Photochemical and Thermal Transformations of 1-Aryloxy-2- and 4-Azidoanthraquinones

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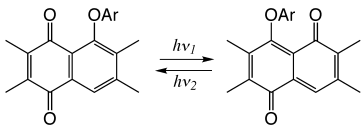
Abstract: The photolysis of 1-aryloxy-2-azidoanthraquinones (**3**) in benzene is described herein which gave 1-hydroxy-2-arylaminoanthraquinones (**4**) and two types of 5*H*-naphtho[2,3-*c*]phenoxazine-8,13-diones (**5** and **6**). Thermolysis of **3** yielded only one of phenoxazines **5** and small amount of **4**. On the other hand thermolysis of **3** in the presence of phenols gave phenoxazine **6** as a major product. The mechanism of the photolysis and thermolysis of 2-azido-1-aryloxyanthraquinones (**3**) is proposed and supported by the results from semiempirical calculations. A relative contribution of the primary photoreactions—azido group dissociation and aryl group migration was estimated to be 3:1. Photolysis and thermolysis of 4-azido-1-(*p*-*tert*-butylphenoxy)-9,10-anthraquinone (**8**) gave 3-(*p*-*tert*-butylphenoxy)-anthra[1,9-*cd*]-izoxazole-6-one (**9**) as the only product.

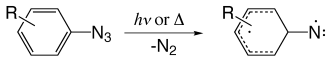
Keywords: azides · photolysis · quinones · semiempirical calculations · thermolysis

Introduction

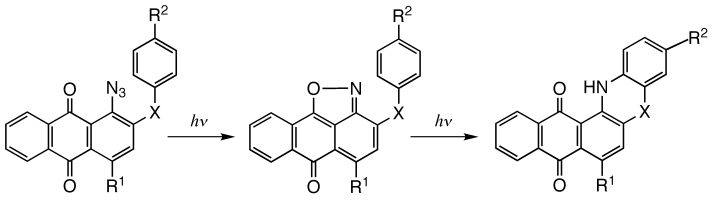
The targets of this study were substituted anthraquinones with two potentially photoactive azido and aryloxy groups. The photochemical reaction of the aryl group migration for aryloxy derivatives of anthra- and naphthacenequinones is well documented and these quinones are known as photochromic materials.[1]



The photochemical reactions of aryl azides are also well known[2] and are widely used in synthetic organic chemistry,[2a] photolithography[3] and photoaffinity labeling of biopolymers.[4] Very reactive singlet arylnitrenes with open-shell electronic configuration are the key intermediates of the thermal and photochemical reactions of aryl azides.[2]



The thermal and photochemical reactions of 1-azidoanthraquinone (**1**) resulting in anthra[1,9-*cd*]izoxazol-6-one are known since 1916.[5] In the presence of aryloxy- or arylthio groups in position 3, the latter are subject to further phototransformation into corresponding phenoxazines and phenothiazines (Scheme 1).[6]



X = O, S; R^1 = H, OH; R^2 = CH_3, *t*Bu

Scheme 1. Phototransformation into phenoxazines and phenothiazines.

There are no data available in the literature so far on the photochemistry of 2-azidoanthraquinones **2**, although **2** was used in photoaffinity labeling of phylloquinone-binding polypeptides[7] and for the substitution of ubiquinone in photosynthetic reaction center.[8] Thermolysis, however, of **2** gave 2-aminoanthraquinone with the yield of 8.6% as the only product identified.[5c]

Recently[9] we have studied the photolysis and thermolysis of 1-arylthio-2-azidoanthraquinones. The major products in both cases were corresponding 5*H*-naphtho[2,3-*c*]phenothia-

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zine-8,13-diones. In this case there is only one photoreactive center—azido group, aryl group does migrate neither thermally nor photochemically.[9]

Therefore the formation of the heterocyclic products, 5*H*-naphtho[2,3-*c*]phenoxazine-8,13-diones, is expected in the photolysis and thermolysis of 1-aryloxy-2-azidoanthraquinones **3**. Note, that the sulfur and nitrogen containing heterocyclic anthraquinone derivatives are used as a components of recording materials, and the synthesis of new derivatives are gratefully acknowledged.[10] However, the existence of two potentially photoactive centers in the 2-azido substituted 1-aryloxyanthraquinones can substantially complicate the synthesis; also, unusual products are to be expected. Therefore, the goal of this paper is to elucidate the pathways of photochemical and thermal transformations of 2- and 4-azido derivatives of 1-aryloxyanthraquinones containing two photoactive groups and to determine their relative efficiency.

