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The Effect of the Nature of the Lowest Unoccupied Molecular Orbital (LUMO) of Some Arylmethylsulfonium Salt Derivatives on Photochemical and Redox Behavior

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Abstract: The results of AM1 molecular orbital calculations on two series of arylmethylsulfonium salt derivatives have indicated that the nature of the lowest unoccupied molecular orbital (LUMO) switches from σ^* when aryl = phenyl, 1-naphthyl, and 9-anthryl to π^* when aryl = 5-naphthacenyl. Electrochemical, photochemical, fluorescence quantum yield, and singlet-lifetime data were found to support the conclusions from the calculations.

It is well known that electron-withdrawing groups such as cyano and nitro attached directly to an aromatic ring lower the energy of the π^* lowest unoccupied molecular orbital (LUMO) and concomitantly increase the energy of the highest occupied molecular orbital (HOMO). The electron-withdrawing 8-S-3[1] sulfonium group is rather unique in this respect, in that both aryl and alkyl groups can be attached directly to sulfur in its +4 oxidation state. Much of the physicochemical behavior, i.e., photochemical and redox, of sulfonium salts is due to the presence of a σ^* LUMO level located on a sulfur-carbon (S–C) bond, which is at lower energy than the perturbed aryl π^* molecular orbitals when the aryl ring is phenyl and naphthyl.[2] This conclusion was based solely on the electrochemical behavior of these systems.

We now describe the results of AM1 calculations[3] which indicate that one must go to naphthacene before there is a crossover between the π^* lowest energy molecular orbital of the aryl ring and the σ^* LUMO level of the S–C bond when the alkyl substituents are methyl and *p*-cyanobenzyl or both methyl. The σ^*/π^* crossover is intuitively unexpected and serves to demonstrate the usefulness of the AM1 calculations.

Experimental Section

Equipment. A Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer were used in the standard three-electrode configuration to obtain reduction potentials by cyclic voltammetry. A platinum-inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a standard calomel electrode (SCE). The electrolyte was 0.1 N tetrabutylammonium fluoroborate (TBAF) previously recrystallized from an ethyl acetate/pentane solvent mixture in dry methylene chloride. The electrochemical peak potentials (E_p) were measured in volts vs SCE at a 100 mV/s scan rate.

Absorption spectra were run on a Perkin-Elmer Model 330 spectrophotometer equipped with a Model 3600 data station and a Model 660 printer. ^{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 an Ealing 3130-Å interference filter for quantum-efficiency studies. Actinometry was performed with Aberchrome 540 to determine the flux (photons/s) of the 200-W Hg–Xe lamp.[4] Combustion analyses and mass spectrometry were performed by the Analytical Sciences Division of the Kodak Research Laboratories. Fluorescence excitation and emission spectra were measured with a Perkin-Elmer Model LS-5 spectrofluorimeter equipped with a Perkin-Elmer Model 7500 Laboratory Computer. Singlet lifetimes were determined by the time-correlated single-photon counting technique using the PRA System 3000 (Photochemistry Research Associates, London, Ontario).

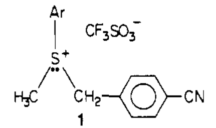
Materials. Compounds **1a**, **1b**, **2a**, and **2b** were synthesized as previously described.[2] Compounds **1c**, **2c**, **1d**, and **2d** were synthesized from the corresponding aryl methyl sulfides as described below.

