

## Reference and Notes

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- (24) There is, of course, a difference in basicity of the thiosalicyl and thiophenol leaving groups which can affect the relative rate ratio. The  $\text{p}K_{\text{a}}$  of thiosalicylic acid<sup>25</sup> is 7.79 while that of thiophenol<sup>26</sup> is 6.43. Employing a suitable correction<sup>27</sup> for this difference in basicity an upper limit on the ratio  $k_{\text{H,A}}^{\text{th}}/k_0^{\text{th}}$  becomes  $3 \times 10^4$ . However, the  $\text{p}K_{\text{a}}$  of 7.79 is that of a species with the carboxyl group ionized and may not reflect the leaving group  $\text{p}K_{\text{a}}$ , which will depend upon the extent of proton transfer from the carboxyl group in the transition state. An estimate<sup>27</sup> of the thiosalicyl leaving group  $\text{p}K_{\text{a}}$  (un-ionized carboxyl) would be 5.7 with which the ratio  $k_{\text{H,A}}^{\text{th}}/k_0^{\text{th}}$  becomes 50.
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## On the Electron-Donating Properties of Oxygen vs. Sulfur. Redox Potentials for Some Perylium and Thiapyrylium Salts

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**Abstract:** The redox levels for two series of perylium and thiapyrylium salts were measured by cyclic voltammetry. This information was utilized to provide a quantitative comparison of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) which is a measure of the thermodynamic stabilities to electron transfer of oxygen vs. sulfur adjacent to carbon cation, radical, and anionic centers in a single system. In one of the series [i.e., 4-(4'-diethylaminophenyl)-2,6-diphenyl-pyrylium (thiapyrylium) system] dicationic, cationic, radical, and anionic centers were compared. The ionic and radical species were found to be thermodynamically more stable in the sulfur analogue (less stable in oxygen analogue) in every case except when the HOMO and/or LUMO level is localized on the diethylaminophenyl moiety. The order of the greatest sulfur preference or least oxygen preference is the following: anion > radical and radical > cation for the HOMO and LUMO levels, respectively. The wavelength of the intramolecular charge transfer band and the electrochemical reduction potentials indicate that the thiapyrylium moiety is more electron withdrawing than pyrylium.

### Introduction

There has been considerable interest in the relative electron-donating behavior of oxygen and sulfur and their effect on stabilizing adjacent carbon ions (cation and anion) and radical centers.<sup>1</sup> Caserio et al.<sup>1</sup> have recently provided an excellent assessment of the current view of sulfur vs. oxygen stabilization. The fundamental variations between the electron-donating and -withdrawing ability of oxygen and sulfur relate to differences in their  $\pi$  and  $\sigma$  donor properties.

CNDO/2 calculations<sup>2</sup> have indicated that the higher carbocation stabilization effect of sulfur in comparison to oxygen is related to the greater capability of the  $\sigma$ -bivalent sulfur to take up excess charge into the sp-valence shell. This explanation does not take into consideration sulfur d orbitals. However, stabilization of adjacent carbocations by sulfur relative to oxygen from CNDO/2 calculations,<sup>3</sup> on the other hand, requires the involvement of sulfur d orbitals. There are then a number of factors, including the  $\pi$ -donating ability of oxygen vs. sulfur, that are involved in determining the stabilizing and destabilizing effects of the two atoms. Most experimental studies designed to probe the electronic properties of oxygen

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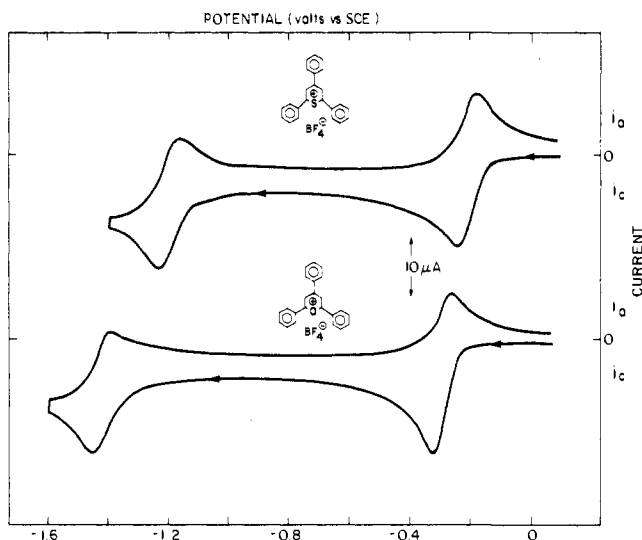


