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Squaraine Chemistry. Effect of *N*-Pyrrolidino Substitution on the Synthesis and Solid State Properties of Squaraines

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ABSTRACT

Several symmetrical and unsymmetrical squaraines bearing N-*pyrrolidino groups have been synthesized by condensation of* N-*pyrrolidinoaniline derivatives with squaric acid or a 1-aryl-2-hydroxycyclobutene-3,4-dione derivative. As compared to squaraines synthesized from* N,N-*dimethylanilines, a consistently higher synthetic yield was obtained for the* N-*pyrrolidino-squaraines synthesized in the work. The yield improvement is attributable to the high nucleophilicity of* N-*pyrrolidinoanilines, owing to the rigidized* N-*pyrrolidino ring structure.* N-*Pyrrolidino substitution is shown to have very little effect on the physical and spectroscopic properties of squaraine. Examinations of the solid state properties of* N-*pyrrolidino substituted squaraines, by solid state absorption spectroscopy and by X-ray powder diffraction reveal that the* N-*pyrrolidino group is the only* N-*alkyl substituent identified thus far that exerts no effect on the aggregation of squaraine molecules in the microcrystalline state. This implies that* N-*pyrrolidino squaraines should be photoconductive and indeed photoconductivities have been observed in xerographic devices incorporating them.*

1 INTRODUCTION

Bis-(4-dimethylaminophenyl)squaraine (**HSq**) and its derivatives are known to possess interesting semiconductive and photoconductive properties.[1]

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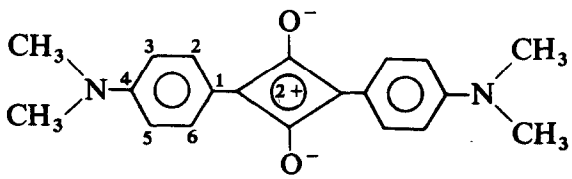


HSq

These compounds exhibit sharp and intense absorption in the visible region in solution.[2] In the solid state, owing to the strong intermolecular donor and acceptor interactions, the absorption becomes very intense and panchromatic, covering most of the visible region and extending to the near-IR.[3] These optical characteristics, coupled with their known photoconductivity, make squaraines very attractive for xerographic copier and printer applications. Squaraines are traditionally synthesized by condensing one equivalent of squaric acid with two equivalents of *N,N*-dialkylaniline derivative in an azeotropic solvent.[4] Squaraines synthesized by this procedure are, however, often found to exhibit low charge-accepting properties and high dark-conductivity in bilayer xerographic devices.[1,5] Structural modification of squaraine to improve the processability and the performance of these materials for xerographic applications has been documented. C-2 substituents have been shown to have very little effect on the spectroscopic and solid state properties (aggregation) of squaraine. As a result, C-2 substituted squaraines generally exhibit good photoconductive properties in xerographic devices.[1,3] Unfortunately, these squaraines are pigmentary. They can be neither purified by solvent recrystallization nor dispersed in polymer solution easily for solution coating in device fabrication. An improvement in their processability is needed prior to any practical applications. On the other hand, *N*-benzyl[5] and *N*-alkyl[6] substituents increase the solubility and consequently the processability of the squaraine. These substituents unfortunately perturb the aggregation of squaraine molecules in the microcrystalline state, whereby their photoconductivity in xerographic devices is adversely affected.[3]

In this work, the effect of *N*-pyrrolidino substitution on the synthesis and the solid state properties of squaraine is examined. A series of *N*-pyrrolidinosquaraines, **Sq 1–Sq 6**, was prepared and structurally characterized. Our data show that the *N*-pyrrolidino substituent not only increases the yield of the squaraine synthesis, but also exerts no adverse effect on the solid state properties. The increase in chemical yield is attributable to the high nucleophilicity of *N*-pyrrolidinoanilines. The absence of an *N*-alkyl effect on the solid state properties is discussed in terms of the small rigidized *N*-pyrrolidino ring structure.

