3278 J. Org. Chem. 1992, 57, 3278-3286

Articles

Squaraine Chemistry. Synthesis, Characterization, and Optical Properties of a Class of Novel Unsymmetrical Squaraines: [4-(Dimethylamino)phenyl](4′-methoxyphenyl)squaraine and Its Derivatives[1]

Kock-Yee Law* and F. Court Bailey

Xerox Webster Research Center, 800 Phillips Road, 0114-39D, Webster, New York 14580

Received October 2, 1991

A class of novel, unsymmetical squaraines, namely [4-(dimethylamino)phenyl](4′-methoxyphenyl)squaraine and its derivatives **USq-1-13**, which were designed to improve the spectral response of photoconductive squaraines in xerographic devices in the visible region, have been synthesized by condensation of 1-aryl-2-hydroxycyclobutene-3,4-diones **3-5** with various *N,N*-dimethylaniline derivatives. The effects of reaction solvent, temperature, and concentration of drying reagent (tributyl orthoformate) on the yield of squaraine formation were studied systematically using the synthesis of **USq-1** as a model reaction. Results show that an optimal yield can be obtained when the condensation reaction is carried out in refluxing 2-propanol (90 min) in the presence of ≥ 3 equiv of tributyl orthoformate. Esterification of the cyclobutenedione reactant is shown to be the major side reaction of the synthesis. The ester formed in the side reaction was not detectable during our side-product analysis, but it was shown to undergo further arylation with the aniline reactant to produce an isolable polymeric side product. The scope of the squaraine synthesis was examined by reacting **3-5** with various aniline derivatives. Our data consistently show that the reaction condition developed in this work is superior to that reported earlier by Sprenger and Ziegenbein, where squaraines were prepared in an azeotropic cosolvent containing benzene and 1-butanol. The improvement in yield is attributable to the use of 2-propanol as a reaction solvent, which suppresses the side (esterification) reaction of the reactant by a steric effect and also minimizes the secondary reaction of the squaraine product by lowering the reaction temperature. Since **3-5** were synthesized by a [2 + 2] cycloaddition reaction, the synthesis reported here represents the first general synthesis of photoconductive squaraine where the use of the expensive squaric acid is avoided. Studies of the spectroscopic and solid-state properties of **USq-1-13** reveal that their properties are similar to those of bis[4-(dimethylamino)phenyl]squaraine (**2**), a model photoconductive squaraine. A general hypsochromic shift on the solution absorption maxima of **USq-1-13**, relative to that of **2**, is observed and is attributable to the incorporation of a less electron-releasing methoxy group in these compounds. This hypsochromic shift has led to a similar hypsochromic shift in the solid-state absorption, resulting in an increase in absorptivity at 400-500 nm and an improvement in spectral response in the visible region for **USq-1-13** in xerographic photoreceptor devices.

Introduction

Photoconductive squaraines are 1,3-disubstituted products synthesized by condensing 1 equiv of squaric acid with 2 equiv of a *N,N*-dimethylaniline derivative.[2-4] This class of compounds exhibits sharp and intense absorption in the visible region in solution.[5] In the solid state, due to the extensive intermolecular charge-transfer interactions, the absorption becomes very broad. It covers most of the visible region and extends to the near-IR where the solid-state diode lasers emit.[6] These optical characteristics have made squaraines very attractive for a number of industrial applications, e.g., xerographic photoreceptors,[7-11] organic solar cells,[12-16] and optical recording.[17-19]

The synthetic procedure for squaraine is simple and versatile, and squaraines of a variety of substitutions have been synthesized.[20-26] Squarines synthesized by this procedure are, however, often found to exhibit high dark-conductivity and low charge-acceptance values in xerographic devices.[7] An additional purification procedure to improve the xerographic properties is needed and has yet to be developed. Structural modification of squaraines improves their solubility in organic solvents, enabling them to be purified by conventional techniques; substitution, however, perturbs the solid-state properties of squaraines and results in a decrease in photosensitivity.[6,21] Law and

---

* To whom correspondence should be addressed.

(1) A preliminary account of this work has appeared in: Law, K. Y.; Bailey, F. C. *J. Chem. Soc., Chem. Commun.* **1990**, 863.

(2) For the nomenclature of squaraine compounds, see: Schmidt, A. H. In *Oxocarbons*; West, R., Ed.; Academic Press: New York, 1980.

(3) The photoconductivity of this class of compounds was first reported by: Kampfer, H.; Verhille, K. E. U.S. Patent 3,617,270, 1971.

(4) For reviews of the synthesis of photoconductive squaraines, see: (a) Schmidt, A. H. Synthesis **1980**, 961. (b) Sprenger, G. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530; (c) Maahs, G.; Hegenberg, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 888.

(5) Law, K. Y. *J. Phys. Chem.* **1987**, *91*, 5184.

(6) Law, K. Y.; Facci, J. S.; Bailey, F. C.; Yanus, J. F. *J. Imaging Sci.* **1990**, *34*, 31.

(7) Law, K. Y.; Bailey, F. C. *J. Imaging Sci.* **1987**, *31*, 172.

(8) Tam, A. C.; Balanson, R. D. *IBM J. Res. Develop.* **1982**, *26*, 186.

(9) Wingard, R. E. *IEEE Ind. Appl.* **1982**, 1251.

(10) Tam, A. C. *Appl. Phys. Lett.* **1980**, *37*, 978.

(11) Melz, R. J.; Champ, R. B.; Chang, L. S.; Chiou, C.; Keller, G. S.; Liclican, L. C.; Neiman, R. B.; Shattuck, M. D.; Weiche, W. J. *Photogr. Sci. Eng.* **1977**, *21*, 73.

(12) Loutfy, R. O.; Hsiao, C. K.; Kazmaier, P. M. *Photogr. Sci. Eng.* **1983**, *27*, 5.

(13) Morel, D. L. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 127.

