SQUARYLIUM DYES BASED ON 2,6-DI-*TERT*-BUTYLSELENOPYRYLIUM OR TELLUROPYRYLIUM NUCLEI

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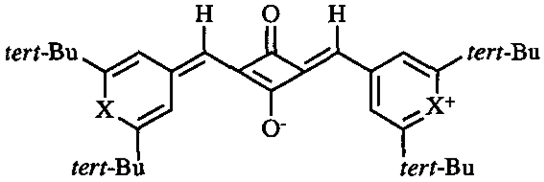
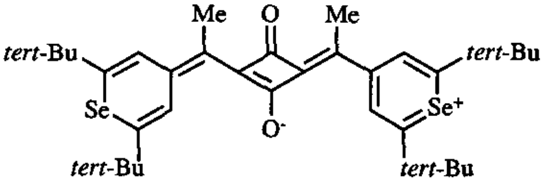
Abstract - The condensation of 2,6-di-*tert*-butyl-4-methylselenopyrylium and -telluropyrylium salts with squaric acid gives squarylium dyes with absorption maxima at 847 and 910 nm, respectively, in dichloromethane. The condensation of a 2,6-di-*tert*-butyl-4-ethylselenopyrylium salt with squaric acid gives the corresponding dimethyl-substituted squarylium dye with an absorption maximum at 906 nm in dichloromethane. Electrochemical reduction and oxidation potentials of these dyes are compared to those of the corresponding squarylium dyes based on pyrylium and thiopyrylium nuclei.

INTRODUCTION

The condensation of 2-methyl- and 4-methylpyrylium and thiopyrylium salts with 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) has produced squarylium dyes with absorption maxima in the near-infrared region. While many of these dyes are sparingly soluble, squarylium dyes (**1**) and (**2**), prepared from 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate and 2,6-di-*tert*-butyl-4-methylthiopyrylium perchlorate, are sufficiently soluble to be coated in thin films for a variety of applications. Dyes (**1**) and (**2**) have been utilized in optical recording elements with near-infrared-emitting diode lasers,[1] in liquid crystal cells,[2] in thermal printing,[3] as electrophotographic photoconductors for laser printers,[4] as near-infrared filter dyes,[4] and as dye sensitizers on the Van der Waals surfaces of tin disulfide photoanodes.[5] While heavier chalcogen analogues of **1** and **2** have been claimed in the patent literature,[1-4] no examples of selenium- and/or tellurium-containing squarylium dyes have been described. The strong narrow bands associated with (**1**) and (**2**) have made these dyes particularly well suited for use with diode lasers. In other classes of chalcogenopyrylium dyes, the maxima of absorption move to longer wavelengths as the heteroatom of the chalcogenopyrylium nucleus increases in size[6] and one might expect selenium- and tellurium-containing analogues to be compatible with light-emitting diodes emitting at 830 nm or longer. Herein, we report the syntheses of dyes (**3**) and (**4**), the first squarylium dyes based on selenopyrylium and telluropyrylium nuclei, as well as the synthesis of a methyl-substituted analogue, dye (**5**). From the spectral and electrochemical properties of these dyes, one would predict substituent effects in these systems to be identical to those found in other polymethine chalcogenopyrylium dyes.



1, X = O
2, X = S
3, X = Se
4, X = Te



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RESULTS AND DISCUSSION

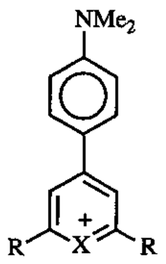
The dyes were prepared by the condensation of 4-methyl-2,6-di-*tert*-butylselenopyrylium trifluoromethanesulfonate, 4-methyl-2,6-di-*tert*-butyltelluropyrylium tetrafluoroborate, and 4-ethyl-2,6-di-*tert*-butylselenopyrylium hexafluorophosphate with squaric acid in refluxing ethanol in the presence of pyridine or diisopropylethylamine to give dyes (**3-5**), respectively. For the purpose of comparison, the known dyes (**1**) and (**2**) were prepared in a similar manner. The spectral properties of dyes (**1-5**) are compiled in Table I. As with other series of chalcogenopyrylium dyes, the maxima of absorption increase in wavelength as the hetroatoms become larger.[6] Similarly, the introduction of methyl substituents at "non-starred" carbons gives bathochromic shifts in absorption maxima.[6]

Table I. Absorption maxima and values of log ε and oxidation and reduction potentials for dyes (**1-5**) in dichloromethane.

