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Comparative photochemical behavior of some anthracenyl and naphthacenyl sulfonium salt derivatives

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Abstract

A series of anthracenyl and naphthacenyl mono- and bis-sulfonium salts was synthesized and their spectroscopic, redox and photoacid behavior investigated. When the thermodynamics of photoinduced electron transfer (PET) bond cleavage in the sulfonium salt derivatives is weakly exothermic, i.e. $\Delta G^\circ_{\mathrm{ET}} = -1.8$ kcal mol^{-1}, the rate of PET does not compete effectively with the rate of decay of the first excited singlet state by fluorescence emission. When $\Delta G^\circ_{\mathrm{ET}}$ is more exothermic than about 5 kcal mol^{-1}, the fluorescence emission is quenched and PET bond cleavage takes place. The quantum yield of acid formation ($\phi_{\mathrm{H^+}}$) in acetonitrile for the napthacenyl and anthracenyl sulfonium salt derivatives is in the range 0.003–0.28. In the anthracenyl sulfonium salts, the electron-withdrawing requirements of the substituent groups on the sulfonium moiety are greatly relaxed over the naphthacenyl derivatives due to the higher energy π^* level of the anthracene moiety.

Keywords: Redox; Photoacid; Photoinduced electron transfer

1. Introduction

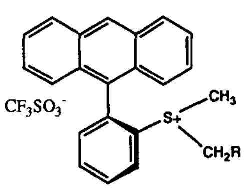
Photochemically induced bond cleavage reactions of onium salts are of considerable scientific and technological importance [1,2]. The technological relevance is related to the photoproduction of a Brönsted acid that can be used in epoxide polymerization [1], photoresists [2], protonic conduction and the control of vesicle formation [3]. Understanding the mechanistic aspects of photoinduced electron transfer (PET) bond cleavage that leads to ion, radical and ion–radical intermediates is of scientific interest and crucial for the design of more efficient photoacid systems [4].

We report the physicochemical behavior of two anthracenyl and two naphthacenyl mono- and bis-sulfonium salt derivatives to provide a better insight into the intramolecular PET bond cleavage processes and the chemical transformations involving high-energy intermediates.

2. Results and discussion

2.1. Mono-sulfonium salts

The following phenyldimethyl (**1a**, **2a**) and phenylmethylperfluorophenylbenzyl (**1b**, **2b**) sulfonium salts containing the anthracene and naphthacene chromophores were synthesized to determine the effect of the alteration of PET and back electron transfer (ET) thermodynamics on photoacid behavior.



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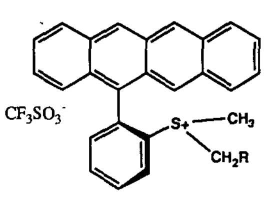
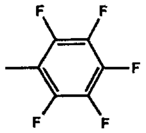


2

R = H

1a, 2a



1b, 2b

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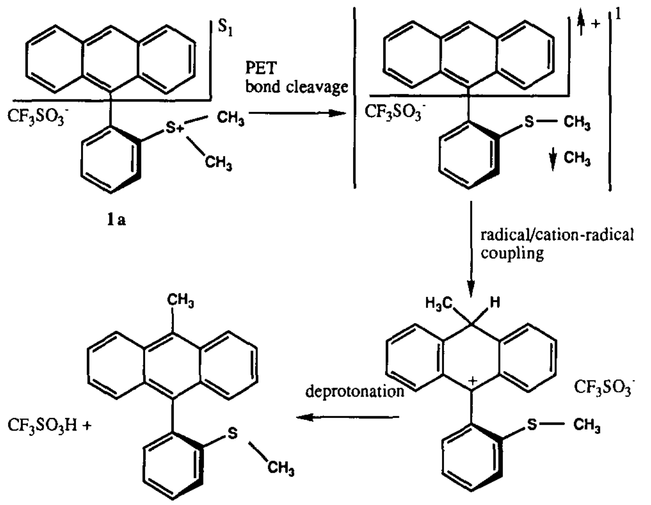
The electronic absorption, fluorescence, photoacid and redox properties were measured in acetonitrile for each of the sulfonium salt derivatives and the results are presented in Table 1. Compound **1a** exhibits quenched fluorescence, and a quantum yield of acid formation of 0.27 (see Table 1). On the other hand, compound **2a** exhibits a fluorescence quantum yield of 0.47 and a quantum yield of photoacid formation of 0.003.