2 EXPERIMENTAL

2.1 Materials

Squaric acid (98%), aniline (99%), *m*-fluoroaniline (99%), 1,4-dibromobutane (99%) and acetic acid anhydride (99+%) were purchased from Aldrich. Sodium carbonate (anhydrous), 1-butanol, ether (anhydrous), methanol, toluene and iodine (resublimed crystals) were certified ACS reagent grade and they were from Fisher. The precursors for the unsymmetrical squaraine synthesis, 1-4'-methoxyphenyl-2-hydroxycyclobutene-3,4-dione, 1-3',4'-dimethoxyphenyl-2-hydroxycyclobutene-3,4-dione and 1-4'-dimethylaminophenylocyclobutene-3,4-dione were synthesized by a cycloaddition/hydrolysis reaction sequence. Detailed procedures for the preparaton of these compounds have been reported earlier.[7–9]

2.2 General techniques

Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and were uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 1750 FTIR. Proton-NMR spectra were recorded on a Bruker AM360 spectrometer. Absorption spectra were taken on a Hewlett-Packard 8451 diode array spectrophotometer. Mass spectra were recorded on a Varian VG7035 mass spectrometer at the University of Rochester, NY. Elemental analyses were performed by Galbraith Laboratories. X-ray powder diffraction patterns were performed in-house on a Scintag PAD V X-ray diffractometer.

2.3 Synthesis of *N*-pyrrolidino-*m*-fluoroaniline and *N*-pyrrolidinoaniline

Sodium carbonate (45 g, 0·43 mol) and iodide (0·86 g) were suspended in 650 ml of 1-butanol in a 1 liter three-necked flask. The mixture was stirred and brought to reflux. 1,4-Dibromobutane (93·5 g, 0·43 mol) and *m*-fluoroaniline (48 g, 0·43 mol) were introduced separately into the reaction flask. The addition rates of both reactants were adjusted in such a fashion that they were introduced evenly (in terms of molarity) and slowly over about 6 h. After the addition was completed, the reaction mixture was cooled to room temperature. Sodium carbonate was removed by filtration. After evaporation of all the solvent, a clear brown liquid (47·7 g) was obtained; this was then stirred overnight with 50 ml of acetic acid anhydride. The mixture was transferred to a 2 liter beaker and was chilled by an ice–water bath. Concentrated hydrochloric acid

was added carefully to the ice cold acetic acid anhydride solution, and the acidic solution was extracted with ether (3 × 300 ml) to remove any neutral or acidic impurities. After the extraction, it was transferred back to a 2 liter beaker, chilled by an ice–water bath and then strongly basified by NaOH pellets. The alkaline solution was extracted with ether (3 × 250 ml). The ether extracts were combined and were dried over $MgSO_4$. After gravity filtration and solvent evaporation, a brown liquid resulted. *N*-Pyrrolidino-*m*-fluoroaniline was isolated as a colorless liquid by reduced-pressure distillation at 122 to 125°C at *c.* 8·3 mmHg. Yield 39·1 g (55%); proton-NMR ($CDCl_3$): δ 1·98–2·03 (m, 4H), 3·26 (t, J = 6·6 Hz, 4H), 6·21–6·26 (m, 1H), 6·30–6·36 (m, 2H) and 7·13 (q, J = 8 Hz, 1H); mass spectrum (*m/z*): 165 (M+).

Calc. for $C_{10}H_{12}NF$:	C 72·70, H 7·32, N 8·48, F 11·50
Found:	C 72·50, H 7·30, N 8·52, F 11·36

Similarly, *N*-pyrrolidinoaniline was synthesized and purified from aniline and 1,4-dibromobutane. Yield 58%; b.p. 118·5–119·5°C at *c.* 11 mmHg; proton-NMR ($CDCl_3$): δ 1·94–2·5 (m, 4H), 3·29 (t, J = 6·5 Hz, 4H), 6·59 (bd, J = 7·5 Hz, 2H), 6·67 (t, J = 7·1 Hz, 1H) and 7·23 (bt, J *c.* 8 Hz, 2H); mass spectrum (*m/z*): 147 (M^+).

