Oxidation of aryl-substituted cycloheptatrienes by photoinduced electron transfer

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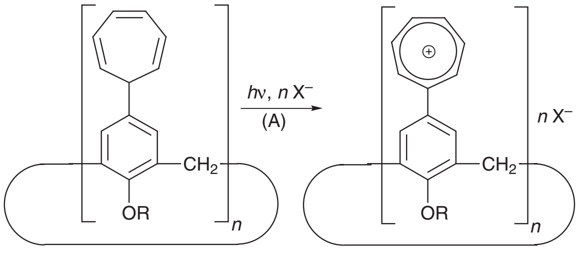
The photooxidation of the aryl-substituted cycloheptatrienes 7-(*p*-methoxyphenyl)cycloheptatriene (**1a**), 7-, 1- and 3-(*p*-dimethylaminophenyl)cycloheptatriene (**1b**, **1c** and **1d**) in deaerated acetonitrile solution at room temperature to the corresponding radical cations is accomplished by electron transfer to the electronically excited acceptors 9,10-dicyanoanthracene (**A2**), *N*-methylquinolinium perchlorate (**A3**), *N*-methylacridinium perchlorate (**A4**), 2,4,6-triphenylpyrylium tetrafluoroborate (**A5**) and 1,1′-dimethyl-4,4′-bipyridinium dichloride (**A6**). In the case of **1** back electron transfer is unimportant**.** The primarily formed radical cation deprotonates and the resultant cycloheptatrienyl radical undergoes a self reaction thus forming bitropyl. By contrast, **1b**, **1c** and, **1d** decompose only very slightly, bitropyl is not formed and the acceptors are not consumed.

Notably, the photooxidation of **1a** in air-saturated acetonitrile solution containing HBF_4 (3.2×10^{-2} M) and one of the acceptors results in the formation of tropylium salt. A tentative mechanism for this process is postulated.

Introduction

Recently, it has been shown that arylbitropyls can be transformed into the related tropylium cations *via* the radical cations of bitropyls generated by photoinduced electron transfer.[1] In the case of an aryl-substituted cycloheptatriene **1** cleavage of one C–H bond in the seven-membered ring has to proceed in order to enable a second oxidation step yielding the aryltropylium ion. Commonly, deprotonation of radical cations is observed.[2]

The generation of aryltropylium ions from arylcycloheptatrienes is of special interest because various molecular properties such as shape, color and electron acceptor strength of the cycloheptatrienes differ strongly from those of the tropylium cations. Accordingly, the properties of macrocycles[3] illustrated in Scheme 1 and supramolecular systems such as rotaxanes and catenanes containing cycloheptatriene building blocks are expected to undergo significant changes in response to the absorption of light.



Scheme 1

Recently, the oxidation of 7-(*p*-methoxyphenyl)cyclohepta-1,3,5-triene (**1a**) induced by electron transfer to photo-excited triphenylpyrylium ion (**A5**) or to photo-excited *p*-benzoquinone (**A1**), was studied[4] and it turned out that the tropylium ion was formed in the case of **A5** provided that the UV-irradiation was performed in aerated solution containing HBF_4. This finding has prompted us to study in some detail the donor behavior of arylcycloheptatrienes during the electron transfer to electronically excited acceptors in order to get insight into the mechanism of the stepwise oxidation of cycloheptatrienes to tropylium salts. The experiments comprised various electron acceptors and apart from **1a** also 7-, 1- and 3-(*p*-dimethylaminophenyl)-cyclohepta-1,3,5-triene (**1b**, **1c** and **1d**). The chemical structures of these compounds are illustrated in Chart 1.

Since the singlet and triplet energies of the acceptors listed in Chart 1 are lower than those of the arylcycloheptatrienes, energy transfer from electronically excited **A** to **1**, *i.e.* the reaction $\mathbf{A}^* + \mathbf{1} \rightarrow \mathbf{A} + \mathbf{1}^*$, can be excluded. Therefore, any observable photoreaction between the reactants suggests the occurrence of electron transfer. Actually, electron transfer is quite feasible in these cases as can be inferred from the free energy change ΔG^0_{et} which is estimated with the aid of the Rehm–Weller equation (1).[5] Here, the Coulomb term is

$$\Delta G^0_{et} = E^0_{ox}(\mathbf{1}) - E^0_{red}(\mathbf{A}) - E_{S\,or\,T}(\mathbf{A}) \qquad (1)$$

neglected. $E^0_{ox}(\mathbf{1})$ and $E^0_{red}(\mathbf{A})$ denote the oxidation and the reduction potential of **1** and **A**, respectively. $E_{S\,or\,T}(\mathbf{A})$ is the singlet or triplet energy of electronically excited **A**. Relevant values of E^0_{ox}, E^0_{red} and $E_{S\,or\,T}$ are compiled in Table 1 and from Table 2 it can be seen that in all cases electron transfer from **1** to **A*** is highly exergonic and, therefore, its occurrence is quite feasible.

The photo-induced electron transfer (PET) from **1** to electronically excited **A** results in the formation of the radical ions $\mathbf{1}^{\cdot+}$ and $\mathbf{A}^{\cdot-}$, as is depicted in Scheme 2. Back electron transfer (BET) from the reduced electron acceptor to the cycloheptatriene radical cation is prevented if the latter undergoes fast deprotonation thus forming radical $\mathbf{1}^{\cdot}$. Provided a suitable electron acceptor **X** is present radical $\mathbf{1}^{\cdot}$ can be oxidized to the tropylium ion **3**.

Regarding the experiments described below it was intended to study the photo-reactivity of the acceptors listed in Chart 1 towards arylcycloheptatrienes with the aid of fluorescence measurements. Moreover, we tried to detect intermediates by applying the flash photolysis technique and to identify final products by product analysis studies in conjunction with continuous irradiations.

Table 1a Reduction potentials,[a] excitation energies and selected extinction coefficients of acceptors

	A1	A2	A3	A4	A5	A6
E^0_{red}/V (*vs.* SCE)	−0.62	−0.89[c]	−0.85	−0.58	−0.50	−0.45
E_{00}/eV	2.25 (T)[b]	2.86[c]	3.53[d]	2.77[e]	2.82 (S)[f] 2.30 (T)[c]	3.08 (T)[c]
$\varepsilon_{347\ nm}$/M^{-1} cm^{-1}		2.37×10^3			3.28×10^4	

[a] Own measurements (SCE) unless otherwise noted. [b] Ref. 8. [c] Ref. 29. [d] Ref. 24. [e] Ref. 30. [f] Ref. 31.

