Synthesis, crystal structures, and laser flash photolysis of 3-nitro-7a,15-methanonaphtho[1',2':6,7][1,3]oxazepino[3,2-*a*]indole derivatives

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Abstract

The condensation of 1-substituted 9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-ones with 2-hydroxy-6-nitro-1-naphthaldehyde afforded 1′-carbamoylmethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indole] derivatives, which underwent intramolecular cyclisation to derivatives of 3-nitro-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole upon treatment with a strong base. Laser excitation of the obtained uncoloured molecules of *trans*- and *cis*-3-nitro-7a,15-methano-naphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole induced the formation of short-lived photo-generated species, which absorb in the visible spectrum and thermally revert to the ground state on a nanosecond time scale.

Keywords: Indoles, spiro[benzo[*f*]chromene-3,2′-indoles], [1,3]oxazepino[3,2-*a*]indoles, single crystal X-ray analysis, flash photolysis

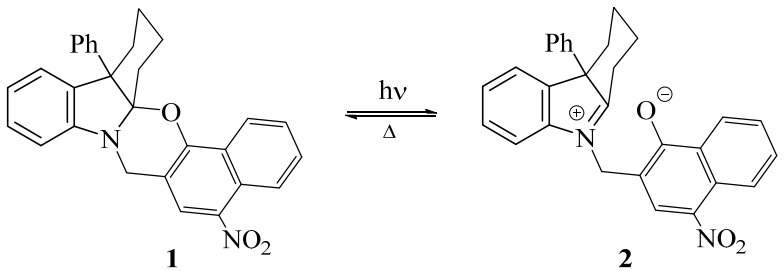
Introduction

Derivatives of heterocyclic compounds are used widely in the preparation of chromogenic "smart materials".[1-4] One of the most important classes of chromogenic materials is photochromic 6-nitro-1′,3′-dihydrospiro[chromene-2,2′-indoles], also known in the literature as 6-nitrospiro[2*H*-1-benzopyran-2,2′-indolines], which have been extensively studied due to their potential applications in various areas of materials science and advanced technologies.[5-8] The aforementioned compounds under UV-irradiation undergo rapid C-O bond cleavage, converting

to the planar, coloured *trans*-merocyanine form.[9,10] The synthesis of 1′,3′-dihydrospiro-[chromene-2,2′-indoles] is usually based on the condensation of 2-methylideneindoline derivatives with such aryl aldehydes as 5-nitrosalicylaldehyde.[1,11] Similar reactions of the aforementioned indolines with various 2-hydroxynaphthaldehydes afforded spiro[benzo[*f*]-chromene-3,2′-indoles], which, like spiro[chromene-2,2′-indoles], change colour when subjected to such external stimulus as UV-irradiation or treatment with active nucleophiles.[12-14]

In our previous work, we showed that the condensation of 1-substituted imidazo[1,2-*a*]-indolones with 2-hydroxy-1-naphthaldehyde gave 1-carbamoylmethylspiro[benzo[*f*]chromene-3,2′-indoles], which, under treatment with a strong base, underwent intramolecular cyclisation to bridged 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole derivatives.[15,16] The latter compounds were used in the preparation of imprinted polymer stationary phases.[17]

The aim of the present work is the synthesis and investigation of 3-nitro-7a,15-methano-naphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole derivatives. In principle, such compounds have the potential to exhibit chromogenic properties, as their structure includes the nitro-2,3-dihydro-1*H*-benzo[*f*]chromene structural unit, a source of the coloured 6-nitro-2-naphtholate chromophore. It was shown recently that the UV-laser excitation of such heterocyclic ring systems as 2-nitro-indolo[2,1-*b*][1,3]benzoxazines or 6-nitro-1′,3,3′,4-tetrahydrospiro[chromene-2,2′-indoles] generates coloured zwitterionic species, which incorporate the 3*H*-indolium cation and the 4-nitrophenolate anion. These photogenerated short-lived species are thermally unstable and revert to the ground state on a nanosecond time scale.[18-21] Molecules of 5-nitronaphtho[2′,1′:5,6]-[1,3]oxazino[2,3-*k*]carbazole **1** under UV-laser excitation undergo a similar ring-opening to afford the unstable zwitterionic compound **2**, possessing the 4-nitro-1-naphtholate chromophore, and revert to the closed form in a few nanoseconds (Scheme 1).[22] Derivatives of nitroindolo[2,1-*b*][1,3]benzoxazines have found application in the development of photoswitchable fluorescent probes,[23] luminescent quantum dots[24] and chemosensors.[25,26]



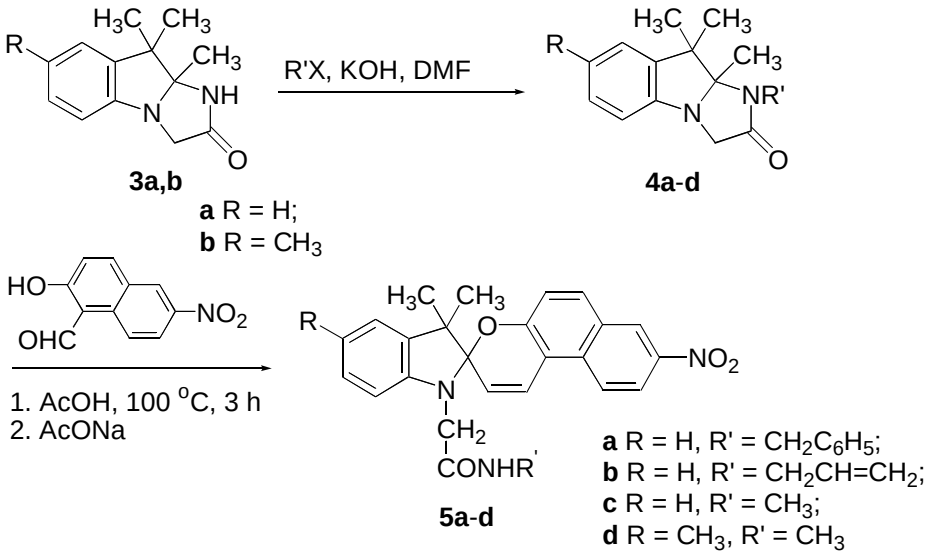
1 **2**

Scheme 1. Photochromism of nitronaphtho[1,3]oxazine derivative **1.**

Results and Discussion

The starting 1-substituted imidazo[1,2-*a*]indolones **4a-c** were prepared by alkylation of compound **3a** with benzyl chloride, allyl bromide and methyl iodide, as described elsewhere.[27] 1,7-Dimethylimidazo[1,2-*a*]indolone **4d** was obtained by a similar method by treatment of

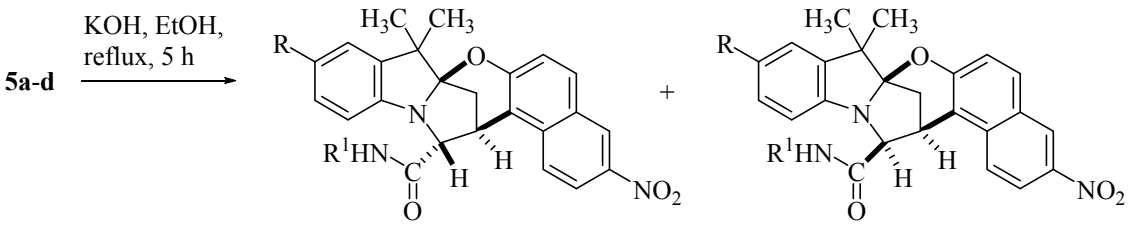
7-methylimidazo[1,2-*a*]indolone **3b** with methyl iodide in DMF in the presence of KOH (Scheme 2).



Scheme 2. Synthesis of 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles].

The condensation of 1-substituted imidazo[1,2-*a*]indolones **4a-d** with 2-hydroxy-6-nitro-1-naphthaldehyde was carried out in acetic acid. Work-up of the reaction mixture with sodium acetate afforded 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] **5a-d**. The ^{1}H NMR spectra of compounds **5a-d** exhibited a characteristic doublet of the methynic proton in the area of 5.82-5.88 ppm with vicinal ^{3}J = 10.5 Hz giving evidence for a *cis*-allocation of pyrane ring protons in the molecule. The corresponding ^{13}C NMR spectra contained the characteristic signal of the quaternary spiro-carbon at 105.0-105.3 (C-O) ppm.