Compound **2b** exhibits a low fluorescence quantum yield and a ϕ_{H^+} value of 0.28, while **1b** exhibits quenched fluorescence and a ϕ_{H^+} value of only 0.05. The phenylanthracene and phenylnaphthacene chromophores exhibit reversible oxidation and reduction potentials, while the electrochemical reduction of the sulfonium group is irreversible due to reductive bond cleavage. Experimental evidence indicates that electrochemical reductive cleavage of the phenyldimethyl sulfonium group is a stepwise process involving a sulfuranyl radical intermediate [5]. There is no direct evidence, however, that the reductive cleavage of phenylmethylperfluorophenylbenzyl sulfonium is concerted or stepwise. The thermodynamics of forward ET from the photoexcited aryl chromophore to the sulfonium moiety is thermodynamically favorable by about −2 to −13 kcal mol^{-1}, while back ET is highly exothermic ranging from −49 to −69 kcal mol^{-1}. Since significant fluorescence quenching was observed in compounds **1a**, **1b** and **2b**, a singlet lifetime could only be measured for **2a**. A value of τ_{S^1} of 12.9 ns was measured for **2a** in acetonitrile.

It is clear that, in **2a**, PET from photoexcited naphthacene to the dimethylsulfonium group does not compete effectively with the rate of fluorescence (3.6×10^7 s^{-1}). In **1a**, **1b** and **2b**, the rate of PET is significantly greater than 10^7 s^{-1} since the fluorescence is almost totally quenched. The actual rate of PET in these systems could not be measured due to the lack of singlet lifetime information. The quantum yields of acid formation for **1a** and **2b** are comparable, i.e. 0.27 and 0.28 respectively. It is clear that the photogeneration of acid depends not only on the PET bond cleavage but also on the efficiency of subsequent chemical transformations that lead to acid formation. Photoacid generation from intramolecular sensitized systems, such as **1** and **2**, appears to take place by the following mechanism [4].



PET from the aryl chromophore in its first excited singlet state through-space or through-bond to the sulfonium moiety can produce bond cleavage if the rate of bond cleavage is faster than the rate of back ET. The rate of the highly exothermic back ET should be slow due to the existence of a Marcus inverted region [6]. PET bond cleavage produces a singlet radical/cation radical pair. The radical pair can then undergo radical coupling to produce a carbocation capable of deprotonating to form a fully aromatic structure. In other words, PET bond cleavage initiates the formation of radical intermediates that couple prior to base-assisted deprotonation.

Compound **1b** exhibits the most exothermic forward ET, yet it only generates acid with a quantum yield of 5%. PET bond cleavage should occur in **1b**; however, the chemistry of the singlet radical/cation radical pair may be responsible for the low value of ϕ_{H^+}.

Table 1

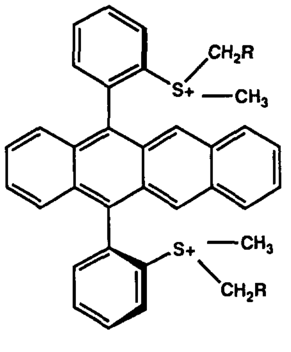
Quantum yield of fluorescence, ϕ_{H^+}, redox behavior and thermodynamics of forward and back electron transfer for compounds **1a**, **1b**, **2a** and **2b**

Compound	ϕ_f	ϕ_{H^+}	λ_{max} (nm)	$E^{o\prime}_{ox}$ (eV)	$E^{o\prime}_{red}$ (eV)	$E_p^{red\,a}$ (eV)	ΔG^o_{ET} (kcal mol^{-1}) Forward	Back
1a	<0.01	0.27	388	1.45	−1.95	−1.54	−4.7	−69
1b	<0.01	0.05	388	1.49	−1.96	−1.15	−12.9	−61
2a	0.47	0.003	486	1.03	−1.67	−1.44	−1.8	−57
2b	0.016	0.28	486	1.08	−1.58	−1.06	−9.7	−49

[a] 100 mV s^{-1} scan rate.