Figure 1. Cyclic voltammogram for 2,4,6-triphenylpyrylium fluoroborate (**1b**) and 2,4,6-triphenylthiapyrylium fluoroborate (**2b**) in  $\text{CH}_3\text{CN}$  vs. SCE.

and sulfur have employed different systems to investigate the stabilities of ions and radical centers.<sup>1-5</sup> In some instances it is difficult to sort out kinetic vs. thermodynamically controlled reactions. One issue that has not been addressed is the quantitative preference of sulfur vs. oxygen stabilized cation, radical, and anion species in a single system. The pyrylium (thiapyrylium) salts are unique in this respect since the cation/dication, cation/radical, and radical/anion thermodynamic redox levels in a rigid six-membered heterocyclic system can all be measured unequivocally. The relative *stability* of the oxygen and sulfur analogues then refers to the thermodynamic stability in terms of electron transfer reactivity, i.e., electron transfer, to the lowest unoccupied and from the highest occupied molecular orbitals.

It has been reported by Maccoll<sup>6</sup> that reversible polarographic half-wave oxidation potentials ( $E_{1/2}^{\text{ox}}$ ) and reduction potentials ( $E_{1/2}^{\text{red}}$ ), can be related to the energy of the highest occupied ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbitals ( $E_{\text{LUMO}}$ ). The redox potentials of a molecule are related to the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  levels as follows:

$$E_{1/2}^{\text{ox}} = E_{\text{HOMO}}(\text{solvent}) + C \quad (1)$$

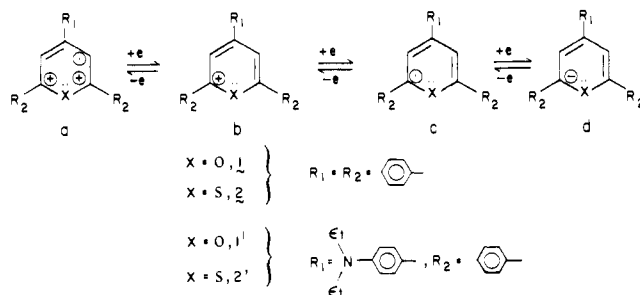
$$E_{\text{HOMO}}(\text{solvent}) = \text{IP} + \Delta E_{\text{sol}}^{\text{R}^-} \quad (2)$$

$$E_{1/2}^{\text{red}} = E_{\text{LUMO}}(\text{solvent}) + C \quad (3)$$

$$E_{\text{LUMO}}(\text{solvent}) = \text{EA} - \Delta E_{\text{sol}}^{\text{R}^+} \quad (4)$$

The term  $C$  is a constant which includes the potential of the reference electrode on an absolute scale.<sup>7</sup> The solvation terms  $\Delta E_{\text{sol}}^{\text{R}^-}$  and  $\Delta E_{\text{sol}}^{\text{R}^+}$  are the differences in real solvation energies between the reduced and oxidized form of the molecule and the molecule in the gas phase. EA and IP are the gas-phase molecular electron affinity and ionization potential, respectively. The  $E_{1/2}^{\text{ox}}$  values for oxygen and sulfur analogues of a specific molecule provide a comparison of the  $E_{\text{HOMO}}$  of the two molecules in the specific solvent employed for the electrochemistry. The potential of the reference electrode, i.e., the  $C$  term, will cancel out when the  $E_{1/2}^{\text{ox}}(\text{S})$  of the sulfur system is subtracted from  $E_{1/2}^{\text{ox}}(\text{O})$  of the oxygen system.

