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Photoionization of anthracene and anthracene derivatives

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Abstract

Anthracene (**III**) and the derivatives 9-methoxymethylanthracene (**IV**), 9-cyanoanthracene (**V**) and (E-3-phenyl-prop-2-ene-1-yl)-(anthracene-9-methyl)-ether (**I**) were subjected to irradiation at $\lambda_{\text{inc}}=347$ nm in dilute deoxygenated acetonitrile solution at room temperature. With the aid of the flash photolysis method employing fluorescence, optical absorption and electrical conductivity measurements the monophotonic photoionization and the formation of free ions was evidenced for compounds **III–V**. In the case of the bichromophoric compound **I** a photocurrent was not observed although a transient optical absorption attributable to the radical anion of the anthracene moiety was detected. Moreover, the fluorescence lifetime of **I** was found to be definitely shorter than that of **IV** (model compound). On this basis it was concluded that a certain fraction of electronically excited singlet states of **I** is deactivated via intramolecular electron transfer. The transient zwitter ions formed in this way, overwhelmingly undergo a self-reaction thus regenerating **I**, but a small portion undergoes an intramolecular Diels–Alder reaction forming **VI**, the only photoproduct. The quantum yield is $\Phi(\text{VI})\leq 0.04$. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The monophotonic ionization of aromatic compounds in dilute solutions of polar solvents has been evidenced in several cases [1–5]. For instance, anthracene (**III**) dissolved in acetonitrile was found to yield a transient photocurrent and a transient optical absorption signal at 700 nm, both attributed to ions, upon flash photolysis at $\lambda_{\text{inc}}=355$ nm [3]. Regarding the ionization mechanism at photon energies lower than the gas phase ionization potential two processes are to be considered for irradiation of aromatic compounds in the absence of additives: (a) the electronically excited molecule ejects an electron that is solvated by the surrounding solvent molecules



(b) The electronically excited molecule undergoes an electron transfer process with a nonexcited molecule



In the presence of an additive ionization can occur via electron transfer between the electronically excited aromatic molecule and the additive molecule provided the latter can function as an electron donor or acceptor according to reactions (4) and (5), respectively:



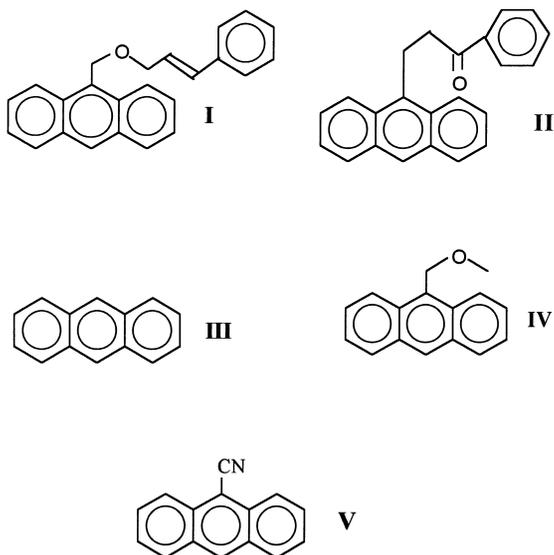
Principally, such charge transfer (CT) processes can occur also intramolecularly in the case of molecules consisting of two moieties: an aromatic one, functioning as light absorber and an electron donating or accepting one, respectively.

At the present time, intramolecular CT processes of this kind are investigated rather intensely [6–16]. Regarding bichromophoric compounds containing an anthryl moiety the phenomena of charge and energy transfer have been dealt with in a recent review article by Becker [17]. Our own interest in this subject concentrated recently on compound **I** (E-3-phenyl-prop-2-ene-1-yl (9-anthracenylmethyl)-ether) consisting of a styrene and a 9-methyl anthracene moiety connected by an ether bond.

In this connection it is interesting to refer to work concerning CT deactivation of electronically excited ω -(9-anthryl) ketones such as ω -(9-anthryl)-propiophenone (**II**) and some of its derivatives [7]. Regarding compounds of

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type **II** the occurrence of CT processes was indirectly evidenced by comparing the fluorescence quantum yields measured with bichromophoric compounds and monochromophoric reference compounds, respectively [7]. In the present work, the flash photolysis method operated in conjunction with optical absorption and electrical conductivity measurements was employed to directly evidence photoionization of monochromophoric compounds, namely anthracene (**III**), 9-methoxymethylanthracene (**IV**) and 9-cyanoanthracene (**V**), and intramolecular electron transfer in compound **I**.



2. Experimental

2.1. Product characterization

High resolution mass spectra (HRMS) were obtained by electron impact ionization at 70 eV with the aid of an instrument of Finnigan MAT (95 ST). ^{13}C NMR spectra were recorded at 100 MHz and ^1H NMR spectra at 400 MHz with a Bruker instrument (WH-400). ^1H NMR chemical shifts are reported in ppm relative to residual protonated solvent resonance of CDCl_3 at $\delta=7.26$. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are given in units of Hz. ^{13}C NMR chemical shifts are given in ppm relative to the solvent resonance of CDCl_3 at $\delta=77.0$. Peaks of the ^{13}C NMR spectra are denoted as “o” for carbons with zero hydrogens attached, “+” for carbons with one or three hydrogens attached, and “-” for carbons with two hydrogens attached, based on the DEPT (distorted enhancement of polarization transfer) spectra.

2.2. Materials

Acetonitrile was used as obtained from Merck (Uvasol Spectrograde). Anthracene (**III**) and 9-cyanoanthracene (**V**),

purchased from Aldrich, were purified by sublimation prior to use. The other compounds were synthesized as described below [18,19]:

9-Methoxymethylanthracene (IV). Sodium hydride (0.27 g, 7.0 mmol) was suspended in 50 ml of dry THF and a solution of 9-hydroxy-methylanthracene (Aldrich) in THF (0.27 g/20 ml, 1.3 mmol) was slowly added. After stirring for 2 h methyl iodide (2.0 g, 7.0 mmol) was added and the reaction mixture was refluxed for 2 h. Excess methyl iodide was removed by distillation. After hydrolysis with 100 ml water the aqueous layer was extracted twice with 100 ml MTB ether. The organic layer was dried over sodium sulfate and the solvent evaporated to yield 1.27 g (80%) of the product. ^1H NMR (CDCl_3): δ 3.59 (s, 3H), 5.42 (s, 2H), 7.48 (t, 2H, $J=7$ Hz), 7.53 (t, 2H, $J=7$ Hz), 8.05 (d, 2H, $J=7$ Hz), 8.41 (d, 2H, $J=7$ Hz), 8.45 (s, 1H); ^{13}C NMR (CDCl_3): δ 131.4 (o), 131.0 (o), 129.0 (+), 128.7 (o), 128.4 (+), 126.2 (+), 125.0 (+), 124.3 (+), 66.6 (-), 58.4 (+); HRMS (EI, 70 eV): calculated for $\text{C}_{16}\text{H}_{14}\text{O}$ 222.1053, found 222.1045.