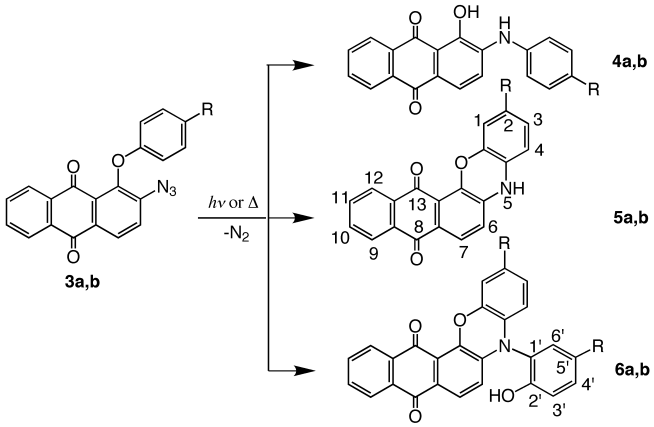
Results

The 2- and 4-azidoderivatives of 1-aryloxyanthraquinones (**3a**,**b** and **8**) were prepared according to known procedure from 1-aryloxy-2- and 4-aminoanthraquinones.[11] The latter were synthesized from commercially available 1-chloro-2 and 4-aminoderivatives of anthraquinone and substituted phenols as described in ref. [12].

Photolysis of 1-aryloxy-2-azidoanthraquinones (3a,b): Photolysis of 1-aryloxy-2-azidoanthraquinones (**3a**,**b**) in benzene gave 1-hydroxy-2-arylaminoanthraquinones (**4a**,**b**) and two types of heterocyclic derivatives of anthraquinone (**5a**,**b** and **6a**,**b**) as the major products (Scheme 2). The chromatographically pure products were identified using ^{1}H and ^{13}C NMR, IR spectroscopy and MS spectrometry. There was complete conversion of the starting material after 7–8 h of irradiation ($\lambda \geq 320$ nm). The total yield of the identified products was 57 and 69% for the conversion of **3a** and **3b**, respectively.

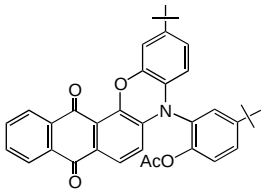
One of the products, 1-hydroxy-2-arylaminoanthraquinones, **4a**,**b**, has been synthesized previously by Smiles rearrangement of 1-aryloxy-2-aminoanthraquinones.[12] 5*H*-Naphtho[2,3-*c*]-phenoxazine-8,13-diones **5a**,**b** are the expected products of the photolysis of the azides **3a**,**b**. The isomeric naphtho[2,3-*a*]-phenoxazine-8,13-diones were obtained previously[6] by photolysis and thermolysis of 1-azido-2-aryloxyanthraquinones (Scheme 1). Similarly, we proposed that a substituent in a *para*-position relative to an oxygen atom in the aryloxy group of **3b** is in the *para*-position relative to a nitrogen atom in **5b** (Scheme 2).

The formation of phenoxazine derivatives **6a**,**b** was difficult to predict according to the data available in the literature. However, **6a**,**b** were unambiguously assigned based on the spectroscopic data. The mass spectra of **6a**,**b** testified the presence of an additional aryloxy group. The ^{1}H NMR spectrum of **6b** contains six protons of the anthraquinone: The characteristic signals of α and β-protons of the unsubstituted anthraquinone ring and the signals of two protons of



Scheme 2. Photolysis of 1-aryloxy-2-azidoanthraquinones **3a**,**b**.

the substituted anthraquinone ring. The chemical shifts and the splitting of these signals are similar to those in the spectrum of phenoxazine **5b**. In addition, the ^{1}H NMR spectrum contains two sets of the similar signals of three aromatic protons whose pattern of splitting is typical of 1,2,4-trisubstituted benzenes. Thus, compound **6b** is the derivative of phenoxazine **5b** in which the nitrogen atom of phenoxazine cycle is bound to the additional aryloxy group. The presence of a hydroxy group in the compound **6b** was proved by its acylation. The C=O stretch vibration band typical of the acetoxy group was found at 1770 cm^{-1} in the IR spectrum of acetoxy substituted product **6c**.



