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Synthesis and characterization of novel squarylium dyes

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Abstract

Squarylium dyes based on 2,6-di-tert-butylpyrylium and 2,4-di-tert-butylpyrylium nuclei have been synthesized and characterized by elemental analysis, ^{1}H NMR, IR- and electronic impact mass spectroscopy. The dyes exhibit high melting points, good solubility in organic solvents and absorption maxima in the range of 711–763 nm with high extinction coefficients. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Squarylium dyes were first synthesized about 30 years ago [1]. This class of cyanine dyes is distinguished by their good photochemical stability and sharp absorption with high extinction coefficients in solution in the red and near IR region [2]. Due to the availability of easily modulating near-IR laser diodes, the preparation of squarylium dyes that are suitable for application as active media in optical information recording systems and other electrooptical areas has been of increasing interest.

A wide range of squarylium dyes has been synthesized. While many of these dyes are sparingly soluble in most common solvents, the solubility is, to some extent, an important criterion for the use of these squarylium dyes in near-IR region. As is well known, for the same length of polymethine chain, pyrylium nuclei and its derivatives give large bathochromic shifts when incorporated in methine and polymethine dyes, much larger than with most other heterocyclic nuclei [3,4]. Squarylium dyes based on 2,6-di-tert-butyl pyrylium nuclei or 2,4-di-tert-butylpyrylium nuclei (dye **1**,**5**) not only have absorption maxima in the near-IR region, but also are sufficiently soluble to be coated in thin film for a variety of applications. The patent literatures [5–8] has reported the use of these dyes in optical recording systems, thermal printing, liquid crystal cells and other areas.

It is known that increasing the effective electron releasing ability of terminal groups, or modifying the polymethine bridge between the termini by introducing electron-withdrawing or donating groups at the appropriate position, can result in a bathochromic shift in the absorption spectrum of a cyanine dye. We have now synthesized five squarylium dyes based on 2,6-di-tert-butylpyrylium nuclei and 2,4-di-tert-butylpyryliun nuclei (Chart 1) and studied their absorption spectra.

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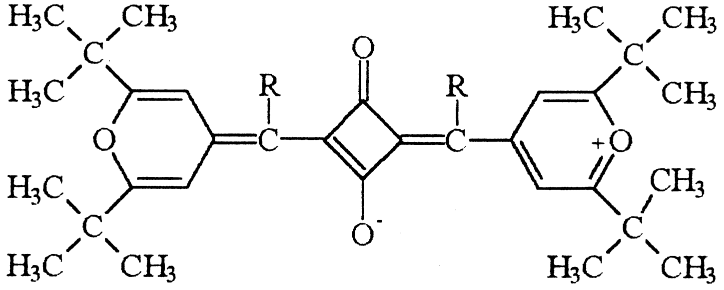

1. R = H

2. R = CH_3

3. R = CH_2CH_3

4. R = 

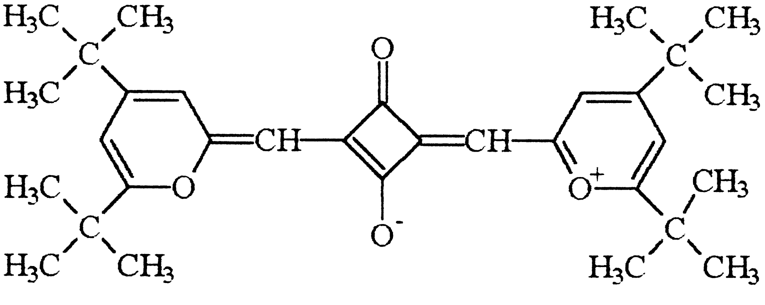

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Chart 1. Structures of the squarylium dyes.

2. Results and discussion

2.1. Synthesis of squarylium dyes

Traditionally, squarylium dyes are synthesized by condensing 1 equiv. of squaric acid and 2 equiv. of electron-rich aromatic, heteroaromatic or olefinic compounds in an azeotropic solvent. This procedure has been reviewed several times in the literature [9–11]. In a similar manner, we condensed 4-methyl-2,6-di-tert-butylpyrylium perchlorate, 4-ethyl-2,6-di-tert-butylpyrylium perchlorate, 4-propyl-2,6-di-tert-butylpyrylium perchlorate, 4-benzyl-2,6-di-tert-butylpyrylium perchlorate and 6-methyl-2,4-di-tert-butylpyrylium tetrafluoroborate with squaric acid in refluxing ethanol in the presence of dry pyridine to give dyes (**1**–**5**), respectively. The results are listed in Table 1.

2.2. Structure elucidation

Elemental analyses and electronic impact mass spectra data are shown in Table 1. The results are consistent with the structure of the dyes (**1**–**5**). In the IR spectra of these squarylium dyes, the skeletal vibration of the pyran heterocycle is observed at 1600–1400 cm^{-1}. The C=O stretching does not appear in the region of 1800–1650 cm^{-1}, but strong absorption bands at ~1630 cm^{-1} are observed, attributable to the C=C stretching in the four-membered ring and the heteroaromatic ring. The absence of any C=O stretching at ~1700 cm^{-1} is a strong indication of extensive bond delocalization in these squarylium dyes.

