

Synthesis and photochromic properties of 11-phenoxy-2-phenylnaphth[2,3-*f*]indole-5,10-dione

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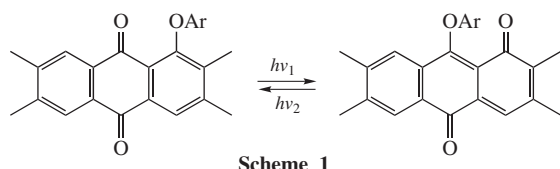
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11-Phenoxy-2-phenylnaphth[2,3-*f*]indole-5,10-dione has been synthesized, its photochromic properties have been studied, and photoinduced 10-phenoxy-2-phenylnaphth[2,3-*f*]indole-5,11-dione has been isolated.

Polycyclic *para*-quinones bearing an aryloxy group at the *peri*-position to the carbonyl undergo a photochemical aryloxytropic rearrangement.^{1–4} It consists in the migration of the aryl group to the carbonyl oxygen accompanied by the reorganization of the π -bond system of the molecule and is usually photochemically reversible (Scheme 1).

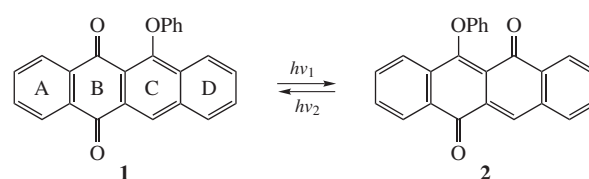


Scheme 1

It was shown previously^{3,5,6} that photoinduced *ana*-quinones are highly reactive towards nucleophiles. Reactions of the photoinduced form with water and other nucleophiles could be the reason for a fatigue of the photochromic aryloxyquinones. Photochromic properties of such compounds (quantum yields of photocoloration and fading, photoequilibrium states, fatigue, etc.) depend on the chemical structure, including the positions and character of substituents.^{2–7} For example, introduction of amino, alkylamino and dialkylamino substituents into the 2-position of 1-aryloxy-9,10-anthraquinones results in the irreversibility of photorearrangement.⁷ At the same time, these substituents reduce significantly the reactivity of the photoinduced forms (*ana*-quinones) towards nucleophiles.^{3,6,7} The most stable of them, 2-alkylamino-9-aryloxy-1,10-anthraquinones, have been isolated in a crystalline state and characterized.⁷ Unlike the amino and N-alkylated amino derivatives, 2-acylamino- and 2-methoxy-substituted 1-aryloxy-9,10-anthraquinones are typical photochromic compounds.³

Annulation of the anthraquinone nucleus at the 2,3-positions by the benzene ring affords an improvement in the photochromic characteristics of *peri*-aryloxyquinones.^{1,2} 6-Phenoxy-5,12-naphthacenequinone **1** is characterized by a low fatigue and comparatively stable *ana*-form **2**, which has been isolated in a crystalline state (Scheme 2).^{1,2} These features allow us to use phenoxyquinone **1** in devices for the optical registration and storage of information and in the light-protective materials.^{2,4,8}

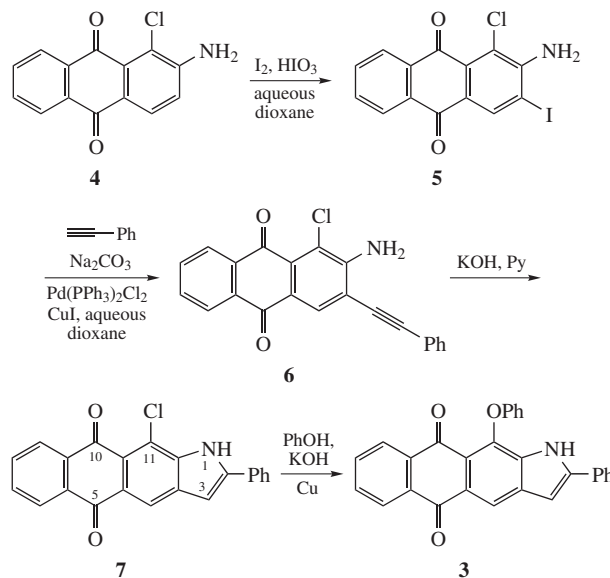
Thus, the introduction of monosubstituted amino groups in the 2-position of 1-aryloxy-9,10-anthraquinone, as well as its 2,3-annulation by the benzene ring, lead to a considerable reduction of reactivity of photoinduced form. It is reasonable to expect the improved photochromic properties of 1-aryloxy-9,10-anthraquinone fused with aromatic π -electron-excessive



