Soluble, Infrared-Absorbing Croconate Dyes from 2,6-Di-*tert*-butyl-4-methylchalcogenopyrylium Salts

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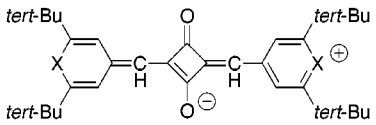
Introduction

Infrared-absorbing dyes have found important applications[1] in thermal imaging, photography, lithography, electrophotography, and optical recording as well as applications as filter elements[1,2] where near-infrared-emitting lasers are employed. Squarylium dyes derived from the condensation of 2-methyl- and 4-methyl-chalcogenopyrylium salts with 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) have narrow absorption maxima in the near-infrared region with large extinction coefficients.[1] Although many squarylium dyes have limited solubility in organic solvents or in coated organic films, squarylium dyes **1** (Chart 1) derived from 2,6-di-*tert*-butyl-4-methylchalcogenopyrylium salts (**2**)[3] are soluble and have been coated in organic thin films for a variety of applications.[4−6]

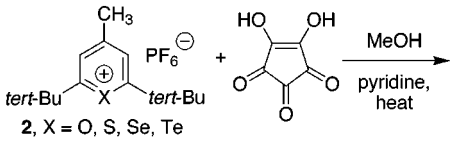
Near-infrared-absorbing dyes can also be prepared by condensation reactions with 4,5-dihydroxy-4-cyclopentene-1,2,3-trione (croconic acid).[7] Calculations and experiment have shown that the croconate dyes have maxima of absorption that are approximately 100 nm longer than the corresponding squarylium dyes.[7c] As with the squarylium dyes, many of the croconate dyes show minimal solubility in organic solvents and in organic thin films. The pyrylium croconate dye **3a** bearing *tert*-butyl substituents has been reported and has sufficient solubility in organic thin films for utility in several applications.[8−10] The heavier chalcogen analogues **3b**−**d** have not been reported. In this paper, we describe the synthesis and properties of all four of the chalcogenopyrylium analogues of croconate dyes **3** and compare selected properties to those of the corresponding squarylium dyes **1**. The croconates are readily prepared, are soluble in organic solvents, and have absorption maxima that cover a broad range of laser emission lines from gallium−arsenide diode lasers (≥820 nm) to the neodinium-YAG laser (1064 nm).

Chart 1

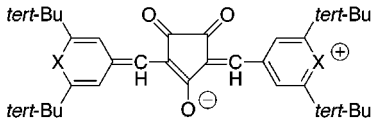


1a, X = O
1b, X = S
1c, X = Se
1d, X = Te

Scheme 1



2, X = O, S, Se, Te



3a, X = O
3b, X = S
3c, X = Se
3d, X = Te

Results and Discussion

Synthesis. The croconate dyes **3** were prepared by the condensation of 4-methylchalcogenopyrylium salts **2** with croconic acid in MeOH with a stoichiometric quantity of pyridine as shown in Scheme 1. Pyrylium dye **3a**, thiopyrylium dye **3b**, seleninium dye **3c**, and tellurinium dye **3d** were all isolated in good yield (75, 63, 81, and 56% yields, respectively) by this route. Thiopyrylium dye **3b** was best prepared by heating the reaction mixture at 80 °C for 3 h while the other three dyes were prepared at 100 °C. At 100 °C, dye **3b** was isolated in only 12% yield. While the products crystallized from the reaction mixture, unidentified impurities were best removed by

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Table 1. Comparison of the Linear Optical and Electrochemical Properties of Squarylium Dyes 1 and Croconate Dyes 3

dye	X	λ_{max},[a] nm	log ϵ[a]	$\nu_{1/2}$,[b] cm^{-1}	ox[c,d,e] Ep_a	red[c,e] Ep_c	red[c,e] Ep_a
1a	O	713	5.58	590	0.53	−0.90	−0.82
1b	S	804	5.53	560	0.48	−0.77	−0.69
1c	Se	847	5.53	560	0.54	−0.67	−0.59
1d	Te	910	5.54	530	0.48	−0.60	−0.52
3a	O	845	5.11	620	0.42	−0.59	−0.51
3b	S	950	5.26	570	0.38	−0.52	−0.44
3c	Se	999	5.15	590	0.41	−0.37	−0.29
3d	Te	1081	5.20				
		970[f]	4.63				