In this manner the relative energy of the HOMO levels for the pyrylium (**1b**) and the thiapyrylium (**2b**) species can be calculated directly from the difference in oxidation potentials between the oxygen and sulfur systems in the solvent employed. The first oxidation potential for **1b**, which is also the reduction potential for **1a**, provides both the  $E_{\text{HOMO}}$  for **1b** as well as



the  $E_{\text{LUMO}}$  for **1a**. This is true only when the redox process is reversible. The first reduction potential of **1b**, on the other hand, provides the relative energy of the LUMO level of **1b**. Also, the first reduction potential for **1b** is equal to the oxidation potential for **1c** and provides the  $E_{\text{HOMO}}$  for **1c**. In a similar manner, the second reduction potential, which is the relative energy of the radical/anion redox levels, provides the  $E_{\text{LUMO}}$  and **1c** and  $E_{\text{HOMO}}$  for **1d** as described above. Using the electrochemical redox potentials to provide the relative energies of the HOMO/LUMO levels, a direct comparison between the thermodynamic stability to electron transfer of oxygen vs. sulfur systems and the effect on cationic, radical, and anionic centers in the pyrylium (thiapyrylium) heterocyclic systems is provided in the following sections.

## Experimental Section

**A. Materials.** 4-(4'-Diethylaminophenyl)-2,6-diphenylpyrylium fluoroborate (**1b**, mp 275–276 °C) and 4-(4'-diethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate (**2b**, mp 229–230 °C) were synthesized as previously described.<sup>8</sup>

2,4,6-Triphenylpyrylium fluoroborate (**1b**, mp 246–248 °C dec) was synthesized by the reaction of 2,4,6-triphenylpyrylium chloride (0.01 mol, mp 218 °C dec), purchased from Eastman Organic Chemicals, and  $\text{AgBF}_4$  (0.01 mol) in 90/10 (v/v) methanol/water solution (400 mL) at room temperature for 1 h. The reaction mixture was then filtered through a fine sintered glass filter funnel to remove silver chloride. The solvent was evaporated until the solution clouded and the reaction mixture was allowed to stand at room temperature. The product (**1b**), which crystallized as yellow needles, was filtered (0.007 mol, 70% yield), air dried, and recrystallized from ethanol. Anal. Calcd for  $\text{C}_{23}\text{H}_{17}\text{OBF}_4$ : C, 69.73; H, 4.32; B, 2.73; F, 19.18. Found: C, 69.43; H, 4.35; B, 2.61; F, 19.37.

2,4,6-Triphenylthiapyrylium fluoroborate (**2b**, mp 195–196 °C) was synthesized from **1b** by the procedure described by Wizinger and Ulrich.<sup>9</sup> **1b** (0.005 mol) was dissolved in 50 mL of acetone in a 100-mL round-bottomed flask. A solution of sodium sulfide (4.8%  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ /15 mL of  $\text{H}_2\text{O}$ , 0.02 mol) was added dropwise and the mixture stirred for 1 h at room temperature. The red mixture was then poured into a fluoroboric acid solution (30 mL of acid and 50 mL of  $\text{H}_2\text{O}$ ) and allowed to stir for 1 h. The resulting yellow precipitate (0.003 mol, 60% yield) was filtered, air dried, and recrystallized from benzene. Anal. Calcd for  $\text{C}_{23}\text{H}_{17}\text{SBF}_4$ : C, 67.01; H, 4.16; S, 7.78; B, 2.62; F, 18.43. Found: C, 67.12; H, 4.10; S, 7.85; B, 2.65; F, 18.49.

**B. Instrumentation.** Electronic spectra were run on a Cary 17D spectrophotometer and cyclic voltammetry was carried out with a PAR Model 170 electrochemistry system (Princeton Applied Research Corp., Princeton, N.J.) at room temperature. A conventional three-electrode cell was used in all experiments. The working electrode was a Beckman platinum inlay electrode. All potentials were measured with respect to an aqueous saturated calomel electrode (SCE) in either  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  (Burdick and Jackson Laboratories, Inc.) using 0.1 M tetrabutylammonium fluoroborate (TBAF) (Southwestern Analytical Chemicals, Inc.: Austin, Texas) as the electrolyte. The concentration of the electroactive species was  $1.0 \times 10^{-4}$  M.

