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Squaraine Chemistry: Synthesis, Characterization and Xerographic Properties of Bis(4-methylbenzylaminophenyl)-squaraine and Its Derivatives

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SUMMARY

*Bis(4-methylbenzylaminophenyl)squaraine and a number of its derivatives (*N*-benzylsquaraines) have been synthesized by condensation of squaric acid with the corresponding* N*-benzylaniline derivatives. Two azeotropic solvent systems, namely 1-heptanol and 1-butanol/toluene, were used. Consistently higher yields, but less pure samples, were obtained in 1-heptanol. The higher yield is attributable to the favorable arylation reaction of the n-heptyl squarate intermediate rather than its esterification reaction in 1-heptanol in the squaraine synthesis. Although the spectroscopic properties of* N*-benzylsquaraines are found to be very similar to those of* N*-alkyl-substituted squaraines, the physical and the electrical properties between these two groups of squaraines are quite different.* N*-Benzyl squaraines exhibit high melting points, low solubility in organic solvents and moderate-to-high xerographic sensitivity in bilayer photoreceptor devices. Our results show that* N*-benzyl-substitution of squaraine is probably the only viable approach to modify the solubility of squaraine without significantly reducing the xerographic sensitivity. The xerographic properties of* N*-benzylsquaraines are found to be sensitive to the synthetic history of the sample (reacting solvent, recrystallization) and these results are discussed in terms of an impurity effect.*

INTRODUCTION

Bis(4-dimethylaminophenyl)squaraine, HSq, and many of its derivatives are known to have interesting semiconductive and photoconductive properties.

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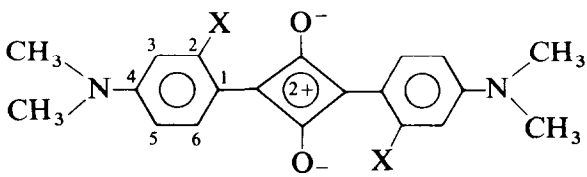
Owing to the exciton interactions, they generally exhibit intense and panchromatic absorption (400–1000 nm) in the solid state and have been shown to be useful for xerographic applications,[1-4] organic solar cells[5-9] and ablative optical recording.[10-12]

Structural modification of squaraines has been a very popular research topic since the original report of the synthesis.[13] Two kinds of substituents, namely substitution in the phenyl ring and substitution at the nitrogen, have been studied. As a result of these efforts, a large number of squaraine derivatives have been synthesized.[14-18] Among the squaraines reported so far, HSq and its 2-substituted derivatives (FSq, HOSq and MeSq) are the only group found to be particularly useful for xerographic applications.[1-4,19] Common features among these compounds are that they all have *N*,*N*-dimethylamino groups, high melting points, low solubility in organic solvents and a very similar X-ray powder diffraction pattern.[19]



X = H	HSq
X = F	FSq
X = OH	HOSq
X = CH_3	MeSq

In contrast to squaraines with substitution in the phenyl ring, squaraines with substitution at the nitrogen (alkyl groups) usually have lower melting points,[20] higher solubility in organic solvents,[20] and different X-ray powder diffraction patterns in the solid.[21] Most photoreceptor devices fabricated from these squaraines are insensitive ($E_{0.5} > 100\,\text{erg cm}^{-2}$); the insensitivity has been attributed to perturbation of the intermolecular interactions of squaraine molecules in the solid state as revealed by the X-ray powder diffraction patterns, and consequently this results in the reduction of photogeneration efficiency in the photoreceptor device. (For examples of the effect of molecular interaction on the photogeneration efficiency, see refs 22 and 23.) The insensitivity might also be a fabrication effect, resulting from dissolution and recrystallization of squaraine molecules into an undesirable form during device fabrication.[5]

HSq and its 2-substituted derivatives are insoluble pigments and are usually used as synthesized. Additional purification and processing steps to improve their xerographic properties have yet to be developed. The objective of the present work is to synthesize xerographically active, soluble squaraines that are processable by conventional recrystallization technique and to study the effect of purification on the xerographic properties of these materials. We describe here the synthesis and the structural characterization of a number of *N*-benzyl-substituted squaraines (*N*-benzylsquaraines). The differences in physical and spectroscopic properties between *N*-

benzylsquaraines and *N*-alkylsquaraines are presented. The xerographic properties of the *N*-benzylsquaraines synthesized in this work were studied in bilayer photoreceptor devices. Effects of synthesis and recrystallization on the xerographic properties of *N*-benzylsquaraines are reported and discussed.

EXPERIMENTAL

Materials

Squaric acid, *m*-fluoroaniline, *N*-methylaniline, trimethyl orthoformate, 1-heptanol, 2-chloroethanol, benzyl chloride, *p*-fluorobenzyl chloride, *p*-chlorobenzyl chloride and *m*-chlorobenzyl chloride were obtained from Aldrich. Toluene and 1-butanol were spectro-analyzed grade from Baker. All these materials were used as received.

General techniques

Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and are uncorrected. Infrared spectra were determined on a Perkin–Elmer infrared spectrophotometer 283. Proton NMR were recorded on a Bruker WP-80 spectrometer. Absorption spectra were taken on a Cary 17 spectrophotometer. Mass spectra were recorded either on a Nuclide 12-90 GCMS single-focusing magnetic-sector spectrometer or on a Varian VG 7035 mass spectrometer with an electron energy of 70 eV. Elemental analysis was performed by Galbraith Laboratories.

N-Methyl-*m*-fluoroaniline

N-Methyl-*m*-fluoroaniline was synthesized according to the procedure described by Roberts and Vogt.[24] To a mixture of 124·7 g (1·12 mol) of *m*-fluoroaniline and 178·6 g (1·68 mol) of trimethyl orthoformate was added, with stirring, 4·6 g of concentrated sulfuric acid. The flask was then attached to a vacuum-jacketed Vigreux distilling column ($\frac{3}{4}$ in diameter × 12 in long) and the mixture was heated with stirring at an oil-bath temperature of ~120°C. About 175 ml of methanol was distilled over in an hour. The bath temperature was then increased slowly to ~205°C and was maintained for 30 min. An additional amount of volatile materials (~25 ml) was distilled over during this time.

