Photoreduction of oxoisoaporphines. Another example of a formal hydride-transfer mechanism

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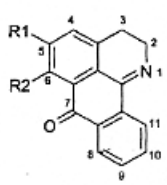
Photoreduction of 5,6-dimethoxy-, 5-methoxy- and 2,3-dihydro-7*H*-dibenzo[*de*,*h*]quinolin-7-one (**A**) by tertiary amines in oxygen-free solutions generates long-lived semi-reduced metastable photoproducts, A–NH^-, *via* a stepwise electron–proton–electron transfer mechanism with a limit quantum yield of about 0.1 at high TEA concentrations. These metastable photoproducts revert thermally to the initial oxoisoaporphine nearly quantitatively in the presence or absence of oxygen. We present spectrophotometric, NMR and UV-vis data for the metastable photoproducts. The spectrophotometric results and PM3 and ZINDO/S calculations support the proposed mechanism for the photoreduction of the oxoisoaporphines.

Introduction

In the photoreduction of several chromophoric compounds by electron donors, excited-state quenching by electron transfer from the reductant leads to transient ion–radical pairs, but, due to rapid back electron transfer, there are no permanent chemical changes.[1] For some compounds, electron-transfer quenching generates basic radical anions that are easily protonated, and semi-reduced free radicals can accumulate.[1,2] Disproportionation of the radicals can generate, among other compounds, stable or metastable products of two-electron reduction or dihydro compounds. This type of photoreaction has been reported for ketones, quinone derivatives and thioindigo dyes,[3,4] and, more recently, for quinoxalin-2-ones[5,6] and electron-deficient azaarenes.[7]

Oxoisoaporphines are a family of oxoisoquinoline-derived alkaloids that have been isolated from *Menispermaceae*, the only known natural source. Since 1983, nine oxoisoaporphines have been isolated from *Menispermun dauricum*.[8] The rhizomes of the plants are used in traditional Chinese medicine as an analgesic and antipyretic. Although some cytotoxicity studies have been published,[9] to our knowledge, these are the first photochemical studies that have been reported for these compounds, whose structure is analogous to that of some biologically relevant quinone imines.[10]

In this work, we study the photochemical behavior in the presence of amines of three synthetic oxoisoaporphine derivatives: 5-methoxy-, 5,6-dimethoxy- and 2,3-dihydro-7*H*-dibenzo[*de*,*h*]quinolin-7-one, designated compounds **A1**, **A2** and **A3**, respectively.



A1: R1 = R2 = MeO-
A2: R1 = MeO-; R2 = H-
A3: R1 = R2 = H-

In oxygen-free solutions in the presence of amines, these compounds are cleanly photoreduced to persistent metastable photoproducts. UV-vis and ^{1}H-NMR spectral data has been used to characterize the metastable photoproducts, and a mechanism for their formation is proposed.

Results and discussion

Photochemistry

The oxoisoaporphines studied do not fluoresce in solution, and are not degraded after 48 h of photolysis at 366 nm, regardless of the presence or absence of oxygen in the solution. In N_2-purged acetonitrile solutions of compounds **A1**–**A3** in the presence of amines, after a few minutes of photolysis, significant UV-vis spectral changes indicate an efficient photoreaction. However, with amines in aerated acetonitrile, the samples were unchanged after 48 h of irradiation. The lack of photoreaction in the presence of oxygen (from air) and the absence of fluorescence suggest that the photoreactions proceed mainly, if not exclusively, from the triplet manifold of the oxoisoaporphines studied.