Since the squarylium dyes prepared in this work have good solubility, solution ^{1}H NMR spectra were able to be recorded. Results in Table 2 show that the chemical shifts of all tert-butyl protons are observed at 1.11~1.27 ppm. Two singlets at δ~6.20 and δ~8.50 ppm are assigned to the heteroaromatic protons. In dye **1** and dye **5**, a signal at 5.80 ppm is observed due to the =CH– group between the heteroaromatic ring and squaric-acid ring. In dyes **2**, **3** and **4**, this signal disappears, but signals for the methyl, ethyl and phenyl protons, respectively, are observed in the expected region.

2.3. Absorption spectra

The squarylium dyes exhibited intense and sharp absorption bands in the near-IR. Their absorption maxima (λ_{max}) varied from 711 to 763 nm, with a high extinction coefficients, $>10^5$ cm^{-1}M^{-1}; abortion data are given in Table 2.

Bigelow and Freund have studied theoretically the ground-state and the excited-stated electronic structures of bis [4-(dimethyl amino) phenyl]

Table 1
Synthesis and characterization data

Compound	Yield	MP	EI mass spectroscopy		Elemental Analyses	
	(%)	(°C)	M/Z	Rel. int (%)	C (Found)	H (Found)
1	60	240–242	490	100	78.36 (78.04)	8.57 (8.71)
2	57	269–272	518	100	78.76 (78.43)	8.88 (8.96)
3	35	232–234	547	100	79.12 (79.22)	9.16 (9.30)
4	30	278–280	643	100	82.24 (82.12)	7.79 (7.89)
5	30	239–240	490	100	78.36 (78.26)	8.57 (8.68)

Table 2
Spectroscopic properties of the squarylium dyes

Compound	IR (cm^{-1})	^{1}H NMR CDCl$_3$ (**1,2,3,5**), CD$_2$Cl$_2$ (**4**), ppm from TMS	λ_{max} (nm)	logϵ (CHCl$_3$)
1	1638(s), 1600(m), 1560(w), 1488(s), 1458(w)	1.20(s,18H), 1.27(s,18H), 5.80(s, 2H), 6.18(s, 2H), 8.60(s, 2H)	711	5.52
2	1638(s), 1951(m), 1560(w), 1470(s), 1472(m)	1.26 (s, 36H), 2.20 (s, 6H), 6.25(s, 2H), 8.75 (s, 2H)	763	5.39
3	1632(s), 1600(m), 1560(w), 1460(s), 1415(s)	1.03(t, 6H), 1.23(s, 36H), 2.75-2.90 (m,4H), 6.27(s,2H), 8.61 (s,2H)	759	5.35
4	1634(s), 1608(s), 1560(w), 1458(m), 1415(w)	1.11-1.20 (m,36H), 6.02 (s,2H), 7.12-7.35 (m,10H), 8.58(s,2H)	759	5.22
5	1632(m), 1598(s), 1537(w), 1480(s), 1427(s)	1.18(s,18H), 1.21(s,18H), 5.81(s,2H), 6.03(s,2H), 8.83(s,2H)	730	5.02

squaraine [12]. From their study, we can conclude that both S_0 and S_1 states are intramolecular donor–acceptor–donor charge transfer (D–A–D CT) states. The heteroaromatic moieties and the oxygen atoms are electron donors and the central four-membered ring is an electron acceptor. There is a charge-transfer during $S_0 \rightarrow S_1$ electronic excitation, but the CT is primarily confined in the central C_4O_2 unit. It is implied that this localization of electronic transition has resulted in the narrow absorption band in solution, and the introduction of electron-releasing groups at the methine chain has given bathochromic shifts in absorption maxim.

A more detailed study on the effect of structural changes on the electronic spectra of these squarylium dyes is being performed and will be reported later.

3. Experimental

3.1. Materials

Squaric acid, 4-methyl-2,6-di-tert-butyl pyrylium perchlorate, 4-ethyl-2,6-di-tert-butylpyrylium perchlorate, 4-propyl-2,6-di-tert-butylpyrylium perchlorate, 4-benzyl-2,4-di-tert-butylpyrylium perchlorate and 6-methyl-2,4-di-tert-butylpyrylium tetrafluoraborate were prepared as described in the literature [13,14]. All solvents were of commercial quality and were used without further purification.

3.2. General

All melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed on a MOD-1106 and electron impact mass spectra were recorded on an HP 5989A spectrometer. Proton-NMR spectra were taken on an AM-300 (300 MHz) instrument at room temperature. IR spectra were obtained on a 5SXC spectrometer (KBr) and absorption spectra on a Shimadzu UV-260.

3.3. Preparation of dyes

Squaric acid (5 mmol) and the substituted pyrylium perchlorate or tetrafluoraborate (10 mmol) were dissolved in 30 ml of refluxing ethanol and 11 mmol of pyridine in 8 ml ethanol was then added dropwise. The resulting solution was stirred at reflux for 12–15 h. The reaction mixture was concentrated *in vacuo* and the residue was purified via chromatography on silica gel (100–200 mesh) using dichloromethane–ethyl acetate (16:10) as eluent.

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