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INTRAMOLECULAR PHOTOINDUCED ELECTRON TRANSFER (PET) BOND CLEAVAGE IN SOME SULFONIUM SALT DERIVATIVES. EFFECT OF DISTANCE AND THERMODYNAMICS ON PET RATE

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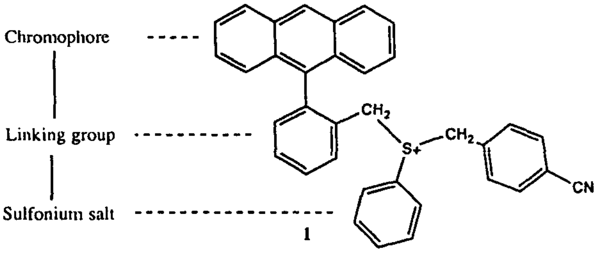
The rate of intramolecular photoinduced electron transfer (PET) between a naphthacene electron donor (D) and a sulfonium electron acceptor (A) was found to be dependent on the thermodynamics for PET and distance between D and A. The slopes of ln k_{ET} vs through-bond and through-space distance plots was found to be $-0{\cdot}60$ and $-0{\cdot}91$ Å^{-1}, respectively. The product distribution obtained from the photolysis of regioisomeric naphthacenyl sulfonium salt derivatives was found to be independent of distance. Photolysis of three regioisomeric naphthacenyl phenylmethyl-*p*-cyanobenzylsulfonium salts produced unsubstituted thiomethylphenylnaphthacene and mono-, di- and tri-*p*-cyanobenzyl-substituted thiomethylphenylnaphthacene. The appearance of the out-of-cage di- and trisubstituted photoproducts suggests that secondary photochemistry and intermolecular electron transfer bond-cleavage reactions are occurring when the concentration of the sulfonium salt in acetonitrile is 10^{-2} and 10^{-3} M and the degree of conversion is high. The primary photoproduct is the mono-substituted naphthacene derivative.

INTRODUCTION

Brønsted 'photoacids' are of interest both scientifically and technologically as they relate to photoinduced bond cleavage reactions[1] and their use in acid-catalyzed chemistry for photocuring[2] and photoresist applications.[3] We have recently presented a scheme that utilizes intramolecular photoinduced electron transfer (PET) bond cleavage[4] to produce single-component, long wavelength light-activated Brønsted 'photoacids.' Photoacids based on this concept contain an electron-rich chromophore connected to an electron-deficient sulfonium group through a linking group as shown for the phenylanthracene sulfonium salt derivative **1**.



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The light-absorbing anthracene chromophore, in this case, is separated from the sulfonium moiety by a benzyl group twisted out of the plane of the anthracene ring system. The electronic absorption spectrum of **1** is virtually identical with that of 9-phenylanthracene between 350 and 400 nm, indicating the lack of a charge-transfer interaction between the donor and acceptor moieties. The photoexcited anthracene chromophore can transfer an electron either through-bond[5,6] or through-space to the σ^* lowest unoccupied molecular orbital (LUMO) localized on the sulfonium moiety. The LUMO of the molecule must be σ^* and localized on the sulfonium group for this concept to be viable.[4] The key intermediate produced after PET and bond cleavage, we believe, is a singlet cation-radical–radical pair.[4] The intermediacy of the singlet pair is consistent with in-cage radical coupling products in addition to out-of-cage products resulting from electron transfer from the radical to the cation-radical.[4]

The ability to produce PET bond cleavage in these systems is dependent on the rate of PET being faster than or competitive with the rate of energy decay pathways such as fluorescence, intersystem crossing (ISC)

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and non-radiative decay. In addition, bond cleavage must be faster than back electron transfer. With this in mind, two series of naphthacenyl sulfonium salts were synthesized. The major difference between the two series is the electron-accepting ability of the sulfonium group. Within a series the sulfonium group is positioned at different distances from the chromophore. The rate of PET, fluorescence lifetime, fluorescence quantum yield, free energy change for PET and quantum yield for acid formation were investigated as a function of distance between the light-absorbing electron-donor chromophore (D) and the site of bond cleavage on the electron-accepting sulfonium moiety (A) within each series. This information will provide a more detailed understanding of the mechanistic aspects of PET bond-cleavage processes.