## Results and Discussion

The electrochemical results for the pyrylium and thiapyrylium compounds **1b**, **2b**, **1'a**, and **2'b** are presented in Figures 1 and 2 and are summarized in Table I. Table I also provides some electronic absorption data.

The electrochemical half-wave potential is the voltage re-

Table I

compd	$E_{1/2}^{\text{red}}, \text{V}^a$	$E_{1/2}^{\text{ox}}, \text{V}^a$	$\lambda_{\text{max}}, \text{nm}^a$	$\epsilon$
<b>1b</b>	-0.29 rev (-0.17 rev)	>2.6 (>2.0)	405 (417)	30 400 (27 200)
	-1.42 rev		355 (368)	39 500 (39 100)
<b>2b</b>	-0.21 rev (-0.07 rev)	>2.6 (>2.0)	~405 sh (420 sh)	21 900 (23 100)
	-1.20 rev (-1.15 rev)		368 (382)	27 000 (30 800)
<b>1'b</b>	-0.59 rev (-0.47 rev)	1.30 rev	542 (558)	78 000 (82 000)
	-1.56 <sup>b</sup>	( $E_p = 1.48$ irr)	366 (381)	22 900 (20 600)
<b>2'b</b>	-0.46 rev (-0.33 rev)	1.23 rev	583 (598)	66 600 (66 900)
	-1.30 <sup>c</sup> rev	( $E_p = 1.40$ irr)	368 (384)	15 600 (12 900)

<sup>a</sup> Volts vs. SCE using 0.1 M tetrabutylammonium fluoroborate as electrolyte and  $\text{CH}_3\text{CN}$  ( $\text{CH}_2\text{Cl}_2$ ) as solvent. <sup>b</sup> Extrapolated value obtained from a plot of peak separation vs.  $E^0$  ( $P_c = -1.63$  V,  $P_a = -1.55$  V, peak separation  $\approx 80$  mV at 1 V/s scan rate). <sup>c</sup> Extrapolated value ( $P_c = -1.37$  V,  $P_a = -1.28$  V, peak separation  $\approx 90$  mV at 500 mV/s).

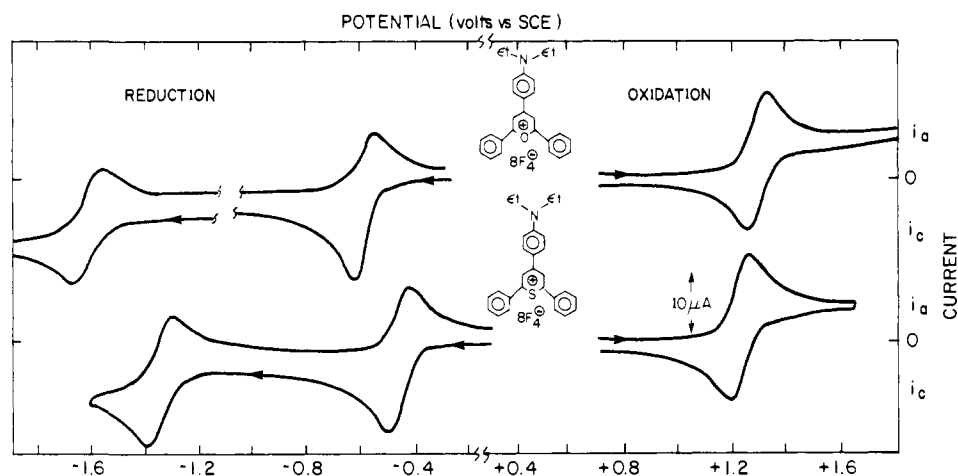
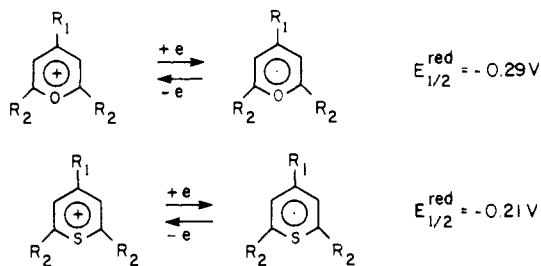


Figure 2. Cyclic voltammogram for 4'-(4-diethylaminophenyl)-2,6-diphenylpyrylium fluoroborate (**1b**) and 4'-(diethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate (**2b**) in  $\text{CH}_3\text{CN}$  vs. SCE.

quired to reduce or oxidize a compound under equilibrium conditions, i.e., the rate for the forward electron transfer reaction at the electrode surface is equal to the rate for the reverse electron transfer. Under thermodynamically controlled conditions we can write the following half-reactions for the **1b**, **2b** system.



