Dyes and Pigments 9 (1988) 187–200

Squaraine Chemistry. Synthesis, Structural Characterization and Xerographic Properties of Mixtures of Halosquaraines

Kock-Yee Law, Samuel Kaplan and Raymond K. Crandall

Xerox Webster Research Center, 800 Phillips Road, 0114-39D Webster, NY 14580, USA

(Received 12 May 1987; accepted 26 May 1987)

SUMMARY

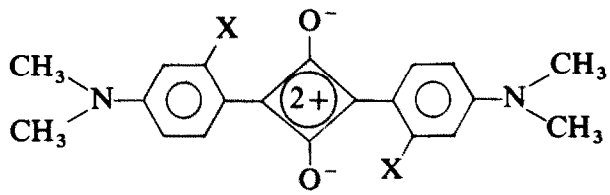
A number of mixtures of halosquaraines have been synthesized by co-reacting mixtures of N,N-*dimethylaniline and* N,N-*dimethylhaloaniline with dibutyl squarate in water-saturated 1-butanol. Yield decreases as the concentration of* N,N-*dimethylhaloaniline increases and this decrease is attributable to the low reactivity of* N,N-*dimethylhaloaniline. This low reactivity is also revealed in the lower than expected halogen incorporation in all the mixtures studied. The chemical composition of each mixture was studied by high-resolution proton NMR spectroscopy and mass spectrometry. The merit of these two techniques in the identification and quantification of individual squaraines in the mixtures is presented and discussed.*

The xerographic properties of each mixture were studied by xerographic photodischarge technique in bilayer photoreceptor devices; improvement in photosensitivity is observed for squaraine mixtures synthesized from N,N-*dimethylaniline (DMA) and 3-fluoro-*N,N-*dimethylaniline (3-FDMA). At a DMA/3-FDMA ratio of 75/25, the fluorosquaraine composition synthesized exhibits photosensitivity similar to the pure fluorosquaraine synthesized from 3-FDMA. The yield of such a composition is 30%, an improvement of 11% from the pure fluorosquaraine synthesized from 3-FDMA.*

1 BACKGROUND

Bis(4-dimethylaminophenyl)squaraine, HSq, and many of its derivatives are known to possess useful photoconductive properties (for nomenclature, see Ref. 1). They exhibit intense and panchromatic absorption (400–1000 nm) in the solid state and have been shown to be useful for diode laser printer and multifunction printer–copier photoreceptor applications.[2–5]

The synthesis of squaraines is reviewed in Refs 6–8. They are generally prepared by condensing one equivalent of squaric acid with two equivalents of *N,N*-dialkylanilines in an azeotropic solvent. This synthesis is simple and versatile and a large number of squaraines have been synthesized by this procedure.[9–13] Squaraine pigments synthesized by this procedure are, however, often found to exhibit high dark-conductivity and low charge-acceptance values in photoreceptor devices.[14,15] (There are four key steps in xerography, namely charging, photodischarge, image transfer and development and cleaning. In order to achieve high imaging quality, a photoreceptor device should have high charge-acceptance and low dark-conductivity values. For a discussion on xerography, see Ref. 16.)



HSq: X = H

FSq: X = F

We have recently found that squaraines can also be prepared from dialkyl squarate and *N,N*-dialkylaniline in the presence of water and acid catalyst.[17] This procedure overcomes the above-described technological disadvantages. For example, HSq, a high dark-decay ($-300\,V\,s^{-1}$) pigment from the squaric acid procedure, has been synthesized in ~45% yield via the dialkyl squarate procedure with a dark-decay value better than $-80\,V\,s^{-1}$.[18] In that study, we have also been able to reduce the dark-decay value of another high dark-decay pigment, FSq, from $-300\,V\,s^{-1}$ to $\sim -80\,V\,s^{-1}$. In addition to the low dark-decay value, FSq exhibits the highest photosensitivity among all the squaraines reported.[18] The yield of FSq from this new procedure is, however, low (<19%). In this paper, we report our efforts in resolving this yield-sensitivity dilemma. Through systematic variation of the concentrations of 3-fluoro-*N,N*-dimethylaniline and *N,N*-dimethylaniline in the synthesis, a fluorosquaraine mixture of photosensitivity similar to that of FSq has been prepared. Synthetic work has also been extended to mixtures synthesized from 2-fluoro-*N,N*-dimethylaniline and 3-chloro-*N,N*-dimethylaniline. Methodologies for structural identification and quantification of individual squaraines in the mixtures are presented.