[a] In CH_2Cl_2. [b] Bandwidth at half-height. [c] In CH_2Cl_2 at a Pt-disk electrode with a scan rate of 0.1 V s^{-1} with 0.2 M Bu_4NBF_4 as supporting electrolyte with the ferrocene/ferricinium couple as the reference electrode. [d] Irreversible peak potential. [e] V (vs Fc/Fc^+). [f] Shoulder.

purifying the dyes via chromatography on SiO_2 eluted with 5−7% EtOH in CH_2Cl_2.

Properties. The absorption maxima of croconate dyes **3** were 130−170 nm longer than absorption maxima of the corresponding squarylium dyes **1** although the molar extinction coefficients of dyes **3** were somewhat smaller (Table 1). The absorption bands of croconate dyes **3** were sharp with bandwidths at half-height in the range of 570−620 cm^{-1}, which are comparable to the values of 530−590 cm^{-1} observed for squarylium dyes **1** (Table 1). The absorption maxima of dyes **3** (845−1080 nm) cover a range of laser emission wavelengths including various gallium−arsenide diode lasers, dye lasers, and the neodinium-YAG laser (1064 nm).

As the heteroatoms in the rings become larger, the absorption maximum moves to longer wavelengths as has been observed in other chalcogenopyrylium dyes series.[11] The oxidation and reduction potentials measured for dyes **1** and **3** suggest that the differences in absorption maxima are LUMO driven rather than HOMO driven.[11] While the oxidation potentials of squarylium dyes **1** are roughly 0.1 V more positive than the corresponding croconate dyes **3**, the reduction potentials of dyes **3** are 0.23−0.31 V less cathodic than the reduction potentials of dyes **1** (Table 1). As a consequence, the narrowing of the HOMO−LUMO gap in dyes **3** relative to dyes **1** is driven by changes in LUMO energy levels.[11]

The croconate dyes **3** are quite soluble in dichloromethane, which is a typical coating solvent for organic thin films. Pyrylium analogue **3a**, thiopyrylium analogue **3b**, and seleninium analogue **3c** were soluble at 180 mg/mL of CH_2Cl_2 while tellurinium dye **3d** was slightly less soluble at 155 mg/mL of CH_2Cl_2.

Experimental Section

General Methods. Solvents and reagents were used as received from Sigma-Aldrich Chemical Co. (St. Louis, MO) unless otherwise noted. Squarylium dyes **1** were prepared as reported in ref 3. 4-Methylchalcogenopyrylium salts **2b**−**d** were prepared from the corresponding Δ-4*H*-2,6-di-*tert*-butylchalcogenopyran-4-ones, which were prepared as described in ref 12. Elemental analyses were conducted by Atlantic Microanalytical, Inc.

Preparation of 2,6-Di-*tert*-butyl-4-methylpyrylium Hexafluorophosphate (2a). A. Preparation of Δ-4*H*-2,6-Di-*tert*-butylpyran-4-one. Potassium hydroxide (0.443 g, 7.89 mmol) was dissolved in 25 mL of ethanol. 1,5-Di-*tert*-butyl-1,4-pentadiyn-3-one (0.500 g, 2.63 mmol) was added, and the resulting solution was stirred at ambient temperature for 15 h. The reaction mixture was poured into water (50 mL), and the product was extracted with hexanes (3 × 25 mL). The organic extracts were dried over magnesium sulfate, concentrated to approximately one-third volume, and chilled. The white crystals were collected by filtration to give 0.17 g (31%) of the pyranone: mp 77−79 °C; ^1H NMR ($CDCl_3$) δ 6.15 (s, 2 H), 1.30 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 180.0, 174.7, 109.0, 35.87, 27.4. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.76; H, 9.54.

