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The products of the photolysis of 2-(4-alkyl(or phenyl)piperazino)-3-amino-1,4-naphthoquinones, their structures and subsequent thermal transformations

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Photolysis of 2-(4-alkyl(phenyl)piperazino)-3-amino-1,4-naphthoquinones affords 2-alkyl(phenyl)-1,2,3,4,12,12a-hexahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyrazine-6,11-diols which recyclize at elevated temperatures to yield 1,2,3,4-tetrahydro-13-alkyl(phenyl)-3,1-(iminoethano)benzo[*g*]quinoxaline-5,10-diols. The latter are oxidated with atmospheric oxygen to the corresponding diones. On the basis of deuterium exchange data a mechanism for the recyclization is proposed.

Key words: 1,4-naphthoquinone; 1,2,3,4,12,12a-hexahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyrazine-6,11-diol; 1,2,3,4-tetrahydro-13-alkyl(phenyl)-3,1-(iminoethano)benzo[g]quinoxaline-5,10-diol(-dione); photolysis; thermolysis; recyclization; ^{1}H and ^{13}C NMR spectra.

We have found previously[1] that the irradiation ($\lambda >$ 400 nm) of 2-(4-alkyl(phenyl)piperazino)-3-amino-1,4-naphthoquinones (**1a—c**) at 80 °C in benzene affords 1,2,3,4-tetrahydro-13-alkyl(phenyl)-3,1-iminoethano-benzo[g]quinoxaline-5,10-diones (**2a—c**) identical to those obtained by thermolysis of the corresponding azides. In the case of compound **1c**, which has a more electron accepting phenyl group in position 4 of the piperazine ring, in addition to the main product, tetrahydro-benzo[g]quinoxalinedione **2c**, the reaction gives ~4 % of naphthoimidazopyrazinedione (**3**). At the same time, photolysis of compounds **1a—c** at 20 °C in the presence of atmospheric oxygen leads to unstable naphthodihydro-imidazolediones, as have been shown with 2-(4-(2-cyanoethyl)piperazino)-3-amino-1,4-naphthoquinone **1a**. Naphthodihydroimidazoledione (**4a**), detected in C_6D_6, is not converted to the benzo[g]quinoxaline derivative **2a** after further heating at 80 °C (Scheme 1).

In the previous paper[2] we showed by ^{1}H and ^{13}C NMR spectroscopy that imidazolyl derivatives (structures type **3** and **4a**) detected upon photolysis of 3-amino-substituted 2-dialkylamino-1,4-naphthoquinones[3,4] arise from subsequent thermal transformations of the primary photolysis products, naphthodihydroimidazolediols. This paper describes a study of the mechanism of formation of tetrahydrobenzoquinoxalinediones **2** in the course of

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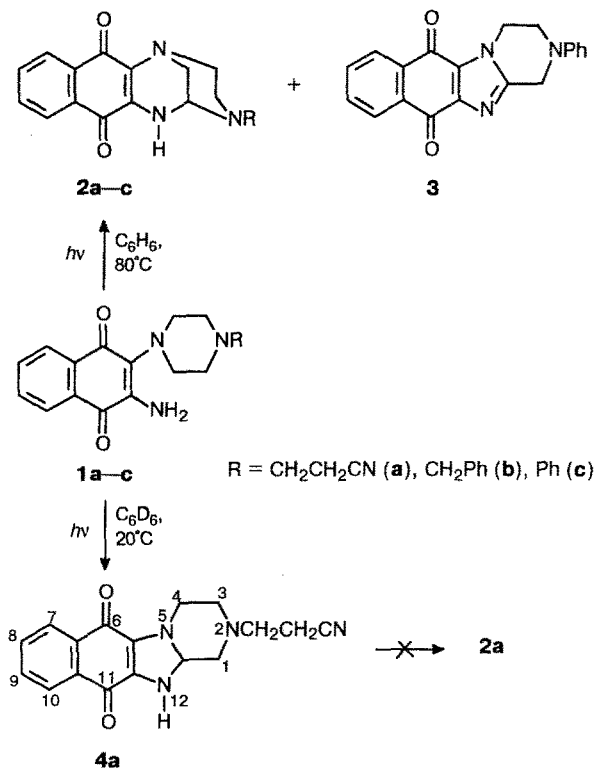
Scheme 1



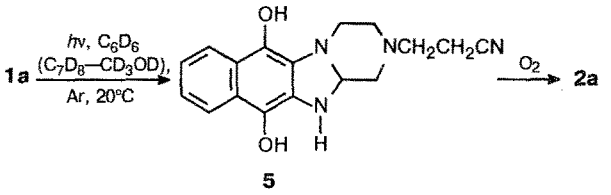
photolysis of-2-(4-alkyl(phenyl)piperazino)-3-amino-1,4-naphthoquinones (**1**).