2 EXPERIMENTAL

2.1 Materials

Squaric acid, *N,N*-dimethylaniline (DMA), *m*-fluoroaniline, *o*-fluoroaniline and *m*-chloroaniline were purchased from Aldrich. Di-*n*-butyl squarate, 3-

fluoro-*N*,*N*-dimethylaniline (3-FDMA), 2-fluoro-*N*,*N*-dimethylaniline (2-FDMA) and 3-chloro-*N*,*N*-dimethylaniline (3-CIDMA) were synthesized as previously described.[17] All solvents used were reagent grade from Fisher and were used without further purification.

2.2 Techniques

Solution proton NMR spectra were recorded on a WH-400 spectrometer (at the University of Rochester) in $CDCl_3$ (99·996% d_1 from Merck). The high field was necessary to resolve peaks from individual compounds in the mixtures and to enhance the signal sensitivity in the very dilute solutions used in the present work. The relative concentration of individual squaraines in the mixture was determined from the relative ratio of the *N*-methyl protons of each squaraine. Since each NMR solution was prepared by dissolving extremely small quantities of sample in $CDCl_3$, it is possible that the quantitative results might be distorted due to the difference in solubility of each individual component. This solubility question was eliminated because the least soluble compound in the mixture, FSq, was found to be totally soluble under the concentration range studied ($\sim 10^{-5}$–10^{-6} M).

Electron impact mass spectra were recorded on a Varian VG7035 mass spectrometer at the University of Rochester with an electron energy of 70 eV. Details on the procedures have been documented earlier.[19] Elemental analyses were performed by Galbraith Laboratories.

2.3 General procedure for the synthesis of halosquaraine mixtures

Dibutyl squarate (1·13 g, 5 mmol), concentrated sulfuric acid (0·1 ml) and water-saturated 1-butanol (5 ml) were charged in a 100 ml three-neck flask, which was equipped with a magnetic stirbar and a nitrogen inlet. This mixture was stirred and brought to reflux under a N_2 atmosphere. A mixture of anilines ($\sim$ 10·1 mmol in total; see Table 1 for structures and molar ratios) was added slowly through a pressure-equalizing tunnel over a period of 6–8 h. The product solution turned light green in color at the end of the addition and was further heated for 40 h. After cooling to room temperature, $\sim$ 30 ml of methanol was added, the precipitated product was separated by filtration using a fine sintered glass funnel, then washed with methanol until the filtrate was light blue. The composition of the product was analyzed by elemental analysis, proton NMR spectroscopy and mass spectrometry.

2.4 Xerographic measurements

The xerographic properties of the pigments synthesized were studied in bilayer photoreceptor devices, which consist of a squaraine Charge

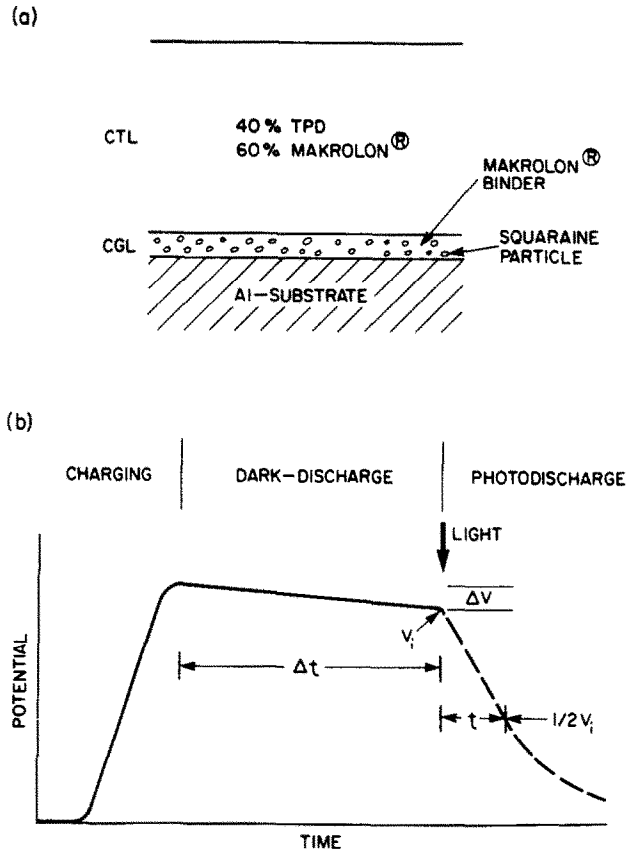


Fig. 1. (a) A cross-section of a bilayer photoreceptor device. (b) Schematic of a photodischarge curve.