E-3-phenylprop-2-ene-1-yl-(9-anthracenyl methyl)-ether (I): Sodium hydride (0.1 g, 2.6 mmol) was suspended in 50 ml of dry THF and a solution of 9-hydroxy-methylanthracene in THF (0.27 g (1.3 mmol)/20 ml,) was slowly added. After stirring for 2 h a solution of cinnamyl bromide in THF (0.25 g/5 ml, 1.3 mmol) was added and the reaction mixture was refluxed for 2 h. After hydrolysis with 100 ml water the aqueous layer was extracted twice with 100 ml MTB ether. The organic layer was dried over sodium sulfate and the solvent evaporated to yield 0.4 g (95%) of the product. ^1H NMR (CDCl_3): δ 4.39 (d, 2H, $J=6.0$ Hz), 5.55 (s, 2H), 6.42 (dt, 1H, $J_d=15.0$ Hz, $J_t=6.0$ Hz), 6.70 (d, 1H, $J=15.0$ Hz), 7.6–7.3 (m, 8H), 8.03 (d, 2H, $J=9.0$ Hz), 8.43 (d, 2H, $J=9.0$ Hz), 8.50 (s, 1H); ^{13}C NMR (CDCl_3): δ 64.1 (-), 71.0 (-), 124.4 (+), 125.0 (+), 126.1 (+), 126.2 (+), 126.5 (+), 127.7 (+), 128.4 (+), 128.6 (+), 128.7 (o), 129.0 (+), 131.0 (o), 131.4 (o), 132.9 (+), 136.7 (o); HRMS (EI, 70 eV): calculated for $\text{C}_{24}\text{H}_{20}\text{O}$ 324.1514, found 324.1507.

2.3. Characteristics of photoproduct

Diels–Alder-product (VI): ^1H NMR (CDCl_3): δ 2.41 (m, 1H), 2.80 (d, 1H, $J=3.5$ Hz), 3.01 (dd, 1H, $J=4.0$ Hz, 5.5 Hz), 4.02 (dd, 1H, $J=4.0$ Hz, 4.0 Hz), 4.32 (s, 1H), 4.56 (d, 1H, $J=4.5$ Hz), 5.05 (d, 1H, $J=4.5$ Hz), 6.78 (m, 2H), 7.10–7.25 (m, 7H), 7.35 (d, 2H, $J=3.5$ Hz), 7.50 (d, 2H, $J=3.5$ Hz); NOE (%): 2.41/4.02, 1.8, 2.41/2.80, 1.4, 2.41/4.56, 1.4, 2.41/6.78, 2.0, 2.80/3.01, 2.5, 2.80/4.32, 4.5, 2.80/6.78, 3.0, 3.01/4.02, 8.3; ^{13}C NMR (CDCl_3) δ 145.5 (o), 143.7 (o), 143.425 (o), 140.0 (o), 138.6 (o), 129.0 (+), 128.3 (+), 127.5 (+), 126.9 (+), 126.5 (+), 126.3 (+), 126.0 (+), 125.7 (+), 123.0 (+), 122.6 (+), 119.5 (+), 71.4 (-), 66.0 (-), 55.0 (+), 54.4 (o), 52.9 (+), 47.6 (+); HRMS (EI, 70 eV): calculated for $\text{C}_{24}\text{H}_{20}\text{O}$ 324.1514, found 324.1515.

2.4. Fluorescence measurements

Fluorescence spectra were recorded under continuous irradiation at room temperature using a SPEX FluoroMax spectrofluorimeter equipped with a modified Czerny–Turner spectrometer (detection range: 180–680 nm) in excitation and emission mode. The spectra were corrected with an internal correction file (DM 3000F software). Fluorescence lifetimes were measured with the aid of the time-correlated single-photon-counting technique. The excitation pulse ($\lambda=310$ nm, fwhm=5–10 ps) was generated by a frequency doubled, cavity-dumped rhodamine 6G dye laser (Spectra Physics Mod.375) that was pumped by an Ar ion laser, mode-locked at 514.5 nm (Spectra Physics Mod.171). A microchannel plate PMT detector (Hamamatsu R2809U-07) was used. It was shielded by a band-pass filter (IL 40 or IL 45, Balzers). The time-resolution of the setup was about 70 ps. Acetonitrile solutions were used throughout. They were saturated with argon prior to the measurement.

2.5. Transient optical absorption and photocurrent measurements

A ruby laser (Korad model KI QS2) operated in conjunction with an ADP frequency doubler was used ($\lambda=347$ nm, duration of flash: 20 ns). A flow system containing a rectangular quartz cell with two platinum electrodes was used. By directing the light beam generated by a xenon lamp through the space between the electrodes it was possible to measure simultaneously changes in the optical density and in the electrical conductivity ($R=333 \Omega$) of the solution in the cell.

2.6. Continuous irradiations

For product analysis acetonitrile or methanol solutions were irradiated with light emitted from a 450 W xenon high pressure arc lamp (Osram, XBO 450 OFR). The reaction vessel was equipped with two necks, one sealed with a septum and the other connected to an argon line. Prior to irradiation the solutions were degassed with argon for at least half-an-hour. During irradiation the solutions were kept under an argon atmosphere and the outer wall of the vessel was thermostated at 25°C. The progress of the reaction was monitored by periodically taking samples for GC analysis. Since compound **I** was found to cyclize thermally in the injector at 200°C the GC analysis was inappropriate in this case and the progress of the reaction was monitored by recording NMR spectra.

