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Synthesis and Spectral Characteristics of Some Highly Soluble Squarylium Cyanine Dyes

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ABSTRACT

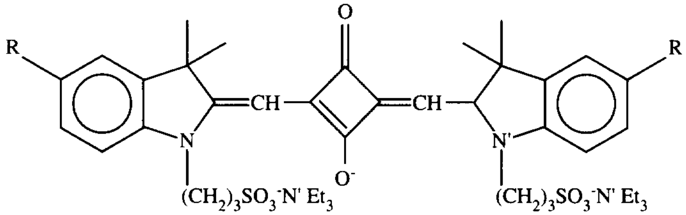
The synthesis of eight novel squarylium cyanine dyes is described. The dyes exhibit high solubility in organic solvents due to the introduction of the 1-sulfonatopropyl group onto the N-atom of the indolenine moiety. The condensation of the indolenine with squaric acid preceded smoothly, the reaction being catalyzed by a weak base. Spectral parameters of the dyes were correlated with the nature of the 5-substituent in the indolenium moeity. All the substituents studied in this work gave a bathochromic effect on absorption and emission, as well as enhancing the fluorescence quantum yield. The effects increased with the electron-donating ability of the substituent, due to involvement of the donor moiety in $S_0 \rightarrow S_1$ *excition and stabilization of the excited state. © 1997 Elsevier Science Ltd*

INTRODUCTION

Squarylium dyes have attracted a great deal of attention because of their potential application in xerography [1, 2], photovoltaics [3, 4], optical recording media [5, 6], nonlinear optics [7–9] and photography [10], and their spectral properties, such as photoconductivity, and sharp and intense absorption in the visible or near IR regions [11–13]. Many squarylium have been synthesized [14, 15], but their poor solubility restricts some potential end-uses [17]. We have now improved the solubility of such dyes by introducing the 1-sulfonatopropyl group onto the N-atom of the heterocyclic moiety, followed by subsequent quaternization.

The structural modification of squaraines has been a very popular research topic since the original report of their synthesis [14]. Essentially three types of substituents have been investigated, namely different substitutents on the C- or N-atom of the aromatic heterocycle, or the use of different N-heterocycles. Among the squaraines reported so far, some reports have described the influence of changing the N-heterocycle [16] and introducing alkyl (mainly methyl or ethyl) on the N-heteroatom.

In contrast to squarylium dyes with different substituents at the N-atom of the heterocycle, the influence of substituents in the carbocyclic ring have been less reported. However, according to our research on cyanine dyes, such substituents can affect the photophysical and photochemical properties of the dyes. We have therefore synthesized a series of indolenium squarylium cyanine dyes with different substituents in the carbocyclic ring, in order to study their effects on some photophysical and photochemical properties. We report here initially, the synthesis and spectral characterization of general formula **1**.



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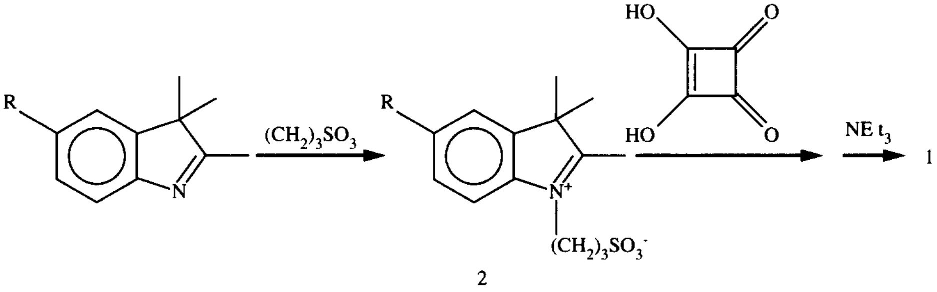
RESULTS AND DISCUSSION

Dye synthesis

The squaraines were synthesized (Scheme 1) from squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) and 5-substituted-(1-sulfonatopropyl-2,3,3-triethylindolenine (**2**), by reference to established literature procedures, but with a few modifications [18].



