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Theoretical and spectroscopic studies of the photochemistry of 3-(4-dimethylaminophenyl)-7-methoxy-cyclohepta-1,3,5-triene

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Abstract

In this paper the photophysics and photochemistry of the title compound has been examined by laser, flash lamp and steady state methods. In protic solvents, photoheterolysis is able to compete with a rapid 1,7-hydrogen shift reaction to give the substituted tropylium methoxide, with the lifetime of the tropylium ion strongly depending on the nature of the alcohol. Hydrogen bonds between the solvent and the methoxy group of the cycloheptatriene derivative favor bond breakage and the solvation of the methoxide ion by protic solvents increases the lifetime of the free ions. Ab initio calculations suggest that the photoheterolysis in the gas phase takes places via a consecutive photohomolysis under formation of a radical pair, which then is undergoing an intra-pair electron transfer to form the tropylium and the methoxide ions.

The 1,7-hydrogen shift reaction leads exclusively to the production of 5-(4-dimethylaminophenyl)-1-methoxy-cyclohepta-1,3,5-triene. The fluorescence of the title compound exhibits a very large Stokes shift indicating considerable geometrical changes in the relaxed excited state and according to semi-empirical and ab initio calculations, the seven-membered ring is planar in the fluorescing state.

Keywords: Cycloheptatrienes; Sigmatropic hydrogen shift; Photoheterolysis; Tropylium ion; Ab initio calculation; Fluorescence

1. Introduction

Cyclohepta-1,3,5-triene (CHT) belongs to a group of compounds suitable for studying the course of photoinitiated pericyclic reactions such as the 1,7-hydrogen shift reaction and the electrocyclization [1].

Because the hydrogen shift reaction of the parent compound is degenerate, the photoproducts of substituted cycloheptatrienes are more easily studied, in particular aryl substituents attached to the seven-membered ring offer some advantages such as selective excitation of reactants and fluorescence [1].

According to ab initio calculations, [2] the 1,7-hydrogen shift of CHT proceeds by passing two conical intersections (S_2–S_1 and S_1–S_0) in the time scale of about 50 fs. Substituents at the 1-position of CHT control the direction of the hydrogen shift, for example, electron acceptors such as the cyano group direct into the two-substituted CHT; electron donors such as the methoxy group control the formation of the seven-substituted derivative. These results are due to the presence of barriers on the excited state surface; the energy required to overcome these barriers depends on the type of substituent at position-1 [2]. Another important result of the quantum mechanical calculations, confirmed by experiments, is the strong change in the conformation of the seven-membered ring. Whilst the boat-like conformation exists in the ground state, during the photoreaction, the formation of a more or less flat ring becomes a prerequisite of the hydrogen shift [2].

The strong influence of substituents on the direction and the selectivity of both the hydrogen shift reaction and the electrocyclization has also been observed with phenyl cycloheptatrienes bearing different substituents in the phenyl ring, [3,4] in particular, the 4-dimethylaminophenyl group allows the photoreactions to be reversible and selective. 3-(4-Dimethylaminophenyl)-7-methoxy-cyclohepta-1,3,5-triene (compound **1**) bears two electron donating groups, the methoxy group is attached directly at the CHT-ring and the dimethylamino group can work only through the π-system of the phenyl ring. The photochemistry of compound **1** differs from all aryl substituted cycloheptatrienes investigated due to the occurrence of an additional photoreaction; in methanol solution a photoheterolysis leads

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to the formation of the substituted tropylium methoxide which thermally reacts back to the 7-methoxy-x-aryl-CHT (x = 1, 2, 3) [5]. This change between a tropylium ion and a cycloheptatriene may be useful in order to control the coconformation of rotaxanes incorporating related cycloheptatrienyl stations [6]. With this in mind the question then arises as to whether the heterolysis and the sigmatropic 1,7-hydrogen shift reaction are competing photoreactions. Only a 7-methoxy-CHT derivative is able to undergo the formation of a tropylium ion, thus any hydrogen shift reaction prevents the CHT derivative from undergoing tropylium ion formation.

This paper is concerned with the photophysical and photochemical deactivation behavior of the compound **1** modeling the photoswitch of the rotaxanes. The fluorescence studies and quantum mechanical calculations examined in this paper will be useful in gaining a deeper insight into the course of photoreactions.

2. Experimental

2.1. General methods

NMR spectra were recorded on a Bruker DPX 300 (300 MHz) or a Bruker AMX 600 (600 MHz) with either the solvent or TMS as the internal standard. Chemical shifts are given in ppm relative to TMS. UV-Vis-spectra were recorded employing a Shimadzu UV 2101 PC spectrometer. Corrected fluorescence emission and fluorescence excitation spectra of solutions with an absorbance $A = 0.02 - 0.06$ were measured with the aid of a SLM AMINCO AB2 spectrofluorimeter.

Fluorescence quantum yields (±10%) were determined using quinine bisulfate in 0.1 N sulfuric acid as standard ($\Phi_F = 0.51$ [7]) and refractive index corrections were made [8] to adjust for the differing solvents used. The quantum yield changes with temperature variation were corrected both with respect to the refractive index and density changes of the solvent [9].

Fluorescence decay times were determined using the time-correlated single photon counting technique [10], and then analyzed with multi-exponential decay fits in the absence of iterative re-convolution using the Microcal Origin^{TM} 6.0 software kit. In order to determine quantum yields photochemical reactions were carried out by the irradiation of the cycloheptatriene solution contained in a quartz cuvette 1 × 1 cm. A high pressure mercury lamp with a narrow spectral range separation produced by a diffraction grid monochromator was used as the irradiation source. 1-(4-Dimethylaminophenyl)-cyclohepta-1,3,5-triene was used as a secondary actinometer ($\Phi_r^{365\,nm} = 0.01$, EtOH, 296 K [11]).

Laser flash and flashed xenon lamp experiments in order to record transient optical absorption and to measure the absorption decay were described elsewhere [5]. Quantum yields for the generation of compound **4** have been determined as described in previous studies [5].

2.2. Calculation details

Ab initio calculations on the HF/6-31G(d) and Becke3LYP/6-31G(d) theory level were carried out using Gaussian 98 [12]. The excited states were calculated with the single configuration interactions (CIS) of 25 occupied and 25 unoccupied orbitals. The full optimization of the ground and excited states was performed by vibrational analysis for the determination of stable and transition geometries. The S_1 state reaction of the model compound **6** (3-(4-diaminophenyl)-7-hydroxy-cyclohepta-1,3,5-triene) was studied by the calculations of the structures with a fixed distance between the carbon atom of the seven-membered ring and the oxygen atom of the OH group with full optimization of the other geometrical parameters.