(14) Merritt, V. Y. *IBM J. Res. Develop.* **1978**, *22*, 353.

(15) Morel, D. L.; Ghosh, A. K.; Feng, T.; Stogryn, E. L.; Purwin, P. W.; Shaw, R. F.; Fishman, C. *Appl. Phys. Lett.* **1978**, *32*, 495.

(16) Merritt, V. Y.; Hovel, H. J. *Appl. Phys. Lett.* **1976**, *29*, 414.

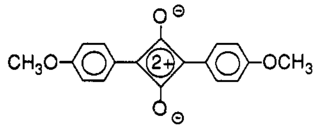
(17) Gravesteijn, D. J.; Steenbergen, C.; Vander Veen, J. *Proc. SPIE Int. Soc. Opt. Eng.* **1988**, *420*, 327.

0022-3263/92/1957-3278$03.00/0

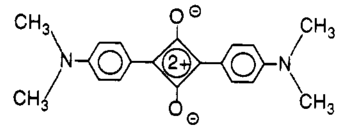
Bailey recently reported that photoconductive squaraines could also be synthesized from dialkyl squarates and *N*,*N*-dimethylaniline derivatives.[27] Xerographic measurements showed that squaraines synthesized by this procedure consistently exhibit better xerographic properties, namely lower dark-conductivity and higher charge-acceptance values. The improvement was shown to be a purity effect.[7] So far, all literature procedures for photoconductive squaraines start with squaric acid, which, by itself, has to be synthesized by a series of complex, multistep, low-yield reactions.[28] It would thus be advantageous from the viewpoint of cost and synthetic simplifications to develop new synthetic methods for photoconductive squaraines so that the use of squaric acid can be avoided.

The spectral response of photoconductive squaraines in devices usually matches their solid-state absorptions. The photosensitivity is high and flat from 500 to 900 nm and decreases at shorter wavelengths.[12] The major drawback of the spectral response is the insufficient sensitivity in the blue region (400–500 nm) which is needed for high-quality copier applications. Since the output of the diode laser for laser printers is at 780 nm[29] and photoresponses beyond 800 nm are unused anyway, one of our approaches to improve the spectral response is to induce a hypsochromic shift on the solid-state absorption of these materials by ~50–100 nm, so that they will have flat and high photoresponse from 400 to 800 nm.

Recent theoretical[30] and spectroscopic studies[5] revealed that both the ground state and the excited state of squaraine are intramolecular donor–acceptor–donor charge-transfer states. Since it is known from our previous work that the energy of transition between charge-transfer states increases as the difference in redox potentials between the donor and the acceptor group increases,[31] we synthesized bis(4-methoxyphenyl)squaraine (1) and examined its optical and photoconductive properties.

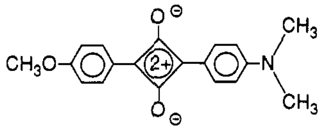


1



2

While the solution absorption of 1 is blue-shifted as expected from that of bis[4-(dimethylamino)phenyl]squaraine (2), their solid-state absorption spectra and their photoconductive properties are markedly different due to an aggregational effect.[32] We attributed the change in aggregation from 2 to 1 to the drastic change in electronic distribution induced by the two methoxy groups in 1. Since the methoxy group is known to produce a hypsochromic effect on the solution absorption of squaraine, the next set of target compounds would be unsymmetrical squaraine **USq-1** and its derivatives. Here we report the synthesis of **USq-1–13**, using a cycloaddition-condensation reaction sequence. The goal of synthesizing photoconductive squaraines without using squaric acid is accomplished. The yield, the scope, and the mechanism of the synthesis will be described. The spectroscopic data of **USq-1–13** will be presented and discussed.



USq-1

Experimental Section

Materials. (4-Methoxyphenyl)acetic acid (99%), (3,4-dimethoxyphenyl)acetic acid (98%), (3,4,5-trimethoxyphenyl)acetic acid (99%), thionyl chloride (gold label), *p*-chlorophenol (99%), triethyl orthoformate (98%), ethylene glycol dimethyl ether (99+%), and triethylamine (99+%) were purchased from Aldrich. Tributyl orthoformate was bought from Pfaltz & Bauer. *n*-Hexane, ether (anhydrous), acetone, toluene, tetrahydrofuran, methylene chloride, methanol, and chloroform were certified grade from Fisher. All these materials were used as received.

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 infrared spectrophotometer 283 or on a Perkin-Elmer model 1750 FTIR. Proton NMR spectra were recorded on a Bruker WP-80 spectrometer. Absorption spectra were taken on a Cary 17 spectrophotometer or on a Hewlett-Packard 8451 diode array spectrophotometer. Mass spectra were recorded on a Varian VG 7035 mass spectrometer at the University of Rochester. Elemental analyses were performed by Galbraith Laboratories. X-ray diffraction data were obtained from Molecular Structure Corp.

Synthesis of Acid Chlorides. All acid chlorides used in this work were synthesized from the corresponding carboxylic acid and thionyl chloride using the procedure described by Farnum and co-workers.[33]

(4-Methoxyphenyl)acetyl chloride: yield 95%; bp ~137 °C (5 mmHg) (lit.[33] yield 88%, bp 125 °C (9 mmHg)).

(3,4-Dimethoxyphenyl)acetyl chloride: yield 84%, bp ~137 °C (0.9 mmHg); IR (CCl_4) 1800 cm^{-1} (C=O).

(3,4,5-Trimethoxyphenyl)acetyl chloride: yield 67%, bp ~168 °C (0.07 mmHg); IR (KBr) 1792 cm^{-1} (C=O).

Synthesis of 1-Aryl-2-hydroxycyclobutene-3,4-diones 3–5. 1-(*p*-Methoxyphenyl)-2-hydroxycyclobutene-3,4-dione (3) was synthesized according to the procedure reported by Bellus.[34] A slight modification was made in this work to improve the workup after the synthesis. The procedure is summarized as below.