RESULTS

The first naphthacenyl sulfonium salt series contains the dimethylsulfonium group on the *ortho* (**2**), *meta* (**3**) and *para* (**4**) positions on the phenyl ring of 5-phenylnaphthacene. The distance between the naphthacene ring and sulfonium group was systematically altered to provide mechanistic insight into the PET bond-cleavage process. The singlet lifetime (τ_{S_1}), quantum yield for fluorescence (ϕ_f), quantum yield for acid formation (ϕ_{H^+}), free energy change for PET (ΔG^0_{ET}), and electronic absorption behavior were measured for compounds **2**–**4** in acetonitrile and are presented in Table 1.

The free energy change for PET was obtained from the redox behavior (see Table 2) and the energy of the longest wavelength electronic transition for **2**–**4** using the Weller equation.[7] The oxidation and reduction potentials for the naphthacene moiety are reversible and are thermodynamic values. The reduction potential for the sulfonium group, on the other hand, is irreversible at all scan rates owing to the apparent concerted nature of the electrochemical reductive cleavage process.[8] The E_p value for the electrochemical reduction of the sulfonium moiety was obtained by measuring E_p as a function of scan rate and extrapolating to zero scan rate. The concerted nature, on the electrochemical time scale, of the electrochemical reductive cleavage of the sulfonium group is critically important for the PET bond-cleavage process. Although the E_p values are not thermodynamic potentials, they provide a good estimate of the energy of the σ^* LUMO level.[8]

In the second series, compounds **5**, **6** and **7** possess a *p*-cyanobenzyl group in place of a methyl on sulfur to produce a more electron-deficient sulfonium group.

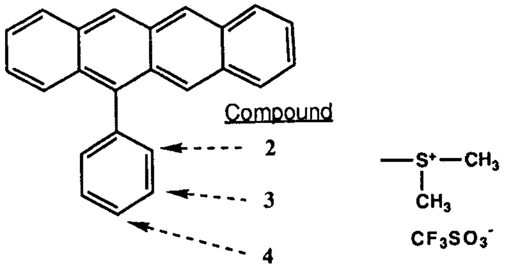


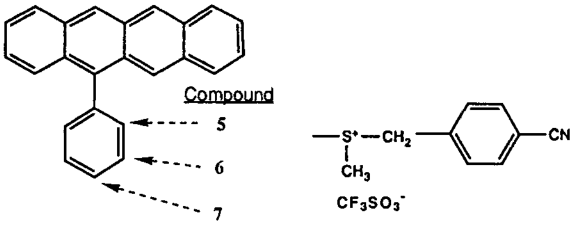
Table 1. Singlet lifetime (τ_{S_1}), fluorescence quantum yield (ϕ_f), quantum yield for acid formation (ϕ_{H^+}), wavelength of lowest energy electronic transition (λ_{max}) and free energy change for PET (ΔG^0_{ET}) for compounds 2–7 in acetonitrile

Compound	τ_{S_1} (ns)	ϕ_f	ϕ_{H^+}	λ_{max} (nm)	ΔG^0_{ET} (kcal mol^{-1})
2	12·9	0·47	~0·01	486	~ −1·8
3	5·5	0·27	<0·01	481	~ −2·5
4	5·9	0·34	<0·01	481	~ −3·5
5	0·80	0·042	0·06	486	~ −11·4
6	5·5	0·052	0·14	482	~ −10·8
7	8·4	0·042	0·12	482	~ −9·6

Table 2. Electrochemical oxidation and reduction potentials for some naphthacenyl sulfonium salts vs. SCE in acetonitrile

Compound	$E^{0\prime}_{ox}$(V)	E_p(V)[a]	$E^{0\prime}_{red}$(V)
2	+1·03	(−1·44)	−1·67
3	+0·97	(−1·46)	−1·53
4	+0·97	(−1·51)	−1·62
5	+1·053	(−1·01)	−1·53
6	+0·985	(−1·12)	−1·573
7	+0·98	(−1·18)	−1·523
5-(2-Thiomethylphenyl-1-napththacene)	(+0·840)[a]		−1·735
5-(3-Thiomethylphenyl)naphthacene	+0·822		−1·633
5-(4-Thiomethylphenyl)naphthacene	+0·932		−1·579

[a] E_p values were obtained from a plot of log[scan rate (mV s^{-1})] vs. measured formal potential (V vs SCE) and extrapolating to zero scan rate.



