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Squaraine Chemistry. Synthesis and Characterization of Squaraine Dyes Having Self-Organizing Properties

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ABSTRACT

A series of mono-substituted N-alkylsquaraines of chain length varying from 2 carbons to 18 carbons have been synthesized by condensing 1-p-dimethylaminophenyl-2-hydroxycyclobutene-3,4-dione with N-methyl-N-alkylanilines. All the N-alkylsquaraines synthesized were soluble in chlorinated solvents and were purified by a solvent extraction technique. Their spectroscopic properties (IR, VIS, ^{1}H NMR and MS) were found to be typical of squaraines. Examinations of the solid-state properties of these materials, by solid-state absorption spectroscopy and by X-ray powder diffraction technique, indicate that the molecules of N-alkylsquaraines form microcrystalline aggregates, analogous to those observed in their photoconductive pigmentary analogs, in the solid state. This observation is in contrast to that seen in other soluble squaraines, where the aggregation is usually perturbed by solubilizing groups. This unique aggregational behavior leads us to propose that there exists a dual intermolecular interaction in the microcrystalline state of N-alkylsquaraines. In addition to the expected intermolecular donor–acceptor interaction between the squaraine chromophores, a hydrophobic interaction between N-alkyl groups occurs. The N-alkyl groups in these materials not only solubilize the squaraine but also provide a proper orientation for the aggregation process. This model suggests that N-alkylsquaraines should have the ability to self-organize and form photoconductive aggregates under various processing conditions. This ability has been verified in the case of solution cast thin films by absorption spectroscopy.

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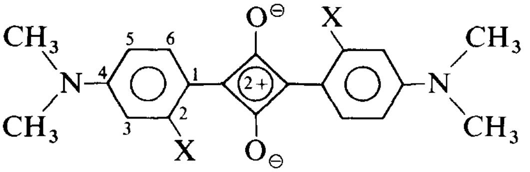
1 INTRODUCTION

Organic materials, such as dyes and pigments, have been widely used as colorants for cottons and fabrics for centuries. More recently, they are also found to be useful as functional materials in modern electronic devices.[1] High-technology applications include the use of colorants in photographic films, toners, inks, etc., as light absorbers in color filters, optical discs or displays; and as photoconductors in solar cells or xerographic photoreceptors. In these applications, the colorant molecules not only have to possess the desirable spectral characteristics, but also the intended electronic function. However, there has always been a controversy as to whether a dye or a pigment should be used. A dye is a soluble material and can be purified and processed by conventional techniques. The drawback in using a dye in devices is that the light and wet fastness of dyes are usually worse than those of pigments. Moreover, dye molecules form aggregates in devices. The aggregation of the dye may vary, depending upon the thermodynamics of the system and the kinetics of the processing conditions.[2,3] As a result, variation in electronic properties occurs. Although manipulation of a dye into a specific aggregated form is possible, such a manipulation generally translates into a narrower process latitude and an increased processing cost. Pigments, on the other hand, are insoluble materials. Being insoluble, the choice of the aggregated form may be limited; but once a desirable aggregation is attained, it would not be altered easily. The water and light fastnesses of pigments are generally good. Unfortunately, the insolubility of pigments has led to purification and processing problems. The dilemma of choosing a dye or a pigment continues.

Bis(4-dimethylaminophenyl)squaraine (HSq) and its 2-substituted derivatives are well-known IR-sensitive photoconductors for xerographic application.[4] They can be synthesized either by condensing one equivalent of squaric acid with two equivalents of an aniline derivative under an azeotropic condition,[5] or by reacting a dialkylsquarate with an aniline derivative in the presence of an acid catalyst in water-saturated 1-butanol.[6]



HSq, $X = H$

HSq and its derivatives are pigmentary and are used as synthesized in xerographic devices. Procedures to purify them to improve their xerographic performance have yet to be developed. Structural modification of squaraine using solubilizing groups, which enables processability and purification, has been a popular research topic.[7] Unfortunately, solubilizing groups usually disturb the aggregation of squaraine and adversely affect the photoconductivity.[8] The goal of synthesizing a soluble, photoconductive squaraine remains a challenge.

Here a novel concept for synthesizing soluble, photoconductive squaraines is described. In this new approach, the aggregation of the squaraine chromophores in the microcrystalline state is controlled by two different intermolecular interactions, namely donor–acceptor interaction between squaraine chromophores and hydrophobic interaction between solubilizing groups. A series of mono-substituted *N*-alkylsquaraines were synthesized and are shown to meet the design goal of aggregation. These materials exhibit excellent solubility in chlorinated solvents, while forming aggregates analogous to that of HSq in the solid state.

