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Syntheses, Characteristics and Electrophotographic Properties of New Dithiosquarylium Dyes

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ABSTRACT

A new class of dithiosquarylium dyes (DTSQ) has been synthesized by the reaction of squarylium dye (SQ) with Lawesson's reagent or P_4S_{10}. The λ_{max}, of DTSQ dyes undergoes a bathochromic shift of about 25 nm compared with corresponding SQ dyes. The visible absorption spectra of DTSQ dyes are well accounted for by Pariser-Parr-Pople Molecular Orbital (PPP-MO) calculations. Electrophotographic characteristics of negatively charged dual layered photoreceptors with DTSQ for charge generation materials (CGM) and 1-phenyl-1,2,3,4-tetrahydroquinoline-6-carboxyaldehyde-1',1'-diphenylhydrazone as a charge transport material (CTM) have been investigated. The photoreceptor that used DTSQs exhibited high photosensitivity at white light.

Keywords: Dithiosquarylium dyes (DTSQ), electrophotographic, thin film, dark decay, photosensitivity.

INTRODUCTIONS

Squarylium dyes have been studied for their ability to color optical recording media [1], organic solar cell [2] and electrophotographic photoreceptors [3, 4]. We have previously reported syntheses [5, 6] and electrochromic properties [7]

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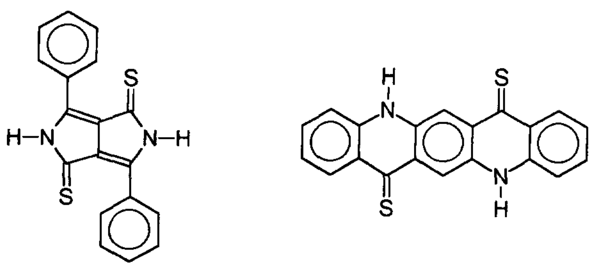
of squarylium and aminosquarylium dyes containing indoline moiety. Nucleophilic transformations at the carbonyl group of 1,4-diketo-pyrrolo(3,4-c) pyrrole (DPP) [8] and quinacridone without cleavage of the cyclic ring system were primarily aimed at the formal replacement of O by S. 1,4-Dithioketo-3,6-diphenyl-pyrrolo(3,4-c) pyrrole (DTPP), shown in Fig. 1, is a thionated derivative of DPP, which has recently appeared on the market as a red pigment.

The solid-state properties of DTPP have been extensively studied, especially in connection with photoconductive behavior and its application to electrophotographic photoreceptors [9, 10]. 7, 14-Dithioketo-5, 7, 12, 14-tetrahydroquinolino- (2, 3-b)-acridine (DTQ) is a thionated derivative of linear trans-unsubstituted quinacridone that is known as a violet pigment. Thionation of quinacridone causes an appearance of an intense near-IR absorption in the solid state [11]. Because of this, DTQ has recently attracted attention as a material suitable for GaAsAl-diode laser prints [11] and optical recording systems [12].

To our knowledge, there are, as yet, no published studies on synthesis and characteristics of dithiosquarylium dyes. In this paper, we wish to report the new syntheses of dithiosquarylium dyes (DTSQ), which are structural analogue of squarylium dye (SQ). Also, the color-structure correlations for a DTSQ are discussed on the basis of PPP-MO calculations. We also have investigated the electrophotographic characteristics of dual-layered photoreceptors using DTSQ as a charge generation material.

EXPERIMENTAL

Melting points were determined using an Electrothermal IA900 and are uncorrected. Visible and IR spectra were measured using Shimadzu UV-2100 and Nicolet Magna-IR500 Spectrophotometers, respectively. Elemental



DTPP DTQ

Fig. 1. Structure of DTPP and DTQ.

analysis were recorded on a Carlo Elba Model 1106 Analyzer. 2,4-Bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent), hexamethylphosphoramide (HMPA) and phosphorous pentasulfide were used without further purification.

Starting materials (SQ dyes 4a–c)

The starting materials **4a**, **4b** and **4c** were prepared using previously described procedures [5, 6]. Structures were confirmed from data described in the literature and from data shown below.