Calc. for $C_{10}H_{13}N$:	C 81·58, H 8·90, N 9·51
Found:	C 81·42, H 8·73, N 9·56

2.4 Synthesis of symmetrical squaraines

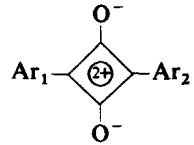
Symmetrical squaraines were prepared by condensing squaric acid and an *N*-pyrrolidinoaniline derivative in an alcoholic solvent.[4,5] Typically, squaric acid (1·14 g, 10 mmol) and the *N*-pyrrolidinoaniline derivative were heated to reflux in a mixture of toluene (40 ml) and 1-butanol (40 ml) at a bath temperature of 125°C. Water was removed by a Dean–Stark trap. After 8 h, the reaction mixture was cooled to room temperature and the product isolated by filtration.

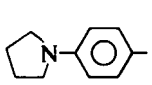
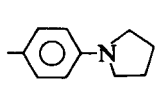
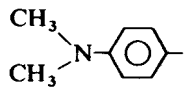
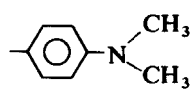
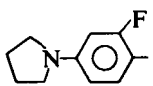
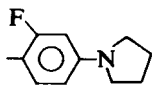
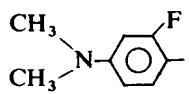
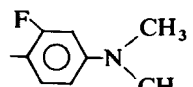
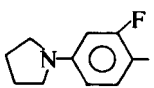
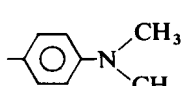
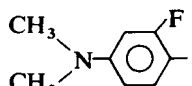
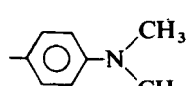
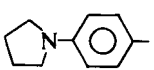
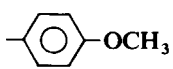
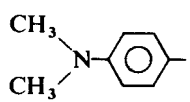
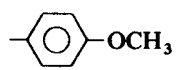
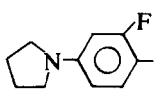
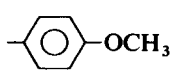
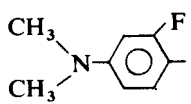
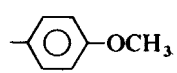
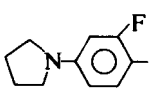
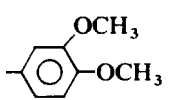
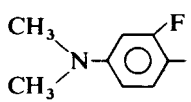
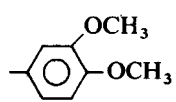
2.5 Synthesis of unsymmetrical squaraines

Unsymmetrical squaraines were prepared by condensing a cyclobutenedione precursor with an *N*-pyrrolidinoaniline derivative in 2-propanol in the presence of tributylorthoformate. Detailed procedures for **Sq 3** and **Sq 4–6** are given in references 9 and 8, respectively.

TABLE 1

A Comparison of Chemical Yields Between Squaraines Synthesized from *N*-Pyrrolidinoanilines and *N,N*-Dimethylanilines



Symbol	*Ar_1*	*Ar_2*	*Yield (%)*	*Ar_1*	*Ar_2*	*Yield (%)*	*Ref.*
Sq 1			74			40–60	10
Sq 2			34			23	10
Sq 3			20			3·8	9
Sq 4			82			67	7,8
Sq 5			62			32	7,8
Sq 6			72			59	7,8