The sulfonium salt derivatives were synthesized by adding silver trifluoromethanesulfonate to a methylene chloride solution of a aryl methyl sulfide and either methyl iodide or *p*-cyanobenzyl bromide. All the reagents were added in equimolar quantities. The reaction mixture was then stirred at room temperature for 3 h. The insoluble silver salts were then filtered off, and the volume of methylene chloride was reduced prior to dropping the reaction mixture into diethyl ether. The crude product was filtered and air dried prior to recrystallization from an acetonitrile/diethyl ether solvent mixture. Compounds **1c**, **2c**, **1d**, and **2d** provided a ^{1}H NMR spectrum, mass spectrum, and combustion analysis that were consistent with their structure. The melting point and percent yield are listed below for compounds **1c**, **1d**, **2c**, and **2d**:

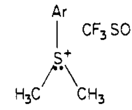
compd	**1c**	**1d**	**2c**	**2d**
mp, °C dec	139–40	98–100	175–6	141–2
% yield	61	35	70	44

Results and Discussion

Electrochemical, photochemical, fluorescence quantum yield, and singlet-lifetime data support the conclusions from the AM1 calculations for the following two series of arylsulfonium salts.



1



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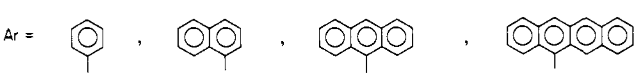
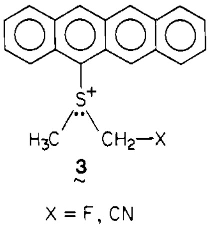


a, b, c, d

The results of AM1 calculations for series **1** are presented in Figure 1. As the aryl ring increases in size from phenyl to naphthacenyl, the π HOMO level increases in energy by ~2.2 eV, while the σ^* LUMO level shows a more modest energy increase of ~0.5 eV. The lowest energy π^* level, on the other hand, decreases in energy by almost 1 eV. When the aryl ring is naphthacenyl, a crossover from a σ^* LUMO to a π^* LUMO takes place. It is expected that the crossover should be signaled by an abrupt change in physicochemical behavior. The crossover between the σ^* and π^* states can be further modified by substituting an electron-withdrawing group such as fluoro or cyano for a hydrogen on a methyl group as in structure **3**.



3

X = F, CN

σ^* LUMO from AM1 calculations

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Scheme I

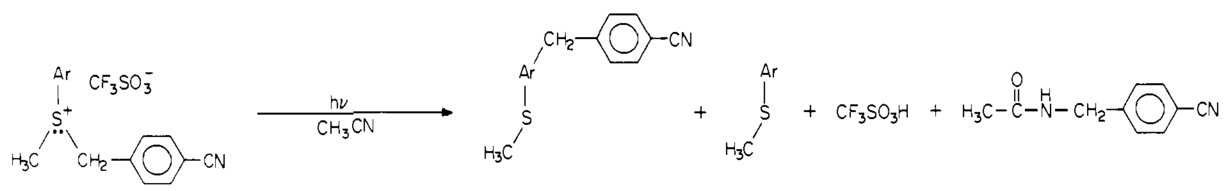
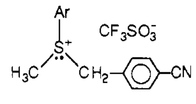
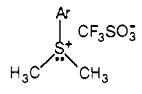
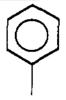
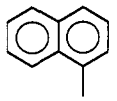
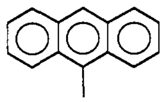
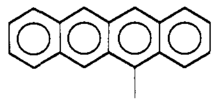


Table I. Fluorescence Quantum Yield (ϕ_f), Excited Singlet State Lifetimes (τ_s), and Electrochemical Peak Potentials (E_p) for Reduction of Substituted Arylmethylsulfonium Trifluoromethanesulfonate Salts


1


2

Ar	Compound	ϕ_f	τ_s, ns	E_p, V
	**1a (2a)**	0.0047 (0.26)	<0.5 (2.4)	-0.78 (-1.51)
	**1b (2b)**	0.0010 (0.48)	<0.5 (7.0)	-0.74 (-1.35)
	**1c (2c)**	0.0015 (0.97)	<0.5 (2.0)	-0.77 (-1.06)
	**1d (2d)**	0.10 (0.25)	6.6 (6.0)	-0.64 (-0.81)

The electrochemical reduction potentials for the sulfonium salts were all irreversible, and the peak potentials (E_p) are provided in the table. For series **1** the E_p values for **1a–c** are fairly constant, and the crossover between states is indicated by a decrease of ~0.1 V to a less cathodic value in the case of **1d**. The aryl ring influences the E_p values in series **2** to a greater extent than in series **1** due to an increased contribution of the aryl-S bond to the σ^* LUMO in series **2** over series **1**.