Subsequently, the reaction mixture was cooled to room temperature and the distillation apparatus was connected to a vacuum pump. The product, *N*-methyl-*m*-fluoroformanilide, was isolated and purified by vacuum

distillation (at ~78°C at 0·19 mm Hg). Yield 108·4 g (63%); IR(CCl_4): 1690 cm^{-1} (C=O).

N-Methyl-*m*-fluoroformanilide (108·4 g; 0·71 mol) was hydrolyzed by refluxing for 2 h with 350 ml 10% hydrochloric acid. The mixture was cooled to room temperature and was made basic with 15% KOH solution. The organic layer was then separated. The aqueous layer was first saturated with K_2CO_3 and then extracted with ether (2 × 400 ml). The organic fractions were combined, washed with water and dried over anhydrous $MgSO_4$. After removing the ether, *N*-methyl-*m*-fluoroaniline was isolated as a colorless liquid by reduced-pressure distillation at 80°C at ~10 mm Hg. Yield 76·5 g (87%); IR(CCl_4): 3450 cm^{-1} (N—H); NMR (CD_2Cl_2): δ 2·8 (s, 3H), 3·92 (bs, 1H, exchangeable), 6·2–6·6 (m, 3H) and 6·95–7·4 (m, 1H): mass spectrum (*m/z*): 125 (M^+).

Calc. for C_7H_8NF: C, 67·2; H, 6·4; N, 11·2; F, 15·2. Found: C, 67·2; H, 6·4; N, 11·3; F, 14·9.

Synthesis of *N*-methyl-*N*-benzylaniline and its derivatives

N-Methyl-*N*-benzylaniline and its derivatives were synthesized from *N*-methylaniline (or *N*-methyl-*m*-fluoroaniline) and benzyl chloride derivatives according to the procedures described by Desai.[25] Typically, 0·14 mol of *N*-methylaniline derivative and 0·14 mol of benzyl chloride derivative were allowed to react at a bath temperature of ~110°C in the presence of 11·9 g anhydrous sodium acetate and 0·12 g iodine for ~16 h. The reaction mixture was then cooled and was transferred to a 250 ml separating funnel with 100 ml of water. The product solution was made basic with sodium hydroxide and was then extracted with ether (4 × 80 ml). The combined ether extract was washed with water and then dried over anhydrous $MgSO_4$. After removing the ether, the product was isolated by vacuum distillation. The yields, physical properties and spectroscopic data of the *N*-methyl-*N*-benzylaniline derivatives thus synthesized are summarized in Table 1.

Squaraine synthesis

Squaraines were synthesized by two published procedures and these are outlined as follows. The yields, the physical properties and the spectroscopic data of the squaraines prepared are tabulated in Tables 2 and 3.

Method A[14]

Squaric acid (1·14 g, 10 mmol) and the *N*-methyl-*N*-benzylaniline derivative (20 mmol) were heated to reflux in a mixture of toluene (40 ml) and 1-butanol

(40 ml) at a bath temperature of ~130°C. Water was removed by a Dean–Stark trap. After 8 h, the reaction mixture was cooled to room temperature. The product was isolated by filtration.

Method B[26]
Squaric acid (1·14 g, 10 mmol) and the *N*-methyl-*N*-benzylaniline derivative (20 mmol) were allowed to react in 50 ml 1-heptanol at an oil bath temperature of ~105°C under a reduced pressure of ~70 mm Hg. Water was distilled off azeotropically under this condition and was collected by a Dean–Stark trap. After 20–24 h, the mixture was cooled and the product was isolated by filtration.

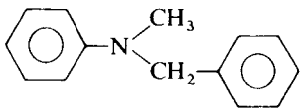
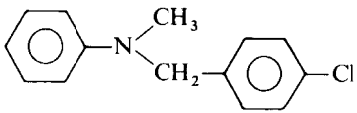
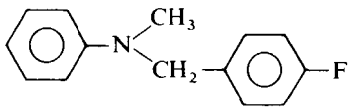
Device fabrication and evaluation

The xerographic properties of squaraine were studied in bilayer photoreceptor devices, which consist of a squaraine Charge Generation Layer (CGL) and a triaryl amine Charge Transporting Layer (CTL) on an aluminum substrate. The CGL is ~0·5 μm thick and contains ~40% (by wt) of a squaraine compound in a Makrolon® binder (a polycarbonate from Mobay Chemical Company). The CTL is ~30 μm thick and is a solid-state solution of 40% of *N*,*N*-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD)[27] in Makrolon® Details of the formulation and the fabrication procedure have been reported earlier.[28] A schematic of the cross-section of a bilayer photoreceptor device is given in Fig. 1a.

Xerographic measurements were made on a flat-plate scanner using 2 in × 2·5 in samples. Typically, the bilayer device was charged negatively to about −1000 V by a corotron device. The surface potential of the device was monitored with a capacitively coupled ring probe connected to a Keithley electrometer (Model 610C) in the Coulomb mode. The output of the electrometer was displayed on a strip-chart recorder (HP Model 740A) which was calibrated by applying known voltage on an uncoated aluminum substrate. The exposure wavelength and the intensity were selected and adjusted using interference and neutral density filters, respectively. With the shutter closed, the dark decay of the device ($\Delta V/\Delta t$) was measured. With the shutter open, the device could be exposed to an intense erase light to determine the residual potential (V_R) or to a monochromatic radiation of known intensity (I erg cm^{-2} s^{-1}) to determine the photosensitivity of the device, which is expressed as $E_{0.5}$, the energy required to photodischarge half of the initial potential (V_i). $E_{0.5}$ is the product of I and t, where t is the time for I to photodischarge the device from V_i to $\frac{1}{2}V_i$: the lower the $E_{0.5}$ value, the higher the photosensitivity. Schematics of the photodischarge curves are given in Fig. 1b.