When 8-nitrospiro[benzo[*f*]chromene-3,2′-indoles] **5a-d** were heated with potassium hydroxide in ethanol, a mixture of the diastereomeric *trans*/*cis*-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **6a-d** and **7a-d** was formed (Scheme 3). The assignments of *trans/cis* configurations to **6a-d** and **7a-d** were based on comparisons with ^{1}H NMR spectra of the most relevant compounds[16,28,29] and data from single-crystal X-ray analyses. For example, the ^{1}H NMR spectrum of **6a** contained a singlet of 14-H at 4.47 ppm characteristic of the *trans*-diastereomer, while in the corresponding spectrum of **7a**, the 14-H proton signal appeared as a doublet at 4.19 ppm ($^{3}J_{14,15}$ = 4.2 Hz), confirming the *cis*-configuration of the molecule.[16,28]



Scheme 3. Synthesis of *trans*- and *cis*-3-nitro-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino-[3,2-*a*]indoles.

To obtain unequivocal evidence for configuration of compounds *trans*-**6a** and *cis*-**7a**, we performed single-crystal X-ray analyses of these compounds. The molecule of *trans*-**6a** consists of indoline and 3,4-dihydro-2*H*-benzo[*f*]chromene structural units possessing common atoms with the central pyrrolidine ring (Figure 1, the crystallographic numbering does not represent the systematic numbering).[30] The dihedral angle between the planes, in which the indole and 6-nitro-2-naphthol units are situated, is 110°. The pyrrolidine hydrogen atoms at C(12) and C(13) are situated relative to the pyrrolidine ring plane in a mutual *trans*-disposition, while the dihedral angle H-C(12)-C(13)-H is 98.16°. The sum of the indoline nitrogen valence angles is 356.21° in *trans*-**6a**, indicating sp^2-dominant hybridisation of the valence electrons (ca. 88%). The N(1)-C(8) bond length is 1.395 Å and corresponds to the bond length of aniline derivatives possessing sp^2 hybridised nitrogens.[31] The indoline nitrogen lone electron pair and the C(2)-O(15) bond are in the same plane. The amide group is in an *s*-*Z*-conformation. The benzylic phenyl ring and the indole moiety are situated in almost parallel planes.

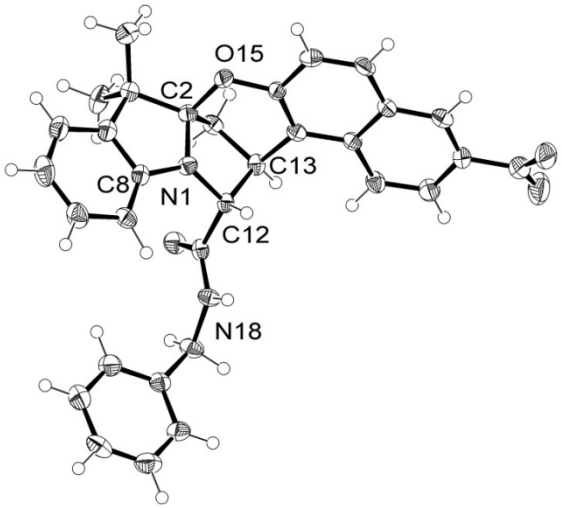
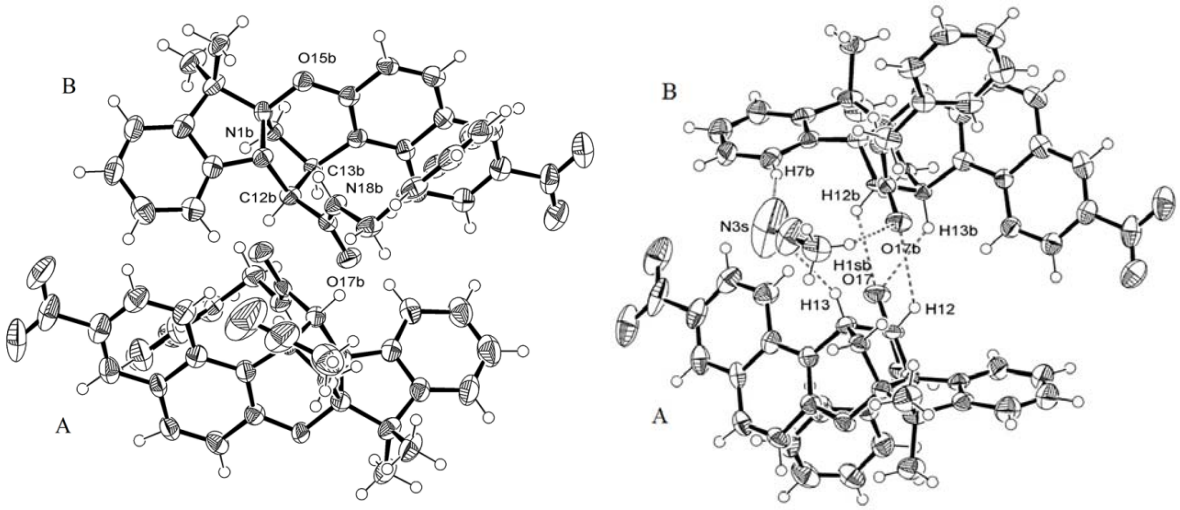


Figure 1. Ortep view of compound *trans*-**6a.**



(a) (b)

Figure 2. Ortep views of compound *cis*-**7a**: (a) view of the crystallographic forms **A** and **B** together with a molecule of acetonitrile; (b) view of hydrogen bonds in the asymmetric unit.

The asymmetric unit of *cis*-**7a** consists of the two independent crystallographic forms **A** and **B** of **7a** and a molecule of the solvent, acetonitrile.[32] Numbering of atoms is done only for form **B** for clarity, as the two structures are very similar, and the differences are minimal. The molecule of *cis*-**7a** involve the same structural units as the molecule *trans*-**6a**, but the dihedral angle between the planes in which the indoline and 3,4-dihydro-2*H*-benzo[*f*]chromene structural units are situated is ca. 54° (Figure 2). The pyrrolidine hydrogen atoms at C(12b) and C(13b) are situated relative to the pyrrolidine ring main plane in a mutual *cis*-disposition, while the dihedral angle H-C(12b)-C(13b)-H is 33.8°. The sum of the indoline nitrogen valence angles is only 331.43° in *cis*-**7a**, indicating that the nitrogen atom is tetrahedral (91% sp^3 hybridisation). The C(8b)-N(1b) bond length is 1.432 Å, confirming the greater share of sp^3 hybridised electrons in the corresponding bond formation.[31] The amide moiety is in an *s*-*Z* conformation, where the C=O bond is in the *anti*-position to the C(12b)-N(1b) bond. The acetonitrile molecule is held in the crystal by three hydrogen bonds connecting two crystallographically independent forms **A** and **B**. Due to the asymmetrical distribution of hydrogen bonds (one bond with form **A** and two bonds with form **B**), the molecules of *cis*-**7a** have some small differences in these crystallographically independent forms. The angle between the phenyl ring and naphthalene moiety, for example, is 62° in form **A** and 65° in form **B**.

The UV-Vis absorption spectra of **6a-d** and **7a** from solutions in acetonitrile were obtained at room temperature. As a representative example, the steady-absorption spectrum of *trans*-**6a** is shown in Figure 3 (black curve). It shows a strong absorption band at 360-380 nm that has been assigned to the 6-nitro-2-naphthoxy moiety and resembles the ground-state absorption of nitronaphtho[1,3]oxazine derivative **1,** possessing a 4-nitro-1-naphthoxy moiety.[22] The steady-state absorption spectra of compounds **6b-d** and **7a** were very similar (Table 1).