Semi-empirical calculations using AM1 Hamiltonian [13] were carried out by AMPAC 6.0 [14]. The calculations of transition energies and oscillator strengths for cations were carried out using the CNDO/s-CI method with the interaction of 100 singly excited configurations and parameters sets as described in reference [15] for fully optimized AM1 ground state structures.

2.3. Materials

All reagents and solvents were purchased from Aldrich Company and were used as supplied. Solvents for UV-Vis- and fluorescence spectroscopy were of UVASOL quality (Merck).

2.3.1. 3-(4-Dimethylaminophenyl)-7-methoxy-cyclohepta-1,3,5-triene (*1*)

To 0.27 g $NaHCO_3$ (3.22 mmol) in MeOH (2 ml) *p*-dimethylaminophenyltropylium perchlorate (1 g, 3.23 mmol) in MeOH (150 ml) was added over a 3 h period. After stirring at normal temperature for 3 h the solution was filtered, the solvent evaporated and the residue dissolved in ether. The solution was dried (Na_2SO_4) and the solvent evaporated; the residue was then dissolved in *n*-hexane (20 ml). By cooling the solution to −77 °C; compound **1** precipitated and could be filtered off. After repeating the procedure three times, pure compound **1** was obtained as a pale yellow solid (0.2 g 25.6%), m.p. 68.5 °C.

^1H NMR ($CDCl_3$, 300 MHz), $\delta = 7.39$ (d, $J = 9$ Hz, 2 H, phenyl), 6.94 (d, $J = 6$ Hz, 1 H, CHT, H-4), 6.74 (d, $J = 9$ Hz, 2 H, phenyl), 6.32 (d, $J = 10$ Hz, 1 H, CHT, H-2), 6.24 (m, 1 H, CHT, H-5), 5.66–5.51 (m, 2 H, CHT, H-1 and H-6), 3.46 (br s, 4 H, CHT, H-7 and OCH_3), 2.97 (s, 6H, NMe_2).

$C_{16}H_{19}NO$ (241.33): calcd. C 79.63, H 7.94, N 5.80; found C 79.48, H 8.06, N 5.87. Compound **2** was available according to reference [16].

*2.3.2. 5-(4-Dimethylaminophenyl)-1-methoxy-cyclohepta-1,3,5-triene (**3**)*

Compound **1** (0.005 g, 0.021 mmol) in CD_3CN (1 ml) was irradiated in a NMR-tube with light of 350 nm (Rayonet-Reactor, 4 RPR-3500 Å Lamps) for 2 h. Compound **1** was consumed to 100%. Compound **3**, therefore was identified by means of ^1H NMR spectroscopy without isolation.

^1H NMR (CD_3CN, 600 MHz), $\delta = 7.21$ (d, $J = 9$ Hz, 2 H, phenyl), 6.70 (d, $J = 9$ Hz, 2 H, phenyl), 6.63 (m, 1 H, CHT, H-3), 6.52 (dd, $J = 1$, 10 Hz, 1 H, CHT, H-4), 5.46 (t, $J = 7$ Hz, 1 H, CHT, H-6), 5.42 (d, 1 H, CHT, H-2), 3.60 (s, 3 H, OCH_3), 2.91 (s, 6H, NMe_2), 2.54 (d, $J = 7$ Hz, 2H, CHT, H-7).

3. Results

3.1. Fluorescence data

The chromophore of **1** is the 3-(4-dimethylaminophenyl)-cyclohepta-1,3,5-triene (compound **2**) and therefore both the absorption and the fluorescence spectrum of compound **1** should resemble those of compound **2**. This is indeed the case, the spectral characteristics of both compounds are identical as illustrated in Figs. 1 and 2.

The large Stokes shift observed with the fluorescence band as a result of excitation within the long-wavelength absorption band is characteristic of aryl cycloheptatriene derivatives [17]. The fluorescence quantum yield of compound **1** is small but considerably larger than that of the comparable compound **2** ($\Phi_F = 0.040$ versus 0.005 in acetonitrile solution). Results obtained with compound **1** are shown in Table 1. The fluorescence quantum yield is shown to be dependent on temperature in the range of 171–293 K (see Fig. 3). However, at 77 K a significant hypsochromic shift for the fluorescence was noted (see Fig. 2). The excitation spectra recorded at room temperature and at 77 K are in accordance with the absorption spectrum (as shown in Fig. 2 for room temperature).

3.2. Photochemistry

Compound **1** differs from compound **2** by the additional methoxy group that was introduced in the position-7 of the seven-membered ring. Apart from the quantum yield this substituent does not affect on the fluorescence spectrum (compare Figs. 1 and 2). Accordingly, the question arises as to whether the photoinduced hydrogen shift is also similar in both compounds. The 1,7-hydrogen shift observed with compound **2** has been shown to result in the formation of 2-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene (**5**) [18].

The UV-spectra following the photoreaction initiated by an excitation wavelength of 365 nm both in compound **1** and **2** exhibit three isosbestic points and indicate a simple photoreaction A → B in acetonitrile solution (compare Fig. 4a and b).

The NMR spectra recorded after different irradiation time of compound **1** reveal the formation of only one product that was assigned to compound **3**. Consequently, it has been shown that the methoxy group does not influence the photoreactivity in acetonitrile. Only the 1,7-hydrogen shift is observed. Instead, the donor substituent at the 3-position of the ring governs the remarkable selectivity of the 1,7-hydrogen shift. It is worthwhile noting that the quantum yield of the sigmatropic hydrogen shift is smaller in protic