3 RESULTS AND DISCUSSION

3.1 Synthesis of *N*-pyrrolidino squaraines

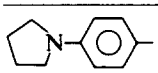
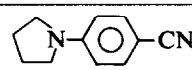
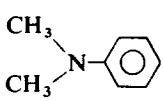
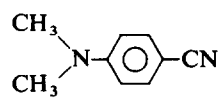
Symmetrical squaraines, **Sq 1** and **2**, were synthesized by condensing squaric acid with *N*-pyrrolidinoaniline and *m*-fluoro-*N*-pyrrolidinoaniline, respectively, in an azeotropic solvent. Unsymmetrical squaraines, **Sq 3–6**, were prepared by condensing the corresponding cyclobutenedione precursor with a *N*-pyrrolidinoaniline. Details of the procedures have been given elsewhere.[5–9] The isolated yields of **Sq 1–6** are summarized in Table 1. The yields of analogous squaraines synthesized from *N*,*N*-dimethylanilines are given for comparison. The data show that, without exception, higher yields are obtained for *N*-pyrrolidino substituted squaraines. We attribute the high yield to the relatively high nucleophilicity of *N*-pyrrolidinoanilines, which is evident by comparing the relative electron donicity of *N*-pyrrolidino and *N*,*N*-dimethyl groups in intramolecular charge-transfer compounds such as *p*-cyano-*N*,*N*-dimethylaniline and *p*-cyano-*N*-pyrrolidinoaniline. For instance, the data in Table 2 clearly show that *p*-cyano-*N*-pyrrolidinoaniline not only has a lower ionization potential (IP), but also a 'more' planar geometry (a smaller twist angle).[11]

3.2 Physical and spectroscopic properties

3.2.1 Physical properties

N-Pyrrolidino squaraines are blue or purple microcrystalline powders in the solid state. Most of them decompose at the melt at a relatively high temperature, >210°C (Table 3). The melting range, between 210 and

TABLE 2
A Comparison of Between Yield of Squaraine Synthesis and Electron-donating Ability of the Aniline Precursors

Symmetrical squaraine synthesis		p-*Cyanoaniline*	*IP (eV)*[a,b]	*χ (degree)*[b,c]
Precursor	*Yield (%)*			
	74		8·39	0
	40–60		8·51	4

[a] Ionization potential.
[b] Data taken from Ref. 11.
[c] The angle between the phenyl ring and the C—N—N framework.

TABLE 3
Physical Properties of *N*-Pyrrolidino Squaraines

Squaraine	*Appearance*	*m.p. (°C)*		*C*	*H*	*N*	*F*
Sq 1	Blue-green	258 (dec.)	Calc.:	77·39	6·50	7·52	
			Found:	77·32	6·55	7·52	
Sq 2	Blue-green	247 (dec.)	Calc.:	70·58	5·43	6·86	9·30
			Found:	70·30	5·46	6·87	9·94
Sq 3	Dark blue	227 (dec.)	Calc.:	72·51	5·81	7·69	
			Found:	71·79	5·64	7·50	
Sq 4	Purple-blue	243–245	Calc.:	75·66	5·74	4·20	
			Found:	75·41	5·74	4·23	
Sq 5	Purple	216 (dec.)	Calc.:	71·78	5·16	3·99	5·41
			Found:	72·09	5·27	4·00	4·84
Sq 6	Dark blue	210 (dec.)	Calc.:	69·28	5·29	3·67	4·98
			Found:	69·12	5·36	3·76	4·76

260°C, is comparable to that of *N*-benzyl substituted squaraines[5] and is much higher than that of *N*-alkyl substituted squaraines, which melt below 200°C.[6] In terms of solubility in organic solvents, **Sq 1–3** are pigmentary. Their maximum solubility in chloroform was estimated to be $\leq 10^{-4}$ M. **Sq 4–6** are readily soluble in chlorinated solvents and can be purified by the conventional solvent extraction technique. The solubility characteristics of *N*-pyrrolidinosquaraines are found to be similar to other symmetrical and unsymmetrical squaraines bearing a dimethylamino group.[1,6–9] We conclude that *N*-pyrrolidino substitution has relatively little effect on the physical properties of squaraine.

3.2.2 Proton NMR

All *N*-pyrrolidinosquaraines synthesized exhibit sufficient solubility in $CDCl_3$ for examination on a 360 MHz NMR spectrometer. The results in Table 4 show that the methylene protons in the *N*-pyrrolidino ring are at $\delta \simeq 2{\cdot}0$ and 3·5 with a 1 : 1 ratio. The singlets for the *N*-methyl and methoxy protons are at $\delta \simeq 3{\cdot}1$ and $\delta \simeq 3{\cdot}9$, respectively. The chemical shifts of these aliphatic protons are consistent with the chemical structures of these compounds.