Table 1b Oxidation potentials and extinction coefficients of cycloheptatrienes

	1a	1b	1c	1d	2b (3,3′)	cyclohepta-1,3,5-triene
$E_p{}^a$/V[a] (*vs.* SCE)	1.23	0.60	0.55	0.52	0.55	1.43
$\varepsilon_{347\ nm}$/M^{-1} cm^{-1}	≈0	121.3				

[a] Peak potential measured *vs.* the saturated calomel electrode (SCE) calibrated *vs.* the ferrocene/ferrocenium couple (0. 31 V).

Table 2 ΔG_{et} (in eV) of the photo-induced electron transfer from **1** to excited acceptors and of the thermal electron transfer from cycloheptatrienyl type radicals to acceptors in the ground state

	A1	A2	A3	A4	A5	A6
1a	−0.4 (T)	−0.7 (S)	−1.5 (S)	−1.0 (S)	−1.1 (S) −0.6 (T)	−1.4 (T)
1b	−1.0 (T)	−1.4 (S)	−2.1 (S)	−1.6 (S)	−1.7 (S) −1.2 (S)	−2.0 (T)
1a$^\bullet$	0.26	0.53	0.49	0.22	0.14	0.09
1b$^\bullet$	0.11	0.38	0.34	0.07	−0.01	−0.06

Calculated according to eqn. (1) with the aid of the oxidation peak potentials listed in Table 1.

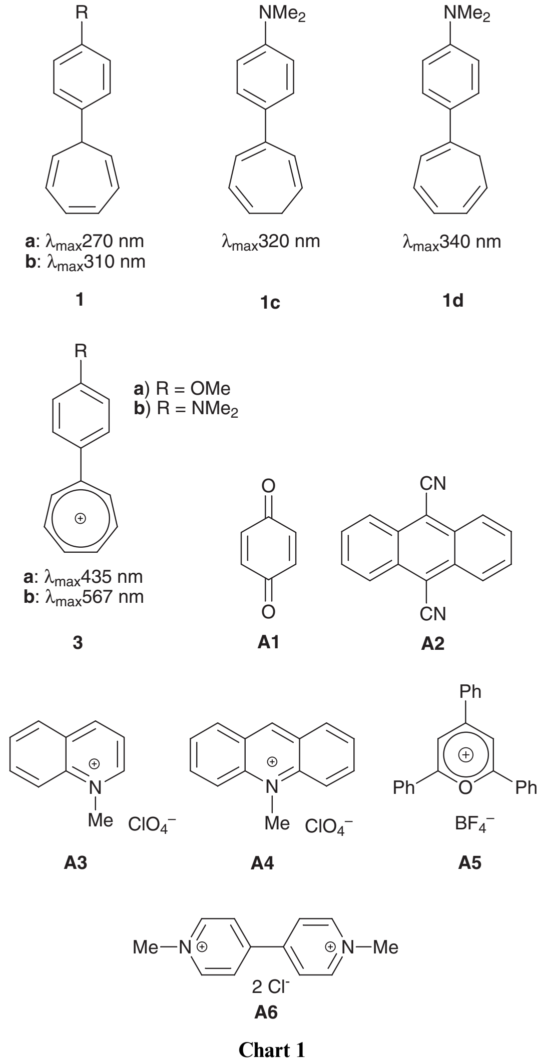
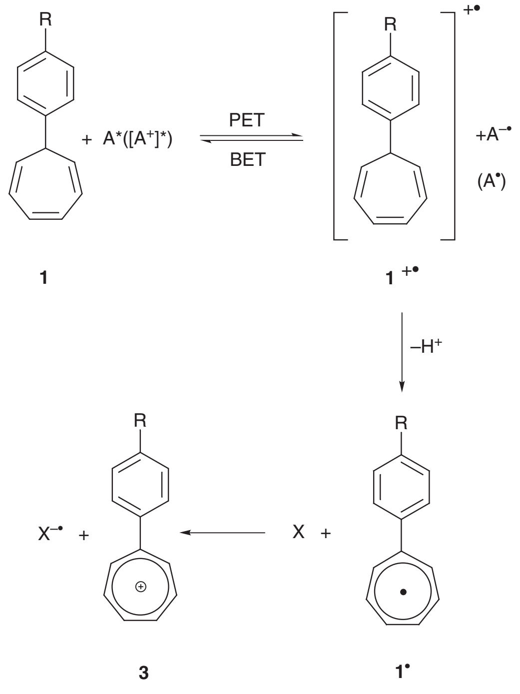


Chart 1



Scheme 2

Results

1. Fluorescence quenching

Experiments performed at room temperature with acetonitrile solutions of the acceptors **A2**, **A3**, **A4** and **A5** showed that the fluorescence of these compounds is effectively quenched by both **1a** and **1b**. In the cases of **A2** and **A5** the dependence of the fluorescence intensity on the quencher concentration was measured. Stern–Volmer plots yielded straight lines and the following rate constants k_q in M^{-1} s^{-1} are obtained with τ_S(**A2**) = 16 ns[6] and τ_S(**A5**) = 4.2 ns[7]: 1×10^{10} (**A2**/**1a**), 2×10^{10} (**A2**/**1b**),

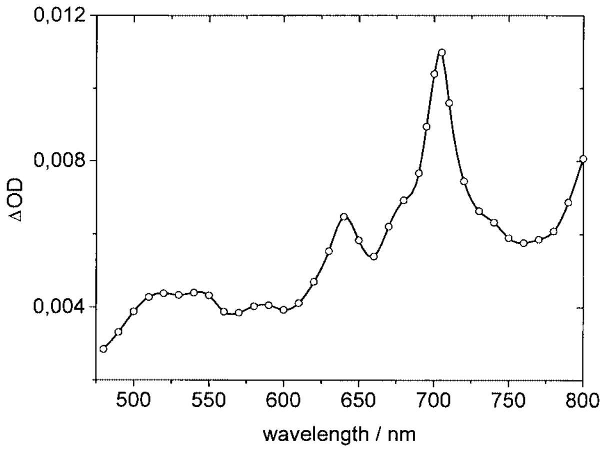


Fig. 1 Transient absorption spectrum observed at the flash photolysis of **A2** (2.5×10^{-4} M) in deaerated acetonitrile solution containing **1a** (6×10^{-3} M). The spectrum was recorded 200 ns after the laser pulse.