6c

The assignment of compound **6b** is also supported by the ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum contains two signals of the carbons of C=O groups at 181.3 and 181.6 ppm typical of 9,10-anthraquinone derivatives.[13] There are also six signals of the carbon atoms bound to heteroatoms (O or N) in the region 139.9–151.2 ppm. The total number of the signals of carbon atoms (34) also coincides with our assignment (structure **6b**). In addition **5b** and **6b** have very similar UV/Vis spectra.

To understand the origin of the product **6**, we performed photolysis of the diluted toluene solutions of the azide **3b**. Photochemical changes were controlled by the UV/Vis spectroscopy and thin-layer chromatography (TLC).

Figure 1 shows changes in the UV/Vis spectrum of **3b** upon irradiation at 313 nm. The optical spectrum of **3b** with a maximum at 370 nm was replaced by new spectrum with long wavelength maxima at 446 and 515 nm (Figure 1). According to TLC, the major products were phenoxazine **5b** and 1-hydroxy-derivative of anthraquinone **4b**. There were no traces of **6b** in the reaction mixture. The long wavelength maxima of the compounds **4b** and **5b** almost coincide, 515 and 516 nm, respectively. Therefore, a maximum at 515 nm in the UV/Vis spectrum (Figure 1, spectrum 4) belongs to these products.

It was mentioned above, that 1-aryloxy derivatives of anthraquinone (as **3a**,**b**) are the subject for the photochemical

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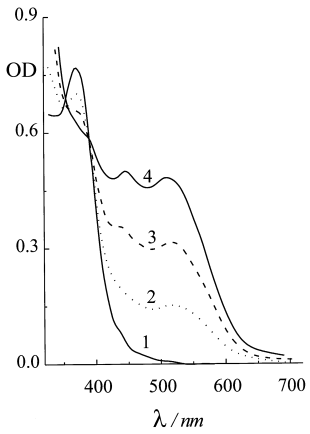
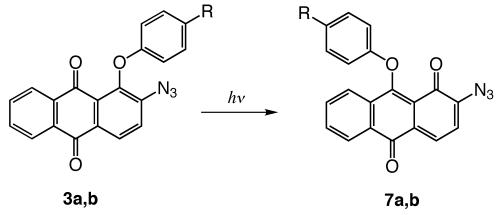


Figure 1. UV/Vis spectrum of 1-(*p-tert*-butylphenoxy)-2-azidoanthraquinone (**3b**, 1.4×10^{-4} mol L^{-1}) before (spectrum 1) and after irradiation at 313 nm for 1 min (spectrum 2), 4 min (spectrum 3) and 16 min (spectrum 4) in toluene at ambient temperature.

migration of aryl group resulting in 9-aryloxy-1,10-anthraquinone derivatives (**7a**,**b** in our case).



Derivatives of 9-aryloxy-1,10-anthraquinone display a strong absorption band in the region 450–550 nm.[1b] Thus, the second maximum at 446 nm (Figure 1, spectrum 4) can be assigned to **7b**.

It is known[14] that 1,10-anthraquinones readily react with water, alcohols and amines to form adducts. The UV/Vis spectra of the adducts have the long wavelength absorption maxima in the range of 330–390 nm.[14b] When we added methanol to the photolitic mixture, the band at 446 disappeared (Figure 2, spectrum 2), which indicates that 1,10-anthraquinone **7b** is one of the photolysis products.

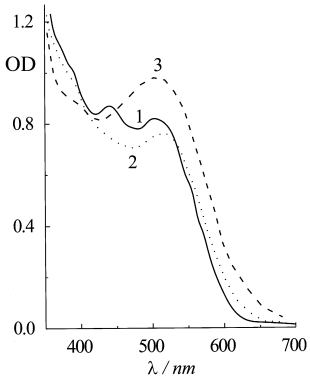


Figure 2. UV/Vis spectrum recorded after 16 min irradiation of 1-(*p-tert*-butylphenoxy)-2-azidoanthraquinone (**3b**, 2.3×10^{-4} mol L^{-1}) in toluene at ambient temperature (spectrum 1), its change after addition of methanol (5% vol.) (spectrum 2), and UV/Vis spectrum recorded after irradiation of **3b** for 16 min in toluene in the presence of 0.1 mol L^{-1} of *p-tert*-butylphenol (spectrum 3).

