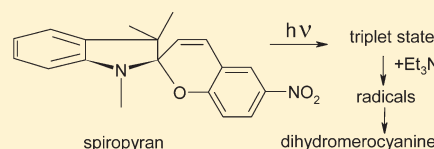


Direct Photoreduction and Ketone-Sensitized Reduction of Nitrospirobenzopyranindolines by Aliphatic Amines

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ABSTRACT: The photoreduction of 6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (N1) and two derivatives (N2 and N3) by diethylamine or triethylamine (TEA) in solution was studied by pulsed and steady-state photolysis. The quantum yield of coloration of the ring-closed Sp form, due to photoinduced ring opening, decreases in acetonitrile with increasing the TEA concentration. The main reason is reaction of TEA with the triplet-excited open merocyanine form. Quenching of this triplet state by amines is rather inefficient for N1–N3; the rate constant for triplet quenching by TEA is $k_6 = (2-3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The secondary transient with an absorption maximum at 420 nm is ascribed to the radical anion. This and the corresponding α -aminoethyl radical subsequently undergo slow termination reactions, yielding a relatively stable product with a maximum at 420–450 nm, which is attributed to a ring-opened dihydromerocyanine (MH^-). The mechanisms of the two subsequent reduction reactions are discussed. Using acetone as sensitizer the same dihydropyran product was obtained with the Sp form as acceptor, indicating a reaction sequence from photogenerated radicals via a ring-opened radical to MH^-/MH_2 . The effect of TEA concentration on the direct and ketone-sensitized reduction mechanisms was analyzed. Photoreduction by amines, due to competing triplet quenching, is strongly decreased on admission of oxygen.

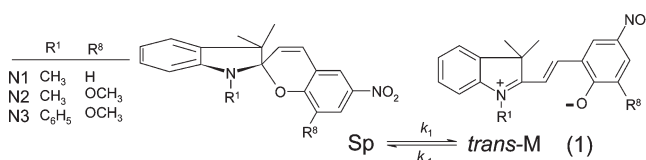


INTRODUCTION

The photochromism of spiro[2H-1-benzopyran-2,2'-indolines] and several 6-nitro-substituted derivatives (nitroS) has been intensively investigated.^{1–22} For nitroS in polar solvents at ambient temperature an equilibrium is established between the ring-closed colorless (Sp) form and the most stable isomer of the strongly colored open merocyanine forms (*trans*-M). The coloration of nitroS is strongly enhanced upon UV irradiation,^{1–5} and this ring-opening photoprocess takes place in the picosecond range.² A triplet state is involved in the photoprocesses upon excitation of the Sp form and at low temperatures also upon excitation of *trans*-M.^{1–15} The quantum yield (Φ_c) of coloration is large in solvents of low polarity; for example, in cyclohexane and toluene $\Phi_c = 0.8$ for parent 6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (N1), its 8-methoxy derivative (N2), and its 1'-phenyl derivative (N3),^{4,5} see Scheme 1. When the light is switched off, the absorbance in the red spectral range decreases and returns to its original equilibrium value. This thermal rearrangement defines a thermal relaxation time which depends on the structure, solvent, and temperature.^{1,5,15} Structural and kinetic information has also been obtained by infrared spectroscopy.¹⁶ Photochemical and thermal reactions of the ring-opened form with amino acids have been reported for a nitroS and several spirooxazines.^{17,18}

NitroS have a wide application potential.^{19–22} The use of nitroS as a photochromic system is, however, limited by the reductive or oxidative photodamage involving free radicals.^{23–28} For N2 in air-saturated toluene an oxidative photosplitting has been reported with 5-nitrovanillin as the major product of the nitrobenzene part and with 3,3-dimethyloxindol and 1,3,3-trimethyloxindol as the corresponding fragments. An increase of fatigue resistance has been found for a nitroS in aerated toluene

Scheme 1



in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), and therefore, involvement of singlet molecular oxygen and a quenching reaction by DABCO have been considered.²³ On the other hand, relatively little attention has been paid to the reduction of spiro compounds. From electrochemical studies with nitroS it is known that the radical anion has an absorption maximum at 450 nm.²⁸ It is well known that DABCO reacts with excited states of aromatic molecules via electron transfer. Electron transfer from an amine may take place also to the triplet state of nitroS. Moreover, nitrosoaromatics are known to play a role in the photoreactions of amines with nitroaromatic compounds.^{29–32} It seems therefore desirable to obtain deeper insight into the photoinduced electron transfer from amines to nitroS.