Compounds **1a–c** undergo photochemistry to produce intramolecular-rearrangement as well as bond-cleavage products as shown in Scheme I.[5] In contrast, compounds **1d** and **2a–d** were found to be photochemically inactive under the experimental conditions where compounds **1a–c** were completely photolyzed. The $\pi \rightarrow \sigma^*$ electronic transition, which is expected to be of low molecular extinction, has been tentatively assigned to a long-wavelength shoulder in the electronic spectrum of **1b** and **1c**. Irradiation within the long-wavelength electronic transition provided the photoproducts previously described. The lack of photochemistry in series **2** compounds (**a–c**), which possess a σ^* LUMO level as indicated by AM1 calculations, is attributed to the strength of the S–CH_3 bond due to the instability of the methyl radical as compared to the *p*-cyanobenzyl radical. Our understanding of the mechanism of photorearrangement is that photochemical excitation produces the sulfonium salt in the singlet excited state, which may then undergo bond cleavage to produce a singlet cation-radical/radical pair if the rate of cleavage can compete with the radiative- and nonradiative-decay modes.[5,6] In fact, the photostability of **1d** and **2a–d** is reflected by the fluorescence quantum yield and excited singlet state lifetimes (see Table I).

The fluorescence quantum yield (ϕ_f) for compounds **1a–c** in CH_2Cl_2 is less than 0.005, while ϕ_f for compound **1d** is a factor of 20–100 higher. The ϕ_f values for **2a–d** range between 0.25 and 0.97. The singlet lifetimes for **1a–c** are considerably shorter than those for **2a–d** and **1d**, reflecting the involvement of a competing rate process, i.e., bond cleavage, that shortens the lifetime of the excited singlet state. The effect of bond cleavage as a competitive process deactivating the excited singlet state is clearly represented by both the fluorescence quantum yield and singlet-lifetime data.

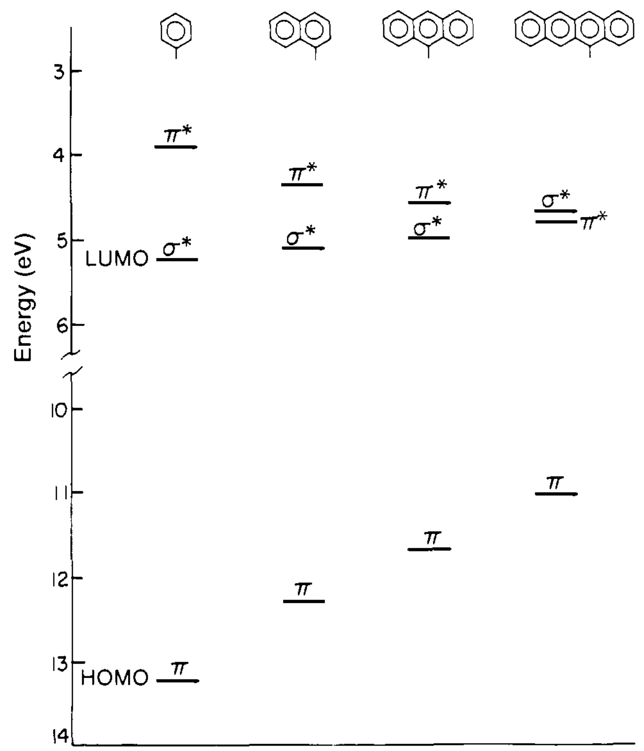


Figure 1. AM1 Molecular Orbital Calculations of the Highest Occupied (HOMO) and Lowest Unoccupied (LUMO) Molecular Orbitals (π^* and σ^*) for $CH_3S^+Ar(CH_2C_6H_4CN)\ CF_3SO_3^-$.

