

Photophysics of arylsubstituted tropylium ions

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Abstract

Phenyl tropylium ion (TRPH) bearing different donor substituents were investigated both experimentally (absorption and fluorescence) and theoretically (semiempirical and ab initio calculations for ground and excited state structures and transitions). Generally, an increased donor strength of the substituent leads to a favoring of the planar geometry in the ground state. In the S_1 -state, however, energetic minimum develops for orthogonal structures, which are characterized by strong charge shift (CSh) (electron transfer from the substituted aryl to the tropylium fragment), forbidden transition moments and near-zero singlet–triplet energy gaps. These results can serve as a basis to interpret the completely non-emissive behavior of the tropylium derivatives with strong donor substituents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorescence; Tropylium ions; Ab initio calculation; Biradicaloid structure; Electron transfer

1. Introduction

p-Tolyl tropylium salts are known to exhibit only a weak fluorescence ($\lambda_f = 537$ nm, $\Phi_f = 0.039$, CH_2Cl_2 , 295 K) [1,2]. Information related to the fluorescence of aryl tropylium ions bearing stronger electron donor groups (e.g. OCH_3 , $\text{N}(\text{CH}_3)_2$) is lacking. It can be expected that such donor substituted aryl tropylium ions should emit even more weakly. Comparable cations such as the dimethylaminophenyl pyridinium ion (DAPY) at room temperature also exhibit a fluorescence with a very small quantum yield ($\lambda_f = 508$ nm, $\Phi_f = 0.008$, EtOH, 295 K) [3–5].

The question arises as to the nature of the deactivation processes, which reduce the fluorescence of such electron donor–acceptor compounds. In order to answer this question we decided to study the photophysical deactivation behavior of the phenyl tropylium ion (TRPH) in comparison to the *p*-methoxyphenyl and the *p*-*N*,*N*-dimethylaminophenyl tropylium ion (TROM and TRDA). Semiempirical as well as ab initio calculations of the model cations (TROH and TRAM) were carried out in order to support the conclusions (Scheme 1).

2. Experiment and calculation

2.1. Materials

The cations were prepared in the form of the perchlorate salts by known methods [6] and purified by recrystallization. The product was checked for purity by fluorescence after each recrystallization step as described in a previous paper [3]. The solvents (dichloromethane, acetonitrile and butylchloride) were of spectroscopic quality (MERCK UVASOL and FLUKA, respectively).

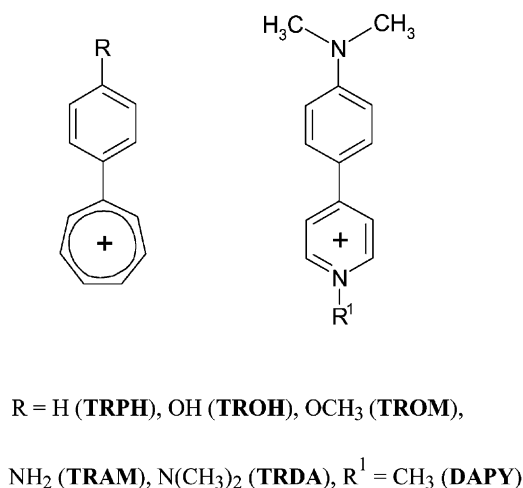
2.2. Apparatus and methods

Absorption spectra were recorded with an ATI Unicam UV2 spectrophotometer (United Kingdom). Corrected fluorescence emission and fluorescence excitation spectra of solutions with an absorbance $A = 0.02$ – 0.06 were measured with the help of a SLM AMINCO AB2 spectrofluorimeter.

Fluorescence quantum yields ($\pm 10\%$) were determined using 9,10-diphenylanthracene (EtOH, 295 K) as standard ($\Phi_f = 0.95$ [7]). The refractive index corrections were made [8] to adjust for the different 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].

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Scheme 1. Tropylium ions investigated and the related pyridinium cation.

2.3. Computational details

Ab initio calculation at the HF/6-31G* theory level was carried out for the cations using Gaussian 98 [10]. The excited states were calculated with singly excited configuration interaction (CIS) using 25 occupied and 25 unoccupied orbitals. Full optimization of the ground and excited states including vibrational analysis was performed to detect stable minimum and transition geometries. The study of the fragment rotation in the S₀-, S₁- and T₁-state was carried out by fixing the torsional angle between the fragments optimizing all other geometrical parameters.

The calculations of transition energies and oscillator strength for the cations were carried out using the CNDO/S-CI method with interaction of 100 singly excited configurations and the parameter sets described in the literature [11] for fully optimized HF/6-31G* ground state structures.

3. Results and discussion

3.1. Absorption of the tropylium ions

The data of the absorption spectra for the investigated cations (Fig. 1 and Table 1) show that the long wavelength absorption band is shifted to the red and the intensity is increased in the cation series TRPH, TROM and TRDA. The reasons for this behavior can be explained by different equilibrium geometries of the cations in the S₀ ground state and by the electronic properties of the substituents. Therefore, the investigation of the geometries and the nature of the lowest singlet excited state for the different tropylium ions were carried out.