3×10^{10} (**A5**/**1a** and **A5**/**1b**). These values are close to that calculated for encounter-controlled processes in acetonitrile at room temperature (1.9×10^{10}).[8] From these results it can be inferred that electron transfer occurs quite effectively.

2. Flash photolysis

The aim of these experiments was to detect radical ions or radicals that were expected to be formed according to the general mechanism depicted in Scheme 2 upon electron transfer from **1a** or **1b** to electronically excited non-ionic or ionic acceptors. For this purpose the non-ionic acceptor **A2** and the ionic acceptor **A5** were selected as typical representatives of the two acceptor classes and exposed to 20 ns flashes of 347 nm light in argon-saturated acetonitrile solutions. The donor concentrations were chosen low enough to guarantee that the photolyzing light was totally or almost totally absorbed by the acceptor.

2.1 Experiments with A2. Fig. 1 shows the transient absorption spectrum recorded with the system **1a**/**A2** at the end of the flash. It has maxima at about 640 nm and 705 nm and resembles fairly well the spectrum of the radical anion of **A2** reported in the literature.[9] Obviously, electron transfer from **1a** to **A2*** occurs, but only the spectrum of the radical anion $\mathbf{A2}^{\bullet-}$ and not that of the radical cation $\mathbf{1a}^{\bullet+}$ is detectable.

The formation of ionic species upon the reaction of **A2*** with **1a** was substantiated by electrical conductivity measurements. Simultaneously with the formation of the absorption due to $\mathbf{A2}^{\bullet-}$ a current was formed. Actually, a photocurrent was also formed when **A2** was irradiated in the absence of **1a** with a 20 ns flash of 347 nm light. In this case light absorption induces the ejection of an electron from excited **A2** molecules, *i.e.* some of the excited **A2** molecules undergo photoionization [eqn. (2)].

$$\mathbf{A2}^* \longrightarrow \mathbf{A2}^{\bullet+} + e^- \qquad (2)$$

Notably, the photocurrent was significantly increased when **1a** was present in the solution indicating that the reaction of **A2*** with **1a** results in the formation of ionic species. Both the decay of the photocurrent and the decay of the intermediate radical anion of **A2** follow second order kinetics. The rate constant of the decay of the radical anion of **A2** was determined to be 3×10^8 M^{-1} s^{-1} ($\varepsilon = 7700$ M^{-1} cm^{-1} for $\mathbf{2}^{\bullet-}$ [10]).

2.2 Experiments with A5. Upon absorption of light the 2,4,6-triphenylpyrylium cation (**A5**) is known to be transformed to the long-lived excited triplet state ^{3}**A5*** with a rather high yield. Reportedly, the intersystem crossing and fluorescence quantum yields and the triplet and singlet lifetimes are: $\Phi_{ISC} = 0.48$ and $\Phi_F = 0.52$, and $\tau_T = 10$ µs[11] and $\tau_S = 4.2$ ns.[7] Interestingly, both excited states ^{1}**A5** and ^{3}**A5** can act as electron acceptors with appropriate donors. At sufficiently low donor concentration only triplet quenching occurs whereas both singlets and triplets are quenched at substantially high donor concentration. The absorption spectrum of the 2,4,6-triphenylpyranyl radical ($\mathbf{A5}^{\bullet}$) generated in this process possesses a broad absorption band extending from about 440 to 600 nm with a peak around 540 nm.[12] At the rather high concentration of 2.2×10^{-3} M **1a** acts as a quencher of both excited states and the transient absorption spectrum recorded 2 µs after the 20 ns flash (*vide* Fig. 2) is identical with the absorption spectrum of $\mathbf{A5}^{\bullet}$ reported in the literature. Apart from the band assigned to $\mathbf{A5}^{\bullet}$ the transient absorption spectrum also exhibits a negative peak at about 410 nm indicating bleaching of the strong absorption band of **A5** located at this wavelength.

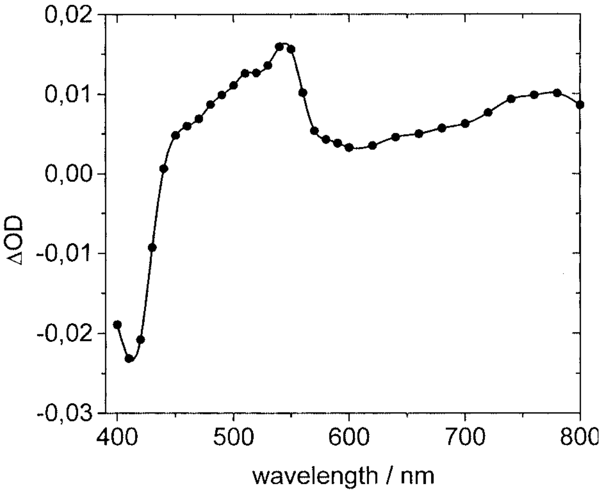


Fig. 2 Transient absorption spectrum observed at the flash photolysis of **A5** (2×10^{-5} M) in deaerated acetonitrile solution containing **1a** (2.2×10^{-3} M). The spectrum was recorded 800 ns after the laser pulse.

At low concentration of **1a** the characteristic optical absorption of ^{3}A5* between 600 and 800 nm[11] was observed. In the absence of **1a** the triplet lifetime (measured at 750 nm) was 11.6 µs. It decreased with increasing concentration of **1a** and on the basis of the concentration dependence of the 1st order halflife the rate constant k_q (^{3}**A5*** + **1a**) = 5×10^9 M^{-1} s^{-1} was obtained.