Scheme 1 Synthesis of squarylium cyanine dyes.

Typically, 2,3,3-trimethylindolenine and 3-propansultone were heated at 100–120°C for 9 h to give 1-sulfonatoprophyl-2,3,3-trimethyl indolenine (**2**) [19]. Squaric acid and **2** in 1-butanol/pyridine were refluxed for 6–8 h, giving a green-coloured solution. After cooling, the precipitate was filtered, washed, and then quaternized with triethylamine and column chromatography then afforded bright green crystals of **1a** in 11.8% yield.

In the condensation, pyridine acted as catalyst; this implies that the reaction is base-catalyzed. However, when pyridine was replaced by a stronger base such as triethylamine, the reaction failed to produce product **1**. Instead, a brownish solution was obtained, which was not studied further.

Chromatography was necessary in many cases to obtain pure **1**, and yields were consequently low. When R was a halogen, purification could be affected by recrystallization and in these cases, yields were in the order of 30%.

Vis, IR and ^{1}H NMR spectra of the squaraines

Vis spectra

The results in Table 1 show that all squaraines exhibit an intense absorption ($\epsilon > 3{\cdot}0 \times 10^5$ cm^{-1} M^{-1}) in the visible region in methanol solution, similar to those of other squaraines reported in the literature. The large extinction coefficient and narrow bandwidths are consistent with the D–A–D electron-transfer (CT) character of the $S_0 \rightarrow S_1$ absorption.

Substituent at C-5 of the indolenium moiety generally produced bathochromic effects on the λ_{max} (Table 1). The red shifts are small (< 24 nm), however, and are attributable to the minor involvement of the D moiety in the CT excitation [19]. Since the excited state of squaraine is a D–A–D CT state, it is intuitively expected that the red-shift should increase as the electron-donating ability of the substituent at C-5 increases. Accordingly, the expected order of red-shift should be $OCH_3 > CH_3 >$ Br, Cl, F $> CO_2H > NO_2$,

TABLE 1

Absorption and Fluorescence Data of Dyes[a]

Compound	λ_{max}^{ab} *(nm, lgε)*	λ_{max}^{ex} *(nm)*	λ_{max}^{em} *(nm)*	ϕ_f
1a	628 (5.45)	632.5	651.0	0.09
1b	636 (5.40)	639.5	660.0	0.15
1c	650 (5.19)	640.0	672.0	0.15
1d	628 (5.51)	632.5	652.0	0.08
1e	634 (5.36)	639.0	658.0	0.17
1f	634 (5.35)	639.5	660.0	0.15
1g	640 (5.19)	642.5	663.5	0.37
1h	652 (5.48)	641.5	680.0	0.01

[a] Solvent: methanol.

but the reverse order was observed. Compounds **1g** and **1h** also exhibited a larger red-shift, which can be attributed to the involvement of the COOH and NO_2 groups into the π system.

Halogeno substitution at the C-5 position was expected to give interesting results because of its σ electron-withdrawing nature and π electron-releasing nature. Since an electron-withdrawing group is expected to produce a blue-shift on λ_{max}, the observed red-shift for Cl and Br at C-5 is indicative of CT stabilization in the excited state. For substitution λ_{max} was equivalent to that of the unsubstituted dye, which implies that the contribution of the two opposing effects (−I, +M) balance out for their overall influence on λ_{max}.

In addition to the relatively large red-shifts, a decrease in ϵ was also observed. It is known that the absorption of the coefficient of the CT state decreases as the CT interaction between the D–A moiety increases [20].

IR spectra

All the squaraines exhibited IR absorption at $\sim 1600\ cm^{-1}$, as shown in Table 2. These bands are attributable to the C—C band stretching of the aromatic heterocycle and the four-membered ring. The absence of any C=O stretching at $\sim 1700\ cm^{-1}$, expected for **1g**, is an indication of the extensive band delocation in these squaraines. Similar results have been reported for other squaraines [21].