3.2. Ground state geometry of the tropylium cations

The structures of the fully optimized geometries of the cations and the atom numbering are shown in Fig. 2 and

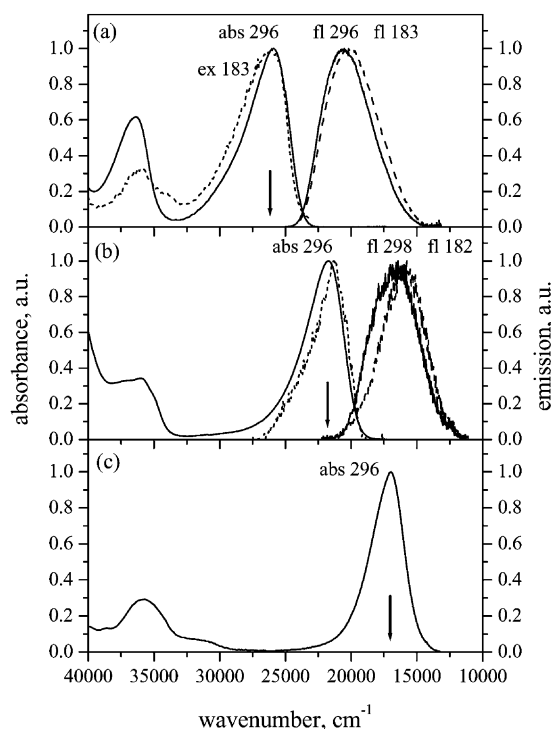


Fig. 1. The normalized absorption (abs), corrected fluorescence (fl) and fluorescence excitation spectra (ex) of (a) TRPH; (b) TROM; (c) TRDA in CH₂Cl₂ at different temperatures (296, 182 K). The arrows show the excitation wavelength used to record the fluorescence spectra.

some relevant geometrical parameters are presented in Table 2. According to ab initio calculations of the various theory levels, the cation with the substituent having a stronger electron donor character is more planar. The torsional angle is decreased going from TRPH to TRDA (around 40, 35 and 27° for TRPH, TROM and TRDA, Table 2). The activation barrier of the internal rotation to reach the planar geometry is also decreased and that of the twisted geometry is increased in that order (see Table 3).

The tropylium ions TRPH and TROM exhibit the ordinary geometrical characteristics of phenyl and tropylium rings. The introduction of a dimethylamino group into the phenyl ring gives rise to a contraction of the bonds 9–10 and 12–13 in the phenyl ring. The bond 11–14 connecting the strong electron donor group and the phenyl ring is also unusually short. The nitrogen of the dimethylamino group of TRDA has sp² character leading to a short distance between N14 and the carbon atom 11 (1.3450' and 1.3553' by HF and B3LYP, respectively) and a planar arrangement of the attached atoms. Therefore, the aryl fragment of TRDA resembles a quinoid geometry.

The theoretical results obtained are supported by the experimental study of TRDA. The X-ray structure [12] is nicely approached by calculating the planar transition state of TRDA, which is shown in Fig. 2. It possesses an analogous quinoid structure of the aryl fragment (Table 2).

Table 1

Experimental (CH_2Cl_2 , 296 K) and theoretical characteristics (CNDO/S-CI) of the absorption transition for the tropylium cations obtained for the fully optimized equilibrium geometry (HF/6-31G*)

| Characteristics | TRPH | TROM | TRDA |
|---|---------------------------------|----------------------------------|---------------------|
| Experimental transition energy of the long wavelength absorption band (eV) (ν , cm^{-1} ; $-\epsilon$, $\text{M}^{-1}\text{cm}^{-1}$) | 3.21 (25910–18600) ^a | 2.69, (21690–22500) ^a | 2.10, (17120–39950) |
| Calculated transition energy (eV) (oscillator strength) | 3.76 (0.2294) | 3.33 (0.3120) | 3.03 (0.4438) |
| Transition dipole orientation | z-axis | z-axis | z-axis |
| Main configurations in configuration interaction (coefficient) | HOMO–LUMO (0.9714) | HOMO–LUMO (0.9741) | HOMO–LUMO (0.9683) |
| Charge of the tropylium fragment in S_1 (S_0) | 0.250 (0.710) | 0.058 (0.785) | 0.039 (0.738) |
| Assignment | Partial CSh ^b | CSh ^b | CSh ^b |

^a From [13].

^b Charge shift.

3.3. Nature of the lowest singlet excited state

The results of the CNDO/S-CI calculations (Table 1) performed for the HF/6-31G* optimized ground state equilibrium geometry are in reasonably good agreement with the experimental data. The energy of the long axis polarized longest wavelength transition decreases in the cation series TRPH, TROM, TRDA (3.76, 3.33 and 3.03 eV). In the same order, the absorption intensity increases (oscillator strength is 0.23, 0.31 and 0.44). The transition corresponds to a nearly pure HOMO–LUMO configuration and produces a

charge shift (CSh) from the aryl fragment to the tropylium ring. Therefore, the charge of the seven-membered ring is decreased upon excitation (from 0.710 to 0.250 for TRPH, from 0.785 to 0.058 for TROM and from 0.738 to 0.039 for TRDA). Therefore, the nature of the electronic transition of these charged molecular systems can be called CSh [5,14]. The data obtained in this paper are in accordance with those data calculated for the cations TRPH and TROM by the help of the Hückel approach [6].