The *p*-cyanobenzyl group alters the E_p for the reductive cleavage of the sulfonium group by approximately 0·4 eV to less cathodic values (see Table 2). The singlet lifetime, quantum yields for fluorescence (acid formation) and free energy change for PET are also presented in Table 1.

Photoproduct studies of 5, 6 and 7

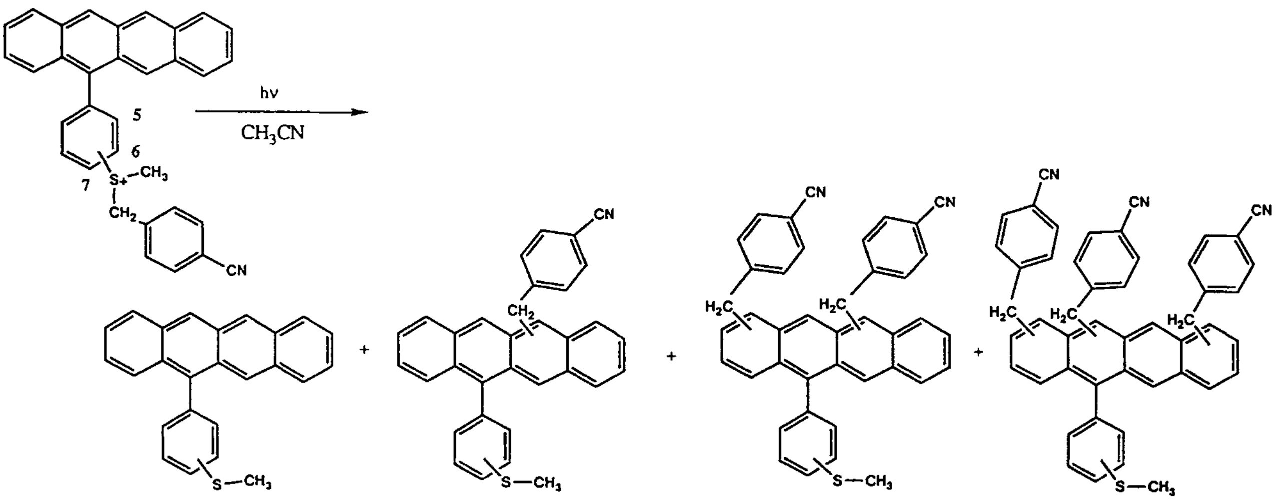
Photochemical irradiation of **5**–**7** in acetonitrile solvent produces four photoproducts with a similar product distribution as shown.

A more detailed analysis of the photoproducts is presented in the Discussion section.

DISCUSSION

The singlet lifetime for the regioisomers **2**–**4** varies from 12·9 to 5·5 ns. The singlet lifetime for each of the salts is considerably longer than the 3·7 ns lifetime observed for 5-phenylnaphthacene itself in acetonitrile. The fluorescence quantum yield for **2**–**4** varies from 47 to 27%. Again, these values are higher than that obtained for 5-phenylanthracene ($\phi_f = 0 \cdot 18$) in the same solvent. For each of the members in this series ϕ_{H^+} is less than 0·01. Since PET is necessary for bond cleavage and Brønsted acid production, it is clear that within the dimethylsulfonium salt series the rate of PET is not competitive with the radiative rate and other decay modes for S_1. The radiative rate for the 5-phenylnaphthacene chromophore is $4 \cdot 9 \times 10^7\ s^{-1}$ in air-saturated acetonitrile. The thermodynamic driving force for PET in **2**, **3** and **4** is modestly exothermic and the average rate of PET is *ca* $5 \cdot 6 \times 10^6\ s^{-1}$.

The variation in τ_{S_1} and ϕ_f between compounds **2**–**4** and 5-phenylnaphthacene is attributed to the effect of the electron-withdrawing sulfonium group on the relative positions of the S_1 and T_2 energy states.[9] The primary deactivation pathway for the S_1 state of 5-phenylnaphthacene in benzene solution has been found to be ISC with $\phi_{ISC} = 0 \cdot 65$.[9] The rate of ISC from S_1 to T_1 through T_2 appears to decrease in the order **2** < **4** < **3** ≪ 5-phenylnaphthacene. The rationale for the presumed change in the rate of ISC as indicated involves the lowering of the energy of the S_1 state in **2**–**4** relative to the energy of the T_2 state. In 5-phenylnaphthacene ISC is the major pathway for deactivation of the S_1 because T_2 is slightly below S_1 in energy. This results in rapid ISC owing to good vibrational overlap between the singlet and triplet manifold.