Here, the photoreduction of the ring-closed compounds N1–N3 (Scheme 1) in the presence of diethylamine (DEA) and triethylamine (TEA) were studied. A major photoproduct other than the nitroso compound was generated by electron transfer from the aliphatic amines to the observable triplet state

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of the ring-opened merocyanine, which is attributed to a dihydromerocyanine.

EXPERIMENTAL SECTION

The three nitroS were the same as used previously.^{5–8} The solvents (Merck) were of the purest spectroscopic quality, e.g., acetonitrile: Uvasol. TEA was purified by distillation, and DEA was used as received. The absorption spectra were monitored on a spectrophotometer (HP, 8453). Molar absorption coefficients of $\epsilon_{366} = 8 \times 10^3$ and $\epsilon_{604} = 3.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for Sp and *trans*-M of N1 in toluene and of $\epsilon_{580} = 4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for N2 in acetonitrile have been reported.^{5,7} For photoconversion the 366 nm line of a 1000 W Xe–Hg lamp combined with a monochromator were used. The concentration was adjusted such that the absorbance (in a 1 cm cell) was 1–3 at λ_{irr} . Conversion was carried out after vigorous bubbling by argon prior to and during irradiation.

An excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns, and energy <100 mJ) was used for excitation at 308 nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). The absorbance of neat TEA at 308 nm is ca. 1 in a 1 cm cell, but for the much lower TEA concentrations of <0.1 M used here, this has virtually no effect on the excitation of the spiro compounds since the contribution of TEA to the total absorption at 308 nm is below 1%. On the other hand, using acetone, acetophenone, or benzophenone, the sensitizer concentration was adjusted such that the contribution was 50–95% of the total absorption at 308 nm. For benzophenone/TEA (1 mM) without nitroS, the triplet state is the initial transient and the ketone radical anion is the secondary transient.³³ For benzophenone/2-propanol, the triplet is the initial transient and the ketyl radical and radical anion were identified as secondary transients at pH below 8 and at pH 10–11, respectively.³³ In all cases with ketone, TEA, and nitroS it has been verified that the initial observable transient is the ketone radical anion, keeping in mind that the ketone triplet state escapes observation in the nanoseconds time range. The secondary transient with an absorption maximum at 420–440 nm is assigned to the merocyanine radical, see below. The decay in the absence of oxygen followed second-order kinetics; the half-life ($t_{1/2}$ after subtraction of a constant part in most cases) was found to depend strongly on the amount of traces of oxygen, and the presented values refer to those after vigorous bubbling by argon. Note that this colored product formation can even be slightly enhanced by the analyzing light (on an even longer time scale). This, however, was prevented by appropriate filters. A Nd laser (GWU Lasertechnik) with $\lambda_{\text{exc}} = 354 \text{ nm}$ served as second method, but the results presented here refer to $\lambda_{\text{exc}} = 308 \text{ nm}$ only.

Electrochemical measurements were performed in an airtight cell under an argon atmosphere in anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte using a potentiostat (EG&G, 273A) with a 0.01 N AgNO_3/Ag electrode in acetonitrile as the reference electrode. Two glassy carbon disk electrodes embedded in an insulating polymer were used as working and counter electrodes, respectively. Reversibility of the reduction was determined by examination of the forward and reverse peak currents at different scan rates between 0.1 and 3 V s^{-1} . Small amounts of ferrocene were added after completion of the measurements as internal standard. The formal potentials were obtained under conditions of reversibility, are given with respect to the ferrocenium/ferrocene

Table 1. Quantum Yields of Coloration and Triplet Formation and Triplet Lifetime^a

| compd ^b | solvent | Φ_c | Φ_T | τ_T (μs) |
|--------------------|--------------|----------|----------|----------------------------|
| N1 | toluene | 0.84 | 0.9 | 10 |
| | acetonitrile | 0.16 | 0.14 | 12 |
| N2 | toluene | 0.74 | 0.77 | 12 |
| | acetonitrile | 0.20 | 0.22 | 15 |
| N3 | toluene | 0.63 | 0.72 | 12 |
| | acetonitrile | 0.14 | 0.16 | 14 |

^a In argon saturated at room temperature, $\lambda_{\text{irr}} = 366 \text{ nm}$, $\lambda_{\text{exc}} = 308 \text{ nm}$.

^b See also refs 5–8.

