Generation of aryltropylium ions from the corresponding bitropyls by electrochemical and photoinduced electron transfer

Dirk Jacobi,[a] Werner Abraham,*[a] Uwe Pischel,[a] Lutz Grubert[a] and Wolfram Schnabel[b]

[a] *Humboldt-University, Institute of Chemistry, D-10115 Berlin, Hessische Str. 1-2, Germany*
[b] *Hahn-Meitner-Institut GmbH, Department of Physical Chemistry, D-14109 Berlin, Glienicker Str. 100, Germany*

Received (in Cambridge) 17th September 1998, Accepted 22nd March 1999

The photoinduced electron transfer from aryl-substituted bitropyls bearing 4-methoxyphenyl (**1**) and 4-(*N*,*N*-dimethylamino)phenyl substituents (**2**) to *N*-methylacridinium perchlorate (**AcrH$^+$**), 2,4,6-triphenylpyrylium tetrafluoroborate (**TPP$^+$**), and the *p*-methoxyphenyltropylium ion (**3**) was studied with the help of steady state photolysis and laser flash spectroscopy. Intermediates detected revealed the occurrence of electron transfer. It affords the formation of radical cations of **1**. C–C bond cleavage occurring in the radical cation can compete with back electron transfer. In this way, compounds **1** and **2** are transformed into the corresponding tropylium ions (**3** and **4**). Electrochemically, both processes, **2**→**4** and **4**→**2**, were performed by altering the current direction, and several **2**→**4**→**2** cycles were achieved.

Introduction

Coupling between single electron transfer, activated electrochemically[1] or stimulated by light,[2] and bond dissociation is presently a field of active investigation.[3] It has been shown that both 7- and 1- or 3-[*p*-(dimethylamino)phenyl]cycloheptatriene are capable of undergoing photoinduced electron transfer to neutral and cationic electron acceptors.[4] Generally, the radical cation formed from an aryl-substituted cycloheptatriene can be converted into the tropylium ion in a further oxidation step provided cleavage of one C–H bond in the seven-membered ring in conjunction with proton release occurs. In the case of [*p*-(dimethylamino)phenyl]cycloheptatriene deprotonation of the radical cation fails because back electron transfer dominates.[4] In this context it is interesting to compare the behaviour of aryl-substituted cycloheptatrienes and that of the bitropyls **1** and **2** with respect to consecutive reactions of the radical cation, *i.e.* cleavage of the C–H *vs.* C–C bond.

Compounds of types **1** and **2** can be considered to be dimers of the corresponding aryl-substituted cycloheptatrienes. Actually, the electron transfer from bitropyls having aryl-substituents of different donor strength [*p*-methoxyphenyl and *p*-(dimethylamino)phenyl groups] to the cationic acceptors *N*-methylacridinium perchlorate (**AcrH$^+$**), triphenylpyrylium tetrafluoroborate (**TPP$^+$**) and *p*-methoxyphenyltropylium perchlorate (**3**), was studied. Formulae of these compounds are given in Chart 1. Intermediates were detected with the help of time-resolved optical absorption spectroscopy and stable products were identified by steady state photolysis and subsequent high pressure liquid chromatography (HPLC) analysis.

Redox peak potentials, obtained by electrochemical measurements, served to evaluate the free energy change accompanying the electron transfer reactions.

Results

Cyclic voltammetry

Cyclic voltammetric measurements showed that the oxidation peak potentials of the dimers **1** and **2** are very similar to the oxidation peak potentials of the corresponding cycloheptatrienes reported elsewhere.[4] This can be seen from Table 1. Notably, in all cases the oxidation is chemically irreversible and, therefore, standard potentials cannot be obtained.

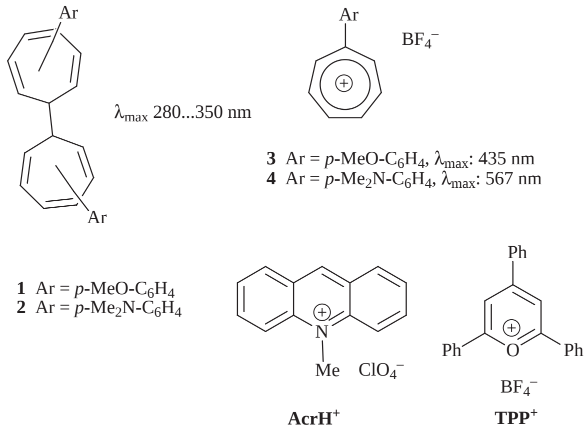


Chart 1

Controlled potential electrolysis

The bitropyls **1** and **2** were oxidised to the tropylium ions **3** and **4** at a constant anode potential. The total conversion of **1** and **2**, achieved by a charge consumption of 2 F ($F = 96.485$ C mol^{-1}), resulted in yields of **3** and **4** of 50 and 95%, respectively. Electrochemically formed **4** was reduced at the cathode and, thereby, **2** was regenerated in a yield of about 90%. Actually, several **2**→**4**→**2** cycles were realised by altering the current direction. However, after four redox cycles the yield of **4** was reduced to 40%.

Photochemistry

Laser flash photolysis. Upon direct laser excitation of **2** in acetonitrile solution in the absence of an electron acceptor at $\lambda_{inc} = 266$ nm a transient absorption spectrum possessing maxima at 370 nm and 560 nm was observed at the end of the flash as can be seen from Fig. 1a. The two bands are assigned to the cycloheptatrienyl type radical **5** (370 nm) and to the tropylium ion **4** (560 nm). Additional evidence for the formation of an ionic species was obtained by measuring the electric conductivity of the solution. A photocurrent i_{photo}, non-linearly depending on the absorbed dose per flash D_{abs}, was generated during the flash ($i_{photo} \propto D_{abs}^{1.4}$).

Similar observations were made upon excitation of **2** at

Table 1 Oxidation peak potentials of the bitropyls **1** and **2** and of the corresponding arylcycloheptatrienes, estimated oxidation potential of **2**, estimated oxidation potentials of the radicals **5** and **6** (*vs.* SCE) and the free enthalpy of the electron transfer to **AcrH$^+$** (initial electron transfer: ΔG_{ET}*; second electron transfer ΔG_{ET})

	Aryl bitropyl	Aryl cycloheptatriene (3-isomer)	Radical[b]	$\Delta G_{ET}{}^{*c}$/eV	$\Delta G_{ET}{}^{d}$/eV
R = OMe (**1**)	1.15 V	1.2 V	(**6**) −0.37 V	−1.1	0.1
R = N(Me)$_2$ (**2**)	0.53 V (0.07 V)[a]	0.55 V	(**5**) −0.53 V	−1.6	−0.07

[a] Derived from the measured peak potential with the aid of $E_p(\mathbf{2}) - E^0_{ox}(\mathbf{2}) = RT[0.783 - \frac{1}{2}\ln(RTk/nFv)]/nF$,[12] where k is the rate constant of the decomposition of $\mathbf{2}^{+\bullet}$, and v is the sweep rate in V s^{-1}, $F = 96495$ C mol^{-1} and $n = 1$. With $k = 3 \times 10^7$ s^{-1} one obtains $E^0_{ox}(\mathbf{2}) = 0.7$ V as the lowest limiting value ($E_p - E^0_{ox} < -0.15$ V). [b] The oxidation potential $E^0_{ox}{}^{(5,6)}$ of the radicals is assumed to be equal to the reduction potential of the corresponding tropylium ions. These reduction potentials can be calculated with the aid of the peak potentials[4] and the known radical dimerization rate constant k of **5** and **6**[13] according to $E_p(\mathbf{4}) - E^0_{red}(\mathbf{4}) = RT[\ln(kc_o{}^*RT/nFv) - 3.12]/3F$,[14] where $k = 2 \times 10^6$ dm^3 mol^{-1} s^{-1}, $c_o{}^*$ (**3** or **4**) = 1 mmol dm^{-3}, $F = 96495$ C mol^{-1} and $n = 1$. [c] Calculated with E^0_{red} (**AcrH$^+$**) = −0.46 V[15] and E(**AcrH$^+$**) = 2.8 eV.[16] [d] $\Delta G_{ET} = E^0_{red}$ (**AcrH$^+$**) $- E^0_{ox}{}^{(5,6)}$.

