependent absorbances. The substituent steric volume and character strongly influence the charge transfer within the system. Arylamino-substituted derivatives are strongly NH acidic and their spectra are highly sensitive to even a weak base such as DMF.

1. Introduction

The development of photoactive devices for sensing and reporting of chemical species is currently of significant importance for both chemistry and biology [1]. Chemosensors for detection and measurement of transition metal ions are being actively investigated, because these metals are essential trace elements in biological systems and important elements in environmental chemistry [2–10]. Fluorescent 1,8-naphthalimide derivatives serve as dyes for synthetic polymers and textile materials [11], liquid-crystal additives [12], electrooptically sensitive materials in laser technology [13], DNA intercalators [14] and fluorescent markers [15] in medicine and biology. Diamino-1,8-naphthalimide derivatives have been developed as signal molecules for transition metal ions [16,17]. However important and useful naphthalimides (1H-benz[de]isoquinoline-1,3(2H)-diones) are, some structure motifs remain unexplored. Herein we present 4-amino-3-nitro substituted 1,8-naphthalimides – potential photoactive sensors and starting compounds for further transformations to fluorescent sensors. The spectroscopic and structural properties are clarified by means of single crystal X-ray diffraction, UV–vis absorption and NMR spectroscopy.

2. Materials and methods

2.1. Synthesis

All new synthesized compounds were purified by column chromatography and characterized on the basis of NMR and micro-analytical data. NMR spectra were recorded on Bruker Avance II+ 600 (^{1}H at 600.1 MHz; ^{13}C at 150.9 MHz) spectrometer, with TMS as the internal standard; *J* values are given in Hertz. Flash chromatography was performed on Silica Gel 60 (0.040–0.063 nm, Merck). Elemental analyses were performed by the Microanalytical Service Laboratory of Faculty of Chemistry, University of Sofia, using Vario EL*III* CHNS(O).

2.2. Electronic spectroscopy

The absorption spectra were recorded on Thermo Spectronic Unicam UV 500 UV–Visible double-beam spectrophotometer using 1 cm quartz cells. Data processing was performed using the Vision-Pro software package. Samples were scanned from 190 to 900 nm. All experiments were carried out at room temperature.

2.3. X-ray crystallographic analysis

Crystals of **3**–**5** suitable for X-ray analyses were obtained after re-crystallization of the compounds. Afterwards a crystal was mounted on a glass capillary and all geometric and intensity data were taken from that crystal. Diffraction data were

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collected at room temperature by ω-scan technique, on an Agilent Diffraction SuperNova Dual four-circle diffractometer equipped with Atlas CCD detector using mirror-monochromatized MoKα (λ = 0.7107 Å) radiation from micro-focus source. The determination of cell parameters, data integration, and scaling and absorption correction were carried out using the CrysAlis Pro program package [18]. The structures were solved by direct methods [19] and refined by full-matrix least-square procedures on F^2 [19].

Crystals of **3**–**5** suitable for X-ray structural analysis were obtained as follows: **3** and **5**: after recrystallization and slow evaporation of cyclohexane/DCM 4:1 solution at room temperature; **4**: slow evaporation of hexane/Et_2O 1:4 (v/v) solution at room temperature.

2.4. General procedure for synthesis of N-aryl substituted 6-amino-7-nitro-benz[de]isoquinoline-1,3(2H)-diones

4-Bromo-5-nitro-1,8-naphthalic anhydride was mixed with 4 equivalents of the appropriate primary amine in a closed vessel and the reaction mixture was heated at the boiling point of the amine for 24 h. After cooling to room temperature propionic acid was added and the heating was continued for another 24 h at 140 °C. After evaporation of the volatiles in vacuo the residues are purified by flash chromatography eluting with cyclohexane:DCM = 3:2.

2.4.1. 2-Mesityl-6-(mesitylamino)-5-nitro-1H-benzo [de]isoquinoline-1,3(2H)-dione (**3**), yield: 89%