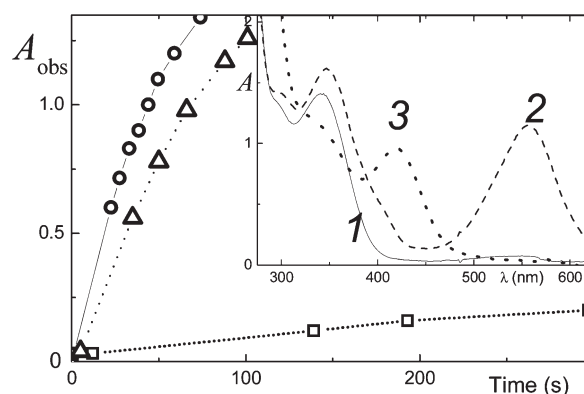


Figure 1. Plots of A_{560} of N1 in argon-saturated acetonitrile as a function of the time of irradiation at 366 nm in the presence of 0 (circles), 0.03 (triangles), and 0.2 M (squares) of TEA; (inset) spectra with 0.2 M TEA prior to (1) and after 50 s of irradiation under either air (2) or argon (3).

reference redox couple, and are converted into SCE units by addition of 0.16 V. All measurements refer to 24°C .

RESULTS AND DISCUSSION

Photoreactions of NitroS. Continuous UV irradiation of various nitroS enhances the coloration with one maximum in the UV and another (λ_t) in the red spectral range at 550–620 nm.^{1–9} The quantum yield of coloration is large for N1–N3 in benzene or toluene, $\Phi_c = 0.6$ –0.8, but relatively small, $\Phi_c = 0.1$ –0.2, in acetonitrile as an example of a nonaqueous polar solvent (Table 1). For N1 and N2 in acetonitrile, a minor part of the colored *trans*-merocyanine remains after thermal relaxation, whereas for N3 only the colorless ring-closed Sp form is present, i.e., in the latter case equilibrium 1 in Scheme 1 is shifted toward the left side. This occurs also for N1–N3 in solvents of low polarity with a maximum at $\lambda_{\text{Sp}} = 330$ –360 nm.⁵ For N1–N3 in cyclohexane or toluene, $\Phi_c = 0.7$ –0.8.^{5,7,8} For N2 in toluene $\Phi_c = 0.59^4$ and 0.84^9 have been reported. Other literature values are $\Phi_c = 0.55$ for N1 in cyclohexane¹¹ and $\Phi_c = 0.88$ for N2 in acetonitrile.¹⁰ On the other hand, Φ_c of N1–N3 is 5–10 times smaller in acetonitrile than in solvents of low polarity; the main reason is successful internal conversion prior to photoinduced ring opening.^{5–8}

Plots of the coloration as a function of the time of irradiation at $\lambda_{\text{irr}} = 366 \text{ nm}$ of N1 and N3 are shown in Figures 1–3 (circles). Similar results occur upon pulsed excitation at 308 nm. The colored merocyanine conformers have a zwitterionic or quinoid

Scheme 2

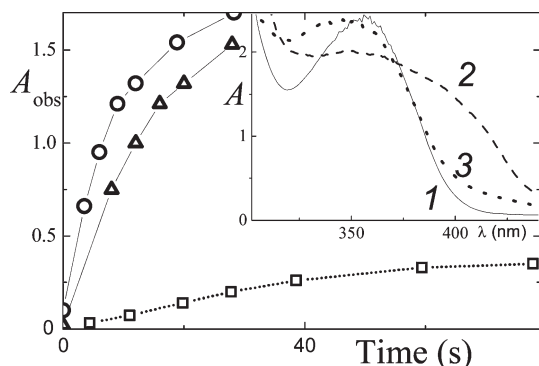
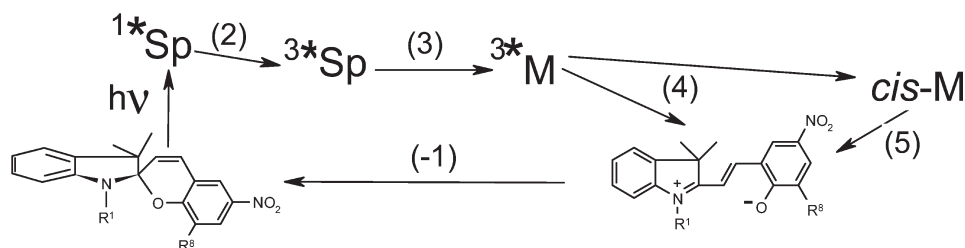