TABLE 1

Synthesis, Properties and Spectroscopic Data of *N*-Benzylanilines

N-*benzylaniline*	*Yield* (%)	*B.p.* (°C)	*Analysis*					M^+ (*m/z*)	^{1}*H-NMR* (*in* CD_2Cl_2, *ppm from TMS*)
			C	*H*	*N*	*Cl*	*F*		
	79	157 at 0·18 mm Hg (lit. 162 at 8 mm Hg)						197	2·99 (s, 3H), 4·45 (s, 2H), and 6·5–7·5 (m, 10 H)
	58	158 at 0·25 mm Hg	Calc.: 72·57 Found: 72·44	6·09 6·02	6 04 6·03	15·30 15·68		231	3·03 (s, 3H), 4·53 (s, 2H), 6·55–6·90 (m, 3H), and 7·1–7·4 (m, 6H)
	59	128 at 0·14 mm Hg	Calc.: 78·11 Found: 78·25	6·56 6·73	6·51 6·51		8·83 8·76	215	3·0 (s, 3H), 4·5 (s, 2H), and 6·6–7·4 (m, 9H)

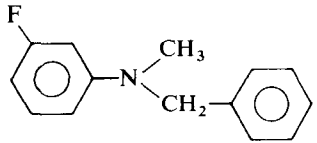
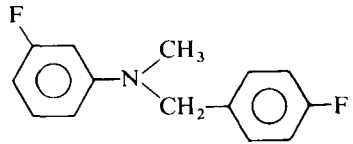
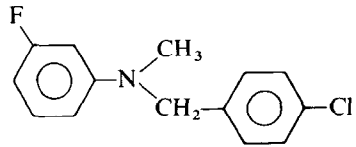
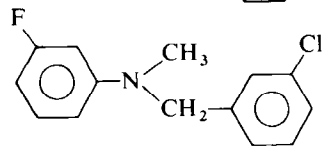
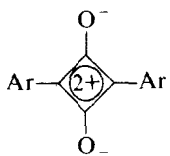
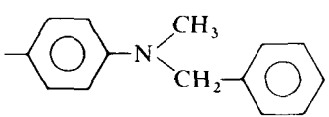
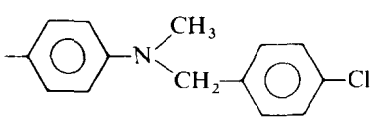
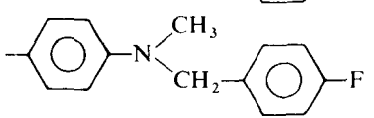
	90	135 at 0·05 mm Hg	Calc.: Found:	78·11 78·14	6·56 6·72	6·51 6·54		8·83 8·76	215	3·02 (s, 3H), 4·53 (s, 2H), 6·2–6·6 (m, 3H), and 6·9–7·4 (m, 6H)
	72	135 at 0·2 mm Hg	Calc.: Found:	72·09 72·00	5·62 5·64	6·00 5·92		16·29 16·14	233	3·05 (s, 3H), 4·53 (s, 2H), 6·2–6·4 (m, 3H), and 6·8–7·4 (m, 5H)
	78	170 at 0·14 mm Hg	Calc.: Found:	67·34 67·45	5·25 5·22	5·61 5·58	14·20 14·31	7·61 7·47	249	3·04 (s, 3H), 4·52 (s, 2H), 6·2–6·4 (m, 3H), and 7·0–7·4 (m, 5H)
	84	172 at 0·07 mm Hg	Calc.: Found:	67·34 67·20	5·25 5·39	5·61 5·77	14·20 14·42	7·61 7·70	249	3·05 (s, 3H), 4·54 (s, 2H), 6·2–6·4 (m, 3H) and 6·9–7·4 (m, 5H)

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



Ar	*Symbol*	*Yield (%) (m.p. (°C))*			*Analysis*				
		Method A	*Method B*		*C*	*H*	*N*	*Cl*	*F*
	BzHSq	43 (254–255)	63 (252–253)	Calc.: Found:	81·33 81·48	5·97 6·05	5·93 5·90		
	ClBzHSq	29 (260–260·5)	63 (256·5–257·5)	Calc.: Found:	70·98 71·06	4·84 4·84	5·17 5·15	13·09 12·96	
	FBzHSq	20 (242·5–243)	63 (241–242)	Calc.: Found:	75·58 75·49	5·15 5·41	5·51 5·46		7·47 7·49

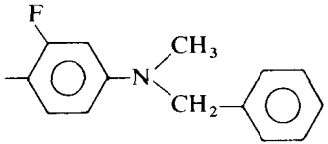
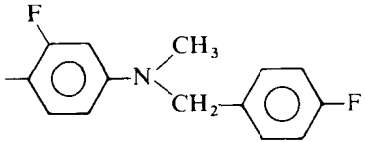
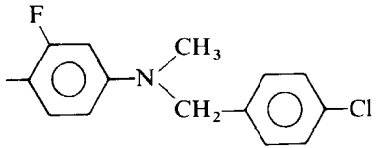
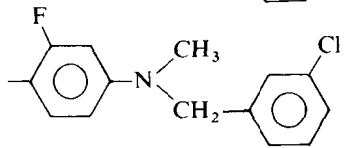
	BzFSq	4·5 (247–249)	29 (246–247)	Calc.:	75·58	5·15	5·51		7·47
				Found:	75·43	5·10	5·68		7·38
	F. BzFSq	< 1	28 (237–238)	Calc.:	70·58	4·44	5·14		13·96
				Found:	70·60	4·50	5·03		14·17
	Cl. BzFSq	0	29 (245·5–247)	Calc.:	66·56	4·19	4·85	12·28	6·58
				Found:	66·50	4·33	4·76	12·27	6·54
	*m*-Cl. BzFSq	0	7 (232–233)	Calc.:	66·56	4·19	4·85	12·28	6·58
				Found:	66·67	4·30	4·86	12·28	6·72