Generation Layer (CGL) and a triaryl amine Charge Transporting Layer (CTL) on an aluminum substrate. The CGL is ~0·5 μm thick and contains ~30% (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)[20] in Makrolon®. Details on the formulation and the fabrication procedure have been reported earlier.[21] A schematic of the cross-section of a bilayer photoreceptor device is given in Fig. 1(a).

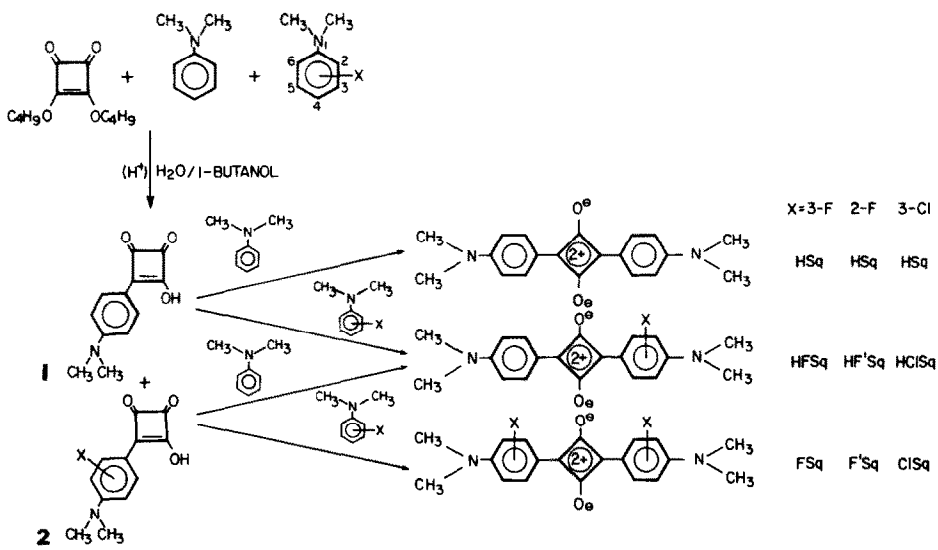
Xerographic measurements were made on a flat plate scanner using 5 cm × 6·3 cm (2 in × 2·5 in) samples. Details of the apparatus and the measuring procedure have been reported earlier.[21] Typically, the bilayer device was charged up negatively to about −1000 V by a corotron device. With the shutter closed, the dark decay of the device ($\Delta V/\Delta t$) was measured. With the shutter open, the device was exposed to a monochromatic

radiation of known intensity (I in erg cm^{-2} s^{-1}) to determine the photosensitivity of the device. The photosensitivity of the device 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 $\frac{1}{2}V_i$. A schematic of a photodischarge curve is given in Fig. 1(b).

3 RESULTS AND DISCUSSION

3.1 Synthesis

Mixtures of halosquaraines were synthesized from dibutyl squarate and aniline mixtures. The compositions of the aniline mixtures used in the present work are summarized in the first column of Table 1. The mechanism of squaraine formation and the synthetic aspects of this reaction have been discussed in an earlier report.[17] Because aniline mixtures are used in this work, two kinds of intermediates, namely 1-(*p*-dimethylaminophenyl)-2-hydroxycyclobutene-3,4-dione (**1**) and 1-(*p*-dimethylaminohalophenyl)-2-hydroxycyclobutene-3,4-dione (**2**) will be formed. These two intermediates undergo further arylation with the aniline in the mixture to generate three squaraine products, two symmetric squaraines HSq and XSq and one unsymmetric squaraine, HXSq (see Scheme 1). The data on the yields of the syntheses and the elemental analysis results are tabulated in Table 1. The



Scheme 1. Synthesis of mixture of halosquaraines.