Figure 2. Plots of A_{600} of N3 in argon-saturated toluene as a function of the time of irradiation at 366 nm in the presence of 0 (circles), 0.03 (triangles), and 0.2 M (squares) of TEA; (inset) spectra with 0.2 M TEA prior to (1) and after 10 s of irradiation (2) and after 20 h (3) thermal relaxation.

character, and four conformers with the central transoid segment can a priori be expected for nitroS after thermal or photochemical cleavage of the C–O bond;^{1,2,14,16} the most stable merocyanine isomer is indicated as *trans*-M. For practical reasons N3 is favored, as the phenyl substituent strongly accelerates the thermal ring closure, in contrast to N1, where in acetonitrile the lifetime of *trans*-M is ca. 160 s.⁵ A thermal relaxation is shown in Figure 3 (full circles).

The previously suggested deactivation reactions of nitroS not involving amines are briefly summarized (Scheme 2).^{5–8,14} The first observed intermediate upon pulsed excitation at 308 nm is the triplet state of the open merocyanine (3M), generated by steps 2 and 3. It is worth mentioning that the excited singlet (1^*Sp) and lowest triplet (3Sp) states of the ring-closed form are not accessible by 10 ns photolysis. The observed 3M state decays into the ring-opened ground state *trans*-M form directly and indirectly via other isomers. One intermediate (denoted here as *cis*-M) has been detected, reactions 4 and 5 (Scheme 2).^{5,7} Here, $1-\alpha$ and $1-\beta$ are the fractions of 3M leading to *cis*-M in the absence and presence of oxygen, respectively. Quenching of 3M by oxygen (step 4') yields the *trans* and *cis* merocyanine forms in amounts which are essentially independent of the O_2 concentration, i.e., $\alpha \approx \beta$. The observed triplet state appears concomitant with the laser pulse; the decay is first order, and the lifetime is $\tau_T = 10\text{--}20\ \mu\text{s}$ in solution at room temperature. It is quenched by oxygen; the rate constant for triplet quenching is $k_{4'} = (1\text{--}3) \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$. The T–T absorption spectrum of N2 in acetonitrile, for example, shows two broad bands with maxima at 450 nm and approximately 560 nm and levels off at 700 nm. Note that the absorption coefficient of the

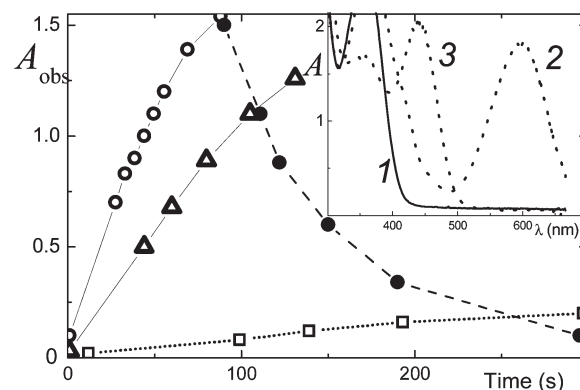
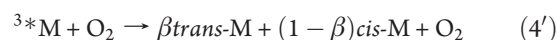
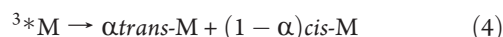


Figure 3. Plots of A_{600} (open) of N3 in argon-saturated acetonitrile as a function of the time of irradiation at 366 nm in the presence of 0 (circles), 0.03 (triangles), and 0.3 M of TEA (squares), thermal relaxation (full); (inset) spectra with 0.3 M TEA prior to (1) and after 100 s irradiation under air (2) and argon (3).

3M state at 450 nm is only 20–30% of that of the ring-opened *trans*-M form at 560–600 nm.



The quantum yield (Φ_T) of formation of the ring-opened triplet state upon UV excitation of the *Sp* form is substantial for N1–N3 in nonpolar solvents and decreases in polar solvents.⁵ The triplet quantum yields and lifetimes are compiled in Table 1. The spectrum subsequent to T–T absorption of N1–N3 in acetonitrile, showing two bands with maxima at 420 and 560–610 nm, is due to both the *trans*- and the *cis*-merocyanines. The lifetime of *cis*-M at room temperature is in the milliseconds time range.^{5–8}

Irradiation of NitroS in the Presence of Amines. Coloration of N1–N3 in argon-saturated acetonitrile, upon irradiation at 366 nm, occurs also in the presence of amines, e.g., at concentrations of 0.002–0.2 M. Nevertheless, efficient interaction of the 3M state with TEA can take place. Examples of the absorption spectra are shown in Figure 1 (inset) for N1 in argon-saturated acetonitrile in the presence of 0.2 M TEA. Φ_c decreases with the TEA or DEA concentrations. Further examples of the photo-induced absorption spectra in the presence of TEA are shown for N3 (insets of Figures 2 and 3). The TEA concentration, where Φ_c is lowered to 50% of the value in the absence of the amine, is $[\text{TEA}]_{1/2} = 0.07\text{--}0.18\ \text{M}$ (Table 2).

