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The Influence of *N*-Alkyl Groups on the Properties of Squarylium Cyanine Dyes

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ABSTRACT

Dyes with strong intermolecular interactions often exhibit low solubility, which restricts their application in some areas. Solubility can be improved by introducing substituent groups with a steric hindrance capacity. By enlarging the intermolecular distance, the interaction can be reduced, and so the solubility is higher. In this report, bis(2,3,3-trimethylindolenium-2-ylidene) squaraines with different branch chain alkyl groups on the nitrogen atom were synthesized and the relationship between substituents and solubility in different solvents, melting point and photophysical properties in solution are discussed. © 1998 Elsevier Science Ltd. All rights reserved

1 INTRODUCTION

Squarylium cyanine dyes have attracted much attention because of their potential application in optical recording media [1], electrophotographic receptors [2], gas sensors [3] and solar cells [4]. They often exhibit sharp and intense absorption in the visible region in solution. In the solid-state, owing to strong intermolecular donor–receptor charge transfer interactions [5], the absorption becomes very broad, typically exhibiting two bands, one of which is blue-shifted (500–600 nm) and the other red-shifted, spreading into, the NIR region [6].

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For bis(2,3,3-trimethylindolenium-2-ylidene) squaraines, their absorption and reflection properties at 600–650 nm in film make them potentially useful in recording media for DVD-ROM.[†] One of the drawbacks, however, is their low solubility.

One approach in structural modification is to introduce an alkyl group onto the N-atom of the heterocyclic moiety in order to improve solubility. We have synthesized a series of indolenium squaraine dyes containing a 3-sulfonatopropyl (triethyl amino salt) group on the N-atom of the indolenium moiety [7]. This structural modification, whilst giving increased solubility, resulted in another difficulty, i.e. the dyes were readily soluble in water, and this factor was severely detrimental to their use in optical recording media. In order to obtain an ideal material for the DVD-ROM, it seemed necessary to correlate the nature of the *N*-alkyl group with solubility.

Since the main reason for the low solubility is the strong intermolecular interaction, and this interaction is dependent on the intermolecular distance, it was thought that an increase of the intermolecular steric hindrance would produce a large intermolecular distance, thus decreasing the lattice energy and giving good solubility. We therefore synthesized a series of bis(2,3,3-trimethylindolenium-2-ylidene) squaraines with different branch chain alkyl groups on the N-atom, in order to correlate the effect of substituent chain branching on the melting point, absorption and emission behavior of the dyes.

2 RESULTS AND DISCUSSION

2.1 Synthesis

The synthesis of the dyes is shown in Fig. 1. Alkylation of the indolenine was carried out by heating the indolenine and alkyl iodide at 100–120°C; excess alkyl iodide (*ca.* 3–5 equal.) was often necessary because the indolenine was readily oxidized at high temperature. After cooling, the precipitate was filtered and recrystallized; the resulting pure indolenium alkyl iodides were obtained at a yield of 60–80%.

The squaraine was obtained by condensation of squaric acid and the appropriate indolenium alkyl iodide in *n*-butanol/pyridine (5:1 v/v) under reflux. After concentration, isolation and recrystallization from alcohol, the pure dyes were obtained at a 40–60% yield. Product data are given in Table 1.

[†] This is from our experimental result and we will report our result in a later paper.

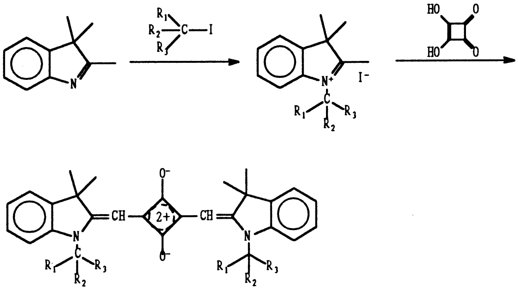

Fig. 1. Synthesis of the indolenium squaraine dyes.