3. Results

3.1. Fluorescence measurements

Fig. 1 shows the ground state absorption and the fluorescence spectra of compounds **III–V** and **I**. Notably, all

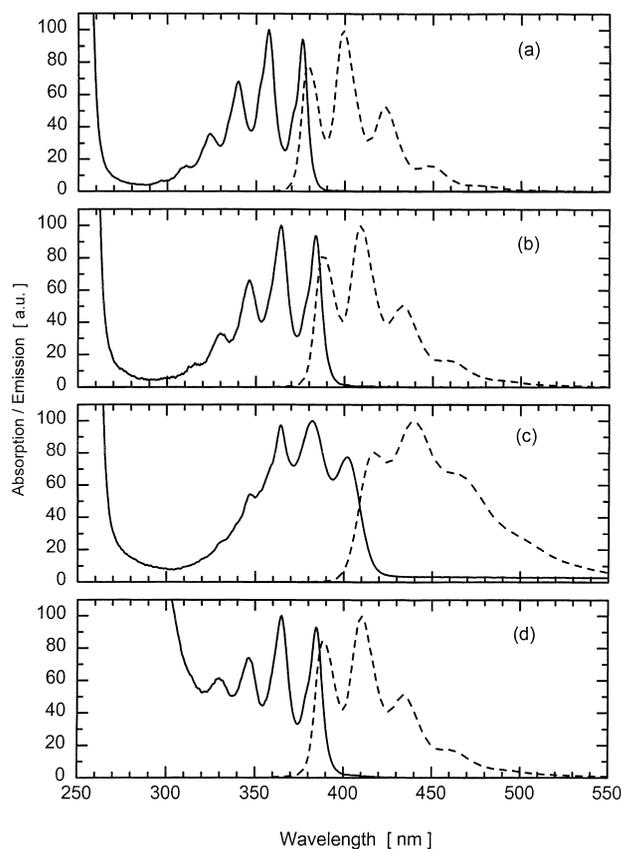


Fig. 1. Ground state absorption (—) and fluorescence (---) spectra recorded in air-saturated acetonitrile solution. $\lambda_{\text{exc}}=347$ nm. (a) **III**]= 7.0×10^{-5} mol dm $^{-3}$; (b) **IV**]= 4.3×10^{-5} mol dm $^{-3}$; (c) **V**]= 4×10^{-5} mol dm $^{-3}$; (d) **I**]= 1.3×10^{-4} mol dm $^{-3}$.

emission spectra exhibit the structure of the anthracene spectrum as a consequence of exciting the anthracene chromophore at $\lambda_{\text{exc}}=347$ nm. The close resemblance of the emission spectra of **I** and **IV** reflects the similarity of the chemical nature of the chromophores in these cases. In the case of **V** both the absorption and the emission spectrum is shifted to longer wavelength.

The fluorescence lifetimes (τ_{fl}) and quantum yields (Φ_{fl}) are listed in Table 1, and it is noted that in the case of **I** τ_{fl} is 2.3 times shorter and Φ_{fl} is 2.3 times lower than the corre-

Table 1

Fluorescence lifetimes (τ_{fl}) and quantum yields (Φ_{fl}) recorded in Ar-saturated acetonitrile solution at ambient temperature ($\lambda_{\text{exc}}=310$ nm)

Compound	λ_{obs} (nm) ^a	τ_{fl} (ns)	Φ_{fl} ^c
I	420–470	0.75	0.06
III	400	5.3 ^b	0.27 ^d
IV	380–430	1.75	0.14
V	420–470	16.9	0.74

^a Band pass filters were used.

^b Reported by O'Connor et al. [20,21] for deoxygenated ethanol and cyclohexane solution.

^c Relative to Φ_{fl} of **III**.

^d Reported by Dawson and Windsor [22].

sponding values found for the analogous compound **IV**. This is taken as an indication for the occurrence of an intramolecular deactivation process in the case of **I** involving its excited singlet state. In accordance with a former work a very large Φ_{fl} value (0.74) was determined for **V**. $\Phi_{\text{fl}}=0.85$ in ethanol and petroleum ether has been reported by Melhuish [23].

3.2. Flash photolysis experiments with compounds **I** and **III–V**

3.2.1. Transient optical absorption measurements

Transient optical absorption spectra recorded at the end of the 20 ns flash with compounds **I** and **III–V** are shown in Fig. 2. These spectra possess relatively weak absorption bands at $\lambda > 500$ nm that are characteristic of radical ions. Moreover, in the cases of **I**, **III** and **IV** there is an additional rather strong absorption band in the wavelength range between 400 and 450 nm that is characteristic of the triplet state of these compounds (T-T absorption bands) [24,25].

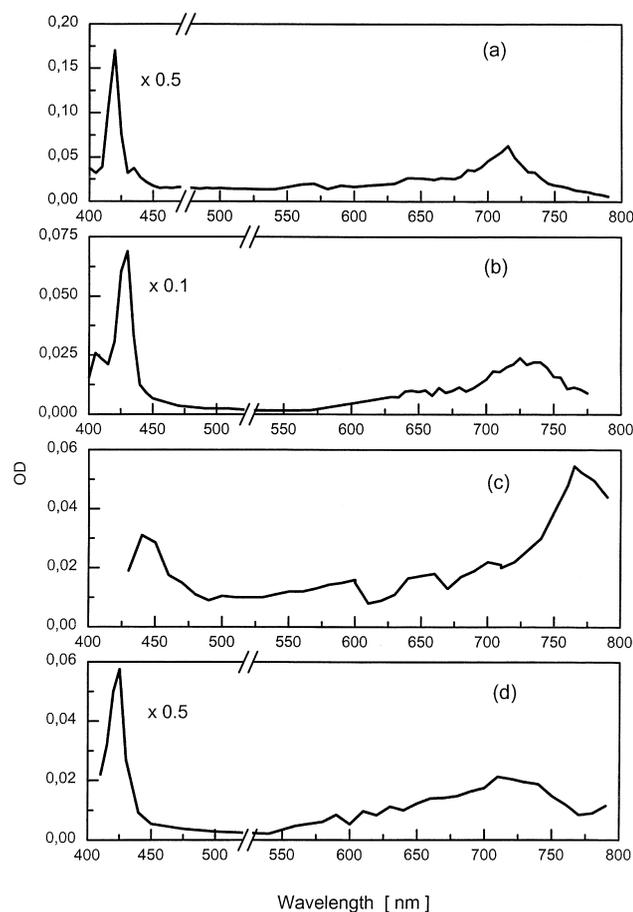
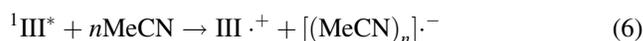


Fig. 2. Transient absorption spectra recorded at the end of the 20 ns laser flash ($\lambda_{\text{inc}}=347$ nm) with Ar-saturated acetonitrile solutions at ambient temperature. (a) $[\text{III}]=3 \times 10^{-5}$ mol dm $^{-3}$; (b) $[\text{IV}]=5.0 \times 10^{-5}$ mol dm $^{-3}$; (c) $[\text{V}]=4.0 \times 10^{-5}$ mol dm $^{-3}$; (d) $[\text{I}]=3.9 \times 10^{-5}$ mol dm $^{-3}$. $D_{\text{exp}}=75\text{--}90$ mJ/flash.