TABLE 1
Synthesis and Properties of Mixtures of Haloquaraines

Molar ratio of aniline reactant	*Yield (%)*[a]	*Elemental analysis (%)*					*Expected*[a] *F or Cl (%)*	*Xerographic data*	
		C	*H*	*N*	*F*	*Cl*		$\Delta V/\Delta t$ ($V\ s^{-1}$)	$E_{0.5}$ *at 800 nm* ($erg\ cm^{-2}$)
DMA/3-FDMA									
100/0[b]	45	75·11	6·46	9·06				−95	4·1
70/30	43	74·12	6·64	8·51	1·08		3·44	−55	3·5
50/50	35	73·28	6·29	8·49	2·75		5·61	−88	3·4
25/75	30	70·46	6·20	8·21	6·30		8·20	−95	2·7
0/100[b]	19	67·58	5·35	7·79	10·81		10·67	−95	2·8
DMA/2-FDMA									
25/75	5·2	74·64	6·29	8·63	0·45		8·20	−60	6·6
0/100[b]	0								
DMA/3-ClDMA									
25/75	5·9	73·03	6·43	8·53		1·60	14·29	−45	5·4
0/100[b]	0								

[a] Based on the assumption that the haloaniline is incorporated into the squaraine statistically.
[b] Data taken from Ref. 17.

yields of the syntheses of HSq and FSq are also included for comparison. For the DMA/3-FDMA series, yield decreases as the concentration of 3-FDMA increases, indicating that the reactivity of 3-FDMA is lower than that of DMA in the synthesis. The low reactivity of 3-FDMA may be attributed to the electron-withdrawing and steric effects exerted by the fluorine atom on the adjacent reacting carbon. This low reactivity is further revealed by the elemental analysis results where the fluorine content of the product mixtures is consistently lower than those expected from statistical incorporation. Whilst the incorporation of fluorine certainly suggests that there are three squaraines, namely HSq, HFSq and FSq, in the product mixtures, the relative concentrations of individual compounds cannot be determined from the elemental analysis alone.

When 2-FDMA or 3-ClDMA is used in the squaraine synthesis, very low yield of squaraine formation and very low halogen incorporation are observed. The level of halogen incorporation suggests that unsymmetric squaraines (HXSq) and symmetric halosquaraines (XSq) are formed; the exact compositions of the product mixtures remain to be determined.

The low yield and the low halogen incorporation suggest that the reactivities of 2-FDMA and 3-ClDMA are even lower than that of 3-FDMA in the squaraine synthesis. The low reactivity of 3-ClDMA relative to 3-FDMA might be attributed to the bulky chlorine atom adjacent to the reacting carbon. The explanation for the low reactivity of 2-FDMA is less straightforward. We have recently studied the proton NMR spectrum of 2-FDMA and results show that the two *N*-methyl groups in 2-FDMA are not magnetically equivalent.† This is in contrast with the results of 3-FDMA, where only one *N*-methyl signal is observed.† These results suggest that there is hindered rotation around the C–N bond of 2-FDMA, and that the lone-pair electrons at the nitrogen are twisted out of the molecular plane of the phenyl ring due to steric repulsion. This in turn reduces the nucleophilicity of the *para* reacting carbon and leads to a low reactivity of 2-FDMA in the squaraine synthesis.

3.2 Structural characterization

3.2.1 Proton NMR spectroscopy

Extremely dilute $CDCl_3$ solutions ($\sim 10^{-5}$–10^{-6} M) of all the halosquaraine mixtures synthesized in this work were studied by high-resolution (400 MHz) NMR spectroscopy. The *N*-methyl protons of squaraines are well resolved from solvent and solvent-impurity peaks and thus information

† Proton NMR spectral data in $CDCl_3$: (a) 2-Fluoro-*N*,*N*-dimethylaniline: δ 2·95 (s, 3H, N—CH_3), 2·965 (s, 3H, N—CH_3) and 6·8–7·2 (m, 5H). (b) 3-Fluoro-*N*,*N*-dimethylaniline: δ 2·96 (s, 6H, N—CH_3), 6·75–6·6 (m, 3H) and 6·95–7·3 (m, 2H).