Compd	λ_{max}, nm	log ε	$E_{\lambda max}$, eV	$E_{ox}'^{\circ}$,	$E_{ox}''^{\circ}$, V vs SCE	$E_{red}'^{\circ}$,	$E_{red}''^{\circ}$,	ΔE,[a] V
1	713	5.58	1.74	0.58	1.16	-0.89	--	1.47
2	804	5.53	1.54	0.48	0.88	-0.73	--	1.21
3	847	5.53	1.47	0.54	0.85	-0.63	--	1.17
4	910	5.54	1.36	0.48	1.09	-0.56	-1.48	1.04
5	906	5.38	1.37	0.37	0.56	-0.66	--	1.03

[a] $\Delta E = E_{ox}'^{\circ} - E_{red}''^{\circ}$.

In series of mono- and trimethine chalcogenopyrylium dyes, the energies of the absorption maxima correlate linearly with the energy of the HOMO-LUMO gap.[6] In such series of dyes, the HOMO (the oxidation potential) increases in energy and the LUMO (the reduction potential) decreases in energy as the chalcogen atoms become larger, thus narrowing the HOMO-LUMO gap. The HOMO-LUMO gap can be approximated by the difference in energy of the first oxidation potential and the first reduction potential. The squarylium dyes (**1-5**) can be thought of as pentamethine dyes which are substituted at the 3-, 4-, and 5-carbons of the methine bridge. The oxidation and reduction potentials for the pentamethine squarylium dyes (**1-5**) as determined by cyclic voltammetry and the energy of the absorption maximum ($E_{\lambda max}$) are compiled in Table I.



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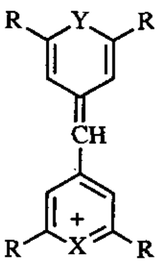

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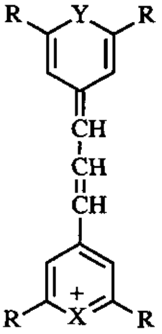

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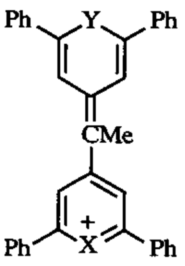

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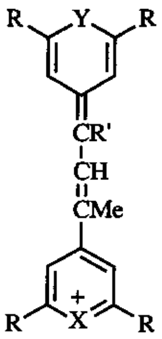

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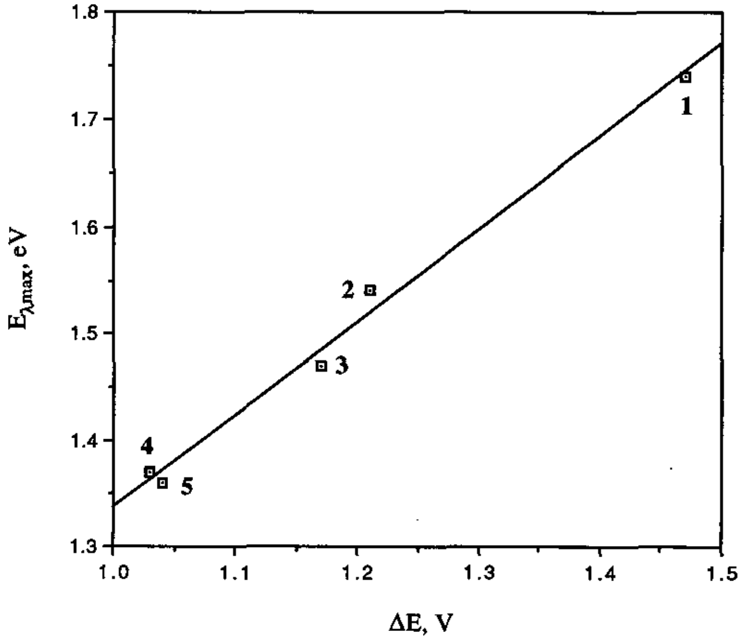
X,Y = O, S, Se, Te
R = Ph, *tert*-Bu
R' = H, Me

Figure 1. A plot of $E_{\lambda max}$ vs ΔE (data from Table I) for dyes(**1**-**5**).