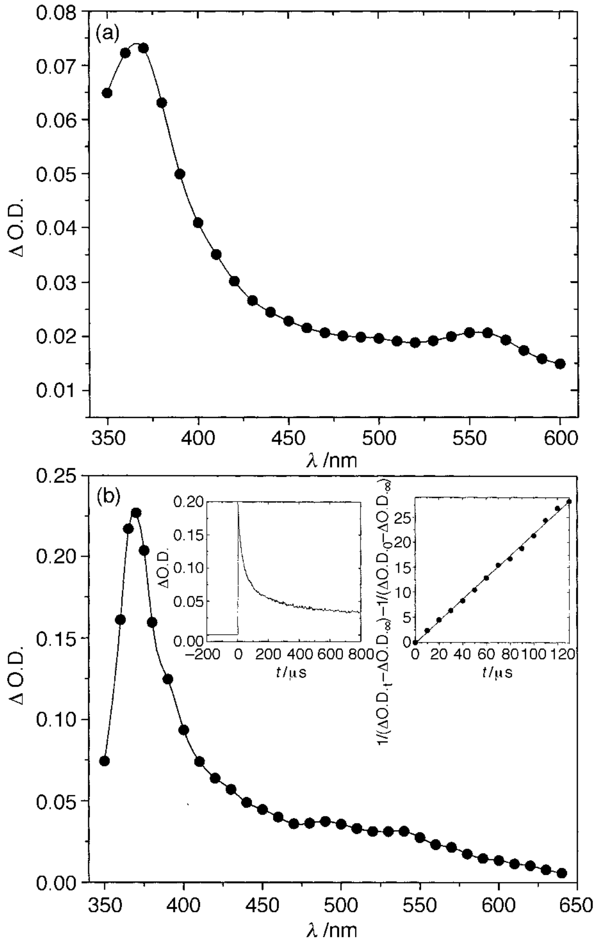
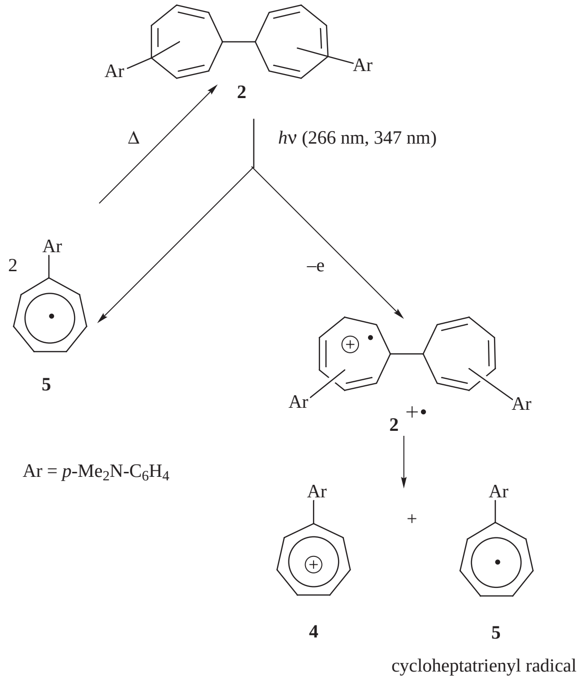


Fig. 1 Transient absorption spectra observed upon laser-flash photolysis of **2** (0.038 mmol dm^{-3}) in deaerated acetonitrile solution at $\lambda_{inc} = 266$ nm (a) and $\lambda_{inc} = 347$ nm (b). Inset 1b: kinetic trace referring to changes in the optical absorption at $\lambda = 370$ nm and plot according to the second order decay.

$\lambda_{inc} = 347$ nm. As can be seen from Fig. 1b the band around 560 nm contributes much less to the absorption spectrum than in the case of excitation at $\lambda_{inc} = 266$ nm indicating a lower yield of the tropylium ion at $\lambda_{inc} = 347$ nm. Fig. 1b contains insets referring to the decay of the absorption at $\lambda_{inc} = 370$ nm. The plot of the reciprocal optical density *vs.* time yields a straight line demonstrating that the decay follows second order kinetics. A possible mechanism for the formation of the two intermediates is depicted in Scheme 1.

In another experiment an acetonitrile solution containing **2** and **AcrH$^+$** both at a concentration of 0.04 mmol dm^{-3} was irradiated with 347 nm flashes. In this case the incident light was absorbed by both compounds in equal amounts. As can be seen from Fig. 2a a transient absorption spectrum with maxima at 370, 510 and 560 nm was formed during the flash.



Scheme 1

Whereas the bands at 370 and 560 nm are assigned to the cycloheptatrienyl type radical and the tropylium ion, respectively, that at 510 nm is attributed to the intermediates arising from the reaction of excited **AcrH$^+$**. Reportedly, the *N*-methylacridinyl radical (**AcrH$^\bullet$**) has an absorption maximum at 510 nm.[5] Regarding the band at 560 nm it is seen from Fig. 2 that one portion is formed during the flash and a second, not insignificant, portion of the absorption builds up after the flash. It will be shown below in the Discussion section that the build-up of the second portion reflects the formation of the tropylium ion *via* the reaction of the cycloheptatrienyl type radical with **AcrH$^+$**.

Steady-state photolysis. When acetonitrile solutions containing **1** or **2** and **AcrH$^+$**, **TPP$^+$** or **3** were continuously irradiated with UV light electron transfer was evidenced in each case by the detection of the stable tropylium ion. However, quite different yields of the tropylium salts were found as can be seen from the following subsections dealing with the experiments performed with the various systems. In some cases the presence of O_2 is a prerequisite of the formation of the tropylium ion.

System AcrH$^+$/1 (3,3′-isomer). Upon irradiation of the system **1**/**AcrH$^+$** at $\lambda_{inc} = 365$ nm (only **AcrH$^+$** absorbs light at this wavelength) in deaerated acetonitrile solution containing tetrafluoroboric acid (0.01–1 mol dm^{-3}) **1** was consumed and the tropylium salt **3** was formed. Notably, only about 50% of the consumed **1** was converted into **3**. The course of the reaction was followed spectroscopically and with the aid of

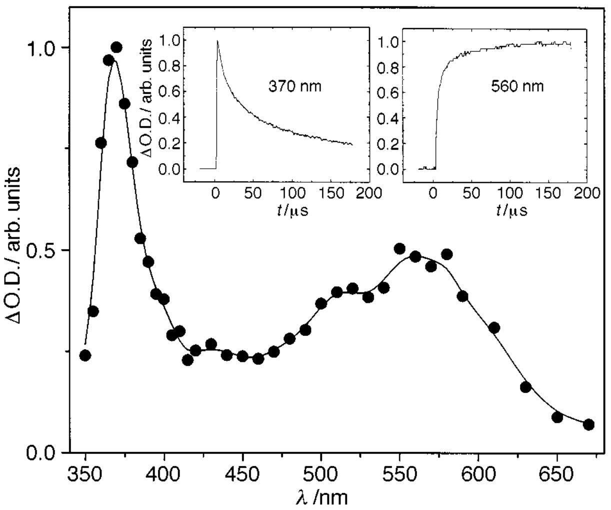


Fig. 2 Laser-flash photolysis of the system **AcrH**$^+$/**2** in deaerated acetonitrile solution at λ_{inc} = 347 nm. [**AcrH**$^+$] = [**2**] = 0.04 mmol dm^{-3}. Transient optical absorption spectra recorded at the end of the 20 ns flash. Insets: kinetic traces referring to changes in the optical absorption at λ = 370 nm and λ = 560 nm.