Photoreduction of the three studied dyes in the presence of triethylamine (TEA) resulted in the rapid appearance of new absorption bands with isosbestic points in the UV-vis spectra (306 and 360 nm, 301 and 379 nm, and 360 nm in the photoreduction in the presence of TEA of **A1**, **A2** and **A3**, respectively). Isosbestic points indicate clean formation of products in a constant ratio or formation of a single product. Prolonging the photolysis time has no effect on the final spectrum of the photoreduced dye. Fig. 1 shows the spectra obtained during the

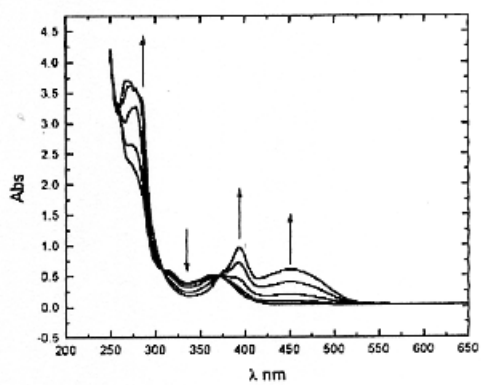


Fig. 1 UV-vis spectra obtained after 0, 1, 3, 7 and 16 min of photolysis during the photoreduction of **A2** (5×10^{-5} M) in the presence of TEA (10^{-2} M) in acetonitrile.

photoreduction of 5×10^{-5} M **A2** in the presence of 10^{-2} M TEA in acetonitrile.

Photoproduct quantum yields, ϕ_{Prod}, were measured against Aberchrome 540 by assuming a stoichiometric relationship between the initial oxoisoaporphine and the metastable photoproduct, as suggested by the isosbestic points. The procedure is described in the Experimental section. Photoproduct quantum yields depend on the molar ratio between amine and dye. When the ratio is less than or close to unity, the extent of photoreaction is nearly proportional to the amine concentration. When this ratio is greater than unity, plateau values are reached. At a ratio of TEA/dye > 100, ϕ_{Prod} values were 0.10, 0.11 and 0.09 for oxoisoaporphines **A1**, **A2** and **A3**, respectively, in N_2-purged acetonitrile.

Samples photoreduced up to total conversion and stored in darkness revert slowly and nearly quantitatively to the initial reactant within 24 to 120 h, as shown for compound **A1** in Fig. 2. The time required for total reversion is proportional to the initial concentration of photoreduced oxoisoaporphine, suggesting a bimolecular reaction, and does not depend on the amine concentration. During the recovery reaction, isosbestic points also appear, showing clean conversion of the metastable photoproduct back to the initial dye. Permanent minor spectral changes that appear at 280 nm are attributed to amine oxidation products.

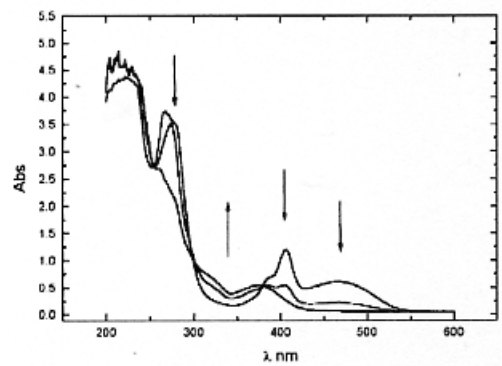


Fig. 2 UV-vis spectra of **A1** (5×10^{-5} M) photoreduced in the presence of TEA (10^{-2} M) in acetonitrile, and stored in darkness for 0, 15 and 40 h after photoreduction.

Air admitted into the reaction cell quickly converts the reaction product back to the initial oxoisoaporphine, frustrating any attempt to isolate the photoproducts. Photoreduction also occurs with other tertiary amines, such as tri-n-propylamine, tri-n-butylamine and tribenzylamine, in acetonitrile or benzene. In either solvent, the metastable photoproducts revert thermally in darkness, and more rapidly if air is admitted into the cell. However, neither secondary nor primary amines produced a reaction, probably because their oxidation potentials[11] are higher than that of TEA, preventing electron transfer to the excited oxoisoaporphine.