2 EXPERIMENTAL

2.1 Materials

Iodoethane, iodobutane, bromooctane and bromododecane were purchased from Eastman (Rochester, NY, USA) and bromohexadecane, and *N*-methylaniline from Aldrich (Milwaukee, USA). Sodium acetate (anhydrous), 2-propanol, *N*,*N*-dimethylformamide, chloroform and ether (anhydrous) were certified grade from Fisher (Pittsburgh, USA). Tributyl orthoformate was obtained from Pfaltz & Bauer (Waterbury, CT, USA). The precursor for the squaraine synthesis, 1-*p*-dimethylaminophenyl-2-hydroxycyclobutene-3,4-dione, was synthesized by a cycloaddition–reductive alkylation–condensation reaction sequence. Procedure for the synthesis has been detailed elsewhere.[9]

2.2 General techniques

Melting points were taken on a capillary melting-point apparatus (invented by Thomas Hoover) and were uncorrected. Infrared spectra were determined on a Perkin-Elmer (Pittsford, USA) Model 1750 FTIR. Proton NMR spectra were recorded on a Bruker AM360 spectrometer. Absorption spectra were taken on a Hewlett-Packard (Fairport, USA) 8451 Diode Array Spectrophotometer. Mass spectra were recorded on a Varian (Palo Alto, USA) VG7035 mass spectrometer at the University of Rochester. Elemental analyses were performed by Galbraith Laboratories

TABLE 1

Synthesis, Properties and Spectroscopic Data of *N*-Methyl-*N*-alkylanilines

$C_6H_5NCH_3R$	*Yield (%)*	*B.p. (°C)*		*Analysis*			*M^+ (m/z)*	*^1H NMR (in CD_2Cl_2, ppm from TMS)*
				C	*H*	*N*		
R = C_2H_5	65	121°C at ~33 mm Hg	Calcd:	79·95	9·69	10·36	135	1·09 (t, *J* = 7·0 Hz, 3H), 2·87 (s, 3H), 3·37 (q, *J* = 7·0 Hz, 2H), 6·55–6·75 (m, 3H) and 7·1–7·25 (m, 2H)
			Found:	79·48	9·81	10·18		
R = C_4H_9	68	151°C at 25 mm Hg	Calcd:	80·92	10·50	8·58	163	0·94 (t, *J* = 7·3 Hz, 3H), 1·34 (sextet, *J* = 7·65 Hz, 2H), 1·54 (quintet, *J* = 7·2 Hz, 2H), 2·89 (s, 3H), 3·29 (t, *J* = 7·4 Hz, 2H), 6·55–6·7 (m, 3H) and 7·12–7·20 (m, 2H)
			Found:	81·07	10·64	8·49		
R = C_8H_{17}	82	130°C at 0·04 mm Hg	Calcd:	82·13	11·49	6·38	219	0·88 (t, *J* = 6·7 Hz, 3H), 1·22–1·36 (m, 10H), 1·5–1·6 (m, 2H), 2·89 (s, 3H) 3·26 (t, *J* = 7·5 Hz, 2H), 6·55–6·70 (m, 3H) and 7·14–7·2 (m, 2H)
			Found:	81·42	11·68	5·96		
R = $C_{12}H_{25}$	75	136°C at 0·06 mm Hg	Calcd:	82·84	12·07	5·08	275	0·88 (t, *J* = 6·6 Hz, 3H), 1·22–1·35 (m, 18H), 1·5–1·6 (m, 2H), 2·89 (s, 3H) 3·28 (t, *J* = 7·4 Hz, 2H), 6·56–6·7 (m, 3H) and 7·12–7·2 (m, 2H)
			Found:	82·95	12·23	4·60		
R = $C_{16}H_{33}$	74	210°C at 0·04 mm Hg	Calcd:	83·31	12·46	4·22	331	0·88 (t, *J* = 6·6 Hz, 3H), 1·22–1·35 (m, 26H), 1·5–1·6 (m, 2H), 2·89 (s, 3H) 3·27 (t, *J* = 7·4 Hz, 2H), 6·56–6·70 (m, 3H) and 7·12–7·20 (m, 2H)
			Found:	83·53	12·45	4·74		
R = $C_{18}H_{37}$	67	236°C at 0·05 mm Hg	Calcd:	83·49	12·61	3·89	359	0·88 (t, *J* = 6·6 Hz, 3H), 1·20–1·38 (m, 30H), 1·5–1·6 (m, 2H), 2·89 (s, 3H) 3·28 (t, *J* = 7·4 Hz, 2H), 6·56–6·75 (m, 3H) and 7·10–7·22 (m, 2H)
			Found:	83·42	12·68	3·75		

(Knoxville, USA). X-ray powder diffraction patterns were obtained from Molecular Structure Corporation (Texas).

2.3 Synthesis of *N*-methyl-*N*-alkylanilines

N-Methyl-*N*-alkylanilines were prepared from *N*-methylaniline and alkyl halides according to the procedures described by Desai.[10] Typically, 0·07 moles of *N*-methylaniline and 0·07 moles of an alkyl halide were allowed to react at a bath temperature of ~120°C in the presence of 5·95 g sodium acetate and 0·06 g iodine for ~16 h. The reaction mixture was cooled to room temperature and was transferred to a 250-ml separating funnel with 50 ml of water. It was then made basic with sodium hydroxide and was extracted with ether (4 × 40 ml). The combined ether extract was washed with water (once), dilute HCl (once, 3 ml conc. HCl in 50 ml of water) and then water (3 × 50 ml). It was then dried over $MgSO_4$. After removal of the ether on a rotatory evaporator, the product was isolated by vacuum distillation. The yields, physical properties and spectroscopic properties of the N-methyl-*N*-alkylanilines synthesized are tabulated in Table 1.