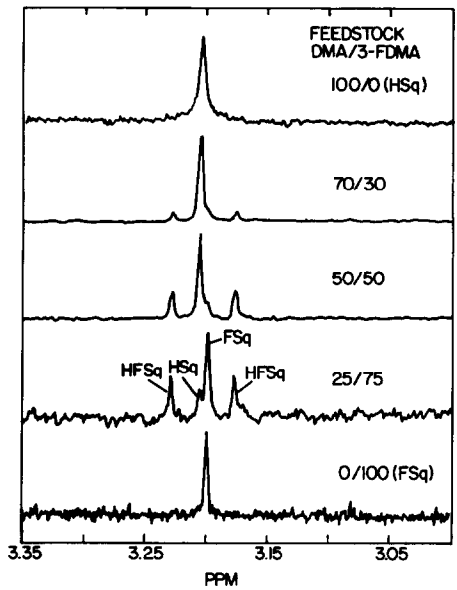
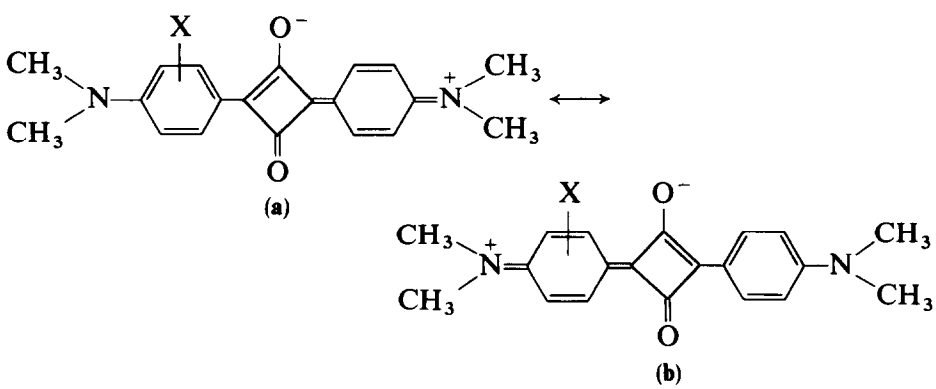


Fig. 2. Proton NMR spectra of mixtures synthesized from varying ratios of DMA/3-FDMA.

can be obtained by studying them. The results are given in Figs 2 and 3. The spectra of the *N*-methyl protons of HSq and FSq are also included for reference. Our results show that the relative amount of FSq in the mixture increases as the concentration of 3-FDMA increases. At the same time, two peaks, one at higher field, the other at lower field relative to the *N*-methyl protons of HSq, are observed. The intensity of these two peaks also increases as the concentration of 3-FDMA increases. These two peaks are assigned to the *N*-methyl protons of unsymmetric squaraine HFSq. Although this assignment cannot be verified unambiguously due to the lack of authentic sample, there is evidence from the mass spectra (see Section 3.2.2) that the third component in the mixture is indeed HFSq.



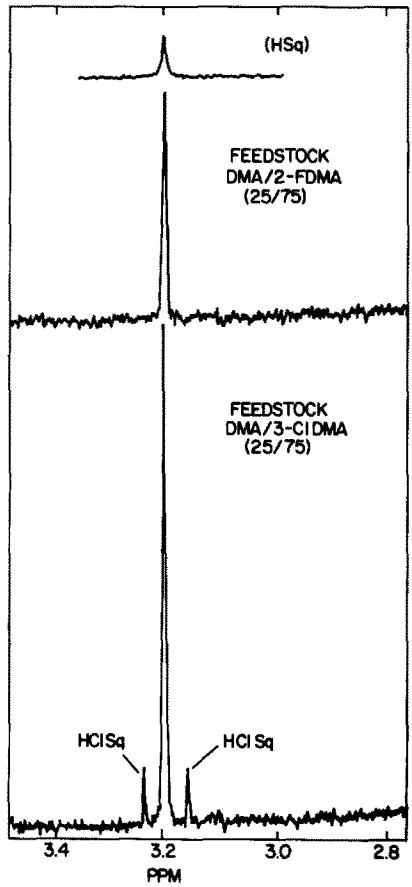


Fig. 3. Proton NMR spectra of mixtures synthesized from DMA/2-FDMA (25/75) and DMA/3-ClDMA (25/75).

The observation of two *N*-methyl signals for unsymmetric squaraine HFSq is not surprising. In the case of the symmetric squaraine, the resonance structures (a) and (b) are equally weighted and the *N*-methyl protons thus become magnetically equivalent. Due to the difference in the anilino moieties in unsymmetric squaraine, which results in unsymmetric charge distribution, the two *N*-methyl groups are no longer magnetically equivalent. This results in two *N*-methyl peaks in unsymmetric squaraines.