^{1}H NMR (600.13 MHz, $CDCl_3$): δ 2.10 (s, 6H, 18′-, 22′-H), 2.17 (s, 6H, 11′-, 15′-H), 2.36 (s, 3H, 20′-H), 2.41 (s, 3H, 13′-H), 7.04 (s, 2H, 19-, 21-H), 7.06 (s, 2H, 12-, 14-H), 7.35 (dd, 1-H, 8-H, *J* = 8.7, 7.4 Hz), 7.96 (dd, 1H, 9-H, *J* = 8.7, 1.0 Hz), 8.64 (dd, 1H, 7-H, *J* = 7.4, 1.0 Hz), 9.45 (s, 1H, 4-H), 11.34 (s, 1H, N*H*); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 17.83 (2C, C-11′, -15′), 18.66 (2C, C-18′, -22′), 21.14 (C-20′), 21.22 (C-13′), 111.76, 123.33, 123.44, 126.18, 129.42 (2C), 129.52, 130.32 (2C), 130.47, 130.93, 131.59, 132.70, 134.01 (2C, C-18, -22), 134.38, 135.03 (2C, C-11, -15), 135.06, 138.46, 138.63, 148.27, 161.96, 163.08. Anal: Calcd. for $C_{30}H_{27}N_3O_4$: (%) C 73.01; H 5.51; N 8.51. Found: C 73.00; H 5.41; N 8.70.

2.4.2. 2-(2,6-Diisopropylphenyl)-6-(2,6-diisopropylphenylamino)-5-nitro-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4**), yield: 93%

^{1}H NMR (600.13 MHz, $CDCl_3$): δ 1.06 (d, 6H, H-22, *J* = 6.9), 1.17 (d, 6H, H-13, *J* = 6.9), 1.21 (d, 6H, H-16, *J* = 6.8), 1.26 (d, 6H, H-25, *J* = 6.8), 2.69–2.76 (m, 2H, 12-H, 15-H), 3.07–3.14 (m, 2H, 21-H, 24-H), 7.32 (dd, 1H, 8-H, *J* = 8.8, 7.4 Hz), 7.34–7.37 (m, 2H, 26-H), 7.39–7.41 (m, 2H, 17-H), 7.50 (dd, 1H, 18-H, *J* = 7.8 Hz), 7.55 (dd, 1H, 27-H, *J* = 7.8 Hz), 7.92 (dd, 1H, 9-H, *J* = 8.8, 1.0 Hz), 8.65 (dd, 1H, 7-H, *J* = 7.4, 1.0 Hz), 9.51 (s, 1H, 4-H), 11.73 (br s, 1H, N*H*); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 22.52 (2C, C-22), 23.98 (2C, C-13), 24.05 (2C, C-16), 24.29 (2C, C-25), 29.12 (2C, C-12, -15), 29.17 (2C, C-21, -24), 111.56 (1C), 122.94 (1C), 123.31 (1C), 124.08 (2C, C-26), 125.11 (2C, C-17), 125.70 (1C, C-8), 129.09 (1C), 129.62 (C-18), 129.70 (C-27), 130.54 (1C), 130.71 (C-4), 132.65 (C-9), 133.03 (1C), 134.61 (C-7), 134.68 (1C), 144.76 (2C, C-20, -23), 145.57 (2C, C-11, -14), 148.55 (1C), 162.57 (C-3), 163.69 (C-1). Anal: Calcd. for $C_{36}H_{39}N_3O_4$: (%) C 74.84; H 6.80; N 7.27. Found: C 75.01; H 6.99; N 7.30.

2.4.3. 2-Butyl-6-(butylamino)-5-nitro-1H-benzo [de]isoquinoline-1,3(2H)-dione (**5**), yield: 1.84 g, 80%

2 g (6.21 mmol) 4-bromo-3-nitro naphthalic anhydride was mixed with 3.7 ml n-butylamine (6 equivalents) in 100 ml of ethanol. The reaction mixture was stirred at 75 °C for 6 h, the volatiles were removed in vacuo and the solid residue purified by flash chromatography eluting with ethylacetate–cyclohexane 4:1.

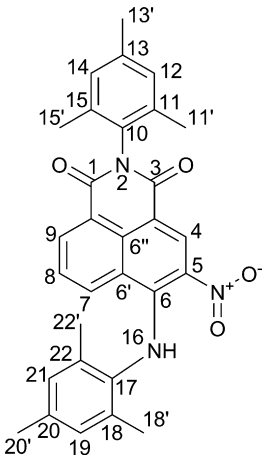


Fig. 1. Arbitrary numbering given for description of the NMR spectral data of compounds **3**–**6**.