Also the transient absorption spectrum of **V** possesses an absorption band between 400 and 450 nm ($\lambda_{\text{max}} \approx 440$ nm). However, this band is assigned to the radical cation rather than to the triplet state of **V**. Notably, intersystem crossing is a very inefficient process in the case of **V**. In acetonitrile solution triplets ($\lambda_{\text{max}}=433$ nm) are formed with a very low quantum yield: $\Phi_{\text{T}}=0.021$ [26]. On this basis a transient optical density $\text{OD}=2 \times 10^{-3}$ at the end of the 20 ns flash is expected assuming $\epsilon=2 \times 10^4$ dm 3 mol $^{-1}$ cm $^{-1}$. Since this value is about one order of magnitude lower than the observed one, T-T absorption can only contribute marginally to the absorption band around 440 nm in the case of **V**.

A more detailed inspection of the transient absorption spectra of **I**, **III** and **IV** reveals the following: both the radical cation and the radical anion of **III** reportedly possess overlapping absorption bands between 700 and 750 nm, that differ somewhat in peak position and band width [27]. However, at the present experimental conditions (error limit, spectral resolution) it is not possible to discriminate between the two species. Following the reasoning of Vauthey et al. [3] it is assumed that upon irradiation of anthracene in acetonitrile solution the radical cation is formed. These authors concluded that in the case of system **III**/MeCN the generation of the photocurrent is due either to electron transfer from singlet excited anthracene, $^1\text{III}^*$, to the solvent (reaction (6)) or to electron capture by $^1\text{III}^*$ from the solvent (reaction (7)).



Since the energy balance yields $\Delta G=+0.34$ eV for (6) and $\Delta G=+2.6$ eV for (7) it was concluded that radical cations rather than radical anions are formed.

A situation quite similar to that encountered with **III** is feasible in the case of compound **IV** and the absorption band peaked at about 720 nm is attributed to the radical cation. In this connection it is noted that, according to the literature, anthracene triplets absorb light only very slightly at $\lambda > 600$ nm [28–30]. According to Meyer et al. [30] in the case of $^3\text{III}^*$ the ratio of the extinction coefficients at $\lambda=420$ nm and $\lambda=720$ nm is quite large: $\epsilon_{420}/\epsilon_{720} \approx 600$. By contrast, much lower values are obtained for this ratio from the spectra presented in Fig. 2(a), (b) and (d). In the case of **III**, e.g., $\epsilon_{420}/\epsilon_{720} \approx 7$ is obtained from the corresponding spectrum (Fig. 2(a)). This strongly indicates that the long wavelength portion of the transient absorption spectra of **I**, **III** and **IV** are not due to the T-T absorption of the anthracene moiety. Regarding **I**, the long wavelength absorption band observed with this compound (see Fig. 2(d)) is assigned to the radical anion rather than to the radical cation which will be explained in Section 4. In the case of compound **V** the absorption spectra of the radical cation and the radical anion differ appreciably and, therefore, the absorption bands peaked at about 440 and 760 nm can be safely attributed to the radical cation. Reportedly, in

Table 2

Decay of the transient absorption at wavelengths corresponding to the T–T absorption (415–430 nm) and to the absorption of radical cations (715–730 nm)

Compound/concentration (mol dm ⁻³)	D_{exp} (mJ/flash)	λ_{obs} (nm)	$(\tau_{1/2})^1$ (μs) ^a	Decay mode
III 3.0×10^{-5}	65	415	0.6	First order
		715	1.8	Second order
IV 5.0×10^{-5}	75	430	1.3	First order
		730	3.0	Undefinable order
I 3.9×10^{-5}	75	420	0.5	First order
		730	3.0	Second order

^a First half-life of decay.

the case of **V** the radical cation possesses two absorption bands with peaks at 435 and 765 nm [31] and the radical anion absorbs in the range from 450 to 780 nm with peaks at 547, 590 and 651 nm [27].

With respect to the assignment of the absorption bands between 400 and 450 nm and 700 and 750 nm to triplets and radical ions, respectively, in the case of compounds **I**, **III** and **IV** it is noticeable that these absorption bands decay at different rates. This proves that they are due to different species. In all three cases the 415/430 nm band decays much faster than the 715/730 nm band. Moreover, the decay of the absorption follows different kinetic laws at the two different wavelengths. Relevant data demonstrating this behavior are presented in Table 2.

Fig. 3 shows plots of the optical density corresponding to the peak wavelength of the radical ions as a function of the absorbed dose. In all cases the OD increases linearly with increasing absorbed dose per flash ($\text{OD} \propto D_{\text{abs}}^n$ with $n=1$) indicating that the photoionization is a monophotonic process. In conclusion, it is inferred from transient absorption spectroscopy that compounds **III–V** undergo monophotonic ionization and that **I** undergoes intramolecular electron transfer upon irradiation at $\lambda_{\text{inc}}=347$ nm in acetonitrile solution.

3.2.2. Photocurrent measurements

The conclusion concerning the photogeneration of ions in acetonitrile solutions containing compound **III–V** arrived at by transient optical absorption measurements was clearly corroborated by measuring the photo-induced changes in the electrical conductivity of the solution. A photocurrent was formed during the flash and the magnitude of the photocurrent recorded at the end of the flash was found to increase linearly with the voltage applied to the platinum electrodes (Ohm's law is fulfilled). As can be seen from Fig. 4, the photocurrent increases linearly with the absorbed dose per flash which also indicates that photoionization occurs monophotonically. Regarding compound **I** it is interesting to note, that a photocurrent was not detectable within the error limit of the measurement. This shows that, compounds **III–V** form free ions and, by contrast, compound **I** does not, although the formation of an ionic species is clearly evidenced by the formation of a transient optical absorption around 725 nm (vide ante).

3.3. Kinetic measurements

As can be seen from the kinetic traces referring to compounds **III–V**, depicted in Fig. 5(a)–(c), both the photocurrent and the transient optical absorption of the radical ions are formed during the 20 ns flash. However, there is no simple correlation between the decay rates. Actually, a first glimpse at the curves reveals that the photocurrent decays faster than the transient absorption.