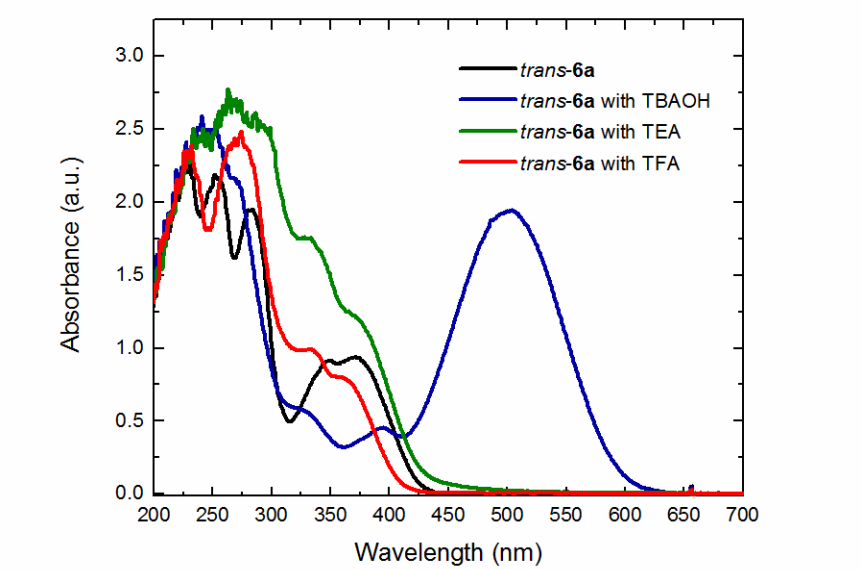
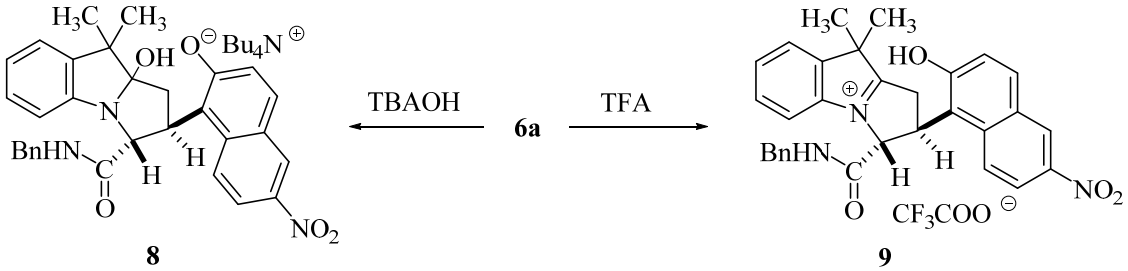


Figure 3. UV-Vis spectra of various forms of *trans*-**6a** in acetonitrile (black: **6a** in pure acetonitrile, blue: chemically opened form of **6a** with TBAOH, green: **6a** with TEA, red: chemically opened form of **6a** with TFA).

When solutions of *trans*-**6a-d** in acetonitrile were treated with a two-fold excess of tetrabutylammonium hydroxide (TBAOH), a coloured product with an absorption maximum at 490-505 nm, characteristic of the 6-nitro-2-naphtholate chromophore,[22] was formed immediately (Table 1). As a representative example, the UV-Vis spectral behaviour of the compound *trans*-**6a** in acetonitrile after the addition of TBAOH is shown in Figure 3 (blue curve). However, adding a non-nucleophilic base, such as triethylamine, to a solution of *trans*-**6a** did not cause any absorption to appear in the visible part of the absorption spectrum (Figure 3, green curve). Therefore, the coloured form that appeared is presumably the adduct **8**, formed *via* ring-opening and hydroxyl anion addition to the indole α-carbon, as shown in Scheme 4. It is known that the formation of similar pseudo-bases occurred when 1,2,3,3-tetrasubstituted 3*H*-indolium salts are treated with alkali.[33,34] It should be noted that the steady-state absorption spectrum of 2-hydroxy-6-nitronaphthaldehyde in acetonitrile exhibited absorption bands at 295 and 340 nm (Figure 4, black curve), while upon addition of TBAOH to the solution, a strong absorption band at 450 nm arose (Figure 4, blue curve) that indicates the formation of the corresponding nitronaphtholate anion.



8 **9**

Scheme 4. Base and acid induced ring-opening reactions of *trans*-**6a.**

Table 1. Absorption maxima (λ_{max}) and molar absorptivity (ε) of 7a,15-methanonaphtho--[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indoles **6a-d** and **7a** in acetonitrile before and after addition of TBAOH

Entry	Compound	λ_{max} (nm)	ε (mM^{-1} cm^{-1})	λ_{max} of chemically opened form (nm)	ε (open form, mM^{-1} cm^{-1})
1	*trans*-**6a**	204 226 253 284 370	44.2 30.0 20.8 17.5 8.4	395 490	4.5 15.4
2	*cis*-**7a**	230 260 280 345 370	22.4 15.0 18.2 8.2 8.1	410 507	12.7 4.7
3	*trans*-**6b**	205 225 250 283 370	42.9 34.0 24.2 20.0 9.8	393 500	5.05 19.2
4	*trans*-**6c**	205 225 250 282 370	37.5 31.5 22.3 18.8 9.1	395 500	4.3 17.7
5	*trans*-**6d**	207 225 253 283 370	32.1 27.3 19.3 15.0 8.1	390 505	3.6 15.3

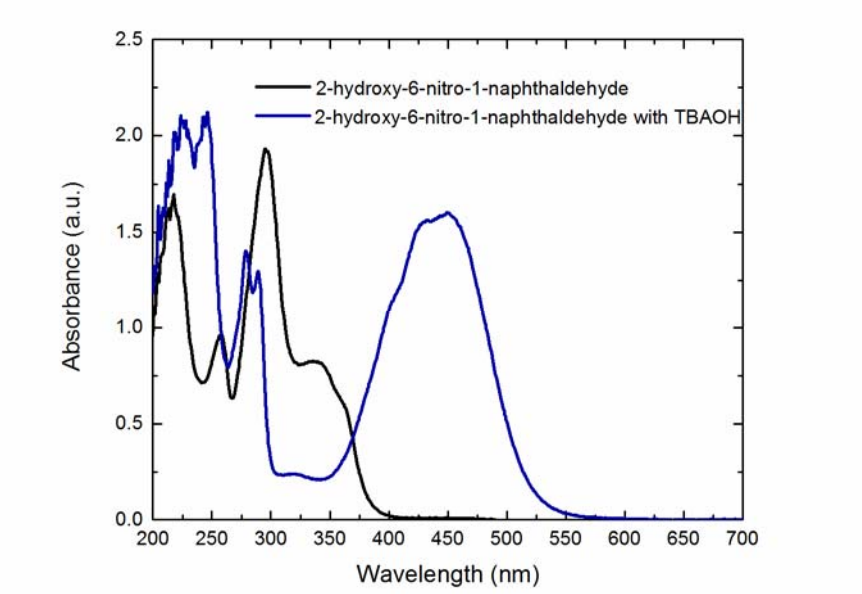


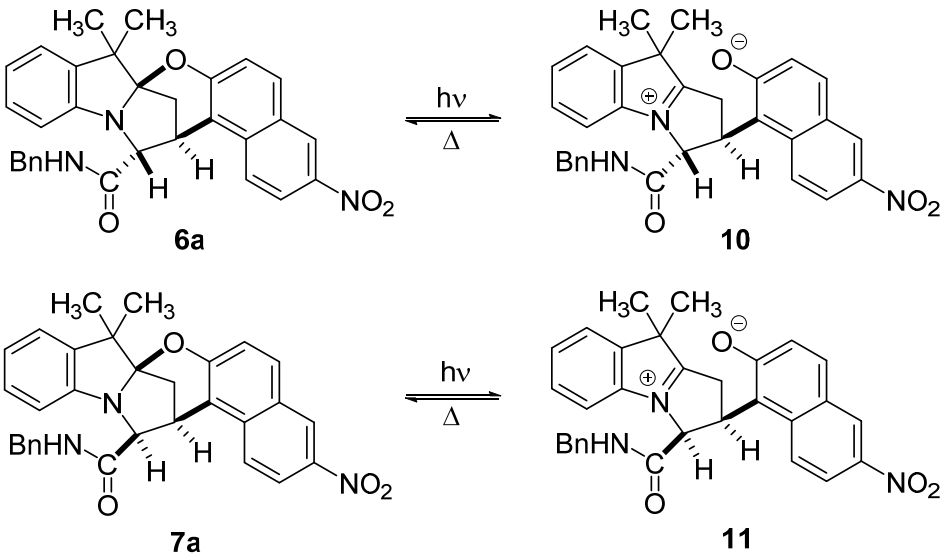
Figure 4. UV-Vis spectra of various forms of 2-hydroxy-6-nitro-1-naphthaldehyde in acetonitrile (black: in pure acetonitrile, blue: after addition of TBAOH).