2.2. Bis-sulfonium salts

The first requirement for a mono- or bis-sulfonium salt photoacid is that the lowest unoccupied molecular orbital (LUMO) be σ^* and located on an S–C bond [4]. This feature was probed for some naphthacenyl and anthracenyl bis-sulfonium salts by AM1 molecular orbital (MO) calculations [7,8]. Calculations on bis-5,12-diphenylnaphthacene sulfonium salt derivatives with the general structure **3** indicate that R must be more electron withdrawing than a *p*-cyanophenyl group. In addition, the phenyl linking group must be approximately orthogonal to the naphthacene π system in order to decouple electronic effects that tend to lower the energy of the naphthacene π^* state relative to the σ^* level. In other words, the inductive effect of the sulfonium groups on the π system of the naphthacene moiety through the phenyl group is less effective when there is a 90° twist between the two π systems. AM1 MO calculations on several derivatives of **3** show that, when R is 3,5-bis-trifluoromethylphenyl (**3a**) or perfluorophenyl (**3b**), the σ^* level lies below the π^* level for the naphthacene ring by 0.91 and 1.20 eV respectively.



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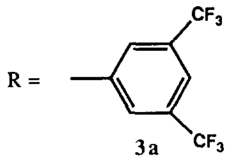
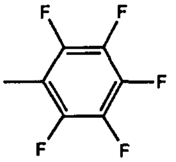
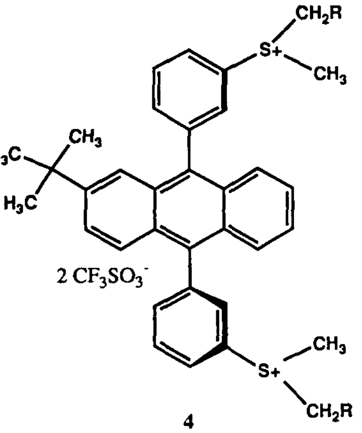




3b

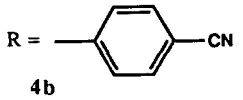
9,10-Diphenylanthracene derivatives (**4**), on the other hand, possess a higher energy π^* state, which allows the use of less electron-withdrawing groups than required with the diphenylnaphthacene chromophore. In this situation R can even be H. The σ^* MO is localized predominantly on both the S–benzyl and S–CH_3 bonds and lies below the anthracene π^* state in energy. The 2-tert-butylanthracene chromophore was chosen because of solubility considerations.