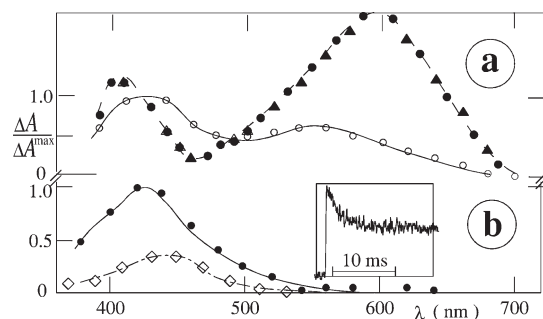


Figure 7. Transient absorption spectra of N3 in (a) air- and (b) argon-saturated acetonitrile in the presence of 0.2 M of TEA (a) at 30 ns (○), 100 μs (●), 1 ms (▲), and 0.1 s (◇) after the 308 nm pulse; (insets) kinetics at 420 nm.

cis ring-opened forms, i.e., triplet quenching by oxygen competes successfully with that by TEA. The photoinduced changes under these conditions are faster than in the absence of oxygen and mimic those in the absence of the amine. In the presence of TEA (0.03–0.1 M) formation of the triplet state of N1–N3 in argon-saturated acetonitrile occurs within the pulse width and the absorbance at 440–470 nm follows first-order decay kinetics. The intermediate, overlapping with T–T absorption and merocyanine formation, has a maximum at 420 nm and a half-life of 5–20 ms. It should be assigned to the radical anion of the merocyanine $M^{\bullet-}$. The electrochemically generated radical anion of N1 or N2 has $\lambda_{\max} = 430\text{--}455$ nm and no strong band above 500 nm.^{26,28} From pulse radiolysis of N2 in ethanol a molar absorption coefficient of $\epsilon_{450} = 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ has been reported.³⁶ For nitroS, in contrast to various other nitroaromatic compounds,^{29–32} the ϵ value of the radical anion of the acceptor is smaller than that of the triplet state.

The subsequently formed third species shows the 420–430 nm band nearly unchanged but only little absorbance in the visible range. Owing to its amplitude extending to >1 s, this species is a photoproduct. Examples for N1 and N3 in argon-saturated acetonitrile are shown in Figures 6b and 7b, respectively. The signal ΔA_{580} at 1 ms decreases on increasing the TEA concentration. From this dependence, a half-concentration was obtained. The results are in agreement with the $[\text{TEA}]_{1/2}$ values, see Table 2.

For N1–N3 in acetonitrile the rate constant k_6 for triplet quenching by TEA is ca. 3 orders of magnitude below the diffusion-controlled limit. This is consistent with the free energy change (but not in full agreement) using the Rehm–Weller relationship.³⁷

$$\Delta G_{\text{et}} = E_{\text{ox}} - E_{\text{red}} - E_{\text{T}} - E_{\text{C}}$$

Here, E_{ox} is the oxidation potential of the amine, E_{red} the reduction potential of the acceptor, E_{T} is the energy of the quenchable triplet state, and E_{C} is the Coulombic term accounting for ion pairing, 0.06 V in acetonitrile. The three nitroS in acetonitrile exhibit a reversible one-electron reduction at the same potential of $E_{\text{red}} = -1.44$ V. Literature values for N1 and N2 are $E_{\text{red}} = -1.38$ and -1.40 V, respectively.²⁸ For the level of the 3^+ *trans*-M state only a rough estimate could be made since it has to be similar to or lower than that of the fluorescent 1^+ *trans*-M state of 1.7 V. Assuming for E_{T} a value of 1.7 V and the oxidation potential of DEA with $E_{\text{ox}} = 0.7$ V, it follows that ΔG_{et} is positive (0.4 V). For the case of TEA with $E_{\text{ox}} = 0.78$ V the ΔG_{et} values of

Table 3. Reduction Potential and Rate Constant k_6 ($10^6 \text{ M}^{-1} \text{ s}^{-1}$) for Triplet Quenching^a

| compd | $-E_{\text{red}}$ (V) ^b | k_6 : TEA | k_6 : DEA |
|-------|------------------------------------|-------------|-------------|
| N1 | 1.46 (1.38) | 2.6 | 3.2 |
| N2 | 1.44 (1.38) | 2.5 | |
| N3 | 1.45 (1.37) | 3.0 | 3.4 |

^a In argon-saturated acetonitrile at room temperature, $\lambda_{\text{exc}} = 308$ nm.