B. Addition of Methylmagnesium Bromide. Methylmagnesium bromide (1.4 M in ether, 47 mL, 66 mmol) was added dropwise to a solution of Δ-4*H*-2,6-di-*tert*-butylpyran-4-one (2.29 g, 11.0 mmol) in 100 mL of anhydrous THF. After addition was complete, the reaction mixture was heated at reflux for 3 h. The reaction mixture was cooled to ambient temperature and was added slowly to 450 mL of cold 10% HPF_6. The white precipitate was collected by filtration and washed with water and ether. The crude salt was recrystallized from acetonitrile/ether to give 3.51 g (91%) of **2a** as a white powder: mp 203−204 °C dec (lit.[11] mp 203−204 °C); ^1H NMR (CD_2Cl_2) δ 7.80 (s, 2 H), 2.81 (s, 3 H), 1.51 (s, 18 H).

Preparation of 2,6-Di-*tert*-butyl-4-methylthiapyrylium Hexafluorophosphate (2b). Methylmagnesium bromide (1.4 M in ether, 66 mL, 92 mmol) was added dropwise to a solution of Δ-4*H*-2,6-di-*tert*-butylthiopyran-4-one (4.15 g, 18.5 mmol) in 100 mL of anhydrous THF. After addition was complete, the reaction mixture was heated at reflux for 3 h. The reaction mixture was cooled to ambient temperature and was added slowly to 450 mL of cold 10% HPF_6. The white precipitate was collected by filtration and washed with water and ether. The crude salt was recrystallized from acetonitrile/ether to give 5.18 g (76%) of **2b** as a white powder: mp 193−194 °C (lit.[11] mp 193−194 °C); ^1H NMR (CD_2Cl_2) δ 7.80 (s, 2 H), 2.81 (s, 3 H), 1.51 (s, 18 H).

Preparation of 2,6-Di-*tert*-butyl-4-methylseleninium Hexafluorophosphate (2c). Methylmagnesium bromide (1.4 M in ether, 47 mL, 66 mmol) was added dropwise to a solution of Δ-4*H*-2,6-di-*tert*-butylselenopyran-4-one (3.00 g, 11.0 mmol) in 100 mL of anhydrous THF. After addition was complete, the reaction mixture was heated at reflux for 3 h. The reaction mixture was cooled to ambient temperature and was added slowly to 450 mL of cold 10% HPF_6. The white precipitate was collected by filtration and washed with water and ether. The crude salt was recrystallized from acetonitrile/ether to give 3.51 g (91%) of **2c** as a white powder: mp 203−204 °C (lit.[11] mp 200−201 °C); ^1H NMR (CD_2Cl_2) δ 8.34 (s, 2 H), 2.83 (s, 3 H), 1.66 (s, 18 H).

Preparation of 2,6-Di-*tert*-butyl-4-methyltellurinium Hexafluorophosphate (2d). Methylmagnesium bromide (1.4 M in ether, 27 mL, 38 mmol) was added dropwise to a solution of Δ-4*H*-2,6-di-*tert*-butylpyran-4-one (2.40 g, 7.50 mmol) in 100 mL of anhydrous THF. After addition was complete, the reaction mixture was heated at reflux for 3 h. The reaction mixture was cooled to ambient temperature and was added slowly to 450 mL of cold 10% HPF_6. The white precipitate was collected by filtration and washed with water and ether. The crude salt was recrystallized from acetonitrile/ether to give 2.47 g (71%) of **2a** as a white powder: mp 185−187 °C (lit.[11] mp 185−187 °C); ^1H NMR (CD_2Cl_2) δ 8.58 (s, 2 H), 2.56 (s, 3 H), 1.55 (s, 18 H).