The photolysis of quinone **1a**, when carried out in a NMR ampule under an inert atmosphere (C_6D_6, 20 °C), brings about the decoloration of the solution and the appearance of a white, finely dispersed precipitate. This precipitate dissolves when a few drops of DMSO-d_6 are added and a flow of argon is simultaneously passed through the solution. As shown by ^1H and ^{13}C NMR spectroscopy, the photolysis gives 2-(2-cyanoethyl)-1,2,3,4,12,12a-hexahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyrazine-6,11-diol (**5**) (Scheme 2). Compound **5** is obtained as well when quinone **1a** in a toluene-d_8—methanol-d_4 mixture (1:1 v/v) is irradiated under similar conditions.

These results indicate that the dihydroimidazolediol derivatives are the primary products in the photolysis of 2-piperazino-3-amino-1,4-naphthoquinones as well.[2] Benzo[*g*]quinoxalinediones[2] are probably formed in the dark transformations of these compounds.

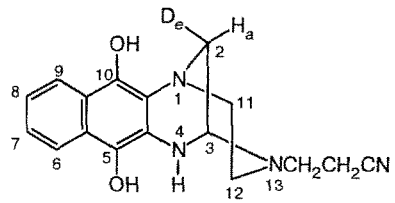
Heating a sealed NMR ampule containing the precipitate obtained on the photolysis of **1a** in C_6D_6 leads to the dissolution of the precipitate at 80 °C. The ^1H and ^{13}C NMR spectra of the resulting solution recorded at 25 °C exhibit substantial broadening of the signals which is especially pronounced in the region of resonance of aromatic protons. Increasing the temperature to 80 °C does not result in narrowing of the signals. It may be supposed that this broadening is caused by some

Scheme 2

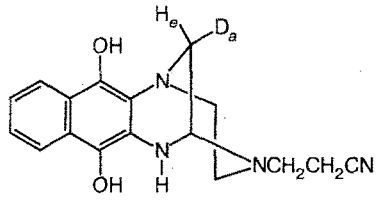


kind of paramagnetic particles present in the solution. Due to the insufficient quality of the spectra we could not unambiguously determine the structure of the compound obtained. However, it can be said with confidence that its structure differs from that of compound **5**. Interaction of this product with atmospheric oxygen after opening of the sealed ampule affords the benzo[*g*]quinoxaline derivative **2a**. The latter has also been obtained on a preparative scale by the thermolysis of dihydroimidazole **5*** followed by oxidation with atmospheric oxygen. (The oxidation is manifested by a rapid change in the color from pale yellow to dark red which follows the opening of the ampule.)

On the basis of the foregoing data it may be inferred that compound **2a** is formed upon oxidation of the product of the thermolysis of dihydroimidazole **5**. In order to determine the structure of the thermolysis product and the mechanism of its formation we carried out the reaction in a toluene-d_8—methanol-d_4 mixture in a NMR ampule. It was found that the thermolysis of compound **5** in the absence of oxygen gave an equimolar mixture of two isotopomers (**6**) which differ in the spatial orientation** of the deuterium atom in position 2 of compound **6**.