4

R = H

4a



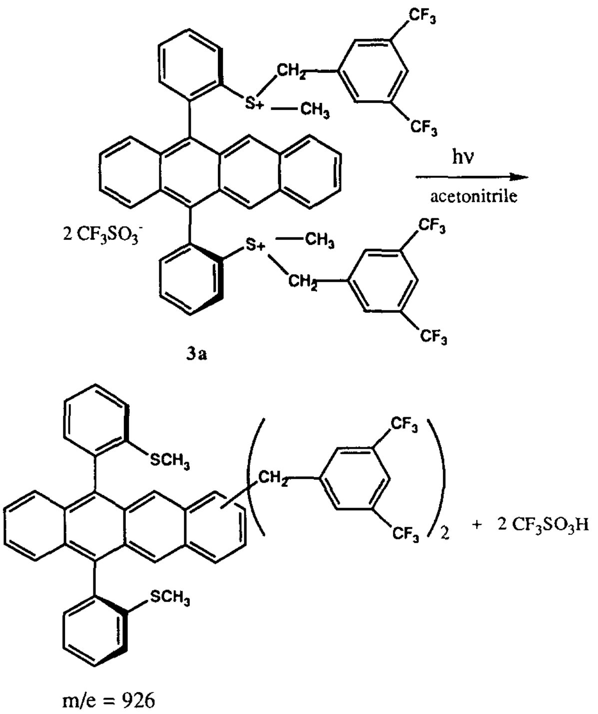
4b

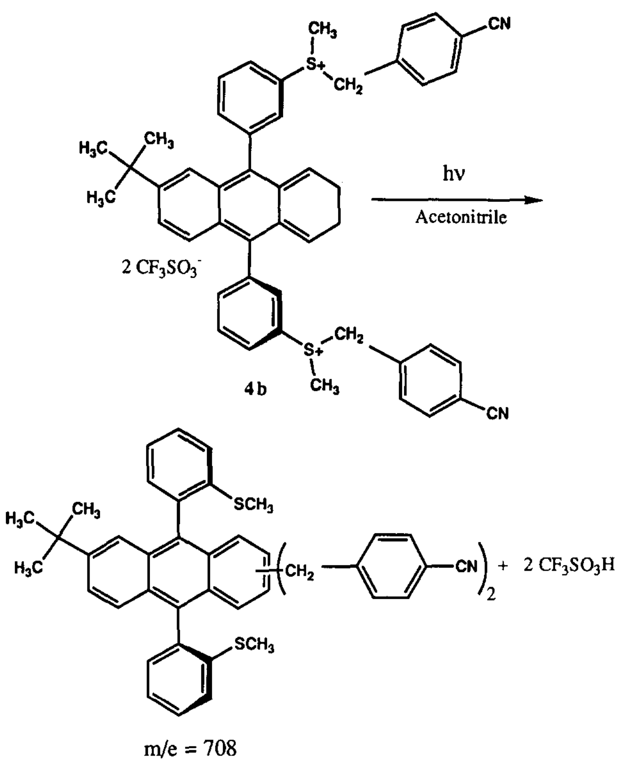
2.3. Photochemistry

The bis-sulfonium salt **3a** possesses an excited state lifetime ot 10 ns and a quantum yield of fluorescence of 0.40 in ethyl acetate. These values can be compared with the photophysical behavior of 5,12-diphenylnaphthacene where $\tau_{S1} = 15.2$ ns, $\phi_{ISC} = 0.17$ and $\phi_f = 0.8$ in benzene [9], which indicates a shortening of τ_{S1} due to PET in the bis-salt. The quantum yield of acid formation ϕ_{H^+} was determined to be 0.18 in acetonitrile solvent using a 488 nm interference filter. The procedure for determining the quantum yields in acetonitrile has been described previously [10]. The quantum yield of acid formation for compound **3b** was found to be 0.17.

Direct photolysis of compounds **3a** and **3b** in dry acetonitrile with a Corning 3-73 cut-off filter (approximately 440 nm) produced the dibenzyl-substituted naphthacenyl sulfide shown below. Photolysis of the naphthacenyl derivatives was carried out at high dilution, i.e. less than 10^{-4} M, to eliminate secondary intermolecular photochemistry.

Photolysis of the anthracenyl sulfonium salt derivatives **4a** and **4b** provided the neutral disubstituted anthracenyl dithiomethyl derivatives. Compounds **4a**





and **4b** exhibited a quantum yield of acid formation in argon-purged acetonitrile of 0.08 using an Ealing 366 nm interference filter.

The bis-sulfonium salts clearly provide two equivalents of acid by a sequential process involving at least two photons.

3. Experimental section

3.1. Equipment

Absorption spectra were run on a Perkin–Elmer model Lambda 9 spectrophotometer equipped with a Perkin–Elmer 7700 professional computer and a Hewlett-Packard ColorPro eight-pen plotter. Proton nuclear magnetic resonance (^{1}H NMR) spectra were run on a GE Nicolet 300 MHz spectrometer. The sulfonium salts were photolyzed with an Oriel 200 W Hg–Xe lamp in combination with either an Ealing 488 nm or 366 nm interference filter for quantum efficiency studies. Actinometry was performed using Aberchrome 540 to determine the flux (photons s^{-1}) of the 200 W Hg–Xe lamp [11]. The quantum yield of photoacid formation was determined potentiometrically as described previously [10]. The general procedure involved taking a 0.1 M acetonitrile solution of the sulfonium salt (4.0 ml) and irradiating the solution for 10 min through an Ealing interference filter. The entire sample was poured into 10 ml of deionized argon-purged water. The pH of the solution was measured using a Corning model 125 pH meter equipped with a Corning combination electrode containing a 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 about 1%. From the pH, the number of molecules of acid formed was obtained and compared with the number of photons absorbed to provide the quantum yield of acid formation.

Mass spectrometry and combustion analyses were performed by the Analytical Technology Division of Eastman Kodak Company. Fluorescence excitation and emission spectra were measured using a Perkin–Elmer model LS-5 spectrofluorometer equipped with a Perkin–Elmer model 7500 laboratory computer and a Hewlett-Packard two-pen plotter. Singlet lifetimes were determined by the time-correlated, single-photon-counting technique using the PRA System 3000 (Photochemistry Research Associates, London, Ont.). Electrochemical measurements were made with a BAS 100a electrochemical analyzer with a Faraday cage and PA1 preamplifier (Bioanalytical Systems, Inc., West Lafayette, IN).