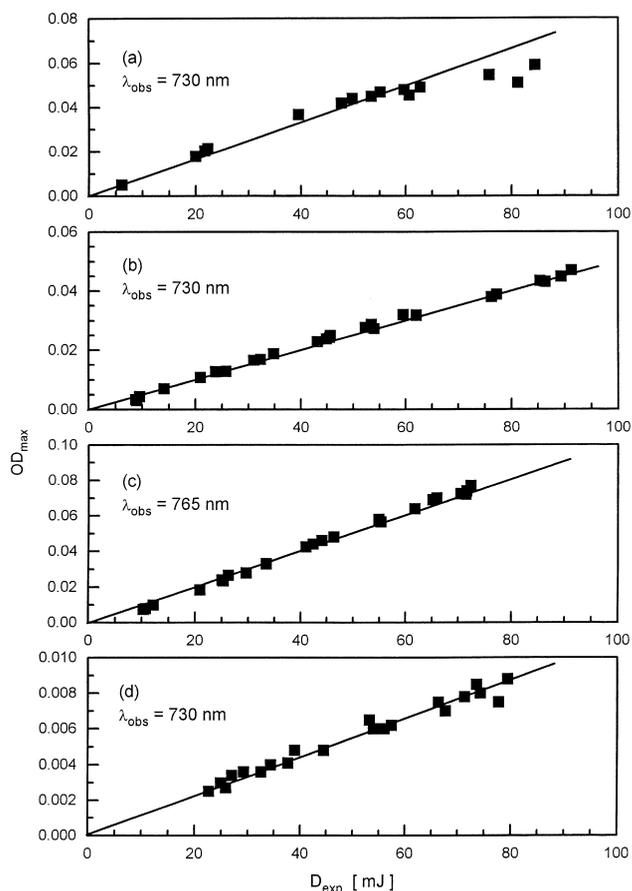


Fig. 3. OD_{max} recorded at the end of the flash as a function of the exposure dose per flash. (a) **[III]** = 3.0×10^{-5} mol dm⁻³; (b) **[IV]** = 5.0×10^{-5} mol dm⁻³; (c) **[V]** = 4.0×10^{-5} mol dm⁻³; (d) **[I]** = 3.9×10^{-5} mol dm⁻³.

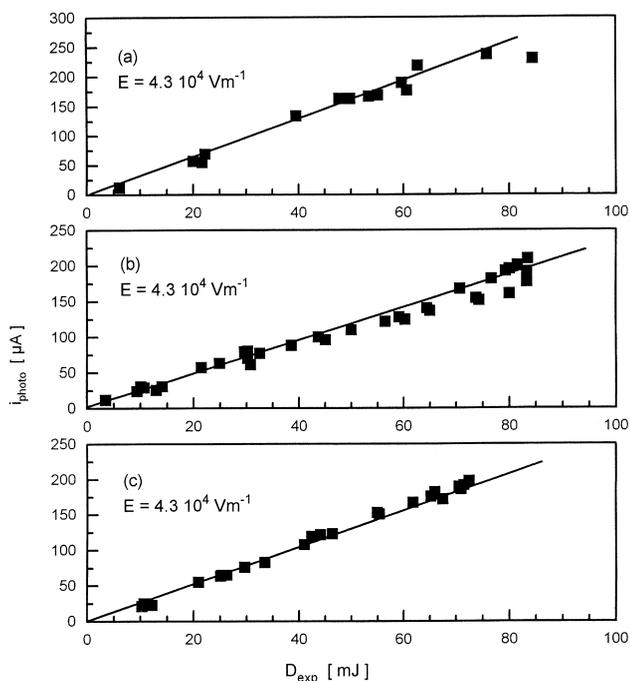


Fig. 4. The photocurrent recorded at the end of the flash as a function of the exposure dose per flash. (a) $[III]=3.0 \times 10^{-5} \text{ mol dm}^{-3}$; (b) $[IV]=5.0 \times 10^{-5} \text{ mol dm}^{-3}$; (c) $[V]=4.0 \times 10^{-5} \text{ mol dm}^{-3}$.

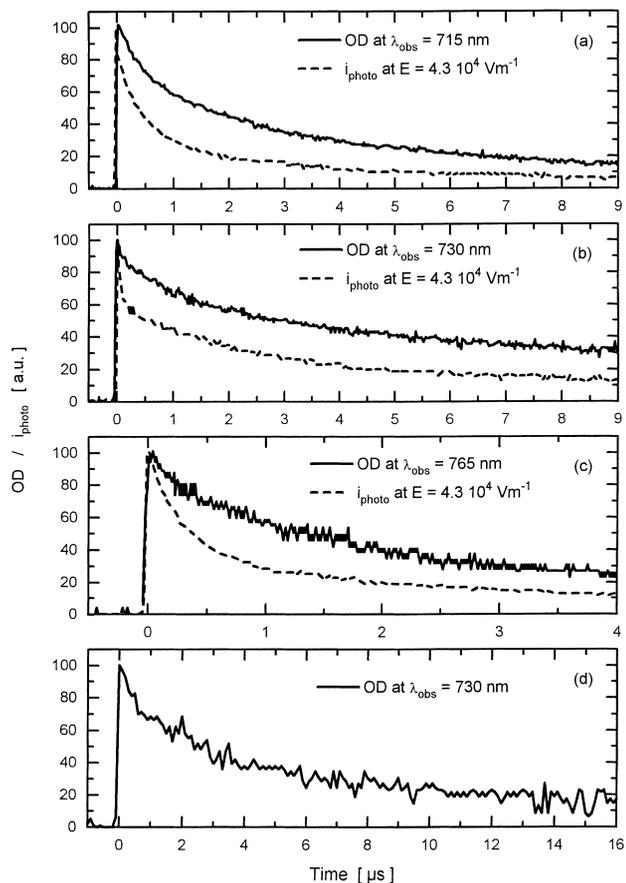


Fig. 5. Kinetic traces depicting formation and decay of the transient optical absorption and the photocurrent. For experimental conditions: see legend of Fig. 2.