4a M.p. 270~272°C. U.V. λmax (nm), ($CHCl_3$), ($\varepsilon \times 10^{-5}$), 654 (1.33). Found: C; 78.45, H; 6.20, N; 7.09%; Calcd.: C; 78.75, H; 6.10, N; 7.06%.

4b. M.p., > 300°C. U. V., λmax (nm), ($CHCl_3$), ($\varepsilon \times 10^{-5}$), 633 (3.21) Found:C, 79.03, H; 6.86, N; 6.70% Calcd.: C; 79.21, H; 6.64, N; 6.60%.

4c M.p., 299°C. U.V. λ max (nm), ($CHCl_3$), ($\varepsilon \times 10^{-5}$), 639 (8.3). Found: C; 78.52, H; 6.75, N; 7.28%; Calcd.: C; 78.64, H; 6.98, N; 7.42%.

Synthesis of dithiosquarylium dye (DTSQ), 5a–c

Method A

One gram (2.5 mmol) of SQ dye 4a and 1.2 g (2.5 mmol) of 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) were suspended in a mixture of 15 ml xylene and 1 ml of hexamethylphosphoramide (HMPA). The suspension was refluxed for 5 h under efficient stirring. The mixture was evaporated and chromatographed on silicagel (Waco-gel C-300; chloroform) to give 1.93 g of **5a**

Method B

0.8 g (2 mmol) of SQ dye **4a** and 1 g (2.3 mmol) of phosphorous pentasulfide in 34 ml of pyridine were refluxed for 5 h. The solvent was removed in vacuum and submitted to column chromatography on silicagel.

Preparation of evaporated films

The evaporated films for measurement of visible absorption spectra were prepared on plain glass. The evaporation was carried out at about 200°C under a vacuum of 10^{-6} torr.

Fabrication of photoreceptors

A negative charging dual layer photoreceptor device configuration was used to evaluate the DTSQs as a charge generation material (Fig. 2).

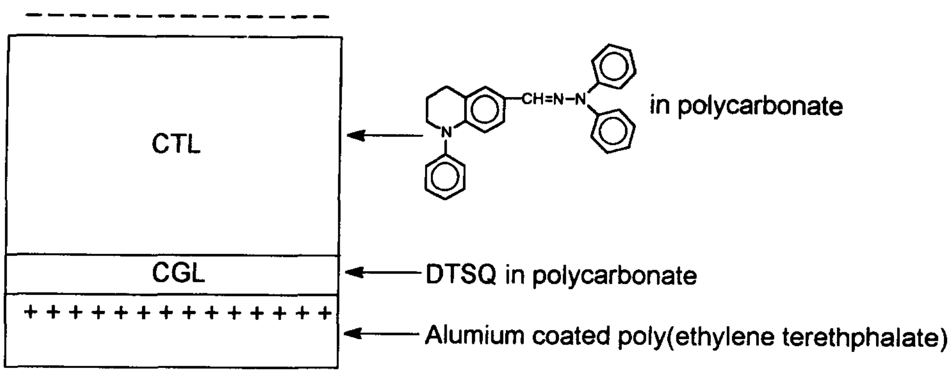


Fig. 2. Composition of dual layer photoreceptor.

The charge generation materials (CGM) used were the three kinds of DTSQ, and the charge transport material was 1-phenyl-1,2,3,4-tetrahydroquinoline-6-carboxyaldehyde-1′,1′-diphenylhydrazone. Photoreceptors were coated by wire bar solvent coating on aluminized Mylar film. Each charge generation layer (CGL) was ~ 0.5 μm thick and contains 30 wt.% of DTSQ in bisphenol-A-polycarbonate (PC).

Charge transport layers (CTL) were composed of 40 wt.% charge transport material (CTM) prepared by dissolution in polycarbonate and methylene chloride, and coated onto the CGL at thickness ~30 μm.