The adducts of 9-aryloxy-1,10-anthraquinones with water are very unstable and easily convert to 1-hydroxyanthraquinones and substituted phenols.[14c] Upon preparative photolysis of **3b** (7–8 h), a noticeable amount of *p-tert*-butylphenol will be formed due to the reaction of 1,10-anthraquinone (**7b**) with the traces of water in the solvent. The resulting phenol can participate in the formation of the unexpected product, that is substituted phenoxazine **6b**. Indeed, it was found that photolysis of **3b** in the presence of the excess of *p-tert*-butylphenol (0.1 mol L^{-1}) gives only substituted phenoxazine **6b** on the expense of the products **4b** and **5b** (Figure 2, spectrum 3). Note that **6b** does not form upon irradiation of individual compounds **4b** and **5b** in the presence and absence of *p-tert*-butylphenol.

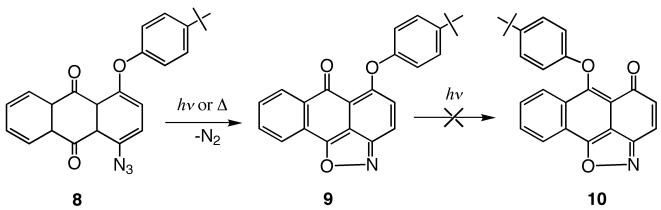
Unlike the photolysis in benzene and toluene, photolysis of **3b** in methylcyclohexane at room temperature gave only 1-hydroxy-2-(4′-*tert*-butylphenyl)aminoanthraquinone (**4b**) as a major product. The irradiation of **3b** in methylcyclohexane at lower temperatures (−100 °C) also gave only **4b**. Compounds **4b**–**6b** were not found among the products of **3b** photolysis in a glassy matrix of methylcyclohexane at 77 K.

Thermolysis of 1-aryloxy-2-azidoanthraquinones (3a,b): We have also performed thermolysis of azides **3a**,**b** in DMSO and triethylenglycol (TEG) at 150 °C. The composition of the reaction products differs from that of the photolytic mixture. The major products of the thermolysis are phenoxazines **5a**,**b** (28–35%). The amount of products **4a**,**b** is much lower. 1-Aryloxy-2-aminoanthraquinones are also found in 15–19% yield. Substituted phenoxazines **6a**,**b** were not formed even in a trace amount. However, with excess *p-tert*-butylphenol (0.1 mol L^{-1}) both the thermolysis and photolysis of **3b** gave **6b** in a high yield (>85%).

The thermolysis of azides **3a**,**b** in the presence of basic reagents gave an interesting result. The heating of **3a**,**b** at 50 °C in DMSO in the presence of KOH for 1 h led to the formation of **4a**,**b** in quantitative yields. The same process can be performed at room temperature for 10 h.

Photolysis and thermolysis of 1-(*p-tert*-butylphenoxy)-4-azidoanthraquinone: 1-(*p-tert*-Butylphenoxy)-4-azidoanthraquinone (**8**) was synthesized using the same reaction scheme as for azides **3a**,**b**. However, we have failed to isolate azide **8**. During the reaction, it partially transforms into 5-(*n-tert*-butylphenoxy)-anthra[1,9-*cd*]-izoxazole-6-one (**9**). The photolysis and thermolysis of a mixture of **8** and **9** lead to the complete transformation of **8** into izoxazolone **9** (Scheme 3).

Izoxazolone **9** is the expected product of photochemical and thermal transformations of azide **8**. It results from the intramolecular reaction of a singlet nitrene generated upon



Scheme 3. Synthesis of **9**.

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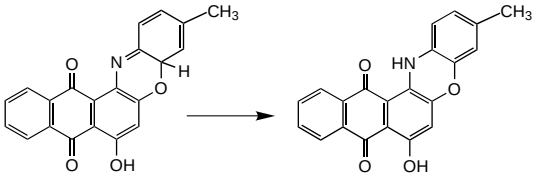
photodissociation of the azido group. The prolonged irradiation of the benzene solution of **9** ($\lambda > 320$ nm) causes no further changes. Therefore there is no photoinduced migration of the aryl group in the case of compound **9**.