A m/e = 350	B m/e = 465	C m/e = 580	D m/e = 695
5 - 1.0	5 - 1.88	5 - 0.67	5 - 0.13
6 - 1.0	6 - 2.22	6 - 1.05	6 - 0.38
7 - 1.0	7 - 1.91	7 - 1.27	7 - 0.43

The effect of the electron-withdrawing sulfonium group on phenyl appears to provide a lowering of S_1 relative to T_2 so that S_1 now lies below T_2 in energy. This energy-level restructuring appears to lower the rate of ISC and is consistent with singlet lifetimes and fluorescence quantum yields presented in Table 1.

The maximum transmission of the inductive effect of the sulfonium substituent on the naphthacene ring system occurs in **2** and **5** owing to the close proximity of the D and A groups. This is clearly evident in the effect on the redox behavior and electronic absorption spectrum. In **2** and **5** the phenyl ring is expected to be nearly orthogonal to the plane of the naphthacene ring system. AM1[10] molecular orbital calculations indicate the dihedral angle between the phenyl and the naphthacene ring system to be 88°, 72° and 64° for **2**, **3** and **4**, respectively.

The effect of increasing the thermodynamic driving force for PET by replacing methyl on sulfur with *p*-cyanobenzyl is dramatic. The *p*-cyanobenzyl radical is clearly more stable than the methyl radical and the electrochemical reductive cleavage process for the methyl-*p*-cyanobenzyl sulfonium moiety occurs at considerably less negative potential than is observed for the dimethyl sulfonium group (see Table 2).

The τ_{S_1} value for **5** is 0·80 ns, which is shortened considerably from 12·9 ns for **2**. In **6**, τ_{S_1} is comparable to that observed for **3**, whereas τ_{S_1} for **7** is actually longer than the S_1 lifetime for **4**. The fluorescence quantum yield for **5**, **6** and **7**, which ranges between 4 and 5%, is considerably lower than the values for **2**–**4**. Correspondingly, the quantum yield for acid formation for **5**, **6** and **7** is significantly larger than for **2**, **3** and **4** owing to an increase in driving force and rate for PET (see Table 1). The free energy change for PET ranges between *ca* −9·6 and *ca* −11·4 kcal mol^{-1} (1 kcal = 4·184 kJ) for compounds **5**, **6** and **7** depending on the position of substitution. The average rate of PET for **5**, **6** and **7** is *ca* 4×10^7 s^{-1}, comparable to the rate of fluorescence.

Photoexcitation of the naphthacene π electrons to a π^* state is the lowest energy electronic transition. The photoexcited π^* electron must reach the lower energy sulfonium σ^* level (LUMO) for bond cleavage and chemistry to occur. The electron transfer process from a π^* to a σ^* state can take place either through-bond[5,6] or through-space, as previously mentioned. Once the photoexcited electron has reached the σ^* molecular orbital, bond cleavage occurs, we believe, with a rate of *ca* 10^{11}–10^{12} s^{-1}, i.e. similar to the rate of a single molecular vibration. Electrochemical evidence indicates that one-electron reductive cleavage of sulfonium salts appears to be a concerted process in which electron acceptance is concomitant with bond cleavage.[8] However, we realize that photoinduced electron transfer bond cleavage is uniquely different from the electrochemical experiment in that the absence of an electron in the HOMO offers the opportunity for facile back electron transfer. Visualization of the coefficients of the wavefunction, from AM1 molecular orbital calculations, for the π highest occupied molecular orbital (HOMO), π^* photo excited state, and the σ^* LUMO for **5** show the π and π^* orbitals to be localized on the naphthacene ring, as expected, while the σ^* molecular orbital is localized predominantly on the sulfur benzylic carbon bond[10] (AM1 molecular orbital calculations were performed on a Tektronic Model CA55R stereo high-performance CAChe system).