Tetraethoxyethylene, which was freshly synthesized using the procedure of Bellus et al.[35] (59.6 g, 0.29 mol), triethylamine (63.7 g), and *n*-hexane (1350 mL) were discharged in a 3-L three-neck flask, which was equipped with a mechanical stirrer and a nitrogen inlet. (*p*-Methoxyphenyl)acetyl chloride (113.1 g, 0.61 mol) was added slowly through a pressure-equalizing funnel over a 2-h

---

(18) Jipson, V. P.; Jones, C. R. *J. Vac. Sci. Technol.* **1981**, *18*, 105.

(19) Jipson, V. P.; Jones, C. R. *IBM Tech. Discl. Bull.* **1981**, *24*, 298.

(20) Law, K. Y.; Bailey, F. C.; Bluett, L. J. *Can. J. Chem.* **1986**, *64*, 1607.

(21) Law, K. Y.; Bailey, F. C. *Dyes Pigm.* **1988**, *9*, 85.

(22) Treibs, A.; Jacob, K. *Liebigs Ann. Chem.* **1968**, *712*, 123; **1966**, *699*, 153.

(23) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 553.

(24) Ziegenbein, W.; Sprenger, H. E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 893.

(25) Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.*, **1966**, *5*, 894.

(26) Treibs, A.; Jacob, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 694.

(27) Law, K. Y.; Bailey, F. C. *Can. J. Chem.* **1986**, *64*, 2267.

(28) Paine, A. J. *Tetrahedron Lett.* **1984**, *25*, 135 and reference cited therein.

(29) Mortensen, P. *Laser Focus World* **1989**, *25*(12), 111.

(30) Bigelow, R. W.; Freund, H. J. *Chem. Phys.* **1986**, *107*, 159.

(31) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2803 and references cited therein.

(32) Law, K. Y. *J. Phys. Chem.* **1988**, *92*, 4226.

(33) Farnum, D. G.; Johnson, J. R.; Hess, R. E.; Marshall, T. B.; Webster, B. *J. Am. Chem. Soc.* **1965**, *87*, 5191.

(34) Bellus, D. *J. Am. Chem. Soc.* **1978**, *100*, 8026.

(35) Bellus, D.; Martin, P.; Sauter, H.; Winkler, T. *Helv. Chim. Acta* **1980**, *63*, 1130.

period. A white precipitate of triethylamine hydrochloride was formed during the addition. After the addition was completed, the mixture was stirred at room temperature for ~4 h. It was then warmed by a warm water bath (~60 °C) for 0.5 h and was filtered through a 1.5-L medium sintered glass funnel. The solid obtained was washed with warm *n*-hexane (3 × 1300 mL). The *n*-hexane solutions were combined; after the solvent was removed under reduced pressure, a light yellow liquid (96.4 g) resulted. This yellow liquid was then dissolved in ~3500 mL of ether, 1000 g of basic alumina (from Fisher, activity III) was added, and the resulting slurry was stirred for 6 h. The slurry was filtered, and the alumina was washed thoroughly with ether. After the solvent was evaporated 73 g of yellow liquid was obtained. This yellow liquid was hydrolyzed with 400 mL of 18% hydrochloric acid at reflux for 4 h. The hydrochloric acid was evaporated under reduced pressure. The residue, a brown gummy solid, was then digested with *n*-hexane on a steam bath, resulting in a brown solid product. The crude product was recrystallized from a mixture of toluene and acetone: yield of **3** 35 g (57%); mp 221–223 °C (lit.[34] mp 220 °C lit.[36] mp 205–207 °C); IR (KBr) 1723 and 1794 cm^{-1} (C=O); NMR (acetone-d_6) δ 3.91 (s, 3 H, OCH$_3$), 7.17 (d, 2 H, J = 9.4 Hz), and 8.07 (d, 2 H, J = 9.4 Hz); MS (m/z) 204 (M$^+$).

1-(3′,4′-Dimethoxyphenyl)-2-hydroxycyclobutene-3,4-dione (**4**) was prepared similarly, except that the alumina treatment was omitted: yield 42%; mp 238–239 °C; IR (KBr) 1713 and 1790 cm^{-1}; NMR (acetone-d_6) δ 3.91 (s, 3 H, OCH$_3$), 3.94 (s, 3 H, OCH$_3$), 7.17 (d, 1 H, J = 7.9 Hz) 7.64 (d, 1 H, J = 2 Hz), and 7.75 (ABq, 1 H, J_A = 7.9 Hz, J_B = 2 Hz); MS (m/z) 234 (M$^+$).

Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.30; H, 4.41.

1-(3′,4′,5′-Trimethoxyphenyl)-2-hydroxycyclobutene-3,4-dione (**5**) was synthesized as **4**: yield 30%; mp 202.5–204.0 °C; IR (KBr) 1728 and 1790 cm^{-1}; NMR (acetone-d_6) δ 3.91 (s, 3 H, OCH$_3$), 3.94 (s, 6 H, OCH$_3$), and 7.65 (s, 2 H); MS (m/z) 264 (M$^+$).

Anal. Calcd for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 58.90; H, 4.78.

Preparation of Organic Salts of 3–5 and *N,N*-Dimethylaniline Derivatives. For convenience, the two components used in the squaraine synthesis were pre-formed as organic salts which would be used as starting materials for the synthesis. These salts were prepared by simply mixing equivalent amounts of **3–5** and a *N,N*-dimethylaniline derivative in THF at room temperature. After the solvent was removed, a creamy whie solid was obtained. The solid was digested with diethyl ether and was collected by filtration. Yields are nearly quantitative (>90%). The melting points and the IR spectral data of these salts are summarized as follows:

3 and *N,N*-dimethylaniline: mp 125–130 °C; IR (KBr) 1681 and 1750 cm^{-1} (C=O).