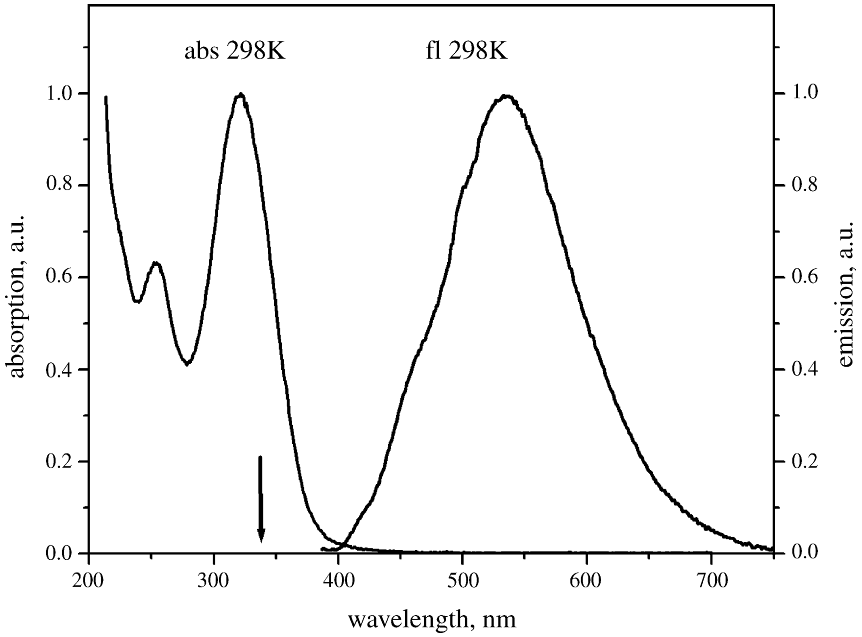


Fig. 1. Absorption and fluorescence spectra of compound **2** in acetonitrile solution.

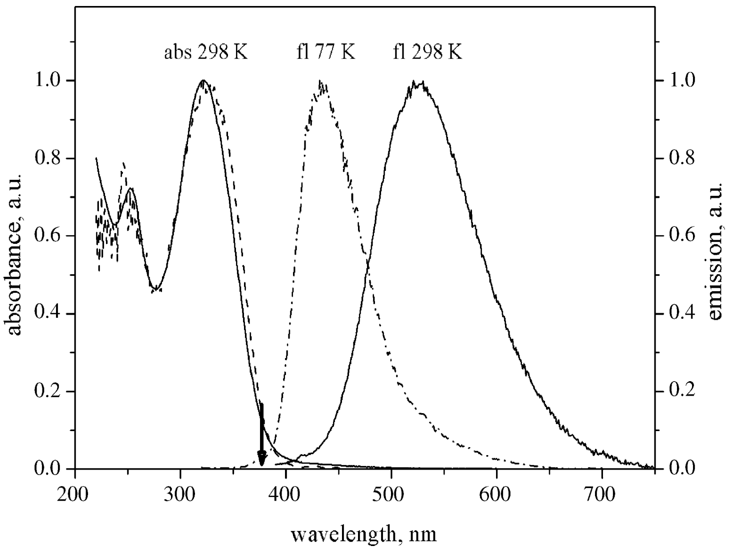


Fig. 2. Absorption (solid line), excitation (dashed line) and fluorescence spectra of compound **1** at 298 K and the fluorescence spectrum at 77 K in methanol solution.

Table 1
Absorption (λ_A) and fluorescence maxima (λ_F), Stokes shift ($\Delta\nu_{A-F}$), fluorescence quantum yields (Φ_F), quantum yields of the H-shift (Φ_r) and quantum yields of the tropylium ion formation (Φ_{ion}) for compound **1**

Solvent	λ_A (nm) (ε, $M^{-1}\,cm^{-1}$)	λ_F (nm)	$\Delta\nu_{A-F}$ (cm^{-1})	τ_F (ns)	Φ_F[a]	Φ_r[a]	Φ_{ion}[a]
Hexane	318 (18 560)	n.d.	n.d.	n.d.	<0.001	0.20	n.d.
Acetone	321 (18 250)	505	10 870	n.d.	0.06	0.07	n.d.
THF	326 (17 280)	485	10 050	n.d.	0.05	0.12	n.d.
EtOH	322 (17 861)	511	11 780	n.d.	0.05	0.08	0.04
MeOH	322 (16 366)	533	12 300	1.5	0.02	0.03	0.09
MeOH:CH_3CN[b]	323 (17 755)	n.d.	n.d.	n.d.	n.d.	0.04	n.d.
Acetonitrile	321 (18 716)	525	12 100	1.2[c]	0.04	0.08	n.d.

n.d.: not determined.
[a] Error 10%.
[b] 1:1 mixture.
[c] Biexponential decay ($\tau_1 = 1.15$ (84%); $\tau_2 = 3.13$ (16%)).

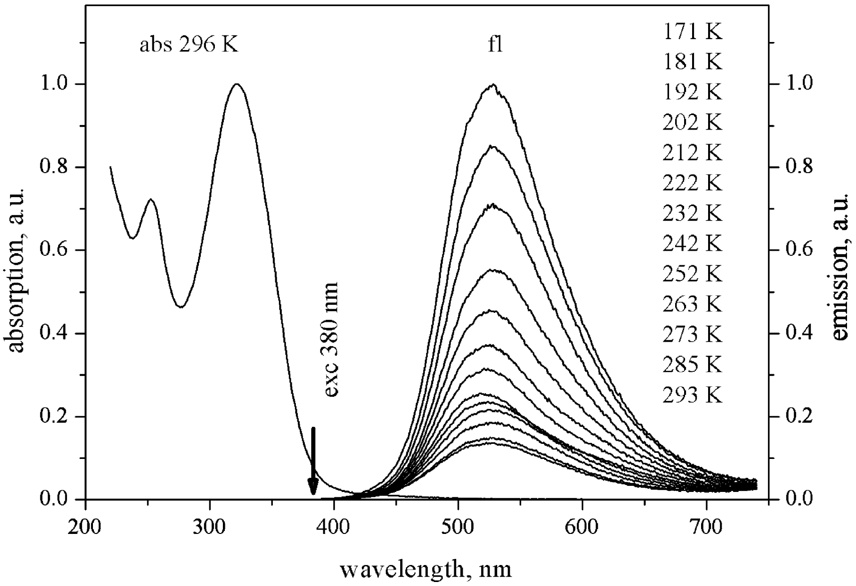


Fig. 3. Fluorescence spectra of **1** in methanol solution at different temperatures.