Table 2. Summary of photochromic parameters of the investigated compounds

Entry	Compound	λ_{max} of the photoinduced form (nm)	Quantum yield, Φ (%)	Relaxation time, τ (ns)
1	*trans*-**6a**	445 515 (shoulder)	3.8	26; 290
2	*cis*-**7a**	440 (shoulder) 535	4.5	27; 86
3	*trans*-**6b**	450 510 (shoulder)	6.5	10; 65; 1090
4	*trans*-**6c**	440 505 (shoulder)	8.1	17; 140
5	*trans*-**6d**	440 500 (shoulder)	6.4	8; 124

It is known that the treatment of 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole derivatives with strong protic acids, such as perchloric or tetrafluoroboric acid, results in heterolytic cleavage of the C–O bond to yield pyrrolo[1,2-*a*]indolium salts.[16] The ^{13}C NMR spectrum of compound *trans*-**6a**, registered in TFA-*d*, revealed signals that indicated the cleavage of the bicyclic ring system and the formation of the cation **9** (Scheme 4). Thus, a signal

at 204.5 ppm was unambiguously assigned to the carbon of the $C=N^+$ group, while the signals of the remaining three carbon atoms of the pyrrolium ring were observed at 35.5 (CH_2), 43.1 (CH) and 71.1 (CH) ppm. When a large excess of TFA was added to a solution of *trans*-**6a** in acetonitrile,the UV-Vis spectrum revealed an absorption maximum at 335 nm (Figure 3, red curve), which was blue-shifted approximately 10 nm compared to the absorption maximum of *trans*-**6a** in pure acetonitrile and can be attributed to the 6-nitro-2-naphthol chromophore of the ring-open form **9**. The transient absorption spectra of compounds *trans*-**6a-d** and *cis*-**7a** in acetonitrile were recorded in the nanosecond domain after UV-laser excitation and in all cases revealed absorption bands situated in the visible region of the electromagnetic spectrum (Table 2). As representative examples, the corresponding transient absorption spectra recorded for *trans*–**6a** and *cis*-**7a** are shown in Figures **5** and **6**. In the case of compound *trans*-**6a**, the transient absorption band maximum was located at 440, with a shoulder at 505 nm, while in the case of compound *cis*-**7a**, the maximum was at 535 nm, with a shoulder at 440 nm. In both cases, the presence of absorption maxima in the visible region of the electromagnetic spectrum can presumably be attributed to the formation of zwitterionic forms **10** and **11**, incorporating the 6-nitro-2-naphtholate chromophore (Scheme 5).



Scheme 5. Photoinduced transformation of *trans*-**6a** and *cis*-**7a** to the coloured zwitterionic isomers **10** and **11.**

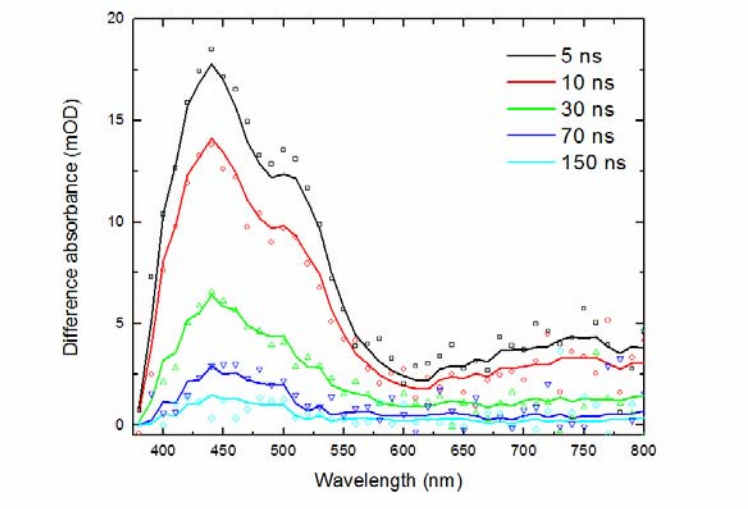


Figure 5. Transient absorption spectra (0.075 mM, acetonitrile, 20 °C) of *trans*-**6a** recorded on a nanosecond scale after laser excitation (355 nm, 3.5 mJ).

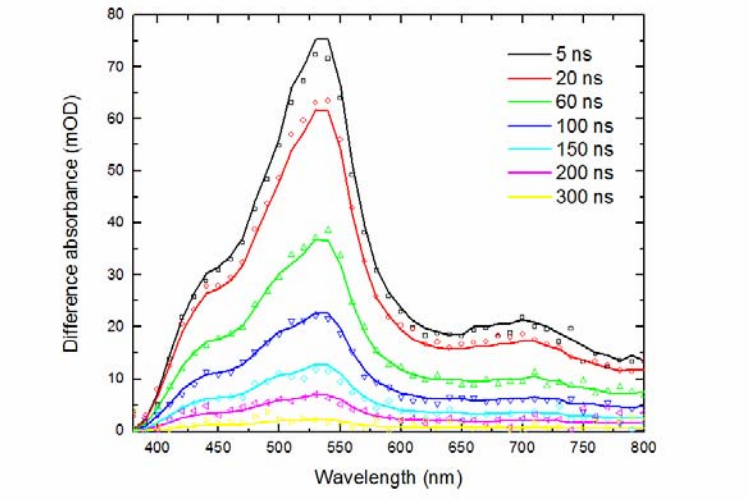


Figure 6. Transient absorption spectra (0.08 mM, acetonitrile, 20 °C) of *cis*-**7a** recorded on a nanosecond scale after laser excitation (355 nm, 3.5 mJ).

Kinetic traces monitored at a variety of wavelengths (Figure 7) indicated that the coloured species were formed during the excitation pulse (ca. 6 ns). In all instances, the induced absorbance decays to zero as the ring-opened isomers *trans*-**10** and *cis*-**11** revert *via* thermal pathways to the original compounds *trans*-**6a** and *cis*-**7a**. Relaxation times, estimated from global fitting of the transient data (Table 2), revealed that the thermal reversion of *trans*-**10** and *cis*-**11** to the original form is fast and proceeds in nanosecond time scale. Similar results were obtained in the case of flash photolysis of compounds *trans*-**6b-d**.

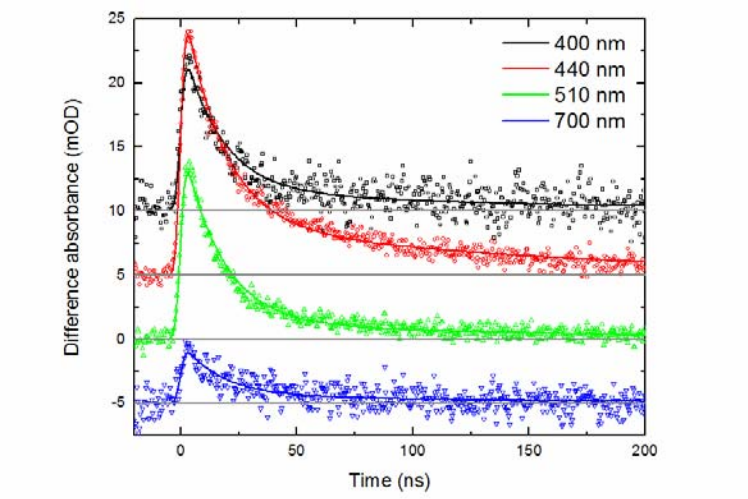


Figure 7. Transient absorption kinetics of 0.075 mM *trans*-**6a** in acetonitrile pumped with 355-nm light and probed at selected wavelengths.

The quantum yields of the photochromic reactions were estimated using the molar extinction coefficients of the TBAOH-induced ring-opened forms (Table 1) obtained from the steady state absorption spectra measurements, as described elsewhere.[18] The corresponding quantum yields of the investigated photochemical reactions were estimated to be ca. 3.8-8.1% (Table 2).

Conclusions

New 7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole derivatives bearing an 8-nitro group were synthesised by the intramolecular cyclisation of 1′-carbamoylmethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indole] derivatives upon treatment with a strong base. The relative *trans*/*cis*-configuration of the prepared bridged compounds was established by means of ^{1}H NMR spectroscopy and confirmed by single-crystal X-ray analysis. Their steady-state spectra in acetonitrile exhibited the main absorption band at approximately 370 nm, which is characteristic of the 6-nitro-2-naphthoxy chromophore. The addition of TBAOH to a solution of the aforementioned compounds in acetonitrile led to the ring-opening of the bridged system and generation of the 6-nitro-2-naphtholate chromophore with a λ_{max} of approximately 500 nm. UV laser excitation of the uncoloured molecules of *trans*- and *cis*-8-nitro-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole induces the formation of short-lived photogenerated species, presumably zwitterionic compounds, which absorb in the visible spectrum and thermally revert to the ground state on a nanosecond time scale.