The calculational results parallel the experimental ones regarding the influence of the substituents on the absorption

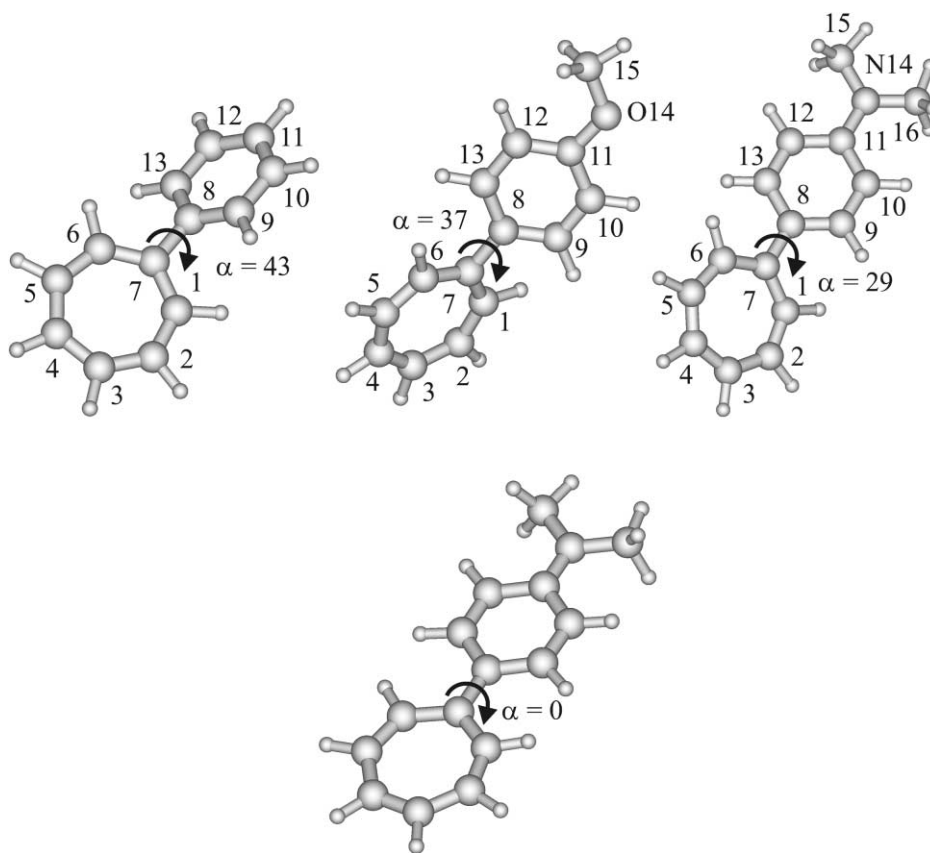


Fig. 2. The S_0 -state equilibrium structures of TRPH, TROM and TRDA (top) and the planar transition state structure of TRDA (bottom) calculated by HF/6-31G*.

Table 2

Selected bond distances and twist angles for the equilibrium geometry of the tropylium ions in the S₀-state obtained by HF/6-31G*

| Bond (Å) and angle (°) | TRPH | TROM | TRDA equilibrium geometry | TRDA geometry of the planar transition state | TRDA |
|------------------------|-----------|-----------|---------------------------|--|------------|
| | HF/6-31G* | HF/6-31G* | HF/6-31G* | HF/6-31G* | X-ray [12] |
| 1–2 | 1.3792 | 1.3737 | 1.3659 | 1.3618 | 1.372 |
| 2–3 | 1.3973 | 1.4033 | 1.4124 | 1.4168 | 1.368 |
| 3–4 | 1.3754 | 1.3690 | 1.3601 | 1.3541 | 1.357 |
| 1–7 | 1.4047 | 1.4109 | 1.4207 | 1.4285 | 1.417 |
| 7–8 | 1.4840 | 1.4695 | 1.4494 | 1.4449 | 1.460 |
| 8–9 | 1.3954 | 1.3954 | 1.4092 | 1.4181 | 1.419 |
| 9–10 | 1.3822 | 1.3803 | 1.3654 | 1.3616 | 1.343 |
| 10–11 | 1.3865 | 1.3934 | 1.4176 | 1.4194 | 1.422 |
| 11–14 | – | 1.3233 | 1.3450 | 1.3388 | 1.362 |
| 15–14 | – | 1.4117 | 1.4558 | 1.4578 | 1.484 |
| 9–8–7–1 | 43.14 | 36.59 | 28.96 | 0.02 | 2.70 |

energy, and two major factors of influence can be derived: (a) increasing planarity of the aryl tropylium ions which results (b) from the increase of the electron donor property of the substituent, thus increasing the CSh character of the excitation.

3.4. Radiative deactivation of aryl tropylium ions

TRPH exhibits a weak fluorescence at room temperature in CH₂Cl₂ solution ($\nu_f = 20,530 \text{ cm}^{-1}$, $\Phi_f = 0.08$, Table 4, Fig. 1a). Cooling down to 183 K leads to only an insignificant shift of the fluorescence band and a small increase of the quantum yield ($\nu_f = 20,200 \text{ cm}^{-1}$, $\Phi_f = 0.09$, CH₂Cl₂). No emission was observed at 77 K in glassy *n*-butylchloride solution.