^{1}H NMR

All the squaraines were sufficiently soluble in methanol for the ^{1}H NMR studies. Table 3 shows that all the dyes showed two singlets, one at $\delta 5.90 \sim 6.02$ which is assigned to the =CH- group between the indolium and squaric ring, the other at $\delta 1.75$–1.76 which is assigned to the methyl group at the C-3 of the indolium moiety.

TABLE 2
IR and ^{1}H NMR Spectra Data of the Dyes

Compound	IR[a] (cm^{-1})	^{1}H HMR[b]							
1a	1614, 1595	1.30(*t*)	1.76(*s*)	2.30(*f*)	3.02(*t*)	3.20(*q*)	4.35(*t*)	6.02(*s*)	7.20–7.50(*m*)
1b	1615, 1596	1.30(*t*)	1.76(*s*)	2.35(*f*)	3.08(*t*)	3.20(*q*)	4.35(*t*)	5.98(*s*)	7.10–2.02(*s*) 7.30(*m*)
1c	1595, 1552	1.30(*t*)	1.76(*s*)	2.25(*f*)	3.02(*t*)	3.30(*q*)	4.30(*t*)	5.90(*s*)	7.00–3.85(*s*) 7.40(*m*)
1d	1620, 1597	1.30(*t*)	1.76(*s*)	2.25(*f*)	2.98(*t*)	2.98(*q*)	4.33(*t*)	5.98(*s*)	7.10–7.40(*m*)
1e	1597, 1491	1.30(*t*)	1.76(*s*)	2.28(*f*)	2.98(*t*)	2.98(*q*)	4.33(*t*)	6.02(*s*)	7.30–50(*m*)
1f	1595, 1491	1.30(*t*)	1.75(*s*)	2.25(*f*)	2.95(*t*)	2.95(*q*)	4.33(*t*)	6.00(*s*)	7.30–60(*m*)
1g	1776, 1610								
	1693,								
1h	1610 1487								

[a]KBr; [b]CD_3OD as solvent.

The aromatic protons in the phenyl ring are at δ7.00–7.60 ppm; the N-ethyl- group of the triethylamino residue shows a quartet at δ3.20–3.30 ppm and a triplet at δ1.30 ppm with an integration of 2–3. The sulfonatoprophyl group shows one quintet at δ2.25–2.30 ppm and two triplets at δ4.30–4.35 and 2.95–3.08 ppm, respectively. The methylene group attached to the N-atom of the indolenium system has a larger chemical shift than that attached to the sulfonate group.

Fluorescence spectra

Figure 1 shows the absorption and emission spectra of **1a** in methanol. The fluorescence spectrum is a reasonably good mirror image of the absorption spectrum and the Stokes' shifts are rather small, within the range of 23–28 nm, indicating negligible reorganization effects and small geometry changes between the ground and excited singlet state. This result is consistent with the earlier MNDO and CNDO calculation results of Bigelow and Freund, who showed that the $S_0 \rightarrow S_1$ transition of bis[4-(dimethyl amino)phenyl]-squaraine on optical-excitation is primarily confined in the central C_4O_2 unit [19]. Such a transition would lead to negligible reorganizational and structural changes. In each case, the excitation spectrum was found to be independent of the monitoring wavelengths and was identical with the absorption spectrum. The spectral results, which are summarized in Table 1, show that the C-5 substituent exerts a relatively minor bathechromic effect on the emission, as compared to absorption and excition.

Fluorescence quantum yield

The results in Table 1 show that substituents at the C-5 position exert a large effect on the ϕ_f value. The fact that the ϕ_f increases as the electon-donating