Electrophotographic measurements

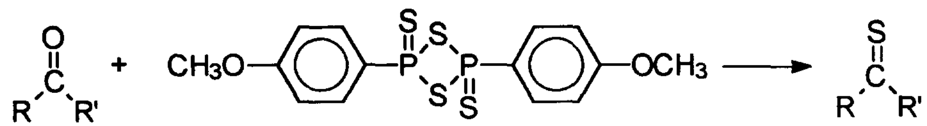
The electrophotographic discharge measurements were carried out in a computer controlled flat-plate scanner. The samples were charged up negatively to about −600 V by a corotron device. The surface potential was measured by probe connected to a Trek electrometer (Model 3601).

RESULTS AND DISCUSSION

Synthesis of dithiosquarylium dyes (DTSQs) 5a–c

We have reported that the reaction of squaric acid **1** with two equivalents of **2** gave squarylium dye 4a. The reaction of **2** with alkyl iodide in acetonitrile gave **3a** and **3b**. Similar reaction of **3a** and **3b** with squaric acid **1** gave the corresponding SQ dye **4b** and **4c**.

Ketones react smoothly of p-methoxyphenylthionophosphine sulfide, Lawesson's reagent **6**, to give in most cases the corresponding thioketones [13].



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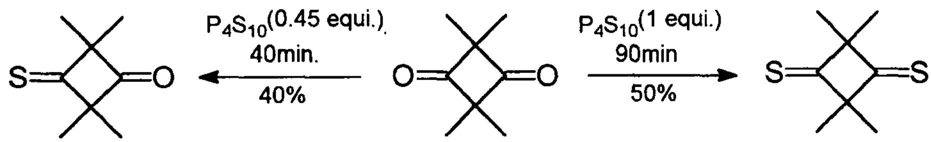
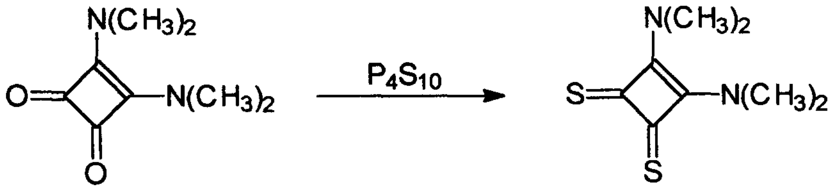
As is the case with other reagents, the reaction of P_4S_{10} with diketones can result in the formation of either monothio or dithio compounds, depending upon the conditions used. Thus thionation of cyclobutane-dione **7** gave either the monothiodione **8** or the dithione **9** as the major product, depending on the amount of P_4S_{10} used and the reaction time [14].



8 7 9

A wide range of compounds in which the thioketone is stabilized by conjugation to a heteroatom have been reported [15]. An area that has received considerable attention is that of derivatives of squaric acid, for example the dithione **10**, prepared by thionation of corresponding diketone [16], for a detailed overview of the area, the review by Schmidt should be consulted [17].