Although, the PET process within compounds **5**–**7** is not precisely isoenergetic, in a thermodynamic sense, one can attempt to measure the effect of distance on the rate of PET, albeit with three points. First, it is assumed that every PET produces bond cleavage and subsequently a proton. The rate of PET, i.e. k_{ET}, is determined from the quantum yields for acid formation and the fluorescent lifetime, by the relationship $k_{ET} = \phi_{H^+}/\tau_{S_1}$. The assumption that every PET produces bond cleavage is reasonable in view of the fact that the electrochemical reductive cleavage process appears to be concerted electron acceptance and bond cleavage, especially in those cases where stabilized radicals are produced.[8] A plot of ln k_{ET} vs through-bond distance in ångströms for **5**, **6** and **7** is shown in Figure 1. The distance between D and A was taken as the sum of the bond lengths (taken from Refs 11 and 12) between the naphthacene ring and sulfur.

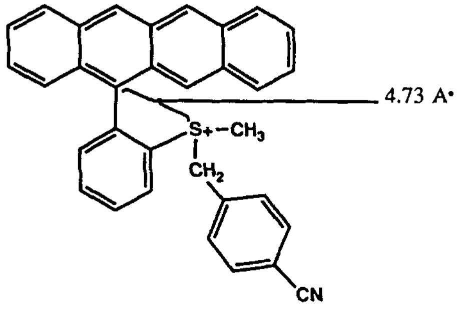
The phenyl linking group between the naphthacene ring system and the sulfur moiety will influence electron transfer between the D and A functionalities by mixing its electronic states with that of D and A.

Empirically, the distance dependence of the electron transfer rate constant is given by

$$\ln k_{ET} = \alpha(r - r_0) + \ln k_0 \qquad (1)$$

where k_0 is the highest rate constant for electron transfer at contact between D and A, r is the D–A distance, r_0 is the distance at van der Waals contact, at which the largest rate occurs, and α is a constant.[13]

The correlation coefficient for the plot of through-bond distance vs ln k_{ET} shown in Figure 1 is 0·97 with



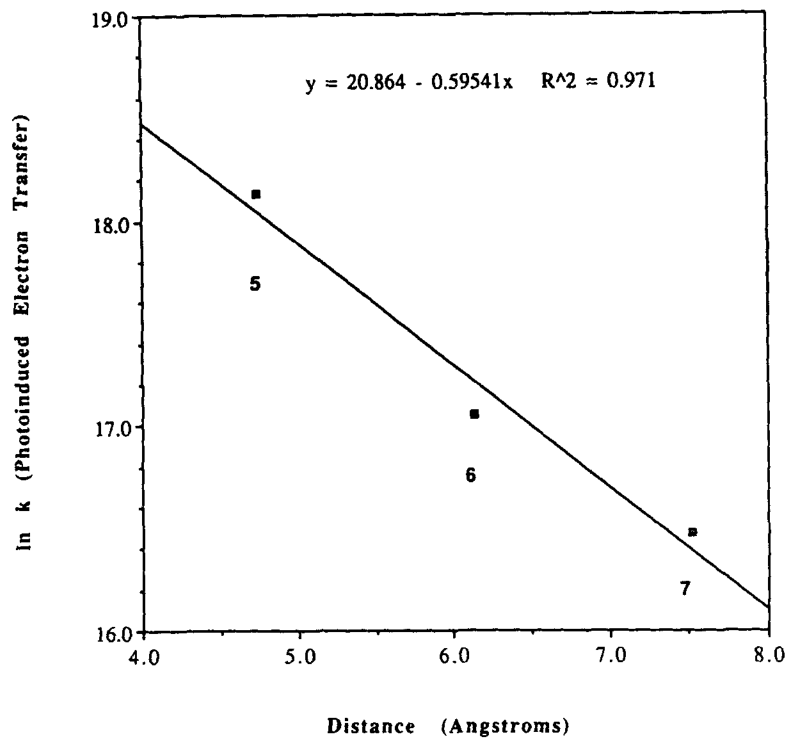
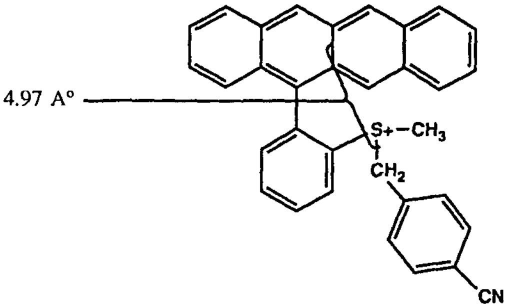