When photolyses were carried out in the presence of diazabicyclo[2,2,2]octane (DABCO) or 2,2-6,6-tetramethylpiperidine (TMP), whose oxidation potentials are lower than that of TEA, spectral changes were not observed, although electron transfer must take place. The radical cation of DABCO is a poor hydrogen donor and TMP has no α-hydrogen to donate; therefore, it appears that it is necessary for the amine to have a transferable α-hydrogen for generation of the metastable photoproducts to occur. When DABCO or TMP are used, back electron transfer dominates proton or hydrogen transfer from the radical cation of the amine to the dye radical anion generated in the single-electron transfer. However, hydrogen atom or proton transfer can take place when there is an α-hydrogen in the donating amine and if the latter has a suitable oxidation potential. Such coupled electron–proton transfers are known to occur in the photoreduction of several heterocyclic compounds.[5-7,12-15]

These results suggest the following mechanism: excitation of ground-state oxoisoaporphine A to the first excited singlet, A^1 (eqn. 1), followed by intersystem crossing to the lowest excited triplet, A^3 (eqn. 2). This A^3 is efficiently quenched by oxygen in aerated systems (eqn. 3). In N_2-purged systems, a single-electron transfer quenching of the first excited triplet by the amine occurs (eqn. 4), followed by competition between back electron transfer (eqn. 5) and hydrogen atom (eqn. 6) or proton (eqn. 7) transfer, in the presence of α-hydrogen amines, leading to photoreduction.

$$A \xrightarrow{h\nu} A^1 \quad (1)$$

$$A^1 \xrightarrow{k_{ISC}} A^3 \quad (2)$$

$$A^3 + O_2 \xrightarrow{k_q} \text{quenching} \quad (3)$$

$$A^3 + R_2N\text{–}CH_2R' \xrightarrow{k_{ET}} A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \quad (4)$$

$$A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \xrightarrow{k_{-ET}} A + R_2N\text{–}CH_2R' \quad (5)$$

$$A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \xrightarrow{k_H} AH^- + R_2N^+{=}CHR' \quad (6)$$

$$A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \xrightarrow{k_{H^+}} AH^{\bullet} + R_2N\text{–}C^{\bullet}HR' \quad (7)$$

If the sequence of reactions were single electron transfer (eqn. 4) followed by proton transfer (eqn. 7), the metastable photoproduct would be a radical. However, the product is too long-lived (24–120 h) to be a radical and we disregard this reaction path as an explaination for the formation of the metastable photoproduct.

It is well known that the $TEA^{\bullet+}$ radical cation is a strong acid and that its deprotonation to the neutral $Et_2N\text{–}C^{\bullet}HCH_3$ radical generates a stronger reducing agent than TEA.[16,17] A second electron transfer should take place, with the formation of AH^- and $Et_2N^+{=}CHCH_3$ (eqn. 8), resulting in a net hydride transfer.

$$AH^{\bullet} + R_2N\text{–}C^{\bullet}HR' \xrightarrow{k_{ET'}} AH^- + R_2N^+{=}CHR' \quad (8)$$

Hydrogen atom transfer (eqn. 6) would also generate the same product, but it is unlikely that H atom transfer, which requires the heterolytic cleavage of a C–H bond, can compete with the more facile stepwise transfer of H^+ followed by electron transfer (eqn. 8). The stepwise mechanism is generally accepted for photoreduction by TEA and, therefore, the same argument can be applied to other tertiary amines that can donate an α-hydrogen.

Eqn. 1 to 8 should be accompanied by back H atom transfer (eqn. 9) and by back transfer of H^+ (eqn. 10).

$$AH^- + R_2N\text{–}C^{\bullet}HR' \xrightarrow{k_{-H}} A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \quad (9)$$

$$AH^{\bullet} + R_2N\text{–}C^{\bullet}HR' \xrightarrow{k_{-H^+}} A^{\bullet-} + R_2N^{\bullet+}\text{–}CH_2R' \quad (10)$$

The primary reaction path leading to metastable products is thus suggested to be a photoinduced electron transfer (eqn. 4), followed by proton transfer (eqn. 7) and a second electron transfer (eqn. 8). Similar reactions with formal hydride transfer *via* sequential steps of electron–proton–electron transfer have been reported for several dye–amine pairs.[2-7,16,18,19]

The iminium cation formed in either eqn. 6 or 8 can react with adventitious water to form the respective aldehyde and secondary amine *via* eqn. 11.

$$R_2N^+{=}CHR' + H_2O \rightarrow R'CHO + R_2NH^+ \quad (11)$$

The relatively low quantum yields for formation of metastable photoproducts could be due to a low triplet quantum yield or to relatively efficient back electron transfer (eqn. 5).