In another experiment performed with **1b** at a rather low concentration (1.9×10^{-5} M) the transient absorption spectrum shown in Fig. 3 was recorded 1 µs after the flash. Apart from the absorption band at $\lambda < 600$ nm this spectrum also contains a rather strong band at $\lambda > 600$ nm with an intensity steadily increasing up to the experimentally accessible limit (800 nm). This part of the spectrum is assigned to the triplet state ^{3}**A5***. Reportedly, the absorption spectrum of ^{3}**A5*** possesses a maximum at 850 nm.[13] Fig. 3 also shows kinetic traces recorded at 410, 540 and 790 nm. It can be seen that the bleached absorption band at 410 nm recovers with a rate equal to the decay rate of the triplet–triplet absorption at 790 nm. On the other hand it is noticeable that the absorption at 540 nm does not decrease down to zero, as does the absorption at 790 nm, but approaches a level definitely above zero. This indicates that $\mathbf{A5}^{\bullet}$ is formed concomitantly with the decay of ^{3}**A5***.

2.3 Conclusions of the flash photolysis experiments. The results described above yield evidence for the formation of the radical anion $\mathbf{A2}^{\bullet-}$ in solutions containing **A2** and of the radical $\mathbf{A5}^{\bullet}$ in solutions containing **A5**. These intermediates are expected to be formed upon electron transfer from **1a** and **1b** to these acceptors. In both cases, it was, however, not possible

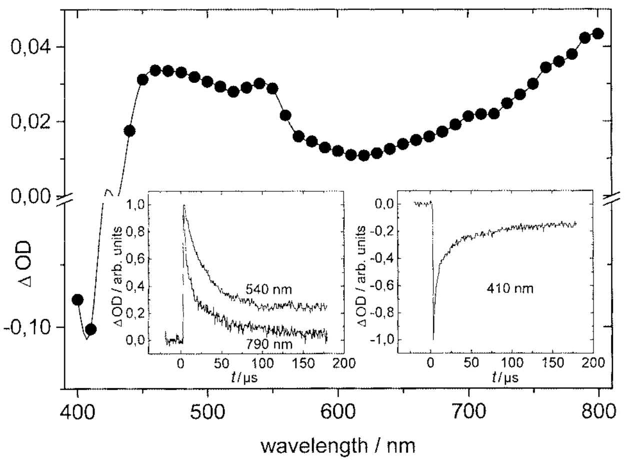


Fig. 3 Transient absorption spectrum observed at the flash photolysis of **A5** (1.9×10^{-5} M) in deaerated acetonitrile solution containing **1b** (2×10^{-5} M). The spectrum was recorded 1 μs after the laser pulse. Insets: kinetic traces depicting the decay of the optical density at 410 nm, 540 nm and 790 nm.

to detect the corresponding radical cations or intermediates resulting from reactions of the radical cations.

3. Continuous irradiations

3.1 Photoexcitation in the absence of oxygen and acid. *3.1.2 HPLC Measurements.* Degassed acetonitrile solutions containing **1a** or **1b** and **A2**, **A4** or **A5** were irradiated with UV light at λ_{inc} = 365 or 405 nm, where **A** only is excited, and the progress of the reaction was followed by high pressure liquid chromatography (HPLC). In all experiments performed with **1a** bitropyls **2a** were formed in high yield. Isomers of **2a** were identified with the help of authentic samples. By contrast, bitropyl was not formed when solutions containing **1b** and **A** were irradiated. In this case, the HPLC analysis revealed that the acceptors are photostable. **1b** was slightly decomposed, but the conversion was too low to detect reaction products.

3.1.2 EPR Measurements. As pointed out above (Section 2.3) the radical cations of **1a** and **1b** were not detectable in the flash photolysis experiments. The existence of $\mathbf{1b}^{\bullet+}$ could be evidenced, however, when EPR measurements were performed with the system **1b**/**A4** in another solvent (dioxane–hexafluoropropan-2-ol, 75/25, v/v) at −60 °C. As can be seen from Fig. 4 the EPR spectrum recorded upon irradiation of the solution with the unfiltered light of a Hg/Xe-lamp compares fairly well with the simulated spectrum of $\mathbf{1b}^{\bullet+}$ (obtained with the aid of the program Compar 2). Apparently, the spectrum of $\mathbf{1b}^{\bullet+}$ does not have the spectrum of the acridinyl radical $\mathbf{A4}^{\bullet}$, which is generated simultaneously with $\mathbf{1b}^{\bullet+}$, superimposed onto it, because $\mathbf{A4}^{\bullet}$ dimerizes rapidly.[14]

3.2 Photoexcitation in the presence of oxygen and acid. Irradiation of air-saturated acetonitrile solutions containing **1a** and **A2**, **A3**, **A4** or **A5** and in addition HBF_4 (3.2×10^{-2} M) at λ_{inc} = 365 or 405 nm resulted in the formation of tropylium ion **3a** and H_2O_2 (detected according to the method of Fukuzumi *et al.*[15]). Typical results are shown in Fig. 5 where optical absorption spectra of the system **1a**/**A4** recorded before and after irradiation for given times are presented. Obviously, the bands characteristic of the tropylium ion at 230, 275 and 430 nm grow with increasing time of irradiation.