endo-**6**

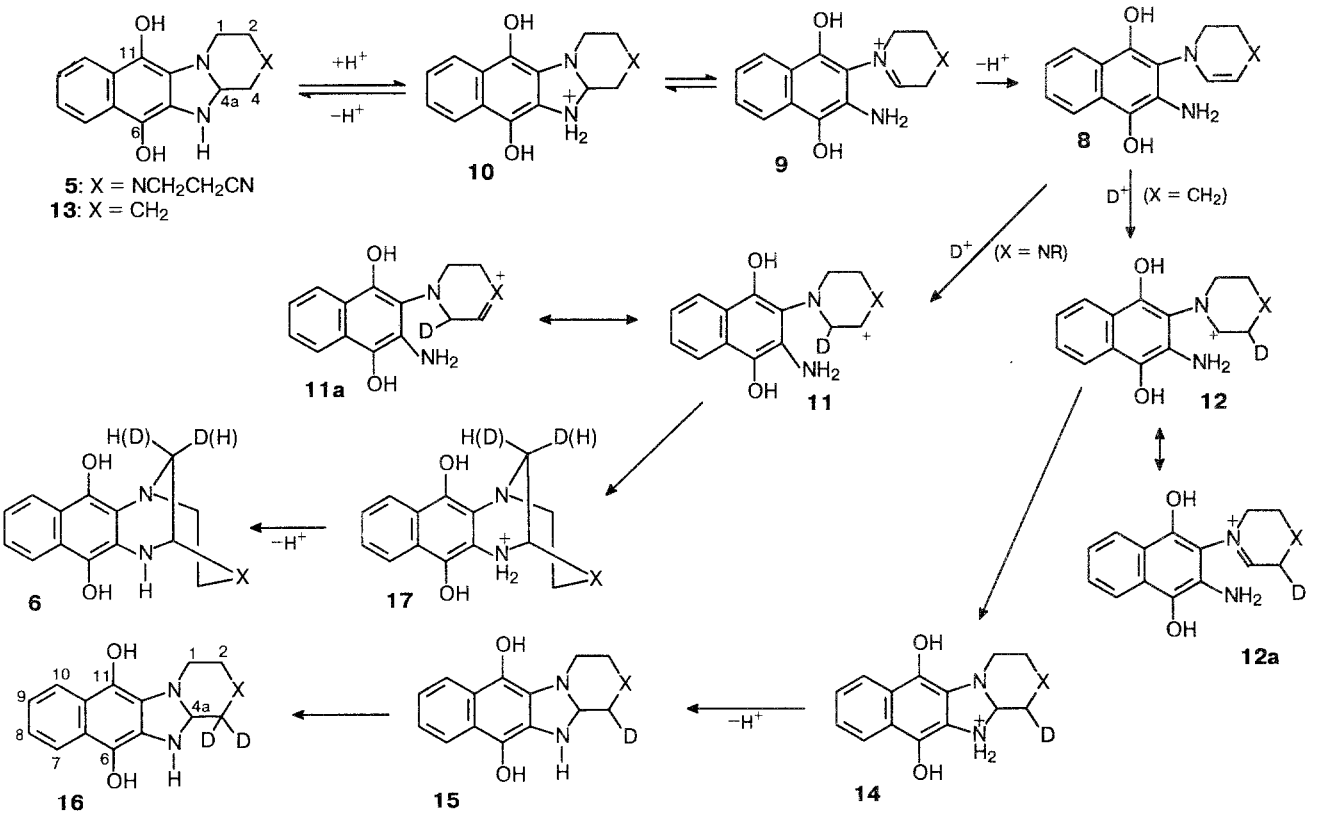


exo-**6**

* Dihydroimidazolediol **5** was obtained by irradiating compound **1a** in a toluene—methanol mixture under conditions similar to those of photolysis in a NMR ampule, and then it was subjected to thermolysis under an inert atmosphere without isolation.

** The following symbols are used: *a* — axial, *e* — equatorial, a — according to nomenclature.

Scheme 3



The ^{1}H NMR spectrum of the mixture of isomers **6** displays signals of H(2*a*) at 3.44 ppm and H(2*e*) at 2.76 ppm; their intensities correspond to 0.5 H. The distinction between the chemical shifts of the H(3) signals of the two isomers, *endo*-**6** and *exo*-**6**, is small (0.003 ppm). As shown by the double resonances, H(2*a*) is coupled with H(3) of the corresponding isomer ($^3J_{H-H}$ = 2.0 Hz). The remaining signals in the ^{1}H NMR spectrum have practically equal chemical shifts for both isomers **6**. We could not obtain a signal for C(2) in the ^{13}C NMR spectrum due to the difference in the chemical shifts of *exo*- and *endo*-**6** and to coupling of C(2) with the deuterium nucleus, which markedly lowers the intensity of the signal. The chemical shifts of the C(3) signals for *endo*- and *exo*-**6** differ by 0.07 ppm, whereas the signals of the other atoms practically coincide. It should be noted that on passing from dihydroimidazole **5** to benzo[*g*]quinoxazoline derivative **6** the doublet at 78.11 ppm, corresponding to the C(4a) atom of compound **5**, disappears from the ^{13}C NMR spectrum, while two other doublets, at 63.35 and 63.28 ppm (C(3)), appear. These changes confirm the formation of the bicyclic structure of **6**.

To rule out the possibility of a mistake, we replicated the experiment under the same conditions in a toluene-d_8—CD_3OH mixture. The product of this reaction was 1,2,3,4-tetrahydro-13-(2-cyanoethyl)-3,1-iminoethanobenzo[*g*]quinoxaline-5,10-diol (**7**). The ^{1}H NMR spectrum of **7** exhibits signals of H(2*a*) and H(2*e*) at 3.50 and 2.81 ppm, respectively (^2J = 12.5 Hz). The signals of C(2) and C(3) in the ^{13}C NMR spectrum occur at 52.5 and 63.70 ppm, respectively.

The presence of deuterium in position 2 of tetrahydrobenzo[*g*]quinoxalinediol points to the fact that in the course of the reaction an intermediate species emerges, which is capable of interacting with the proton. This is probably the reduced form of enaminoquinone (**8**) which is formed as shown in Scheme 3. An equilibrium between type **5** and **9** structures is known[5] to exist in an acidic medium. Addition of D^+ to the double bond of compound **8** in the case of X = NR proceeds preferably with the formation of cation **11**, rather than **12**. The attack of D^+ at the double bond from above and from below is equally probable, so, the resulting mixture of isotopomers **6** is eqiumolar.