^{1}H NMR (600.13 MHz, $CDCl_3$): δ 0.90 (t, 3H, 19-H, *J* = 7.4 Hz), 0.93 (t, 3H, 14-H, *J* = 7.3 Hz), 1.32–1.39 (m, 2H, 18-H), 1.43–1.49 (m, 2H, 13-H), 1.58–1.63 (m, 2H, 17-H), 1.75–1.80 (m, 2H, 12-H), 3.87–3.93 (m, 2H, 16-H), 4.01–4.07 (m, 2H, 11-H), 7.60–7.64 (m, 1H, 8-H), 8.55–8.61 (m, 2H, 7-H, 9-H), 9.15 (s, 1H, 4-H), 9.86 (br s, 1H, N*H*); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 13.91 (1C, CH_3), 13.99 (1C, CH_3), 20.33 (1C, CH_2), 20.43 (1C, CH_2), 30.27 (1C, CH_2), 33.46 (1C, CH_2), 40.11 (1C, CH_2), 47.56 (1C, CH_2), 117.11 (1C), 122.95 (1C), 123.19 (1C), 124.04 (1C), 126.14 (1C), 126.60 (1C), 127.13 (1C), 127.72 (1C), 134.96 (1C), 137.66 (1C), 164.15 (1C), 164.72 (1C). Anal: Calcd. for $C_{20}H_{23}N_3O_4$: (%) C 65.03; H 6.28; N 11.37. Found: C 64.92; H 6.20; N 11.39

2.4.4. 2-tert-Butyl-6-(tert-butylamino)-5-nitro-1H-benzo[de] isoquinoline-1,3(2H)-dione (**6**), yield: 0.472 g, 84%

4-Bromo-3-nitro naphthalic anhydride 0.490 g (1,52 mmol) was mixed with 2.31 ml tert-butylamine (14.4 equivalents) and the reaction was stirred and refluxed for 4 h. Acetic acid (10 ml) was then added and the reaction was heated at 120 °C for additional 24 h All volatiles were removed in vacuo and the solid residue was recrystallized from acetic acid-pyridine (2:1 vol) ^{1}H NMR (600.13 MHz, DMSO-d_6): δ 1. 17 (s, 18H, 6CH_3), 7.55 (dd, 1H, 8-H, *J* = 7.7 Hz), 8.32 (dd, 1H, 9-H, *J* = 7,4, 1,1 Hz), 8.58 (dd, 1H, 7-H, *J* = 7.9, 1.1 Hz), 8.80 (s, 1H, 4-H); ^{13}C NMR (150.9 MHz, DMSO-d_6): 27.12 (6C) δ 50.85 (2C), 94.61 (1C), 117.77 (1C), 124.50 (1C), 131.91 (1C), 133.01 (1C) 133.06 (1C), 133.45 (1C), 134.29 (1C), 134.43 (1C), 160.29 (1C), 162.24 (1C), 169.17 (1C). Anal: Calcd. for $C_{20}H_{23}N_3O_4$: (%) C 65.03; H 6.28; N 11.37. Found: C 65.20; H 6.40; N 11.30

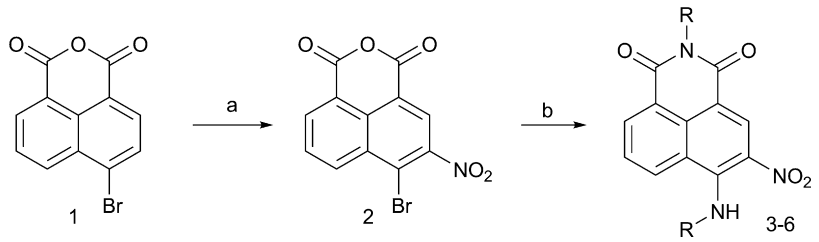
3. Results and discussion

The desired compounds were synthesized starting from the commercial 4-bromo-1,8-naphthalic anhydride by the following synthetic scheme [20] (Scheme 1).

3.1. Absorption spectra

The UV–vis absorption properties of the systems were studied in various solvents of different polarity. Three notable characteristics distinguish these naphthalimides: (i) presence of two major absorption maxima for all compounds; (ii) sensitivity to the media polarity and basicity; (iii) dependence of spectral properties from the 4-NH(R)-substituent volume (Fig. 1).

Representative spectra of the investigated compounds in acetonitrile are shown in Fig. 2. The longest wavelength absorption of the systems is characterized by a broad band with main maximum



Scheme 1. Synthesis of **3**–**6**. Reagents and conditions: (a) HNO_3/H_2SO_4; (b) RNH_2 **3**: R = 2,4,6-trimethylphenyl; **4**: R = 2,6-diisopropylphenyl; **5**: R = n-Bu; **6**: R = t-Bu.