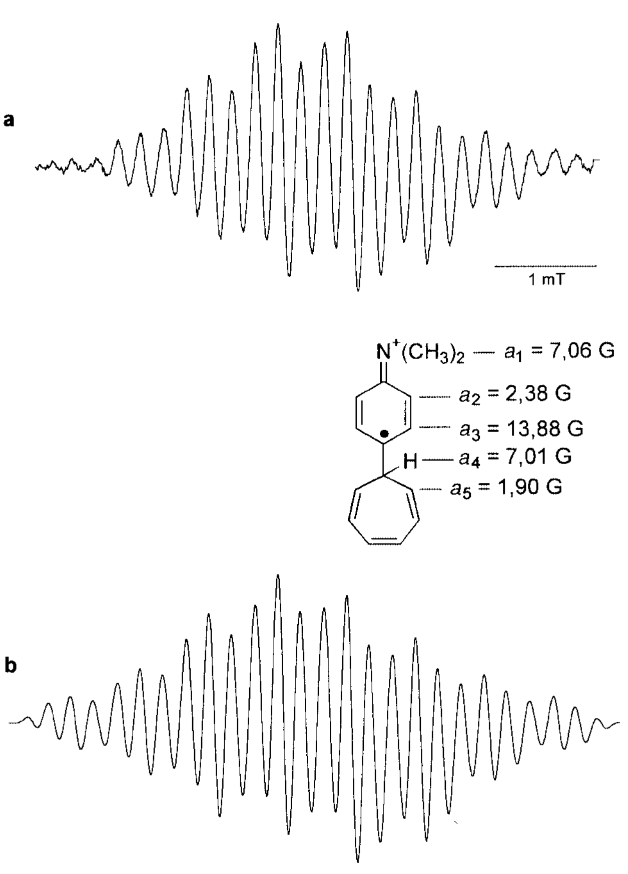


Fig. 4 EPR spectra. (**a**) Spectrum recorded at −60 °C with the system **1b**/**A4** in deaerated solution, [**1b**] = 6×10^{-2} M, [**A4**] = 3×10^{-2} M. Solvent: dioxane–hexafluoropropan-2-ol (75/25, v/v). (**b**) Spectrum of the radical cation $\mathbf{1b}^{\bullet+}$ simulated (program Compar 2) on the basis of the hyperfine coupling constants given in the graph.

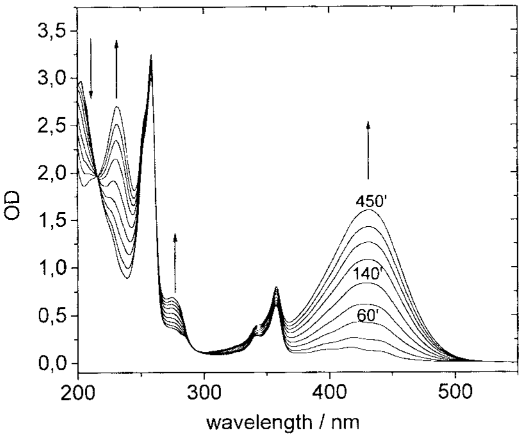


Fig. 5 Optical absorption spectra observed at the photooxidation of **1a** (8×10^{-5} M) upon irradiation of **A4** (3×10^{-5} M) in air-saturated acetonitrile solution containing HBF_4 (3.2×10^{-2} M).

On the other hand, the intensity of the bands characteristic of **A4** at 250 nm and 360 nm does not decrease simultaneously with the increase in the absorption due to the tropylium ion indicating that the acceptor is not consumed. Actually, the bands at 250 nm and 360 nm become larger to some extent. This increase is assigned to the contributions of the absorption of the tropylium ion to the total absorption at these wavelengths. In this respect it is notable that analogous observations (according to UV-Vis and HPLC-studies) were made with the other acceptors used in these experiments (**A2**, **A3** and **A5**), *i.e.* they were not consumed while **3a** and H_2O_2 were formed. Notably, **3a** was not formed in air-equilibrated solutions in the absence of protons.

The quantum yield of the formation of **3a**, Φ(**3a**), was measured in the case of the system **1a**/**A5** and it turned out (see Fig. 6, inset) that Φ(**3a**) increases with increasing concentration of **1a** and eventually approaches a limiting value of about 0.3. Moreover, it can be seen from Fig. 6 that the reciprocal quantum yield depends linearly on the reciprocal concentration of **1a**.

Discussion

1. Photooxidation in the absence of oxygen and acid

The photoinduced electron transfer from **1** to electronically excited acceptors **A** is expected to be favored in all cases according to the free energy change ΔG^0_{et} calculated with the aid of eqn. (1) (*vide* Table 2). Indeed, the occurrence of a fast reaction between photo-excited acceptors **A2** and **A5** and the donors **1a** and **1b** was evidenced by the results of the flash photolysis and the fluorescence quenching experiments, and this fast reaction is very likely to involve electron transfer. The fact that time resolved absorption spectroscopy permitted the detection of radical anions or radicals only and not that of the corresponding radical cations is puzzling. Probably, the absorptivity of the radical cations is low and, therefore, the transient optical absorption spectra of these species are relatively weak, *i.e.* undetectable in the present work. In the case of systems of type **1a/A** evidence for the generation of radical cations $\mathbf{1}^{\cdot+}$ comes from the product analysis studies according to which **2a** is formed in high yield. According to the mechanism presented in Scheme 3 radical cations $\mathbf{1a}^{\cdot+}$ deprotonate rapidly and the cycloheptatrienyl radicals generated in this way combine thus forming **2a**. Actually, the fate of the radical cation $\mathbf{1}^{\cdot+}$ depends on the competition between various reactions. Apart from deprotonation it can undergo addition to the solvent, dimerization and back electron transfer. Regarding deprotonation a prognosis on the basis of pK_a-values of the radical cations $\mathbf{1}^{\cdot+}$ is not possible since those values are not accessible. On the other hand, the deprotonation of $\mathbf{1a}^{\cdot+}$ must be an important process, provided the mechanism depicted in Scheme 3 holds, since **2a** is formed in a high yield. Analogously, it is concluded that back electron transfer is unimportant in this case. Principally, the radical $\mathbf{1a}^{\cdot}$ could be converted to **3a** provided the acceptor (in the ground state) used for the photooxidation of **1a** would also be capable of undergoing reaction (3). However, it

$$\mathbf{1a}^{\cdot} + \mathbf{A} \longrightarrow \mathbf{3a} + \mathbf{A}^{\cdot-} \qquad (3)$$

can be excluded that the **A** compounds tested in this work can play this role because of the endergonicity of reaction (3). As can be seen from Table 2 the ΔG^0_{et} values are positive in all cases. Therefore, radicals $\mathbf{1a}^{\cdot}$ are very likely to dimerize.

Regarding the compounds **1b, 1c** and **1d** it is noteworthy that neither dimer **2b** nor the tropylium ion **3b** is formed. Actually, the oxidation of radical $\mathbf{1}^{\cdot}$ is feasible as far as the system **1b/A5** is concerned because of the exergonicity ($\Delta G^0_{\mathrm{et}} = -0.01$ eV) of the reaction $\mathbf{1b}^{\cdot}$ + **A5**, but **3b** is not formed. Therefore, it is concluded that the radical cations $\mathbf{1b}^{\cdot+}$, $\mathbf{1c}^{\cdot+}$ and $\mathbf{1d}^{\cdot+}$ do not deprotonate but undergo back electron transfer leading to the bimolecular decay of the reduced acceptors observed with **A2** and **A5**. Also in the case of the electron transfer from **1b** to **A5** in the triplet state the back electron transfer is fast. Therefore, a delay between the decay of the triplet state of **A5** and the recovery of **A5** from its radical was not observed (see Fig. 3). A back electron transfer faster than the deprotonation of the radical cation is feasible because of the diminished acid strength of these radical cations (relative to $\mathbf{1a}^{\cdot+}$) and also because of the smaller exergonicity of the back electron transfer (−1.1 eV) with respect to **1a** (−1.7 eV). Assuming that the back electron transfer occurs in the Marcus inverted region it should proceed faster than in the case of **1a**.