This electrochemical information indicates that in  $\text{CH}_3\text{CN}$  the  $E_{\text{LUMO}}$  for pyrylium **1b** is 0.08 eV (2.0 kcal/mol) higher in energy than the  $E_{\text{LUMO}}$  for the corresponding thiapyrylium **2b**. Since  $E_{\text{LUMO}}$  for **1b** is equal to  $E_{\text{HOMO}}$  for **1c**, this level lies 2 kcal/mol above the  $E_{\text{HOMO}}$  in the sulfur analogue **2c**. Table II provides a summary of the relative energies of the HOMO and LUMO levels for the thiapyrylium-pyrylium salts investigated. In system **1/2** the energy of the LUMO level ( $E_{\text{LUMO}}$ ) of the closed-shell **1b/2b** and open-shell radicals **1c/2c** is 2.0 and 5.1 kcal/mol higher in energy in the pyrylium than in the sulfur analogue, respectively. Also, the  $E_{\text{HOMO}}$  of the radicals **1c/2c** and anions **1d/2d** is 2.0 and 5.1 kcal/mol higher in energy in the pyrylium than the thiapyrylium analogue, respectively.

The effect of the electron-donating diethylamino group in the compounds **1'b** and **2'b** is to make the oxidation potential experimentally accessible and the reduction potentials (see

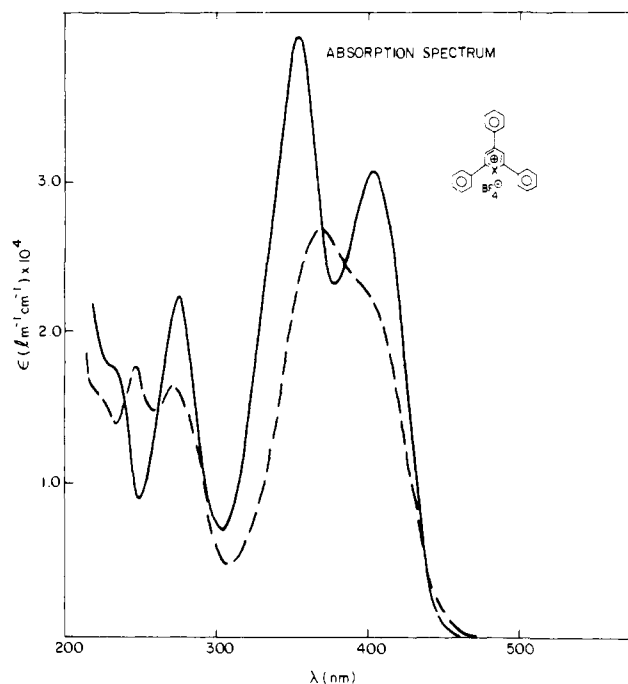
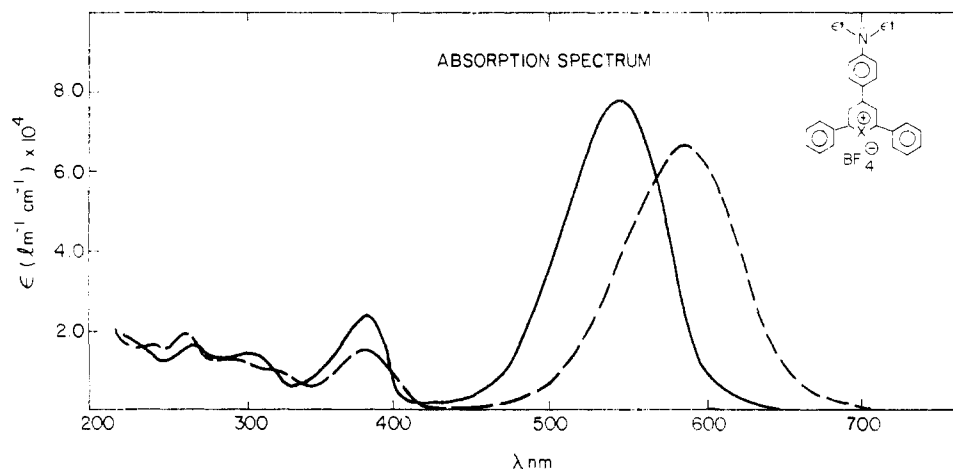