NMR experiments

Direct photoreduction of N_2-purged solutions of **A1**, **A2** or **A3** in the presence of excess TEA ([TEA]/[oxoisoaporphine] > 10) in CD_3CN allows structural characterization of the metastable photoproducts from their ^{1}H-NMR spectra. In the first few minutes of photolysis of the TEA–**A** system, the NMR spectrum shows new signals due to metastable photoproducts.

Fig. 3 shows the evolution of the ^{1}H-NMR spectrum during the photoreduction of oxoisoaporphine **A3**. The spectra show the appearance of new broad signals that are finally resolved at $t = 70$ min, when nearly all the initial oxoisoaporphine has been converted. At this point, photolysis was discontinued because no further spectral changes were evident. The longer photolysis time used for the NMR experiments compared with that in the UV-vis experiments is due to the concentration of oxoisoaporphine used in the former and to the lower photon flux impinging on the NMR tube. The observed signal broadening may be attributed to a fast electron exchange,[20–22] probably between the paramagnetic radical $AH^{\bullet}$, formed in eqn. 7, and the anion AH^-, formed in eqn. 8. Alternatively, it is possible to attain a non-Boltzmann distribution of proton spins due to a residual chemically induced dynamic nuclear polarization,[23,24] caused by interaction between the spins of the protons of the metastable photoproduct and the spins of the unpaired electrons of the radical intermediates. However, our attempts to detect these radicals by using electronic paramagnetic resonance were unsuccessful, probably due to a very low stationary concentration of radical species. This suggests that these radicals evolve rapidly to the metastable photoproduct, in agreement with a fast electron exchange.

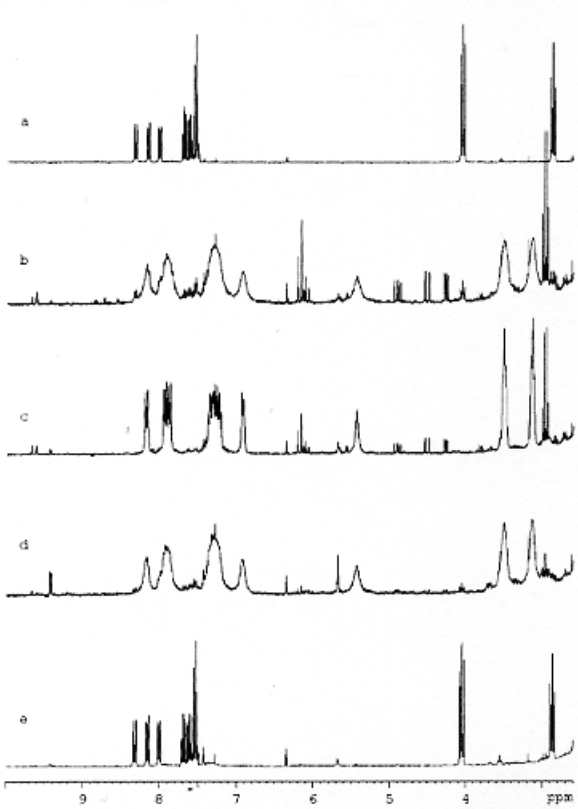


Fig. 3 ^{1}H-NMR spectra obtained during photoreduction of **A3** ($\sim 5 \times 10^{-3}$ M) in the presence of TEA ($\sim 2 \times 10^{-2}$ M) in acetonitrile-d_3: (a) photolysis time $t = 0$; (b) $t = 40$; (c) $t = 70$; (d) $t = 70$, then stored overnight in darkness; (e) $t = 70$ min, then exposed to air. The upfield shift of the aromatic proton resonances is consistent with the increased charge density of the metastable anion. The upfield shift of the C2 methylene proton signals and the downfield shift of the C3 methylene proton resonances are also evident (see text).