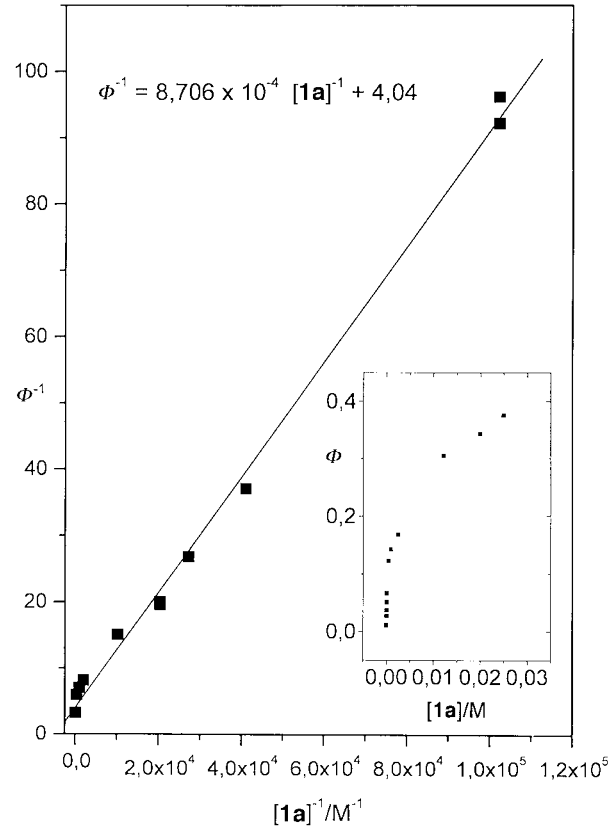
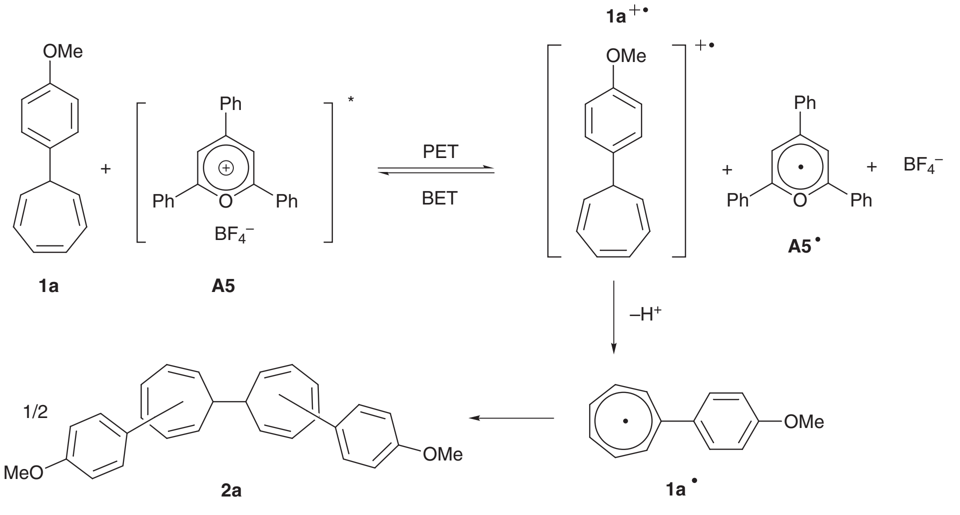


Fig. 6 Dependence of the reciprocal quantum yield of **3a** formation *vs.* the reciprocal concentration of **1a**. Inset: plot of the quantum yield of **3a** formation on the concentration of **1a**.

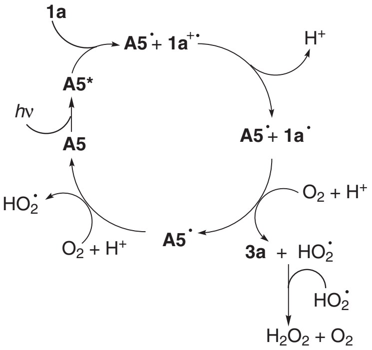
2. Photooxidation in presence of oxygen and acid

Concerning the photolysis in acidic, air-equilibrated aceto-



Scheme 3

nitrile solution O_2 is regarded to play the role of a one-electron oxidant which enables the oxidation of the cycloheptatrienyl radical. A mechanism illustrating how the acceptor **A5** acts as a photosensitizer for the oxidation of **1a** by O_2 is proposed in Scheme 4. The essential feature of this mechanism is the electron transfer from $\mathbf{1a}^{\bullet}$ to O_2 and the subsequent protonation of $O_2^{-\bullet}$ [reactions (4) and (5)]. At a sufficiently high proton concentration the equilibrium (5) is shifted to the right side (in water p$K = 4.88$;[16] in acetonitrile p$K = 12$[17]) thus guaranteeing irreversibility of electron transfer according to reaction (4). In the absence of acid the occurrence of reaction (5) is rather improbable because of its endothermicity, *i.e.* the oxidation potential of $\mathbf{1a}^{\bullet}$ (−0.36 V) is more positive than the reduction potential of O_2 (−0.86 V).[18] However, the occurrence of reaction (4) becomes feasible if the reduction potential of O_2 effective in the presence of HBF_4 is larger than −0.86 V. Actually, a shift of the reduction potential of O_2 to more positive values upon the addition of acid has been proven by various authors, *e.g.* by Sawyer *et al.*[19] and by Fukuzumi.[20]



Scheme 4

$$\mathbf{1a}^{\bullet} + O_2 \longrightarrow \mathbf{3a} + O_2^{-\bullet} \qquad (4)$$

$$O_2^{-\bullet} + H^+ \rightleftharpoons HO_2^{\bullet} \qquad (5)$$

Regarding the mechanism depicted in Scheme 4 it should be noted that the observation that the acceptor is not consumed during the oxidation of **1a** to **3a** has been accounted for. It is assumed that in the presence of a protonic acid the radical $\mathbf{A5}^{\bullet}$ is oxidized to **A5** by O_2. Principally, the oxidation of **1a** to **3a** can be initiated both by singlet- and triplet-excited **A5** molecules as is depicted in Scheme 5.