Scheme 2

pyrrole ring, although the loss of reversibility could not be excluded. This prompted us to synthesize 11-phenoxy-2-phenylnaphth[2,3-*f*]indole-5,10-dione **3** and to study its photochromic properties.

The synthesis of quinone **3** is presented in Scheme 3. To form the pyrrole ring, a general approach based on *vic*-functionalized arylacetylenic precursors has been applied.^{9,10}



Scheme 3

2-Amino-1-chloro-9,10-anthraquinone **4** was iodinated by a mixture of I_2 and HIO_3 .¹¹ 2-Amino-1-chloro-3-iodo-9,10-anthraquinone **5**, obtained in 75% yield, was introduced into Pd,Cu-catalyzed cross-coupling with phenylacetylene (the Sonogashira reaction). A convenient modified procedure was employed.¹⁰ The reaction was carried out in aqueous dioxane in the presence of $Pd(PPh_3)_2Cl_2$ and CuI with Na_2CO_3 as a base at 85–87 °C. Under these conditions, the cross-coupling was completed within 15 min, the yield of 2-amino-1-chloro-3-phenylethynyl-9,10-

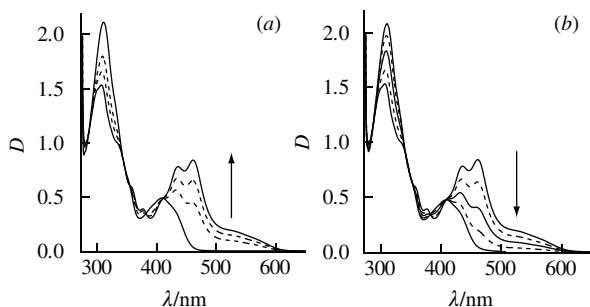


Figure 1 (a) The electronic absorption spectrum of 11-phenoxy-2-phenyl-naphth[2,3-*f*]indole-5,10-dione **3** in benzene at room temperature ($C = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$) and its changes upon irradiation at 436 nm for 10, 30 and 70 s. (b) The electronic absorption spectrum recorded after photolysis of **3** in benzene at 436 nm for 240 s and its changes upon irradiation at 546 nm for 1, 3, 6, 12 and 18 min.

anthraquinone **6** was 90%. Cyclization of acetylene **6** occurred in pyridine in the presence of powdered KOH at 115 °C and afforded 11-chloro-2-phenyl-naphth[2,3-*f*]indole-5,10-dione **7** in 69% yield. Substitution of the chlorine atom by the phenoxy group in compound **7** proceeded under the action of phenol and KOH in the presence of a copper powder at 170–175 °C to give phenoxyquinone **3**. The yield of **3** was 65%.[†]

peri-Phenoxy-*para*-quinone **3**, like other analogous quinone derivatives, rearranges on irradiation with UV and visible light.[‡] Figure 1(a) shows typical changes in the electronic absorption spectrum of a benzene solution of **3** upon irradiation at 436 nm. In the course of irradiation, the intensity of absorption bands of **3** ($\lambda_{\text{max}} = 311$ and 411 nm) decreases and new absorption bands ($\lambda_{\text{max}} = 437$ and 461 nm) and a shoulder (at ~520 nm) appear in the visible region of the spectrum. Irradiation of the sample for additional 170 s does not result in further spectral changes.