2.4 Synthesis of *N*-alkylsquaraines

N-Methyl-*N*-alkylaniline (2·76 mmoles), 2-propanol (25 ml) and tributyl orthoformate (2 ml) were charged into a 100-ml 3-neck flask, which was equipped with a magnetic stirbar and a nitrogen inlet. The mixture was stirred and brought to reflux. A solution containing 1-*p*-dimethylaminophenyl-2-hydroxycyclobutene-3,4-dione (0·30 g, 1·38 mmoles) in 4 ml of DMF was added slowly and evenly through a pressure-equalizing funnel in a 3-h period. After the addition was completed, the product mixture was kept at reflux for another 3 h. The green precipitate which formed was collected by filtration, and after washing with cold 2-propanol and ether, a green or blue solid was obtained. The pure squaraine dye was separated from the crude product by dissolving in hot chloroform through a Soxhlet Extractor. After removal of the solvent and vacuum drying, a metallic green solid resulted. The yields, physical properties and spectroscopic data of the squaraine dyes are summarized in Tables 2, 3 and 4.

3 RESULTS AND DISCUSSION

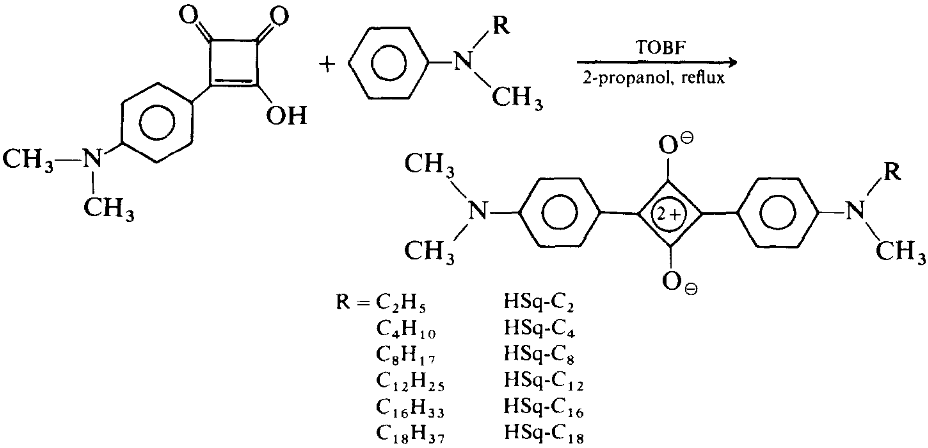
3.1 Synthesis of *N*-alkylsquaraine dyes

N-Alkylsquaraine dyes were synthesized by condensing 1-*p*-dimethylaminophenyl-2-hydroxycyclobutene-3,4-dione with an *N*-methyl-*N*-alkyl-

TABLE 2
Synthesis and Physical Properties of *N*-alkylsquaraines

Squaraine	*Yield*	*m.p. (°C)*		*C*	*H*	*N*
HSq-C_2	31%	230·0–230·5	Calcd:	75·42	6·63	8·38
			Found:	74·82	6·64	8·11
HSq-C_4	34%	205·0–206·0	Calcd:	76·21	7·23	7·73
			Found:	75·72	7·18	7·63
HSq-C_8	21%	209·5–210·5	Calcd:	77·48	8·19	6·69
			Found:	76·84	8·26	6·44
HSq-C_{12}	24%	201·0–202·5	Calcd:	78·44	8·92	5·90
			Found:	78·44	9·01	5·95
HSq-C_{16}	20%	192·0–194·0	Calcd:	79·20	9·50	5·28
			Found:	79·23	8·95	5·01
HSq-C_{18}	20%	196·5–198·0	Calcd:	79·52	9·74	5·01
			Found:	79·86	9·46	4·69

aniline in refluxing 2-propanol. Water is the by-product of the synthesis and is removed chemically by an in-situ drying reagent, tributyl orthoformate. Details on the reaction mechanism and the optimization of the reaction condition have been reported elsewhere.[9] The synthesis is summarized in Scheme 1, the yields and the physical properties of these materials are tabulated in Table 2.



Scheme 1

All the *N*-alkylsquaraines synthesized were soluble in chlorinated solvents, giving red-fluorescing blue solutions. The presence of an *N*-alkyl group in these materials apparently increases their solubility drastically. Except for HSq-C_2, which is a blue powder, HSq-C_4, HSq-C_8, HSq-C_{12}, HSq-C_{16} and HSq-C_{18} are metallic green solids. They have sharp melting points and the melting point decreases as the length of the *N*-alkyl chain increases.