The new signals in the aromatic region (see Fig. 3) are assigned to the aromatic protons of the semi-reduced heterocycle. The H2 and H3 methylene proton signals shift in opposite directions, moving closer together, suggesting changes in the charge density on these carbon atoms. For **A2**, the MeO– proton signal remains at 3.85 ppm, the same occurs for **A1**, where the MeO– signals do not shift on photoreduction. The new signal that appears at 5.4 ppm, (s, 1H) for all oxoisoaporphines studied, disappear upon D_2O addition, indicating an exchangeable proton on the metastable photoproduct.

Another minor signal (quartet at 9.65 ppm) is assigned to the CHO proton of acetaldehyde, probably formed by hydrolysis of an intermediate iminium ion by adventitious water. Acetaldehyde has been observed in similar reactions.[2,6,7,18] The signals at 6.2 ppm and between 4.2 and 5.0 ppm are assigned to an oxidation product of TEA, probably formed from the iminium cation.

The ^{1}H-NMR spectra of samples stored overnight in darkness show a slow reversion to the starting material. Upon exposure to air, the NMR signals convert to those of original oxoisoaporphine **A3**, confirming essentially quantitative recovery of the starting material. A COSY experiment carried out on the photoproduct showed a correlation of the exchangeable proton signal at 5.4 ppm with that due to the H2 methylene protons (data not shown), allowing the signal at 5.4 ppm to be assigned to the N–H proton.

Experiments carried out with **A3** and tripropylamine showed the same behavior, but the signal assigned to the CHO proton is a triplet, as expected for formation of propanal. It is noteworthy that the signals between 4.2 and 5.0 ppm and at 6.2 ppm do not appear when tripropylamine is used as the reducing agent. From these data, and considering that the shift of all the aromatic proton signals to high field is consistent with an increase in charge density in the semi-reduced metastable photoproduct, we conclude that the photoproduct is the N-hydrogenated oxoisoaporphine anion (Fig. 4), the ^{1}H- and ^{13}C-NMR assignments for which are summarized in Table 1. The ^{13}C-NMR chemical shifts were obtained from HMQC bidimensional experiments.

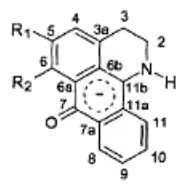


Fig. 4 Structure of the metastable photoproduct A–NH$^-$.

The broadening of the ^{1}H-NMR spectrum observed during the thermal back reaction strongly suggests the involvement of paramagnetic species, possibly radicals initiated by traces of oxygen in the medium.

Semiempirical PM3 and ZINDO/S calculations[25–29]

Molecular orbital calculations (HyperChem 6.01 software) provide more support for the structure of the metastable photoproduct. Calculated spectra, employing ZINDO/S and the PM3 minimized geometries of A–NH$^-$ anions were obtained and compared with the experimental UV-vis spectra of the semi-reduced metastable anions. Although these spectra were calculated for the isolated anions, disregarding any solvent effects, they fit nicely with the experimental spectra in respect of the

Table 1 Partial ^1H–^{13}C-NMR assignments for initial oxoisoaporphines **A2** and **A3** and the respective metastable photoproducts **A2**–NH^- and **A3**–NH^-

	A2		**A2**–NH^-		**A3**		**A3**–NH^-	
C atom[a]	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	—	—	—	—	—	—	—	—
2	4.102	48.64	3.442	41.845	4.05	48.86	3.5	42.3
3	2.927	25.896	3.067	30.851	2.86	25.29	3.15	31.39
4	7.551	108.69	7.163	96.182	7.54	132.47	6.92	120.86
5	—	—	—	—	7.52	133.88	7.23	125.24
6	7.153	120.54	6.596	114.485	8	125.55	7.93	120.48
8	8.232	127.1	7.822	121.534	8.15	127.22	7.87	122.04
9	7.682	131.64	7.202	122.763	7.61	131.69	7.29	124.06
10	7.769	134.62	7.317	124.96	7.68	134.47	7.33	125.21
11	8.403	125.28	8.109	122.31	8.32	125.39	8.17	123.26
12	3.931	56.26	3.834	55.26				