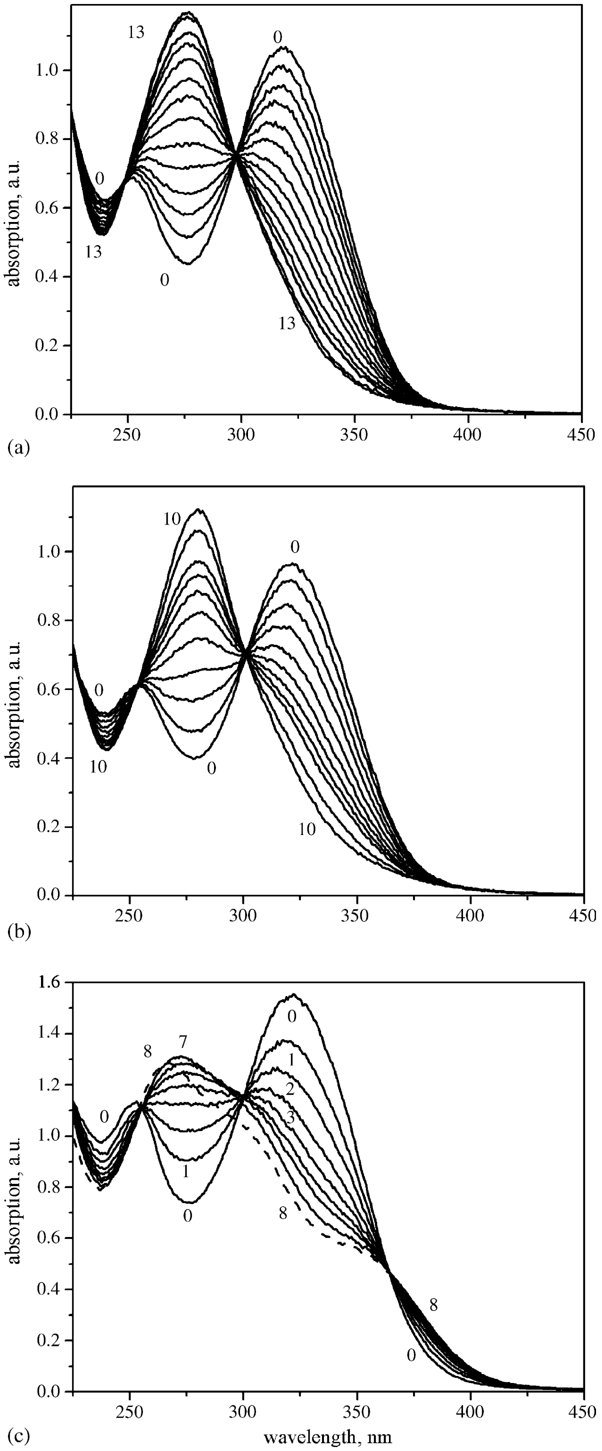


Fig. 4. Absorption spectra recorded after various irradiation times (irradiation wavelength 365 nm): (a) compound **2** in methanol solution 0–720 s; (b) compound **1** in acetonitrile solution 0–420 s; (c) compound **1** in methanol solution 0–580 s.

solvents compared with those in nonpolar solvents (Table 1). An influence of the methoxy group on the photoreactivity of compound **1** is noted in methanol solution. A simple photoreaction was not observed in this solvent indicating an additional reaction to occur (compare Fig. 4b and c).

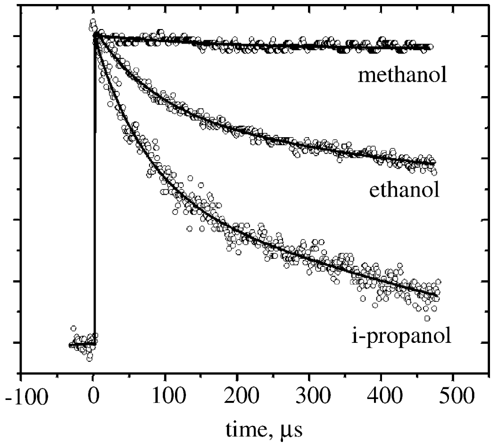


Fig. 5. The decay kinetics of the transient absorption of **4** in different alcohols monitored at 570 nm.

This second type of photoreaction observed with compound **1** [5] can only be observed in alcoholic solvents and results in the formation of the transient *p*-dimethylaminophenyl-tropylium ion (compound **4**). The lifetime of this ion depends on the nature of the alcohol solvent used (see Fig. 5 and Table 2).

However, not only the lifetime but also the quantum yield of tropylium ion formation is dependent on the alcoholic solvent used (Table 2). In addition, the lifetime of compound **4** can also be altered by adding acetonitrile to the methanol solution of compound **1** (Table 2).

The transient absorption spectrum depicted in Fig. 6 exhibits, apart from the absorption band of the tropylium ion (at 570 nm), a shoulder on the short-wavelength site around 440 nm; this can be separated from the main absorption band by Gauss-functions.

The ratio of these two transient absorption bands depends on the type of alcohol used as a solvent (Table 3).

Whereas a transient absorption band that is attributed to the tropylium ion is not observed in acetonitrile solution (see above), a transient absorption band peaking at 430 nm (see Fig. 7) is recorded and the appearance of this transient absorption band is accompanied by a transient electrical conductivity of the solution (see Fig. 8).

Table 2
Quantum yields of the formation of **4** in different alcohols characterized by the hydrogen bond donor solvent parameter α and the lifetimes (mono- or biexponential) of **4** in alcohols and mixtures of acetonitrile and methanol

Solvent	α [24]	Φ_{ion}	τ_1 (%), s	τ_2 (%), s
Methanol	0.93	0.09	0.1 (47)	1.1 (53)
Ethylene glycol	0.90	0.08	1.4 (100)	
Ethanol	0.83	0.04	0.005 (75)	0.03 (25)
i-Propanol	0.76	0.007	0.002 (100)	
Methanol:acetonitrile (5:95)	n.d.	n.d.	1.1 (25)	16.7 (75)

n.d.: not determined.

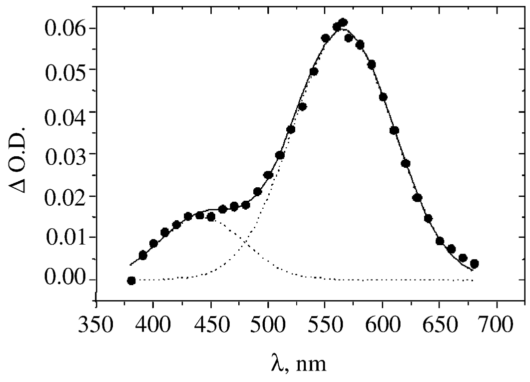


Fig. 6. Absorption spectra of transients recorded with **1** in ethanol solution (2×10^{-5} M, purging with Ar) recorded 700 ns after the 347 nm excitation flash and calculated band separation.