3 and 3-hydroxy-*N,N*-dimethylaniline: mp 170–174 °C; IR (KBr) 1694 and 1760 cm^{-1} (C=O).

3 and 3-methyl-*N,N*-dimethylaniline: mp 122–126 °C; IR (KBr) 1685 and 1758 cm^{-1} (C=O).

3 and 3-fluoro-*N,N*-dimethylaniline: mp 135–138 °C; IR (KBr) 1720 and 1760 cm^{-1} (C=O).

3 and 3-methoxy-*N,N*-dimethylaniline: mp 120–124 °C; IR (KBr) 1684 and 1755 cm^{-1} (C=O).

3 and *N*-benzyl-*N*-methylaniline: gummy solid; IR (KBr) 1733 and 1762 cm^{-1} (C=O).

4 and *N,N*-dimethylaniline: mp 127–128 °C; IR (KBr) 1684 and 1762 cm^{-1} (C=O).

4 and 3-hydroxy-*N,N*-dimethylaniline: mp 170–171 °C; IR (KBr) 1690 and 1759 cm^{-1} (C=O).

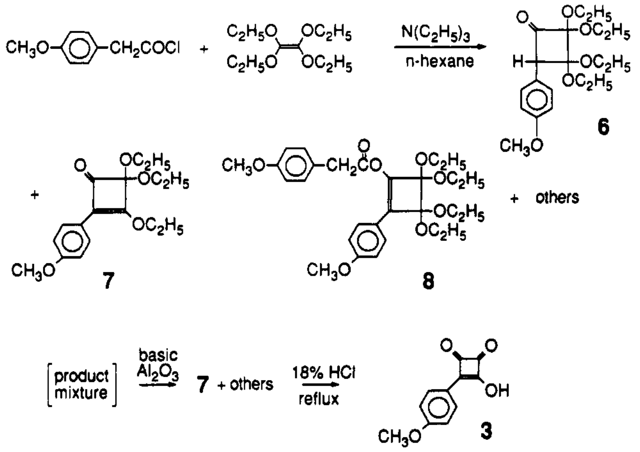
4 and 3-methyl-*N,N*-dimethylanine: mp 118.5–120 °C; IR (KBr) 1692 and 1752 cm^{-1} (C=O).

4 and 3-fluoro-*N,N*-dimethylaniline: mp 130.0–130.5 °C; IR (KBr) 1681 and 1758 cm^{-1} (C=O).

4 and 3-methoxy-*N,N*-dimethylaniline: mp 114.0–116.5 °C; IR (KBr) 1695 and 1753 cm^{-1} (C=O).

Squaraine Synthesis. Squaraines were synthesized by two different procedures, and they are outlined as follows. The yields, the physical properties, and the spectroscopic data of the squaraines prepared are tabulated in Tables II–V.

Scheme I



Method A. The above-prepared organic salt (1.25 mmol) was suspended in 10 mL of 2-propanol containing 1 mL of tributyl orthoformate. The mixture was stirred and was brought to reflux under a nitrogen atmosphere. The salt usually went into the solution as soon as reflux began. After 90 min of reflux, the mixture was cooled to ice-cold temperature. The precipitated squaraine product was isolated by filtration and was washed with 1–2 mL of cold 2-propanol and ~10 mL of diethyl ether. After vacuum drying, analytically pure squaraines were obtained. The only exception was **USq-6**; the product isolated from filtration was impure, and recrystallization (from methylene chloride and methanol) was required.

Method B. The above organic salt (0.3 g) was heated to reflux in a mixture of benzene (25 mL) and 1-butanol (15 mL) at a bath temperature of ~125 °C.[21] The progress of the reaction was monitored by TLC (on silica gel using chloroform as eluent) and absorption spectroscopy. After 5 h of reflux, the mixture was cooled to room temperature, with the exception of **USq-2**, **USq-8**, and **USq-13** in which they were precipitated out of the product solution and were isolated by filtration. Other squaraines prepared by this procedure are very soluble in the product mixture. The product solutions were then diluted with chloroform, and the yields were determined by absorption spectroscopy.

Results and Discussion

Synthesis of Precursors: 1-Aryl-2-hydroxycyclobutene-3,4-diones 3–5. The titled compounds were synthesized by a [2 + 2] cycloaddition reaction between methoxy-substituted phenyl ketenes and tetraethoxyethylene as described by Bellus.[34] The reaction for **3** is outlined in Scheme I.

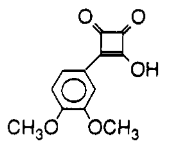
Under our reaction conditions, the [2 + 2] cycloadduct, **6**, could not be detected. Only **7** and **8** were discernible by IR analysis.[37] Compound **8** was converted smoothly to **7** in the mixture by an alumina treatment. Hydrolysis of the product mixture in 18% hydrochloric acid at reflux converted **7** to **3**, from which **3** can be isolated and purified by solvent recrystallization. The overall yield of **3** is 57% based on tetraethoxyethene.

Reactions of (3,4-dimethoxyphenyl)ketene and (3,4,5-trimethoxyphenyl)ketene with tetraethoxyethylene yield primarily cycloadducts of type **7**. This is indicated by the presence of C=O stretching at ~1750 cm^{-1} in the IR spectra of the reaction mixtures[37] and by the lack of spectral changes after the alumina treatment. The alumina treatment was therefore omitted, and yields of **4** and **5** are 42% and 30%, respectivley, after hydrolysis and recrystallization.

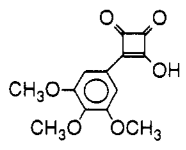
---

(36) Schmidt, A. H.; Reid, W. *Synthesis* 1978, 1.