Also TROM exhibits a very weak fluorescence ($\nu_f \approx 16,400 \text{ cm}^{-1}$, $\Phi_f < 0.001$, CH₂Cl₂, Table 4, Fig. 1b) at room temperature and at 183 K. In this case, the fluorescence could be recorded only for solutions with a large concentration (approximately $1 \times 10^{-4} \text{ M}$) where the fluorescence quantum yield could not be determined. The weak fluorescence of TROM under these conditions might be assigned to narrowly spaced ion pairs the fraction of which is increased for increased concentrations [2]. Similar as obtained for TRPH, TROM does not fluoresce at 77 K in glassy matrix (*n*-butylchloride).

Table 3

Activation barrier ΔE^\ddagger of the fragment rotation of the cations to the planar ($\varphi = 0^\circ$) and the twisted ($\varphi = 90^\circ$) geometry relative to the equilibrium geometry (φ_{eq}) with the absolute energy E^0 (HF/6-31G*)

| Cation | ΔE^\ddagger ($\varphi = 0^\circ$) (kcal/mol) | E^0 (a.u.) φ_{eq} , ° | ΔE^\ddagger ($\varphi = 90^\circ$) (kcal/mol) |
|--------|--|--|---|
| TRPH | 4.50 | −498.240645 (43.14) | 2.32 |
| TROH | 3.17 | −573.093633 (37.21) | 3.65 |
| TROM | 2.92 | −612.090290 (36.59) | 3.96 |
| TRAM | 2.11 | −553.260808 (30.86) | 5.84 |
| TRDA | 1.58 | −631.252623 (28.96) | 6.32 |

Table 4

Photophysical parameters of the aryl tropylium ions studied in CH₂Cl₂ solution

| Parameter | TRPH | TROM | TRDA |
|------------------------------------|--------|--------|--------|
| ν_a (cm ^{−1} , 295 K) | 25910 | 21690 | 17120 |
| ν_f (cm ^{−1} , 296 K) | 20530 | 16450 | – |
| ν_f (cm ^{−1} , 183 K) | 20200 | 15750 | – |
| ν_f (cm ^{−1} , 77 K) | – | – | – |
| Φ_f (296 K) ^a | 0.081 | <0.001 | <0.001 |
| Φ_f (183 K) ^b | 0.087 | <0.001 | <0.001 |
| Φ_f (77 K) ^{b,c} | <0.005 | <0.005 | <0.005 |
| τ_f (ns) ^d | 3.00 | – | – |

^a 9,10-Diphenylanthracene (EtOH, 295 K) as standard ($\Phi_f = 0.95$ [7]).^b Excitation in the long wavelength absorption band.^c In *n*-butylchloride glass.^d From [2].

No emission was observed from TRDA for all conditions (296, 184 and 77 K, concentration up to 10^{-5} M) (Table 4). This finding is contrary to the emission properties of DAPY, the fluorescence quantum yield of which is increased from 0.008 at room temperature to 0.49 at 140 K and is further increased at 77 K [4]. The lack of fluorescence from TRDA cannot be explained by a specific interaction between the cation and a solvent molecule because the fluorescence is absent also in acetonitrile and in butyronitrile solution at temperatures from 296 to 200 K. Alcoholic solvents cannot be used in the case of TRDA because of the nucleophilic attack of these solvents on the cation and the resulting bleaching of the solution.

Photoreactions of the tropylium ions TROM and TRDA can also not be responsible for the absence of fluorescence, because prolonged irradiation of the solutions at room temperature in the long wavelength absorption band results in only very small changes of the absorption spectra. In contrast, irradiation of the TRPH solution leads to strong absorption changes. It was found earlier that the photostability of aryl tropylium ions is drastically increased in tropylium ions, which bear strong electron donor groups [1,2].

Table 5

Some bond distances and twist angles of the equilibrium geometry for the tropylium cations in the S_0 - and S_1 -state from ab initio optimization (HF/6-31G*)

| Bond (Å) and angle (°) | TRPH | | TROH | | | TRAM | | |
|------------------------|-------------------------|-------------------------|--------------|-------------------------|-------------------------|--------------|-------------------------|-------------------------|
| | S_1 -state TRPH_32 | S_1 -state TRPH_90 | S_0 -state | S_1 -state TROH_00 | S_1 -state TROH_90 | S_0 -state | S_1 -state TRAM_00 | S_1 -state TRAM_90 |
| 1–2 | 1.3682 | 1.3495 | 1.3746 | 1.3683 | 1.3497 | 1.3679 | 1.3691 | 1.3504 |
| 2–3 | 1.4204 | 1.4508 | 1.4023 | 1.4169 | 1.4506 | 1.4100 | 1.4171 | 1.4506 |
| 3–4 | 1.3698 | 1.3396 | 1.3701 | 1.3701 | 1.3397 | 1.3624 | 1.3676 | 1.3398 |
| 4–5 | 1.4204 | 1.4508 | 1.4023 | 1.4143 | 1.4506 | 1.4100 | 1.4171 | 1.4506 |
| 5–6 | 1.3682 | 1.3495 | 1.3747 | 1.3734 | 1.3497 | 1.3679 | 1.3691 | 1.3504 |
| 6–7 | 1.4322 | 1.4345 | 1.4098 | 1.4272 | 1.4335 | 1.4181 | 1.4293 | 1.4322 |
| 7–8 | 1.4446 | 1.4484 | 1.4718 | 1.4559 | 1.4508 | 1.4546 | 1.4598 | 1.4542 |
| 8–9 | 1.4364 | 1.4493 | 1.4038 | 1.4375 | 1.4451 | 1.4086 | 1.4327 | 1.4378 |
| 9–10 | 1.3653 | 1.3575 | 1.3715 | 1.3591 | 1.3529 | 1.3668 | 1.3560 | 1.3495 |
| 10–11 | 1.4024 | 1.4132 | 1.3954 | 1.4098 | 1.4242 | 1.4082 | 1.4184 | 1.4374 |
| 11–14 | – | – | 1.3299 | 1.3117 | 1.2905 | 1.3437 | 1.3332 | 1.3114 |
| 9–8–7–1 | 32.22 | 0.00 | 37.21 | 0.00 | 90.00 | 30.86 | 1.76 | 90.00 |