Figure 1. Effect of through-bond distance on electron transfer rate for 5, 6 and 7

a slope of $\alpha = -0{\cdot}60$. The constant α has been shown generally to vary between 1 and 2 Å^{-1}, although lower values have been reported.[13] A plot of ln k_{ET} vs through-space distance taken from the center of the naphthacene ring to the center of the S—CH_2 bond being cleaved in AM1 calculated structures provides a plot with a correlation coefficient of 0·85 and $\alpha = -0{\cdot}91$.

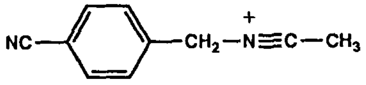
Although, the through-bond distance plot provides a better correlation, it is not possible to eliminate the contribution from through-space PET, especially in 5, and to account for the changes in dihedral angle between the phenyl bridging group and the naphthacene ring system which will effect electronic coupling.



Photoproduct studies

The distribution of photoproducts from the photolysis of 5–7 is essentially independent of distance. The ratio of monosubstituted naphthacene (B) to unsubstituted naphthacene (A) is *ca* 2 for the three regioisomeric sulfonium salts 5, 6 and 7. In addition to a monosubstituted photoproduct (B), di- (C) and trisubstituted (D) photoproducts were also observed. The existence of the out-of-cage di- and trisubstituted products suggests either the presence of *p*-cyanobenzyl carbocation and indiscriminate electrophilic reaction with the naphthacene or the thiomethylphenyl ring systems or the involvement of secondary photochemistry. The benzylic carbocation intermediate produced by one-electron oxidation of the benzyl radical could possibly react with acetonitrile solvent to produce a stabilized electrophilic species. In the absence of nucleophiles such as water, the formation of the acetonitrile adduct is reversible.[14]

The primary photoproduct, we believe, is the monosubstituted naphthacene derivative B which is formed in the highest yield. In 10^{-2} and 10^{-3} M solutions of 5–7, irradiation of B can provide A and C by an intermolecular electron transfer reaction. Irradiation of C in the presence of 5–7 can provide D and A in a similar manner. In an attempt to differentiate between the two mechanisms, a trap for the benzyl carbocation was



added to the acetonitrile solutions which were then irradiated at wavelengths greater than 400 nm. Phenol (10^{-2} M) was added to an acetonitrile solution containing **7** (10^{-3} M) to trap the benzyl carbocation in an intermolecular reaction. No phenol–benzyl carbocation adducts were observed. We conclude that that the experimental observations are consistent with compounds A, C and D being formed by secondary photo chemistry.

In summary, the rate of intramolecular photoinduced electron transfer between a naphthacene electron donor and a sulfonium electron acceptor was found to be dependent on the free energy change for electron transfer, the stability of the radical and the distance between D and A. The slope of ln k_{ET} vs through-bond and through-space distance plots are $-0{\cdot}60$ and $-0{\cdot}91$ Å^{-1}, respectively.

The primary photoproduct obtained from the photolysis of the regioisomeric **5**, **6** and **7** was found to be the monosubstituted naphthacene derivative B and that photoproducts A, C and D arise from secondary photochemistry.

EXPERIMENTAL

Equipment and quantum yield determinations. Absorption spectrometry, fluorescence excitation and emission spectrometry, photochemistry[15] and mass spectrometry were performed using equipment described previously.[4] The quantum yields for acid formation were determined by the following general procedure. A 0·1 M acetonitrile solution of the sulfonium salt (4·0 ml) was irradiated for 10 min through an Ealing 488·0 nm interference filter and the entire sample was poured into 10 ml of deionized argon-purged water. The pH of this solution was measured using a Corning Model 125 pH meter equipped with a Corning combination electrode containing saturated KCl solution. Control experiments on solutions kept in the dark indicated that acid was not formed in the dark during the experimental procedure. The degree of conversion was *ca* 1%. From the solution pH the number of molecules of acid formed was obtained and compared with the number of photons absorbed to provide the quantum yield for acid formation.