(37) The product mixture of the cycloaddition reaction exhibits strong vibrational bands at 1755 and 1775 cm^{-1} which can be assigned to the C=O stretchings of intermediates 7 and 8 respectively.[34]



4



5

Unsymmetrical Squaraine Synthesis. a. Synthesis and Yield Optimization. Unsymmetrical squaraines were synthesized by direct condensation of compounds **3–5** with an *N,N*-dimethylaniline derivative.

Using **3** and *N,N*-dimethylaniline as model reactants, the conditions for the formation of unsymmetrical squaraine **USq-1** were optimized. Preliminary test-tube tests revealed that 2-propanol was the best solvent among 10 other alcoholic and nonalcoholic solvents examined. Since water is the byproduct of the synthesis and elimination of water in the mixture was shown to be essential in driving the reaction in the product-forming direction, we attempted to facilitate this process using external drying reagents, such as molecular sieves and tributyl orthoformate (TBOF). Experimentally, a drastic yield increase, as judged from the color of the testing solution, was observed when a drying reagent was used. In this work, we selected TBOF as an in situ homogeneous drying reagent for the synthesis. Systematic study indicates that an optimal yield of **USq-1** can be obtained when $\geq$3 equiv of TBOF are used.

Using an optimal amount of TBOF, the effect of solvent on the yield of **USq-1** formation was reexamined systematically. The progress of the reaction in each solvent was monitored closely by TLC and absorption spectroscopy. The optimized reaction time was usually ~90-120 min. The results, which are tabulated in Table I, show that **USq-1** was only formed (indicated by the purple color) at reaction temperatures higher than 78 °C. In 1-alkanols, the optimal refluxing temperature is ~78–98 °C. The decrease in yield at higher temperatures may be attributable to secondary reactions of **USq-1** and *N,N*-dimethylaniline in the product mixture, partly due to the increase in solubility of **USq-1** and partly due to the enhancement of the secondary reactions at higher reaction temperatures.[38] It is interesting to note that the highest yield was obtained in 2-propanol. As discussed later in the mechanistic section, the high yield of **USq-1** in 2-propanol as compared to that in ethanol is probably the result of suppressing the esterification reaction of **3** due to steric effect.

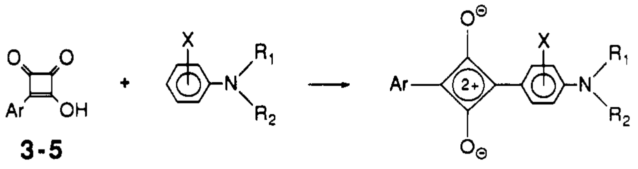
In nonalcoholic solvents, such as acetonitrile and 1,2-dichloroethane, a very low yield of **USq-1** formation was obtained despite the favorable reaction temperature. Since elimination of a water molecule in the reaction complex is a necessity for the squaraine formation step, the specificity of higher chemical yields in alcoholic solvents suggest that the water elimination step may be solvent-assisted.

b. Scope of the Synthesis. A number of unsymmetrical squaraines were prepared by reacting **3–5** with a *N,N*-dimethylaniline derivative using the optimized conditions described above. The yields and the physical properties of these compounds are summarized in Table II. Our results show that the yield of squaraine formation is very sensitive to both electronic and steric factors. For a given 1-aryl-2-hydroxycyclobutene-3,4-dione reactant, yield increases as the nucleophilicity of the aniline increases; namely, consistently higher yields are obtained when hydroxy and methyl anilines are used. On the other hand, bulky substituents adjacent to the reacting carbon exhibit an adverse effect on the chemical yield. The yields of **USq-5** and **USq-11** are consistently lower than those of **USq-1** and **USq-7** despite the presence of the strong electron-releasing group in 3-methoxy-*N,N*-dimethylaniline.

Traditionally, photoconductive squaraines were prepared by reactions of squaric acid with *N,N*-dialkylanilines in 1-butanol.[23] Water is formed in the reaction and is removed by an azeotropic solvent during the synthesis. As noted earlier, this procedure is very versatile and has become a general preparative procedure. In this work, we compare the yields of **USq-1–13** synthesized under the squaric acid conditions (method B) with those developed in this work. The comparative data, which are summarized in Table II also, show that without exception higher yields are obtained when unsymmetrical squaraines are synthesized by our new procedure. Similar to the conclusions reached earlier in the solvent effect study, we attribute the high yields obtained by our procedure to the use of lower reaction temperatures and secondary alcohols, which minimize the secondary reaction of the squaraine product and suppress the esterification reaction of the starting 1-aryl-2-hydroxycyclobutene-3,4-dione reactant.

c. Side-Product Analysis and Reaction Mechanism. Using **3** and *N,N*-dimethylaniline as model reactants, **USq-1** was synthesized in refluxing ethanol in the presence

Scheme II



3-5

Unsymmetrical squaraines

Scheme III

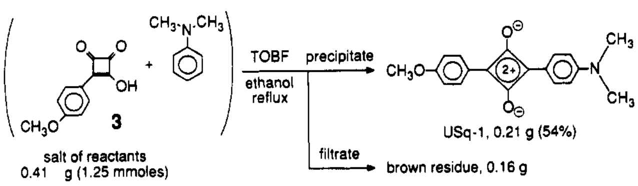


Table I. Effect of Solvent on the Yield of USq-1

solvent	bp[a] (°C)	yield of USq-1 (%)
methanol	64.5	NR[b]
ethanol	78.3	52
1-propanol	97.4	54
1-butanol	117	<5
2-propanol	82.4	65
2-butanol	99.5	49
tetrahydrofuran	66	NR[b]
chloroform	61.7	NR[b]
acetonitrile	81.6	<5
1,2-dichloroethane	83.5	<5

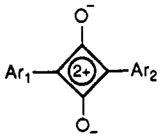
[a] Boiling point data taken from: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972. [b] No reaction (purple color).