Discussion

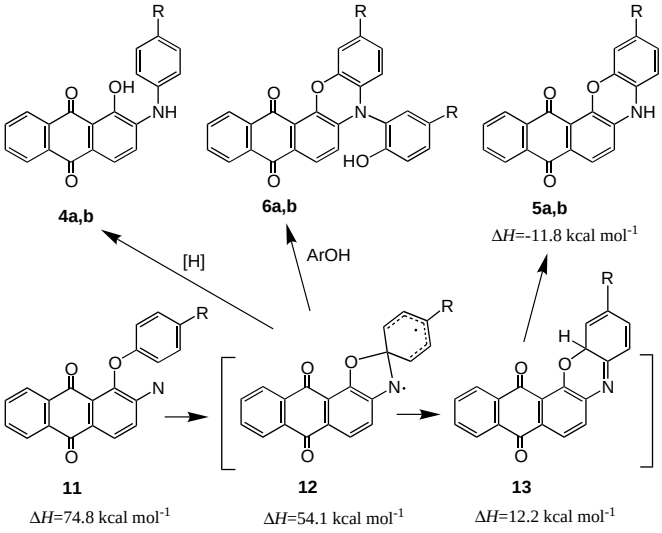
The mechanism of the cyclization reaction of aryl azides containing either arylthio or aryloxy groups in the *ortho*-position has been proposed in the literature.[2a, 15] It was shown that the cyclization was not a simple process of insertion, but involved a positional rearrangement. Therefore it was assumed that the singlet arylnitrene attacks the carbon atom bound to the heteroatom to form a dipolar spiro species.[2a, 6c, 15] Similar positional rearrangement was observed for naphtho[2,3-*a*]-phenoxazine-8,13-diones (Scheme 1).[6] In the latter case the precursor of the phenoxazine, the diene **D**, was directly detected at the low temperature ($-95\,^{\circ}$C).[6d]



In the special case of 2,4,6-trimethylphenoxy substituent, the intermediate **D** was stable enough to record its ^{1}H NMR spectrum and to assign its structure with confidence.[6d]

We were unable to observe a similar intermediate in our case. However, the rearrangement of spiro species **12** into phenoxazine **5** should occur similarly through the intermediate formation of diene **13** (Scheme 4).

According to our semiempirical calculations (AM1 and PM3 methods), the intermediate spiro species is a diradical **12** in contrast to the previously proposed dipolar species.[2a, 6, 15] The energy of the diradical structure was predicted by AM1 method to be lower than that of the dipolar species by 25 kcal mol^{-1}. One of the unpaired electrons of **12** is localized on the nitrogen. The other is delocalized over the ring mainly in *ortho* and *para* positions of the spiro center.



Scheme 4. Formation enthalpies (ΔH) calculated by the PM3 method.

Scheme 4 displays the formation enthalpies (ΔH) calculated by the PM3 method. The AM1 method gave higher values for ΔH for all species. However, the relative values are close to the data calculated by the PM3 method. The calculations show that the proposed intermediates are actually the minima on the potential energy surface and all proposed reactions are exothermal.

Experimental results obtained in this work are in good agreement with the theoretical results given in Scheme 4. Accordingly, products **4**–**6** are formed from a common precursor diradical **12**. The formation of unusual product **6** can be explained by the reaction of radical substitution in the *ortho*-position of the phenol. A significant decrease in the yields of both **4** and **5** in the presence of phenol testifies that not only **5** but also **4** are formed through the diradical **12**. The high yield of **4b** upon photolysis of **3b** in methylcyclohexane can be explained by hydrogen abstraction from a solvent.

The main difference between photolysis and thermolysis of 1-aryloxy-2-azidoanthraquinones **3a**,**b** is the absence of substituted phenoxazines **6a**,**b** among the thermolysis products. It is not surprising, because upon thermolysis no migration of the aryl group resulting in 1,10-anthraquinones occurs and thus no phenol is formed. Since the yield of phenoxazines **6** depends on the amount of phenol resulting from the decomposition of photoinduced ana-quinones **7**, we can roughly estimate a relative contribution of the primary photoreactions azido group dissociation and aryl group migration. As follows from the product yields, upon photolysis, about 25 % of excited molecules are subject to isomerization into ana-quinone **7**, the remaining 75 % dissociate to form the singlet nitrene and molecular nitrogen.

In the case of 4-azido derivatives of 1-aryloxyanthraquinone (**8**) and in contrast to 2-azido derivatives only one of two possible photochemical reactions is realized, that is, the azido group dissociation followed by reaction of cyclization. This is in agreement with a significantly higher rate constant of dissociation of azido group in the α-position of anthraquinone as compared with the β-position.