TABLE 3
IR, VIS-Absorption and ^{1}H-NMR Spectral Data of *N*-Benzylsquaraines

N-*benzylsquaraine*	*IR* (cm^{-1})[a]	λ_{max} (*nm*)[b]	*log* ε (cm^{-1} M^{-1})[c]	^{1}*H-NMR* (*ppm from TMS*)[d]
BzHSq	1 616, 1 590	628·2	5·56	3·24 (s, 6H), 4·74 (s, 4H), 6·9 (d, 4H, $J = 8·6$ Hz), 7·1–7·5 (m, 10H) and 8·32 (d, 4H, $J = 8·6$ Hz)
Cl. BzHSq	1 615, 1 585	626·4	5·55	3·22 (s, 6H), 4·72 (s, 4H), 6·84 (d, 4H, $J = 9$ Hz), 7·22 (AB quartet, 8H, $J = 9$ Hz) and 8·42 (d, 4H, $J = 9$ Hz)
F. BzHSq	1 614, 1 590	626·4	5·52	3·23 (s, 6H), 4·75 (s, 4H), 6·88 (d, 4H, $J = 8·6$ Hz), 7·0–7·3 (m, 8H) and 8·32 (d, 4H, $J = 8·6$ Hz)
BzFSq	1 600 (broad)	632·6	5·50	3·24 (s, 6H), 4·74 (s, 4H), 6·6–6·8 (m, 4H), 7·0–7·5 (m, 10H) and 8·5–8·8 (m, 2H)
F. BzFSq	1 595 (broad)	630·9	5·49	3·20 (s, 6H), 4·70 (s, 4H), 6·4–6·8 (m, 4H), 7·0–7·2 (m, 8H) and 8·6–8·9 (m, 2H)
Cl. BzFSq	1 595 (broad)	630·6	5·30	
m-Cl. BzFSq	1 610 (broad)	630·6	5·45	3·22 (s, 6H), 4·68 (s, 4H), 6·3–6·8 (m, 4H), 6·8–7·4 (m, 8H) and 8·5–8·9 (m, 2H)

[a] In KBr.
[b] In CH_2Cl_2.
[c] Molar extinction coefficient.
[d] In $CDCl_3$.
[e] The solubility of this compound is too low for solution spectrum.

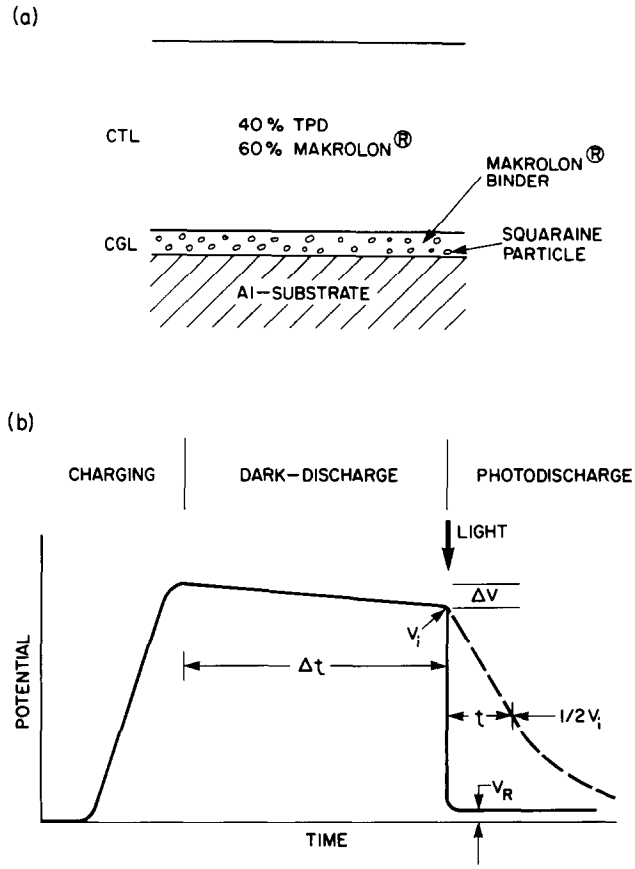


Fig. 1. (a) A cross-section of a bilayer photoreceptor device. (b) Schematics of photodischarge curves: ——, photodischarge by intense erase white light ($I > 10^4$ ergs cm^{-2} s^{-1}); – – –, photodischarge by monochromatic light I at 600 (32·7 ergs cm^{-2} s^{-1}) or 800 (46·1 ergs cm^{-2} s^{-1}) nm.

RESULTS AND DISCUSSION

Synthesis of *N*-methyl-*N*-benzylaniline and derivatives

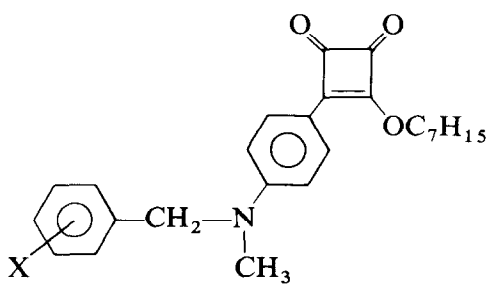
N-Methylaniline and *N*-methyl-*m*-fluoroaniline are the starting compounds in the benzylaniline synthesis. The latter compound, which is not commercially available, was prepared in a two-step synthesis analogous to that described by Roberts and Vogt.[24] The advantage of this approach is that, after a single methylation of *m*-fluoroaniline by trimethyl orthoformate, the nitrogen is protected from further methylation by forming a formanilide. Hydrolysis of the formanilide yields the single methylated

compound cleanly. In the present work, *N*-methyl-*m*-fluoroaniline was obtained in ~55% overall yield. Reaction of one equivalent of *N*-methylaniline (or derivative) with one equivalent of benzyl chloride (or derivatives) under the catalytic effects of iodine and sodium acetate yields *N*-methyl-*N*-benzylaniline or derivatives in 60–90% isolated yields. Satisfactory elemental analyses and spectroscopic data were obtained for all the *N*-methyl-*N*-benzylaniline derivatives synthesized and the data are tabulated in Table 1.