2.2 Absorption and emission spectra

All the dyes exhibited, in ethanol, sharp and intense absorption bands with $\lambda_{\max}$ in the range 626–640 nm; relevant data are summarized in Table 1(a). The small bathochromic shift observed in these compounds is consistent with the MO calculation results in that the charge transfer during excition is primarily confined in the central four-membered cycle of the squaraine moiety. Although there is an inductive stabilization of the excited D-A-D CT state by the *N*-alkyl group, the majority of dyes showed the same absorption maximum at 640 nm indicating that this effect is negligible. The blue shift in dyes **1**, **3**, and **8** is difficult to attribute to the inductive effect and is probably due to solvent effects.

The emission spectrum of dye **1** is shown in Fig. 2 and emission data of the dyes are given in Table 1(a). All the dyes exhibited a similar emission spectrum with reasonable ‘mirror image’ with the absorption; the Stokes’ shifts were small, ranging from 9 to 20 nm, which indicates a small geometry change between the ground and the singlet excited state. As with the absorption data, the *N*-alkyl substituent exerted only a small effect on the emission spectrum, all the dyes having the same emission maxium at 666 nm, except for dyes **1**, **3**, and **8**.

2.3 Solubility

Solubility data of the squarines in *n*-butanol and in chloroform are given in Table 1(b), from which it can be seen that the dyes exhibited very different solubility in these two solvents.

The squaraines can be divided into three main classes according to the nature of the *N*-alkyl group. Where the *N*-alkyl has two equivalent branched chains (dyes **1**, **6**, **7**), the squarine thus has four alkyl groups stretched out of the molecular plane, and the groups are arranged along the two sides of the

TABLE 1
Characterisation Data of the Dyes

(a)

No.	*R_1*	*R_2*	*R_3*	*Yield*	*Found*			*Cal.*		
				(%)	*C*	*H*	*N*	*C*	*H*	*N*
1	$-CH_3$	$-CH_3$	H	58.2	79.55	7.44	5.44	79.97	7.55	5.83
2	$-CH_3$	$-CH_3$	$-CH_3$	46.1	79.88	7.88	5.45	80.13	7.74	5.66
3	$-CH_3$	$-CH_2CH_3$	H	56.6	79.93	7.31	5.30	80.13	7.74	5.66
4	$-CH_3$	$-(CH_2)_2CH_3$	H	35.4	79.64	7.41	5.42	80.28	7.93	5.51
5	$-CH_3$	$-(CH_2)_4CH_3$	H	52.1	80.42	8.05	5.69	80.56	8.26	5.22
6	$-CH_2CH_3$	$-CH_2CH_3$	H	39.3	79.86	8.11	5.97	80.28	7.93	5.51
7	$-(CH_2)_2CH_3$	$-(CH_2)_2CH_3$	H	61.3	80.17	8.05	5.13	80.56	8.26	5.22
8	$-CH_2CH_3$	$-(CH_2)_2CH_3$	H	45.9	79.96	7.81	5.15	80.42	8.10	5.36
9		$-(CH_2)5-$	H	74.3	80.17	7.41	5.13	80.60	7.56	5.53
10	$-(CH_2)_6-$		H	41.7	80.34	7.17	5.11	80.73	7.874	5.38
10	$-(CH_2)_{y-}$		H	38.9	80.75	7.91	5.10	80.86	7.92	5.24

(b)

Compound	*m.p. (°C)*	*Solubility 1 (mg ml^{-1})^a*	*Solubility 2 (mg ml^{-1})^b*	λ_{max}^{ab} *(nm)^c*	λ_{max}^{em} *(nm)^c*
1	288–290	12.8	8.0	630	639
2	256–258	18.6	1.1	646	666
3	308–310	24.1	16.0	628	636
4	262–264	37.7	3.9	646	666
5	258–260	112.0	2.5	646	666
6	260–262	28.1	2.9	646	666
7	256–258	72.5	2.0	646	666
8	322–324	56.0	2.1	626	636
9	262–264	15.9	1.6	646	666
10	260–262	44.0	2.0	646	666
11	258–260	96.0	2.6	646	666

[a] Solvent is chloroform.
[b] Solvent is *n*-butanol.
[c] Solvent is ethanol.

plane (we refer to such dyes as class A). For dyes with two different branched chains, one a methyl group (dyes **1**, **3**, **4**, **5**), and the other a longer branched chain alkyl group, there are two branched chains stretching out of the plane of the dye (we refer to these as class B). Class C dyes were those with a cycloalkyl group (dyes **9**, **10**, **11**); the cycloalkyl group has more rigid properties, and the branched chain is stretched along the molecular plane.