^b Values vs Fc^+/Fc . In parentheses vs SCN from ref 28.

N1–N3 are slightly more positive, and therefore, the k_6 values are slightly smaller than with DEA. For other dyes some deviation from the Rehm–Weller relationship is not unusual.³⁸

Another quenching reaction was observed for N3 in air-saturated acetonitrile. It involves the ΔA_{600} value, which is constant for more than 1 s but shows a decay in the presence of DEA. The rate constant for quenching of the *trans*-M form by DEA was found to be approximately $500 \text{ M}^{-1} \text{ s}^{-1}$. This is in contrast to TEA, which does not interact with *trans*-M at all, in agreement with the slightly smaller oxidation potential of DEA. Note that such a reaction cannot be detected in argon-saturated solution since quenching step 6 decreases the yield ΔA_{600} of the *trans*-M form. Thus, the second quenching reaction by DEA has no consequences on the overall photoreduction under oxygen-free conditions.

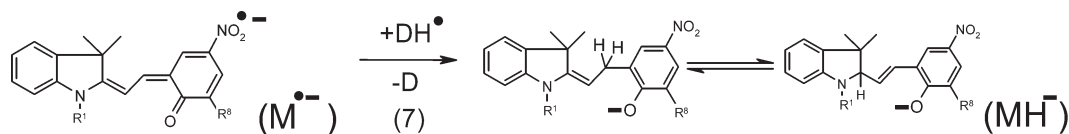
Radical Reactions. The presence of TEA gives rise to secondary transients after quenching of the triplet state. At low amine concentrations (<30 mM) the rate constant k_{obs} , due to triplet decay, shows a linear dependence on the amine concentration. The slope of this plot is $k_6 \approx (2\text{--}3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the two amines examined (Table 3). This corresponds to a TEA concentration for 50% triplet quenching of $[\text{TEA}]_{1/2} = 30\text{--}90$ mM, taking for τ_{T} an upper limit of 10 μs. At higher TEA concentrations an analysis is not possible due to increasing absorbance of the secondary transients in the appropriate range of 400–480 nm.

The transient absorption spectra of N1–N3 in acetonitrile after triplet decay reveal two or three species: The first with a maximum at 420–440 nm and a similar ϵ value as that of the T–T absorption spectrum is assigned to the merocyanine radical, one structure is shown in Scheme 4. The radical anion of N1 absorbs at 400–500 nm, whereby the ϵ_{450} value is almost as large as that of *trans*-M.²⁸ The radicals of *p*-nitrophenol in aqueous solution have two pK_{a} values, the larger one is at 9.8; the corresponding dianion radical has $\epsilon_{450} = 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.³⁹

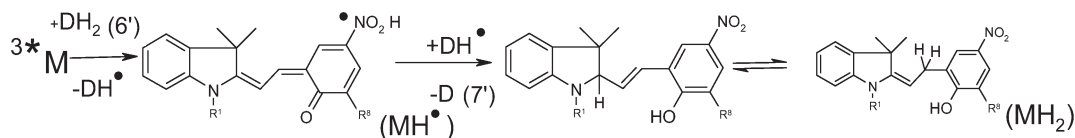
In the nitroS case, $M^{\bullet-}$ is converted into a species with a relatively large ϵ value and one characteristic band at $\lambda_{\text{H}} = 420, 440,$ and 450 nm for N1 (Figure 6b), N2, and N3 (Figure 7b), respectively. These spectra are overlapping with those of the *trans*- and *cis*-merocyanines with a major band at 380–420 nm and a minor at 550–620 nm, the yields of which are reduced on increasing TEA concentration. The stable species contains the 420–450 nm band nearly unchanged but only little absorbance in the visible range. Owing to its amplitude extending to >1 s, this species is a *p*-nitrophenolate photoproduct. From proton transfer studies of the *p*-nitrophenol/TEA system in aprotic solvents, the molar absorption coefficient in acetonitrile and 25 mM of TEA is known to be $\epsilon_{426} = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.³⁵