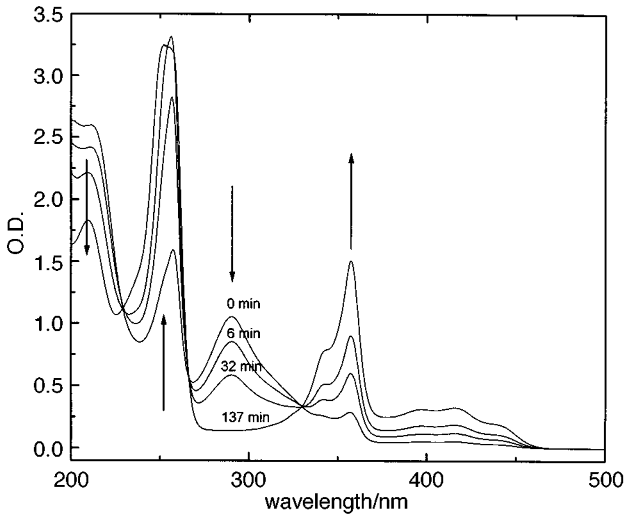


Fig. 4 Irradiation of a deaerated acetonitrile solution containing (**AcrH**)$_2$ (0.05 mmol dm^{-3}) and HBF$_4$ (10 mmol dm^{-3}) at λ_{inc} = 254 nm. UV–VIS spectra recorded after various irradiation times (min) as indicated in the graph.

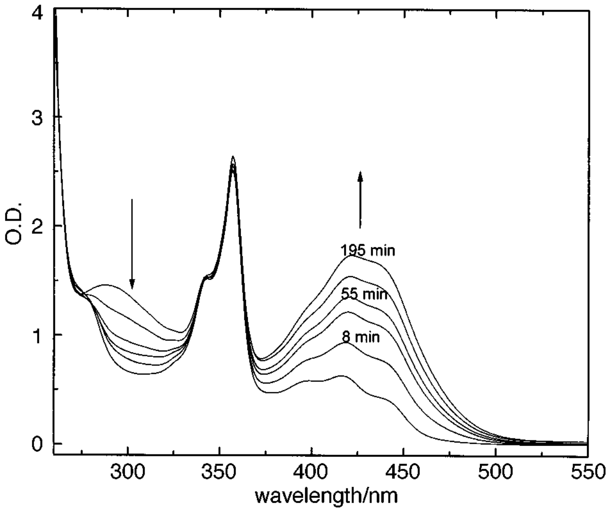


Fig. 3 Photolysis of the system **AcrH**$^+$/**1** (3,3′-isomer) in deaerated acetonitrile solution containing HBF$_4$ (9 mmol dm^{-3}) at λ_{inc} = 365 nm. [**1**] = 0.075 mmol dm^{-3}; [**AcrH**$^+$] = 0.13 mmol dm^{-3}. Optical absorption spectra recorded after various irradiation times (min) as indicated in the graph.

HPLC. UV-VIS spectra recorded after various irradiation times are presented in Fig. 3, where it is seen that the absorption band of the tropylium ion around 435 nm increases with irradiation time and that the absorption of **1** around 300 nm decreases simultaneously.

Notably, the yield of the tropylium ion does not depend on the acid concentration (0.01–1 mol dm^{-3}) but tropylium salt is not formed at all in the absence of acid. Since the absorption due to **AcrH**$^+$ in the range 325 to 375 nm is not altered significantly it is concluded that **AcrH**$^+$ is not consumed but acts as a photocatalyst. Therefore, the question arises of how **AcrH**$^+$ is regenerated. Regarding the mechanism discussed below it is noted that 9,10-dihydro-10-methylacridine, **AcrH**$_2$, was not detected.

In another experiment it was found that **AcrH**$_2$ is able to reduce **3** by hydride transfer yielding 1- and 3-(4-methoxyphenyl)cycloheptatriene and **AcrH**$^+$. In order to elucidate the fate of acridinyl radicals which should be formed primarily by electron transfer from **1** to **AcrH**$^+$ the latter were generated from (**AcrH**)$_2$ as will be described in the next section.

System (AcrH)$_2$/HBF$_4$. (**AcrH**)$_2$ is readily decomposed upon direct excitation at λ_{inc} = 254 nm in deaerated acetonitrile solution containing HBF$_4$ (0.01 mol dm^{-3}). Periodic recording of the UV-VIS spectrum of the irradiated solution revealed the steady state formation of the absorption band of **AcrH**$^+$ at 360 nm and the disappearance of the absorption band of (**AcrH**)$_2$ at 290 nm (see Fig. 4). According to the HPLC analysis **AcrH**$_2$ and **AcrH**$^+$ are formed in the ratio 1 : 1.

When a solution primarily irradiated for 2 min at λ_{inc} = 254 nm was subsequently irradiated at λ_{inc} = 365 nm, where **AcrH**$^+$ is excited, (**AcrH**)$_2$ continued to be decomposed. This decomposition is attributed to the reaction of excited **AcrH**$^+$ with (**AcrH**)$_2$. In this respect it is remarkable that the two-electron oxidation of (**AcrH**)$_2$ by electron acceptors such as oxygen or the trityl cation also leads to **AcrH**$^+$.[6,7]

System AcrH$^+$/2 (isomer mixture). The system **AcrH**$^+$/**2** was irradiated at λ_{inc} = 405 nm, where about 95% of the incident light is absorbed by **AcrH**$^+$. The irradiation resulted in the formation of **4**. Actually, **AcrH**$^+$ was consumed to the same extent as **4** was formed. The yield of **4** turned out to depend strongly on the concentration of **AcrH**$^+$. It varied from 15% at the concentration ratio [**AcrH**$^+$]/[**2**] = 1 ([**AcrH**$^+$] = 0.01 mmol dm^{-3}) to 57% at [**AcrH**$^+$]/[**2**] = 1000 ([**AcrH**$^+$] = 10 mmol dm^{-3}).

System (AcrH)$_2$/4. As will be discussed below (see Scheme 3), apart from **4**, 10,10′-dimethyl-9,9′-biacridine, (**AcrH**)$_2$, might also be formed upon irradiation of the system **AcrH**$^+$/**2**, but it was only detectable at a yield of 20%. In order to find out whether (**AcrH**)$_2$ is decomposed a deaerated acetonitrile solution containing (**AcrH**)$_2$ (0.5 mmol dm^{-3}) and **4** (0.1 mmol dm^{-3}) was irradiated at λ_{inc} = 254 nm where mainly (**AcrH**)$_2$ is excited. It turned out that **2** and **AcrH**$^+$ were formed whereas the concentration of (**AcrH**)$_2$ decreased.

System TPP$^+$/2. Irradiation of the system **TPP**$^+$/**2** in air-equilibrated acetonitrile solution at λ_{inc} = 405 nm, where the light is exclusively absorbed by **TPP**$^+$, resulted in the formation of **4**. As can be seen from Fig. 5, where UV-VIS spectra recorded after various irradiation times are presented, the absorption band of **4** around 560 nm grew rapidly with increasing irradiation time and the absorption band of **TPP**$^+$ around 400 nm was simultaneously depleted indicating that **4** is formed at the same rate as **TPP**$^+$ is consumed.

Under appropriate conditions Φ(**4**), the quantum yield of the formation of **4**, is rather high. For example, Φ(**4**) = 0.2 was found at [**2**] = 0.02 mmol dm^{-3} and [**TPP**$^+$] = 0.04 mmol dm^{-3}.

Actually, the yield of **4** depends on the concentration ratio [**TPP**$^+$]/[**2**] as can be seen from Table 2, where the fraction of **2** converted into **4** is given as a percentage of totally consumed **2**.