In the aromatic region, two sets of signals, at 6 to 7 ppm and 8 to 9 ppm, are observed (Table 4) and they are assigned to protons β- and α- to the four-membered ring of squaraine, respectively.[6,12] Individual protons can be assigned unambiguously based on the coupling pattern and the integration.

TABLE 4
IR, VIS Absorption and ^{1}H-NMR Spectral Data of *N*-Pyrrolidino Squaraines

Squaraine	*IR* (cm^{-1})[a]	λ_{max} (*nm*)[b]	*log* ε (cm^{-1} M^{-1})[c]	^{1}*H-NMR (ppm from TMS)*[d]
Sq 1	1587, 1604	634·6	5·49	2·04 (m, 8H), 3·46 (m, 8H), 6·60 (d, J = 9·0 Hz, 4H) and 8·36 (d, J = 9·0 Hz, 4H)
Sq 2	1598	638·4	5·46	2·05 (m, 8H), 3·45 (m, 8H), ≃6·2 (bd, 2H), ≃6·4 (bd, 2H) and ≃8·6 (m, 2H)
Sq 3	1595, 1620	631·7	5·15	≃2·0 (m, 4H), 3·13 (s, 6H), 3·4 (m, 4H), ~6·24 (bd, 1H), ~6·37 (bd, 1H), 6·70 (d, J = 9·2 Hz, 2H), 8·39 (d, J = 9·2 Hz, 2H) and ≃8·53 (m, 1H)
Sq 4	1590, 1604, 1615	583·8	5·35	2·13 (m, 4H), 3·61 (m, 4H), 3·91 (s, 3H), 6·71 (d, J = 9·2 Hz, 2H), 7·00 (d, J = 9·0 Hz, 2H), 8·42 (d, J = 9·0 Hz, 2H) and 8·51 (d, J = 9·0 Hz, 2H)
Sq 5	1591, 1622	586·5	5·32	2·11 (m, 4H), 3·56 (m, 4H), 3·89 (s, 3H), 6·35 (ABq, J_A = 11 Hz, J_B = 2 Hz, 1H), 6·48 (ABq J_A = 11 Hz, J_B = 2 Hz, 1H), 6·99 (d, J = 9·0 Hz, 2H), 8·46 (d, J = 9·0 Hz, 2H), and ≃8·7 (m, 1H)
Sq 6	1588, 1620	594·9	5·32	≃2·1 (m, 4H), ~3·5 (bm, 4H), 3·93 (s, 3H), 3·95 (s, 3H), 6·33 (ABq, J_A = 11 Hz, J_B ≃ 2 Hz, 1H) 6·47 (ABq, J_A = 9·7 Hz, J_B ~ 2 Hz, 1H), 6·96 (d, J = 8·7 Hz, 1H), ~7·99 (d, J ~ 2 Hz, 1H), 8·17 (ABq, J_A = 8·7 Hz, J_B ≃ 2 Hz, 1H) and 8·66 (m, 1H)

[a] In KBr.
[b] In chloroform.
[c] Molar extinction.
[d] In $CDCl_3$.

3.2.3 IR spectra

Results in Table 4 show that all *N*-pyrrolidinosquaraines exhibit strong IR absorption bands at *c.* 1600 cm^{-1}. These IR bands are attributable to the C⋯C bond stretchings of the phenyl ring and the four-membered ring in squaraine. The absence of any C=O bond stretching at *c.* 1700 cm^{-1} is a strong indication of extensive bond delocalization in squaraines. Similar results were obtained in other squaraines.[5–9]