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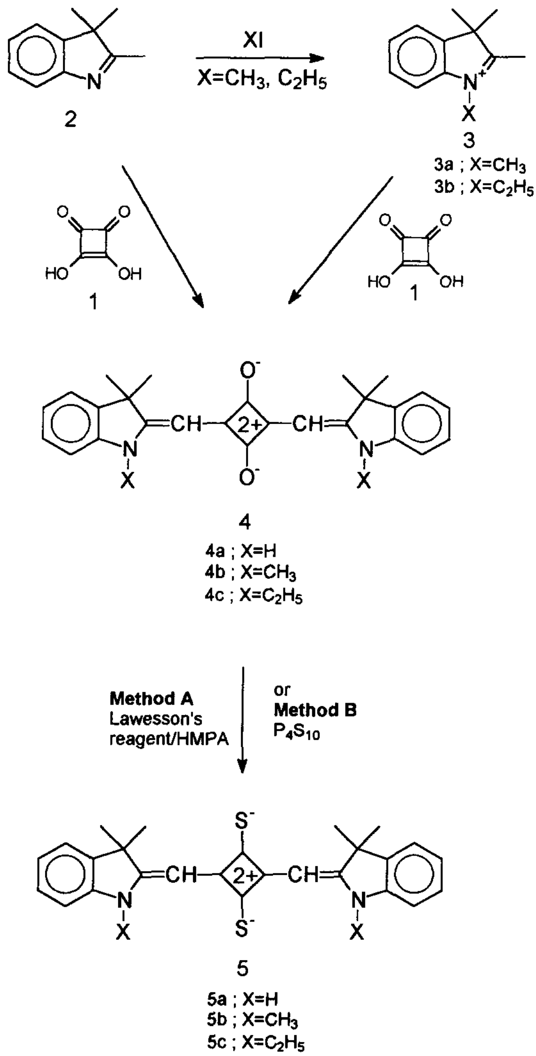
We have found for the first time that thio-analogus of SQ dyes **5a**–**5c**, can be synthesized by the reaction of SQ **4a**–**4c**, with Lawesson's reagent. DTSQ dyes **5a**–**5c** were also prepared from SQ dyes **4a**–**4c**, by using phosphrorous pentasulfide, P_4S_{10}, as the thionation agent. The general synthetic routes to the DTSQ dyes are outlined in Scheme 1. The properties of the prepared DTSQ are listed in Table 1

The reactivity of Lawession's reagent (Method A) against P_4S_{10} (Method B) was very poor. DTSQ dyes generally absorb at much longer wavelength



Scheme 1

than the corresponding SQ dyes. The structural difference between DTSQ and SQ gave quite different physical properties especially in their absorption spectra, as discussed in a later section. X-ray structural analysis of DTSQ are under investigation and will be reported separately.

Visible absorption spectra

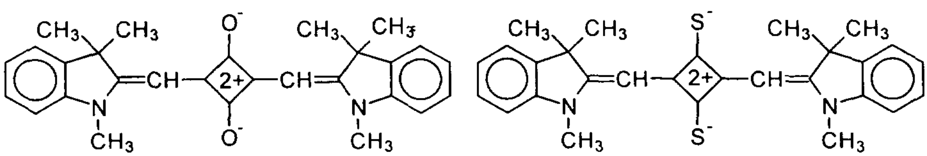
The observed visible absorption spectra in chloroform of DTSQ dyes **5a–5c** together with the corresponding SQ dyes, **4a–4c**, are shown in Table 1. The effect of the two thio groups on the absorption spectra of DTSQ dyes **5a**–**5c**, compared with that of corresponding SQ dyes **4a**–**4c**, were defined as the difference in λ_{max} i.e. $\Delta\lambda$. In dyes **5a**–**5c**, inclusion of thio groups produced a bathochromic shift of 27, 27, 23 nm on corresponding dyes **4a** with **5a**, **4b** with **5b** and **4c** with **5c**. The PPP-MO results reproduced the observed values of λ_{max} and $\Delta\lambda$, values in Scheme 2.

It was found that responsible agreement between experimental and calculated λ_{max} values could be obtained. The π electron density changes accompanying the first excitation are shown in Fig. 3. We found that the calculated

TABLE 1
Data of DTSQ Dyes **5a-5c** and SQ Dyes **4a**–**4c**

Dye	*Yield (%)* Method A	*Yield (%)* Method B	$\lambda_{max}{}^{a}$ (nm)	$\Delta\lambda^{b}$ (nm)	ε^{a} ($\times 10^{-5}$)	M.p (°C)	Analysis (%)[c] Found (Calcd.) C	H	N	S
4a[d]	—	—	654	—	1.33	271	78.45 (78.75)	6.20 (6.10)	7.09 (7.06)	—
5a	46	93	681	27	1.34	268	73.14 (72.89)	5.20 (5.69)	6.29 (6.54)	14.92 (14.95)
4b[d]	—	—	633	—	3.21	300	79.03 (79.21)	6.86 (6.64)	6.70 (6.60)	—
5b	39	53	660	27	0.96	269	73.35 (73.68)	6.13 (6.13)	5.93 (6.13)	13.73 (14.04)
4c[d]	—	—	639	—	8.30	299	78.52 (78.64)	6.75 (6.98)	7.28 (7.42)	—
5c	32	—	658	23	1.37	271	74.47 (74.38)	6.99 (6.60)	5.64 (5.78)	13.41 (13.24)

[a]Measured in $CHCl_3$.
[b]$\Delta\lambda = \lambda_{max\,5a\sim c} - \lambda_{max\,4a\sim c}$.
[c]Elemental analysis of DTSQ.
[d]See ref. 5.