At relatively low concentration of **1a** the singlet pathway is unimportant and practically only $^3\mathbf{A5}^*$ molecules are involved in the formation of **3a**. It is presumed that the rate of the reaction $\mathbf{1a}^{\bullet} + O_2$ is much larger than the rate of deprotonation ($\mathbf{1a}^{\bullet +} \longrightarrow \mathbf{1a}^{\bullet} + H^+$), *i.e.* the rate of the latter reaction determines the formation rate of **3a**. Then, eqn. (9) was derived on the basis of the steady-state approximations (6)–(8).

$$k_{ET}[\mathbf{1a}][^3\mathbf{A5}^*] = (^3k_{BET} + {}^3k_{br})[\mathbf{1a}^{\bullet +}] \qquad (6)$$

$$k_{isc}[^1\mathbf{A5}^*] = (^3k_{ET}[\mathbf{1a}] + {}^3\tau^{-1})[^3\mathbf{A5}^*] \qquad (7)$$

$$\Phi(\mathbf{3a}) = {}^3\tau k_{isc}{}^3k_{br}{}^3k_{ET}[\mathbf{1a}]/(1 + {}^3k_{ET}{}^3\tau[\mathbf{1a}])(^1k_d + k_{isc})(^3k_{BET} + {}^3k_{br}) \qquad (8)$$

A transformation of eqn. (8) leads to eqn. (9).

$$1/\Phi(\mathbf{3a}) = (^1k_d + k_{isc})(^3k_{BET} + {}^3k_{br})/k_{isc}{}^3k_{br} + (^1k_d + k_{isc})(^3k_{BET} + {}^3k_{br})/k_{isc}{}^3k_{br}{}^3\tau k_{ET}[\mathbf{1a}] \qquad (9)$$

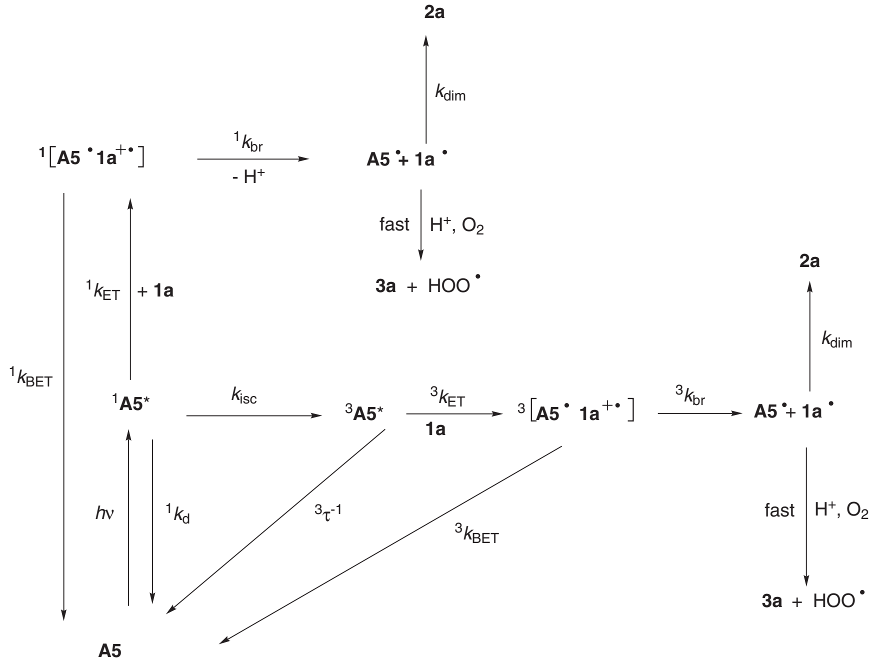
With $a = (^1k_d + k_{isc})(^3k_{BET} + {}^3k_{br})/k_{isc}{}^3k_{br}$, and $m = (^1k_d + k_{isc})$-$(^3k_{BET} + {}^3k_{br})/k_{isc}{}^3k_{br}{}^3\tau k_{ET}$, one obtains eqn. (10) and $a/m = k_{ET}$

$$1/\Phi(\mathbf{3a}) = a + m/[\mathbf{1a}] \qquad (10)$$

$^3\tau$ and $k_{ET} = (a/m)/{}^3\tau$. A plot of $1/\Phi(\mathbf{3a})$ *vs.* $1/[\mathbf{1a}]$ yields a straight line as can be seen from Fig. 6. With *m* and *a*, the slope and the intercept with the ordinate of the straight line, respectively, $k_{ET} = 9 \times 10^8$ M^{-1} s^{-1} is calculated using $^3\tau = 5.4$ µs ($^3\tau$: lifetime of $^3\mathbf{A5}^*$ in air-equilibrated acetonitrile). The k_{ET} value agrees satisfactorily with the k_q value (5×10^9 M^{-1} s^{-1}) obtained from the triplet quenching experiments (see Results 2.2). The extrapolated quantum yield at infinite quencher concentration amounts to 0.25.

Conclusions

1. This paper demonstrates that the photooxidation of aryl-substituted cycloheptatrienes to tropylium ions involves two



Scheme 5

electron transfer steps. The process is governed by the chemical nature of the aryl substituent. The *p*-dimethylaminophenyl substituent on the seven-membered ring hinders the photoinduced oxidation to the tropylium salt.

2. In the case of **1a** deprotonation of the radical cation competes successfully with back electron transfer to the reduced electron acceptor thus making the forward electron transfer irreversible. However, back electron transfer dominates if a powerful donor substituent, namely the dimethylaminophenyl group, is attached to the seven-membered ring and the formation of the cycloheptatrienyl radical is prevented. This obstacle can be circumvented by protonation of the amino group.[21]

3. In the case of **1a** it was shown for the first time that tropylium cations **3a** can be efficiently generated by photoinduced electron transfer. The photooxidation is accomplished with the support of protons and dioxygen. We have shown that macrocycles such as calixarenes incorporating the cycloheptatriene moiety can be transformed into the tropylium derivative with the aid of this method. Work to study the photochemically induced alteration of the complexation properties of these macrocycles is currently in progress.