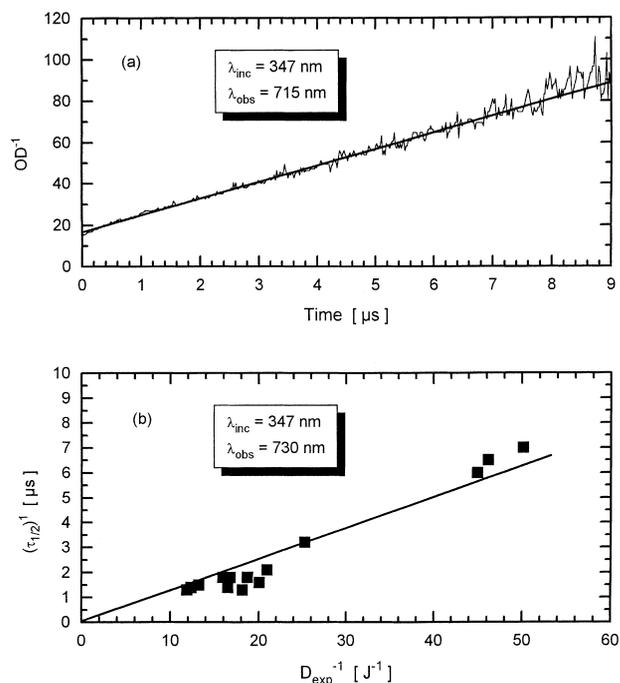


Fig. 6. Flash photolysis of III ($3 \times 10^{-5} \text{ mol dm}^{-3}$) in Ar-saturated acetonitrile solution at $\lambda_{inc}=347 \text{ nm}$. Decay of the optical density OD after the 20 ns flash. (a) Plot of the reciprocal optical density vs. time at $D_{exp}=85 \text{ mJ/flash}$; (b) first half-life of the decay in OD vs. the reciprocal exposure dose.

3.3.1. Optical density

Regarding the formation of ionic species it is important to note that in the cases of **I**, **III** and **IV** the transient absorption of both the triplets and the ionic species was formed simultaneously during the flash. Moreover, the decay of the triplet absorption did not affect the decay kinetics of the absorption of the ionic species. Therefore, it is concluded that radical ions originate from excited singlets rather than from triplets, i.e. that the decay of the triplets does not lead to the formation of ionic species. Concerning the transient absorption of the radical ions a careful inspection of the kinetic traces shows that the decay follows second-order kinetics in the case of **III**. This was evidenced (see Fig. 6) by a plot of OD^{-1} vs. the time and a plot of the first half-life $(\tau_{1/2})^1$ vs. the reciprocal exposure dose $(D_{exp})^{-1}$. D_{exp} is proportional to c_0 , the initial concentration of radical ions, i.e. $(\tau_{1/2})^1 = (c_0 k_2)^{-1} \propto (D_{exp})^{-1}$. In the case of compound **V** a behavior similar to that observed with **III** was found. As can be seen from Fig. 7, the transient optical density attributed to radical ions decayed according to second-order kinetics. In the case of **IV** the decay of the OD around 730 nm could not be related to a certain kinetic order. A reason for this behavior was not revealed.

Also in the case of compound **I** the transient optical density at 720 nm decayed according to second-order kinetics. This is demonstrated in Fig. 8, where plots of OD^{-1} vs. the time and of $(\tau_{1/2})^1$ vs. $(D_{exp})^{-1}$ are presented. This result is surprising insofar as a first-order kinetic law

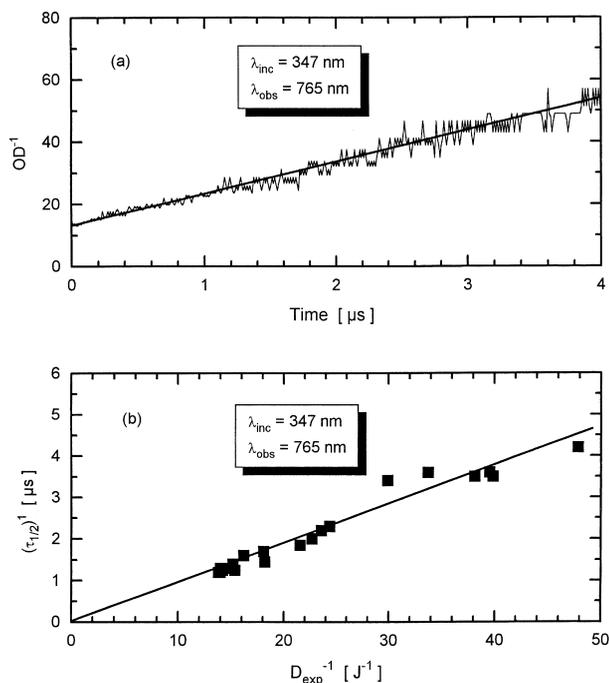


Fig. 7. Flash photolysis of **V** (4×10^{-5} mol dm⁻³) in Ar-saturated acetonitrile solution at $\lambda_{\text{inc}}=347$ nm. Decay of the optical density OD after the 20 ns flash at $\lambda_{\text{obs}}=765$ nm. (a) Plot of the reciprocal optical density vs. time at $D_{\text{exp}}=80$ mJ/flash; (b) first half-life of the decay in OD vs. the reciprocal exposure dose.

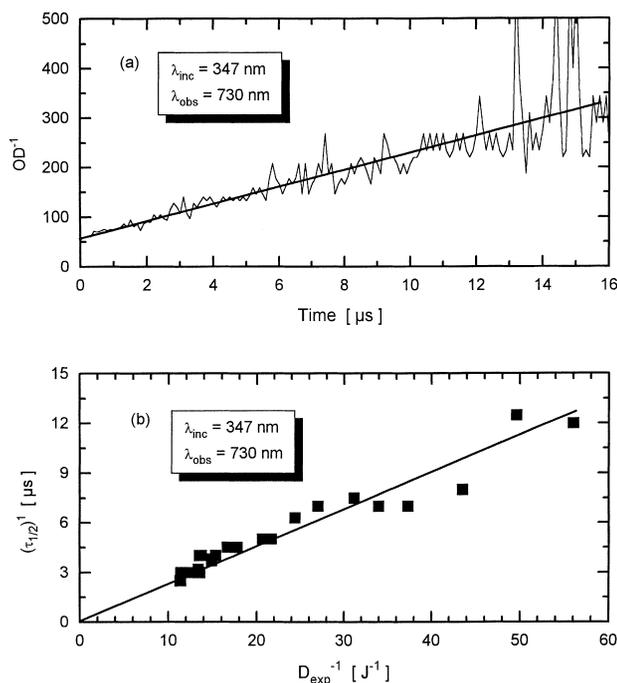


Fig. 8. Flash photolysis of **I** (3.5×10^{-5} mol dm⁻³) in Ar-saturated acetonitrile solution at $\lambda_{\text{inc}}=347$ nm. Decay of the optical density OD after the 20 ns flash at $\lambda_{\text{obs}}=730$ nm. (a) Plot of the reciprocal optical density vs. time at $D_{\text{exp}}=75$ mJ/flash; (b) first half-life of the decay in OD vs. the reciprocal exposure dose.