On the contrary, irradiation of the photolysed sample with long-wavelength light (546 nm), which is absorbed by the photo-induced form only, results in the complete recovery of the initial spectrum of *para*-quinone **3** [Figure 1(b)]. These spectral changes are characteristic of reversible photorearrangement of a *para*-quinoid structure to *ana*-quinoid one.^{1–4,6–8,12,13}

[†] The ¹H NMR spectra were recorded using a Bruker DPX 200 spectrometer in CDCl₃ at room temperature. The IR spectra were recorded using a Bruker Vector 22 spectrometer. The electronic absorption spectra were recorded on a UV-VIS Shimadzu 2401PC spectrometer. The high-resolution mass spectra were measured using a Thermo Electron Corporation DFS spectrometer.

3: mp 284.5–285.5 °C (toluene). ¹H NMR, δ : 6.99 (d, 1H, H³, J 2.1 Hz), 7.00–7.10 (m, 3H, PhO), 7.25–7.35 (m, 2H, PhO), 7.35–7.50 (m, 3H, Ph), 7.60–7.75 (m, 4H, H⁷⁽⁸⁾, Ph), 8.15–8.25 (m, 1H, H⁹⁽⁶⁾), 8.25–8.35 (m, 1H, H⁶⁽⁹⁾), 8.62 (s, 1H, H⁴), 8.80 (br. s, 1H, NH). IR (ν/cm^{-1}): 1594, 1667, 1734 (O=C–C=C=O), 3454 (NH). UV [benzene, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 311 (4.11×10^4), 411 (9.33×10^3).

5: mp 244–245 °C (toluene). ¹H NMR (200 MHz) δ : 5.49 (br. s, 2H, NH₂), 7.70–7.80 (m, 2H, H⁶⁽⁷⁾), 8.15–8.30 (m, 2H, H⁵⁽⁸⁾), 8.65 (s, 1H, H⁴).

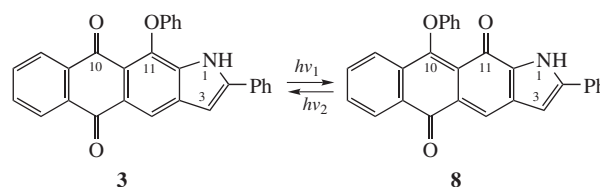
6: mp 216.5–217.5 °C (dioxane–hexane). ¹H NMR, δ : 5.65 (br. s, 2H, NH₂), 7.45–7.55 (m, 3H, Ph), 7.60–7.70 (m, 2H, Ph), 7.75–7.85 (m, 2H, H⁶⁽⁷⁾), 8.25–8.40 (m, 2H, H⁵⁽⁸⁾), 8.44 (s, 1H, H⁴). IR (ν/cm^{-1}): 1599, 1677, 1736 (O=C–C=C=O), 2210 (C≡C), 3403, 3512 (NH₂). UV [benzene, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 327 (4.3×10^4), 420 (5.5×10^3).

7: mp 299.5–300.5 °C (dioxane). ¹H NMR, δ : 7.07 (d, 1H, H³, J 2.2 Hz), 7.40–7.60 (m, 3H, Ph), 7.70–7.85 (m, 4H, H⁷⁽⁸⁾, Ph), 8.25–8.40 (m, 2H, H⁶⁽⁹⁾), 8.64 (s, 1H, H⁴), 9.09 (br. s, 1H, NH). IR (ν/cm^{-1}): 1597, 1673, 1734 (O=C–C=C=O), 3454 (NH). UV [benzene, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 311 (3.9×10^4), 406 (9.4×10^3).

[‡] The photolysis of benzene solutions was performed using the selected 436 or 546 nm lines of a high-pressure Hg lamp equipped with a water filter and a combination of glass filters.