4b 5b

	4b	5b	
Cal.(nm)	644	674	$\Delta\lambda_{cal.}$;30nm
Obs.(nm)	633	660	$\Delta\lambda_{obs.}$;27nm
f(oscillator strength)	1.21	0.92	
ε ($\times 10^{-5}$)	3.21	0.96	

Scheme 2 Comparison between experimental and calculated visible absorption spectra of DTSQ and SQ dye.

electron density changes showed a pronounced migration of electron density from the thiolate group into central bridging carbon atom.

The visible absorption of DTSQ were studied in the different solvent having a different polarity. Results of the bathochromic behavior of DTSQ are given in Table 2. The λmax values of DTSQ showed hypsochromic shift with an increase in the solvent polarity, and these DTSQ thus have a large dipole moment in the ground state than in the excited state.

DTSQ exhibit an intense and narrow absorption peak at around 630–650 nn. In the solid state, the absorption spectra of DTSQ exhibit a broad absorption covering the wavelength region from 500 to 800 nm (Fig. 4). It is well known that the λmax of dyes in the solid shift to longer wavelengths compared with those in solution because of the stronger molecular interactions of dye molecules in the solid state.

Electrophotographic characteristics

The elcctrophotographic properties of the DTSQ synthesized were studied in dual layer photoreceptor devices. The characteristics of photoreceptor was measured by an apparatus, which is shown in Fig. 5.

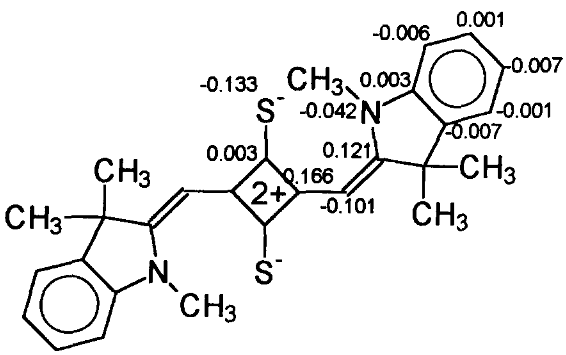


Fig. 3. π-electron density changes accompanying the first excitation of DTSQ dye.

TABLE 2
Absorption Spectra of DTSQ in Organic Solvents

Dye	*Benzene (nm)*	*1,4-Dioxane (nm)*	*$CHCl_3$ (nm)*	*CH_3CN (nm)*	*MeOH (nm)*	$\Delta\lambda^a$
5a	693	688	681	676	677	27
5b	673	665	660	648	647	26
5c	673	665	658	650	648	25

[a] $\Delta\lambda = \lambda_{MeOH} - \lambda_{Benzene}$.

Photoinduced discharge curves (PIDC) were measured in terms of surface potential vs time. V_o is the initial dark potential before white light irradiation. DD is the average potential of dark decay. $E_{1/2}$ is the exposure for surface potential to a half decay. Figure 6 shows a typical charging and photoinduced discharging curve (PIDC) of the negatively charged DTSQ photoreceptor with white light exposure.

Table 3 shows the sensitivity and dark decay properties of these DTSQ. The illumination intensity was fixed at 40 erg cm^{-2}. The results suggest that the introduction of an alkyl group onto the nitrogen of the indoline ring gives increased dark decay and photosensitivity.