An alternative explanation of the nearly quantitative non-radiative deactivation consists in the possible formation of a twisted biradicaloid structure of the arylsubstituted tropylium ions in the excited state which opens a deactivation channel to the ground or the triplet state. In order to explore this deactivation pathway, ab initio calculations of the excited state were carried out for TRPH and the model cations for TROM and TRDA which bear equivalent but smaller substituents: TROH and TRAM.

3.5. Ab initio study of the excited state of TRPH

According to the calculations, the cation TRPH in the S_1 -state possesses an equilibrium geometry TRPH_32 which is more planar (around 32) than the S_0 equilibrium one (43) (Tables 2 and 5, Fig. 3). A comparison between both geometries indicates the TRPH_32 structure of S_1 to be characterized by strong alternation of bond distances for the seven-membered ring (an increase of the bond distances 2–3,

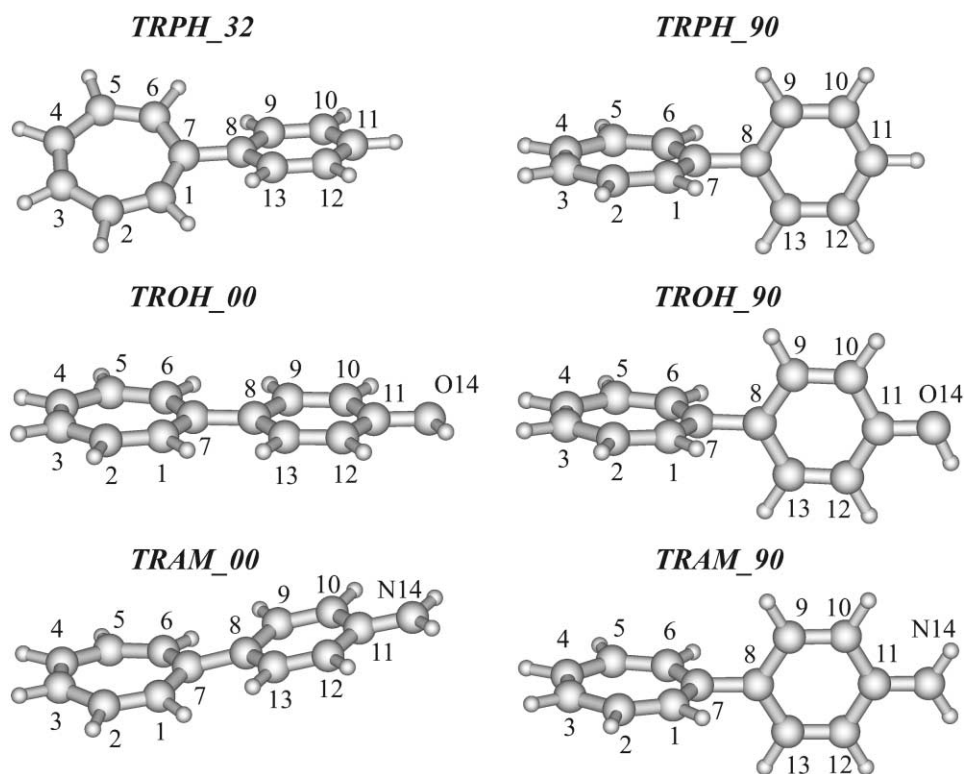


Fig. 3. The equilibrium (TRPH_32, TROH_90, and TRAM_90) and transition state (TRPH_90, TROH_00, and TRAM_00) structures of TRPH (top panel), TROH (mid panel), and TRAM (bottom panel) in the optimized S_1 -state as obtained by HF/6-31G*.

Table 6

Characteristics of the S_1 excited states for the equilibrium (TRPH₃₂) and the orthogonal (TRPH₉₀) structures as well as the FC geometry reached from the equilibrium ground state of the phenyltropylium cation TRPH by HF/6-31G*

| Characteristic | TRPH ₃₂ | FC state | TRPH ₉₀ |
|--|---------------------------|----------------|-------------------------------|
| State symmetry | A | A ₁ | A ₂ |
| Electronic energy (a.u.) (sum of electronic and zero-point energy, a.u.) | -498.295989 (-498.085502) | -498.288190 | -498.290403 (-498.079503) |
| Lowest vibrational frequency (cm ⁻¹) | 52.2 | - | -26.3 ^a |
| Transition energy of $S_1 \rightarrow S_0$ (eV) | 4.15 | 4.37 | 3.84 |
| Oscillator strength | 0.7806 | 0.7268 | 0.0000 |
| S_1 - T_n energy gap (eV) ^b | 1.55 ^c | - | 0.05 ^d |
| Charge of the tropylium fragment in S_1 (S_0) | 0.54 (0.79) | 0.55 (0.82) | 0.23 (0.86) |
| Assignment | Partial CSh | Partial CSh | Biradicaloid with partial CSh |

^a Negative frequency indicates saddle points.