From the integration of these *N*-methyl peaks, the relative molar concentrations of HSq, HFSq and FSq in the sample are determined and are reported in Table 2. The fluorine content of these samples can then be calculated from the composition as determined by NMR. As seen in the third column in Table 2, good agreement is obtained between the NMR calculated values and the values obtained from elemental analyses.

For the fluorosquaraine mixture synthesized from DMA/2-FDMA, only

TABLE 2
Proton NMR Analysis of Mixtures of Halosquaraines

Molar ratio of aniline reactant	*Composition from NMR data* (%)			*Halogen content* (*wt* %)	
				NMR	*Elemental analysis*
DMA/3-FDMA	*HSq*	*HFSq*	*FSq*		
70/30	84	16	0	0·9% F	1·08% F
50/50	59	35	5	2·6% F	2·75% F
25/75	14	42	44	7·4% F	6·3% F
DMA/2-FDMA	*HSq*	*HF'Sq*	*F'Sq*		
25/75	100	0	0	0% F	0·45% F
DMA/3-ClDMA	*HSq*	*HClSq*	*ClSq*		
25/75	81%	19%	0	2·1% Cl	1·6% Cl

the *N*-methyl signal from HSq is detected (Fig. 3). The absence of any other *N*-methyl signals may be due to the very similar chemical shifts of the *N*-methyl groups involved. However, as judged from the similar proton NMR spectra of 3-FDMA and 2-FDMA (Section 3.1, footnote) one would anticipate that the *N*-methyl protons of HF'Sq and F'Sq, if they are formed, should be resolved from that of HSq. The proton NMR data thus suggest that HF'Sq and F'Sq, if formed, must be in very small quantity (<5%). Indeed, very little fluorine incorporation (0·45%) is observed in the elemental analysis (Table 1).

For the chlorosquaraine mixture synthesized from DMA/3-ClDMA, the NMR result in Fig. 3 shows that only HSq and HClSq are formed. ClSq, if formed, is below the detection limit of the spectrometer. From the integration of these *N*-methyl peaks, HSq and HClSq are found to be formed in 81% and 19% respectively. The calculated chlorine content is 2·1% and is in good agreement with the elemental analysis result (1·6%).

TABLE 3
Calculated Mass Numbers of Ions of HSq, HXSq and XSq

Ion	*Mass number*		
	M	$(M+H_2)$	$(M+CH_2)$
HSq	320	322	334
HFSq (or HF'Sq)	338	340	352
FSq (or F'Sq)	356	358	370
HClSq	354	356	368
ClSq	388	390	402

3.2.2 Mass spectrometry

As reported previously, squaraines exhibit unique and characteristic mass spectrometric properties.[19] In addition to the molecular ion, ions at (M + 2) and (M + 14), which are assigned to $M + H_2]^+$ and $M + CH_2]^+$ respectively, are formed for squaraines having *N,N*-dimethylamino groups. Details on the mechanism of the formation of these ions have been described in an earlier report. The calculated mass numbers of ions of all the possible squaraine products in Scheme 1 are summarized in Table 3. The generality of the mass spectral reactions reported earlier suggests that these ions might be used as a benchmark for the formation of individual squaraines in the product mixtures.

The electron impact (EI) mass spectra of the three fluorosquaraine mixtures synthesized from DMA/3-FDMA are given in Fig. 4. By comparison with the mass numbers in Table 3, our mass spectral results show that each mixture consists of three compounds, namely HSq, HFSq