Experimental Section

General: Photolysis of the samples was carried out using a high-pressure mercury lamp with either UFS-1 (280–400 nm), BS-8 (>320 nm) glass filters or a combination of UFS-2 and ZhS-3 glass filters (313 nm). Thin-layer chromatography was performed on Silufol silica gel UV-254 TLC plates. All products were purified by column chromatography (silica gel L, 5–40 μm). IR (KBr): Bruker Vector-22. UV/Vis spectra were recorded using Specord spectrophotometer. ^{1}H NMR ($CDCl_3$): Bruker WP-200SY and DRX-500HI (internal TMS as reference). ^{13}C NMR ($CDCl_3$): DRX-500HI ($CDCl_3$ as reference). MS: Finnigan MAT-8200.

Computational methods: The semiempirical calculations of the geometry and electron structure were performed by AM1[16] and PM3[17] methods using the GAUSSIAN-98 suit of programs[18] and MNDO92 program (author's modification of the MNDO85 program[19]). The latter program gave opportunity to calculate properties of the open-shell singlet biradical

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12 using restricted Hartree–Fock method in half-electron approximation.[20]

1-Aryloxy-2- and 4-azidoanthraquinones (3a,b and 8): A solution of $NaNO_2$ (0.83 g, 12 mmol) in HCl (30%, 3 mL) was added at room temperature to a stirred solution of 1-aryloxy-2- or 4-aminoanthraquinone (3.2 g, ≈10 mmol) in acetic acid (100 mL). The reaction mixture was stirred for 1 h and then cooled to 10 °C and NaN_3 (0.78 g, 12 mmol) was added. Then the mixture was stirred for an additional 30 min in the dark. The precipitated azide was filtered off. Purification by silica gel column chromatography ($CHCl_3$) afforded **3a** (82%) and **3b** (85%). **3a**: m.p. 164 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 6.84-7.35$ (m, 5H; OPh), 7.49 (d, J(H,H) = 8.5 Hz, 1H; 3-H), 7.71 (m, 2H; 6-H, 7-H), 8.09 (m, 1H; 5-H), 8.22 (m, 1H; 8-H), 8.27 (d, J(H,H) = 8.5 Hz, 1H; 4-H); IR (KBr): $\tilde{\nu} = 3077$, 2113, 1673 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 267 (4.59), 370 (3.78); MS: m/z: calcd for $C_{20}H_{11}N_3O_3$: 341.0798; found: 341.0806 [M^+]; **3b**: m.p. 161 °C (decomp); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H; *t*Bu), 6.76 (d, $J = 9$ Hz, 2H; 2′-H, 6′-H), 7.28 (d, J(H,H) = 9 Hz, 2H; 3′-H, 5′-H), 7.49 (d, J(H,H) = 8.5 Hz, 1H; 3-H), 7.72 (m, 2H; 6-H, 7-H), 8.13 (m, 1H; 5-H), 8.23 (m, 1H; 8-H), 8.26 (d, J(H,H) = 8.5 Hz, 1H; 4-H); IR (KBr): $\tilde{\nu} = 2990$, 2109, 1670 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 263 (4.57), 375 (3.74); MS: m/z: calcd for $C_{24}H_{19}N_3O_3$: 397.2422; found: 397.2406 [M^+].

Preparative photolysis of azides 3a and 3b: The solutions of **3a** (0.34 g, 1 mmol) or **3b** (0.4 g, 1 mmol) in benzene (500 mL) were irradiated by the filtered light of a mercury lamp ($\lambda \geq 320$ nm) for 7–8 h at 20 °C until the complete conversion of the starting material (TLC control). The solvent was evaporated and the residue was separated using a silica gel column chromatography (benzene). 1-Hhydroxy-2-arylaminoanthraquinones (**4a**,**b**) isolated from the first fractions were identified by comparison with the samples synthesized as described in ref. [12] The product yields were 19% (**4a**) and 25% (**4b**). The neighboring fractions containing products **5** and **6** were doubly separated using column chromatography ($CHCl_3$). The yields were 15% (**5a**), 16% (**5b**), 23% (**6a**) and 28% (**6b**).

5*H*-Naphtho[2,3-*c*]-phenoxazine-8,13-dione (5a): m.p. 318–321 °C; ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 6.69$ (m, 2H; 2-H, 3-H), 6.82 (d, J(H,H) = 8.5 Hz, 1H; 6-H), 6.92 (m, 2H; 1-H, 4-H), 7.70 (d, J(H,H) = 8.5 Hz, 1H; 7-H), 7.74 (m, 2H; 10-H, 11-H), 8.27 (m, 2H; 9-H, 12-H), 9.05 (s, 1H; NH); IR (KBr): $\tilde{\nu} = 3447$, 2982, 1660, 1631 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 267 (4.58), 310 (3.62), 410 (3.18), 560 (3.83); MS: m/z: calcd for $C_{20}H_{11}NO_3$: 313.0736, found: 313.0743 [M^+].