The photoinduced product is sufficiently stable. Therefore, we succeeded in its isolation from a mixture with **3** using preparative TLC (Silufol plates, benzene–AcOEt). To our knowledge, this is one of the few isolations in the crystalline state of photochemically generated *ana*-quinones.^{1,3,7} The structure of the photoinduced form as 10-phenoxy-2-phenyl-naphth[2,3-*f*]indole-5,11-dione (*ana*-quinone **8**) was entirely confirmed.[§] Figure 2 shows the electronic absorption spectra of *para*-quinone **3** and *ana*-quinone **8**. The long-wavelength absorption maxima of these spectra are 461 nm ($\epsilon = 1.76 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) for **8** and 411 nm ($\epsilon = 9.33 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) for **3**.

As would be expected,⁷ in the ¹H NMR spectrum of *ana*-quinone **8**, the signals of the protons H⁴, H⁹, H³ shifted upfield relatively to the chemical shifts of the above protons in the spectrum of *para*-quinone **3** ($\Delta\delta$ 0.4, ≈ 0.3 , and 0.25 ppm, respectively). *Vice versa*, the signal of the proton at nitrogen atom H¹ is shifted downfield by 0.9 ppm.[§] The high-resolution mass spectrum of **8** also confirms its structure. Thus, the photochromic transformations of *para*-quinone **3** are really described by Scheme 4.



Scheme 4

Irradiation of a benzene solution of **3** at 436 nm affords a photostationary state with a **3**:**8** ratio of 38:62 [Figure 1(b)].[¶] The quantum yields of the coloration and fading reactions^{††} were 0.22 ± 0.02 (436 nm) and 0.015 ± 0.002 (546 nm), respectively. Note that similar quantum yields are known for naph-

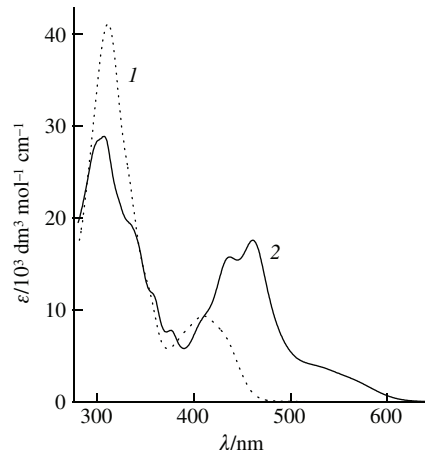


Figure 2 The electronic absorption spectra of (1) 11-phenoxy-2-phenyl-naphth[2,3-*f*]indole-5,10-dione **3** and (2) 10-phenoxy-2-phenyl-naphth[2,3-*f*]indole-5,11-dione **8** in benzene at room temperature.

[§] **8**: mp 222.5–224.5 °C. ¹H NMR, δ : 6.75 (d, 1H, H³, J 2.0 Hz), 6.95–7.10 (m, 3H, PhO), 7.25–7.50 (m, 5H, Ph, PhO), 7.50–7.70 (m, 4H, H⁷⁽⁸⁾, Ph), 7.85–8.00 (m, 1H, H⁹⁽⁶⁾), 8.21 (s, 1H, H⁴), 8.30–8.40 (m, 1H, H⁶⁽⁹⁾), 9.71 (br. s, 1H, NH). UV [benzene, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 307 (2.9×10^4), 437 (1.6×10^4), 461 (1.76×10^4). HRMS: found, 415.1205; calc. for C₂₈H₁₇NO₃, 415.1203.

[¶] An aliquot portion of a benzene solution of compound **3** of known concentration was irradiated to reach a photostationary state. The formed mixture of quinones **3** and **8** was separated by preparative TLC, **3** was quantitatively extracted with a benzene–AcOEt mixture and its content was determined by electronic absorption spectroscopy. The ratio of **3** to **8** in the irradiated solution was calculated. Completeness of the isolation of **3** from the solutions by this procedure was confirmed in special experiments. The accuracy was $\pm 2\%$.