3.2. Materials

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

3.2.1. 9-[2-Thiomethylphenyl]anthracene

2-Bromothioanisole (Aldrich) (5.0 g, 24.6 mmol) was refluxed in anhydrous tetrahydrofuran (THF) together with Mg^0 (0.60 g, 24.6 mmol) for 4 h to produce the corresponding Grignard. Anthrone (6.0 g, 30.9 mmol) was added to the Grignard 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 was extracted with three 100 ml portions of methylene chloride. The combined methylene chloride extracts 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 3.72 g (40% yield) of purified product (melting point (m.p.), 196–198 °C). ^{1}H NMR ($CDCl_3$): δ 7.2–8.5 (m, 13 H), δ 2.62 (s, 3 H); $m/e = 300$. Analysis: calculated for $C_{21}H_{16}S$ (300.4): C, 83.96; H, 5.37; S, 10.67; found: C, 83.90; H, 5.35; S, 10.62.

3.2.2. 5-[2-Thiomethylphenyl]naphthacene

2-Bromothioanisole (Aldrich) (5.0 g, 24.6 mmol) was refluxed in anhydrous THF together with Mg^0 (0.60 g, 24.6 mmol) for 4 h to produce the corresponding Grignard. 5-Naphthacenone (6.0 g, 26.8 mmol) was added to the Grignard 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 was extracted with three 100 ml portions of methylene chloride. The combined methylene chloride extracts 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 3.56 g (38% yield) of purified product (m.p., 156–158 °C). ^1H NMR ($CDCl_3$): δ 7.2–8.8 (m, 15 H), δ 2.26 (s, 3 H); *m/e* = 350. Analysis: calculated for $C_{25}H_{18}S$ (350.48): C, 85.68; H, 5.18; S, 9.15; found: C, 85.63; H, 5.15; S, 9.09.

3.2.3. 5,12-Bis-[2-thiomethylphenyl]naphthacene

2-Bromothioanisole (Aldrich) (5.0 g, 24.6 mmol) was refluxed in anhydrous THF (100 ml) together with Mg^0 (0.60 g, 24.6 mmol) for 4 h to produce the corresponding Grignard. 5,12-Naphthacenequinone (3.2 g, 12.3 mmol) was added to the Grignard as a solid at −76 °C. The reaction mixture was stirred for 45 min at low temperature and heated at reflux for 1 h; 10 ml of 10% aqueous HCl was then added to the reaction mixture and stirred at room temperature for 15 min. The reaction mixture was flash evaporated to remove the THF. Water (200 ml) was added to the reaction mixture and the mixture was extracted with three 100 ml portions of methylene chloride. The combined methylene chloride extracts were dried over $MgSO_4$, filtered and flash evaporated.

The crude diol product was dissolved in acetic acid together with potassium iodide (2.0 g, 24.6 mmol) and sodium hypophosphite (4.3 g, 49.2 mmol) and heated at reflux for 4 h. The reaction mixture was diluted with 200 ml of water and the crude product was collected by suction filtration. The product was purified by Soxhlet extraction with benzene to provide 5.0 of the bis-thiomethyl derivative (33% yield). Field desorption mass spectrometry (FDMS) *m/e* = 472. ^1H NMR (benzene-d_6): δ 1.63 (s, 6 H), δ 6.80–8.50 (m, 18 H); m.p. > 250 °C.

Table 2
Physical characterization of the sulfonium salt derivatives (m.p., ^1H NMR, *m/e*)