2.3.1 Solubility in chloroform

As shown in Table 1(b), the solubility of dyes in chloroform is largely dependent on the length and the number of the branched chains. The solubility increases as the chain length increases, indicating that the branched chain exerts a large effect on the solubility in chloroform. Correlation of the

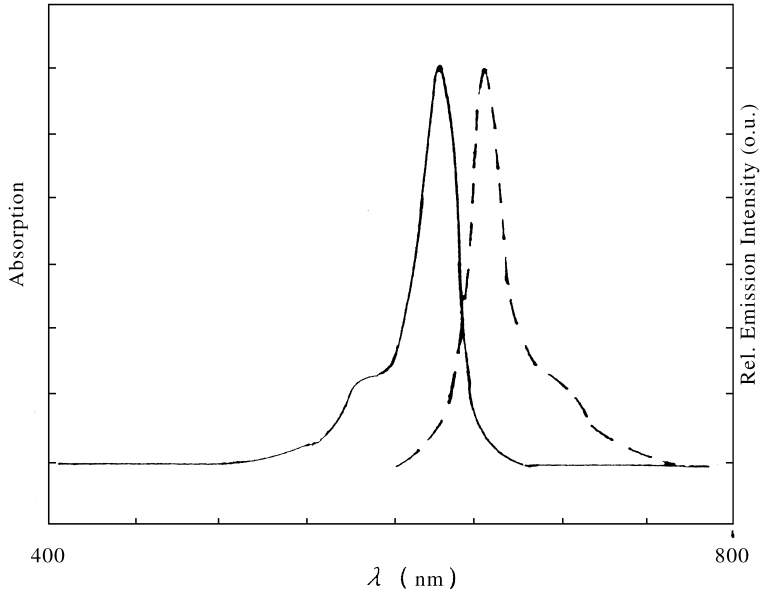

Fig. 2. The absorption and emission spectrum of squaraine 1 in ethanol: — absorption; – – – emission.

solubility with the branch chain length of the alkyl group is illustrated in Fig. 3. The solubility increases in the order: class A > class C > class B, which can be attributed to the substituent lyophilic effect. Since the dyes in class B have half the number of branched chains as the dyes in class A, it could be expected that the same ratio should be observed in the solubility. This is in accordance with the experimental data found when the branch chain was longer. When the branch chain was shorter (1–2 C-atom) the solubility was nearer to dyes in class A. This difference stems from the contribution of the methyl group (R1) to the solubility, this contribution becoming more negligible as the branch chain length increases.

For dyes in class C, although the extent of the branch chains is equal to those of the dyes in class A, the solubility was observed to be less than that of dyes in class A and larger than that of dyes in class B. This implies that the nature of the branch chain also exerts an effect on solubility. In class C, because of the nature of the cyclic system, the alkyl group aligns mainly along the molecular plane as the length increases. The dependence of the direction of the branch chain stretching on solubility indicates that the substituent affects dye–dye molecular interactions. Dye molecules with the substituent stretching out of the molecular plane will hinder the intermolecular strong CT interaction, and therefore dyes in class C have a stronger intermolecular interaction than dyes in class A.

2.3.2 Solubility in n*-butanol*

The results shown in Table 1(b), and correlation of the branch chain length with the solubility for class A, B and C are shown in Fig. 4. The fact that the solubility of the dyes in *n*-butanol was lower than that in chloroform, and decreased with the length and the number of the branched chain, suggests a totally different solvation mechanism of the dyes in butanol, from that in chloroform. The H–bond interaction in butanol results in them exhibiting a stronger solvent–solvent interaction and hydrophilicity. H–bond interaction also occurs between the hydroxyl group in butanol and the O-atom in the squaraines; this interaction is relatively weak because of the steric hindrance effect of the indolenium moiety [8] and because the dyes have the same structural framework, the difference in solubility mainly arises from the substituent effect. Increase in the length and number of the branch chain alkyl groups leads also to an increase of the lyophobic character which decreases solute–solvent interaction. This tendency was observed in dyes of class A and B, while the reverse trend was observed in dyes of class C. This indicates there are other causes beyond the amphiphilicity of the substituent.