Et_3N^{+} , which in acetonitrile solution has a lifetime of up to a few microseconds,⁴⁰ is converted into DH^{\bullet} via deprotonation step 9. Once the α -aminoethyl radical is formed, a reaction with spiropyran/merocyanine radicals is expected, step 7

Scheme 4



Scheme 5



(Scheme 4). Thus, per one initial electron transfer (step 6) to the 3^*M triplet state two radicals should be formed. They react via an intermediate to the corresponding quasi-stable dihydromerocyanine anion $MH^{\bullet-}$, step 7. The structural identity remains open: two possible forms are shown in Scheme 4. Such a dihydro species has not been identified as yet. This assignment would be in analogy with transients observed for the photoreduction of the triplet state of nitroaromatic compounds.^{29–32}

Termination reactions of nitroaromatic radicals could, in principle, yield nitroso compounds. The observed photoproduct should, however, not be attributed to the *trans*-merocyanine nitroso form due to the too large ϵ value. One could propose that $MH^{\bullet-}$ is a species of the quinonemonoxime type.⁴¹ However, a reversible oxidation of a quinonemonoxime has not been reported. There is no obvious reason against a thermal ring closure of any *trans*-nitrosomerocyanine, whereas both structures for $MH^{\bullet-}$ shown in Scheme 4 are expected to be stable as far as oxygen is excluded. Apparently, a nitroso form is not favored vs the dihydromerocyanine anion as product, but the main reason behind this finding is not known as yet.

Most results refer to acetonitrile and the longer lived intermediates to radical ions. The photoreduction in benzene or toluene is slightly different. An example is shown in Figure 2. The reaction of the excited spiro compound with TEA could lead via electron plus proton transfer (reaction 6') to SpH^{\bullet} and MH^{\bullet} type radicals and finally (step 7') to the corresponding dihydromerocyanine/nitrophenol MH_2 , Scheme 5. For nitroaromatic compounds, an equilibrium is operating and should be on the side of the conjugate acid in nonpolar solvents and of the radical anion side in polar solvents.^{30–32} A similar situation is proposed for N1–N3.

Reduction of NitroS via Photogenerated Radicals. UV irradiation of a ketone in argon-saturated acetonitrile in the presence of both a nitroS and an aliphatic amine strongly enhances conversion to the dihydromerocyanine. Here, acetone, acetophenone, or benzophenone were applied as sensitizers. A low amine concentration of 1 mM is sufficient for this sensitized conversion of Sp to $MH^{\bullet-}/MH_2$ since the rate constant for quenching of a ketone triplet state (3^*K) by TEA or DEA is close to the diffusion-controlled limit. An example of radical-induced conversion of Sp to $MH^{\bullet-}$ is shown for N3 in the presence of acetone and TEA (Figure 8, curve 2 vs 1). Subsequent addition of

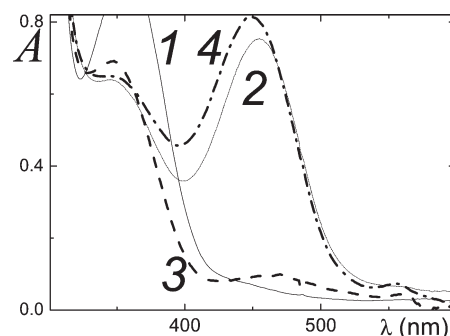


Figure 8. Absorption spectra of N3 in argon-saturated acetonitrile in the presence of 1 M acetone and 1 mM TEA (1) and after 10 s irradiation at 313 nm (2); addition of 1 mM $HClO_4$ (3) and 10 mM of TEA (4).

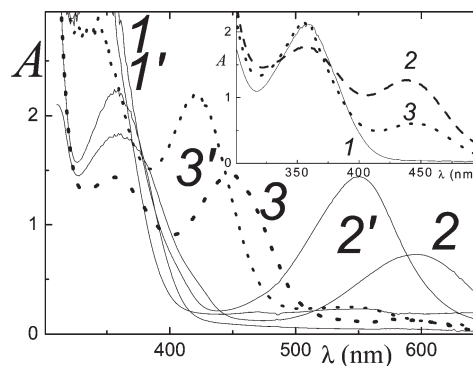


Figure 9. Absorption spectra of N1 (1') and N3 (1) in acetonitrile in the presence of 1 M acetone, 1 mM NaOH, and 1 M 2-propanol and after 9 s irradiation at 313 nm (air saturated, 2,2') and argon-saturated after 20 s irradiation (3, 3'); (inset) absorption spectra of acetone (0.2 M), TEA (50 mM), and N3 in argon-saturated acetonitrile prior to (1) and at 30 s irradiation at 313 nm (2) as well as upon air saturation and 10 min thermal relaxation (3).