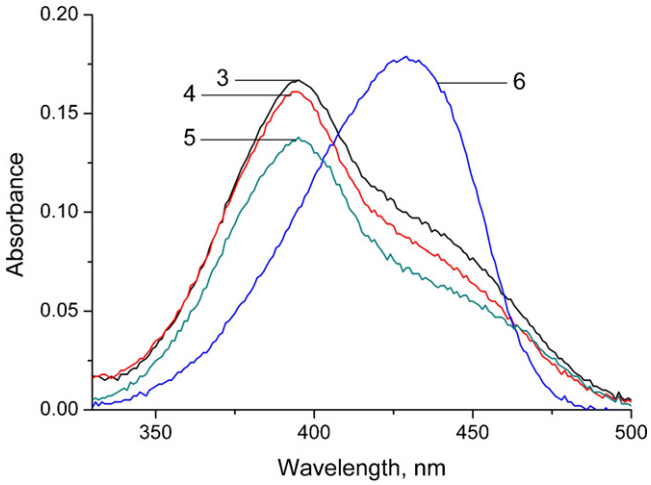


Fig. 2. Absorption spectra of compounds **3–6** in acetonitrile, $c = 1 \times 10^{-5}$ mol l^{-1}.

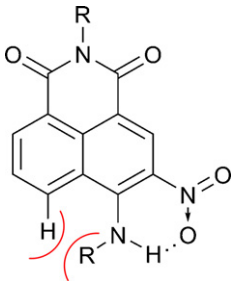


Fig. 4. *Peri* effect illustration.

appearing between 380 and 410 nm and well pronounced shoulder around 440–450 nm. A clear exception is compound **6**, which exhibits main maximum in the visible region (around 430 nm) with a clear sign of asymmetry on the short wavelength edge. In order to perform more detailed analysis of the spectroscopic data we have applied a model for obtaining the absorption spectrum by the superposition of Gaussian-type functions.

Their exact number is difficult to be determined, especially when the vibronic transitions have to be considered, but in first approximation one can estimate the number and position of the main absorption maxima from general considerations about the chromophore structure and electronic effects of the substituents.

As it known from the numerous studies on 4-amino naphthalimides, they possess a broad structureless absorption band around 450 nm, which is usually assigned to an intramolecular charge transfer (ICT) between the electron-donating amino group and the accepting carbonyl moiety [21]. Typical characteristics of this band, which gives evidence of its CT nature, are: the absorption is fairly broad and intense (molar absorptivities in the range of 10000 M^{-1} cm^{-1}) [22]; neither 4-unsubstituted naphthalimides [23] nor naphthylamines [24] exhibit this band.

Another type of electronic transitions typical for these systems are π–π* in the aromatic ring, usually around 340 nm for unsubstituted naphthalimides [25]. It is expected that both substituent types in the present series (electron donating in position four and electron withdrawing in position three) will have hyperchromic effect and cause bathochromic shift of the maximum.

On this basis, neglecting the fine structure typical for the π–π* transition, we applied deconvolution procedure using two Gaussian-type functions (Fig. 3) with initial center positions 440 (CT-band, denoted with *a*) and 380 nm (red-shifted π–π* transitions, denoted with *b*), respectively. The results obtained for the wavelength and molar absorptivity of the maxima are summarized in Table 1.

As can be seen from Table 1 and Fig. 3, compounds **3**–**5** possess similar properties in non-polar solvents such as TCM (CCl_4), with predominant influence of the band *b* (ratio *a*/*b* about 0.45), while the deconvoluted spectrum of compound **6** gives two maxima with similar intensity ($a/b \sim 1$), explaining the different shape of the recorded spectrum. It is known from the literature that monoalkylamino substituents in position 4 cause hyper- and bathochromic shift of the CT-absorption band as compared to the non-alkylated amino derivatives [26]. Further alkylation to dialkylamino group shifts the maximum back to shorter wavelengths and weaker intensity. This is due to the so called *peri* effect–steric interactions between one of the alkyl groups and the hydrogen at the 5-position

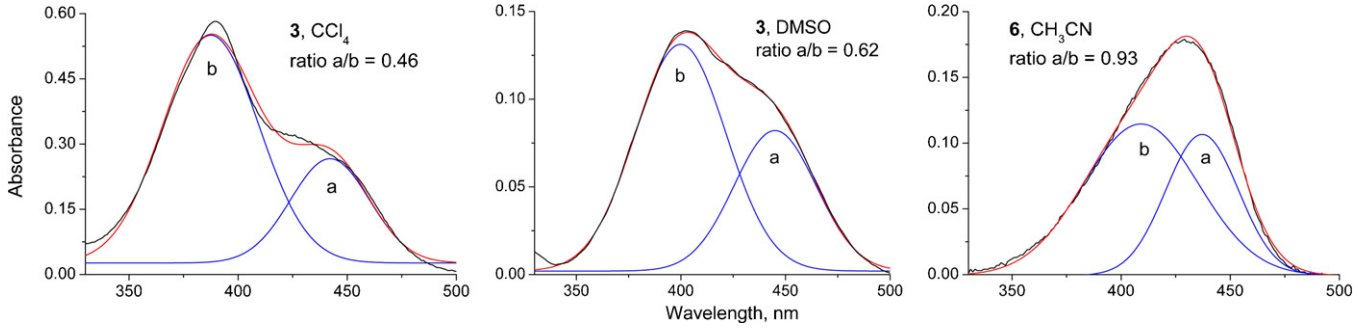


Fig. 3. Representative deconvoluted spectra of **3** and **6** in selected solvents.