The proposed scheme has been also confirmed by the thermolysis of 1*H*-2,3,4,4a-tetrahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyridine-6,11-diol (**13**) obtained on the photolysis of 2-piperidino-3-amino-1,4-naphthoquinone.[2] Heating compound **13** in a 1:1 toluene-d_8—methanol-d_4 mixture under an inert atmosphere at 80 °C affords compound **16**, that is, the deuterium label is introduced into position 4 of dihydroimidazole **13**. The ^{1}H NMR spectrum of compound **16** differs from that of **13** in the following. The former does not contain signals at 1.94 and 1.81 ppm corresponding

Table 1. Characteristics of the compounds obtained

Compound	M.p./°C (solvent)	Molecular mass Found / Calculated	Molecular formula	IR, ν/cm^{-1}	EAS (EtOH), λ_{max}/nm (log ε)	^1H NMR ($CDCl_3$), δ
1c	204—207 (C_6H_6)	333.1491 / 333.1477	$C_{20}H_{19}N_3O_2$	3440, 3340 (NH_2); 1670, 1640 (C=O)	255 (4.40), 281 sh (4.26), 333 sh (3.53), 472 (3.22)	3.22 (m, 4 H, H(2'), H (6')); 3.34 (m, 4 H, H (3'), H(5')); 5.49 (br.s, 2 H, NH_2); 6.92 (m, 3 H, H(3")—H(5")); 7.30 (m, 2 H, H(2"), H(6")); 7.62 (m, 2 H, H(6), H(7)); 8.02 (m, 2 H, H(5), H(8))
1d	183—185 (C_6H_6)	375.1587 / 375.1583	$C_{22}H_{21}N_3O_3$	3380 (NH); 1675, 1630 (C=O)	246 (4.35), 251 (4.35), 283 (4.28), 502 (3.50)	2.24 (s, 3 H, CH_3); 3.31 (m, 4 H, H(3'), H(5')); 3.61 (m, 4 H, H(2'), H(6')); 6.91 (m, 3 H, H(3")—H(5")); 7.25 (m, 2 H, H(2"), H(6")); 7.63 (m, 3 H, H(6), H(7)); 7.99 (m, 2 H, H(5), H(8))
2c	177—180 (precipitated by hexane from benzene)	331.1324 / 331.1321	$C_{20}H_{17}N_3O_2$	3340 (NH); 1670, 1635 (C=O)	250 (4.39), 282 (4.33), 514 (3.20)	2.80 (m, 1 H, H(2)); 2.92 (m, 2 H, H(11)); 3.52 (m, 2 H, H(12)); 3.64 (m, 1 H, H(2)); 5.40 (m, 1 H, H(3)); 6.33 (d, 1 H, NH); 6.93 (m, 3 H, H(3')—H(5')); 7.30 (m, 2 H, H(2'), H(6')); 7.63 (m, 2 H, H(7), H(8)); 8.01 (m, 2 H, H(6), H(9))
3	220—222 ($C_6H_4Cl_2$-*o*)	329.1166 / 329.1164	$C_{20}H_{15}N_3O_2$	1685, 1660 (C=O)	251 (4.70), 251 (4.70), 283 (4.19), 335 (3.49), 380 (3.06)	3.78 (t, 2 H, H(4)); 4.62 (m, 4 H, H(1), H(3)); 7.03 (m, 3 H, H(3')—H(5')); 7.33 (m, 2 H, H(2'), H(6')); 7.72 (m, 2 H, H(8), H(9)); 8.16 (m, 2 H, H(7), H(10))

to the H(4*e*) and H(4*a*) atoms in compound **13**, respectively. The multiplicities of the signals from H(3*a*), H(3*e*), and H(4a) in the spectra of these two compounds are different. The signal from H(4a) appears as a singlet in the spectrum of **16** and as a doublet of doublets in the spectrum of **13**, $^3J_{H(4a)-H(4a)} = 9.6$ Hz, $^3J_{H(4a)-H(4e)} = 2.8$ Hz). The chemical shifts and signal multiplicities from the other protons are practically equal. The chemical shifts of the signals of compounds **13** and **16** in the ^{13}C NMR spectra with complete proton decoupling are also nearly identical, and the intensity of the C(4) signal is considerably lower in the case of the thermolysis product **16**.

The difference in the structure of the thermolysis products derived from the piperazine **5** and piperidine **13** derivatives of dihydroimidazole is a result of proton (D^+) addition to different ends of the double bond of the reduced enaminoquinone **8**, that is, the structure of the product is determined by the relative stability of the two cations formed upon addition of D^+ to the double bond.