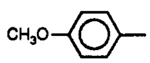
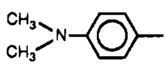
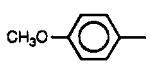
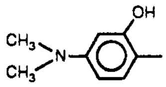
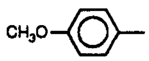
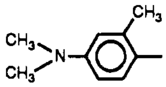
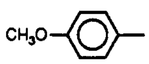
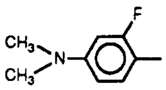
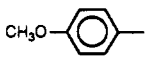
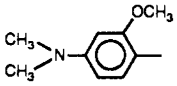
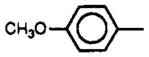
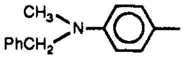
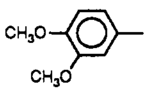
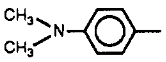
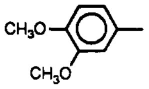
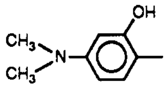
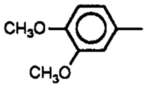
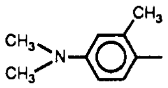
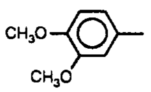
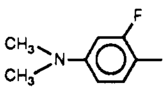
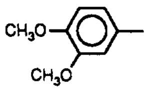
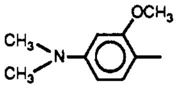
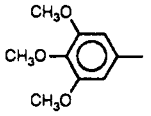
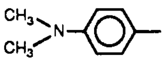
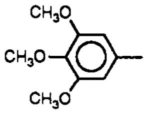
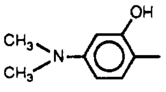
---

(38) Squaraines are known to react with amines to form adducts. In the case of tertiary amines, 1:1 squaraine–amine adducts have been isolated and characterized.[22,39] Due to the increase in solubility of USq-1 at evaluated temperatures, USq-1 may react with *N,N*-dimethylaniline to form a USq-1–aniline adduct and results in a decrease in chemical yield.

(39) Treibs, A.; Jacob, K.; Tribollet, R. *Liebigs Ann. Chem.* **1970**, *741*, 101.

Table II. Synthesis, Physical Properties, and IR Spectral Data of Unsymmetrical Squaraines



squaraine	Ar_1	Ar_2	% yield		mp (°C)	IR[c] (cm^{-1})		C	H	N	F
			method A[a]	method B[b]							
USq-1			67	16	212–214	1596	calcd:	74.25	5.58	4.56	
						1620	found:	74.07	5.78	4.54	
USq-2			86	75[a]	261–262	1592	calcd:	70.58	5.30	4.33	
						1633	found:	70.38	5.28	4.33	
USq-3			73	41	209–211	1594	calcd:	74.74	5.96	4.36	
						1605	found:	74.81	5.80	4.31	
USq-4			32	4.5	214–216	1594	calcd:	70.14	4.96	4.31	5.84
						1620	found:	69.54	4.83	4.27	5.56
USq-5			43	3.0	209–213	1596	calcd:	71.20	5.68	4.15	
						1618	found:	70.56	5.74	3.97	
USq-6			41	26	198.5–199.5	1589	calcd:	78.31	5.52	3.65	
						1625	found:	77.95	5.59	4.09	
USq-7			77	33	215–219	1605	calcd:	71.20	5.68	4.15	
							found:	71.01	5.69	4.73	
USq-8			87	78[a]	249–250	1591	calcd:	67.98	5.42	3.96	
						1630	found:	67.29	5.40	3.82	
USq-9			83	37	223–225	1595	calcd:	71.78	6.02	3.99	
						1610	found:	71.94	6.19	3.88	
USq-10			59	7.7	217–220	1590	calcd:	67.60	5.10	3.94	5.36
						1624	found:	67.47	5.26	3.85	5.35
USq-11			52	32	216–218	1594	calcd:	68.65	5.76	3.81	
						1624	found:	67.94	6.15	3.64	
USq-12			57	-	205–208	1610	calcd:	68.65	5.76	3.81	
							found:	68.21	5.67	4.05	
USq-13			-	51[a]	236–237	1616	calcd:	65.79	5.52	3.65	
						1632	found:	66.39	5.65	3.58	

[a] Isolated yield. [b] Yield determined by absorption spectroscopy, unless specified. [c] In KBr.

of an optimal amount of TOBF in a typical 1.25 mmol run.[40] **USq-1** precipitates from the product solution and was isolated by filtration, yield 0.21 g (54%). The filtrate was a purple-brown solution. After the solvent was removed under reduced pressure, a brown residue, 0.16 g, was obtained.

TLC analysis (on silica gel using chloroform as eluent) revealed that this brown residue consists of primarily an orange-brown unknown substance and a small amount of **USq-1**. The spectroscopic properties of the brown residue are: IR (KBr) ~1740 cm^{-1} (broad); ^1H NMR (CD_2Cl_2) δ ~2.95 (NCH_3), ~3.8 (OCH_3), and 6.4–7.4 (aromatic protons). The IR spectral data suggest that the brown residue is neither the ethyl ester of 3[40] nor any other 1,2-disub-

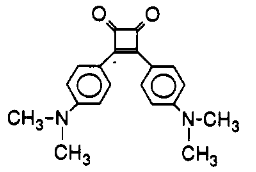
---

[40] Ethanol was chosen as reaction solvent in this study because the probable side product, the ester of 3, could be prepared by esterification of 3 directly in refluxing ethanol, mp: 109–110 °C; IR (KBr) 1740 and 1788 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.57 (t, J = 9.1 Hz, 3 H), 3.91 (s, 3 H), 4.95 (q, J = 9.1 Hz, 2 H), 7.03 (d, J = 10.6 Hz, 2 H), and 8.04 (d, J = 10.6 Hz, 2 H); MS (m/z) 232 (M^+).