Table 1
Absorption maxima of compounds **3**–**6** in solvents with different polarities.

Comp.	λ_{max}, nm (ε, M^{-1} cm^{-1})					
	Solvent					
	CCl_4	CH_2Cl_2	MeOH	CH_3CN	DMF	DMSO
3	442 (10,800)	449 (8567)	444 (6730)	444 (6420)	509 (10,600)	445 (7850)
	387 (23,500)	393 (25,367)	397 (15,700)	393 (14,800)	425 (8960)	399 (12,700)
4	441 (8940)	447 (5350)	443 (6110)	445 (6110)	507 (13,200)	445 (6340)
	386 (21,700)	392 (14,700)	395 (16,100)	392 (16,500)	430 (10,900)	398 (14,200)
5	441 (4140)	450 (3280)	442 (3610)	448 (3980)	396 (10,500)	439 (4590)
	387 (11,600)	393 (9860)	395 (9750)	393 (10,500)	449 (3890)	395 (8320)
6	–	387 (5350)	426 (6320)	437 (8950)	440 (1790)	442 (10,600)
		339 (13,200)	399 (12,200)	409 (9610)	412 (1850)	415 (13,000)

(Fig. 4). It is believed that the hydrogen in the monoalkylamino substituents is aligned toward the *peri* hydrogen while the alkyl group points away, thus minimizing the steric hindrance.

In the compounds studied by us (**3**–**6**) the nitro group presence at position 3 clearly has an impact on the rotation around C_4—N bond, due to both steric repulsion and formation of hydrogen bond. This leads to an unusual alignment in the amino group and stabilization of other possible conformers. The H-bond formation cannot be neglected, since the increased N—H acidity (see below) determines a stronger N—H···O bond which effectively influences the conformer ratio toward the chelate six-membered cycle (see X-ray results). Obviously the *peri* effect and the formation of H-bond act in opposite directions, leading to a specific geometry of compromise. On the other hand, absorption spectra and especially the intensities of CT-bands are very sensitive to the degree of conjugation between the nitrogen lone electron pair and the naphthalimide aromatic system [27]. Indeed, we observed that the stronger the H-bond is, the weaker the CT band gets – the *a*/*b* ratios are smaller in less-polar solvents (Table 1 and Fig. 3). The use of polar solvents like DMSO which effectively interferes in the H-bond formation leads to increase of the relative intensity of CT-bands in compounds **3**–**5**.

Fig. 5 shows the recorded spectra of compound **3** in different solvents. The observed main absorption maximum bathochromic shift with increasing the solvent polarity can be seen as a classical example of positive solvatochromism, due to better solvation of the more polar excited state in solvents like DMSO. Our model for explanation of the spectroscopic data takes into consideration not only the shift but also the change in the shape of band. This leads us to the conclusion that stronger conformational effects, rather than dipole–dipole interactions, influence the spectra. Solvents of different polarity give different stable geometries of the ground state, therefore the observed effect is not solvatochromism.

Compound **6** is the exception that confirmed the rule – **6** does not fit into the pattern set by **3**–**5**. Its absorption maxima are insensitive to the media polarity and show "reversed" *a*/*b* ratio. This observation can easily be explained if the N-substituent steric volume is taken into consideration – the tert-Butyl group is too large, thus the *peri* effect is strong enough to overcome the stabilization via H-bonding, leading to solvent-independent absorption band shape, similar to the one observed for monoalkylated 4-amino derivatives without nitro group.

Another noteworthy result was obtained from the absorption of compounds **3** and **4** in DMF (Fig. 6). These two solutions were red colored – a marked difference from the common pale-yellow color in all other solvents. This phenomenon can be attributed to deprotonation of the amino moiety at C-4 position and formation of negatively charged naphthalimide rings. The increased electron density at the nitrogen shifts the longest wavelength absorption maximum bathochromically with ca. 80 nm.