Table 2 Yield of **4** formed in the photolysis of the system **TPP**$^+$/**2** at λ_{inc} = 405 nm

	1,2′	1,2′	1,2′	2,2′	2,3′	3,3′	mixture of isomers
[**TPP**$^+$]/10^{-5} M	1.3	5.6	8.4	6.6	8.7	8.6	5.7
[**2**]/10^{-5} M	2.1	2.1	2.1	2.6	3.4	3.8	2.7
4 Yield (%)	53	74	74	56	68	62	93

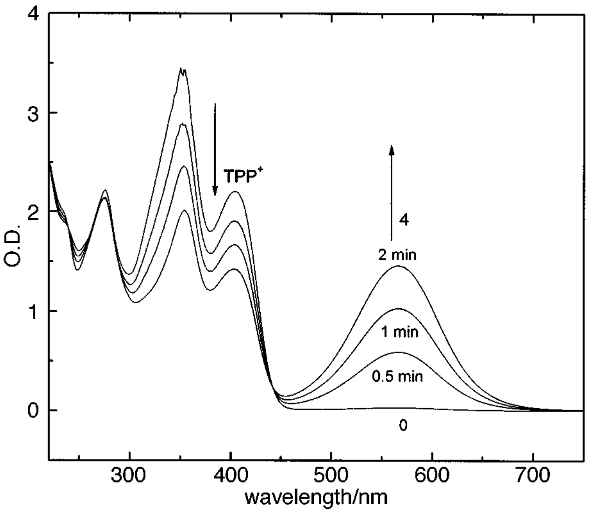


Fig. 5 Photolysis of the system **TPP**$^+$/**2** (1,2′-isomer) in deaerated acetonitrile solution at λ_{inc} = 405 nm. [**TPP**$^+$] = 0.085 mmol dm^{-3}; [**2**] = 0.038 mmol dm^{-3}. Optical absorption spectra recorded after various irradiation times as indicated in the graph.

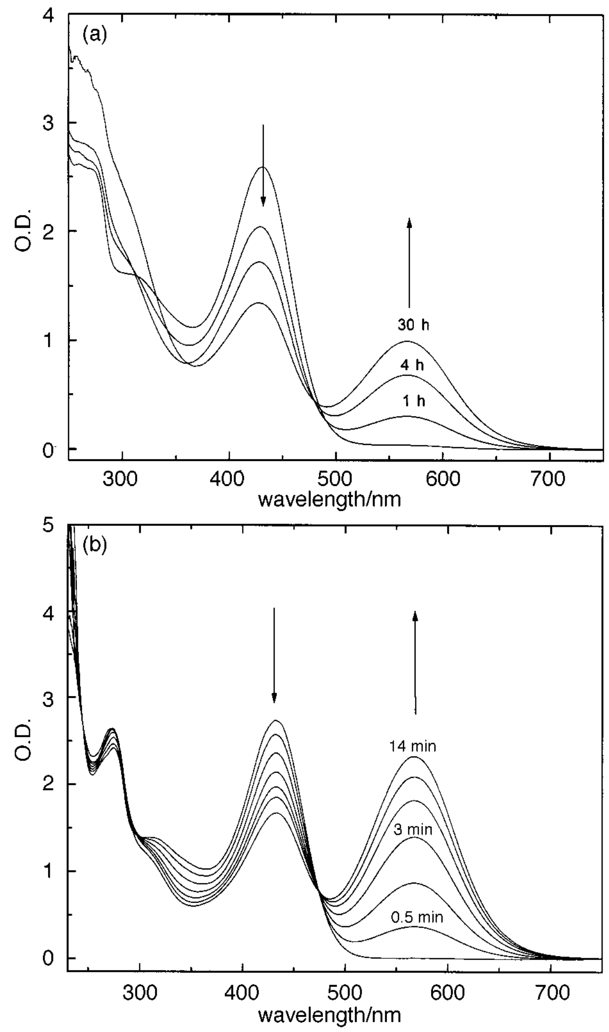


Fig. 6 Photolysis of the system **3**/**2** (isomer mixture) in deaerated acetonitrile solution at λ_{inc} = 436 nm (a) and λ_{inc} = 313 nm (b). [**3**] = 0.15 mmol dm^{-3}; [**2**] = 0.04 mmol dm^{-3}. Optical absorption spectra recorded after various irradiation times as indicated in the graph.

The yield of **4** varies from 50 to 90%, and it seems that it also depends on the nature of the isomer of **2**.

Notably, **4** was not formed in the absence of O_2, although **2** also undergoes photochemical alterations in this case. This was inferred from the fact that upon irradiation of a solution containing neat 2,3-isomer of **2** and **TPP**$^+$ a mixture of isomers of **2** was formed. A reaction mechanism dealing with this effect will be proposed in the Discussion section.

System 3/2. Compound **3** has an absorption maximum at 435 nm and the isomer mixture of **2** has absorption maxima between 290 and 350 nm. Upon irradiation at λ_{inc} = 436 nm only **3** was excited. Compound **2** was consumed and **1** and **4** were formed, as was inferred from HPLC and absorption spectroscopy, respectively. As can be seen from Fig. 6a the band of **4** at 560 nm grew steadily with increasing time of irradiation. The HPLC studies revealed that only 19% of the consumed **2** was converted into **4**.

When, in another experiment, the system **3**/**2** was irradiated at λ_{inc} = 313 nm, where mainly **2** is excited, 46% of the consumed **2** was converted into **4** (Fig. 6b). The oxidation of **2** by **3** was enhanced by **TPP**$^+$. Irradiation at λ_{inc} = 365 nm, the absorption maximum of the system **TPP**$^+$, caused the rapid formation of **4** as can be seen from Fig. 7. At the end of the irradiation **4** was formed in a yield of 80%. Compound **3** was consumed to the same extent that **4** was formed. On the other hand, the intensity of the **TPP**$^+$ band at 365 nm did not decrease simultaneously with the increase in the absorption band of the tropylium ion at 560 nm indicating that **TPP**$^+$ is not consumed. The band at 410 nm is the superposition of the absorption bands of **TPP**$^+$ (λ_{max} = 405 nm) and of **3** (λ_{max} = 436 nm) and the (rather small) depletion of the optical density at 365 and 410 nm is attributed to the diminished contributions of the absorption of **3** due to its consumption.

Discussion

Electrochemistry

It is known that the electrochemical oxidation of bitropyl, the parent compound of **1** and **2**, results in the formation of tropylium ions.[8] However, the yield of tropylium salt has not yet been reported. In the electrolysis experiments performed with **1** and **2** during the present work it was found that the yields of **3** and **4** differ considerably. Regarding the mechanism it is assumed that the fast C–C bond cleavage within the primarily formed radical cations of **1** and **2** leads to the formation of the tropylium ion and the cycloheptatrienyl type radical. When the latter is oxidised at the electrode an additional tropylium ion is formed (see Scheme 2). The observed chemical irreversibility can be attributed to this follow up reaction.

The rather low tropylium ion yield in the case of **1** is thought to be due to side reactions of the radical **6** that have not yet been visualised. On the other hand, side reactions appear to be less important in the case of **2**, which is almost quantitatively converted into the tropylium ion.

Photochemistry

Direct excitation of 2. Direct excitation of **2** with a flash at λ_{inc} = 266 nm yields, at the end of the flash, both the tropylium

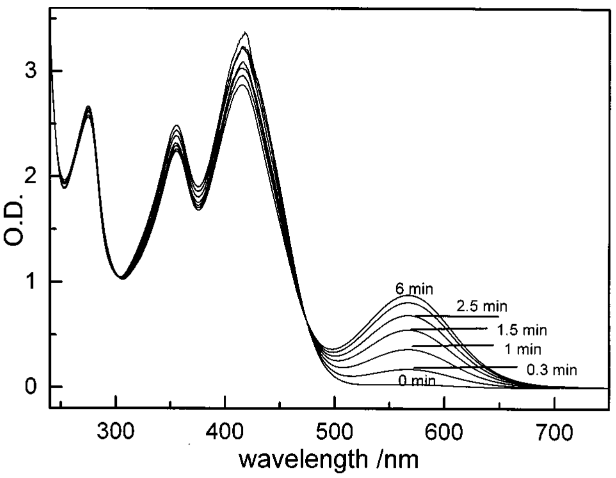
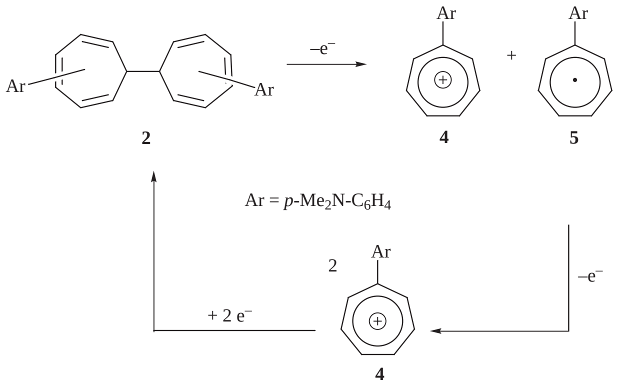


Fig. 7 Photolysis of the system **3**/**2** (isomer mixture) in deaerated acetonitrile solution at $\lambda_{inc} = 365$ nm using **TPP**$^+$ as sensitiser. [**3**] = 0.12 mmol dm^{-3}; [**2**] = 0.015 mmol dm^{-3}; [**TPP**$^+$] = 0.05 mmol dm^{-3}. Optical absorption spectra recorded after various irradiation times as indicated in the graph.