^b The triplet state T_n with the same electronic configuration as S_1 .

^c The S_1 - T_1 energy gap.

^d The S_1 - T_4 energy gap, the S_1 - T_1 energy gap is 0.43 eV.

4–5 and 6–7) and a strong increase of the bond distances 8–9 and 10–11 for the phenyl fragment (Table 5). This structure enables an allowed transition $S_1 \rightarrow S_0^{FC}$ (transition energy 4.15 eV, $f = 0.78$, Table 6) as the result of which the positive charge of the tropylium ring is increased from 0.54 to 0.79 (Table 6). But this CSh from the phenyl group resulting from the electron density transfer from the tropylium ring is rather small. Therefore, the equilibrium structure TRPH₃₂ has a partial CSh nature.

Studies of the torsion of the two aromatic units within the TRPH in the S_1 -state show that the planar and orthogonal geometries of TRPH correspond to energy maxim, i.e. to transition state structures (lowest vibrational frequency is negative, -26.3 cm^{-1} for TRPH₉₀) (Fig. 4 and Table 6). The twisted structure TRPH₉₀ (Fig. 3) possesses a bond alternation which is similar to the alternation in TRPH₃₂

(Table 5) and is characterized by a forbidden transition with the transition energy 3.84 eV (Table 6). This transition results in a very large CSh increasing the positive charge of the tropylium moiety from 0.23 to 0.86 (Table 6). As the orbitals involved in the transition are completely localized on the phenyl and tropylium moieties, respectively, this CSh corresponds to the partial CSh. The energy gap between S_1 - and T_1 -states is less than the gap for the equilibrium structures (0.43 and 1.55 eV, respectively, see Table 6) but the S_1 -state possesses a twin T_n -state involving the same electronic structure as S_1 and which is nearly degenerate to S_1 .

According to the theoretical results, the TRPH in the S_1 -state relaxes from the Franck–Condon twisted structure (43) to a more planar one from which the emission occurs and the small fluorescence quantum yield of TRPH might be attributed to the competing cation photochemistry.

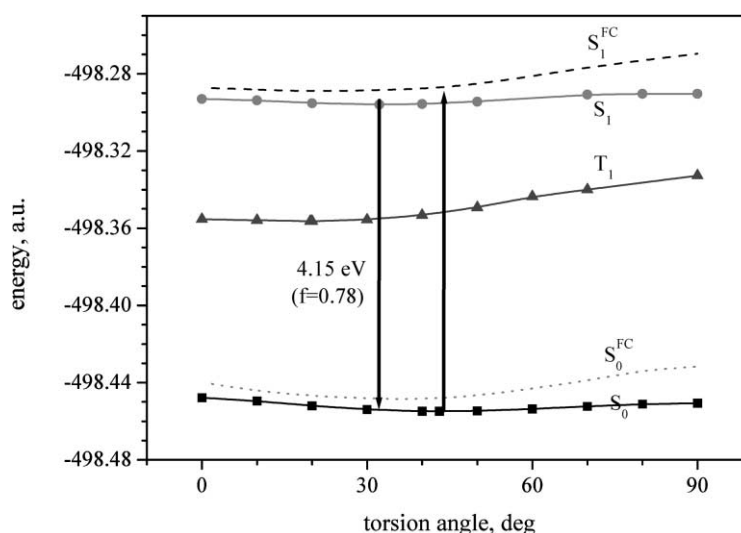


Fig. 4. Ground and excited state potentials of TRPH as calculated by HF/6-31G*. The transition state (at the torsional angles 0 and 90°) and equilibrium (at 43° for the S_0 -state and at 32° for the S_1 -state) structures were calculated with full optimization of all geometrical parameters. Other points of the potentials were calculated for the fixed torsional angle with optimization of all other parameters. The S_1^{FC} and S_0^{FC} energies were obtained for the S_0 and S_1 optimized structures, respectively. The arrows show the transitions from S_0 to S_1 equilibrium geometries.

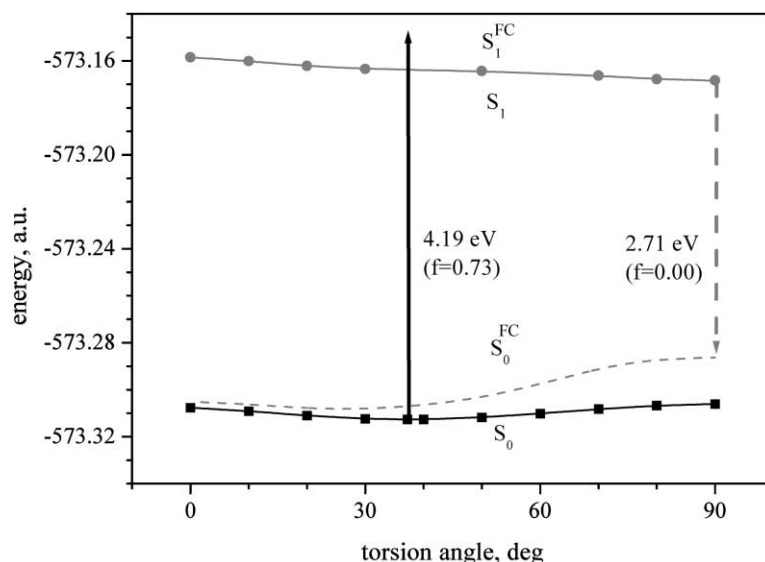


Fig. 5. The ground and excited state potentials of TROH as calculated by HF/6-31G*. The transition state (at the torsional angles 0 and 90°) and equilibrium (at 37° for the S₀-state and at 90° for the S₁-state) structures were calculated with full optimization of all geometrical parameters. For details see Fig. 4 and text.