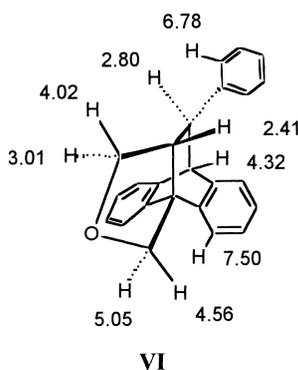
should hold provided the decay of the transient OD would be related to an intramolecular deactivation process. Obviously, this is not the case.

3.3.2. Electrical conductivity

The decay of the photocurrent observed with compounds **III–V**, does not follow a certain kinetic order. Moreover, the decay lifetime does not depend on the exposure dose per flash. Apparently, there is an initial rapid decay which is followed by a rather slow decay extending to the time range where the transient optical absorption is still detectable. It appears feasible to explain this behavior on the basis of the reaction of the highly mobile solvated electrons formed right after ejection with the solvent. In this way the radical anion $\text{CH}_3\text{CN}^{\cdot-}$ or its dimer $(\text{CH}_3\text{CN})_2^{\cdot-}$ is formed. In the solvated state these species are less mobile than the solvated electron and, therefore, contribute much less to the photocurrent.

3.4. Analysis of products of the photoreaction of **I**

27.9 mg of **I** (0.086 mmol) were dissolved in 100 ml of either acetonitrile or methanol. Irradiation for 1 h afforded compound **VI** exclusively, as determined by NMR spectroscopy and HRMS (see Section 2). Other photoproducts were not detected. The stereochemical structure of compound **VI** was determined by measuring nuclear Overhauser effects (NOE) between selected proton resonances.



Irradiation at 2.41 ppm gives rise to NOE signals (all in ppm units) at 4.02 (1.8%), 2.80 (1.4%), 4.56 (1.4%), and 6.78 (2.0%), and irradiation at 3.01 ppm yields NOE signals at 2.80 (2.5%) and 4.02 (8.3%). These results indicate that the 3.01 and the 4.02 protons are in geminal position pointing to the same side as the 2.80 proton. From the NOE signals obtained upon irradiation at 2.41 it is concluded that the 4.02 proton is in closer proximity to the 2.41 proton than the 3.01 proton. The occurrence of a NOE signal at 6.78 (3.0%) upon irradiation at 2.80 supports the assignment to the benzenic hydrogen given in the formula shown above. Since there is a NOE signal between 2.41 and 6.78 of 2.0% one can conclude that the phenyl group and the 2.41 proton point into the same direction.

In another experiment the consumption of **I** was measured by irradiating an acetonitrile solution (5.7×10^{-5} mol dm⁻³)

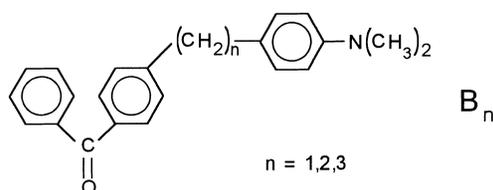
with a large number of 347 nm laser flashes. The absorption bands of the anthryl groups at 365.0 and 384.5 nm decreased linearly with the number of flashes and the quantum yield of consumption $\Phi(-I)=0.04$ was estimated with the aid of the extinction coefficients of anthracene ($\epsilon_{365}=9.35 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{384}=8.85 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Since **VI** is the only detectable product the quantum yield of formation of **VI** cannot exceed the quantum yield of consumption of **I**, i.e. $\Phi(\text{VI}) \leq 0.04$.

4. Discussion

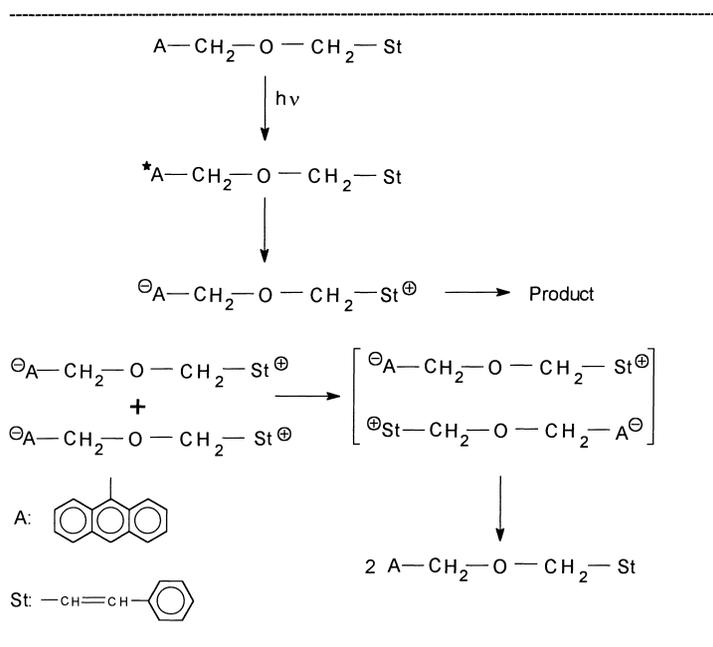
The monophotonic photoionization of the compounds **III–V** in acetonitrile solution resulting in the generation of free ions is clearly evidenced in this work by transient optical spectroscopy and photocurrent measurements. Regarding compound **III** our results widely corroborate those of Vaulthey et al. [3]. These authors reported that the monophotonic ionization of anthracene occurs in acetonitrile solution with a quantum yield of 0.06. The most interesting feature of our work is the finding that compound **I**, in an excited singlet state, undergoes intramolecular charge transfer to some extent. This is concluded on the basis of the following facts: (a) the fluorescence lifetime of **I** is 2.3 times shorter and the fluorescence quantum yield is 2.3 times lower than the corresponding values of **IV** which is considered a model compound of **I**; (b) transient optical absorption spectroscopy reveals the formation of a radical ion; (c) no photocurrent is formed upon irradiation of **I**. Therefore, it is very likely, that a certain fraction of singlet-excited molecules of **I** undergoes a CT process forming a

transient zwitter ion. In this process, the styrene moiety acts as donor and the anthracene moiety as acceptor. On this basis the transient absorption band around 720 nm (Fig. 2(d)) would be attributable to the radical anion located at the anthracene moiety. From the low quantum yield of conversion (0.04) it is inferred that only a small fraction of the transient zwitter ions forms a product and the major fraction deactivates via a self-reaction as indicated in Scheme 1. This reaction is encounter-controlled and, therefore, the decay of the transient absorption attributed to the charge-separated state follows second-order kinetics. Only a small portion of the transient zwitter ions undergoes the intramolecular [4+2] cyclo-addition converting **I** into **VI**. In other words, a Diels–Alder reaction catalyzed by the intramolecular transfer of one electron occurs, but only to a low extent.