Scheme 2

ion **4** and the cycloheptatrienyl type radical **5**. As is depicted in Scheme 1 the formation of **4** requires a precursor: the radical cation **2**$^{+\bullet}$, generated by photoionization. Since the latter was not observed at the time resolution of the detection set-up used in this work its lifetime must be rather short, *i.e.* shorter than about 30 ns ($k > 3.3 \times 10^7$ s^{-1}). In other words homolytic C–C bond cleavage in the radical cation **2**$^{+\bullet}$ leading to **4** and the radical **5** is a rather fast process. Deprotonation of the radical cation yielding **2**$^{\bullet}$ was not observed. Such selective cleavage of the C–C bond of radical cations was also found in the case of **(AcrH)**$_2$[7] and 2-methyl-1,1,2-triphenylpropane.[9]

Principally, cycloheptatrienyl type radicals can be generated also by homolytic C–C bond cleavage in electronically excited bitropyls, *i.e.* ionization can compete with homolytic C–C bond cleavage which exclusively yields **5**. In this respect it is notable that photo-induced homolytic cleavage of C–C bonds was observed upon continuous irradiation of bitropyls substituted with *tert*-butyl groups at low incident light intensity.[10]

The non-linear dose dependence of the photocurrent observed at $\lambda_{inc} = 266$ nm suggests that photoionization is in part due to a biphotonic effect. Provided biphotonic photoionization is not operative at $\lambda_{inc} = 347$ nm the radical ion yield, and consequently the tropylium ion yield, is expected to be lower than that at $\lambda_{inc} = 266$ nm. This corresponds with the conclusion drawn by comparing the transient absorption spectra obtained at $\lambda_{inc} = 266$ nm and at $\lambda_{inc} = 347$ nm (*vide* Fig. 1a and 1b, respectively): the ratio OD_{370}/OD_{560} is much larger at $\lambda_{inc} = 266$ nm than at $\lambda_{inc} = 347$ nm.

Electron transfer from 2 to excited AcrH$^+$

The flash photolysis experiments give evidence for the formation of **AcrH**$^{\bullet}$, **4** and **5**. The mechanism postulated in this case is presented in Scheme 3. The thermodynamic driving force for electron transfer from **2** to [AcrH$^+$]* can be evaluated with the aid of the Rehm–Weller equation [eqn. (1)], where E^0_{red}(**AcrH**$^+$)

$$-\Delta G = E^\circ_{red}(\mathbf{AcrH^+}) - E^\circ_{ox}(\mathbf{2}) + E(\mathbf{AcrH^+}) \qquad (1)$$

is the standard reduction potential of **AcrH**$^+$, E^0_{ox}(**2**) is the standard oxidation potential of **2** and E(**AcrH**$^+$) is the energy of the excited state of **AcrH**$^+$.[11] Accordingly, the electron transfer from **2** to [AcrH$^+$]* is highly exergonic (see Table 1).

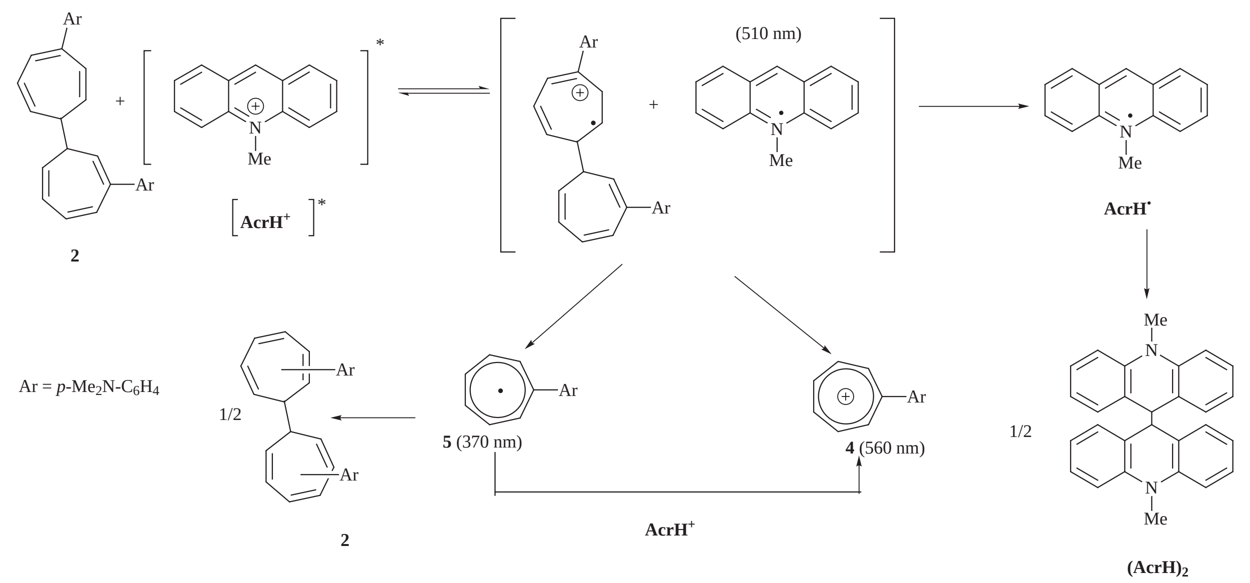
Interestingly, **4** is formed rapidly (during the 20 ns flash), very likely *via* C–C bond cleavage in **2**$^{+\bullet}$ and, additionally, after the flash, presumably, by the reaction of **AcrH**$^+$ with **5**. This process should be only weakly exergonic according to the oxidation potential of the donor **5** (see Table 1). On the basis of this approximation the observed dependence of the yield of **4** on the acceptor concentration [**AcrH**$^+$] becomes comprehensible.

As indicated in Scheme 3 a possible deactivation route of the acridinyl radicals formed during the electron transfer concerns the dimerization to 10,10′-dimethyl-9,9′-biacridine, **(AcrH)**$_2$. The rather low yield of the latter might be explained by taking into account that the (experimentally evidenced) reaction of **(AcrH)**$_2$ with [**AcrH**$^+$]* occurs. This process which is also depicted in Scheme 3 results in the formation of **2** and proceeds in the following way: **(AcrH)**$_2$ reacts with [**AcrH**$^+$]* producing **AcrH**$^{\bullet}$ and **(AcrH)**$_2^{+\bullet}$. The latter decomposes forming **AcrH**$^+$ and **AcrH**$^{\bullet}$. **AcrH**$^{\bullet}$ can principally react with **4** forming **AcrH**$^+$ and **5**. However, this reaction is not very likely to occur because of its estimated free energy change ($\Delta G = 0.07$ eV, Table 1). Finally, two radicals of type **5** can combine and form **2**. Some of the radicals regenerated in this way may undergo side reactions such as hetero-coupling thus lowering the yields of **4** and **(AcrH)**$_2$.