[a] Numbering of carbon atoms is as shown in Fig. 4.

maxima of the absorption bands and the oscillator strengths of the relative molar absorptions intensities at wavelengths over 300 nm, as shown in Fig. 5. Under our experimental conditions, the strong amine absorption at lower wavelengths precludes comparisons below 300 nm. The agreement between the experimental and calculated metastable photoproduct spectra can be attributed to the small changes in the dipole moment of the states involved, which precludes large solvent-induced Stokes shifts.[30]

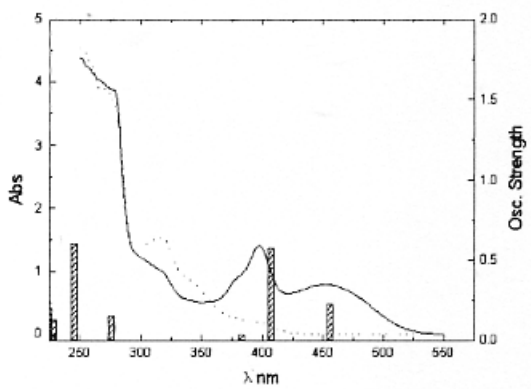


Fig. 5 Experimental UV-vis spectra of oxoisoaporphine **A3** before (···) and after (—) photolysis, and ZINDO/S calculated oscillator strengths (hatched bars).

The changes in the PM3 charge densities on C2 and C3 upon conversion of oxoisoaporphine **A3** to the corresponding **A**–NH^- anion are consistent with the NMR spectral results. Thus, the increase in charge from −0.053 to −0.096 for C2 is consistent with the upfield shift of the C2 methylene protons. For C3, the decrease in the charge density from −0.074 to −0.053 is in agreement with the downfield shift observed in the NMR spectra. For the same oxoisoaporphine and the corresponding **A**–OH^- anion, the change in charge density on C2 is in opposite directions, from −0.053 to −0.014, while that on C3 shows no change. Similar changes in the calculated charge densities were found for **A1** and **A2**, in agreement with the observed ^1H-NMR chemical shifts for the methylene protons of the corresponding photoreduced compounds.

Conclusions

For several donor–acceptor pairs, excited-state quenching proceeds *via* sequential transfer of a single electron, followed by a proton and a second electron transfer, resulting in a net hydride transfer within the quenching complex. This process leads to reactive even-electron ion pairs that are more stable kinetically than ion–radical pairs.[3] These reactions are potentially reversible, with one or both of the reactants recyclable. Nonetheless, examples are relatively rare because the reversibility of the system depends largely on the thermodynamic stabilities of the intermediates or metastable products relative to other reaction pathways.[31]

Our oxoisoaporphines behave in a similar way, with a formal hydride transfer mechanism involving eqn. 4, 7 and 8, with concomitant formation of an iminium ion from the amine. This iminium ion hydrolyzes due adventitious water to the respective aldehyde *via* eqn. 11, as shown by the NMR experiments.

Excitation of oxoisoaporphine to the photoactive triplet state (eqn. 1 and 2) in oxygen-free solution results in single-electron transfer from the amine to generate the ion–radical pair (eqn. 4). The amine radical cation, a kinetically strong acid,[17,19] donates an α-proton to the oxoisoaporphine radical anion, leading to a neutral radical pair, **A**–$NH^{\bullet}$/amine–$H^{\bullet}$ (eqn. 7). A second electron transfer forms the ion pair (eqn. 8). The low quantum yields for metastable photoproducts are probably the result of inefficient intersystem crossing or the competition of relatively efficient back electron transfer with proton transfer.

Although hydrogen abstraction from the amine radical cation should generate the same ion pair (eqn. 6), it is improbable that an homolytic breakdown of the C–H bond occurs. The amine oxidation products observed in photoreductions by TEA probably form *via* reactions between intermediate radical ions, radicals or iminium ions from reactions with the solvent or TEA.