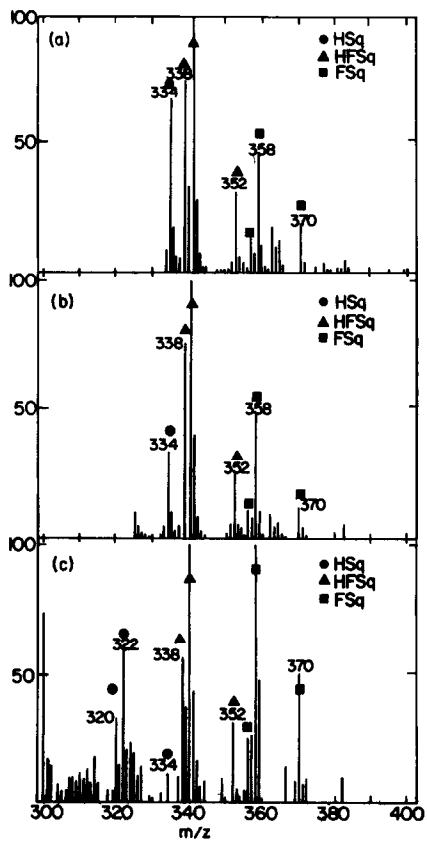


Fig. 4. EI mass spectra of the mixtures synthesized from varying ratios of DMA/3-FDMA: (a) 70/30, (b) 50/50, (c) 25/75.

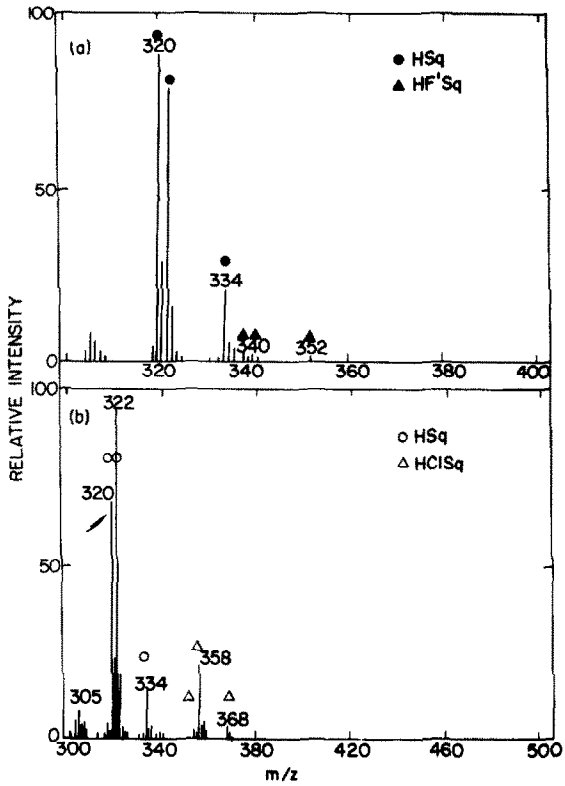


Fig. 5. EI mass spectra of the mixture synthesized from (a) DMA/2-FDMA (25/75); (b) DMA/3-ClDMA (25/75).

and FSq, and that the relative intensities of the ions of HFSq and FSq increase as the concentration of 3-FDMA increases. This is in qualitative agreement with the elemental analysis results and the NMR data. The mass spectral results, however, cannot be more quantitative because of the lack of volatility and ionization data of individual components in the mixture and the complexity of the mass spectral reactions of squaraines.

The EI mass spectra of the fluorosquaraine mixture from DMA/2-FDMA and the chlorosquaraine mixture from DMA/3-ClDMA are given in Figs 5(a) and (b) respectively. By comparison with Table 3, our mass spectral results show that only two squaraines are formed in each mixture, namely HSq and HF'Sq for the fluorosquaraine mixture and HSq and HClSq for the chlorosquaraine mixture. It is worth noting that, due to the low concentration of HF'Sq in the product mixture, it has escaped detection from high-resolution NMR spectroscopy. The results here suggest that although it is not very quantitative, mass spectrometry is very powerful for squaraine structure identification, and is very sensitive in the detection of a minute quantity in a mixture.

3.3 Xerographic data

The xerographic properties of the halosquaraine mixtures synthesized were studied in bilayer photoreceptor devices. The dark-decay ($\Delta V/\Delta t$) and the $E_{0.5}$ values of the devices examined are included in Table 1. Our results show that, for compositions synthesized in the DMA/3-FDMA series, the $E_{0.5}$ value decreases (or photosensitivity increases) as the concentration of 3-FDMA increases. In fact, at a DMA/3-FDMA ratio of 25/75, the composition synthesized exhibits xerographic properties (in terms of $\Delta V/\Delta t$ and $E_{0.5}$ values) very similar to that of FSq. The yield of such a composition is $\sim 30\%$, an improvement of $\sim 11\%$ from FSq. Thus, an optimization of yield and photosensitivity has been achieved.

Very little improvement in photosensitivity is observed for the halosquaraine mixtures synthesized from 2-FDMA and 3-ClDMA. This may be attributable to the low halogen incorporation in these mixtures.