Singlet lifetimes were determined by the time-correlated single-photon counting technique using a PRA System 3000 (Photochemistry Research Associates, London, Ontario, Canada). Electrochemical measurements were made with a BAS 100a Electrochemical Analyzer with a Faraday cage and PA1 preamplifier (Bioanalytical Systems, West Lafayette, IN, USA). Conventional (area *ca* 0·01–0·03 cm^2) and ultramicroelectrodes (UMEs)[16] were used for all fast cyclic and Osteryoung square-wave voltammetric[17] investigations (BAS). All short-time-scale voltammetry was performed with platinum and carbon 10 and 2 μm UMEs. Typical scan rates range from 5 mV s^{-1} to 500 V s^{-1}. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was purchased from Southwestern Analytical Chemicals (Austin, TX, USA) and recrystallized three times from hot ethyl acetate. Diethyl ether was added (10%, v/v) after salt dissolution to improve recovery. The isolated salt was dried under vacuum at 120 °C for 72 h (m.p. 247–249 °C) Before each experiment a sufficient amount of supporting electrolyte was added to the cell to yield a concentration of 0·15 M Voltammetric experiments were carried out in a single-compartment cell. All potentials are reported versus a saturated calomel electrode (SCE), which was separated from the test solution via an isolation compartment containing solvent and supporting electrolyte. In addition, potentials were referenced to the ferrocene [$Fecp_2/Fecp_2^+$] couple. The compound to be studied was weighed and placed in the cell. Using a volumetric pipet, 10 ml of acetonitrile were transferred into the cell. Acetonitrile (high-purity, Burdick & Jackson, Muskegon, MI, USA) was percolated through a glass column packed with Woelm B-super 1 alumina (Woelm Pharma) before use. All solutions were deaerated before use with ultrapure nitrogen (Air Products, Allentown, PA, USA).

The working electrodes were successively polished with 6, 3, 1 and 0·25 μm diamond paste (Buehler, Lake Bluff, IL, USA). All cyclic voltammetric waves were corrected for the solvent background and charging current and for later waves the currents were measured from the estimated decaying faradaic current of the preceding wave following usual practice.[18]

Materials. 5(12*H*)-Naphthacenone and 5-phenylnaphthacene were synthesized as described previously.[4,8]

*5-(2-Thiomethylphenyl)*naphthacene. 2-Bromothioanisole (Aldrich) (5·0 g, 24·6 mmol) was refluxed in anhydrous tetrahydrofuran (THF) with magnesium (0·60 g, 24·6 mmol) for 4 h to produce the corresponding Grignard compound. 5-Naphthacenone (6·0 g, 24·6 mmol) was added to the Grignard compound as a solid at −76 °C. The reaction mixture was stirred at −76 °C for 45 min and heated at reflux for 1 h. Concentrated HCl (10 ml) was then added to the reaction mixture and heated at reflux for 15 min. The reaction mixture was cooled to room temperature and flash evaporated to remove the THF. Water (200 ml) was added to the reaction mixture and the mixture extracted with three 100 ml portions of methylene chloride. The combined methylene chloride extracts

Table 3. Physical characterization of the sulfonium salt derivatives (m.p., ^{1}H NMR, *m/z*)

Compound	Yield (%)	M.P. (°C)	^{1}H NMR (CD_3CN) (δ, ppm)	*m/z*[a]
2	61	103d	3.30 (s, 6 H) 7.30–8.90 (m, 15 H)	365
3	83	172d	3.30 (s, 6 H) 7.30–8.90 (m, 15 H)	365
4	85	250d	3.30 (s, 6 H) 7.30–8.90 (m, 15 H)	365
5	58	120d	3.00 (d, 3H) 4.60 (q. 2 H) 6.50–9.00 (m, 19 H)	466
6	74	113d	3.30 (d, 3 H) 4.94 (q, 2 H) 7.08–8.90 (m, 19 H)	466
7	61	142d	3.38 (s, 3 H) 5.02 (q, 2H) 7.05–8.90 (m, 19 H)	466

[a] By field desorption mass spectrometry.

were dried over $MgSO_4$, filtered and flash evaporated. The crude product was purified by dissolving in hot CCl_4 and passing the solution through a pad of silica gel. An alternative purification procedure is to dissolve the reaction mixture in a minimum amount of dry diethyl ether and cool the mixture in an ice-bath to crystallize the crude product. Recrystallization from CH_3NO_2 provided 3·34 g (40% yield) of purified product, m.p. 196–198 °C; ^{1}H NMR ($CDCl_3$), δ *ca* 7·2–8·8 (m, 15 H), *ca* 2·22 (s, 3H); MS, *m/z* 350.