From the data in Table I, reduction potentials become less negative as the chalcogen atom increases in size from dye (**1**) to dye (**4**). Oxidation potentials do not follow a trend in this series. However, as shown in Figure 1, a plot of $E_{\lambda max}$ vs ΔE is linear for dyes (**1**-**5**) with a slope of 0.87, an intercept of 0.46, and R^2 equal to 0.991.

These results can be compared to a correlation of similar functions in chalcogenopyrylium dyes (**6-8**) where a similar plot gave a slope of 0.89, an intercept of 0.53 and R^2 equal to 0.97.[6] The data for dyes (**1-5**) lie on the same line as the data for dyes (**6-8**) which is consistent with dyes (**1-5**) behaving as polymethine chalcogenopyrylium dyes.

Substituents on the methine backbone of polymethine dyes give both bathochromic and hypsochromic hue shifts from electronic interactions. In dyes (**9**) and (**10**), the electronic contributions from methyl substituents at "non-starred" positions in the methine backbone lead to bathochromic shifts in hue. In monomethine dyes (**9**), the bathochromic hue shift is much larger than in the trimethine dyes (**10**) and is presumably due to increased steric interactions in (**9**) raising the HOMO in energy. In plots similar to that shown in Figure 1, the points associated with dyes (**10**) lie on the same line as those for compounds (**6-8**) which is indicative of similar steric interactions among these compounds. The data points for dyes (**9**) lie more than two standard deviations off the line described for the data for (**6-8**) and (**10**) and indicate that electronic factors alone do not describe the effect of methyl substituents. The point in Figure 1 associated with the methyl-substituted squarylium dye (**5**) lies on the line described by the data points for dyes (**1-4**). These data are consistent with electronic contributions being dominant with methyl substitution in the squarylium dyes (**1-5**).

SUMMARY AND CONCLUSIONS

Squarylium dyes based on selenopyrylium and telluropyrylium nuclei can be prepared and are stable materials. The absorption maxima move to longer wavelengths as the size of the heteroatoms increases. This has been observed in other chalcogenopyrylium dyes of varying structure.[6] Although the zwitterionic character of the squarylium dyes imparts unusual solubility properties to these materials, the stereoelectronic effects observed in dyes (**1-5**) are consistent with those observed in other series of mono-and trimethine chalcogenopyrylium dyes. The design of squarylium dyes based on chalcogenopyrylium nuclei should follow the same rules as are used for the design of other chalcogenopyrylium polymethine dyes.

EXPERIMENTAL SECTION

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian Gemini-200 spectrophotometer. UV-visible-near infrared spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N Analyzer.

Preparation of Dye (1). Squaric acid (0.38 g, 3.3 mmol) was dissolved in 20 ml of refluxing ethanol. 4-Methyl-2,6-di-*tert*-butylpyrylium perchlorate (2.05 g, 6.68 mmol) was added followed by the dropwise addition of 0.60 g (7.6 mmol) of pyridine in 5 ml of ethanol. The resulting solution was heated at reflux for 12 h. The reaction mixture was concentrated in vacuo and the residue was purified via chromatography on silica gel eluted with 2% ethanol and 20% ethyl acetate in dichloromethane. Product yield was 1.37 g (84%) of a copper-bronze solid, mp 239-241 °C: ^{1}H Nmr ($CDCl_3$) δ 8.62 (s, 2 H), 6.17 (s, 2 H), 5.80 (s, 2 H), 1.30 (s, 18 H), 1.24 (s, 18 H).

Preparation of Dye (2). Squaric acid (0.285 g, 2.50 mmol) was dissolved in 20 ml of refluxing ethanol. 4-Methyl-2,6-di-*tert*-butylthiopyrylium trifluoromethanesulfonate (1.86 g, 5.00 mmol) was added followed by the dropwise addition of 0.66 g (5.1 mmol) of diisopropylethylamine in 5 ml of ethanol. The resulting solution was heated at reflux for 12 h. The reaction mixture was concentrated in vacuo and the residue was purified via chromatography on silica gel eluted with 2% ethanol and 20% ethyl acetate in dichloromethane. The dye (2) was recrystallized from 2/1 (v/v) heptane/ether. Product yield was 0.185 g (14%) of a copper-bronze solid, mp 235.5-236.5 °C: ^{1}H Nmr ($CDCl_3$) δ 9.20 (s, 2 H), 6.88 (s, 2 H), 6.04 (s, 2 H), 1.41 (s, 18 H), 1.31 (s, 18 H).