Table 3
Transient absorption maxima of the radical cation (rc) and **4** and the ratio of the optical density measured at the absorption maxima

Solvent	Radical cation (rc) (λ, nm)[a]	Tropylium ion **4** (λ, nm)	ΔO.D. (**4**)/ ΔO.D. (rc)[b]
Methanol	440	566	7
Ethylene Glycol	468	571	8
Ethanol	442	566	4
i-Propanol	440	569	2

[a] From fitting the entire spectrum by Gauss functions.
[b] 0.5–1.0 μs after flash.

The tropylium ion, compound **4**, can be attacked by nucleophiles such as water or alcohols: we therefore chose to estimate the equilibrium constant K of the reaction of compound **4** with methanol (see Schemes 1 and 2).

The estimation of K was performed according to Eq. (1) by measuring the absorbance of compound **4** (used with the perchlorate counter ion) in relation to the concentration. It was discovered that at a low concentration (10^{-6} to10^{-5} M) the equilibrium is on the side of the tropylium ion **4** ($K = 2 \times 10^{-6}$ M).

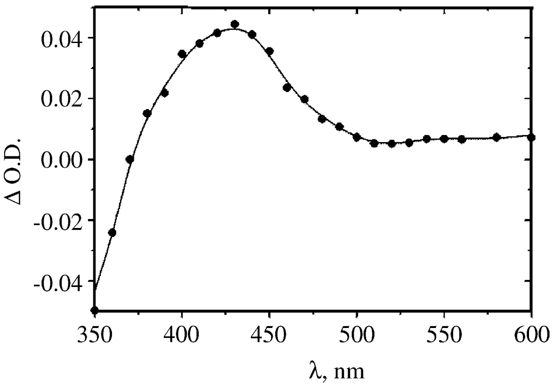


Fig. 7. Absorption spectrum of the transient in MeCN (Ar-purged) recorded 300 ns after the 347 nm excitation.

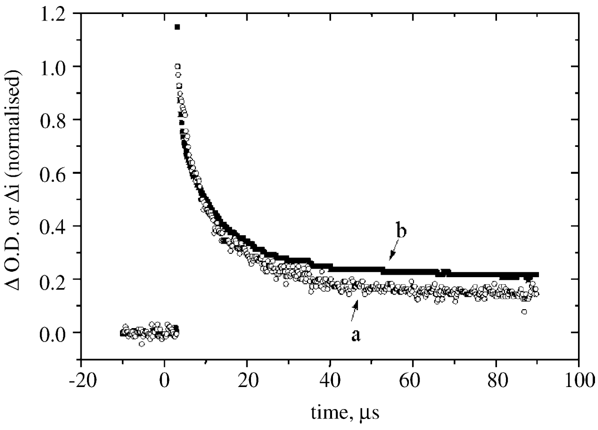


Fig. 8. The decay kinetics of the transient absorption (ΔO.D.) in MeCN monitored at 430 nm (a) and the conductivity (Δ*i*) (b) after the 347 nm flash.

3.3. Calculations

Due to the presence of the boat-shaped cycloheptatriene ring, a number of ground state conformers of compound **1** which bear the methoxy group in the pseudo-axial or -equatorial position are possible (see Scheme 3). Both the photophysical and the photochemical properties may be governed by these conformers. It can be expected that quantum mechanical calculations will provide insight into the most stable conformers in both the ground and the excited states.

In fact, both semi-empirical and ab initio calculations determined the equatorial conformers as being the most stable entities (Table 4) with the conformer e being the most stable (see Scheme 3).

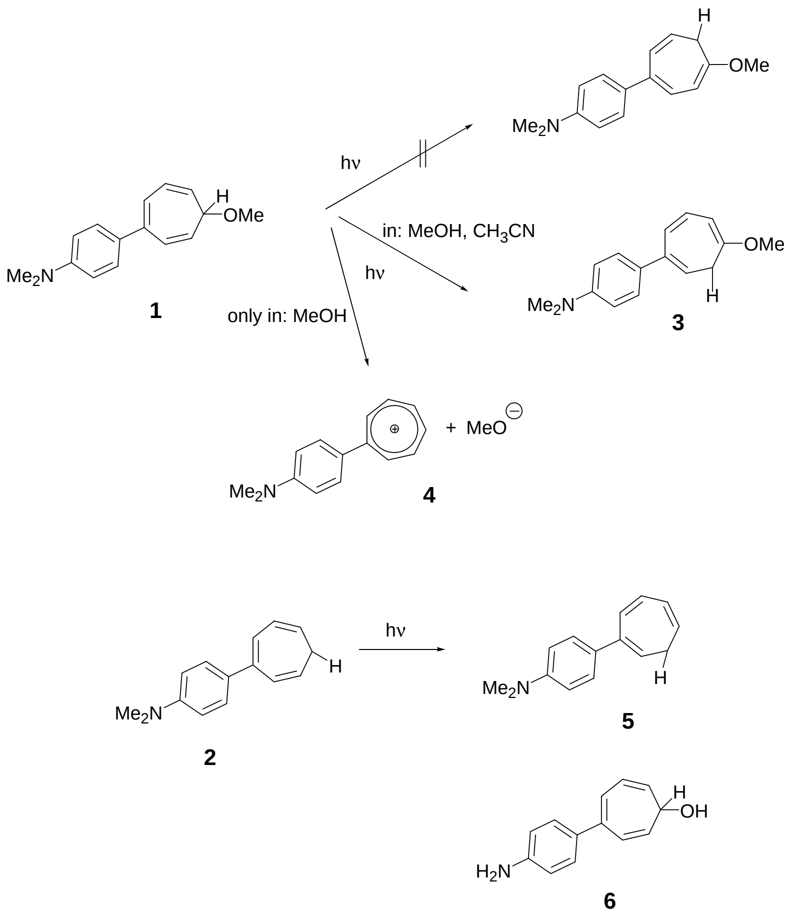
The geometrical parameters of the conformers are identified as being very similar, independent of the calculation methods.

CNDO/s calculations carried out with the AM1 optimized conformers have shown that the $S_0 \rightarrow S_1$-transition, which has a low transition moment, has charge transfer (CT) characteristics (Table 5).