Similar behavior was observed previously (on 4-amino substituted naphthalimides without nitro groups), but only after addition of strong bases —NaOH [28] or $(C_4H_9)_4NF$ [29]. The process has also been found to be reversible – upon reprotonation with hydrochloric acid the color changes back from red to yellow. From this point of view, the ability of compounds **3** and **4** to form stable anions in DMF is unprecedented. Two major factors determine the enhanced N—H acidity of these dyes: (i) the presence of aromatic ring as a substituent to the nitrogen; (ii) the presence of the electron accepting nitro group which further stabilizes the N—H acid's conjugated base. Furthermore, the amino nitrogen atom is not basic at

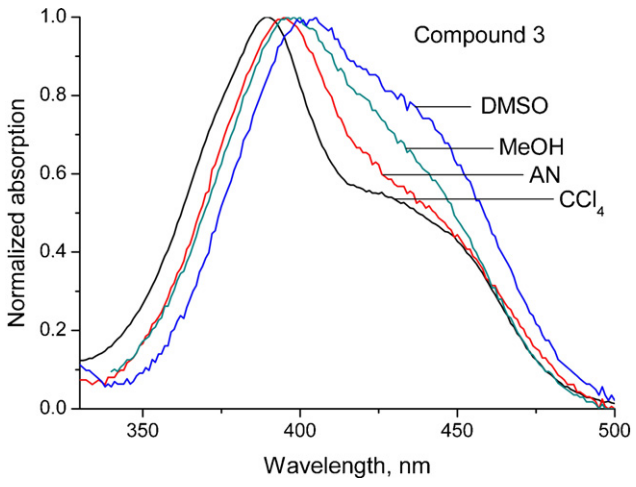


Fig. 5. Normalized absorption spectra of **3** in solvents of different polarity – *a*/*b* ratio dependency on the media.

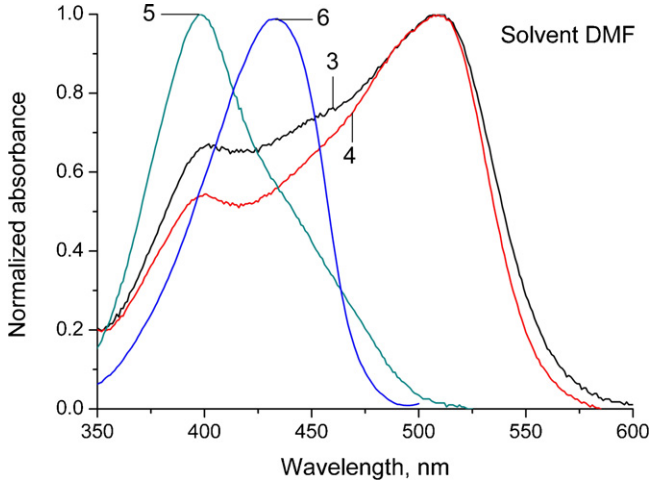


Fig. 6. Normalized absorption spectra of studied compounds in DMF – sensitivity of **3** and **4**.

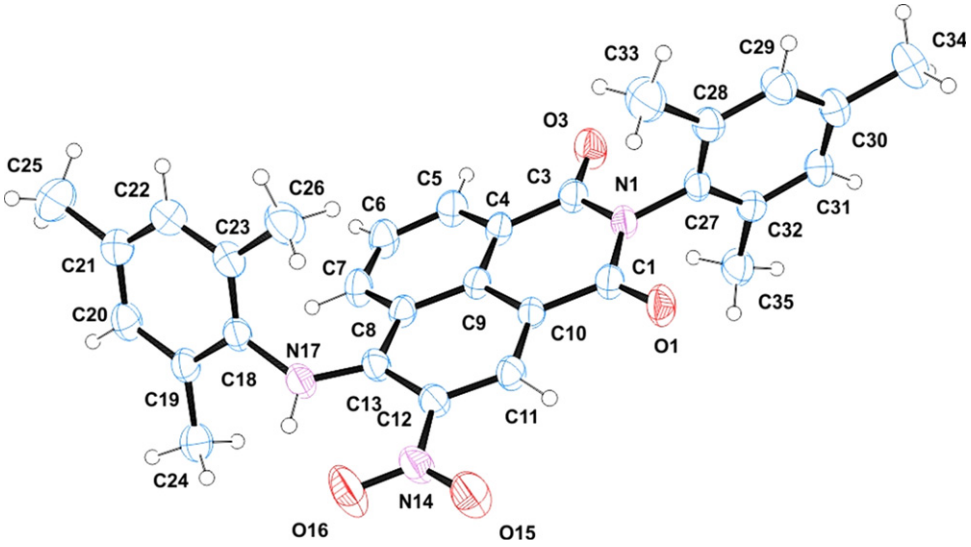


Fig. 7. *ORTEP* view of compound **3** with the atomic numbering scheme; ellipsoids are drawn at 50% probability.