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Conclusions

Electrochemical, photochemical, fluorescence quantum yield, and excited singlet state lifetimes have been found to support the results of AM1 calculations, indicating a crossover between σ^* and π^* LUMO states when the aryl ring is naphthacene in some sulfonium salt derivatives. The preceding conclusions apply in general to other onium salts. Phosphonium salts would be expected to behave in a similar fashion to sulfonium salts, while ammonium and oxonium salts would be expected to show the σ^*/π^* crossover between naphthalene and anthracene.

Characterization of Pd–β-Cyclodextrin Colloids as Catalysts in the Photosensitized Reduction of Bicarbonate to Formate[†,1]

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Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. *Received April 7, 1988*

Abstract: Photosensitized reduction of bicarbonate, HCO_3^-, to formate, HCO_2^-, proceeds in an aqueous system composed of deazariboflavin, dRFl (**1**), as photosensitizer, *N*,*N*′-dimethyl-4,4′-bipyridinium, MV^{2+}, as primary electron acceptor, sodium oxalate as sacrificial electron donor, and in the presence of a Pd colloid stabilized by β-cyclodextrin, Pd–β-CD. The process proceeds with a quantum efficiency, $\phi = 1.1$. Kinetic characterization of the Pd–β-CD catalyst activity reveals the presence of active sites for bicarbonate activation and reduction as well as catalytic sites for H_2 evolution. The HCO_3^- activation sites are specifically inhibited by thiols. The catalytic reduction of HCO_3^- to HCO_2^- and the respective inhibition processes exhibit enzyme-like kinetic properties. The Pd–β-CD colloid shows reversible activities and effects the reduction of MV^{2+} by formate. Kinetic characterization of the catalyzed reduction of HCO_3^- to HCO_2^- and the reverse oxidation of HCO_2^- provides a sequential mechanism for the reactions.

Photoreduction of CO_2, its hydrated form, carbonic acid, or its dissociated ions, bicarbonate and carbonate (eq 1), using visible

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (1)$$

solar light is a challenging subject as a means of mimicking photosynthesis and of solar energy conversion and storage.[2-4] The standard redox potentials[5,6] for the reduction of carbon dioxide (at pH = 7) to C_1-carbon fuel products are given in eq 2–7 and

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^\circ = -0.52 \text{ V} \quad (2)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E^\circ = -0.42 \text{ V} \quad (3)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^\circ = -0.48 \text{ V} \quad (4)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^\circ = -0.38 \text{ V} \quad (5)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^\circ = -0.24 \text{ V} \quad (6)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^\circ = -0.41 \text{ V} \quad (7)$$

compared to that of H_2 evolution. It is evident that reduction of CO_2 in aqueous solutions to several C_1 products is thermodynamically favored over H_2 evolution. Nevertheless, reduction of CO_2 is encountered with severe kinetic difficulties, and extensive efforts are directed toward the activation of CO_2, bicarbonate, and carbonate by transition-metal complexes[7,8] or heterogeneous metal surfaces.[9,10]

Reduction of carbon dioxide could basically be accomplished through various pathways. These include hydrogenation,[11] insertion into transition-metal hydride complexes,[12] carbanion nucleophilic attack,[13] or by electron transfer followed by protonation.[14] The methanation process exemplifies an extensively explored hydrogenation of CO_2 to methane, a process that usually proceeds at elevated temperatures and high pressures.[15] Insertion of CO_2 into various transition-metal hydrides to form the formate ligand was observed.[16] Electrocatalyzed reduction of CO_2 was observed in the presence of various transition-metal complexes, i.e., Ni^{2+}– or Co^{2+}–cyclams,[17] metal porphyrins or phthalocyanins,[18] and iron–sulfur clusters,[19] or by using Ru or Cu metal catalysts as electrodes.[20] Hydrogenation of bicarbonate using

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[†] Dedicated to the memory of Professor David Ginsburg.

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