3.2 Spectroscopic properties

IR spectra

Results in Table 3 show that the *N*-alkylsquaraines show strong IR absorption bands at ~1600 cm^{-1}. These bands are attributable to the C—C

TABLE 3

IR, VIS-Absorption and ^1H NMR Spectral Data of *N*-alkylsquaraines

Squaraine	*IR* *(cm^{-1})*[a]	λ_{max} *(nm)*[b]	*log* ϵ *(cm^{-1} M^{-1})*[c]	*^1H NMR (ppm from TMS)*[d]
HSq-C_2	1620,[e] 1588	626	5·42	1·24 (t, *J* = 7·2 Hz, 3H), 3·15 (s, 3H), 3·20 (s, 6H), 3·57 (q, *J* = 7·2 Hz, 2H). 6·85 (d, *J* = 9·2 Hz, 2H), 6·89 (d, *J* = 9·2 Hz, 2H) and 8·39 (d, *J* = 9·2 Hz, 4H)
HSq-C_4	1610,[e] 1586	628	5·44	1·02 (t, *J* = 7·3 Hz, 3H), 1·44 (sextet, *J* = 7·6 Hz, 2H), 1·71 (septet, *J* = 7·6 Hz, 2H), 3·22 (s, 3H), 3·25 (s, 6H), 3·57 (t, *J* = 7·6 Hz, 2H), 6·91 (bd, 4H) and 8·44 (d, *J* = 9·0 Hz 4H)
HSq-C_8	1620,[e] 1588	630	5·49	0·90 (t, *J* = 6·8 Hz, 3H), 1·25–1·45 (m, 10H), 1·65–1·75 (m, 2H), 3·22 (s, 3H), 3·25 (s, 6H), 3·55 (t, *J* = 7·5 Hz, 2H), 6·93 (d, *J* = 9·0 Hz, 4H), 8·46 (d, *J* = 9·0 Hz, 2H) and 8·47 (d, *J* = 9·0 Hz, 2H)
HSq-C_{12}	1610,[e] 1588	630	5·49	0·86 (t, *J* = 6·8 Hz, 3H), 1·2–1·4 (m, 18H), 1·60–1·72 (m, 2H), 3·17 (s, 3H), 3·20 (s, 6H), 3·49 (t, *J* = 7·3 Hz, 2H), 6·86 (d, *J* = 9·2 Hz, 4H) and 8·40 (bd, 4H)
HSq-C_{16}	1604, 1585	630	5·49	0·84 (t, *J* = 6·8 Hz, 3H), 1·20–1·75 (m, 28H), 3·15 (s, 3H), 3·18 (s, 6H), 3·48, (t, *J* = 6·8 Hz, 2H), 6·85 (d, *J* = 9·2 Hz, 4H) and 8·39 (bd, 4H)
HSq-C_{18}	1605,[e] 1590	630	5·52	0·89 (t, *J* = 6·6 Hz, 3H), 1·25–1·75 (m, 32H), 3·20 (s, 3H), 3·23 (s, 6H), 3·52 (bt, 2H), 6·89 (d, *J* = 9·1 Hz, 4H) and 8·43 (d, *J* = 9·1 Hz, 4H)

[a] In KBr.
[b] In $CHCl_3$.
[c] Molar extinction coefficient.
[d] $CDCl_3$.
[e] Shoulder.

bond stretchings of the phenyl ring and the four membered ring in squaraine. The absence of any $C{=}O$ stretching at ~1700 cm^{-1} is a strong indication of the extensive bond delocalization in squaraine. Very similar results were obtained for other squaraines.[7,11,12]

VIS spectra

Similar to other squaraines, *N*-alkylsquaraines exhibit intense absorption in the visible region in chloroform.[13,14] Their absorption maxima vary from 626 to 630 nm. There is a small but definite bathochromic shift on the λ_{max} and an increase in ε_{max} (from $2{\cdot}63 \times 10^5$ to $3{\cdot}31 \times 10^5\ cm^{-1}\ M^{-1}$) as the chain length of the *N*-alkyl group increases. A similar *N*-alkyl group effect was also observed in our earlier work and the observation is attributable to the stabilization of the donor–acceptor–donor charge-transfer state of squaraine by the *N*-alkyl groups.[13]

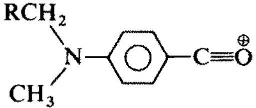
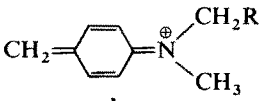
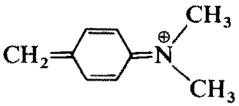
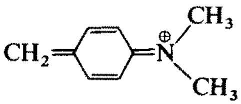
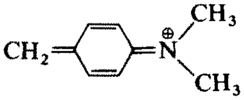
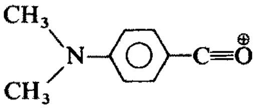
^1H NMR spectra

The ^1H NMR spectral data of *N*-alkylsquaraines are summarized in Table 3. The highest field signal is a triplet at 1 ± 0·2 ppm, which is assigned to the terminal methyl group of the *N*-alkyl chain. *N*-Methyl and *N*-methylene protons are at their characteristic position at 3·2 ± 0·1 (singlets) and ~3·5 ppm (triplets), respectively. In the aromatic region, two sets of doublets, at ~6·9 and ~8·4 ppm are anticipated due to the unsymmetrical structure.[11,15] Experimentally, these doublets are not always resolvable, even on a 360 MHz spectrometer. They sometimes appear as broad doublets.