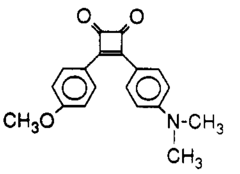
Table III. ^{1}H NMR Spectral Data of Unsymmetrical Squaraines

squaraine	solvent	^{1}H NMR (ppm from TMS)
USq-1	$CDCl_3$	δ 3.27 (s, 6 H, NCH_3), 3.89 (s, 3 H, OCH_3), 6.86 (d, J = 9.3 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 8.34 (d, J = 8.8 Hz, 2 H), and 8.45 (d, J = 9.3 Hz, 2 H)
USq-2	CD_2Cl_2	δ 3.28 (s, 6 H, NCH_3), 3.91 (s, 3 H, OCH_3), 6.14 (d, J = 2.5 Hz, 1 H), 6.53 (ABq, J_A = 9.6 Hz, J_B = 2.5 Hz, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 8.08 (d, J = 9.6 Hz, 1 H), and 8.18 (d, J = 8.8 Hz, 2 H)
USq-3	$CDCl_3$	δ 2.95 (s, 3 H, CH_3), 3.27 (s, 6 H, NCH_3), 3.91 (s, 3 H, OCH_3), ~6.5–6.75 (m, 2 H), 7.0 (d, J = 8.9 Hz, 2 H), 8.46 (d, J = 8.9 Hz, 2 H), and 9.10 (d, J = 10.2 Hz, 1 H)
USq-4	$CDCl_3$	δ 3.26 (s, 6 H, NCH_3), 3.91 (s, 3 H, OCH_3), 6.3–7.2 (m, 3 H), and 8.2–8.8 (m, 4 H)
USq-5	$CDCl_3$	δ 3.27 (s, 6 H, NCH_3), 3.90 (s, 3 H, OCH_3), 4.06 (s, 3 H, OCH_3), 6.03 (s, 1 H), 6.49 (ABq, J_A = 9.1 Hz, J_B = 1.7 Hz, 1 H), 6.98 (d, J = 8.6 Hz, 2 H), 8.41 (d, J = 8.6 Hz, 2 H), and 8.73 (d, J = 9.1 Hz, 1 H).
USq-6	CD_2CL_2	δ 3.32 (s, 3 H, NCH_3), 3.93 (s, 3 H, OCH_3), 4.84 (s, 2 H, NCH_2–), 6.94 (d, J = 9.1 Hz, 2 H), 7.05 (d, J = 8.5 Hz, 2 H), 7.1–7.4 (m, 5 H), 8.40 (d, J = 8.5 Hz, 2 H), and 8.49 (d, J = 9.1 Hz, 2 H)
USq-7	$CDCl_3$	δ 3.30 (s, 6 H, NCH_3), 3.99 (s, 6 H, OCH_3), 6.82 (d, J = 9.4 Hz, 2 H), 6.98 (d, J = 8.9 Hz, 1 H), 7.95 (d, J = 1.7 Hz, 1 H), 8.17 (ABq, J_A = 8.9 Hz, J_B = 1.7 Hz, 1 H), and 8.35 (d, J = 9.4 Hz, 2 H)
USq-8	$CDCl_3$	δ 3.26 (s, 6 H, NCH_3), 3.98 (s, 6 H, OCH_3), 6.12 (d, J = 2.2 Hz, 1 H), 6.47 (ABq, J_A = 9.4 Hz, J_B = 2.4 Hz, 1 H), 6.96 (d, J = 8.2 Hz, 1 H), 7.64 (d, J 2.4 Hz, 1 H), 7.94 (ABq, J_A = 8.2 Hz, J_B = 2.2 Hz, 1 H), and 8.11 (d, J = 9.4 Hz, 1 H)
USq-9	$CDCl_3$	δ 2.96 (s, 3 H, CH_3), 3.29 (s, 6 H, NCH_3), 4.0 (s, 6 H, OCH_3), 6.6–6.8 (m, 2 H), 7.0 (d, J = 8.4 Hz, 1 H), 8.0 (bs, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), and 9.10 (d, J = 9.3 Hz, 1 H)
USq-10	$CDCl_3$	δ 3.26 (s, 6 H, NCH_3), 3.97 (s, 6 H, OCH_3), 6.3–6.7 (m, 2 H), 7.0 (d, J = 8.8 Hz, 1 H), 8.02 (d, J = 8.8 Hz, 1 H), 8.23 (d, J = 8.8 Hz, 1 H), and 8.5–8.8 (m, 1 H).
USq-11	$CDCl_3$	δ 3.26 (s, 6 H, NCH_3), 3.97 (s, 6 H, OCH_3), 4.04 (s, 3 H, OCH_3), 5.98 (d, J = 1.7 Hz, 1 H), 6.46 (ABq, J_A = 8.9 Hz, J_B = 1.7 Hz, 1 H), 6.96 (d, J = 8.4 Hz, 1 H), 7.98 (d, J = 1.7 Hz, 1 H), 8.14 (ABq, J_A = 8.4 Hz, J_B = 1.5 Hz, 1 H), and 8.75 (d, J = 8.9 Hz, 1 H)
USq-2	$CDCl_3$	δ 3.32 (s, 6 H, NCH_3), 3.94 (s, 6 H, OCH_3), 3.98 (s, 3 H, OCH_3), 6.88 (d, J = 8.5 Hz, 2 H), 7.71 (s, 2 H), and 8.52 (d, J = 8.5 Hz, 2 H)
USq-13	$CDCl_3$	δ 3.25 (s, 6 H, NCH_3), 3.93 (s, 9 H, OCH_3), 6.11 (bs, 1 H), 6.49 (bd, J = 9.2 Hz, 1 H), 7.51 (s, 2 H), and 8.12 (d, J = 9.2 Hz, 1 H)

stituted cyclobutene-3,4-dione derivative derived from it.[41] The broad proton signals observed in the NMR spectrum on the other hand suggest that the brown residue is a polymeric material. The ratio of the *N*-methyl, methoxy, and aromatic protons is about 3:6:8, indicating that the polymeric material consists of a *p*-(dimethylamino)phenyl group and a *p*-methoxyphenyl group about 1:1 in ratio. In our earlier mechanistic investigation of the reaction between dibutyl squarate and *N,N*-dimethylaniline, we had shown that the major side product of the reaction was a polymeric material derived from 1,2-bis[*p*-(dimethylamino)phenyl]cyclobutene-3,4-dione (**9**).[27]