4 CONCLUDING REMARKS

A number of mixtures of halosquaraines were prepared by co-reacting mixtures of anilines (*N*,*N*-dimethylaniline and a *N*,*N*-dimethylhaloaniline) with dibutyl squarate. Yield generally decreases as the concentration of *N*,*N*-dimethylhaloaniline increases. This is attributable to the relative low reactivity of *N*,*N*-dimethylhaloanilines. The low reactivity is further manifest in the low halogen incorporation of the halosquaraine mixtures as compared with the calculated statistical incorporation values. From the results in Table 1, the relative reactivity of the anilines studied is: DMA > 3-FDMA > 3-ClDMA > 2-FDMA.

Structural characterization has been performed on the mixtures synthesized in this work using high-resolution NMR spectroscopy and mass spectrometry. Proton NMR has been shown to be quantitative in determining the relative concentration of individual components in squaraine mixtures. However, due to the insufficient NMR data on squaraines in the literature, structure assignment is not conclusive. The well-behaved mass spectral reactions of squaraine have been found to be very useful in unambiguous structure identification of squaraines. Mass spectrometry is also found to be very sensitive in the detection of small quantities of squaraine in a mixture; it is, however, not very quantitative. These two techniques are thus complementary to each other.

The electrical properties of the squaraine mixtures synthesized were studied in bilayer photoreceptor devices. Through systematic variation of the ratio of DMA/3-FDMA, we have been able to identify a fluorosquaraine

composition with performance equivalent to that of FSq with improved synthetic yield from $< 19\%$ to $\sim 30\%$. This work thus demonstrates that the dilemma of yield and photosensitivity can be optimized using mixtures of squaraines.

ACKNOWLEDGEMENT

The authors thank Mr D. Warrenfeltz (University of Rochester) for recording the mass spectra.

REFERENCES

1. R. West, *Oxocarbons*, Chapter 10. New York, Academic Press (1980).
2. A. C. Tam and R. D. Balanson, *IBM J. Res. Develop.*, **26**, 186 (1982).
3. R. E. Wingard, *IEEE Industry Applications*, 1251 (1982).
4. A. C. Tam, *Appl. Phys. Lett.*, **37**, 978 (1980).
5. R. J. Melz, R. B. Champ, L. S. Chang, C. Chiou, G. S. Keller, L. C. Liclican, R. B. Neiman, M. D. Shattuck and W. J. Weiche, *Photogr. Sci. Eng.*, **21**, 73 (1977).
6. A. H. Schmidt, *Synthesis*, 961 (1980).
7. H. E. Sprenger and W. Ziegenbein, *Angew. Chem. Int. Ed. Engl.*, **7**, 530 (1968).
8. G. Maahs and P. Hegenberg, *Angew. Chem. Int. Ed. Engl.*, **5**, 888 (1966).
9. H. Kampfer and K. E. Verhille (Agfa-Gevaert), US Patent 3617270 (1968).
10. R. B. Champ and M. D. Shattuck (IBM Corpn), US Patent 3824099 (1973).
11. N. F. Haley, J. J. Krutak and R. J. Ott (Eastman Kodak), US Patent 4175956 (1978).
12. J. F. Yanus (Xerox Corpn), US Patent 4486520 (1983).
13. K. Y. Law and F. C. Bailey (Xerox Corpn), US Patent 4508803 (1983).
14. M. S. H. Chang and P. G. Edelman (Pitney–Bowes Inc.), US Patent 4353971 (1980).
15. M. S. H. Chang and M. F. Berman (Pitney–Bowes Inc.), US Patent 4391888 (1981).
16. J. W. Weigl, *Angew. Chem. Int. Ed. Engl.*, **16**, 374 (1977).
17. K. Y. Law and F. C. Bailey, *Can. J. Chem.*, **64**, 2267 (1986).
18. K. Y. Law and F. C. Bailey, *J. Imaging Sci.*, **31**, 172 (1987).
19. K. Y. Law, F. C. Bailey and L. J. Bluett, *Can. J. Chem.*, **64**, 1607 (1986).
20. M. Stolka, J. F. Yanus and D. M. Pai, *J. Phys. Chem.*, **88**, 4707 (1984).
21. K. Y. Law, *J. Imaging Sci.*, **31**, 83 (1987).