Compound	Yield (%)	m.p. (°C)	^1H NMR (CD_3CN)	(FDMS) *m/e*
1a	61	198–200	δ 2.82 (s, 6 H), δ 7.30–8.80 (m, 13 H)	315
1b	83	167d	δ 3.08 (s, 3 H), δ 4.69 (q, 2 H), δ 6.85–8.80 (m, 13 H)	481
2a	85	103d	δ 3.30 (s, 6 H), δ 7.30–8.90 (m, 15 H)	365
2b	58	137d	δ 3.12 (d, 3 H), δ 4.90 (q, 2 H), δ 6.70–9.00 (m, 15 H)	531
3a	94	118d	δ 3.00–3.20 (m, 6 H), δ 4.62–4.90 (m, 4 H), δ 6.40–8.70 (m, 24 H)	926
3b	95	160–162	δ 3.20 (m, 24 H), δ 4.70 (q, 2 H), δ 7.20–8.20 (m, 18 H)	810
4a	95	150d	δ 1.22 (s, 9 H), δ 3.20 (s, 9 H), δ 7.20–8.30 (m, 15 H)	508
4b	67	97d	δ 0.80–1.00 (m, 6 H), δ 1.20 (s, 9 H), δ 1.40–1.60 (m, 4 H), δ 1.60–1.82 (m, 4 H), δ 3.62–4.98 (m, 4 H), δ 5.00–6.32 (m, 4 H), δ 7.00–8.20 (m, 23 H)	686

3.2.4. Bis-9,10-[3-thiomethylphenyl]-2-tert-butylanthracene

3-Bromothiomethylbenzene (60 g, 0.245 mol) was dissolved in 300 ml of anhydrous THF together with Mg^0 (0.25 mol) and heated at reflux for 2 h to provide the corresponding Grignard reagent. 2-tert-Butylanthraquinone (32.3 g, 0.122 mol) was added to the reaction mixture as a solid at room temperature. The reaction mixture was heated at reflux for 1 h and stirred at room temperature for 15 h. The reaction mixture was treated with 20 ml of 10% HCl and stirred for 10 min before flash evaporating off the THF. The mixture was extracted with anhydrous ether (3×100 ml) and the combined ether extract was dried over $MgSO_4$, filtered and flash evaporated in a 1 l round-bottomed flask. To the crude diol was added potassium iodide (26 g), sodium hypophosphite (33 g) and 200 ml of acetic acid. The reaction mixture was heated at reflux for 2 h and poured onto 300 g of ice. Diethyl ether (200 ml) was added to the water–product mixture. The mixture was extracted with diethyl ether (2×100 ml). The ether layer was dried over $MgSO_4$, filtered and flash evaporated to provide a 90% yield of the desired product as a pale yellow oil. The crude product can be purified by dissolving in carbon tetrachloride and filtering through a pad of silica gel. ^1H NMR ($CDCl_3$): δ 0.80–1.10 (m, 6 H), δ 1.30 (s, 9 H), δ 1.40–1.60 (m, 4 H), δ 2.90–3.10 (t, 4 H), δ 7.20–7.80 (m, 15 H).

3.3. Sulfonium salt synthesis

All the sulfonium trifluoromethanesulfonate salts were synthesized as described below. Equal molar quantities of the arylmethyl sulfide, methyl iodide and substituted benzyl bromide were dissolved in benzene in a single-neck round-bottomed flask wrapped with aluminum foil. Silver trifluoromethanesulfonate (triflate) complexed with two equivalents of dioxan 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 or AgI. The volume of acetonitrile was reduced and the solution was 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 ether. Table 2 provides the product yield, melting point, mass spectrometric and ^1H NMR characterization for the sulfonium salts described.

4. Conclusions

Eight anthracenyl and naphthacenyl mono- and bis-sulfonium salt derivatives possessing a σ^* LUMO were synthesized and their spectroscopic, redox and photoacid properties were compared to provide further insight into the mechanism of photoinduced bond cleavage chemistry. Fluorescence emission is quenched and PET bond cleavage takes place only when ΔG°_{ET} is more exothermic than about -5 kcal mol^{-1}. Although PET bond cleavage is observed in **1b**, ϕ_{H^+} is low, presumably due to competition from an intramolecular cyclization pathway. Some aryl bis-sulfonium salt Brönsted photoacids were designed and synthesized that can be sequentially activated photochemically to produce two molar equivalents of acid. AM1 MO calculations assisted in the molecular design process by indicating the functionality required to provide a σ^* LUMO localized on the sulfonium moiety rather than a π^* LUMO localized on the aryl ring system. In the anthracenyl bis-sulfonium salts, the electron-withdrawing requirements of the substituent groups on the sulfonium moiety are greatly relaxed over the naphthacenyl derivatives due to the higher energy π^* level of the anthracene moiety.

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