2-*tert*-Butyl-5*H*-naphtho[2,3-*c*]-phenoxazine-8,13-dione (5b): m.p. 289–292 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ (s, 9H; *t*Bu), 6.81 (d, J(H,H) = 8.5 Hz, 1H; 3-H), 7.89 (d, $J = 8.5$, 1H; 6-H), 7.09 (s, 1H; 1-H), 7.18 (d, J(H,H) = 8.5 Hz, 1H; 4-H), 7.70 (d, J(H,H) = 8.5 Hz, 1H; 7-H), 7.74 (m, 2H; 10-H, 11-H), 7.99 (s, 1H; NH), 8.23 (m, 2H; 9-H, 12-H); IR (KBr): $\tilde{\nu} = 3457$, 2962, 1651, 1629 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 265 (4.46), 313 (3.60), 412 (3.25), 567 (3.79); MS: m/z: calcd for $C_{24}H_{19}NO_3$: 369.1365; found: 369.1371 [M^+].

5(2′-Hydroxyphenyl)-naphtho[2,3-*c*]-phenoxazine-8,13-dione (6a): m.p. 185–188 °C; IR (KBr): $\tilde{\nu} = 3440$, 2965, 1662 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 266 (4.70), 310 (3.61), 410 (3.42), 548 (4.03); MS:: calcd for $C_{26}H_{15}NO_4$: 405.1001; found: 405.0975 [M^+].

2-*tert*-Butyl-5(2′-hydroxy-5′-*tert*-butylphenyl)-naphtho[2,3-*c*]-phenoxazine-8,13-dione (6b): m.p. 192–195 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 1.22 (s, 9H; *t*Bu), 1.29 (s, 9H; *t*Bu), 5.94 (d, J(H,H) = 8.5 Hz, 1H; 3′-H), 5.99 (d, J(H,H) = 8.5 Hz, 1H; 6-H), 6.68 (dd, J_1(H,H) = 8.5, J_2(H,H) = 3.0 Hz, 1H; 4′-H), 6.70 (d, J(H,H) = 3.0 Hz, 1H; 6′-H), 7.14 (d, J(H,H) = 3.0 Hz, 1H; 1-H), 7.18 (d, J(H,H) = 8.5 Hz, 1H; 4-H), 7.31 (d, J(H,H) = 8.5 Hz, 1H; 7-H), 7.44 (dd, J_1(H,H) = 8.5 Hz, J_2(H,H) = 3.0 Hz, 1H; 3-H), 7.59 (td, J_1(H,H) = 8.0 Hz, J_2(H,H) = 2.0 Hz, 1H; 10-H), 7.66 (td, J_1(H,H) = 8.0 Hz, J_2(H,H) = 2.0 Hz, 1H; 11-H), 7.75 (s, 1H; NH), 8.00 (dd, J_1(H,H) = 8.0, J_2(H,H) = 2.0 Hz, 1H; 9-H), 8.05 (dd, J_1(H,H) = 8.0, J_2(H,H) = 2.0 Hz, 1H; 12-H); IR (KBr): $\tilde{\nu} = 3400$, 2960, 1660 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 266 (4.78), 313 (3.63), 410 (3.46), 560 (4.02); MS: m/z: calcd for $C_{34}H_{31}NO_4$: 517.2253; found: 517.2241 [M^+].

Photolysis of azide 3b in the excess of *p*-*tert*-butylphenol: The solution of azide **3b** (0.04 g, 0.1 mmol) and *p*-*tert*-butylphenol (0.03 g, 0.2 mmol) in benzene (50 mL) was irradiated with a mercury lamp ($\lambda \geq 320$ nm) for 8 h at room temperature until the complete conversion of starting azide. The solvent was evaporated and the residue was purified by column chromatography on silica gel ($CHCl_3$) to afford 2-*tert*-butyl-5(2′-hydroxy-5′-*tert*-butylphenyl)-naphtho[2,3-*c*]-phenoxazine-8,13-dione (**6b**; 0.04 g, 77%).