Thus, the formation of 1,2,3,4-tetrahydro-3,1-iminoethanobenzo[*g*]quinoxaline-5,10-diones during the photolysis of 2-(4-alkyl(or phenyl)piperazino)-3-amino-1,4-naphthoquinones at 80 °C is the result of three reactions: intermolecular photoreduction to give hexahydronaphthoimidazopyrazinediols, thermal recyclization of the latter affording tetrahydrobenzo[*g*]quinoxalinediols, and their subsequent oxidation by atmospheric oxygen.

Experimental

The electron absorption spectra (EAS) were recorded on a Specord UV VIS spectrophotometer in EtOH; the IR spectra were measured on a UR-20 spectrometer in $CHCl_3$ or in KBr pellets. The molecular mass and elemental composition of the compounds were determined from the accurate mass numbers for the molecular ions using a Finnigan MAT 8200 mass-spectrometer. The found and calculated values are in good agreement.

2-(4-(2'-Cyanoethyl)piperazino)-3-amino-1,4-naphthoquinone (1a) and 2-(4-benzylpiperazino)-3-amino-1,4-naphthoquinone (1b) were prepared by the procedure described in ref. 1; **2-piperidino-3-amino-1,4-naphthoquinone** was synthesized according to ref. 4.

2-(4-Phenylpiperazino)-3-amino-1,4-naphthoquinone (1c) was prepared by the alkaline hydrolysis of 3-acetylamino-2-(4-phenylpiperazino)-1,4-naphthoquinone (**1d**) (*cf.* ref. 4) and purified on a chromatographic column packed with SiO_2 (using C_6H_6 as the eluent), yield 60 %. The characteristics of **1c** and **1d**, together with those of compounds **2c** and **3** are presented in Table 1.

Photolysis procedures. *1.* A refluxed solution of 0.05 mmol of an amino-substituted quinone **1a—c** in 500 mL of absolute benzene was irradiated with a tunsten lamp (300 Wt) until the starting quinone disappeared. The solution was concentrated under reduced pressure and chromatographed on SiO_2 plates (*L* 100/160 μ) with a 4:1 benzene—acetone mixture as the eluent (system **A**, for compounds **1b,c**) or with a 4:1 chloroform—acetone mixture (system **B**, for compound **1a**).

2. Photolysis in NMR ampules ("Wilmad Glass"):

a) in the presence of atmospheric oxygen;

b) in the absence of oxygen. The quinone was dissolved in 0.5 mL of a deuterated solvent, and an argon flow was passed through this solution for 30 min, then the ampule was evacuated and sealed.

The irradiation was carried out with the light of a DRSh-500 lamp through a water filter and a ZhS-11 glass filter. The temperature of the samples submitted to irradiation was maintained by passing a controlled stream of vaporized liquid nitrogen through a Dewar tube. The temperature was monitored using a KhA thermocouple and calibration tables as disclosed in the GOST 3044-77 and ST SEV 1059-78 standards (Table 2). NMR spectra were recorded on Bruker AM-400 and Bruker AC-200 spectrometers.

2-(2-Cyanoethyl)-1,2,3,4,12,12a-hexahydronaphtho[2',3,':4,5]imidazo[1,2-*a*]pyrazine-6,11-dione (4a). ^{1}H NMR (25 °C, C_6D_6), δ: 1.41 (t, 2 H, CH_2CN); 1.60 (m, 2 H, H(1), H(1) (H(3), H(3))); 1.72 (m, 4 H, $C\underline{H}_2CH_2CN$, H(3), H(3), (H(1), H(1))); 2.77 (t, 1 H, H(4)); 3.59 (m, 1H, NH); 4.39 (d, 1H, H(12a)); 4.56 (d, 1H, H(4)); 6.98 (m, 2H, H(8), H(9)); 7.96 (m, 2H, H(7), H(10)).

2-(2-Cyanoethyl)-1,2,3,4,12,12a-hexahydronaphtho[2',3,':4,5]imidazo[1,2-*a*]pyrazine-6,11-diol (5). ^{1}H NMR (27 °C, C_6D_6—DMSO-d_6), δ: 2.31—2.72 (m, 6 H, CH_2CN, $C\underline{H}_2CH_2CN$, H(1*a*), H(3*a*)); 2.79 (m, 1 H, H(3*e*)); 3.07 (m, 1 H, H(1*e*)); 3.44 (m, 1 H, H(4*a*)); 5.05 (m, 2 H, H(12a), H(4*e*)); 5.80 (br.s, 1 H, NH); 7.39 (m, 2 H, H(8), H(9)); 8.23 (s, 1 H, OH); 8.37 (m, 2 H, H(7), H(10)); 8.55 (s, 1 H, OH).