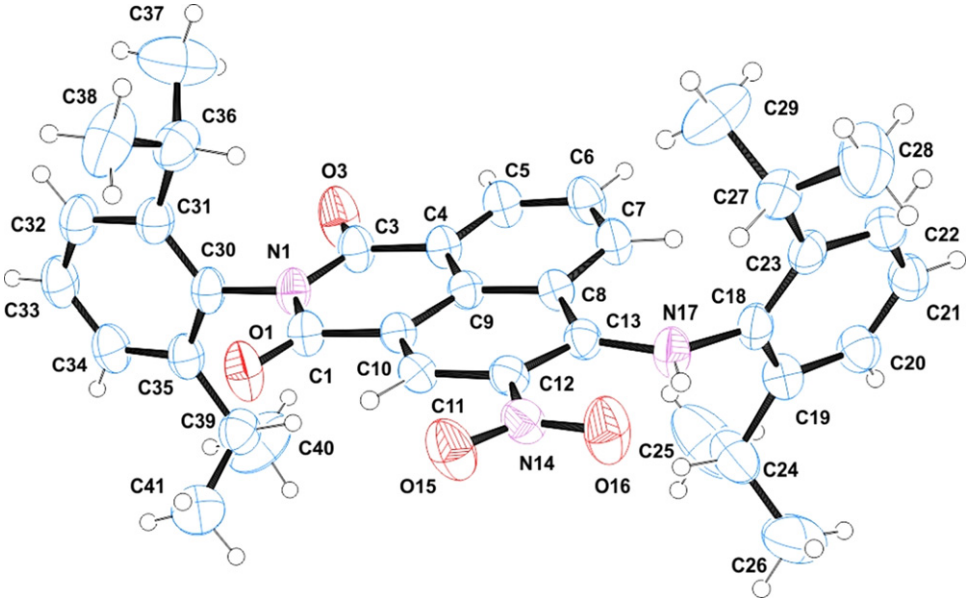


Fig. 8. *ORTEP* view of compound **4** with the atomic numbering scheme; ellipsoids are drawn at 50% probability.

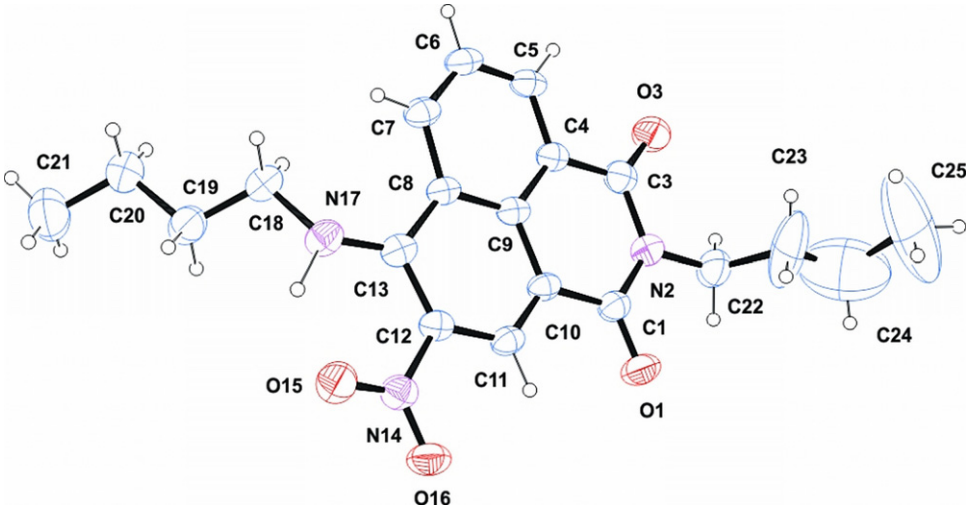


Fig. 9. *ORTEP* view of compound **5** with the atomic numbering scheme; ellipsoids are drawn at 50% probability.

all – in our hands the spectra of compounds **3** and **4** in MeOH could not be influenced even by adding hypermolar amounts of sulfuric acid.

3.2. X-ray crystallography

Crystal structure determination of compounds **3**–**5**.

The solid-state structure of **3** was determined using X-ray crystallography. Compound **3** crystallizes in the centrosymmetric triclinic group *P-1* (SG 2) with one molecule per asymmetric unit (see ESI – Table 1). An *ORTEP* view of the molecule of **3** is shown in Fig. 7 and selected bond distances and bond angles are given (see ESI – Table 2).