Electron impact mass spectra

Squaraines are known to exhibit very unique and anomalous mass spectrometric behavior. As a result of the strong intermolecular donor–acceptor interactions between squaraine molecules in the solid state, squaraines vaporize thermally as aggregates in the mass spectrometer. Fragmentation of these aggregates upon electron impact results in alkylation and hydrogenation of the molecular ion. Thus, fragment ions of mass numbers higher than the molecular ions are generally observed. These intermediate alkylated and hydrogenated ions, $M + CHR]^{+\cdot}$ and $M + H_2]^{+\cdot}$, respectively, further fragment into a set of very characteristic rearranged products, such as structures **a** and **b** in Table 4. Details of the mechanism of the formation of these intermediate ions and their subsequent fragmentation processes have been documented in an earlier report.[11] The *N*-alkylsquaraines synthesized in this work are no exception. They give clean and unique mass spectra. A typical mass spectrum is depicted in Fig. 1. The mass spectral data are summarized in Table 4.

TABLE 4
Mass Spectral Data of N-Alkylsquaraines

Squaraine	*m/z (relative intensity)*						
	M^+		$M + CHR^{]+\cdot}$	 **a**	$M + H_2^{]+\cdot}$	 **b**	*Base peak*
HSq-C_2	334 (0)	R = H CH_3	348 (67) —	148 (73) —	336 (100)	134 (87) 148 (73)	$M + H_2^{]+\cdot}$
HSq-C_4	362 (0)	R = H C_3H_7	376 (69) —	148 (63) —	—	134 (100) 176 (56)	
HSq-C_8	418 (0)	R = H C_7H_{15}	432 (36) 530 (44)	148 (60) —	—	134 (44) 232 (48)	$\dot{M} + H_2^{]+\cdot}$—C_7H_{15}
HSq-C_{12}	474 (0)	R = H $C_{11}H_{23}$	488 (34) —	148 (61) —	—	134 (100) —	
HSq-C_{16}	530 (0)	R = H $C_{15}H_{31}$	544 (36) —	148 (89) 358 (60)	532 (25)	134 (100) 344 (96)	
HSq-C_{18}	558 (0)	R = H $C_{17}H_{35}$	— —	148 (100) 386 (66)	—	134 (95) 372 (58)	

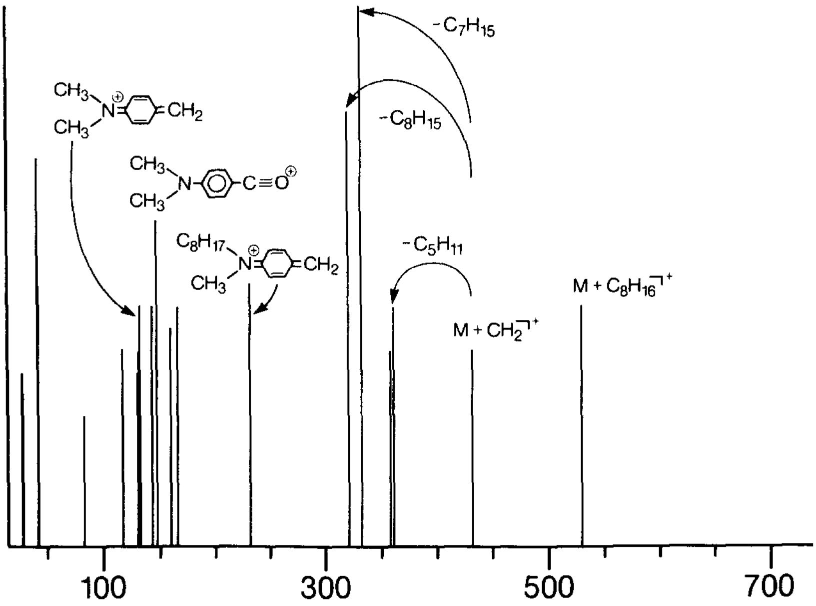


Fig. 1. Electron impact mass spectrum of HSq-C_8.

In addition to the basic fragmentation processes of squaraine, dealkylation reactions of intermediate ions are found to be the only major fragmentation process. For example, the intermediate ion $M + CH_2]^{+\cdot}$ of HSq-C_8 is found to lose a C_5H_{11}, a C_7H_{15} and a C_8H_{15} group to give ions at *m/z* 361, 333 and 321, respectively (Fig. 1). A very similar mass spectrometric behavior has also been observed for squaraines having *N*-benzyl substituents.[7]

3.3 Solid-state properties

Recent investigation on the effect of aggregation on the photogeneration efficiency of organic photoconductors indicates that the photoconductivity and the spectral response of squaraine are governed by the aggregation of squaraines molecules in the microcrystalline state.[16] Photoactive squaraine aggregates are characterized by a broad and panchromatic absorption, which typically consists of two bands, one in the visible (500–650 nm) and the other in the near-IR (~700 nm) range; and by the characteristic X-ray powder diffraction pattern with diffraction lines at 2θ ~11·5°, ~14·5° and ~26°. This set of properties is very characteristic of a highly photoconductive squaraine.[4,8] In this work, we use them as criteria to estimate the potential of *N*-alkylsquaraines as photoconductive materials.