Experimental Section

General. Reagents and solvents were purchased from Sigma-Aldrich and used without further purification. Reactions were monitored by TLC analysis on precoated silica gel plates (Kieselgel $60F_{254}$, Merck). Compounds were visualised with UV light or by treatment with iodine vapour. Column chromatography was performed on silica gel SI 60 (43-60 μm, E. Merck). Melting points were determined in open capillary tubes with a Büchi B-540 melting point apparatus. Infrared spectra were recorded on a Perkin Elmer Spectrum One spectrometer using potassium bromide pellets. ^{1}H NMR spectra were recorded at 300 MHz on a Varian Unity Inova spectrometer, at 400 MHz on a Bruker Avance III spectrometer. ^{13}C NMR spectra were collected using the same instruments at 75, 100 and 175 MHz. The chemical shifts are expressed in ppm downfield relative to TMS, and the coupling constants (*J*), referring to apparent peak multiplicity, are reported in Hz. Diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer at room temperature and at -100 °C. The crystal structures were solved using known programs.[35] Elemental analyses were measured with a CE-440 elemental analyzer, Model 440 CHN/O/S. Low-resolution mass spectra were recorded via direct injection on a Waters Micromass ZQ 2000 mass spectrometer applying positive atmospheric pressure chemical ionization ($APCI^{+}$, 20 V). High-resolution ESI-TOF mass spectra were measured on a Bruker maXis spectrometer. Steady state absorption spectra of the solutions were measured using a Shimadzu scanning spectrophotometer model UV-3101PC.

Flash photolysis experiments were performed using a nanosecond Q-switched Nd:YAG laser (EKSPLA NL301), and pulses of the third harmonic (wavelength – 355 nm, duration – 6 ns) were applied for excitation.[19] The energy of the pulses for flash photolysis was approximately 3.5 mJ. Sample transmission was probed using light flashes with a duration of ~100 μs generated by a laser-synchronised Xe lamp covering the spectral range of 380–850 nm. Temporal changes in the sample transmission were detected by two high-speed photodiodes (Thorlabs DET10A) placed behind two monochromators for the sample and reference beams. The signals were recorded using a 1 GHz bandwidth oscilloscope (Tektronix TDS7104). All nanosecond kinetic traces presented here were obtained by averaging at least 30 experimental measurements. To avoid local over-exposure of the sample, solutions were mixed with a home-built magnetic stirrer. IRF of the experiments was approximately 6 ns.

Nanosecond-resolution flash-photolysis experimental data were analysed using global analysis techniques described elsewhere.[36] All the flash-photolysis data presented here were fitted using a linear evolution model with the smallest number of compartments necessary to provide a satisfactory fit. One or two kinetic components were adequate to describe the data presented herein.

The quantum yields of photochromic transformations were determined following the calibration method described elsewhere.[18] Briefly, benzophenone was used as a standard with its intersystem crossing quantum yield assumed to be unity. The quantum yield of the photoinduced ring opening was determined with Equation 1:

$$\Phi = \frac{\chi \varepsilon_{bzP} \Phi_{bzP}}{\chi_{bzP} \varepsilon} \quad (1)$$

The terms χ and χ_{bzP} are the slopes of linear portions of the plots of the maximum amplitude of induced absorption measured at λ_{max} against the pump pulse energy ($A=f(E_{laser})$) of the ring-opened compound and benzophenone, respectively. The molar extinction coefficients ε of the investigated compounds were determined by chemically inducing the opening of the ring with TBAOH; ε_{bzP} for its triplet absorption at 520 nm is 6.5 $mM^{-1}cm^{-1}$.[37]

1,7,9,9,9a-Pentamethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (4d). 7,9,9,9a-Tetramethyl-9,9a-dihydro-1*H*-imidazo[1,2-*a*]indol-2(3*H*)-one (**3b**) (2.61 g, 11.3 mmol) was dissolved in 25 ml DMF and finely powdered KOH (0.95 g, 16.95 mmol) was added. Iodomethane (4.81 g, 2.1 ml, 33.9 mmol) was added dropwise to the solution and the mixture was stirred for 2 h at rt. Then the reaction mixture was poured into water (100 ml) and extracted with ether (3 × 50 ml). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo* and the residue was subjected to flash chromatography on silica gel (hexane/acetone 3:1) to yield the title compound **4d**. Yellowish oil, yield 1.99 g (72%). IR: ν_{max} 3035, 2968, 1704 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.15 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.46 (3H, s, CH_3), 2.29 (3H, s, CH_3), 2.93 (3H, s, CH_3), 3.74 (1H, AB-d, *J* 15.6 Hz, CH), 4.00 (1H, AB-d, *J* 15.6 Hz, CHH′), 6.67 (1H, d, *J* 8.0 Hz, 5-H), 6.83 (1H, d, *J* 0.4 Hz, 8-H), 6.97 (1H, dd, *J* 8.0, 0.4 Hz, 6-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.2 (CH_3), 21.8 (CH_3), 24.2 (CH_3), 28.0 (CH_3), 28.3 (CH_3), 49.5 (C-9), 55.0 (CH_2), 92.6 (C-9a), 113.7 (CH), 122.9 (CH), 128.9 (CH), 131.9 (C), 140.8 (C), 146.7 (C), 171.9 (C=O). HRMS (ESI TOF): $[M+H]^+$, found 245.1650, $[C_{15}H_{20}N_2O+H]^+$ requires 245.1648.

***N*-Benzyl-2-(3′,3′-dimethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indol]-1′(3′*H*)-yl)acetamide (5a).** A mixture of imidazo[1,2-*a*]indol-2-one **4a** (500 mg, 1.63 mmol) and 2-hydroxy-6-nitronaphthaldehyde (355 mg, 1.63 mmol) in acetic acid (7 ml) was heated at 100 °C for 2 h. Then the reaction mixture was poured into aqueous 5% sodium acetate solution (50 ml), diethyl ether (15 ml) was poured on the top and the mixture was stored at 5 °C for 16 h. The precipitated crystalline material was filtered, washed with cold ethanol (1 ml) and recrystallized from acetonitrile to give **5a**. Yellowish crystals, yield 665 mg (81%), mp 121-122 °C (from acetonitrile). IR: ν_{max} 3410 (N-H), 3031, 2989, 1679 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.23 (3H, s, CH_3), 1.34 (3H, s, CH_3), 3.85 (1H, AB-d, *J* 18.0 Hz, CHH′), 4.03 (1H, AB-d, *J* 18.0 Hz, CHH′), 4.45 (2H, d, *J* 5.7 Hz, NHC*H*$_2$), 5.82 (1H, d, *J* 10.5 Hz, C*H*=CH), 6.57 (1H, d, *J* 7.5 Hz, 7-H), 6.89 (1H, d, *J* 9.0 Hz, 5′-H), 6.95-7.01 (2H, m, Ar-H), 7.14-7.29 (7H, m, Ar-H), 7.59 (1H, d, *J* 10.5 Hz, CH=C*H*), 7.75 (1H, d, *J* 9.0 Hz, 6′-H), 8.08 (1H, d, *J* 9.0 Hz, 10′-H), 8.27 (1H, dd, *J* 9.0, 2.4 Hz, 9′-H), 8.67 (1H, d, *J* 2.4 Hz, 7′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.2, 25.8, 43.2, 48.1, 52.3, 105.1 (C-spiro), 107.5, 110.7, 117.9, 119.2, 120.4, 121.1, 122.1, 125.3, 125.4, 127.3, 127.3 (2 × C), 127.5, 128.0, 128.6 (2 × C), 132.5, 132.6, 135.9, 137.7, 143.7, 145.7, 154.6, 169.7, 176.5 (C=O). MS *m/z* (%): 506 ($M+H^+$, 100). Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31. Found: C 72.87; H, 5.48; N, 8.19 %.