Experimental

Acetonitrile was Merck HPLC grade and acetonitrile-d_3 (99%) was Merck spectroscopic grade, and both were used as received. Triethylamine (Fluka) and tripropylamine (Aldrich) were stored over potassium hydroxide pellets and vacuum distilled, trap to trap, sealed into glass tubes at 10^{-4} mm Hg and stored at −18 °C. 2,2,6,6-Tetramethylpiperidine (Aldrich, 99%) was also vacuum distilled and stored in sealed glass tubes. Before each experiment, a new tube was opened to ensure the freshness of the amine. DABCO (Aldrich) was used as received. The DABCO solution was prepared immediately before use.

Quantum yields

The oxoisoaporphine photoreduction quantum yield was measured by using 366 nm absorbance-matched solutions (0.6–0.8) of Aberchrome and the oxoisoaporphine–TEA system. Photoreduction quantum yields, ϕ, were calculated from the initial slopes of absorbance *vs.* time plots at 498 nm for Aberchrome and at the maximum of the lowest energy absorption of the metastable oxoisoaporphine photoproduct. Quantum yields

were calculated as follows: $\phi = [(m_{oxo}/\varepsilon_{oxo})/(m_{Aber}/\varepsilon_{Aber})] \times \phi_{Aber}$, where m_{oxo} and m_{Aber} are the initial slopes of plots of absorbance *vs.* time for the oxoisoaporphine and Aberchrome, respectively. The molar extinction coefficients, ε, were taken at the maximum of the lowest energy band of the metastable oxoisoaporphine photoproduct by comparison with extinction coefficients for fresh oxoisoaporphine. This estimation procedure is possible due to the 1 : 1 stoichiometric relationship between these species. For Aberchrome, $\varepsilon_{Aber} = 8200\ M^{-1}\ cm^{-1}$ at 498 nm, with a quantum yield of $\phi_{Aber} = 0.20$.[32,33]

General procedures for photoreduction studies

Solutions (3 ml) of oxoisoaporphine, with absorbances of between 0.20 and 1.40 at 366 nm, were purged with N_2 for 20 min in a 10 mm quartz fluorescence cell sealed with a septum. Immediately after purging, an aliquot of pure or dilute amine was added through the septum. The solutions were photolyzed with a Black Ray UV lamp equipped with a 366 nm filter, and the spectral absorbance changes with time were followed on ATI Unicam UV2 or UV4 spectrophotometers using Vision 2.11 software.

Metastable products

NMR spectral measurements were performed with a Bruker Avance DRX-300 (300 MHz) spectrometer. Reactions were carried out by direct photoreduction of N_2-purged solutions containing a weighed amount of the appropriate oxoisoaporphine and excess TEA in CD_3CN. N_2-purged solutions were prepared directly in NMR tubes and sealed with septa. During photoreduction, several ^{1}H-NMR spectra were recorded in order to test for maximum concentrations of the metastable species. COSY spectra were collected when no more changes were detected in the NMR spectra. It was not possible to obtain ^{13}C-NMR spectra of the irradiated samples due to the low concentrations of metastable photoproducts and to the reversible character of the reaction, but HMQC experiments allowed assignment of several ^{13}C resonances.

Semiempirical quantum mechanical calculations

Molecular orbital calculations were carried out using a Windows version of HyperChem 6.01 (HyperCube, Inc.) on a PC with a 466 MHz Intel Celeron processor and 256 Mb of RAM. The calculated spectra were obtained with the restricted Hartree–Fock configuration interaction, with orbital criteria using the first 5 unoccupied and 5 occupied MOs, and the proper multiplicity and weighting overlap factor values of 1.267 and 0.585 were used for σ–σ and π–π overlap, respectively.[34] The results obtained by including more MOs (10 + 10) increase the number of absorption lines in the high energy region beyond the range of UV spectrometers without affecting the spectral region of interest.