Synthesis and physical properties of *N*-benzylsquaraines

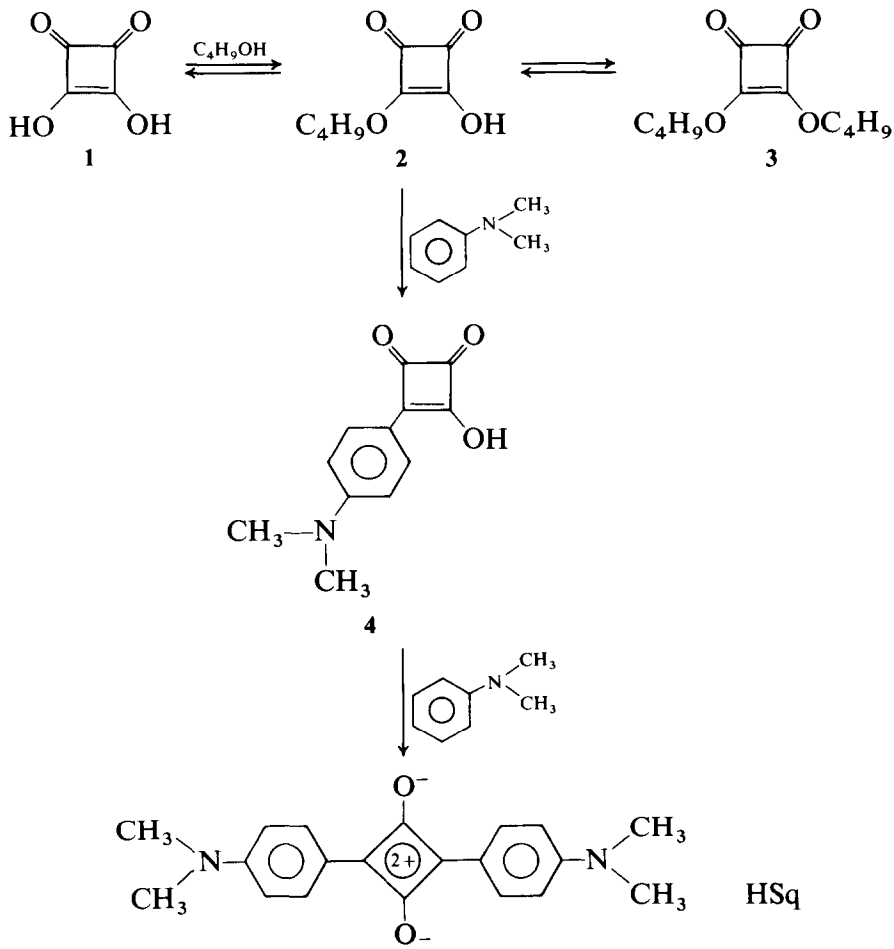
N-Benzylsquaraines were synthesized from squaric acid and *N*-methyl-*N*-benzylaniline (or derivatives). Two azeotropic solvent systems, namely 1-butanol/toluene and 1-heptanol, were used and analytically pure samples were obtained from both procedures. The yields and the physical properties of the *N*-benzylsquaraines synthesized are tabulated in Table 2. The melting points of the *N*-benzylsquaraines synthesized are relatively high, ranging from 230 to ~260°C. This melting point range is lower than that of HSq by about 10–40°C,[13] but is much higher than those of *N*-alkyl-substituted squaraines where their melting points are below 200°C.[20] These results suggest that, in contrast to *N*-alkyl substitution, *N*-benzyl substitution has no significant effect on the melting points of squaraines.

For a given solvent system, yield decreases as the reactivity of the aniline decreases (by the electron-withdrawing halobenzyl group). Fluoro substitution at the *meta*-position reduces the chemical yield of the squaraine synthesis drastically. This is attributable to the electron-withdrawing and steric effects of the fluorine atom exerted on the adjacent reacting carbon. The results in Table 2 also show that consistently higher synthetic yields are obtained in 1-heptanol. This is however accompanied by a decrease in melting points. Since impurities were detected for squaraine samples synthesized in 1-heptanol during the mass spectrometric analyses of squaraines, we attribute the melting-point lowering to an impurity effect. Impurities of the following general structure were detected during the mass



spectrometric analyses of squaraines synthesized in 1-heptanol. Analogous *n*-butyl compounds were not detected for squaraines synthesized in 1-butanol, however.

The squaraine synthesis described above was reported about two decades ago,[13] but the mechanism of squaraine formation remains to be a subject of further investigation. Using squaric acid and *N,N*-dimethylaniline as model reactants, and 1-butanol/toluene as solvent, we have established that *n*-butylsquarate, **2**, is a reaction intermediate in the synthesis (Scheme 1).[29] Arylation of **2** with *N,N*-dimethylaniline gives 1-*p*-(*N,N*-dimethylanilino)-2-hydroxycyclobutene-3,4-dione, **4**, which further reacts with *N,N*-dimethylaniline to give a squaraine product, HSq. The major side-reaction of **2** is to esterify to give dibutylsquarate, **3**, which is known not to give any squaraine product under neutral conditions.[29] Thus, the yield of squaraine



Scheme 1

in the synthesis is primarily controlled by the competitive arylation and esterification reactions of **2**. Consideration of bond dissociation energy shows that the esterification reaction of **2** → **3** is endothermic by ~12 kcal mol^{-1} and that the arylation reaction of **2** → **4** is exothermic by ~8 kcal mol^{-1}. According to Hammond's postulate,[30] the esterification reaction should have a relatively late transition state due to its endothermicity. That is to say, the impact of steric effect on the esterification reaction is greater than that of arylation from 1-butanol to 1-heptanol. The high yield of squaraine formation in 1-heptanol may thus be attributed to the favorable arylation of *n*-heptylsquarate in the reacting solvent.