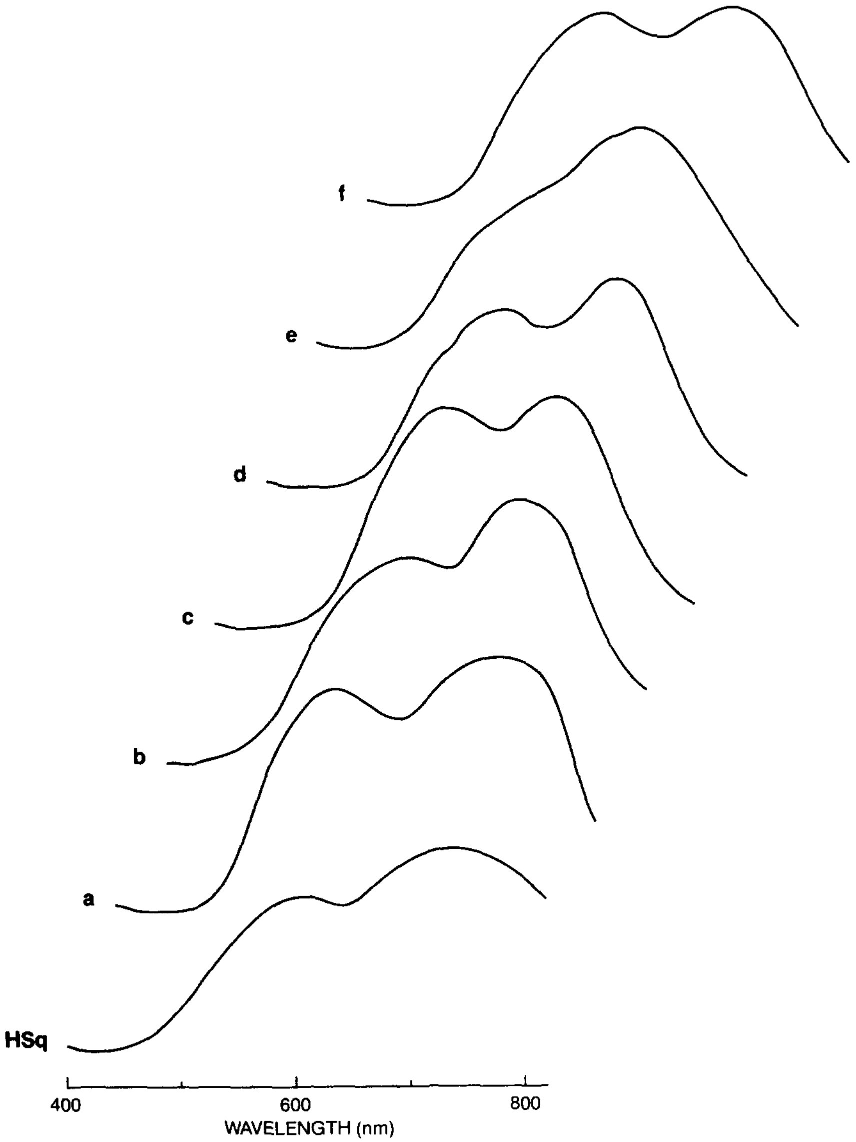


Fig. 2. Solid-state absorption spectra of HSq and *N*-alkylsquaraines in KBr pellets (a) HSq-C_2; (b) HSq-C_4; (c) HSq-C_8; (d) HSq-C_{12}; (e) HSq-C_{16}; (f) HSq-C_{18}.

Figure 2 shows the solid-state absorption spectra of HSq-C_2 to HSq-C_{18} in KBr pellets. The solid state absorption spectrum of HSq is also given. The data indicate that the solid-state absorption spectra of *N*-alkylsquaraines are broad and panchromatic relative to their solution absorption spectra (Table 3). More importantly, comparison with the spectrum of HSq suggests that the aggregation of *N*-alkylsquaraine molecules in

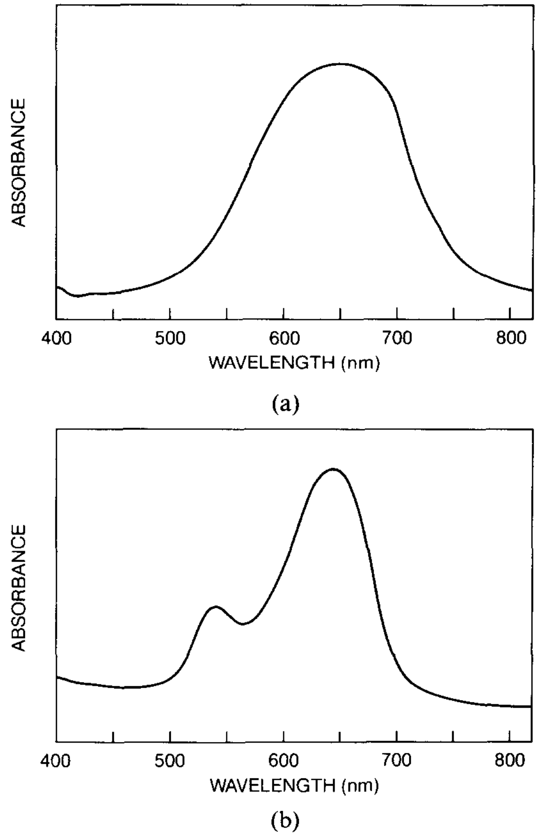
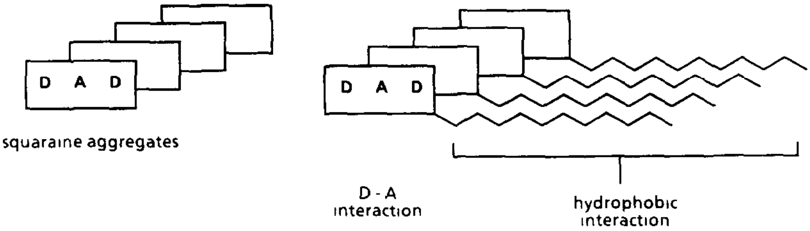