Experimental

1. Instrumentation

Absorption spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer and emission measurements were carried out with a Perkin-Elmer spectrofluorimeter LS 50B. NMR spectra were recorded on a Bruker instrument (DPX 300) and EPR spectra on a ZWG instrument (EPR-300).

1.2 Continuous irradiation. Continuous irradiations were carried out with acetonitrile solutions in 1 cm quartz cuvettes with a 500 W high pressure mercury lamp operated in conjunction with a metal interference filter (Carl Zeiss Jena) or an Oriel monochromator (model 77200). For some irradiations a Rayonet photoreactor (lamp type: RPR 3500 or 4190) was used. Prior to irradiation the solutions were degassed by argon bubbling. Solutions containing HBF_4 (3.2×10^{-2} M) were prepared using aqueous HBF_4 (50%). The absorbed irradiation dose was determined with the aid of the ferric oxalate actinometer.

1.3 Flash photolysis. Laser flash photolysis of acetonitrile solutions was performed in 1 cm quartz cuvettes with the aid of a ruby laser (Korad Model K1 QS2, flash duration 20 ns) operated in conjunction with a frequency doubler ($\lambda = 347$ nm). The solutions were deaerated by argon bubbling.

2. Product analysis

HPLC analysis was performed using RP 18 phases and a diode array detector (Shimadzu SPD-M10A). The mobile phase consisted of a 80:20 mixture of acetonitrile and water that was buffered with triethylamine–H_3PO_4 (pH = 2.7). Tropylium salt yields were determined by analytical HPLC on the basis of a calibration curve obtained with probes of given concentration. The latter was obtained by measuring the optical absorption at 435 nm ($\varepsilon = 2.25 \times 10^4$ M^{-1} cm^{-1}). The rate constant of tropylium salt formation was calculated by the tangent method using plots of the conversion *vs.* the time of irradiation. The H_2O_2 concentration of the (neutralized) reaction solution was determined *via* the oxidation of iodide to iodine using $(C_4H_9)_4NI$.[14] The concentration of I_3^- was determined by measuring the optical density at 365 nm with the aid of a calibration curve.

3. Determination of reduction and oxidation potentials

Rapid scan cyclic voltammetry (1 to 20 V s^{-1}) was performed using a HEKA Elektronik potentiostat (model PG 285) with the aid of an EG&G cell having a planar working electrode (d = 1 mm). A saturated calomel reference electrode (located in a lugging capillary with diaphragm) was employed. The reduction potential $E^0_{red}(\mathbf{3a}) = -0.35$ V was calculated from the measured peak potential $E_p = -0.36$ V according to eqn. (11).[22]

$$E^0_{red}(\mathbf{3a}) = E_p - RT/\{\ln(k_2[\mathbf{1a}]RT/nFv) - 3.12\}/3F \quad (11)$$

Here, F is 96.485 C mol^{-1}, $k_2 = 2 \times 10^6$ M^{-1} s^{-1} [23] is the rate constant of the dimerization of **1a**, $n = 1$, $v = 1$ V s^{-1} (scan rate) and $[\mathbf{1a}] = 1 \times 10^{-3}$ M. Analogously, $E^0_{red}(\mathbf{3b}) = -0.51$ V was obtained. The oxidation potentials of the radicals $\mathbf{1a}^{\bullet}$ and $\mathbf{1b}^{\bullet}$ were assumed to be equal to the reduction potentials of the corresponding tropylium ions **3a** and **3b**, *i.e.* $E^0_{ox}(\mathbf{1a}^{\bullet}) = E^0_{red}(\mathbf{3a})$ and $E^0_{ox}(\mathbf{1b}^{\bullet}) = E^0_{red}(\mathbf{3b})$.

4. Materials

Acetonitrile (Riedel de Haen, HPLC grade) was used as received. The acceptors **A2** and **A5** were commercial products. **A3**[24] and **A4**[25] were synthesized as described in the literature. Cyclohepta-1,3,5-triene (Fluka) was purified by rectification.

The cycloheptatrienes **1a**,[26] **1b**,[26] **1c**,[27] **1d**[28] and the tropylium perchlorates **3a** and **3b**[26] were synthesized as described in the literature and purified by recrystallization.

4.1 Synthesis of 3,3′-bis(4-methoxyphenyl)bi(cyclohepta-1,3,5-trien-7-yl) (2a). A solution of $CrCl_2$ prepared from 9 g (36.2 mmol) $CrCl_3$ in 20 ml HCl (5 m) and 10 g Zn dust (153 mmol) was filtered and transferred under argon into a three-necked flask containing 250 ml of a suspension of 1 g **3a** (3.4 mmol) in HCl (2 m). After stirring for one hour under argon, 40 ml *tert*-butyl methyl ether were added. The mixture was neutralized with NaOH and cooled with ice. Subsequently, the organic layer was separated and the aqueous phase extracted with *tert*-butyl methyl ether. The combined organic extracts were dried and the solvent was evaporated under reduced pressure. 620 mg (94%) of the raw mixture of regioisomers of the substituted bitropyl remained. As concluded from ^1H NMR spectroscopy at least four isomers were formed. This isomer mixture was used to identify the products formed during the oxidation of **1a** by photoexcited **A4** or **A5**.

Successive recrystallization from cyclohexane–hexane (1:1) and from acetonitrile resulted in pale yellow plates of the pure 3,3′-isomer of **2a**. Yield 80 mg (12%), mp: 191–194 °C (Found: C, 84.90; H, 6.50. Calc. for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64%); δ_H ($CDCl_3$) 2.18 (2H, br m, 7-H); 3.85 (6H, s, MeO); 5.43, 5.50 (4H, m, 1-H, 6-H); 6.38 (2H, m, 5-H); 6.44 (2H, 2-H); 6.94 (4H, d, Ar); 7.00 (2H, d, 4-H); 7.47 (4H, d, Ar).

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