Spectroscopic data of *N*-benzylsquaraines

IR spectra

Results in Table 3 show that all *N*-benzylsquaraines exhibit strong IR absorption bands at ~1600 cm^{-1}. These IR bands are attributable to the C···C bond stretching 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 extensive bond delocalization in squaraines. Similar results were obtained in other squaraines.[20]

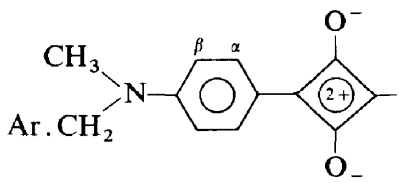
VIS spectra

N-Benzylsquaraines exhibit intense absorption ($\varepsilon \simeq 3 \times 10^5\ cm^{-1}\ M^{-1}$) in the visible region in methylene chloride solution. Their absorption maxima vary from 626 to 631 nm depending on the substitution in the benzyl group and the fluoro substitution in the phenyl ring. More detailed discussion on the effect of structural changes on the electronic spectra of squaraines will be reported elsewhere.[31]

^{1}H-NMR spectra

With the exception of Cl. BzFSq, the solubility of which in chloroform is too low for a solution ^{1}H-NMR spectrum, all other *N*-benzylsquaraines synthesized exhibit sufficient solubility for solution ^{1}H-NMR studies. The results in Table 3 show that they all show two singlets at $\delta \simeq 3{\cdot}2$ and $\delta \simeq 4{\cdot}7$ with an integration ratio of 3 to 2. These two singlets are assigned to the N—CH_3 and the N—CH_2 groups at the nitrogen respectively.

More interesting results are observed in the aromatic region. The aromatic protons in the phenyl ring of the benzyl group are usually at δ 7·0–7·5. For BzFSq, Cl. BzHSq and F. BzHSq, two doublets of coupling constant of ~9 Hz are observed at $\delta \simeq 6{\cdot}9$ and $\delta \simeq 8{\cdot}4$ and they are assigned to the β- and the α-protons in the phenyl ring adjacent to the four-membered ring of squaraine, respectively.



As compared with the chemical shifts of the aromatic protons of *N*-benzylaniline (Table 1), the α-protons are about 1 ppm lower-field than expected. Similar downfield shift was also observed for the α-protons of other squaraines.[20] The mechanism of the deshielding effect on the α-proton has recently been studied and details will be reported elsewhere.[32]

In the cases of BzFSq, F. BzFSq, Cl. BzFSq and *m*-Cl. BzFSq, the ratios of the downfield protons to the high-field protons are 2:4, confirming the assignment of the aromatic protons. Unlike other squaraines with an α-substituent where a doublet is observed for the remaining α-proton,[20] multiplets are observed for the fluoro *N*-benzylsquaraines synthesized in this work. This is attributed to the additional coupling between the α-proton and the fluorine atom in the phenyl ring.

Electron impact mass spectra

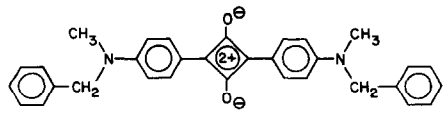
The electron impact mass spectral data of *N*-benzylsquaraines are summarized in Table 4 and representative spectra are given in Figs 2 and 3. As seen in Figs 2 and 3, both BzHSq and BzFSq give clean mass spectra. The striking feature in the mass spectra is the consistent occurrence of ions of mass numbers higher than the molecular ions. These ions are at m/z $(M + 2)$, $(M + 14)$ and $(M + 90)$ and can be assigned to the addition of two hydrogen atoms, a CH_2 group and a $CH.C_6H_5$ group to the molecular ions. This assignment is further supported by the mass spectral data of other *N*-benzylsquaraines (Table 4) where ions at m/z $(M + 108)$ and $(M + 124)$ are observed when the benzyl groups are fluorobenzyl and chlorobenzyl groups respectively. The formation of ions of m/z higher than that of M^+ suggests that some kind of intermolecular H-transfer and alkyl-transfer reactions are occurring in the mass spectrometer.

Similarly to the high mass number ions, lower molecular weight fragment ions also appear to be very characteristic. From the structure–property relationship of the mass spectra of *N*-benzylsquaraines, three kinds of fragment ions of general structures **5**, **6** and **7** (see Scheme 2 for structures) can be deduced. The formation of **5** and **7** is very interesting because the carbon atom adjacent to the four-membered ring of squaraine is bonded neither to an oxygen atom nor to a hydrogen atom and their formation indicates the occurrence of molecular rearrangement processes in the mass spectrometer.

TABLE 4
Mass Spectral Data of *N*-Benzylsquaraines

Squaraine	*m/z (relative intensity)*[a]						
	M^+	$M + CH_2^{\neg\ddagger}$ *and* $M + CHAr^{\neg\ddagger}$	***5***	***6***	$M + H_2^{\neg\ddagger}$	***7***	*Base peak*
BzHSq	472 (39)	486 (38) 562 (100)		237 (7·8)	474 (30)		$M + CH \cdot C_6H_5^{\neg\ddagger}$
Cl. BzHsq	540 (4·5)	554 (1·0) 664 (0·4)	258 (7·3)		542 (0·3)	244 (8·8)	$C_7H_7^+$
F. BzHSq	508 (0·4)	522 (3) 616 (19)	242 (15)	255 (2·4)	510 (6·3)	228 (19)	$C_7H_6F^+$
BzFSq	508 (6·9)	522 (9·8) 598 (4·4)	242 (3·5)	255 (1·4)		228 (91)	$C_7H_7^+$
F. BzFSq	544 (13)	558 (38) 652 (51)	260 (4·9)	273 (5·9)	546 (5·8)	246 (14)	$C_7H_6F^+$
Cl. BzFSq	576 (12)	590 (84) 699 (23)	276 (3·7)	289 (49)	578 (1·6)	262 (18)	$C_7H_6Cl^+$
m-Cl. BzFSq	576 (14)	590 (31) 699 (12)			578 (11)	262 (37)	C_7H_7

[a] For chloro compounds, the contribution from isotropic peaks is included.