The effect of the branch chain alkyl group on the solubility may arise from steric hindrance of interaction between the indolenium moieties of the dye and solvent. The O-atom and N-atom are negative centers, and the stretch of the branch chain out of the plane will block the O-atom in a solvent close to the heterocycles. As the length of the branch chain increases, the distance between the solvent layer and the indolenium moiety increases, and the solvation interaction decreases. The difference in solubility decreases as, the

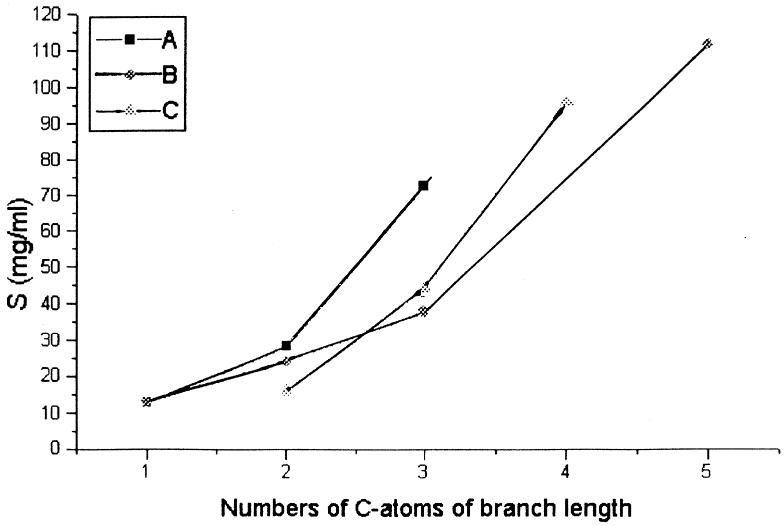

Fig. 3. The solubility of squaraines in chloroform.

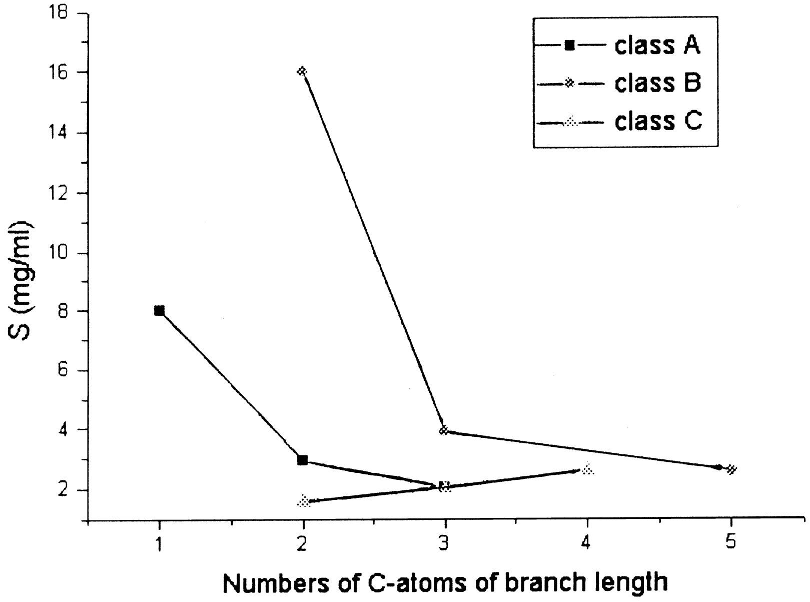

Fig. 4. The solubilities of squaraines in butanol.

length of the branch chain suggests that the steric effect tends to saturation as the chain length increases.

The reverse result was observed in dyes of class C, which exhibited a slight increase in solubility as the chain length increased, indicative of the direction effect of the branch chain on solvation.

2.4 Melting points

As shown in Table 1(b), the melting points of the dyes were high, ranging from 250 to 320°C. The relationship between the melting point (m.p.) and the branch length in classes A, B and C are shown in Fig. 5. The m.p. decreased as the length and number of branch chain alkyl groups increased, which indicates that the interaction among the dyes decreased as the steric hindrance of the branch chain increased, i.e. in accordance with our prediction on the effect of the substituent on lattice energy.