2-(3′,3′-Dimethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indol]-1′(3′*H*)-yl)-*N*-(prop-2-en-1-yl)-acetamide (**5b**)**.** Following the preparation of **5a**, the condensation of imidazo[1,2-*a*]indol-2-one **4b** (2.5 g, 9.75 mmol) with 2-hydroxy-6-nitro-naphthaldehyde (2.12 g, 9.75 mmol) in glacial acetic acid (7 ml) and standard workup gave the title compound **5b**. Yellowish crystals, yield 1.34 g (29%), mp 161-162 °C (from acetonitrile). IR: ν_{max} 3423 (N-H), 3062, 2966, 1641 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (3H, s, CH_3), 1.38 (3H, s, CH_3), 3.75 (1H, AB-d, *J* 17.6 Hz, CHH′), 3.87-3.91 (2H, m, CH_2), 3.97 (1H, AB-d, *J* 17.6 Hz, CHH′), 5.06-5.10 (2H, m, CH_2), 5.72-5.82 (1H, m, CH), 5.88 (1H, d, *J* 10.4 Hz, C*H*=CH), 6.55 (1H, d, *J* 7.2 Hz, 4-H), 6.65 (1H, t, *J* 5.6 Hz, CON*H*), 7.00 (1H, t, *J* 7.2 Hz, 5-H), 7.08 (1H, d, *J* 9.2 Hz, 6‘-H), 7.18 (1H, d, *J* 7.2 Hz, 7-H), 7.23 (1H, dt, *J* 7.2, 0.8 Hz, 6-H), 7.61 (1H, d, *J* 10.4 Hz, CH=C*H*), 7.82 (1H, d, *J* 9.0 Hz, 5‘-H), 8.08 (1H, d, *J* 9.0 Hz, 10-H), 8.27 (1H, dd, *J* 9.0, 2.4 Hz, 9‘-H), 8.69 (1H, d, *J* 2.4 Hz, 7‘-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 20.4, 26.1, 31.1, 41.6, 48.4, 52.3, 105.2 (C-spiro), 107.8, 110.9, 116.4, 118.0, 119.5, 120.6, 121.3, 122.2, 125.5, 125.6, 127.5, 128.2, 132.7, 132.8, 133.9, 136.25, 143.9, 145.9, 154.9, 169.4 (C=O). HRMS (ESI TOF): $[M+H]^+$, found 456.1917; $[C_{27}H_{25}N_3O_4+H]^+$ requires 456.1918.

2-(3′,3′-Dimethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indol]-1′(3′*H*)-yl)-*N*-methylacetamide (**5c**). Following the preparation of **5a**, the condensation of imidazo[1,2-*a*]indol-2-one **4c** (1.86 g, 8.0 mmol) and 2-hydroxy-6-nitronaphthaldehyde (1.75 g, 8.0 mmol) in glacial acetic acid (15 ml) and workup gave the title compound **5c**. Yellowish crystals, yield 1.61 g (46%), mp 170-172 ºC (from acetonitrile). IR: ν_{max} 3417 (N-H), 3076, 2963, 1644 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.31 (3H, s, CH_3), 1.37 (3H, s, CH_3), 2.80 (3H, d, *J* 5.1 Hz, CH_3), 3.69 (1H, AB-d, *J* 18.0 Hz, CHH′), 3.94 (1H, AB-d, *J* 18.0 Hz, CHH′), 5.88 (1H, d, *J* 10.5 Hz, C*H*=CH), 6.51-6.57 (1H, m, CON*H*), 6.52 (1H, d, *J* 7.5 Hz, 7-H), 6.99 (1H, dt, *J* 7.5, 1.2 Hz, 5-H), 7.08 (d, *J* 9.0 Hz, 1H, 5′-H), 7.18 (d, *J* 6.3 Hz, 1H, 4-H), 7.22 (dt, *J* 7.5, 1.2 Hz, 1H, 6-H), 7.60 (1H, d, *J* 10.5 Hz, CH=C*H*), 7.82 (1H, d, *J* 9.0 Hz, 6′-H), 8.07 (1H, d, *J* 9.0 Hz, 10′-H), 8.26 (1H, dd, *J* 9.0, 2.4 Hz, 9′-H), 8.68 (1H, d, *J* 2.4 Hz, 7′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.2, 26.0, 26.1, 48.2, 52.1, 105.0 (C-spiro), 107.7, 110.7, 117.8, 119.3, 120.4, 121.2, 122.1, 125.3, 125.4, 127.3, 128.0, 132.5, 132.6 136.1, 139.9, 143.7, 145.9, 154.7, 170.0 (C=O). MS *m/z* (%): 430 ($M+H^+$, 100). Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 69.92; H, 5.40; N, 9.78. Found: C, 69.65; H, 5.55; N, 9.82%.

***N*-Methyl-2-(3′,3′,5′-trimethyl-8-nitrospiro[benzo[*f*]chromene-3,2′-indol]-1′(3′*H*)-yl)acet-amide (5d).** Following the preparation of **5a**, the condensation of imidazo[1,2-*a*]indol-2-one **4d** (1.9 g, 7.78 mmol) with 2-hydroxy-6-nitronaphthaldehyde (1.69 g, 7.78 mmol) in acetic acid (7 ml) and workup gave the title compound **5d**. Colourless crystals, yield 1.95 g (57%), mp 225-226 °C (from acetonitrile). IR: ν_{max} 3374 (N-H), 3054, 2971, 1658 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.30 (3H, s, CH_3), 1.36 (3H, s, CH_3), 2.36 (3H, s, 5-CH_3), 2.80 (3H, d, *J* 4.8 Hz, NH-*CH*$_3$), 3.64 (1H, AB-d, *J* 18.0 Hz, CHH′), 3.90 (1H, AB-d, *J* 18.0 Hz, CHH′), 5.88 (1H, d, *J* 10.5 Hz, C*H*=CH), 6.42 (1H, d, *J* 7.8 Hz, Ar-H), 6.52-6.56 (1H, m, CONH), 7.00-7.04 (2H, m, Ar-H), 7.09 (1H, d, *J* 9.0 Hz, 5′-H), 7.59 (1H, d, *J* 10.5 Hz, CH=C*H*), 7.82 (1H, d, *J* 9.0 Hz, 6′-H), 8.07 (1H, d, *J* 9.0 Hz, 10′-H), 8.26 (1H, dd, *J* 9.0, 2.4 Hz, 9′-H), 8,68 (1H, d, *J* 2.4 Hz, 7′-

H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.3, 21.2, 26.2, 26.3, 48.5, 52.2, 105.3 (C-spiro), 107.7, 110.9, 118.0, 119.5, 120.6, 122.2, 123.1, 125.5, 125.5, 127.4, 128.4, 130.9, 132.7, 136.5, 143.8, 143.9, 155.0, 170.3 (C=O). Anal. Calcd for $C_{26}H_{25}N_3O_4$ (443.49): C, 70.41; H, 5.68; N, 9.47. Found: C, 70.81; H, 5.84; N, 9.37 %. HRMS (ESI TOF): $[M+H]^+$, found 444.1921. $[C_{26}H_{25}N_3O_4+H]^+$ requires 444.1918.

(7a*R,14*R**,15*S**)- and (7a*R**,14*S**,15*S**)-*N*-Benzyl-8,8-dimethyl-3-nitro-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole-14-carboxamides (*trans*-6a and *cis*-7a).** To a solution of **5a** (500 mg, 0.99 mmol) in ethanol (20 ml) finely powdered KOH (166 mg, 2.97 mmol) was added at rt. The reaction mixture was refluxed for 5 h, then allowed to reach rt and stored at 5 °C for 16 h. The precipitated crystals of *cis*-**7a** were collected by filtration and recrystallized from acetonitrile. The filtrate was poured into water (30 ml), acetic acid was added to the mixture until it became colourless and then diethyl ether (5 ml) was poured on the top. The precipitated crystals were collected by filtration, washed with cold ethanol (1 ml) and recrystallized from ethanol to afford *trans*-**6a**.

Isomer *trans*-**6a**: yellowish crystals, yield 200 mg (40%), mp 213-214 °C (from ethanol). IR: ν_{max} 3302 (N-H), 3028, 2968, 1666 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.25 (3H, s, CH_3), 1.63 (3H, s, CH_3), 2.16 (1H, d, *J* 11.6 Hz, CHH′), 2.61 (1H, dd, *J* 11.6, 4.2 Hz, CHH′), 4.34 (1H, dd, *J* 14.7, 6.0 Hz, CHH′Ph), 4.44 (1H, d, *J* 4.2 Hz, 15-H), 4.47 (1H, s, 14-H), 4.52 (1H, dd, *J* 14.7, 6.0 Hz, CHH′Ph), 6.26-6.31 (2H, m, Ar-H), 6.80 (1H, t, *J* 7.5 Hz, Ar-H), 6.99-7.15 (5H, m, Ar-H), 7.26-7.29 (3H, m, Ar-H), 7.75 (1H, d, *J* 9.0 Hz, 5-H), 8.07 (1H, d, *J* 9.0 Hz, 1-H), 8.19 (1H, dd, *J* 9.0, 2.1 Hz, 2-H), 8.63 (1H, d, *J* 2.1 Hz, 4-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.7, 27.9, 28.2, 41.8, 43.6, 44.7, 67.5, 107.2, 107.9, 119.9, 120.2, 121.1, 122.5, 122.9, 125.4, 126.9, 127.4 (2×C), 127.6, 127.9, 128.7 (2×C), 130.9, 133.5, 137.5, 140.9, 141.2, 141.5, 143.2, 154.5, 169.6 (C=O). MS *m/z* (%): 506 ($M+H^+$, 100). Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31%. Found: C, 73.47; H, 5.41; N, 8.28%.