Preparation of Dye (3). Squaric acid (1.71 g, 15.0 mmol) was dissolved in 80 ml of refluxing ethanol. 4-Methyl-2,6-di-*tert*-butylselenopyrylium trifluoromethanesulfonate (3.03 g, 7.32 mmol) was added followed by the dropwise addition of 1.2 g (15 mmol) of pyridine in 10 ml of ethanol. The resulting solution was heated at reflux for 4 h. The reaction mixture was poured into 400 ml of water and the products were extracted with dichloromethane (4 x 50 ml). The combined extracts were washed with brine, were dried over sodium sulfate, and concentrated. The crude dye was slurried in warm ether, filtered, and dried. Product yield was 1.37 g (84%) of a copper-bronze solid, mp 232-233 °C: ^{1}H Nmr ($CDCl_3$) δ 9.18 (s, 2 H), 6.95 (s, 2 H), 6.21 (s, 2 H), 1.43 (s, 18 H), 1.32 (s, 18 H). Anal. Calcd for $C_{32}H_{42}O_2Se_2$: C, 62.33; H, 6.87. Found: C, 62.49; H, 7.17.

Preparation of Dye (4). Squaric acid (0.114 g, 1.00 mmol) was dissolved in 20 ml of refluxing ethanol. 4-Methyl-2,6-di-*tert*-butyltelluropyrylium tetrafluoroborate (0.814 g, 2.00 mmol) was added followed by the dropwise addition of 0.26 g (2.0 mmol) of diisopropylethylamine in 5 ml of ethanol. The resulting solution was heated at reflux for 3 h. The reaction mixture was concentrated in vacuo and the residue was purified via chromatography on silica gel eluted with 2% ethanol and 20% ethyl acetate in dichloromethane. The red, crystalline dye was slurried in ether and the product was collected by filtration and dried. Product yield was 0.233 g (33%) of a red solid, mp 244.5-245 °C: ^{1}H Nmr ($CDCl_3$) δ 9.13 (s, 2 H), 7.00 (s, 2 H), 6.36 (s, 2 H), 1.44 (s, 18 H), 1.30 (s, 18 H). Anal. Calcd for $C_{32}H_{42}O_2Te_2$: C, 53.84; H, 5.93. Found: C, 54.00; H, 6.08.

Preparation of Dye 5. A mixture of 4-ethyl-2,6-di-*tert*-butylselenopyrylium hexafluorophosphate (3.03 g, 7.08 mmol), squaric acid (1.30 g, 11.4 mmol), and pyridine (0.87 g, 11 mmol) in 75 ml of ethanol was heated at reflux for 3.0 h. The reaction mixture was cooled to ambient temperature precipitating the dye as copper-bronze crystals. The reaction mixture was diluted with 75 ml of water. The crude product was collected by filtration and was then washed with water (4 x 50 ml) and ether (4 x 50 ml). The crude product was filtered from boiling acetonitrile to give 1.33 g (58%) of dye (5) as copper-bronze crystals, mp 254-255 °C: ^{1}H Nmr (CD_2Cl_2) δ 8.54 (s, 4 H), 2.04 (s, 6 H), 1.68 (s, 36 H) [All signals were broadened from rotational exchange.] Anal. Calcd for $C_{34}H_{46}O_2Se_2$: C, 63.35; H, 7.19. Found: C, 62.97; H, 6.92.

Electrochemical Procedures. Cyclic voltammetry was performed employing a Princeton Applied Research Potentiostat/Galvanostat Model 273 in line with an IBM PC-AT. The curves were plotted with a Hewlett-Packard Plotter Model 7550-plus. Sample solutions were prepared in dichloromethane at 1 mM. Each sample was degassed with argon for 5 min prior to use. Tetrabutylammonium tetrafluoroborate was used as supporting electrolyte at 0.2 M. Potentials were measured at a Pt disk at a scan rate of 0.1 V s^{-1}.

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