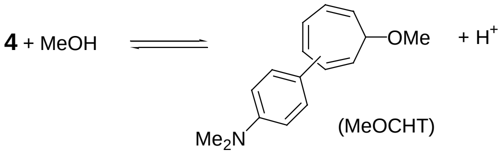
Table 4
Energy of the fully optimized geometry of the axial (a–d) and the equatorial conformers (e–h) of compound **1** calculated by the help of ab initio (HF/6-31G(d)) and semi-empirical (AM1) methods

Configuration.	HF/6-31G(d)		AM1	
	E[a] (a.u.)	ΔH[b] (kcal/mol)	H (kcal/mol)	ΔH (kcal/mol
a	−745.843481	3.64	39.49	4.04
b	−745.841562	4.85	39.79	4.34
c	−745.841718	4.75	39.78	4.33
d	−745.843489	3.64	39.49	4.04
e	−745.849284	0	35.58	0.13
f	−745.846735	1.60	35.72	0.27
g	−745.846736	1.60	35.69	0.24
h	−745.848784	0.31	35.45	0

[a] Sum of electron and zero-point energies.
[b] Energy difference.



Scheme 1.



$$K = \frac{[\mathrm{MeOCHT}]^2}{[\mathbf{4}]} \quad (1) \qquad [\mathrm{MeOCHT}] = [\mathrm{H}^+]$$

Scheme 2.

Charge transfer occurs from the seven-membered ring to the dimethylaminophenyl moiety with the second electronic transition being localized in the seven-membered ring. The energy of both transitions is only slightly different, thus giving rise to the assumption that both transitions can be found within the long-wavelength absorption band.

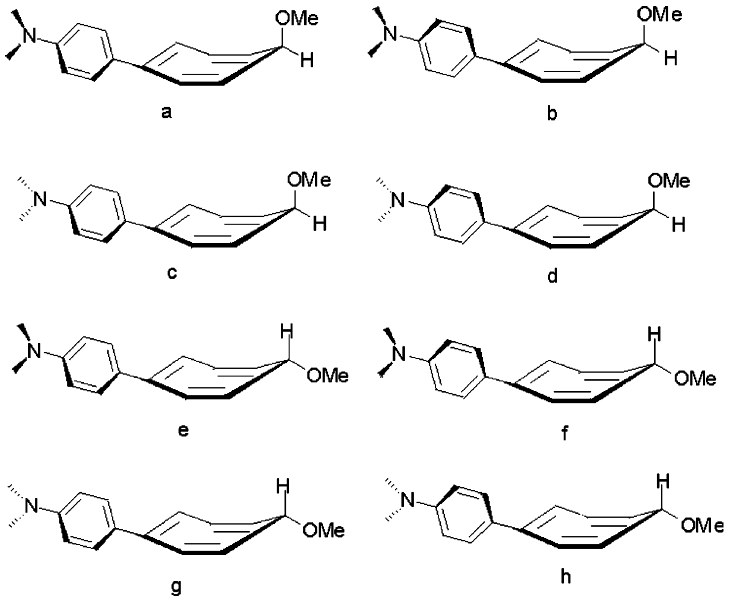
Table 5
Transition energies (eV) (oscillator strength) and the transition nature (CT, Charge Transfer, ππ*) of the most stable axial and equatorial conformers (AM1 optimized structures) as calculated by CNDO/s

Configuration	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_2$
a	4.43 (0.02) CT	4.48 (0.28) ππ*
h	4.42 (0.02) CT	4.48 (0.27) ππ*

Ab initio calculations on 3-(4-aminophenyl)-7-hydroxycyclohepta-1,3,5-triene (compound **6**) indicate that the excited state structure bearing the hydroxy group in the pseudo-axial position is almost planar (see Fig. 9): the calculated parameters of compound **6** in the S_1-state of the two conformers are shown in Table 6.

Table 6
Some parameters of the optimized structures of the model compound **6** calculated by the ab initio method (HF/6-31 G(d)) including configuration interaction

Parameter	e	h
Sum of electronic and zero-point energy (a.u.)	−628.703184	−628.703796
Lowest vibration frequency (cm^{-1})	49.4	48.6
Transition energy of $S_1 \rightarrow S_0$ (eV)	3.51	3.52
Oscillator strength	0.26	0.27
Energy difference between $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions	2.17	2.07
Dipole moment of S_1 (S_0), D	3.07 (2.71)	3.28 (2.87)
Assignment	ππ*	ππ*



Scheme 3.

Additionally, ab initio calculations of the tropylium formation pathway of the model compound **6** were carried out for the gas phase. Results are shown in Fig. 10.

The calculations revealed the formation of a radical pair close to the S_1 planar equilibrium structure (transition energy 3.51 eV) separated by an activation barrier of 34.5 kcal/mol. The radical pair is converted radiationless to the ground state of an ion pair nature because of the small energy gap between the S_1 and S_0^{FC} states (around 0.94 eV) as a result of the electron transfer within the radical pair.

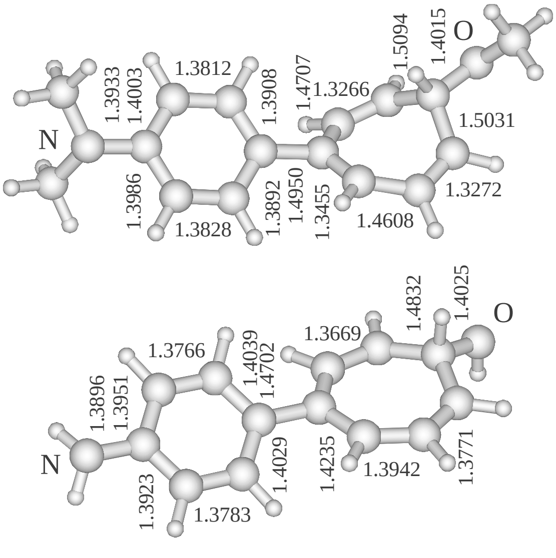


Fig. 9. The optimized structures of compound **1** in the S_0 (top) and of the model compound **6** in the S_1 state (bottom) calculated with HF/6-31G(d).