NMR spectra of compound **6a** registered in TFA-*d* (compound **9**): ^{1}H NMR (400 MHz, TFA-*d*): δ_H 1.77 (3H, s, CH_3), 1.83 (3H, s, CH_3), 3.80 (1H, dd, *J* 21.6, 4.8 Hz, CH), 4.05 (1H, ddd, *J* 21.6, 10.0, 2.8 Hz, CH), 4.42 (1H, d, *J* 14.6 Hz, CHH′Ph), 4.72 (1H, d, *J* 14.6 Hz, CHH′Ph), 5.34–5.39 (1H, m, CH), 5.85 (1H, d, *J* 4.8 Hz, CH), 7.21 (2H, d, *J* 7.2 Hz, Ar-H), 7.30-7.42 (5H, m, Ar-H), 7.57-7.61 (1H, m, Ar-H), 7.72 (2H, d, *J* 4.0 Hz, Ar-H), 7.88 (1H, d, *J* 9.6 Hz, Ar-H), 8.04 (1H d, *J* 9.6 Hz, Ar-H), 8.13 (1H, dd, *J* 9.6, 2.4 Hz, Ar-H), 8.77 (1H, d, *J* 2.4 Hz, Ar-H). ^{13}C NMR (100 MHz, TFA-*d*): δ_C 21.6 (CH_3), 22.4 (CH_3), 35.5 (CH_2), 43.1 (CH), 45.5 (CO*C*H_2), 51.4 (C), 71.1 (CH), 115.5, 117.2, 120.7, 121.7, 123.0, 124.5, 127.1, 128.6 (2×C), 129.2, 129.7 (2×C), 130.4, 131.7, 134.6, 136.1, 136.4, 137.1, 143.8, 146.1, 157.5, 168.6 (C=O), 204.5 (C=N$^+$).

Isomer *cis*-**7a**: yellowish crystals, yield 100 mg (20%), mp 233-234 °C (from acetonitrile). IR (ν_{max}, cm^{-1}): 3362 (N-H), 3048, 2930, 1673 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.526 (3H, s, CH_3), 1.533 (3H, s, CH_3), 2.22 (1H, d, *J* 11.7 Hz, CHH′), 2.33 (1H, dd, *J* 11.7, 4.2 Hz, CHH′), 3.81 (1H, dd, *J* 15.3, 4.5 Hz, CHH′Ph), 4.19 (1H, d, *J* 4.2 Hz, 14-H), 4.28 (1H, dd, *J* 15.3, 8.0 Hz, CHH′Ph), 4.52-4.55 (1H, m, 15-H), 6.34 (2H, d, *J* 7.8 Hz, Ar-H), 6.58 (1H, d, *J* 7.8 Hz, 10-H), 6.92-7.12 (6H, m, Ar-H), 7.16 (1H, d, *J* 9.3 Hz, 5-H), 7.19-7.24 (2H, m, Ar-H), 7.83 (1H, d,

J 9.3 Hz, 5-H), 8.17 (1H, d, *J* 9.3 Hz, 1-H), 8.23 (1H, dd, *J* 9.3, 2.0 Hz, 2-H), 8.65 (1H, d, *J* 2.0 Hz, 4-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 23.1, 26.4, 32.7, 37.2, 42.5, 99.9, 109.9, 110.4, 118.2, 119.9, 120.0, 122.4, 122.6, 124.7, 124.9, 126.7 (2 × C), 126.9, 127.2, 128.2 (2 × C), 128.4, 131.4, 134.4, 134.5, 137.3, 138.5, 143.5, 148.8, 153.6, 169.8 (C=O). MS *m/z* (%): 506 ($M+H^+$, 100). Anal. Calcd for $C_{31}H_{27}N_3O_4$ (505.56): C, 73.65; H, 5.38; N, 8.31. Found: C, 73.14; H, 5.38; N, 8.13 %.

(7a*R,14*R**,15*S**)- and (7a*R**,14*S**,15*S**)-8,8-Dimethyl-3-nitro-*N*-(prop-2-en-1-yl)-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole-14-carboxamides** (***trans*-6b and *cis*-7b**). Following the procedure of preparation of **6a** and **7a**, the spiropyran **5b** (800 mg, 1.75 mmol), potassium hydroxide (295 mg, 5.26 mmol) in ethanol (25 ml) gave isomers *trans*-**6b** and *cis*-**7b**.

Isomer *trans*-**6b**: yellowish crystals, yield 310 mg (39%), mp 225-226 °C (from ethanol). IR: ν_{max} 3412 (N-H), 3062, 2974, 1687 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.35 (3H, s, CH_3), 1.67 (1H, s, CH_3), 2.20 (1H, d, *J* 11.6 Hz, CHH′), 2.61 (1H, dd, *J* 11.6, 4.0 Hz, CHH′), 3.84-3.98 (2H, m, NH*CH*$_2$) 4.47 (1H, s, 14-H), 4.49 (1H, d, *J* 4.0 Hz, 15-H), 5.05-5.13 (2H, m, *CH*$_2$=CH), 5.73-5.82 (1H, m, CH_2=*CH*), 5.97 (1H, t, *J* 5.6 Hz, NH), 6.35 (1H, d, *J* 8.0 Hz, 13-H), 6.84 (1H, t, *J* 7.6 Hz, 12-H), 7.07 (1H, t, *J* 7.6 Hz, 11-H), 7.09 (1H, d, *J* 8.8 Hz, 5-H), 7.17 (1H, d, *J* 7.6 Hz, 10-H), 7.79 (1H, d, *J* 8.8 Hz, 6-H), 8.13 (1H, d, *J* 9.2 Hz, 1-H), 8.25 (1H, dd, *J* 9.2, 2.4 Hz, 2-H), 8.68 (1H, d, *J* 2.4 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 20.6, 28.27, 28.29, 42.0, 42.1, 44.8, 67.5, 107.2, 108.1, 116.8, 120.1, 120.4, 120.5, 121.3, 122.8, 123.1, 125.6, 127.2, 128.2, 131.1, 133.5, 133.7, 141.0, 141.8, 143.5, 154.6, 169.7 (C=O). HRMS (ESI TOF): $[M+H]^+$, found 456.1918. $[C_{26}H_{25}N_3O_4+H]^+$ requires 456.1918.

Isomer *cis*-**7b**: yellowish crystals, yield 106 mg (13%), mp>250 °C (from acetonitrile). IR: ν_{max} 3293 (N-H), 3074, 2965, 1654 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.54 (3H, s, CH_3), 1.57 (3H, s, CH_3), 2.24 (1H, d, *J* 11.6 Hz, CHH′), 2.32 (1H, dd, *J* 11.6, 4.0 Hz, CHH′), 3.23-3.29 (1H, m, NHCHH′), 3.50-3.58 (1H, m, NHCHH′), 4.14 (1H, d, *J* 4.0 Hz, 14-H), 4.36 (1H, ddd, *J* 16.8, 3.2, 1.6 Hz, *trans*-CH*H*=CH), 4.507-4.55 (2H, m, 15-H, *cis*-CH*H*=CH), 4.79-4.89 (1H, m, CH_2=*CH*), 6.56 (1H, d, *J* 7.6 Hz, 13-H), 6.94-6.97 (1H, m, NH), 6.99 (1H, dt, *J* 7.6, 0.8 Hz, 12-H), 7.13-7.19 (2H, m, 10-H, 11-H), 7.22 (1H, d, *J* 9.6 Hz, 5-H), 7.87 (1H, d, *J* 8.8 Hz, 6-H), 8.15 (1H, d, *J* 9.6 Hz, 1-H), 8.25 (1H, dd, *J* 9.6, 2.4 Hz, 2-H), 8.68 (1H, d, *J* 2.4 Hz, 4-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 23.3, 26.6, 32.8, 37.5, 41.0, 45.1, 78.5, 110.2, 110.6, 115.6, 118.5, 120.1, 120.2, 122.5, 122.8, 124.8, 124.9, 127.5, 128.6, 131.6, 133.4, 134.7, 138.7, 143.8, 148.9, 153.8, 169.9 (C=O). HRMS (ESI TOF): $[M+H]^+$, found 456.1920. $[C_{26}H_{25}N_3O_4+H]^+$ requires 456.1918.