Fig. 3. Solid-state absorption spectra of squaraine dyes in KBr pellets (a) bis(4-dibutyl aminophenyl)squaraine; (b) bis(4-dioctadecylaminophenyl)squaraine.

the solid state is very similar to that of a photoconductive squaraine. This is an unusual observation because solubilizing groups are known to alter the aggegation.[8] For comparison purposes, the solid-state absorption spectra of two soluble squaraine dyes are given Fig. 3. The aggregation observed in *N*-alkylsquaraines is therefore unique. We propose that, in contrast to other solubilizing groups, which usually perturb the aggregation, the mono *N*-alkyl groups in *N*-alkylsquaraines play an active role in the aggregation process. It enhances the solubility of the squaraine and at the same time provides a proper orientation for the squaraine chromophores, enabling intermolecular donor–acceptor interaction to occur. A schematic of the proposed interaction is depicted in Scheme 2. Since *N*-alkylsquaraines form aggregates similar to that of HSq, these materials should be photoconductive. Experimentally, photoconductivity of these materials has been observed in xerographic devices.[17] Our goal of synthesizing a soluble photoconductive squaraine is thus accomplished.



Scheme 2

To compliment the solid-state absorption data, the X-ray powder diffraction patterns of HSq-C_2 to HSq-C_{18} were examined. Again, the powder pattern of HSq is used as a reference. The results are highlighted in Fig. 4. The data show that there is a drastic decrease in crystallinity in the solid samples of HSq-C_2 to HSq-C_{18}. The decrease is readily attributable to the *N*-alkyl groups. Despite this complication, careful inspection of the

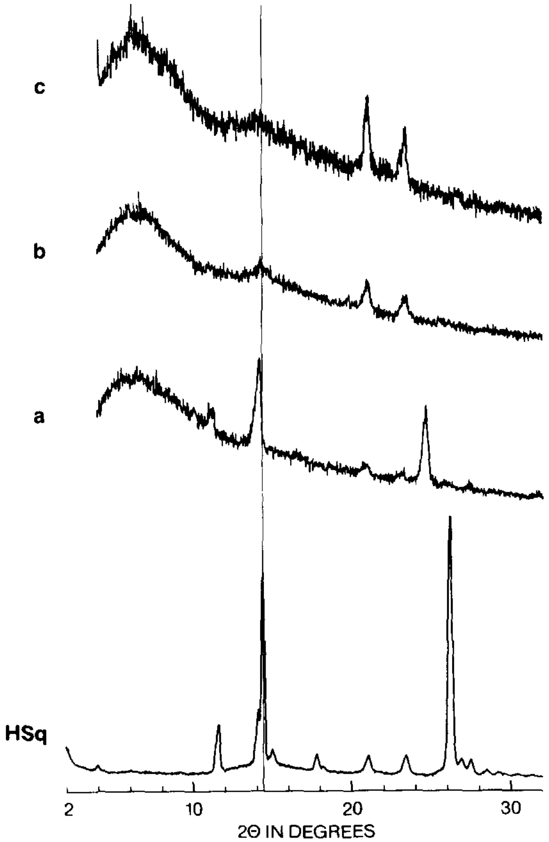


Fig. 4. X-ray powder diffraction patterns of HSq and *N*-alkylsquaraines. (a) HSq-C_2; (b) HSq-C_8; (c) HSq-C_{18}.

powder patterns of HSq-C_2 to HSq-C_{18} suggests that the basic diffraction lines of that of a photoconductive aggregate are discernible. The X-ray data are thus consistent with the aggregation model proposed in Scheme 2.

3.4 Self-organizing and film-forming properties

The occurrence of a dual, cooperative intermolecular interaction in the microcrystalline state of *N*-alkylsquaraines suggests that these materials should self-organize to form photoconductive aggregates regardless of the processing conditions. To examine the self-organizing ability of these materials upon thin-film formation, concentrated chloroform solutions of these dyes were prepared. The chloroform solutions were then cast on glass substrates (both hydrophilic and hydrophobic). Results show that HSq-C_{18} and HSq-C_{16} form good-quality thin films on glass substrates.