4. Discussion

4.1. 1,7-H shift and fluorescence

Assuming that the sigmatropic 1,7-hydrogen shift observed with compound **1** proceeds via a conical intersection the question arises as to whether there is a relationship between fluorescence and hydrogen shift in these types of photoreaction. The strong Stokes shift observed in the fluorescence band can be explained by the planarization of the boat-shaped conformation of the seven-membered ring. Obviously these geometrical changes are hampered at a low temperature: for example the Stokes shift at 77 K is therefore much smaller, as can be seen from Fig. 2. Quantum mechanical calculations (see above) lend support to the geometrical change being planarization. This planarization of the seven-membered ring on the pathway to the conical intersection has also been calculated for the unsubstituted cycloheptatriene. However, looking at the solvent dependency of the quantum yield for the fluorescence and the hydrogen shift reaction as displayed in Table 1, a correlation between these two processes cannot be derived. Nonpolar and slightly polar solvents actually favor the hydrogen shift (Table 1, entries 1–3), but radiative deactivation is not observed in hexane solution and differs only slightly in acetone and THF. It therefore seems, that the formation of the fluorescence minimum does not proceed along the pathway leading to the conical intersection, thus fluorescence is not a useful probe for gaining insight into the reaction pathway. Due to the substantial influence of the donor dimethylaminophenyl group on the reaction pathway a remarkable selectivity of the hydrogen shift is observed. Only one of the two possible directions of the hydrogen shift reaction is realized. A

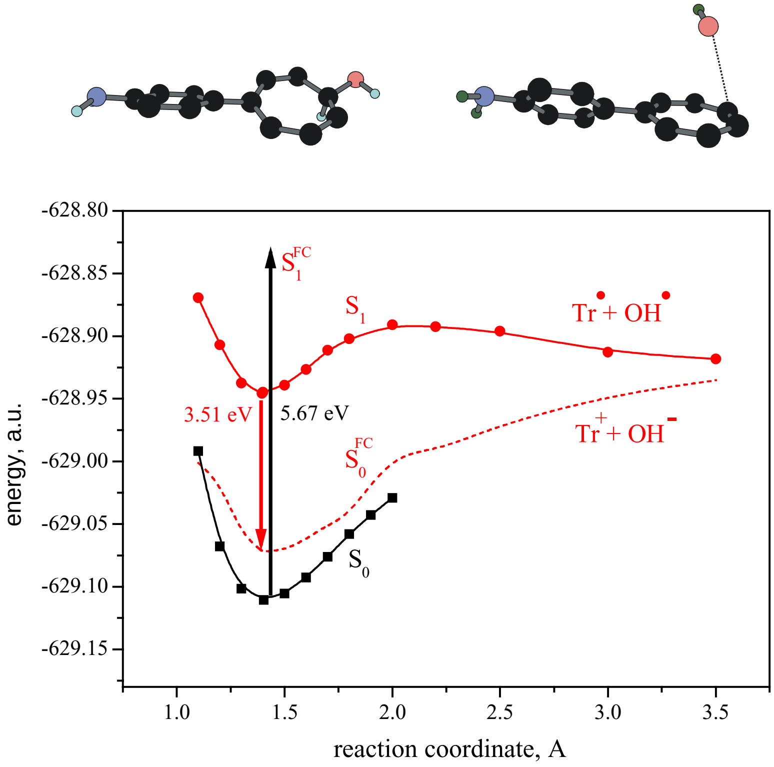


Fig. 10. The S_1 and S_0 potential energy surfaces depending on the distance between the carbon atom of the seven-membered ring and the oxygen atom of OH group (reaction coordinate) calculated by HF/6-31G (d) with the configuration interaction of 25 occupied and 25 unoccupied orbitals for the model compound **6**. The S_0^{FC} surface (dotted line) was calculated for the S_1 state optimized geometries. The structures show the S_1 equilibrium geometries with the connected and the separated OH group.

comparable influence of this electron donor substituent has been also found with other cycloheptatriene derivatives [1]. In contrast, the hydrogen shift of cycloheptatrienes bearing the phenyl substituent is not selective [1].

4.2. *Photoheterolysis*

Heterolytic cleavage of a covalent bond can be imagined to proceed via two steps, namely cleavage of a C–O-bond leading to a contact ion pair and subsequent dissociation yielding free solvated ions. In our case, protic solvents are necessary for bond breakage in the excited state. Among the alcohols, methanol provides the best conditions for tropylium ion formation with the quantum yield for this process correlating well (linear regression, $n = 4$, $r = 0.998$) with the hydrogen bond donor strength (see Fig. 11). This suggests that the solvent coordination via hydrogen bonding to the methoxy group of compound **1** in the excited state is a prerequisite for the ionization. This is in accordance with observations made with the heterolysis of 9-fluorenol [19]; in this case there is the formation of a loose ion pair.

Obviously, hydrogen bonds are not only able to stabilize the formed methoxide ion but also support bond dissociation in the early stage of the bond-breaking process. According to the calculated ionization pathway in the gas phase at first the homolytic bond fission takes place. Afterwards due to the electron transfer in the hot ground state the ion pair is formed. The solvent may support this process. However, the lifetime of a possible radical pair should be very short (<5 ns) as can be estimated from the insensitivity of the tropylium ion quantum yield on the presence of oxygen in air equilibrated solutions (based on diffusion-controlled rate for

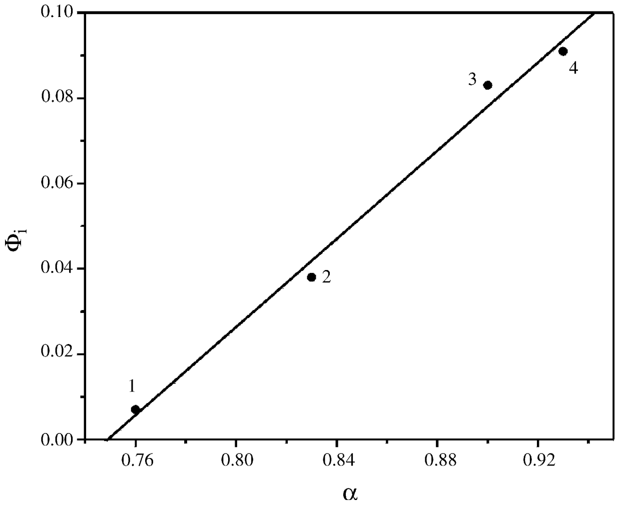


Fig. 11. Dependence of the quantum yield of the formation of **4** on the hydrogen bond donor capacity (α^{24}) of the solvent (1: *i*-PrOH; 2: EtOH; 3: ethyleneglycol: 4: MeOH).

oxygen quenching with $K_{\mathrm{diff}}(\mathrm{MeOH}) = 1.1 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and an error for quantum yield measurements of 10%). The observed independence on oxygen for the reactions suggests that they proceed via the singlet excited state.