5-(3-Thiomethylphenyl)naphthacene. This compound was synthesized by a procedure identical with that for 5-(2-thiomethylphenyl)naphthacene in 81% yield, m.p. 156–158 °C; ^{1}H NMR ($CDCl_3$), δ *ca* 7·2–8·8 (m, 15 H), *ca* 2·26 (s, 3 H); MS, *m/z* 350.

5-(4-Thiomethylphenyl)naphthacene. This compound was synthesized by a procedure identical with that for the 5-(2-thiomethylphenyl)naphthacene derivative in 48% yield, m.p. 178–179 °C; ^{1}H NMR ($CDCl_3$), δ *ca* 7·2–8·8 (m, 15 H), *ca* 2·62 (s, 3 H); MS *m/z* 350.

All the sulfonium trifluoromethanesulfonate salts were synthesized following the procedure described below.

Equal molar amounts of the napththacene sulfide, methyl iodide or substituted benzyl bromide were dissolved in benzene in a single-necked round-bottomed flask wrapped in aluminium foil. Silver trifluoromethanesulfonate (triflate) complexed with two equivalents of dioxane was then added as a solid in the dark. The reaction mixture was stirred for 15 h and flash evaporated. Acetonitrile previously dried over CaH_2 (50 ml) was added to the reaction mixture and filtered to remove the AgBr. The volume of acetonitrile was reduced and the solution added dropwise to ten times the volume of anhydrous diethyl ether in the dark. The purified product, which precipitated from the ether solution, was collected by suction filtration and dried over P_2O_5 in a vacuum oven at room temperature. The product was purified by three repeated precipitations from diethyl ether. Table 3 gives product yields, melting points and mass spectrometric and ^{1}H NMR characterization for the sulfonium salts described.

Photolysis of 5 and characterization of photoproducts. Compound **5** (62 mg) was dissolved in 50 ml of dry acetonitrile previously distilled from CaH_2 and placed in a Pyrex glass vessel. The solution was irradiated with an Oriel 200 W Hg–Xe lamp using a Corning 0-52 cut-off filter, i.e., $h\nu > 340$ nm for 1 h after being purged with argon for 1 h. The solution was continuously purged with argon while being irradiated.

The acetonitrile solution was diluted with 400 ml of dry methylene chloride and poured through a pad (5 g) of silica gel. The ionic starting material adsorbed on the silica gel and the non-ionic photoproducts were eluted with methylene chloride (200 ml). The photoproducts were characterized by ^{1}H NMR and mass spectrometry. The ratio of unsubstituted thiomethylphenylnaphthacene (*m/z* 350) to the mono- (*m/z* 465), bis- (*m/z* 580) and tri- (*m/z* 695) *p*-cyanobenzyl-substituted thiomethylphenylnaphthacene was determined by field desorption mass spectrometry and represents an average of three photochemical experiments for each regioisomer. The distribution of photoproducts for **5**, i.e. A : B : C : D, was found to be 1·0 : 1·88 : 0·67 : 0·13. Washing the silica gel with acetonitrile (100 ml) eluted the polar compounds, which proved to be only the starting sulfonium salt.

Photolysis of 6 and characterization of photoproducts. Compound **6** (62 mg) was dissolved in 50 ml of dry acetonitrile and photolysed as described previously. The distribution of photo products for **6**, i.e. A:B:C:D, was found to be 1·0:2·22:1·05:0·38. Washing the silica gel with acetonitrile (100 ml) eluted the polar compounds, which proved to be only the starting sulfonium salt.

Photolysis of 7 and characterization of photoproducts. Compound **7** (62 mg) was dissolved in 50 ml of dry acetonitrile and photolysed as described previously. The distribution of photoproducts for **7**, i.e. A:B:C:D, was found to be 1·0:1·91:1·27:0·43. Washing the silica gel with acetonitrile (100 ml) eluted the polar compounds, which proved to be only the starting sulfonium salt.

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