TABLE 3

Compound	*R*	*Yield (%)*	*Calculated (%)*			*Found (%)*		
			C	*H*	*N*	*C*	*H*	*N*
1a	H	11.8	62.83	7.67	6.66	62.34	7.34	6.50
1b	CH_3	8.6	63.57	7.89	6.45	63.43	8.21	6.15
1c	OCH_3	10.1	61.31	7.61	7.12	61.23	7.98	6.62
1d	F	20.6	60.25	7.12	6.39	59.98	7.41	6.18
1e	Cl	26.4	58.07	6.87	6.16	58.18	7.08	6.06
1f	Br	30.3	52.91	6.26	5.61	52.64	6.53	5.19
1g	CO_2H	12.3	59.46	6.95	6.03	58.90	6.43	5.91
1h	NO_2	9.1	56.76	6.71	9.03	56.45	6.27	8.84

ability of the substituent increases indicates that the stronger the interaction of the D–A moiety, the more stable is the excited state. It is interesting to note that **1g** exhibits a larger ϕ_f value than the other compounds. This suggests that the CO_2H group is dissociated in solution to the CO_2^- group, which exerts an electron-donating effect.

EXPERIMENTAL

Materials

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, Aldrich) and propane sulfone (Aldrich) were of reagent grade and used without further purification. All the indolenines (5-substituent-2,3,3-trimethylindolenines) were synthesized according to the Fischer–Indole synthesis [22], and were purified by reduced pressure distillation, except for the 5-carbonyl-2,3,3-trimethylindolenine derivative, which was recrystallized. Organic solvents were of reagent grade and were used after distillation, solvents for the spectroscopic determinations were of reagent grade and were dehydrated before use.

General techniques

Visible and IR spectra were meaured using Hitachi UV8451A and Perkin-Elmer 683 spectrometers, respectively. Elemental analyses was performed on a Carlo-Erba 1102; fluorescence spectra were recorded on a Hitachi MPF-4. ^1H NMR was taken using a Brucker AC 200, and TMS as internal

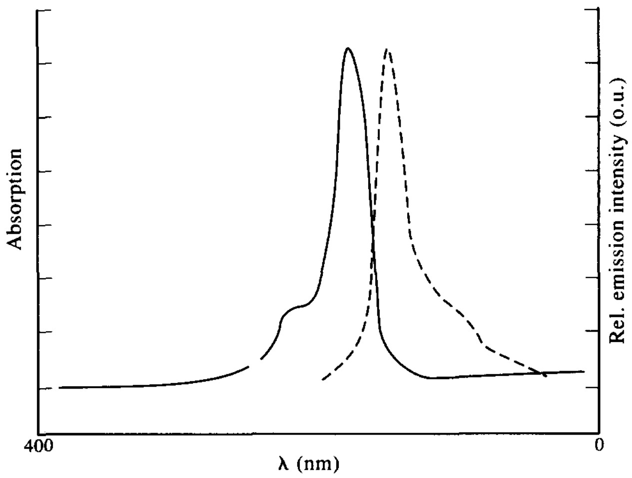


Fig. 1. Absorption and emission spectra of **1a** in methanol.

standard. Fluorescence quantum yield was measured by the relative method. Bis(3-ethylbenzothiazol-2-ylindene)squaraine was used as reference and synthesized according to the literature method [23], and was characterized on the basis of analytical results. Column chromatography was carried out on silica gel (300 mesh) using chloroform/methanol as eluent.

Squaraine synthesis

Equivalent molar amounts of the indolenine and propane sulfone were mixed and heated at 100–120°C for 9 h under nitrogen. After cooling, the black solid was powdered and washed several times. The intermediate *2* was thus obtained and used in later condensations without further purification.

One equivalent of squaric acid and two equivalents of **2** in 1-butanol/pyridine (10:1, v/v) was refluxed for 8 h. Two work-up procedures were used, namely:

*Recrystallization (**1d–f**)*

After cooling, the product was filtered and then washed with ether. After adding a slightly greater equivalent excess of triethylamine, crystals were formed; recrystallization then gave the pure products **1** (from methanol).

*Chromatography (**1a–c,g,h**)*

After cooling, the produce was precipitated by addition of ether and then filtered. After reacting with triethylamine and removing the solvent, the squaraine produce was isolated from the residue by column chromatography on silica gel using choloroform/methanol as eluent.

All products obtained were analytically pure. Pertinent results are given in Table 3.

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