Preparation of 4-[(3-[(2,6-Bis(1,1-dimethylethyl)-4*H*-pyran-4-ylidene)methyl]-2-hydroxy-4,5-dioxo-2-cyclopenten-1-ylidene)methyl]-2,6-bis(1,1-dimethylethyl)pyrylium Inner Salt (3a). 2,6-Di-*tert*-butyl-4-methylpyrylium hexafluorophosphate (**2a**, 1.0 g, 3.2 mmol) and croconic acid (0.23 g, 1.6 mmol) were slurried in 5 mL of MeOH. Pyridine (0.25 g, 3.2 mmol) was added, and the resulting mixture was heated on a steam bath for approximately 3 h. The progress of reaction was followed by UV−vis−near-IR spectroscopy. When starting **2a** had been consumed, the reaction was chilled and the product was collected by filtration. The solid was purified by chromatography on SiO_2 eluted with 7% EtOH in CH_2Cl_2 to give 0.62 g (75%) of **3a** as a copper bronze solid: mp 156 °C dec; ^1H NMR ($CDCl_3$) δ 9.20 (br s, 2 H), 6.61 (br s, 2 H), 6.50 (br s, 2 H), 1.34 (s, 36 H); IR (KBr) 1583 cm^{-1}; FAB(+) MS *m*/*z* 519 ($C_{33}H_{42}O_5$ +

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H^+); λ_{max} (CH_2Cl_2) 845 nm [$\epsilon = (1.3 \pm 0.1) \times 10^5$ M^{-1} cm^{-1}]. Anal. Calcd for $C_{33}H_{42}O_5$: C, 76.41; H, 8.16. Found: C, 76.36; H, 8.24.

Preparation of 4-[(3-[(2,6-Bis(1,1-dimethylethyl)-4*H*-thiopyran-4-ylidene)methyl]-2-hydroxy-4,5-dioxo-2-cyclopenten-1-ylidene)methyl]-2,6-bis(1,1-dimethylethyl)thiopyrylium Inner Salt (3b). 2,6-Di-*tert*-butyl-4-methylthiopyrylium hexafluorophosphate (**2b**, 2.0 g, 5.4 mmol) and croconic acid (0.38 g, 2.7 mmol) were slurried in 15 mL of MeOH. Pyridine (0.43 g, 5.4 mmol) was added, and the resulting mixture was heated at 80 °C for 3 h. The progress of reaction was followed by UV−vis−near-IR spectroscopy. When starting **2b** had been consumed, the reaction was chilled and the product was collected by filtration. The solid was purified by chromatography on SiO_2 eluted with 7% EtOH in CH_2Cl_2 to give 0.94 g (63%) of **3b** as a copper bronze solid: mp 221 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.65 (br s, 2 H), 7.41 (br s, 2 H), 6.76 (br s, 2 H), 1.44 (s, 36 H); IR (KBr) 1626 cm^{-1}; FAB(+) MS *m*/*z* 551 ($C_{33}H_{42}O_3S_2 + H^+$); λ_{max} (CH_2Cl_2) 950 nm [$\epsilon = (1.8 \pm 0.1) \times 10^5$ M^{-1} cm^{-1}]. Anal. Calcd for $C_{33}H_{42}O_3S_2$: C, 71.96; H, 5.70. Found: C, 72.04; H, 5.55.