3.2.4 VIS spectra

N-Pyrrolidinosquaraines show intense and sharp absorption in the visible region in chloroform. Symmetrical squaraines **Sq 1** and **Sq 2** show λ_{max}

at 634·6 and 638·4 nm, respectively, with a molar extinction coefficient of *c.* 3×10^5 cm^{-1} M^{-1} (Table 4). Unsymmetrical squaraine **Sq 3** absorbs in the same region, but the extinction coefficient is lowered due to the unsymmetrical structure.[9] Unsymmetrical squaraines **Sq 4–6** absorb at wavelengths shorter than 600 nm, again with a lowered extinction coefficient. The wavelength of absorption and the extinction coefficient are very typical of unsymmetrical squaraines having methoxy groups.[7,8] We thus conclude that *N*-pyrrolidino substitution has essentially no effect on the absorption properties of squaraines.

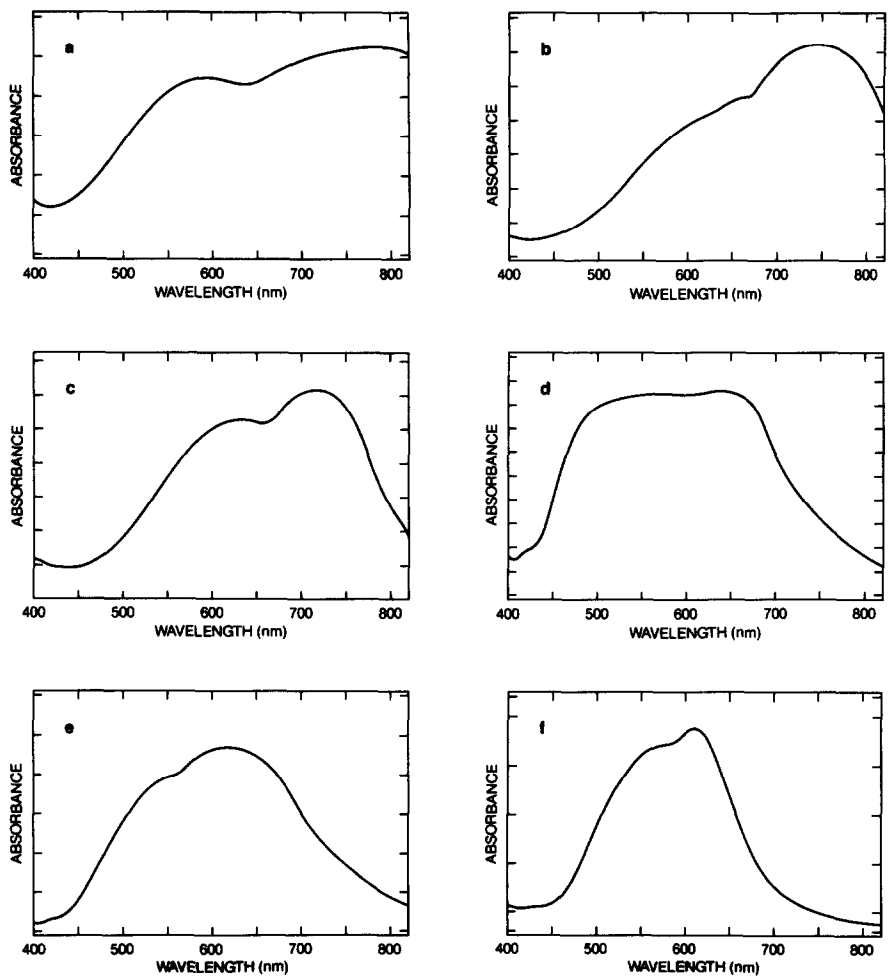


Fig. 1. Solid state absorption spectra (in KBr) of *N*-pyrrolidinosquaraines: a, **Sq 1**; b, **Sq 2**; c, **Sq 3**; d, **Sq 4**; e, **Sq 5**; f, **Sq 6**.