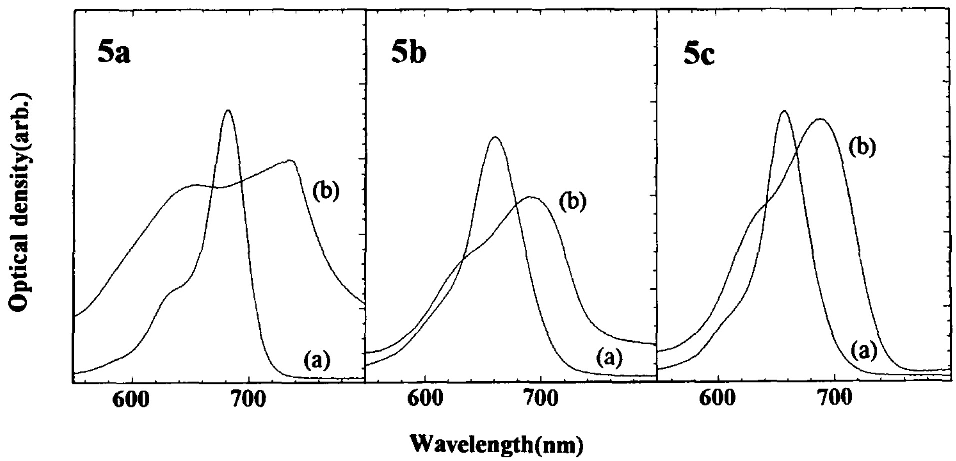


Fig. 4. Absorption spectra of DTSQ (a) in $CHCl_3$, (b) in solid film.

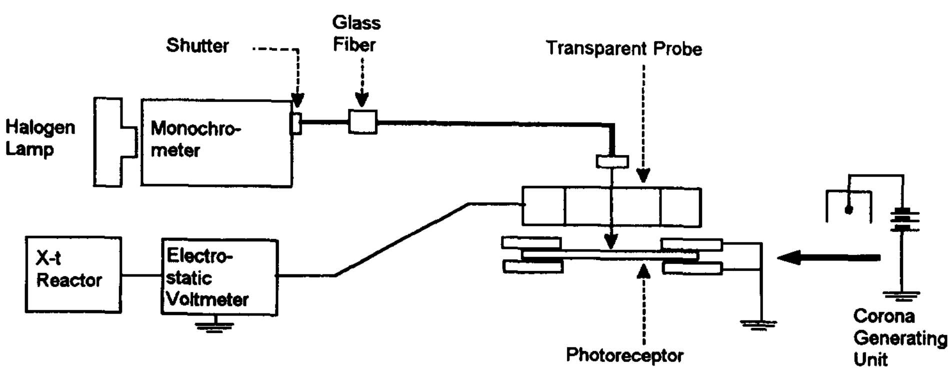


Fig. 5. Schematic illustration of electrophotographic process with charging and photoinduced discharging.

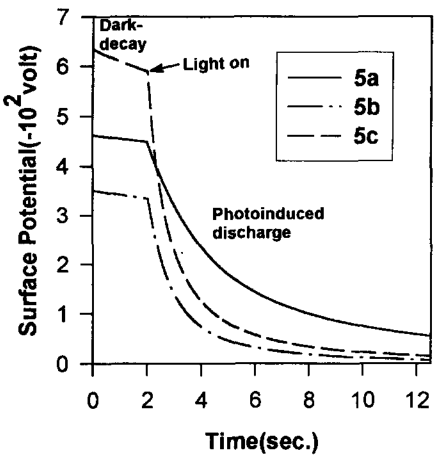


Fig. 6. Charging and photoinduced discharged characteristics of the photoreceptor utilizing DTSQ as the CGM.

TABLE 3
Electrophotographic Evaluation of DTSQ Dyes

Dye	*Initial potential* $(-V)\ V_o$	*Exposure potential* $(-V)\ V_i$	*Dark decay* $(Vs^{-1})\ DD$	*Half exposure* $(erg/cm^2)\ E_{1/2}$
5a	463	450	6.50	86
5b	351	335	8	29.6
5c	634	587	23.5	26.4

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