According to the decisive role of hydrogen bonds in the dissociative process the very strong hydrogen bond donor hexafluoroisopropanol (HFIP) is able to transform compound **1** to **4** whilst in the ground state.

By comparing the quantum yields of the hydrogen shift reaction one can conclude that the photodissociation process competes with the hydrogen shift reaction. For example, in methanol solution the dissociation is clearly more effective than the pericyclic reaction (hydrogen shift) i.e., $\Phi_{\mathrm{ion}} = 0.09$ versus $\Phi_r = 0.03$ in methanol (see Table 1). In contrast, the fluorescence efficiency is not strongly influenced by the presence of protic solvents (entries 3–6 in Table 1). In addition the fluorescence lifetimes as measured in acetonitrile and methanol solutions (see Table 1) do not indicate changes in the rate constants for radiative deactivation.

According to the observed photoconductivity (see above) and the similarity of the transient absorption spectrum with that of the radical cation of *N*,*N*-dimethylaniline ($\lambda_{\max} = 473$ nm by pulse radiolysis of *N*,*N*-dimethylaniline in a Freon mixture [20]), the transient absorption in acetonitrile solution can be assigned to the radical cation of compound **1**, which is formed by electron ejection: unfortunately this solvated electron remains difficult to be detected in acetonitrile solution due to its only weak absorption in the visible wavelength range [21]. Other cycloheptatrienes bearing the dimethylaminophenyl substituent also exhibit photoionization [21], thus electron ejection may also occur in alcoholic solvents leading to a transient absorption at around 440 nm, observed as shoulder on the short-wavelength side of the transient tropylium ion spectrum (see Fig. 6). The solvated electron in alcohol solvents is most likely hidden under the strong absorption of the parallel formed tropylium cation **4**. The formation of a long-lived tropenyl radical by a parallel or preceding photohomolytic process, which would exhibit an absorption band at a maximum of 370 nm [21], can be ruled out based on the lack of a corresponding absorption in the transient spectra. The weaker the hydrogen bonds between the solvent and compound **1** the more dominant is the ionization by electron ejection (Table 3) suppressing any photoheterolysis in acetonitrile ($\alpha = 0.19$).

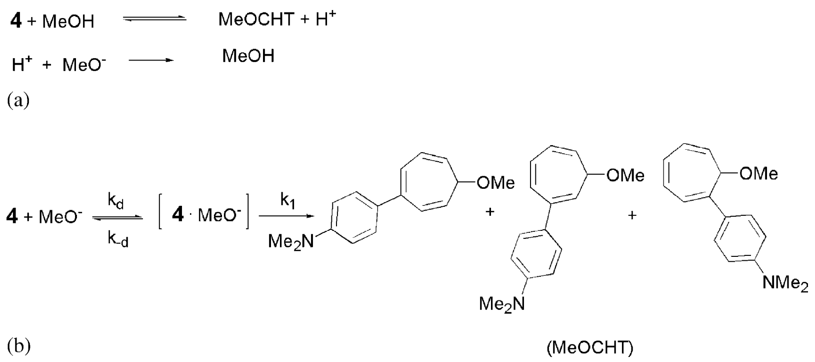
4.3. Thermal back reaction of the tropylium methoxide

The lifetime of the tropylium ion is an important parameter in relation to the intended switch process based on the repulsion of charges; it is controlled by the level of nucleophilic attack in the solution. In methanol solution the nucleophiles are the solvent itself and the stronger nucleophilic anion which is formed by photoheterolysis. The decay of carbenium ions in protic solvents usually follows a single exponential function [22], as does the decay of the transient tropylium ion, however in some cases the decay curve is best fitted in a double exponential fashion indicating the presence of two different species (see Table 2).

According to the related equilibrium constant, the solvolysis of compound **4** with methanol does not occur. However, the methoxide ion formed scavenges the proton thus shifting the equilibrium (reaction a in Scheme 4) towards the recombination product.

The alternative reaction is the direct attack of the methoxide ion (reaction b in Scheme 4). Considering the different concentrations, the reaction with methanol is much more probable. In each case, the two possible regio-isomers shown in Scheme 4 are formed by this reaction, in addition to the starting compound **4** and the H-shifted product **3**. This reversible ionization results in the complex photoreaction observed in methanol solution (Scheme 4 and Fig. 4c).

The solvent has a profound effect on the lifetime of the tropylium ion (see Table 2); this is as expected in a reaction in which the charge density is lower in the activated complex than in the initial reactant molecules. However, it is obvious that the order does not follow the expected reaction rates of a cation with protic solvents (see Fig. 5) [22] otherwise methanol would react faster than ethanol as it was found with other carbenium ions [22]. Again, the hydrogen bond capacity of the alcohol is likely to govern the reactivity, thus reflecting the varied solvation of the methoxide in different alcohols. Furthermore, the increased polarity of alcohols such as methanol and ethylene glycol may contribute. Compared to the other alcohols, methanol and ethylene glycol



Scheme 4.

form stronger solvent shells around the methoxide ion leading to a higher barrier of desolvation. This effect is reflected for both, the reaction of the methoxide ion with compound **4** and the proton according to reaction a or b in Scheme 4. A similar effect was found in the reaction of amines with diarylmethyl cations in aqueous acetonitrile solution [23].

The two species observed according to the biexponential fit of the aryl tropylium ion decay curves may be related to different degrees of solvation, e.g. solvent separated ion pairs and free solvated ions. Surprisingly, solvent mixtures of acetonitrile and methanol support the ionization resulting in a considerably increased lifetime for the tropylium ion, probably due to the diminished concentration of the nucleophile methanol.

5. Conclusions

Photoheterolysis is able to compete with the rapid 1,7-hydrogen shift reaction of compound **1** provided that protic solvents are used. Hydrogen bonds govern both the bond breakage process and the rate of the thermal back reaction of the methoxide ion with the tropylium ion.

The lifetime of the ion pair formed is strongly dependent on the nature of the alcohol used and can be considerably increased by dilution with acetonitrile. Electron ejection rather than tropylium ion formation, is observed in acetonitrile solution, but also occurs in alcoholic solutions. The competition between the two ionization processes is controlled by the hydrogen bond donor capacity of the alcohol and lifetimes of several seconds for the tropylium ions is sufficient for shuttling processes in rotaxanes.

Finally, the influence of the substituent on the direction of the hydrogen shift reaction previously observed in cycloheptatriene derivatives has also been confirmed with compound **1**.

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