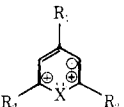
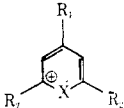
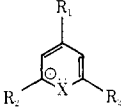
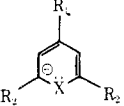
Figure 3. Electronic absorption spectrum of 2,4,6-triphenylpyrylium fluoroborate (**1b**, —) and 2,4,6-triphenylthiapyrylium fluoroborate (**2b**, ----) in  $\text{CH}_3\text{CN}$ .

Figure 2) more cathodic than in the triphenyl series. In the 4-diethylamino derivatives the dication which is presumably localized on the diethylaminophenyl group rather than on the heterocyclic ring possesses a lower energy LUMO level in the oxygen analogue than in the corresponding sulfur analogue



**Figure 4.** Electronic absorption spectrum of 4-(4'-diethylaminophenyl)-2,6-diphenylpyrylium fluoroborate (**1'b**, —) and 4-(4'-diethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate (**2'b**, ----) in  $\text{CH}_3\text{CN}$ .

**Table II.** Relative Energy of HOMO-LUMO Levels in Some Thiapyrylium-Pyrylium Salts in  $\text{CH}_3\text{CN}$  at 25 °C

system	$\Delta E$ , kcal/mol <sup>a</sup>	
	LUMO	HOMO
	<b>1'a/2'a</b>	2.0 (S > O)
	<b>1'b/2b</b> <b>1'b/2'b</b>	2.0 (O > S) 3.0 (O > S)
	<b>1c/2c</b> <b>1'c/2'c</b>	5.1 (O > S) 6.0 (O > S)
	<b>1d/2d</b> <b>1'd/2'd</b>	5.1 (O > S) 6.0 (O > S)

<sup>a</sup>  $\Delta E$  is the difference in energy of HOMO and LUMO levels between the thiapyrylium and pyrylium analogues.

by 2 kcal/mol. The sulfur analogue of the closed-shell monocation and radical possesses lower energy LUMO levels than the oxygen analogue by 3.0 and 6.0 kcal/mol, respectively. The  $E_{\text{HOMO}}$  of the radical and anion of system **1'/2'** is at lower energy in the thiapyrylium species by 3.0 and 6.0 kcal/mol, respectively. The  $E_{\text{HOMO}}$  of the monocations **1'b/2'b**, which is localized on the diethylaminophenyl moiety, is of lower energy in the oxygen analogue. In general, the sulfur analogue is more stable in terms of competitive electron transfer reactions between the oxygen and sulfur analogues in every case where the HOMO and LUMO energy level is localized within the pyrylium-thiapyrylium ring system.