Electron transfer from 1 to excited AcrH$^+$. Interestingly, **3** is formed as a final product only if protons are present in the solution. A mechanism explaining this phenomenon is presented in Scheme 4. The electron transfer from **1** to [**AcrH**$^+$]* results in the formation of the acridinyl radical **AcrH**$^{\bullet}$ and the radical cation **1**$^{+\bullet}$. The reduction potential of **3** (−0.36 V)[4] is more positive than the oxidation potential of **AcrH**$^{\bullet}$ (−0.46 V). From these values $-\Delta G = 0.1$ eV is estimated. Therefore, **AcrH**$^{\bullet}$ and **3** are likely to undergo electron transfer. **6** and **AcrH**$^+$ are formed by the reaction of **3** with **AcrH**$^{\bullet}$ and, subsequently, **1** (*i.e.* a mixture of its isomers) might be regenerated by the combination of two radicals of type **6**. In the presence of protons the acridinyl radical is protonated[17] and the reduction of **3** is prevented. The protonated acridinyl radical (*i.e.* the radical cation of dihydroacridine) is known to disproportionate yielding **AcrH**$^+$ and **AcrH**$_2$.[18]

The formation of **AcrH**$_2$ could not be observed because it reacts with **3** by hydride transfer yielding (4-methoxyphenyl)cycloheptatriene and **AcrH**$^+$.[19] Since **3** is consumed and **AcrH**$^+$ is formed in this reaction it becomes comprehensible why at the photolysis of the system **AcrH**$^+$/**1** the yield of **3** is only 50% and why **AcrH**$^+$ is not consumed. (4-Methoxyphenyl)cycloheptatriene could be detected in small quantities with the help of HPLC. Independent experiments have confirmed that the irradiation of a mixture of **3**, **AcrH**$_2$ and (4-methoxyphenyl)cycloheptatriene leads to the decomposition of the cycloheptatriene derivative.

Electron transfer from 2 to excited TPP$^+$. The reaction mechanism illustrated in Scheme 5 is based on the occurrence of electron transfer from **2** to ^{3}(**TPP**$^+$)*, triplet excited **TPP**$^+$. This reaction results in the formation of the radical cation **2**$^{+\bullet}$ and the triphenylpyrylium radical, **TPP**$^{\bullet}$. Species **2**$^{+\bullet}$ rapidly undergoes C–C bond cleavage yielding **4** and the corresponding

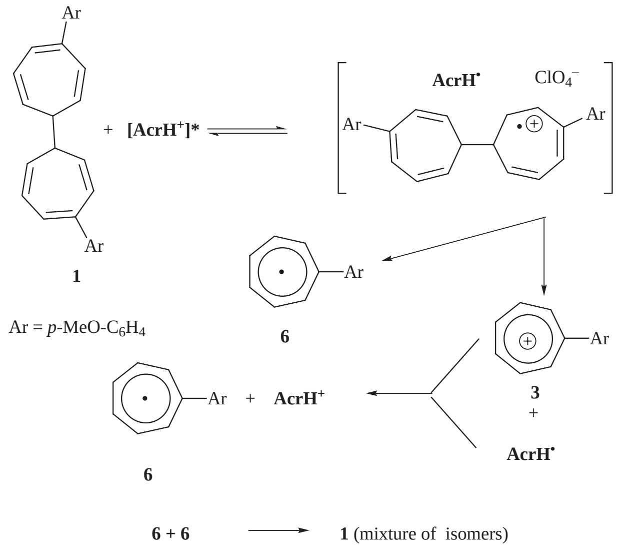


$$(AcrH)_2 + (AcrH^+)^* \longrightarrow (AcrH)_2^{+•} + AcrH^•$$

$$(AcrH)_2^{+•} \longrightarrow AcrH^+ + AcrH^•$$

$$AcrH^• + \mathbf{4} \longrightarrow AcrH^+ + \mathbf{5}$$

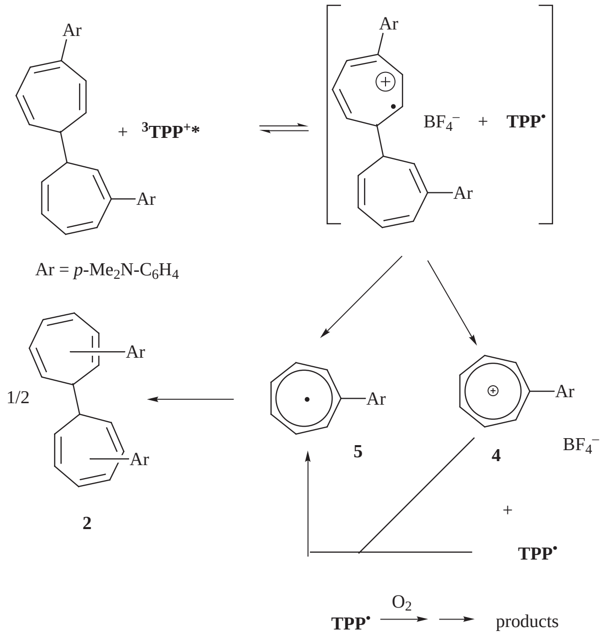
Scheme 3



$$AcrH^• + H^+ \longrightarrow AcrH^{+•}$$

$$2\,AcrH^{+•} \longrightarrow AcrH^+ + AcrH_2$$

Scheme 4



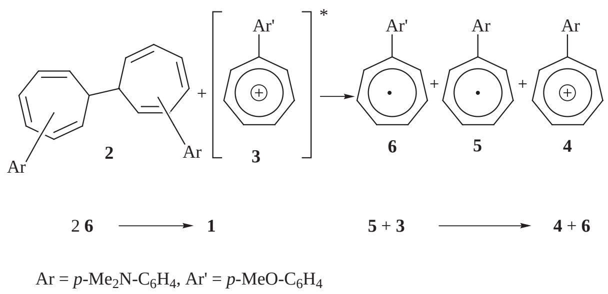
Scheme 5

radical **5**. This is revealed by laser flash photolysis experiments with **2** in the absence of any other compound at $\lambda_{inc} = 266$ nm (see Fig. 1a), where $\mathbf{2}^{+•}$ was formed by photoionization. Simultaneously with the laser flash the absorption of **4** at 560 nm appeared. The high value of the quantum yield $\Phi(\mathbf{4}) = 0.2$ found in the case of system **TPP**$^+$**/2** at a relatively low concentration of **2** supports the assumption that the electron transfer involves the long-lived triplet state of **TPP**$^+$.

The radical **TPP**$^•$ is persistent,[20] and, therefore, homo- and hetero-coupling reactions are unlikely. We could show that electrochemically produced **TPP**$^•$ radicals are capable of reducing **4**.[19] However, in air-equilibrated neutral acetonitrile solution O_2 scavenges **TPP**$^•$ radicals and thus the reduction of **4** by **TPP**$^•$ is prevented.[21] This explains why in the absence of O_2 the tropylium salt is not formed. Nevertheless, it cannot be assumed that under these conditions **2** is photostable. This is inferred from the photo-isomerization occurring upon the irradiation of **TPP**$^+$ in the presence of neat **2**. When a bitropyl-isomer of **2** was irradiated in the absence of O_2 other isomers were formed. This is due to the fact that each **2** isomer is formed with equal probability when two **5** radicals combine.

Notably, electrochemical studies also revealed that in acetonitrile solution **TPP**$^•$ radicals react with O_2, a reaction causing the decomposition of **TPP**$^+$.[22]

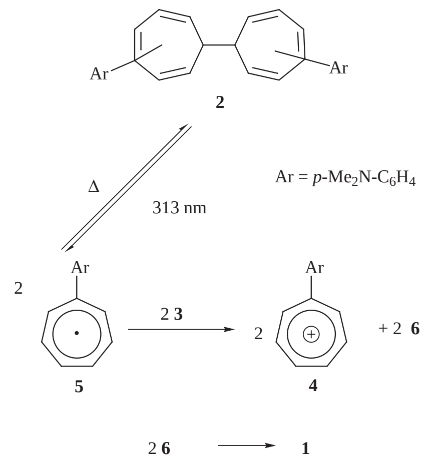
Electron transfer from 2 to excited 3. This system was photolyzed under different irradiation conditions. Irradiation at $\lambda_{inc} = 436$ nm excites the (p-methoxyphenyl)tropylium ion **3** which acts as an acceptor. In other words electron transfer from **2** to **3*** occurs and **4** is formed apart from **6** and **5**. This mechanism is depicted in Scheme 6 which also shows that the self reaction of **6** yields **1**, a final product detected by HPLC.