M. W. 472

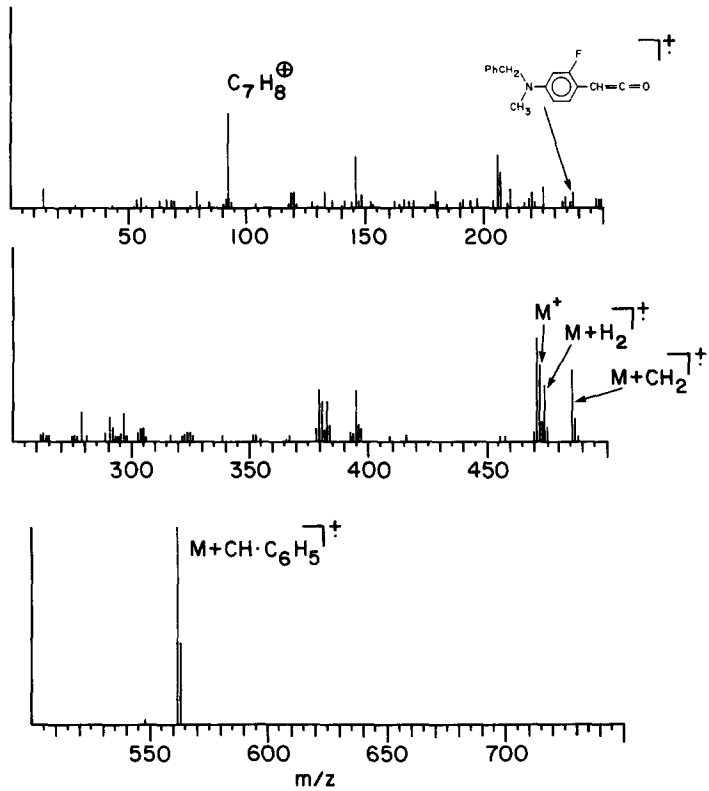


Fig. 2. EI mass spectrum of BzHSq.

The anomalous mass spectrometric behavior of squaraines has been studied in our laboratory.[20] Our results show that, owing to the strong donor–acceptor interactions 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 ions. These alkylated and hydrogenated species further fragment into the characteristic rearranged products of structures similar to those of **5** and **7**. The similarity in the fragmentation pattern between *N*-benzylsquaraines and other *N*-alkylsquaraines suggests that they all have the same sets of mass-spectral reactions, which are summarized in Scheme 2 and mechanistic details of which have been reported previously.[20]

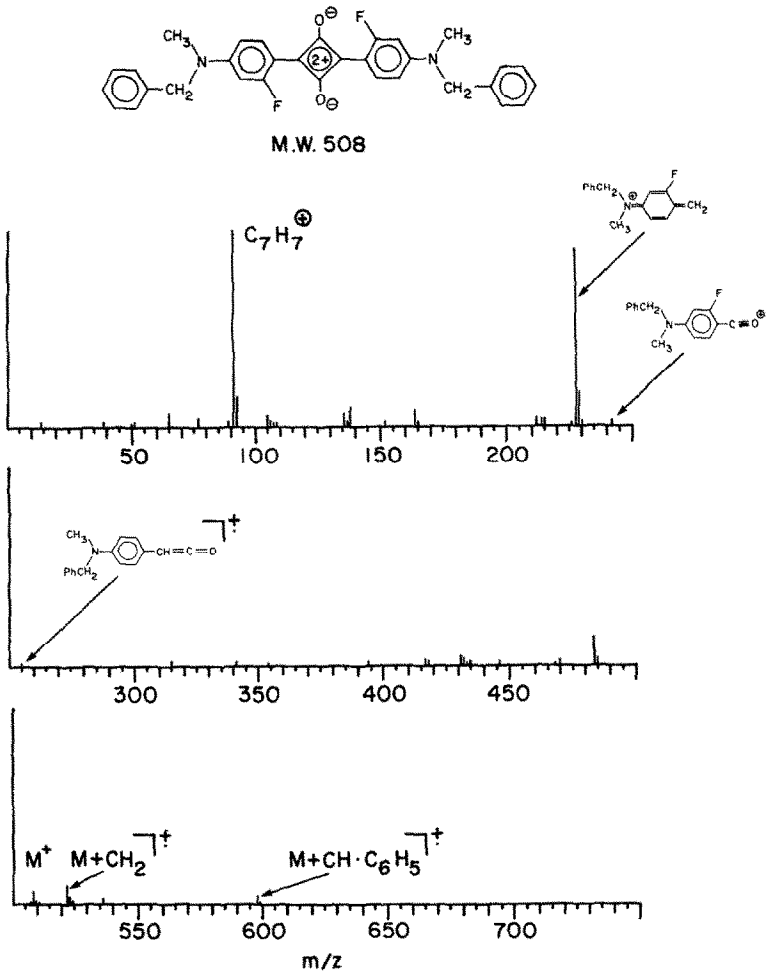
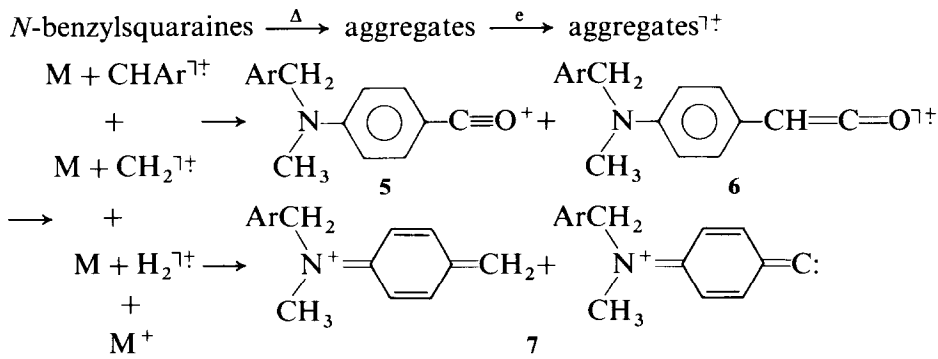


Fig. 3. EI mass spectrum of BzFSq.

In addition to the fragmentation processes described in Scheme 2, dealkylation reactions (—CH_2Ar) are found to be the only major mass-spectral reactions of various ions. A typical example is shown in the mass spectrum of BzHSq (Fig. 2) and major dealkylation reactions are summarized in Table 5. As a result, prominent peaks (often base peaks) at m/z corresponding to $C_6H_5.CH_2^+$ or $X.C_6H_4CH_2^+$ (X = Cl or F) are observed in the EI mass spectra of *N*-benzylsquaraines.