3.6. *Ab initio* study of the excited state of TROH

In the ground state the hydroxyphenyl tropylium ion TROH has both a more planar equilibrium structure (the torsional angle amounts to 37.21°, see Table 5) and more strongly alternating bonds than TRPH in its S₀-state. The internal fragment rotation both to the planar and the perpendicular geometry increases the cation energy (Fig. 5, Table 3). But the activation barrier of the fragment rotation to the planar transition state is smaller than for TRPH and the activation energy to the perpendicular structure is increased (Table 3).

The allowed absorption transition with the energy of 4.19 eV and the oscillator strength of 0.73 results in a Franck–Condon state of CSh nature (Table 7). As a result of this transition, the positive charge is shifted from the seven-membered ring to the aryl fragment. But the CSh is

less than in TROM when comparing to the CNDO/S-CI calculation (Table 1).

In contrast to TRPH, the calculation of the S₁ potential surface for TROH (Fig. 5) indicates that the orthogonal geometry TROH₉₀ (Fig. 3) is a true energy minimum (all eigenvalues of the Hessian matrix are positive). The main feature of this S₁ equilibrium structure (lowest vibrational frequency is 54.4 cm⁻¹, Table 7) consists of very strong bond alternation as compared to the equilibrium geometry of the S₀-state. The bond lengths 2–3, 4–5, 6–7, 8–9 and 10–11 are strongly increased and the bond lengths 1–2, 3–4, 5–6, 9–10 are decreased (Table 5). This bond alternation is stronger than that in TRPH₉₀. The equilibrium structure TROH₉₀ is characterized by a forbidden transition with energy 3.21 eV which shifts the positive charge from the aryl fragment to the seven-membered ring. As a result of this shift, the charge of the ring is increased from 0.22 to 0.85

Table 7

Characteristics of excited states for planar (TROH₀₀) and twisted (TROH₉₀) structures of the hydroxyphenyltropylium TROH by HF/6-31G*

| Characteristic | TROH ₀₀ | FC state | TROH ₉₀ |
|--|---------------------------|-------------|-------------------------------|
| State symmetry | A' | – | A'' |
| Electronic energy (a.u.) (sum of electronic and zero-point energy, a.u.) | –573.158532 (–572.943466) | –573.158805 | –573.168372 (–572.951072) |
| Lowest vibrational frequency (cm ⁻¹) | –103.2 ^a | – | 54.4 |
| Transition energy of S ₁ → S ₀ (eV) | 3.99 | 4.19 | 3.29 |
| Oscillator strength | 1.0706 | 0.7329 | 0.0000 |
| S ₁ –T ₁ energy gap (eV) ^b | 1.56 | – | 0.04 |
| Charge of the tropylium fragment in S ₁ (S ₀) | 0.55 (0.72) | 0.47 (0.79) | 0.22 (0.85) |
| Assignment | Partial CSh | Partial CSh | Biradicaloid with partial CSh |

^a Negative frequency indicates saddle point.

^b The triplet state T₁ with the same electronic configuration as S₁.

(Table 7) very similar to TRPH_90. The reversed charge distribution (as compared to the S_0 -state) and the small S_1 – T_1 energy gap (0.04 eV, Table 7) is characteristic for a biradicaloid character of TROH_90. This singlet–triplet pair with equal electronic configuration is the lowest one in TROH (and TRAM, see below) but is higher lying in TRPH (S_1 – T_4 , Table 6).

The internal fragment rotation leading to the planar geometry increases the tropylium energy in the S_1 -state (Fig. 6 and Table 7). The planar transition state structure TROH_00 (Fig. 3) (with negative vibrational frequency -103.2 cm^{-1} , Table 7) is characterized by a smaller bond alternation as compared to TROH_90 (Table 5) and an increased positive charge of the tropylium ring in comparison to the S_1 twisted structure. But the tropylium charge for this planar structure is smaller than the charge in the ground state (Table 7). The results obtained can be interpreted by the resonance interaction between the two planar fragments of the cation. This interaction results in a strongly allowed $S_1 \rightarrow S_0$ transition with energy 3.99 eV and oscillator strength 1.07 which increases the positive charge of the seven-membered ring from 0.55 to 0.72 (Table 7) corresponding to partial CSh. In contrast, in the fully decoupled perpendicular TROH_90, no resonance interaction is possible, the oscillator strength is zero and the CSh is at its maximum.

Concluding from the ab initio calculations (Fig. 5), TROH in the S_1 -state relaxes from the Franck–Condon geometry to the orthogonal biradicaloid structure TROH_90 which can lead to a fast crossing to the nearly isoenergetic T_1 surface. By this way, an effective fluorescence quenching can occur. Following these arguments the tropylium ions TROH and TROM do not emit and the detected weak fluorescence of TROM at high concentration may be attributed to the emission of ion pairs.