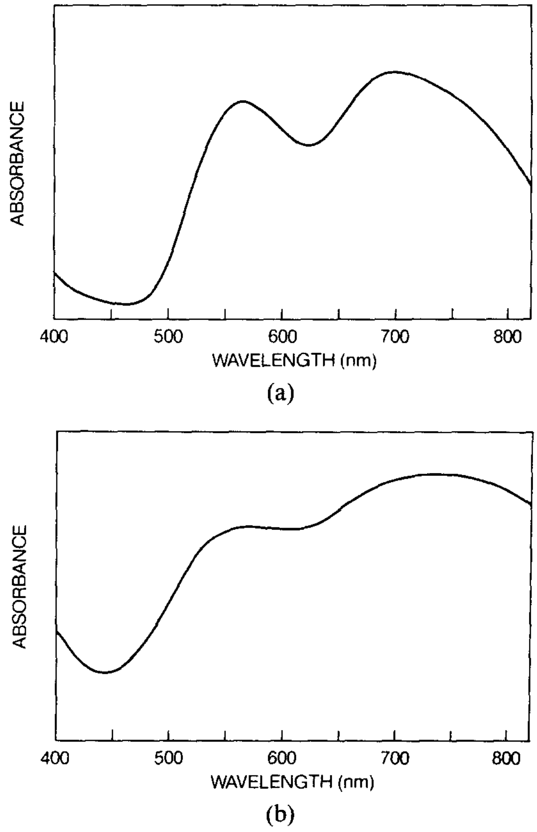


Fig. 5. Absorption spectra of dye films cast from chloroform solutions. (a) HSq-C_{18}; (b) HSq-C_{16}.

The absorption spectra of these films (Fig. 5), which show the characteristic two-band absorption, indicate that these squaraine dyes self-organize to photoconductive aggregates in thin films on glass.

The film-forming ability decreases as the length of the *N*-alkyl group decreases. HSq-C_2 basically crystallizes as blue powder on glass substrates, and HSq-C_4, HSq-C_8 and HSq-C_{12} form poor-quality films. The absorption spectra of these films or powder are found to be very similar to those given in Fig. 2. The spectral data of these solution cast films essentially reaffirm our belief that molecules of *N*-alkylsquaraines can self-organize to a photoconductive aggregated form under various experimental conditions.

4 CONCLUSIONS

Using squaraine as an example, we have demonstrated a viable concept for modifying the solubility of a class of photoactive pigmentary materials, without perturbing the desirable aggregation in the solid state. The success of the approach lies in the active participation of the solubilizing groups in the aggregation process. The present concept appears to be a refinement of our earlier approach on soluble vanadyl phthalocyanine dyes, whereby the central strategy was to minimize the damage produced by the solubilizing groups on the desirable aggregation.[17] We expect the concept described herein to be useful for the modification of other organic electronic materials.

Based on the observed solid-state properties, *N*-alkylsquaraines should be photoconductive. This has indeed been observed experimentally by xerographic discharge technique. Unfortunately, the presence of long alkyl chains in these materials seems to adversely affect the mobility of the photogenerated charges and results in high residual potential in xerographic devices.[18] Since surfactant squaraines are known to form interesting multilayer assemblies when organized by the Langmuir–Blodgett technique,[19] our current plan is to organize these molecules into multilayer assemblies and examine their fundamental photoelectrical properties.

REFERENCES

1. Zollinger, H., *Color Chemistry*, VCH Publishers, New York, USA, 1987.
2. Law, K. Y., *J. Phys. Chem.*, **89** (1985) 2652.
3. Law, K. Y., *Polymer*, **23** (1982) 1627.
4. Law, K. Y. & Bailey, F. C., *J. Imaging Sci.*, **31** (1987) 172.

5. Sprenger, H. E. & Ziegenbein, W., *Angew. Chem. Int. Ed. Engl.*, **5** (1966) 894.
6. Law, K. Y. & Bailey, F. C., *Can. J. Chem.*, **64** (1986) 2267.
7. Law, K. Y. & Bailey, F. C., *Dyes and Pigments*, **9** (1988) 85.
8. Law, K. Y., Facci, J. F., Bailey, F. C. & Yanus, J. F., *J. Imaging Sci.*, **34** (1990) 31.
9. Law, K. Y. & Bailey, F. C., *J. Chem. Soc. Chem. Commun.*, (1991) 1156; and manuscript in preparation.
10. Desai, R. D., *J. Indian Inst. Sci.*, **7** (1924) 235.
11. Law, K. Y., Bailey, F. C. & Bluett, L. J., *Can. J. Chem.*, **64** (1986) 1607.
12. Law, K. Y. & Bailey, F. C., *J. Org. Chem.*, **57** (1992) 3278.
13. Law, K. Y., *J. Phys. Chem.*, **91** (1987) 5184.
14. Law, K. Y., *Chem. Phys. Lett.*, **150** (1988) 357.
15. Law, K. Y., *J. Phys. Chem.*, **93** (1989) 5925.
16. Law, K. Y., *J. Phys. Chem.*, **92** (1988) 4226.
17. Law, K. Y., *Inorg. Chem.*, **24** (1985) 1778.
18. Law, K. Y., unpublished.
19. Law, K. Y. & Chen, C. C., *J. Phys. Chem.*, **93** (1989) 2533.