Compound **4** crystallizes in the centrosymmetric group $P2_1/c$ (SG 14) with one molecule per asymmetric unit (see ESI – Table 1). The *ORTEP* plot with the atomic numbering system of **4** is shown in Fig. 8 and selected bond distances and bond angles are listed (see ESI – Table 2). The bond distance and angles of the benzoisoquinoline and the two diisopropylbenzene moieties are comparable to those observed in other structures [29a,30–34]. The benzoisoquinoline ring is almost planar with *rms* of 0.0267. The oxygens of the nitro group (N14/O15/O16) are slightly out of the plane of the benzoisoquinoline ring thus the angle between the two mean planes is nitro/benzoisoquinoline is 10.5(3)°.

The two substituents, diisopropylbenzene and 2,6-diisopropylaniline are positioned out of the plane of the benzoisoquinoline; the angle between the mean planes of the benzoisoquinoline and aromatic rings is 86.2(4)° and 74.8(4)° for C30/C31/C32/C33/C34/35 and C18/C19/C20/C21/C22/C23, respectively.

A strong intramolecular hydrogen bond, N17–H17···O16 (*D*···*A* distance of 2.587(4) Å) is responsible for the stabilization of the molecules of **4**. The presence of four "bulky" isopropyl groups prevents the formation of additional hydrogen bonds.

Compounds **3** and **4** possess identical benzoisoquinoline core and similar substituents 1,3,5-triisopropylbenzene and 1,3-diisopropylbenzene, respectively. Thus it is not strange if the major structural features of **3** and **4** are comparable: similar bond lengths and angles (see ESI – Table 2), almost planar aromatic rings (*rms* of 0.132, 0.026 and 0.021 for the benzoisoquinoline, C27/C28/C29/C30/C31/C32 and C18/C19/C20/C21/C22/C23 of the respective mean), an angle between the mean planes of the benzoisoquinoline and respective aromatic rings of 82.2(5)° and 63.6(5)° and finally an intramolecular N17-H17···O16 (*D*···*A* distance of 2.598(3) Å) hydrogen bonding interaction.

Compound **5** crystallizes in the centrosymmetric group *C*2/*c* (SG 15) with one molecule per asymmetric unit (see ESI – Table 1). An *ORTEP* view of the molecule of **5** is shown in Fig. 9 and selected bond distances and bond angles are given (see ESI – Table 2) In the case of **5** the identical benzoisoquinoline core to the one present in compounds **3** and **4** is conserved.

On the other hand, instead of the diisopropylbenzene and trimethylbenzene substituents here we have two butanamine substituents (N17–C18–C19–C20–C21 and N2–C22–C23–C24–C25). One could say that the three compounds (**3**–**5**) preserve a similar conformation and thus similar bond lengths and angles. As in **3** and **4** the core of **5** is almost planar (*rms* of 0.092), the two substituents are out of the mean plane of the "core" and a strong intramolecular hydrogen bond, N17-H17···O16 (*D*···*A* distance of 2.614(4) Å) is responsible for the stabilization of the molecules of **5**.

The comparable geometrical features of the three compounds, the presence of stiff benzoisoquinoline fragment and the "similar" positioning of the substituents clearly show the relative structural rigidity (Fig. 10). The overlay of the molecules of **3**–**5** shows

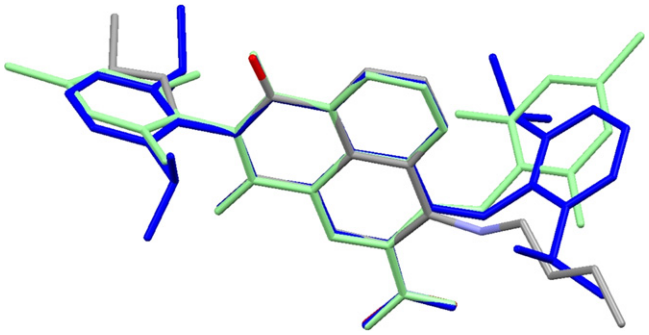


Fig. 10. Overlay of the molecules of **3** (light green), **4** (dark blue) and **5** (light colored) showing the structural deviations.

that the major structural variation concerns the torsion angle C8–C13–N17–C18, −2.8(4)°, −23.5(4)° and 27.8(5)°, respectively.

4. Conclusions

Exploring substitution patterns on naphthalimides continues to reveal their rich spectral properties and provides opportunities for new applications of this class of compounds. The combination of nitro and amino groups on a naphthalimide was never thoroughly studied before and shows that 4-arylamino-3-nitro-1,8-naphthalimides are promising naked eye sensory systems which properties can be fine tuned by changing the steric and electronic properties of N-4.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.10.004.

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