Syntheses

5,6-Dimethoxy- and 5-methoxy-2,3-dihydro-7*H*-dibenzo[*de*,*h*]-quinolin-7-one (A1 and A2). The procedure reported by Favre *et al.* was used.[35] A solution of phthalaldehydic acid in toluene was treated with homoveratrylamine or homopiperonylamine and refluxed with stirring using a Dean–Stark trap for 2 h. The resulting mixture was treated with polyphosphoric acid at 100 °C for 10 min. The red mixture was taken up in water, neutralized with NH_4OH and extracted with $CHCl_3$. The chloroform extracts were dried over anhydrous Na_2SO_4, the solvent evaporated and the residue subjected to silica gel flash chromatography. Elution with hexane–ethyl acetate 95 : 5 (v/v) gave, among other side-products, the methoxy-substituted 2,3-dihydro-7*H*-dibenzo[*de*,*h*]quinolin-7-ones **A1** and **A2** in yields of 30 and 4%, respectively. **A1**: Mp 154–155 °C. ^{1}H-NMR ($CDCl_3$): δ 2.86 (2H, t), 3.96 (3H, *s*), 3.98 (3H, *s*), 4.07 (2H, t), 7.01 (1H, s), 7.59 (1H, ddd, $J = J' = 7.33$ Hz, $J'' = 1.1$ Hz), 7.66 (1H, ddd, $J = J' = 7.29$ Hz, $J'' = 1.3$ Hz), 8.22 (1H, d, $J = 7.55$ Hz), 8.31 (1H, d, $J = 7.13$ Hz). ^{13}C-NMR ($CDCl_3$): δ 26.07, 47.98, 56.64, 61.79, 116.25, 120.23, 124.25, 124.57, 127.16, 131.01, 133.36, 133.61, 133.81, 135.62, 148.76, 155.95, 156.60, 184.09. **A2**: Mp 164–165 °C. ^{1}H-NMR ($CDCl_3$): δ 2.90 (2H, t), 3.93 (3H, s), 4.15 (2H, t), 6.99 (1H, d, $J = 2.14$ Hz), 7.59 (1H, d, $J = 2.31$ Hz), 7.61 (1H, dd, $J = J' = 7.36$ Hz), 7.70 (1H, dd, $J = J' = 6.64$ Hz), 8.28 (1H, d, $J = 7.54$ Hz), 8.39 (1H, d, $J = 7.75$ Hz). ^{13}C-NMR ($CDCl_3$): δ 25.86, 48.54, 56.10, 108.09, 120.27, 120.40, 124.94, 127.27, 130.95, 131.76, 132.33, 133.86, 136.27, 138.68, 155.65, 162.25, 184.29.

2,3-Dihydro-7*H*-dibenzo[*de*,*h*]quinolin-7-one (A3). The procedure used is that described by Walker *et al.*[36] *N*-Phenethylphthalimide was partially reduced with sodium borohydride in MeOH at room temperature and cyclized with hydrochloric acid, to give 5,6,8,12b-tetrahydro-8-isoindolo[1,2-*a*]isoquinolone (90%). The isoquinolone was then oxidized with air in the presence of NaOH/MeOH and dimethyl sulfate to afford, upon heating, 1-(2-methoxycarbonylphenyl)-3,4-dihydroisoquinoline, which was not isolated, but was directly hydrolyzed to the quinolincarboxylic acid with hydrochloric acid. By using fuming sulfuric acid at 0–5 °C, **A3** was obtained as yellowish needles and crystallized in MeOH in 69% yield. Mp 163–164 °C. ^{1}H-NMR ($CDCl_3$): δ 2.96 (2H, t), 4.20 (2H, t), 7.50 (1H, d, $J = 7.39$ Hz), 7.58 (1H, dd, $J = J' = 7.59$ Hz), 7.65 (1H, dd, $J = J' = 6.35$ Hz), 7.73 (1H, dd, $J = J' = 7.47$ Hz), 8.18 (1H, d, $J = 7.50$ Hz), 8.32 (1H, d, $J = 7.63$ Hz), 8.41 (1H, d, $J = 7.36$ Hz). ^{13}C-NMR ($CDCl_3$): δ 25.40, 48.59, 124.99, 125.84, 126.23, 127.28, 127.94, 129.90, 131.14, 131.79, 132.24, 133.05, 133.90, 136.25, 156.05, 184.31.

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