Preparation of 4-[(3-[(2,6-Bis(1,1-dimethylethyl)-4*H*-selenin-4-ylidene)methyl]-2-hydroxy-4,5-dioxo-2-cyclopenten-1-ylidene)methyl]-2,6-bis(1,1-dimethylethyl)seleninium Inner Salt (3c). 2,6-Di-*tert*-butyl-4-methylseleninium hexafluorophosphate (**2c**, 2.0 g, 4.8 mmol) and croconic acid (0.34 g, 2.4 mmol) were slurried in 15 mL of MeOH. Pyridine (0.38 g, 4.8 mmol) was added, and the resulting mixture was heated on a steam bath for approximately 1 h. The progress of reaction was followed by UV−vis−near-IR spectroscopy. When starting **2c** had been consumed, the reaction was chilled and the product was collected by filtration. The solid was purified by chromatography on SiO_2 eluted with 7% EtOH in CH_2Cl_2 to give 1.25 g (81%) of **3c** as a copper bronze solid: mp 221 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.50 (br s, 2 H), 6.90 (s, 4 H), 1.44 (s, 36 H); IR (KBr) 1586 cm^{-1}; FAB(+) MS *m*/*z* 646 ($C_{33}H_{42}O_3{}^{80}Se_2$); λ_{max} (CH_2Cl_2) 999 nm [$\epsilon = (1.4 \pm 0.2) \times 10^5$ M^{-1} cm^{-1}]. Anal. Calcd for $C_{33}H_{42}O_3Se_2$: C, 61.48; H, 6.56. Found: C, 61.36; H, 6.55.

Preparation of 4-[(3-[(2,6-bis(1,1-Dimethylethyl)-4*H*-tellurin-4-ylidene)methyl]-2-hydroxy-4,5-dioxo-2-cyclopenten-1-ylidene)methyl]-2,6-bis(1,1-dimethylethyl)tellurinium Inner Salt (3d). 2,6-Di-*tert*-butyl-4-methyltellurinium hexafluorophosphate (**2d**, 2.0 g, 4.3 mmol) and croconic acid (0.30 g, 2.1 mmol) were slurried in 15 mL of MeOH. Pyridine (0.34 g, 4.3 mmol) was added, and the resulting mixture was heated on a steam bath for approximately 15 min. The progress of reaction was followed by UV−vis−near-IR spectroscopy. When starting **2d** had been consumed, the reaction was chilled and the product was collected by filtration. The solid was purified by chromatography on SiO_2 eluted with 5% EtOH in CH_2Cl_2 to give 0.85 g (56%) of **3d** as a copper bronze solid: mp 213 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.71 (br s, 2 H), 7.59 (br s, 2 H), 7.02 (br s, 2 H), 1.46 (s, 36 H); IR (KBr) 1577 cm^{-1}; FAB(+) MS *m*/*z* 747 ($C_{33}H_{42}O_3{}^{130}Te_2 + H^+$); λ_{max} (CH_2Cl_2) 1081 nm [$\epsilon = (1.6 \pm 0.1) \times 10^5$ M^{-1} cm^{-1}], 970 nm [sh, $\epsilon = (4.3 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}]. Anal. Calcd for $C_{33}H_{42}O_3Te_2$: C, 53.46; H, 5.70. Found: C, 53.43; H, 5.55.

Electrochemical Procedures. The working electrode for cyclic voltammetry was a platinum disk electrode (diameter, 1 mm) obtained from Princeton Applied Research. The auxiliary electrode was a platinum wire. The reference for cyclic voltammetry was the Fc/Fc^+ couple at +0.40 V at a scan rate of 0.1 V s^{-1}. All measurements were conducted in J. T. Baker HPLC-grade dichloromethane that had been stored over 3A molecular sieves. Electrometric-grade tetrabutylammonium fluoroborate (Southwestern Analytical Chemicals, Inc.) was recrystallized from ethyl acetate−ether and then dried overnight at 80 °C before it was used as supporting electrolyte at 0.2 M. Argon was used for sample deaeration.

Solubility Experiments. A 50.0-mg sample of dye **3** was placed in a vial, and CH_2Cl_2 was slowly added via a 500-μL gastight syringe. The addition was stopped when all crystals of the dye had dissolved as viewed under 10× magnification against a diffuse tungsten light source. The volume of solvent was determined by weight.

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Supporting Information Available: Absorption spectra for dyes **3a**−**d** in the visible and near-infrared regions. This material is available free of charge via the Internet at http://pubs.acs.org.

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