In dyes of classes A and B, the net steric effect decreased as the length of the branch increased, which can be attributed to the small rigidity in the alkyl chain. The effective length was about three C–C bonds. In dyes of class C, although these have a greater rigidity in the N-substituent, their small effect on the thickness of the dye makes them exert a minor effect on the lattice energy.

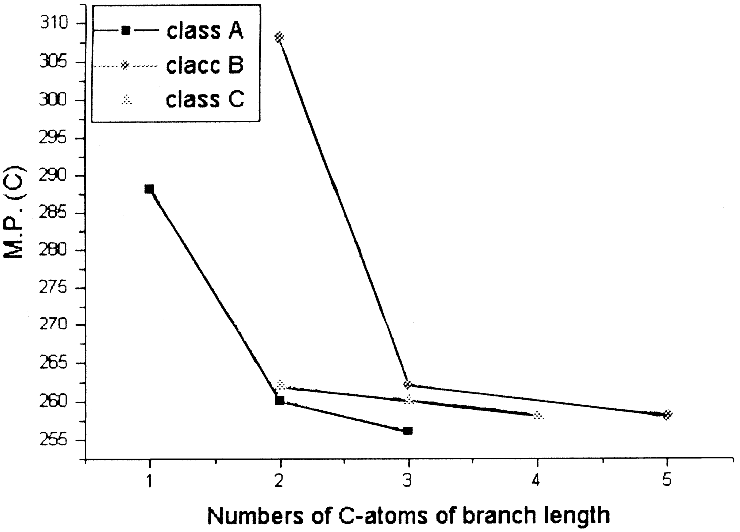

Fig. 5. The melting points of squaraines of classes A, B, and C.

3 EXPERIMENTAL

3.1 Materials and instruments

Squaric acid (Aldrich) was of reagent grade and used without further purification. The 2,3,3-trimethyl indolenines were synthesized according to the Fischer indol method [9], and were purified by reduced pressure distillation. The alkyl iodides were synthesized from the pertinent alcohol and PI_3 [10], and purified by distillation. Organic solvents were of reagent grade and were used after distillation. Visible and fluorescence spectra were measured using Hitachi Uv8451a and Mpf-4 spectrophotometers, respectively. MS were taken on a TRIO 2000 GC-MS.

3.2 Squaraine synthesis

One equivalent of the indolenine and five equivalents of the appropriate alkyl iodide were mixed and heated under reflux or at 100–110°C for 6 h. After cooling, the reaction mixture was stirred into ether and the resulting precipitate filtered, washed with ether, and recrystallized from acetone, to give the 1-alkyl-2,3,3-trimethyl indolenium iodide in a 60–80% yield.

One equivalent of squaric acid and two equivalents of the indolenium iodide in the mixture of 1-butanol/pyridine (5:1 v/v) was refluxed for 8 h, and the reaction solution was then concentrated and the residue recrystallized three times from aq. ethanol to give bright green crystals in a 30–40% yield.

4 CONCLUSIONS

From the results reported, it can be concluded that the branch chain alkyl groups on the N-atom exerted negligible effect on the absorption and emission spectrum. The small blue-shift in the absorption and emission in dyes **1**, **3**, and **8** may be attributed to solvent effects. The substituent effect on the solubility of the dyes can be divided into two factors, viz. branch chain contribution and steric effect. The branch chain contribution obeyed the 'like dissolves like' and so the substituent exerted a larger effect on the solubility in solvents such as chloroform. The solubility increased as the length and number of the substituent increased. In addition to the length and number the 'stretching' direction of the substituent also affected the solubility. This effect was, in fact, due to steric hindrance, which reduced dye–dye interaction. For a hydrophilic solvent such as 1-butanol, the negative effect of the branch chain arises from the nature of the salvation of the dye. Because the intermolecular distance of the dyes does not increase linearly with the length of the branch chain the lyophilic effect was mainly in the long chain alkyl group and so the reverse tendency was observed.

It can therefore be anticipated that the solubility of the dye will be further improved by introducing the branch chain alkyl groups containing a polar group, such as hydroxyl or carboxylate.

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