Scheme 6

Notably, the yield of **4** is expected to be increased *via* the oxidation of radical **5** by **3**. The occurrence of this reaction is feasible since the oxidation potential of the radical **5** [assumed to be equal to the reduction potential of **4** (−0.53 V)] is more negative than the reduction peak potential of **3** (−0.36 V[4]). Regarding the relatively low rate of the formation of **4** found in this case it is noteworthy that the lifetime of **3*** is shorter than 1 ns.[23] Therefore, at the applied concentration of 5×10^{-4} mol dm^{-3} **2** quenches only a very small portion of excited **3**.

Irradiation at $\lambda_{\text{inc}} = 313$ nm predominantly excites **2**. The subsequently occurring C–C bond cleavage generates two radicals **5** which will be oxidised by **3** in its ground state as is depicted in Scheme 7. This reaction sequence is much faster than that *via* the excited state of **3**. Oxidation of **5** by **3** yields **4** and **6**. Regarding the fate of **6** it is likely that a self reaction resulting in the formation of **1** takes place. This reaction is also contained in Scheme 7.



Scheme 7

Conclusions

1. This work demonstrates that the favoured deactivation pathway of radical cations of aryl bitropyls **1** and **2** generated electrochemically or photochemically, either by direct excitation or by photoinduced electron transfer, consists in a C–C bond cleavage yielding cycloheptatrienyl type radicals and tropylium cations. The C–C bond cleavage is faster than the back electron transfer. Experiments with mixtures of the regioisomers of the bitropyls yielded results similar to those obtained with the neat isomers.

2. Long wavelength (313 nm) excitation of bitropyl **2** causes the homolytic cleavage of the central bond thus yielding cycloheptatrienyl type radicals. These radicals can be oxidised by electron acceptors such as **TPP**$^+$ in the presence of oxygen or by aryltropylium cations having a suitable oxidation potential.

3. An electrochemically initiated redox cycle involving the aryl-substituted bitropyl **2** and the corresponding tropylium ion was established. This cycle opens up the possibility of an electrochemical switch. However, for a practical application of this switch undesired side reactions still have to be overcome. In this respect further studies concerning the importance of the aryl substituents at the seven-membered rings are desirable.

Experimental

Instrumentation

Absorption spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer and NMR spectra were recorded on a Bruker instrument (DPX 300).

Electrochemistry

Cyclic voltammograms of **1**, **2** and **4** were measured in acetonitrile solution (1 mmol dm^{-3}) using tetrabutylammonium hexafluorophosphate as supporting electrolyte at a scan rate of 1 V s^{-1}. Electrochemical experiments were carried out using the PG 285 potentiostat connected to a nitrogen-purged three-electrode-cell fitted *vs.* a SCE with a platinum working electrode and a platinum auxiliary electrode. The latter was separated from the working electrode by a porous glass disk. 100 mmol of **1** or **2** were added to 50 ml of an acetonitrile solution of tetraethylammonium perchlorate (100 mmol dm^{-3}). Electrolysis was performed at constant potential (**1**: −1.4 V; **2**: −0.9 V). It was terminated when the current (initially 5–20 mA) had lowered to 0.75 mA. Also here tetrabutylammonium hexafluorophosphate was used as supporting electrolyte.

Irradiations

Steady state photolysis experiments were carried out with acetonitrile solutions using a 500 W high pressure mercury lamp operated in conjunction with a metal interference filter (Carl Zeiss Jena) or a monochromator (Oriel, model 77200). Additional irradiations were performed in a Rayonet photoreactor. The solutions were irradiated in 1 cm quartz cuvettes. The absorbed irradiation dose was determined with the aid of the ferric oxalate actinometer. Laser flash photolysis was carried out with the aid of a ruby laser (Korad, Model K1 QS2, $\lambda = 347$ nm, flash duration 20 ns) and a Nd/YAG laser (J. K. Lasers, $\lambda = 266$ nm, flash duration 20 ns). If desired the acetonitrile solutions were de-aerated by argon bubbling prior to irradiation. Solutions containing tetrafluoroboric acid (0.5–50 mmol dm^{-3}) were prepared using aqueous HBF_4 (50%).

Product analysis

High pressure liquid chromatography, HPLC, and optical absorption spectroscopy were used to determine the concentration of reaction partners.

HPLC analysis was performed using RP 18 columns and a diode array detector (Shimadzu SPD-M10A). The mobile phase consisted of an acetonitrile–water mixture (80:20, vol/vol) containing a buffer system (triethylamine–H_3PO_4) set to pH = 2.7. To separate enantiomers of **2** an OD-H-column (Daicel) was used. A preparative HPLC set-up (Knauer, Berlin) was used to purify the bitropyls. Tropylium salt yields were determined by analytical HPLC on the basis of a calibration with probes of known concentration. The latter was obtained by measuring the optical absorption of **3** at 435 nm ($\varepsilon = 22\,500$ dm^3 mol^{-1} cm^{-1}) and that of **4** at 567 nm ($\varepsilon = 46\,840$ dm^3 mol^{-1} cm^{-1}). The rate constant of tropylium salt formation was calculated by the tangent method from conversion *vs.* the time of irradiation plots.

Materials

Solvent and reactants. Acetonitrile (HPLC grade) was obtained from Riedel de Häen. Commercially available triphenylpyrylium tetrafluoroborate (**TPP**$^+$) was purified by recrystallization. Acridinium perchlorate (**AcrH**$^+$),[24] 10,10′-

dimethyl-9,9′-biacridine **[(AcrH)$_2$]**[25] and **AcrH$_2$**[26] were prepared according to procedures described in the literature.

Bitropyls. The bitropyls **1** and **2** were synthesised as reported in the literature *via* the reduction of the corresponding tropylium salts[27] with Cr(II) under argon atmosphere[28] or by electrolysis at controlled potential. A mixture of regio-isomers of **1** or **2** resulted. In the case of **1** the 3,3′-isomer could be separated and purified by recrystallization.[4] In the case of **2** individual isomers were separated from the mixture containing 1,2′-, 2,3′-, 2,2′- and 3,3′-isomers with the aid of preparative high pressure chromatography (HPLC). The 1,1′-isomer was not formed. Apart from *meso*-compounds, each isomer consists of stereoisomers which were separated by HPLC using chiral phases and detected by their optical activity.

The synthesis was performed in the following way: 9 g Zn dust and 9 g (34 mmol) $CrCl_3$ were dissolved under argon in 80 ml aqueous HCl (5 M). The solution was filtered and transferred into a three-necked flask. Subsequently, a solution of **3** or **4** (6.7 mmol) in 150 ml HCl (2 M) was added dropwise. After stirring for one hour under argon 150 ml of *tert*-butyl methyl ether were added. Upon cooling with ice the mixture was neutralised by the addition of NaOH. After separation of the organic layer from the aqueous phase the latter was extracted with *tert*-butyl methyl ether. The combined organic extracts were dried and the solvent was evaporated under reduced pressure. The solid residue consisted of the regio-isomers of the substituted bitropyl.

Separation of 2 isomers

A mixture of isomers is obtained according to the procedure described above. The isomers were roughly separated from the mixture by fractional recrystallization from methanol. Whereas the 3,3′-isomer is insoluble in methanol, the 2,2′-isomer and the 2,3′-isomer crystallise from the solution, and the 1,2′-isomer is obtained by evaporation of the solvent. The fractions were purified by preparative HPLC with the aid of a RP-18 column. The eluant was methanol–water at a vol/vol ratio of 93:7 in the cases of the 2,2′-, 3,3′- and 2,3′-isomers and of 85:15 in the case of the 1,2′-isomer.