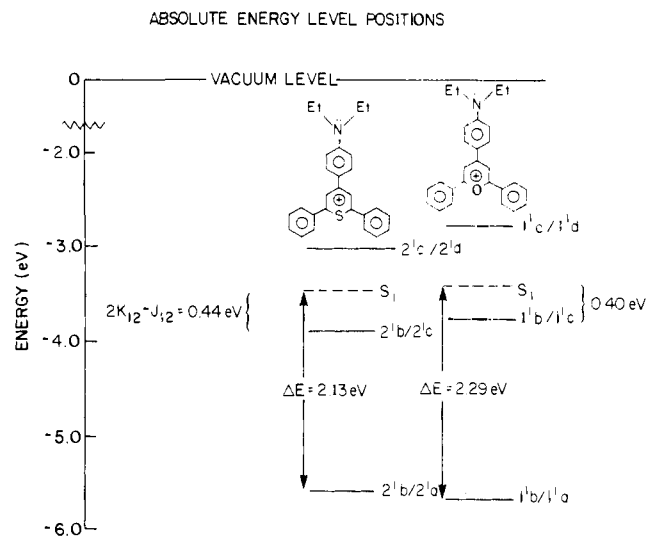
The presence of the electron-donating diethylamino group has little effect on the relative stability of the oxygen and sulfur systems. The sulfur derivative appears to be  $\sim 1$  kcal/mol more stable when the diethylamino group is present than without it. However, there is consistently a larger difference in the stability of the anions than in the radicals between the oxygen and sulfur systems. This may be due to the destabilization of the anion by oxygen rather than stabilization by sulfur, which is consistent with  $\sigma_p^+$  values for  $\text{CH}_3\text{O}^-$  and  $\text{CH}_3\text{S}^-$  substituents<sup>10</sup> from equilibrium-  $\text{p}K_{\text{a}}$  measurements on substituted benzoic acids.<sup>11</sup>

**Effect of S vs. O on Electronic Absorption Spectra.** The energy of the first excited singlet state,  $E_{\text{S}_1}$ , is related to the energy of the HOMO and LUMO levels by the following relationship:<sup>7</sup>

$$E_{\text{S}_1} = E_{\text{HOMO}} - E_{\text{LUMO}} - J_{12} + 2K_{12} \quad (5)$$

$J_{12}$  is the Coulomb repulsion integral and  $K_{12}$  is the exchange integral.<sup>7</sup> Knowledge of the molecular redox levels, which provide  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , and the singlet energy from absorption spectra of the thiapyrylium-pyrylium systems allows the effect of sulfur vs. oxygen on the value of the  $2K_{12} - J_{12}$  term to be determined. The  $2K_{12} - J_{12}$  term is the difference in energy of the lowest unoccupied molecular orbital when occupied by an electron after electronic excitation vs. that when empty in a closed-shell configuration.

The electronic absorption spectrum for compounds **1b** and **2b** (in  $\text{CH}_3\text{CN}$ ) is presented in Figure 3. The effect of sulfur in **2b** is to produce a hypochromic effect on the intensity of the absorption between 300 and 400 nm as well as an apparent decrease in separation between the first and second transitions at  $\sim 410$  and  $\sim 380$  nm, respectively. The effect of the diethylamino group in **1'b** and **2'b** is to produce a substantial red shift in the long-wavelength optical transition (Figure 4), i.e.,  $\sim 140$  nm for pyrylium and  $\sim 178$  nm for thiapyrylium, which appears to possess considerable intramolecular charge transfer (CT) character. The second electronic transition does not exhibit such a shift. The  $\lambda_{\text{max}}$  of the intramolecular CT band also shifts to the red upon going from a polar ( $\text{CH}_3\text{CN}$ ,  $\epsilon \sim 38$ ) to a nonpolar solvent ( $\text{CH}_2\text{Cl}_2$ ,  $\epsilon \sim 9$ ). The shifts in  $\lambda_{\text{max}}$  of the longest wavelength transition in **1'b** and **2'b** from  $\text{CH}_3\text{CN}$  to  $\text{CH}_2\text{Cl}_2$  are  $\sim 16$  and  $\sim 15$  nm, respectively. The rationale for the red shift upon going from a high to a low dielectric constant solvent is consistent with that proposed by Kosower for the absorption shifts in 1-alkylpyridinium iodide complexes,<sup>12</sup> i.e., the polar solvent stabilized the polar ground state relative to the nonpolar first excited singlet state, resulting in a blue shift in absorption. The magnitudes of the  $2K_{12} - J_{12}$  term for **1'b** and **2'b** are  $\sim 0.40$  and  $\sim 0.44$  eV, respectively. The absolute positions of the redox levels are shown in Figure 5 using  $-4.38$  eV as the energy of the SCE ( $\text{CH}_3\text{CN}$ ) Fermi level.<sup>7</sup> The effect of oxygen vs. sulfur on the  $2K_{12} - J_{12}$  term is relatively minor with the value of this term for thiapyrylium (**2'b**) being  $\sim 0.04$  eV larger than that for the pyrylium analogue. It is interesting to note that the singlet state lies above the intramolecular charge transfer state similar to the cyanine dyes, where the  $2K_{12} - J_{12}$  term was found to be  $\sim 0.37$  eV.<sup>7</sup> The lower reduction potential for **2b** and **2'b** than the corresponding pyrylium analogues **1b** and **1'b** indicates that the thiapyrylium