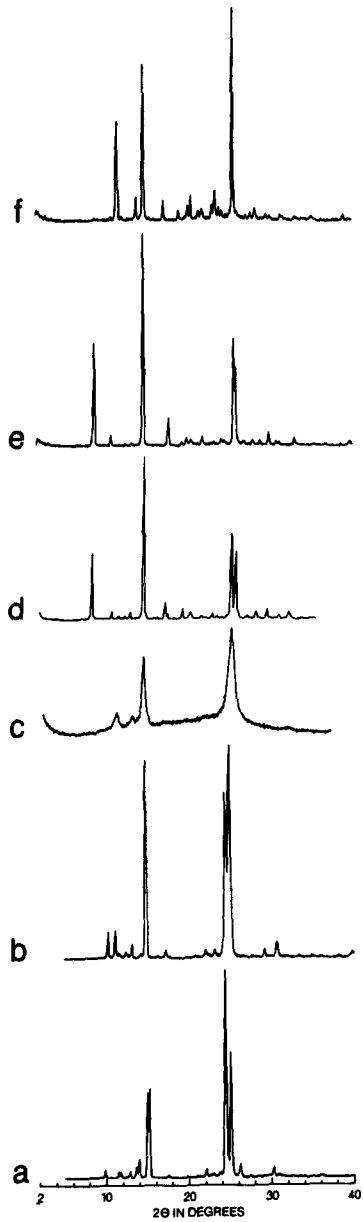


Fig. 2. X-ray powder diffraction patterns of *N*-pyrrolidinosquaraines: a, **Sq 1**; b, **Sq 2**; c, **Sq 3**; d, **Sq 4**; e, **Sq 5**; f, **Sq 6**.

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 squaraine molecules in the microcrystalline state.[13] Photoactive squaraine aggregates are characterized by a broad and panchromatic absorption, which typically consists of two bands, one at longer wavelengths and the other at shorter wavelengths relative to the monomeric absorption, and by the characteristic X-ray powder diffraction pattern with diffraction lines at $2\theta \simeq 11{\cdot}5°$, $\simeq 14{\cdot}5°$ and $\simeq 26°$.[3] This set of properties is very characteristic of a highly photoconductive squaraine. Here we use them as criteria to estimate the potential of *N*-pyrrolidinosquaraines as photoconductive materials.

Figure 1 shows the solid state absorption spectra of **Sq 1** to **Sq 6** in KBr pellets. Without exception, all *N*-pyrrolidinosquaraines, both symmetrical and unsymmetrical, show panchromatic absorption similar to their photoconductive analogs. These results indicate that the aggregation of *N*-pyrrolidinosquaraines in the microcrystalline state is very similar to other photoconductive squaraines, which usually bear *N*,*N*-dimethylamino groups.

The conclusion drawn from the absorption spectral data also gains support from X-ray powder diffraction data (Fig. 2). The X-ray diffraction patterns of **Sq 1** to **Sq 6** are very similar (Fig. 2). More importantly they closely resemble those of photoconductive squaraines, such as **HSq** and its derivatives.[1] It is important to point out that, in our earlier attempts to modify squaraines with *N*-benzyl and *N*-alkyl groups, solid state properties similar to those of **HSq** were not obtained due to the substituent-induced perturbation on the aggregation of squaraine molecules in the solidstate.[3] The data presented here indicate that *N*-pyrrolidino substitution is unique. The minimal perturbation on the solid state properties is probably the result of the small size and the rigidized *N*-pyrrolidino ring structure.

4 CONCLUDING REMARKS

Several symmetrical and unsymmetrical squaraines bearing an *N*-pyrrolidino substituent have been synthesized. Higher synthetic yields are obtained for these materials as compared with squaraines bearing dimethylamino groups. The yield improvement is attributable to the high nucleophilicity of *N*-pyrrolidinoanilines. In contrast to those observed in

N-benzyl- and *N*-alkyl-squaraines, where the aggregation of squaraine molecules in the solid state is perturbed due to substituent effects, *N*-pyrrolidino substitution is shown to have very little adverse effect on the aggregation. This indicates that *N*-pyrrolidinosquaraines should exhibit desirable photoconductive properties. Indeed, photoconductivities have been observed in xerographic devices incorporating these materials.[14]

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