Xerographic properties

There are four key steps in xerography, namely charging, photodischarge, image transfer, and development and cleaning. In order to achieve high



Scheme 2

imaging quality, a photoreceptor device should have high charge-acceptance and low dark-conductivity values (for a discussion on xerography, see ref. 33). The xerographic properties of all the *N*-benzylsquaraines synthesized were studied in bilayer photoreceptor devices. The results in Table 6 show that squaraines synthesized in 1-butanol consistently exhibit better xerographic properties, viz., better charge acceptance, lower dark decay and higher photosensitivity, compared with those synthesized in 1-heptanol. Since lower melting points are also observed in the 1-heptanol samples, we attribute the inferior xerographic properties of these samples to an impurity effect.

The improved solubility of *N*-benzylsquaraines has allowed us to purify these compounds by recrystallization (from 2-chloroethanol and methanol). Data on the melting points and the xerographic properties of the recrystallized samples are summarized in Table 7. Mixed results are obtained in the melting point measurements where three of the recrystallized samples (BzHSq, F.BzHSq and F.BzFSq) actually give lower melting points after recrystallization. Very recently, Wingard[2] showed that squaraines can

TABLE 5
Major Dealkylation Reactions of BzHSq

562	$\xrightarrow{CH_2C_6H_5}$	471	$\xrightarrow{CH_2C_6H_5}$	380	$\xrightarrow{CH_2C_6H_5}$	289
$(M + CHC_6H_5^+)$						
486	$\xrightarrow{CH_2C_6H_5}$	395	$\xrightarrow{CH_2C_6H_5}$	304		
$(M + CH_2^+)$						
474	$\xrightarrow{CH_2C_6H_5}$	383	$\xrightarrow{CH_2C_6H_5}$	292		
$(M + H_2^+)$						
472	$\xrightarrow{CH_2C_6H_5}$	381				
(M^+)						

TABLE 6
Xerographic Properties of *N*-Benzylsquaraines

	BzHSq		*Cl. BzHSq*		*F. BzHSq*		*BzFSq*		*F. BzFSq*		*Cl. BzFSq*		*m-Cl. BzFSq*	
	Method		*Method*		*Method*		*Method*		*Method*		*Method*		*Method*	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*[c]	*B*	*A*[c]	*B*	*A*[c]	*B*
Corotron (kV)	−5·3	−5·25	−6·4	−7·0	−5·25	−7·0	−6·5	−7·0		−5·7		−7·0		−5·75
V_i(V)	−900	−920	−820	[a]	−960	[a]	−800	[a]		−880		[a]		−920
$\Delta V/\Delta t$(V s^{-1})	−90	−70	−140		−110		−190			−125				−100
V_R (V)	−50	−120	−40		−40		−40			−30				−60
$E_{0\,5}$ (erg cm^{-2})														
600 nm	37	54	23		[b]		11·2			18·6				32·6
800 nm	56	66	21		[b]		12·4			18·6				31·7

[a] V_{ddp} worse than −500 V.
[b] $E_{0\,5} > 100$ erg cm^{-2}.
[c] This squaraine could not be prepared by method A.

TABLE 7
Xerographic Properties of Recrystallized *N*-Benzylsquaraines

	BzHSq	*Cl. BzHSq*	*F. BzHSq*	*BzFSq*	*F. BzFSq*	*Cl. BzFSq*	*m-Cl. BzFSq*
M.p. (°C)	247–248	270–272	236–238	247–249	232–234	248–249	232–234
Corotron (kV)	−5·4	−6·0	−5·5	−6·0	−5·4	−7·0	−5·75
V_i (V)	−960	−980	−950	−950	−950	−940	−940
$\Delta V/\Delta t$ (V s^{-1})	·−35	−95	−65	−105	−75	−115	−80
V_R (V)	−20	−50	−50	−40	−20	−30	−20
$E_{0\,5}$ (erg cm^{-2})							
600 nm	38·2	10·9	90	16·8	10·2	5·9	25·6
800 nm	44	8·1	88·5	13·6	8·2	5·9	21·2

form inclusion complexes with chlorinated solvent (chloroform) in the solid state. It is thus possible that the melting point lowering is the result of the solvent incorporation into the microcrystals during recrystallization. Despite this complication, comparison of the results in Tables 6 and 7 show that all recrystallized samples give improved xerographic properties (higher charge acceptance, lower dark decay and higher photosensitivity). We attribute the improvement to the removal of impurities generated in the squaraine synthesis.

The $E_{0.5}$ values of the *N*-benzylsquaraines synthesized are in the range of $\sim$6–80 erg cm^{-2} from the visible to the near-IR and are about a factor of 2–25 larger than those of HSq and its derivatives ($E_{0.5}$ values range from 3 to 15 erg cm^{-2}).[19] Recent electrochemical measurements suggested that the generally low xerographic sensitivity of *N*-benzylsquaraines is not due to any energy mismatch in the bilayer photoreceptor device. Since X-ray diffraction data of *N*-benzylsquaraines indicate that they not only have a different diffraction pattern, but also a relatively low crystallinity, compared with HSq, the low sensitivity may thus be a morphological effect.[21] Nevertheless, results in Table 7 show that Cl. BzFSq is the most sensitive (lowest $E_{0.5}$ value) *N*-benzylsquaraine synthesized in this work. Its $E_{0.5}$ values, which are $\sim$6 erg cm^{-2} from the visible to the near-IR, are comparable with those of HSq ($E_{0.5} \sim 5$ erg cm^{-2})[28] at similar molar concentration in the charge generation layer.

CONCLUSIONS

N-Benzyl substitution of squaraine has been shown to be a viable approach in modifying the solubility of squaraine without total sacrifice of the xerographic sensitivity. Squaraines synthesized from squaric acid usually contain a minute amount of impurity, which results in low charge-acceptance and high dark-decay values in xerographic devices. In this work, due to the enhanced solubility, we have been able to improve the xerographic properties of *N*-benzylsquaraines by solvent recrystallization.

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