(7a*R,14*R**,15*S**)- and (7a*R**,14*S**,15*S**)-*N*,8,8-Trimethyl-3-nitro-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole-14-carboxamides** (***trans*-6c and *cis*-7c**). Following the procedure of preparation of **6a** and **7a**, the spiropyran **5c** (1.1 g, 2.56 mmol), potassium hydroxide (0.43 g, 7.68 mmol) in ethanol (25 ml) gave *trans*-**6c** and *cis*-**7c**.

Isomer *trans*-**6c**: yellowish crystals, yield 0.46 g (42%), mp 251-253 °C (from ethanol). IR: ν_{max} 3404 (N-H), 3025, 2991, 1687 cm^{-1} (C=O). ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ_H 1.38 (3H, s, CH_3), 1.58 (3H, s, CH_3), 2.07 (1H, d, *J* 11.7 Hz, CHH′), 2.65 (3H, d, *J* 4.2 Hz, CH_3), 3.05 (1H,

dd, *J* 11.7, 4.5 Hz, CHH′), 4.33 (1H, d, *J* 4.2 Hz, 15-H), 4.39 (1H, s, 14-H), 6.18 (1H, d, *J* 7.5 Hz, 13-H), 6.68 (1H, t, *J* 7.5 Hz, 11-H), 6.94 (1H, dt, *J* 7.5, 0.9 Hz, 12-H), 7.10 (1H, d, *J* 7.5 Hz, 10-H), 7.18 (1H, d, *J* 9.0 Hz, 6-H), 8.10 (1H, d, *J* 9.0 Hz, 5-H), 8.22-8.29 (2H, m, 1-H, 2-H), 8.36-8.37 (1H, m, NH), 8.92 (1H, d, *J* 1.8 Hz, 4-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 21.2, 25.5, 28.1, 40.9, 44.5, 67.2 106.9, 107.7, 118.6, 119.6, 119.9, 121.0, 121.2, 122.2, 123.9, 125.3, 126.6, 127.4, 131.3, 133.4, 141.0, 142.7, 143.1, 154.3, 169.2 (C=O). MS *m/z* (%): 430 ($M+H^+$, 100). Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 69.92; H, 5.40; N, 9.78. Found: C, 69.64; H, 5.51; N, 9.47%.

Isomer *cis*-**7c**: yellowish crystals, yield 0.185 g (17%), mp 272-273 °C (from acetonitrile). IR (ν_{max}, cm^{-1}): 3296 (N-H), 3046, 2967, 1654 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.53 (3H, s, CH_3), 1.56 (3H, s, CH_3), 2.22 (1H, d, *J* 11.7 Hz, CHH′), 2.24 (3H, d, *J* 5.1 Hz, NCH_3), 2.32 (1H, dd, *J* 11.7, 4.2 Hz, CHH′), 4.12 (1H, d, *J* 4.8 Hz, 14-H), 4.50 (1H, t, *J* 4.2 Hz, 15-H), 6.53 (1H, d, *J* 7.5 Hz, 13-H), 6.77-6.82 (1H, m, NH), 6.98 (1H, dt, *J* 7.5, 0.9 Hz, 12-H), 7.12-7.18 (2H, m, 10-H, 11-H), 7.21 (1H, d, *J* 9.0 Hz, 6-H), 7.85 (1H, d, *J* 9.0 Hz, 5-H), 8.15 (1H, d, *J* 9.3 Hz, 1-H), 8.24 (1H, dd, *J* 9.3, 2.4 Hz, 2-H), 8.65 (1H, d, *J* 2.4 Hz, 4-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 23.1, 25.5, 26.4, 32.6, 37.3, 44.9, 78.3, 110.0, 110.4, 118.3, 119.8, 120.0, 122.3, 122.6, 124.6, 124.8, 127.1, 128.3, 131.4, 134.3, 138.4, 143.6, 148.7, 153.5, 170.6 (C=O). MS *m/z* (%): 430 ($M+H^+$, 100). Anal. Calcd for $C_{25}H_{23}N_3O_4$ (429.47): C, 68.48; H, 5.52; N, 9.58. Found: C, 68.43; H, 5.41; N, 9.47%.

(7a*R,14*R**,15*S**)- and (7a*R**,14*S**,15*S**)-*N*,8,8,10-Tetramethyl-3-nitro-14,15-dihydro-8*H*-7a,15-methanonaphtho[1′,2′:6,7][1,3]oxazepino[3,2-*a*]indole-14-carboxamides (*trans*-6d and *cis*-7d)**. Following the procedure of preparation of **6a** and **7a**, the spiropyran **5d** (1.0 g, 2.25 mmol), potassium hydroxide (380 mg, 6.75 mmol) in ethanol (25 ml) gave *trans*-**6d** and *cis*-**7d**.

Isomer *trans*-**6d**: yellowish crystals, yield 380 mg (59%), mp 241-243 °C (from ethanol). IR: ν_{max} 3400 (N-H), 3065, 2975, 1685 cm^{-1} (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.37 (3H, s, CH_3), 1.56 (3H, s, CH_3), 2.05 (1H, d, *J* 11.4 Hz, CHH′), 2.19 (3H, s, 11-CH_3), 2.63 (3H, d, *J* 4.5 Hz, NH-*CH_3*), 3.06 (1H, dd, *J* 11.4, 4.6 Hz, CHH′), 4.30 (1H, d, *J* 4.6 Hz, 15-H), 4.36 (1H, s, 14-H), 6.07 (1H, d, *J* 7.5 Hz, 13-H), 6,74 (1H, dd, *J* 7.5, 0.6 Hz, 12-H), 6.92 (1H, d, *J* 1.5 Hz, 10-H), 7,17 (1H, d, *J* 9.0 Hz, 5-H), 8.10 (1H, d, *J* 9.0 Hz, 6-H), 8.24-8.25 (2H, m, 1-H, 2-H), 8.33-8.37 (1H, m, NH), 8.92 (1H, d, *J* 1.5 Hz, 4-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 20.7, 21.6, 25.5, 28.0, 28.4, 40.9, 44.5, 67.7, 106.9, 108.3, 119.7, 121.1, 121.3, 123.0, 123.9, 125.4, 126.7, 127.37, 127.6, 131.3, 133.5, 141.0, 141.2, 142.8, 154.4, 169.3 (C=O). Anal. Calcd for $C_{26}H_{25}N_3O_4$ (443.49): C, 70.41; H, 5.68; N, 9.47. Found: C, 70.03; H, 5.78; N, 9.36%. HRMS (ESI TOF): $[M+H]^+$, found 444.1919. $[C_{26}H_{25}N_3O_4+H]^+$ requires 444.1918.

Isomer *cis*-**7d**: yellowish crystals, yield 82 mg (8%), mp >250 °C (from acetonitrile). IR (ν_{max}, cm^{-1}): 3320 (N-H), 3025, 2965, 1652 (C=O). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 1.46 (3H, s, CH_3), 1.50 (3H, s, CH_3), 2.07 (3H, d, *J* 4.8 Hz, NH-CH_3), 2.12 (1H, d, *J* 11.6 Hz, CHH′), 2.25 (3H, s, CH_3), 2.30 (1H, dd, *J* 11.6, 4.8 Hz, CHH′), 3.94 (1H, d, *J* 4.8 Hz, 14-H), 4.49 (1H, t, *J* 4.8 Hz, 15-H), 6.30 (1H, d, *J* 7.6 Hz, Ar-H), 6.92 (1H, d, *J* 7.6 Hz, Ar-H), 7.01 (1H, s, Ar-H), 7.27 (1H, d, *J* 8.8 Hz, Ar-H), 7.54-7.57 (1H, m, NH), 8.11 (1H, d, *J* 9.2 Hz, Ar-H), 8.15 (1H, s, Ar-

H), 8.87 (1H, s, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 20.6, 23.1, 25.3, 26.1, 32.0, 36.9, 44.32, 77.7, 99.5, 109.7, 110.0, 118.8, 120.1, 122.8, 124.8, 125.1, 126.7, 128.3, 130.0, 131.4, 134.1, 138.5, 142.7, 146.8, 153.6, 169.7. HRMS (ESI TOF): $[M+H]^+$, found 444.1919. $[C_{26}H_{25}N_3O_4+H]^+$ requires 444.1918.

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