$HClO_4$ causes protonation of $MH^{\bullet-}$ (curve 3 vs 2). Finally, deprotonation of MH_2 can be achieved by addition of more TEA (curve 4 vs 3). The product $MH^{\bullet-}$ with a peak at $\lambda_H = 450$ nm disappears at pH below 8, whereas MH_2 is present or appears at pH 10–11.

Alternatively, an alcohol concentration of 0.1 M is sufficient for 2-propanol as donor since the rate constant for quenching of

Scheme 6

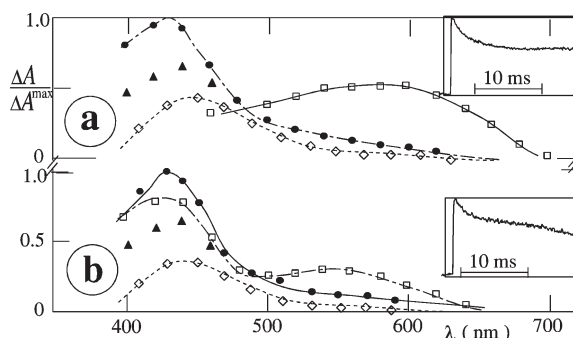
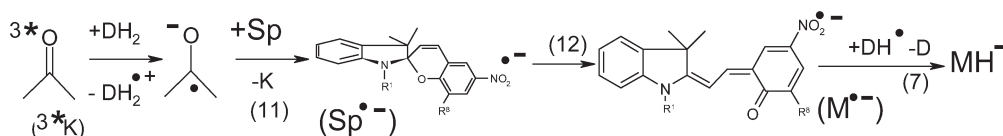


Figure 10. Transient absorption spectra of N3 in argon-saturated acetonitrile in the presence of 1 mM of TEA at 10 μ s (\square), 100 μ s (\bullet), 1 ms (\blacktriangle), and 0.1 s (\diamond) after excitation of (a) benzophenone and (b) acetone by the 308 nm pulse; (insets) kinetics at 430 nm.

the triplet state of benzophenone by 2-propanol is ca. $10^6 \text{ M}^{-1} \text{ s}^{-1}$. Examples are shown in Figure 9. UV irradiation of air-saturated acetone in the presence of N1 (curve 2') or N3 (curve 2), NaOH, and 2-propanol yields essentially the ring-opened merocyanine via step 4'. In contrast, exclusion of oxygen yields MH^- with $\lambda_{\text{H}} = 428$ and 450 nm, respectively (curves 3', 3). Oxidation reaction 10 is, in principle, possible for dihydro photoproducts. Such a thermal back-reaction of 50% within 10 min after air saturation is shown in Figure 9 (inset curve 3 vs 2).

The time-resolved excitation of acetone, acetophenone, or benzophenone in argon-saturated acetonitrile in the presence of TEA yields a radical anion of the ketone ($\text{K}^{\bullet-}$) which reacts with the ring-closed Sp form to form longer-lived radical anions and eventually the product MH^- . Examples are shown in Figure 10a for N3 with benzophenone and 10b with acetone. The ketone-sensitized reduction mechanism including steps 11 and 12 is suggested, see Scheme 6. The first electron transfer leads via the ketone triplet to the ring-closed radical anion ($\text{Sp}^{\bullet-}$). Ring opening and a second electron transfer should lead to the dihydromerocyanine/nitrophenolate.

CONCLUSION

The photoreduction of three 6-nitrospirobenzopyranindolines involves the lowest triplet state of the merocyanine form. Electron transfer from the amine to this triplet state in acetonitrile leads to the radical anion of the merocyanine form. In toluene or benzene an H-adduct radical is the secondary transient. These nitrospirobenzopyran radicals and the amine-derived radical, at least under conditions of pulsed excitation, react bimolecularly to produce the nitrophenol(ate) photoproducts. The photoreduction steps occur in substantial yield, as long as the TEA or DEA concentrations are large enough and oxygen is carefully excluded. The same dihydroproduct was obtained upon excitation of a ketone, indicating a reaction sequence involving the photogenerated ketone and merocyanine radicals. The

strong enhancement of the product yield upon sensitized reduction is ascribed to the low triplet yield upon direct excitation in polar solvents.

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