Characterisation of 2 isomers

1,2′-Bis[4-(dimethylamino)phenyl]bi(cyclohepta-2,4,6-trien-1,1′-yl). The 1,2′-isomer was a racemic mixture of two enantiomers that were separated at the chiral phase (eluent n-hexane–i-PrOH, 98:2, vol/vol), 1st fraction (+)-enantiomer; 2nd fraction (−)-enantiomer. Yield 80 mg (8%), mp 68 °C (Found: C, 85.48; H, 7.73; N, 6.38. Calc. for $C_{30}H_{32}N_2$: C, 85.67, H, 7.67; N, 6.66%); λ_{max}(MeCN)/nm (log ε): 283 (4.51), 350 (sh) (4.21); δ_H ($CDCl_3$) 2.97 (1 H, m, 7-H), 2.91 (6 H, s, Me_2N), 2.97 (6 H, s, Me_2N), 3.91 (1 H, t, 7-H), 5.37 (2 H, m, 1-H, 6-H), 5.63 (1 H, t, 6-H), 6.12 (1 H, m, 5-H), 6.32 (2 H, m, 2-H, 5-H), 6.45 (2 H, m, 3-H, 4-H), 6.5 (2 H, m, 3-H, 4-H), 6.68 (2 H, d, Ar), 6.71 (2 H, d, Ar), 7.06 (2 H, d, Ar), 7.46 (2 H, d, Ar).

2,2′-Bis[4-(dimethylamino)phenyl]bi(cyclohepta-2,4,6-trien-1,1′-yl). The 2,2′-isomer was a racemic mixture of two enantiomers that were separated at the chiral phase (eluent n-hexane–i-PrOH, 98:2, vol/vol), 1st fraction (−)-enantiomer; 2nd fraction (+)-enantiomer. Yield 260 mg (26%), mp 180 °C (Found: C, 85.37; H, 7.28; N, 6.45. Calc. for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66%); λ_{max}(MeCN)/nm (log ε): 282 (4.53); δ_H ($CDCl_3$) 2.08 (2 H, br s, 7-H), 2.89 (12 H, s, Me_2N), 5.43 (4 H, m, 1-H, 6-H), 6.23 (2 H, m, 5-H), 6.65 (4H, d, Ar), 6.78 (2 H, m, 4-H), 6.91 (2 H, d, 3-H), 7.24 (4 H, d, Ar).

2,3′-Bis[4-(dimethylamino)phenyl]bi(cyclohepta-2,4,6-trien-1,1′-yl). Yield 200 mg (20%), mp 82 °C (Found: C, 85.29; H, 7.48; N, 6.56. Calc. for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66%); λ_{max}(MeCN)/nm (log ε): 287 (4.54), 325 (sh); δ_H ($CDCl_3$) 2.11 (1 H, m, 7-H), 2.20 (1 H, m, 7-H), 2.96 (6 H, s, Me_2N), 2.99 (6 H, s, Me_2N), 5.47 (4 H, m, 1-H, 6-H), 6.36 (2 H, m, 5-H, 5′-H), 6.46 (1 H, d, 2′-H), 6.71 (2 H, d, Ar), 6.76 (2 H, d, Ar), 6.8; 7.0 (3 H, m, 3-H, 4-H, 4′-H), 7.31 (2 H, d, Ar), 7.43 (2 H, d, Ar).

3,3′-Bis[4-(dimethylamino)phenyl]bi(cyclohepta-2,4,6-trien-1,1′-yl). The 3,3′-isomer was a racemic mixture of two enantiomers that were separated at the chiral phase (eluent n-hexane–i-PrOH 95:5, vol/vol), 1st fraction (−)-enantiomer; 2nd fraction (+)-enantiomer. Yield 190 mg (19%), mp 168 °C (Found: C, 85.29; H, 7.54; N, 6.36. Calc. for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66%); λ_{max}(MeCN)/nm (log ε): 321 (4.48), 255 (4.34); δ_H ($CDCl_3$) 2.09 (2 H, br s, 7-H), 2.92 (12 H, s, Me_2N), 5.32, 5.43 (4 H, m, 2-H, 6-H), 6.30 (2 H, m, 5-H), 6.38 (2 H, d, 2-H), 6.69 (4H, d, Ar), 6.92 (2 H, d, 4-H), 7.4 (4 H, d, Ar).

Acknowledgements

The technical assistance of K. Buck is gratefully acknowledged. This research was in part financially supported by the Fonds der Chemischen Industrie.

References

1 H. Lund and M. M. Baizer (eds.), *Organic Electrochemistry*, Marcel Dekker, New York, 1991.
2 G. B. Schuster, *Adv. Electron Transfer Chem.*, 1991, **1**, 163.
3 T. Linker and M. Schmittel, *Radikale und Radikalionen in der Organischen Synthese*, Wiley-VCH, Weinheim 1998.
4 D. Jacobi, PhD Thesis, Humboldt-University, 1998.
5 D. T. Poulos, G. C. Hammond and M. E. Burton, *Photochem. Photobiol.*, 1981, **34**, 169.
6 S. Fukuzumi and T. Yorisue, *J. Chem. Soc.*, *Perkin Trans 2*, 1991, 1607.
7 S. Fukuzumi and Y. Tokuda, *J. Phys. Chem.*, 1992, **96**, 8409.
8 D. H. Geske, *J. Am. Chem. Soc.*, 1959, **81**, 4145.
9 A. Albini, E. Fasani and N. d'Alessandro, *Coord. Chem. Rev.*, 1993, **125**, 269.
10 G. Vincow, M. L. Morrell, F. R. Hunter and H. J. Dauben, Jr., *J. Chem. Phys*, 1968, **48**, 2876.
11 D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834.
12 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, p. 453.
13 B. Dreher, W. Abraham and F. Pragst, *J. Prakt. Chem.*, 1983, **325**, 104.
14 M. L. Olmstead, R. G. Hamilton and R. S. Nicholson, *Anal. Chem.*, 1969, **41**, 260.
15 P. Hapiot, J. Moiroux and J.-M. Savéant, *J. Am. Chem. Soc.*, 1990, **112**, 1337.
16 P. S. Mariano, J. L. Stavinoha and E. Bay, *Tetrahedron*, 1981, **37**, 3385.
17 M. Fujita, A. Ishida, T. Majima, S. Fukuzumi, S. Takamuku, *Chem. Lett.*, 1995, 111.
18 S. Fukuzumi, Y. Tokuda, T. Kitano, T. Okamoto and J. Otera, *J. Am. Chem. Soc.*, 1993, **115**, 8960.
19 D. Jacobi, L. Grubert and W. Abraham, unpublished results.
20 S. Nuzuma, N. Sato, H. Kawata, Y. Suzuki, T. Toda and H. Kokubun, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2600.
21 R. Akaba, S. Ahira, H. Sakuragi and K. Tokumaru, *J. Chem. Soc., Chem. Commun.*, 1987, 1262.
22 M. A. Miranda and H. Garcia, *Chem. Rev.*, 1994, **94**, 1069.
23 W. Abraham, B. Dreher, D. Kreysig, N. A. Sadovskij and M. G. Kuzmin, *J. Prakt. Chem.*, 1987, **329**, 569.
24 S. Fukuzumi, S. Koumitsu, K. Hironaka and T. Tanaka, *J. Am. Chem. Soc.*, 1987, **109**, 305.
25 S. Fukuzumi, T. Kitano and K. Mochida, *J. Am. Chem. Soc.*, 1990, **112**, 3246.
26 A. K. Colter, G. Saito and F. J. Sharom, *Can. J. Chem.*, 1977, **55**, 2741.
27 C. Jutz and F. Voithenleitner, *Chem. Ber.*, 1964, **97**, 29.
28 K. Okamoto, K. Komatsu, O. Murai, O. Skaguchi and Y. Matsui, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1785.

Paper 8/07270A