**Figure 5.** Absolute position of singlet and electrochemical redox levels for 4-(4'-diethylaminophenyl)-2,6-diphenylpyrylium fluoroborate (**1'b**) and 4-(4'-diethylaminophenyl)-2,6-diphenylthiapyrylium fluoroborate (**2'b**) in  $\text{CH}_3\text{CN}$ .

moiety is more electron withdrawing than pyrylium. The wavelength of the intramolecular charge transfer electronic transition in thiapyrylium (**2'b**), i.e., red shifted from pyrylium (**1'b**), also supports this conclusion.

### Conclusion

Measurement of the redox levels for two series of pyrylium and thiapyrylium salts has provided a quantitative comparison of the effect of oxygen vs. sulfur on the thermodynamic stabilities to electron transfer of nitrogen-cationic, carbon-radical,

and carbon-anionic centers in a single system. The ionic and radical species localized on the pyrylium–thiapyrylium ring system prefer to be adjacent to sulfur. The order of greatest sulfur preference in the 4-(4'-diethylaminophenyl)-2,6-diphenylpyrylium (thiapyrylium) system is the following: anion > radical and radical > cation for the HOMO and LUMO levels, respectively. The wavelength of the intramolecular charge-transfer band and the electrochemical reduction potentials indicate that the thiapyrylium moiety is more electron withdrawing than pyrylium. Sulfur was found to produce a somewhat larger separation between the energy of the first excited singlet ( $E_{S_1}$ ) and the energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), obtained electrochemically, than oxygen in the thiapyrylium–pyrylium system studied.

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## Reactivity in Methyl Transfer Reactions. 4. Powerful Methylating Agents with Neutral Nucleophiles

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**Abstract:** Rates and activation energies for methyl transfer to a series of substituted phenyl methyl sulfides from methyl trifluoromethanesulfonate (triflate) and from trimethyloxonium tetrafluoroborate are reported, along with rates for reaction of a few substituted dimethylanilines and pyridine with methyl triflate and dimethyl sulfate. The rate constants (in sulfolane) are not very high; varying from about 70 for pyridine and methyl triflate to  $9.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  for dimethyl sulfate with *N,N*-dimethyl-*m*-nitroaniline (at 30 °C) and do not provide consistent support for a loss of selectivity with increasing reactivity. With the uncharged phenyl methyl sulfide, trimethyloxonium ion is less than three times more reactive than methyl triflate, in contrast to the factor of 75 reported earlier for the *p*-nitrothiophenoxide ion. The substantial values of the Hammett  $\rho$ , the fairly large activation energies, and the persistence of considerable selectivity all suggest that these reactions do not have highly reagent-like transition states. The similarities of rates and activation energies for the reaction of the sulfides with the charged trimethyloxonium ion and the neutral methyl triflate, however, suggest that product solvation is not far along at the transition state.

In previous papers<sup>2-4</sup> methyl transfer rates have been studied with respect to the influence of the leaving group X on the relative reactivities of several nucleophiles  $\text{Nu}_i^-$  in reaction 1.



Not surprisingly, the reactions (with  $\text{Nu}_i^- = \text{Ar}_i\text{O}^-$  and

$\text{Ar}_i\text{S}^-$ ) fitted the Hammett equation for variation in  $\text{Ar}_i$  within normal error limits. One aim was to look for a trend toward loss of selectivity ( $\rho$  closer to zero) for the most reactive methylating agents. Small effects in this direction were observed, but it was unclear that the differences in  $\rho$  were anything other than random fluctuations, except in the extreme case where there was a possible diffusional limitation.

An unselective, early transition state, case should be char-