^{1}H NMR (27 °C, C_7D_8—CD_3OD), δ: 2.40 (t, 2 H, CH_2CN); 2.49 (m, 1 H, H(1*a*)); 2.52 (m, 1 H, H(3*a*)); 2.61 (m, 2 H, CH_2CH_2CN); 2.76 (m, 1H, H(3*e*), $^2J_{H(3e)-H(3a)}$ = 10.9 Hz, $^3J_{H(3e)-H(4a)}$ = 3.1 Hz, $^3J_{H(3e)-H(4e)}$ = 2.7 Hz, $J_{H(3e)-H(1e)}$ = 1.6 Hz); 2.96 (m, 1 H, H(1*e*), $^2J_{H(1e)-H(1a)}$ = 10.2 Hz, $^3J_{H(1e)-H(12a)}$ = 3.2 Hz, $^3J_{H(1e)-H(3a)}$ = 1.6 Hz); 3.58 (m, 1 H, H(4*a*), $^2J_{H(4a)-H(4e)}$ = 13.1 Hz, $^3J_{H(4a)-H(3a)}$ = 11.6 Hz, $^3J_{H(4a)-H(3e)}$ = 3.1 Hz); 5.02 (dd, 1 H, H(12a), $^3J_{H(12a)-H(1a)}$ = 9.2 Hz, $^3J_{H(12a)-H(1e)}$ = 3.2 Hz); 5.09 (dt, 1 H, H(4*e*), $^2J_{H(4e)-H(4a)}$ = 13.1 Hz, $^3J_{H(4e)-H(3e)}$ = 2.7 Hz, $^3J_{H(4e)-H(3a)}$ = 2.7 Hz); 7.60 (m, 2 H, H(8), H(9)); 8.44 and 8.53 (both m, 2 H, H(7), H(10)).

^{13}C NMR (27 °C, C_7D_8—CD_3OD), δ: 16.11 (t, $\underline{C}H_2CN$); 46.31 (t, $\underline{C}H_2CH_2CN$); 52.34 (t, C(4)); 54.48 (t, C(3)); 58.02 (t, C(1)); 78.11 (d, C(12a)); 120.15 (s, CN); 120.96, 121.84, 123.30, and 124.20 (all d, C(7), C(8), C(9), C(10)); 125.06 and 127.97 (both s, C(5a), C(11a)); 128.48 and 128.58 (both s, C(6a), C(10a)); 129.81 and 131.61 (both s, C(6), C(11)).

1,2,3,4-Tetrahydro-13-(2-cyanoethyl)-3,1-iminoethanobenzo[*g*]quinoxaline-5,10-diol (7) was obtained by heating the photolysis product **5** in a toluene-d_8—methanol-d_3 mixture under an inert atmosphere at 80 °C for 16 h.

^{1}H NMR (25 °C, C_7D_8—CD_3OH), δ: 2.17—2.25 (m, 2 H, H(11*e*), H(11*a*)); 2.34 (t, 2 H, $C\underline{H}_2CN$); 2.41 (m, 1 H, $C\underline{H}HCH_2CN$); 2.77 (m, 1 H, $C\underline{H}HCH_2CN$); 2.81 (dt, 1 H, H(2*e*), $^2J_{H-H}$ = 12.5 Hz); 3.04 (dm, 1 H, H(12*e*)); 3.36 (dt, 1 H, H(12*a*)); 3.50 (dd, 1 H, H(2*a*), $^2J_{H-H}$ = 12.5 Hz); 4.15 (br.s, 1 H, H(3)); 7.29 and 7.48 (both m, 2 H, H(7), H(8)); 8.26 and 8.39 (both m, 2 H, H(6), H(9)).

^{13}C NMR (25 °C, C_7D_8—CD_3OH), δ: 16.89 (t, $\underline{C}H_2CN$); 44.96 (t, $\underline{C}H_2CH_2CN$); 51.34 (t, C(12)); 52.26 (t, C(2)); 54.83 (t, C(11)); 63.70 (d, C(3)); 118.30 (s, CN); 120.48 and 120.81 (both s, C(9a), C(5a)); 121.03, 121.99 123.69, and 126.30 (all d, C(6, C(7), C(8), C(9)); 127.54 (s, C(10a), C(4a)); 131.09 (s, C(5)); 142.27 (s, C(10)). The signals which were not mentioned overlap with those of the solvent. It is possible that the positions of the signals from C(5), C(10a), C(4a), C(9a), and C(5a) could be interchanged.

Isotopomers 6 were prepared by heating dihydroimidazolediol **5** in a toluene-d_8—methanol-d_4 mixture under the conditions described for the preparation of compound **7**.