Acylation of 2-*tert*-butyl-5(2′-hydroxy-5′-*tert*-butylphenyl)-naphtho[2,3-*c*]-phenoxazine-8,13-dione (6b): The solution of phenoxazine **6b** (0.05 g, 0.1 mmol) in a mixture of Ac_2O (10 mL) and pyridine (5 mL) was stirred for 1 h at 100 °C and subsequently poured into water. The precipitate was recrystallized from EtOH to afford 2-*tert*-butyl-5(2′-acetoxy-5′-*tert*-butylphenyl)-naphtho[2,3-*c*]-phenoxazine-8,13-dione (**6c**; 0.044 g, 82%). M.p. 93–95 °C; IR (KBr): $\tilde{\nu} = 2960$, 1770, 1670 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 263 (4.64), 540 (3.85); MS: m/z: calcd for $C_{36}H_{33}NO_5$: 559.2412; found: 559.2466 [M^+].

Thermolysis of azides 3a,b: The solutions of compound **3a** (0.34 g, 1 mmol) or **3b** (0.4 g, 1 mmol) in DMSO or TEG (20 mL) were heated for 1 h at 150 °C. Subsequently the reaction mixture was poured into water. The precipitate was separated using column chromatography (benzene). For **3a**: isolated products **4a** (0.02 g, 5%), **5a** (0.08 g, 28%), and 1-phenoxy-2-aminoanthraquinone (0.05 g, 16%); for **3b**: isolated products **4b** (0.02 g, 6%), **5b** (0.13 g, 35%), and 1-(*p*-*tert*-butylphenoxy)-2-aminoanthraquinone (0.07 g, 19%).

Thermolysis of azide 3b in the presence of *p*-*tert*-butylphenol: A solution of azide **3b** (0.04 g, 0.1 mmol) and *p*-*tert*-butylphenol (0.15 g, 1 mmol) in DMSO (20 mL) was heated for 1 h at 150 °C. The reaction mixture was poured into water. The precipitate was separated by column chromatography ($CHCl_3$) to afford **6b** (0.043 g, 85%).

Thermolysis of azides 3a and 3b in the presence of KOH: Granulated KOH (0.06 g, 1 mmol) was added to the stirred solutions of **3a** (0.34 g, 1 mmol) or **3b** (0.4 g, 1 mmol) in DMSO (30 mL) and solutions were kept at room temperature for 10 h or at 50 °C for 1 h. The reaction mixture was poured into water. The precipitate was filtered and dried to afford compounds **4a** or **4b** with the yields of 95% each.

Photolysis of 1-(*p*-*tert*-butylphenoxy)-4-azidoanthraquinone (8): The starting material azide **8** (purity ≈80%) was contaminated with 5-(*p*-*tert*-butylphenoxy)anthra[9,1-*cd*]izoxazole-6-one (**9**). The solution of a mixture of **8** and **9** (0.4 g, ≈1 mmol) in benzene (500 mL) was irradiated by a mercury lamp ($\lambda \geq 320$ nm) for 1 h at room temperature until the complete conversion of the starting material (TLC control). The solvent was evaporated and the residue was purified by column chromatography ($CHCl_3$) to afford **9** (0.33 g, ~85%).

5-(*p*-*tert*-Butylphenoxy)anthra[9,1-*cd*]-izoxazol-6-one (9): m.p. 222–224 °C; ^{1}H NMR (20 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H; *t*Bu), 6.76 (d, J(H,H) = 9 Hz, 2H; 2′-H, 6′-H), 7.28 (d, J(H,H) = 9 Hz, 2H; 3′-H, 5′-H), 7.49 (d, J(H,H) = 8.5 Hz, 1H; 3-H), 7.72 (m, 2H; 6-H, 7-H), 8.13 (m, 1H; 5-H), 8.23 (m, 1H; 8-H), 8.26 (d, J(H,H) = 8.5 Hz, 1H; 4-H); IR (KBr): $\tilde{\nu} =$ 2975, 1675, 1650 cm^{-1}; UV/Vis (ethanol): λ (lgε) = 248 (4.42), 306 (3.90), 442 (4.07), 457 (4.02); MS: m/z: calcd for $C_{24}H_{19}NO_3$: 369.1365, found 369.1365 [M^+].

Thermolysis of 1-(*p*-*tert*-butylphenoxy)-4-azidoanthraquinone (8): The solution of a mixture of **8** and **9** (0.4 g, ≈1 mmol) in DMSO (20 mL) was heated for 1 h at 150 °C. The solvent was evaporated and the residue was purified by column chromatography ($CHCl_3$) to afford izoxazole **9** (0.30 g, ≈80%).

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