thacenequinone **1** (0.34–0.6 and 0.049 in aromatic hydrocarbons).^{12,13}

As was mentioned above, the fatigue of the photoinduced *ana*-anthraquinones is predominantly determined by their reactivity towards nucleophiles (H₂O, ROH, NHR₂, etc.).^{3,6} To compare the reactivity of synthesized *ana*-quinone **8** and known *ana*-naphthacenequinone **2**, we measured the kinetics of their destruction in 96% ethanol. The rate constants are $(7.6 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$ ($\tau = 3.7 \text{ h}$) for **8** and $(1.1 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$ ($\tau = 2.5 \text{ h}$) for **2**. It indicates the lesser reactivity of **8** towards the nucleophiles in comparison with **2**. Hence, the replacement of benzene ring D in phenoxynaphthacenequinone **1** by the pyrrole one slightly enhances the stability of the photoinduced *ana*-quinone and reduces fatigue of new photochromic quinone **3**.

In conclusion, 11-phenoxy-2-phenylnaphth[2,3-*f*]indole-5,10-dione **3**, a heterocyclic analogue of known photochrome 6-phenoxy-5,12-naphthacenequinone **1**, has been synthesized for the first time. On irradiation, this compound undergoes reversible photoisomerization to give a sufficiently stable 10-phenoxy-5,11-quinone (*ana*-quinone). The photoinduced *ana*-quinone was isolated and characterized. Spectral characteristics of the photochromic *para*-quinone and its photoinduced *ana*-form were determined and the quantum yields of both photochemical steps were measured.

References

- 1 Yu. E. Gerasimenko and N. T. Poteleschenko, *Zh. Org. Khim.*, 1971, **7**, 2413 (in Russian).
- 2 V. A. Barachevsky, in *Organic Photochromic and Thermochromic Compounds*, eds. J. C. Crano and R. Guglielmetti, Plenum Press, New York, 1999, vol. 1, p. 267.
- 3 N. P. Gritsan and L. S. Klimenko, *J. Photochem. Photobiol. A: Chem.*, 1993, **70**, 103.
- 4 *Organicheskie fotokhromy*, ed. A. V. Eltsov, Khimia, Leningrad, 1982, p. 224 (*Organic Photochromes*, ed. A. V. Eltsov, Consultants, Bureau, New York, 1990, p. 210).
- 5 N. P. Gritsan, L. S. Klimenko, Z. V. Leonenko, I. Ya. Mainagashev, V. I. Mamatyuk and V. P. Vetchinov, *Tetrahedron*, 1995, **51**, 3061.
- 6 L. S. Klimenko, Z. V. Leonenko and N. P. Gritsan, *Mol. Cryst. Liq. Cryst.*, 1997, **297**, 181.
- 7 E. P. Fokin, S. A. Russkikh, L. S. Klimenko and V. V. Russkikh, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978, no. 7(3), 110 (in Russian).
- 8 F. Buchholtz, A. Zelichenok and V. Krongauz, *Macromolecules*, 1993, **26**, 906.
- 9 S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2005, **105**, 2873.
- 10 M. S. Shvartsberg, I. I. Barabanov and L. G. Fedenok, *Usp. Khim.*, 2004, **73**, 171 (*Russ. Chem. Rev.*, 2004, **73**, 161).
- 11 M. S. Shvartsberg, A. V. Piskunov and A. A. Moroz, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1101 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 987).
- 12 J. Malkin, A. Zelichenok, V. Krongauz, A. S. Dvornikov and P. M. Rentzepis, *J. Am. Chem. Soc.*, 1994, **116**, 1101.
- 13 Y. Yokoyama, S. Fukui and Y. Yokoyama, *Chem. Lett.*, 1996, 355.
- 14 N. P. Gritsan and N. M. Bazhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1275 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 897).
- 15 N. P. Gritsan and N. M. Bazhin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 280 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 210).
- 16 N. P. Gritsan, *Ph.D. (Phys.-Math.) Thesis*, Novosibirsk, 1979, pp. 129–132 (in Russian).

^{††} Photolysis quantum yields were measured using the isomerization of 2-dialkylamino-1,4-naphthoquinones^{14,15} as an actinometric photoreaction with a quantum yield of 0.1 for the photoisomerization of 2-dimethylamino-3-chloro-1,4-naphthoquinone in benzene.¹⁶

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