^{1}H NMR of the mixture of isotopomers **6** (25 °C, C_7D_8—CD_3OD), δ: 2.07 (dd, 1 H, H(11*e*)); 2.15 (t, 2 H, $CH_2C\underline{H}_2CN$, $^3J_{H-H}$ = 7.0 Hz); 2.21 (td, 1 H, H(11*a*), $^3J_{H(11a)-H(12a)}$ = 12.7 Hz, $^2J_{H(11a)-H(11e)}$ = 12.0 Hz, $^3J_{H(11a)-H(12e)}$ = 3.6 Hz); 2.32 (m, 1 H, $C\underline{H}HCH_2CN$, $^2J_{H-H}$ = 12.7 Hz, $^3J_{H-H}$ = 7.0 Hz); 2.64 (m, 1 H, $CH\underline{H}CH_2CN$, $^2J_{H-H}$ = 12.7 Hz, $^3J_{H-H}$ = 7.0 Hz); 2.76 (m, 0.5 H, H(2*e*)); 2.97 (dd, 1 H, H(12*e*), $^2J_{H(12e)-H(12a)}$ = 13.2 Hz, $^3J_{H(12e)-H(11a)}$ = 3.6 Hz); 3.30 (td, 1 H, H(12*a*), $^2J_{H(12a)-H(12e)}$ = 13.2 Hz, $^3J_{H(12a)-H(11a)}$ = 12.7 Hz, $^3J_{H(12a)-H(11e)}$ = 3.8 Hz); 3.44 (d, 0.5 H, H(2*a*), $^3J_{H(2a)-H(3)}$ = 2.0 Hz); 4.013 (s, H(3)); 4.016 (d, H(3), $^3J_{H(3)-H(2a)}$ = 2.0 Hz)*; 7.36 and 7.55 (both m, 2 H, H(7), H(8)); 8.38 and 8.56 (both m, 2 H, H(6), H(9)).

^{13}H NMR of the mixture of isotopomers **6** (25 °C, C_7D_8—CD_3OD), δ: 16.75 t ($\underline{C}H_2CN$); 44.63 (t, $\underline{C}H_2CH_2CN$); 51.12 (t, C(12)); 54.57 (t, C(11)); 63.28 (d, C(3)); 63.35 (d, C(3)); 117.96 (s, CN); 120.09 and 120.32 (both s, C(9a), C(5a)); 120.86, 121.99, 123.68, and 126.29 (all d, C(6), C(7), C(8), C(9)); 127.28 (s, C(10a), C(4a)); 130.55 (s, C(5)); 142.03 (s, C(10)).

Table 2. Photolysis of 3-amino-2-(4-R-piperazino)-1,4-naphthoquinones

Compound	Photolysis procedure	*T*/°C	τ/h	*C*/*M* (solvent)	Reaction product (yield)
1a	*1*	80	2.5	$1.00 \cdot 10^{-3}$ (C_6H_6)	**2a** (65 %)
	2a	20	0.25	$1.29 \cdot 10^{-2}$ (C_6D_6)	**4a**
	2b	20	0.5	$1.29 \cdot 10^{-2}$ (C_6D_6)	**5***
	2b	20	0.75	$1.94 \cdot 10^{-2}$ (C_7D_8—CD_3OD)	**5**
1b	*1*	80	2	$1.00 \cdot 10^{-3}$ (C_6H_6)	**2b** (40 %)
1c	*1*	80	1.75	$1.00 \cdot 10^{-3}$ (C_6H_6)	**2c** (44 %) **3** (4 %)

* The photolysis product precipitates.

* The sum of the integrals of the H(3) signals for *endo*- and *exo*- isotopomers is equal to 1 H.

The signals from C(2) could not be detected due to the low signal/noise ratio.

1,2,3,4-Tetrahydro-13-(2-cyanoethyl)-3,1-iminoethanobenzo[*g*]quinoxaline-5,10-dione (2a). 0.050 g of quinone **1a** in 30 mL of a toluene—methanol mixture (1:1 v/v) was placed into a quartz ampule, and a flow of argon was passed through the solution for 1 h. Then the ampule was evacuated and sealed. Irradiation was carried out at 20 °C for 3.5 h according to the procedure described in ref. 2, then the reaction mixture was kept at 80 °C for 26 h. The ampule was opened, the solution was exposed to the air for 24 h, concentrated, and chromatographed on Silufol plates with a 4:1 benzene—acetone solvent mixture to give 0.045 g (90 %) of **2a**.