Concerning the rather long lifetime of the charge-separated state of **I** it is interesting to refer to the work of Masuhara et al. [32] who investigated the photo-induced intramolecular charge transfer in another donor–insulator–acceptor system containing benzophenone and *N,N*-dimethylaniline as acceptor and donor moieties, respectively.



In acetonitrile solution, these compounds denoted as B_n (with $n=1-3$) exhibited a behavior similar to that of compound **I**, i.e. the charge-separated state formed rapidly after



Scheme 1. Photoreactions of compound **I**.

the flash in the ns-range and the decay occurred in the μs range and followed second-order kinetics. It seems that, in these cases, the lifetime of the charge-separated state is so long because back electron transfer is a very inefficient process. Otherwise it would be conjectured that the lifetime of the charge-separated state is short because of the flexibility of the insulator group linking donor and acceptor. Long lifetimes of charge-separated states extending to the μs range were found for donor–insulator–acceptor molecules with rigid insulator bridges of linearly connected norbornane and bicyclo[2.2.0] hexane type units [33]. Here, back electron transfer seems to be important, since the lifetime of the charge-separated state increases with increasing length of the insulator link.

Commonly, the Gibbs free energy change ΔG is taken as a measure for the probability of the occurrence of an electron transfer reaction. Regarding the photoionization via the reaction of an electronically excited donor with the solvent ΔG is obtained with the aid of the Rehm–Weller equation [34,35] using the modified Coulomb term [36]:

$$\Delta G = E_{\text{ox}} - E_{\text{red}} - E_{00} - \frac{6.242 \times 10^{18} e^2}{2n^2 4\pi\epsilon_0 (r_{\text{D}} + r_{\text{solv}})}. \quad (8)$$

Here, E_{00} is the excited state energy (in eV), E_{ox} and E_{red} denote the oxidation potential of the donor and the reduction potential of the solvent, respectively, (in eV); e the elementary charge (1.602×10^{19} A s); ϵ_0 the electric field constant (8.85×10^{-12} A s V^{-1} m $^{-1}$); r_{D} and r_{solv} the radii (in m) of the donor and the solvent molecule, respectively; n is the mean refractive index of donor and solvent.

The applicability of this method crucially depends on the availability of reliable values of E_{ox} and E_{red} . With $E_{\text{red}} = -3.5$ eV, the reduction potential of acetonitrile reported by Rifi and Covitz [37], $E_{\text{ox}} = 0.95$ eV, $E_{00} = 3.30$ eV and $r_{\text{D}} + r_{\text{solv}} = (1.7 + 2.74) \times 10^{-10}$ m Vauthey et al. [4] obtained a slightly positive (endergonic) free energy change $\Delta G = +0.37$ eV for **III**. The endergonicity was thought to be reflected by the rather low quantum yield of photoionization (0.06) and the rather low rate constant of photoionization via interaction of electronically excited **III** with the solvent ($k_{\text{ion}} = 3 \times 10^6$ dm 3 mol $^{-1}$ s $^{-1}$).

For **IV** and **V** literature values of E_{ox} were not available. Cyclic voltammetry performed in acetonitrile solution indicated irreversibility of the oxidation process in both cases¹. With the aid of the peak oxidation potentials obtained in this way ($E_{\text{p}} = 1.25$ eV (**IV**) and $E_{\text{p}} = 1.6$ eV (**V**)) positive ΔG values (0.6 and 1.1 eV for **IV** and **V**, respectively) were calculated indicating endergonicity. Because of the irreversibility of the oxidation process these ΔG values can be weighted qualitatively only, but it can be anticipated that photoionization should be a minor process. Nevertheless, it

was unambiguously evidenced by the experimental results in all three cases (**III–V**).

In the case of intramolecular charge transfer in bichromophoric compounds the free energy change has been estimated with the aid of the following equation [11]:

$$\Delta G = E_{\text{ox}} - E_{\text{red}} - E_{00} - C \quad (9)$$

with

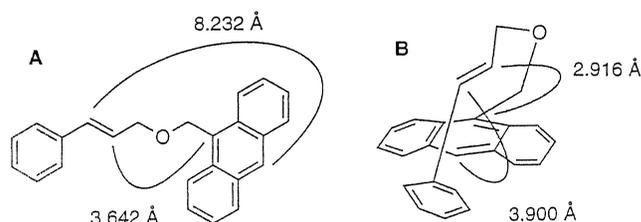
$$C = \frac{6.242 \times 10^{18} e^2}{4\pi\epsilon_0} \left[\frac{1}{\epsilon_s R_c} - \frac{1}{r} \left(\frac{1}{37} - \frac{1}{\epsilon_s} \right) \right], \quad (10)$$

and for acetonitrile with $\epsilon_s = 37$

$$C = \frac{6.242 \times 10^{18} e^2}{4\pi\epsilon_0 \epsilon_s R_c}. \quad (11)$$

Here ϵ_s denotes the static dielectric constant of the solvent; R_c the distance of the charge centers and r is the ionic radius.

Regarding compound **I** ΔG was calculated according to Eq. (9) with $E_{00} = 3.22$ eV using for E_{ox} the oxidation peak potential $E_{\text{p}} = 1.68$ eV of Ph–CH=CH–OCH $_3$ ¹ and $E_{\text{red}} = -1.88$ eV of anthracene [38] for R_c equal to 8×10^{-10} and 4×10^{-10} m, the approximated R_c values corresponding to the two conformers of **I** depicted below:



Slightly endergonic ΔG values (+0.37 and +0.31 eV, respectively) were obtained indicating that intramolecular electron transfer in compound **I** is not very likely. This is in accord with the low quantum yield of conversion.

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¹The measurements were performed at the Institute for Organic and Bioorganic Chemistry, Humboldt-University Berlin, courtesy of Prof. W. Abraham.

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