3.7. Ab initio study of the excited state of TRAM

The model tropylium ion TRAM containing the amino group has an equilibrium geometry in the S_0 -state which is more planar than that for TROH (the torsional angle is 30.86° , Table 5) but less planar than for TRDA bearing the stronger dimethylamino electron donor group (Table 2). The torsional motion of the two aromatic units towards the orthogonal transition state structure increases the energy. The activation barrier of this rotation is higher than the barrier of the rotation, which leads to the planar geometry (Fig. 6 and Table 3).

Taking into account the S_1 energy minimum at 90° (Fig. 6) and the positive charge concentration on the aminophenyl group and the small S_1 – T_1 energy gap (0.04 eV) (Fig. 6 and Table 8) it can be concluded also in this case that TRAM relaxes from the Franck–Condon state having partial CSh nature to an equilibrium orthogonal geometry (lowest vibrational frequency 55.4 cm^{-1}) having biradicaloid nature with full CSh. The geometrical characteristics of this structure TRAM_90 (Fig. 3 and Table 5) indicate a strong bond alternation of long bonds (1–2, 3–4, 5–6) with short ones (2–3, 4–5) in the seven-membered ring and 8–9, 10–11 with 9–10 in the aniline moiety. This quinoid like structure is analogous to the twisted structure TROH_90 and is characterized by a forbidden transition $S_1 \rightarrow S_0$ with the energy 2.70 eV which increases the positive charge of the seven-membered ring from 0.19 to 0.83 (Table 8). Similar as for TROH, the fast conversion of the S_1 -state to the T_1 -state for the twisted biradicaloid structure can be expected to lead to efficient deactivation of the fluorescent excited state of TRAM.

In contrast to TROH, the planar S_1 transition structure is bent (TRAM_00, Fig. 3) but is characterized by a similar

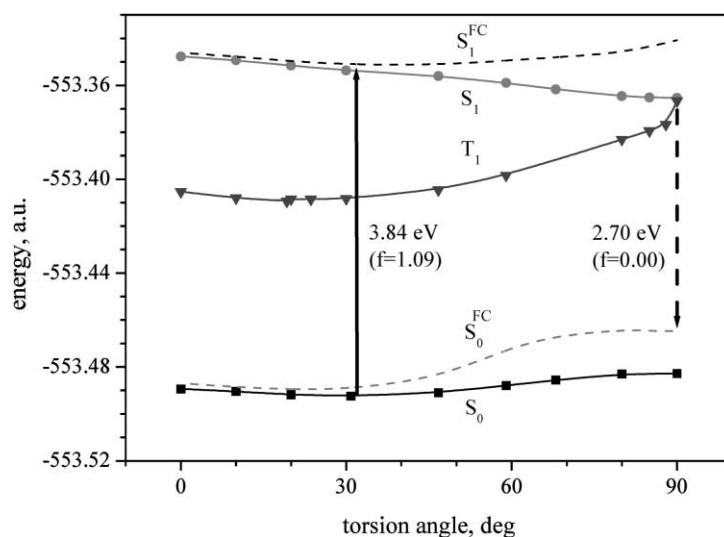


Fig. 6. Ground and excited state potentials of TRAM as calculated by HF/6-31G*. The transition state (at the torsional angles 0° and 90°) and equilibrium (at 31° for the S_0 -state and at 90° for the S_1 -state) structures were calculated with full optimization of all geometrical parameters. For details see Fig. 4 and text.

Table 8
 Characteristics of excited states for planar (TRAM_00) and twisted (TRAM_90) structures of the aminophenyltropylium TRAM by HF/6-31G*

| Characteristic | TRAM_00 | FC state | TRAM_90 |
|--|---------------------------|-------------|-------------------------------|
| State symmetry | A' | – | A'' |
| Electronic energy (a.u.) (sum of electronic and zero-point energy, a.u.) | –553.347690 (–553.119600) | –553.347688 | –553.365296 (–553.134090) |
| Lowest vibrational frequency (cm ⁻¹) | –83.9 ^a | – | 55.4 |
| Transition energy of S ₁ → S ₀ (eV) | 3.79 | 3.88 | 2.70 |
| Oscillator strength | 1.2955 | 1.2851 | 0.0000 |
| S ₁ –T ₁ energy gap (eV) ^b | 1.55 | – | 0.04 |
| Charge of tropylium fragment of S ₁ (S ₀) | 0.52 (0.66) | 0.50 (0.72) | 0.19 (0.83) |
| Assignment | Partial CSh | Partial CSh | Biradicaloid with partial CSh |

^a Negative frequency indicates saddle point.

^b The triplet state T₁ with the same electronic configuration as S₁.

bond alternation (Table 5) and an analogous allowed transition (Table 8).

4. Conclusion

Experimental investigations of different arylsubstituted tropylium ions have shown that the fluorescence is absent for those cations bearing donor groups such as OCH₃ and N(CH₃)₂. We propose that good donors can lead to twisted excited state structures causing fast radiationless deactivation and effective fluorescence quenching. Ab initio calculations of the excited states of the model cations containing the donor groups OH and NH₂ indicated that the fast deactivation can occur because the twisted structure is an energy minimum in the S₁-state and possesses a very small S₁–T₁ energy gap causing fast intersystem crossing.

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