^{1}H NMR (27 °C, DMSO-d_6), δ: 2.08 (td 1 H, H(11*a*), $J_{H(11a)-H(11e)}$ = −11.6 Hz, $J_{H(11a)-H(12a)}$ = 12.8 Hz, $J_{H(11a)-H(12e)}$ = 3.8 Hz); 2.43 (m, 3 H, C<u>H</u>HCH$_2$CN, H(11*e*), H(2*e*), $J_{H(11e)-H(12a)}$ = 3.8 Hz, $J_{H(11e)-H(12e)}$ = 0.2 Hz, $J_{H(11e)-H(11a)}$ = −11.6 Hz); 2.71 (m, 2 H, C<u>H</u>$_2$CN); 2.83 (m, 1 H, CH<u>H</u>CH$_2$CN); 3.14 (m, 2 H, H(12*e*), H(12*a*), $J_{H(12a)-H(12e)}$ = −13.7 Hz, $J_{H(12a)-H(11a)}$ = 12.8 Hz, $J_{H(12a)-H(11e)}$ = 3.8 Hz, $J_{H(12e)-H(11a)}$ = 3.8 Hz, $J_{H(12e)-H(11e)}$ = 0.2 Hz); 3.27 (dt, 1 H, H(2*a*), $^2J_{H-H}$ = 12.3 Hz, $^3J_{H(2a)-H(3)}$ = 1.4 Hz); 4.42 (m, 1 H, H(3), $^3J_{H(3)-H(4)(NH)}$ = 4.9 Hz); 7.68 and 7.77 (both td, 2 H, H(7), H(8)); 7.92 (m, 2 H, H(6), H(9)); 8.07 (d, 1 H, NH, $^3J_{H(4)-H(3)}$ = 4.9 Hz).

^{13}C NMR (27 °C, DMSO-d_6), δ: 15.20 (t, <u>C</u>H$_2$CN); 43.56 (t, <u>C</u>H$_2$CH$_2$CN); 49.45 (t, C(12)); 50.38 (t, C(2)); 52.55 (t, C(11)); 61.59 (d, C(3)); 119.85 (CN); 124.84 (s, C(5a)); 125.40 and 125.40 (both d, C(7), C(8)); 130.41 (s, C(9a)); 132.13 and 134.38 (both d, C(6), C(9)); 132.57 (s, C(4a)); 143.65 (s, C(10a)); 176.41 and 179.54 (both s, C(10), C(5)).

1*H*-2,3,4,4a-Tetrahydronaphtho[2',3':4,5]imidazo[1,2-*a*]pyridine-6,11-diol 13 was obtained by photolysis of 2-piperidino-3-amino-1,4-naphthoquinone according to procedure 2*b*.

^{1}H NMR (25 °C, C_7D_8—CD_3OD), δ: 1.44 (m, 1 H, H(3*a*)); 1.67 (m, H(3*e*)); 1.77 (m, H(2*a*)); 1.83 (m, H(4*a*)); 1.86 (m, H(2*e*)); 1.95 (m, 1 H, H(4*e*)); 2.99 (td, 1 H, H(1*a*), $^3J_{H(1a)-H(2a)}$ = 12.2 Hz, $^2J_{H(1a)-H(1e)}$ = 12.2 Hz, $^3J_{H(1a)-H(2e)}$ = 3.1 Hz); 4.41 (dd, 1 H, H(4a), $^2J_{H(1a)-H(1e)}$ = 12.2 Hz, $^3J_{H(1a)-H(2e)}$ = 3.1 Hz); 4.41 (dd, 1 H, H(4a), $^3J_{H(4a)-H(4a)}$ = 9.6 Hz, $^3J_{H(4a)-H(2e)}$ = 2.8 Hz); 4.88 (m, H(1*e*)); 7.37 (m, 2 H, H(8), H(9)); 8.20 and 8.28 (both m, 2 H, H(7), H(10)).

Heating compound **13** in a toluene-d_8—methanol-d_4 mixture under an inert atmosphere resulted in the introduction of deuterium to position 4 (the CH_2 fragment is converted to CD_2).

^{1}H NMR spectrum of the resulting compound **16** (25 °C, C_7D_8—CD_3OD), δ: 1.42 (td, 1 H, H(3*a*)); 1.67 (m, H(3*e*)); 1.76 (m, H(2*a*)); 1.85 (m, 1 H, H(2*e*)); 2.99 (td, 1 H, H(1*a*), $^2J_{H(1a)-H(1e)}$ = 12.2 Hz, $^3J_{H(1a)-H(2a)}$ = 12.2 Hz, $^3J_{H(1a)-H(2e)}$ = 3.1 Hz); 4.39 (s, 1 H, H(4a)); 4.88 (m, H(1*e*)); 7.37 (m, 2 H, H(8), H(9)); 8.20 and 8.27 (both m, 2 H, H(7), H(10)).

^{13}C NMR spectrum of compound **16** (25 °C, C_7D_8—CD_3OD), δ: 23.88 (t, C(3)); 26.37 (t, C(2)); 48.37 (t, C(1)); 82.09 (d, C(4a)); 121.09 and 121.81 (both d, C(7), C(10)); 123.23 and 124.16 (both d, C(8), C(9)); 125.03 (s, C(6a)); 128.05, 128.34, and 128.44 (all s, C(10a), C(11), C(5a)); 131.38 and 131.42 (both s, C(11a), C(6)). The signal from C(4) could not be detected due to the low signal/noise ratio.

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