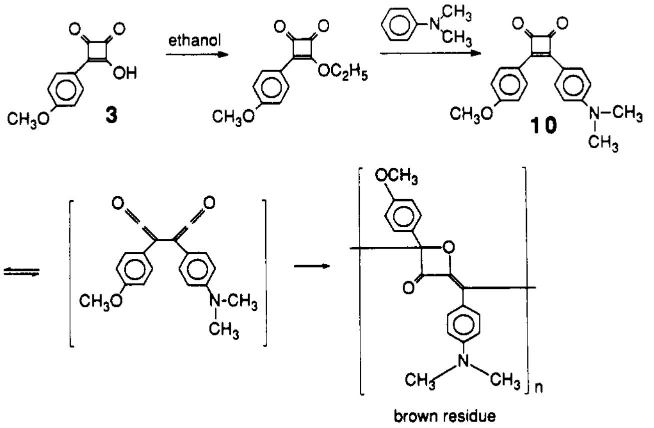
9



10

In view of the similarity in spectroscopic data obtained in this work as compared to our earlier results, we propose that 1-[*p*-(dimethylamino)phenyl]-2-(*p*-methoxyphenyl)-cyclobutene-3,4-dione (**10**) is the major side product in the synthesis of **USq-1**. It is formed presumably through the arylation of the ester of **3** by *N,N*-dimethylaniline. Compound **10** is, however, not stable under our experimental conditions. It undergoes a ring-opening reaction similar to those of 1,2-diphenylcyclobutene-3,4-dione[42] and **9**[27] to give a diketene intermediate, which polymerizes to generate the brown residue isolated in this work (Scheme IV). Since the weight of the brown residue is ~0.16 g, the yield of the side product would be ~42%. The material balance of the product analysis is ~96%.

Scheme IV



Structural Characterization of Unsymmetrical Squaraines. a. IR Spectra. Results in Table II show that all unsymmetrical squaraines exhibit strong IR absorption bands at ~1600 cm^{-1}. The absence of any C=O stretching at ~1700 cm^{-1} indicates that the C–O bonds have very little double bond character and that the π-electrons are fully delocalized in the central C_4O_2 unit despite the asymmetrical charge distribution in the two phenyl rings of these compounds as revealed by proton NMR spectroscopy.

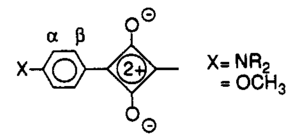
b. Proton NMR Spectra. Owing to the enhanced solubility, all unsymmetrical squaraines synthesized in this work exhibit sufficient solubility in chlorinated solvents for ^{1}H NMR studies on a routine 80-MHz instrument. Spectral results in Table III show that the chemical shifts of the methoxy and the *N*-methyl protons are at their expected positions at δ ~4 and ~3.3 ppm, respectively. The chemical shifts of the aromatic protons are more interesting, at ~6–9 ppm. As reported earlier, the protons in the α-position of the four-membered ring are shifted to lower field by 0.5–1.5 ppm and the protons in the β-position are shifted to higher field by 0–0.5 ppm as compared to the chemical shifts of the aromatic protons in the precursor compounds.[20,21,43] The chemical shift range observed in Table III is therefore expected.

---

[41] 1,2-Disubstituted cyclobutene-3,4-diones normally exhibit two carbonyl stretchings in the region of 1700–1800 cm^{-1}. For IR data, see ref 27.

[42] Blomquist, A. T.; LaLancette, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 1387.

[43] Law, K. Y. *J. Phys. Chem.* **1989**, *93*, 5925.



In unsymmetrical squaraine such as **USq-1**, there are two kinds of α and β protons. Because of the couplings between adjacent protons, four doublets at δ 6.86, 7.00, 8.34, and 8.45 ppm are observed. Spectral assignments can be made by simply comparing similar shifts in model squaraines **1** and **2**. Substitution in the aniline or the anisole ring induces magnetic inequivalency in the aromatic protons of unsymmetrical squaraines and signals corresponding to individual protons are observed. Usually, unambiguous assignments can be made by first separating the aromatic protons into two groups, namely α and β, and then studying their coupling patterns.

c. Electron Impact Mass Spectra. Figure 1 shows the EI mass spectrum of **USq-1**. The mass spectrum appears to be clean, and the most unusual feature of the spectrum is the occurrence of ions of mass number higher than the molecular ion. Identical spectral results were also obtained for **USq-2–13**, and the data are tabulated in Table IV. Our data show that the high m/z ions are at M + 2 and M + 14 (for **USq-6**, an additional ion at m/z M + 90 was also observed). These ions can be assigned to the addition of two hydrogen atoms, a CH_2 group (and a $CH–C_6H_5$ group in the case of **USq-6**) to the corresponding M^+. 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.

Similar to the high mass number ions, lower molecular weight fragment ions also appear to be very unique. From the structure–property relationship of the spectral data in Table IV, nine fragment ions of general structures a–i (see Scheme V for structures) can be deduced. The formations of ions a, b and e, f are 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.

The anomalous mass spectrometric behavior of squaraines has been studied in our laboratory.[20] Our results suggest 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 a–i. The similarity in the fragmentation pattern between the unsymmetrical squaraines synthesized in this work and those of *N*-alkyl squaraines[20] and *N*-benzyl squaraines[21] suggests that all squaraines have a similar set of mass spectral reactions, which are summarized in Scheme V, and mechanistic details of which have been reported previously.[20,44]

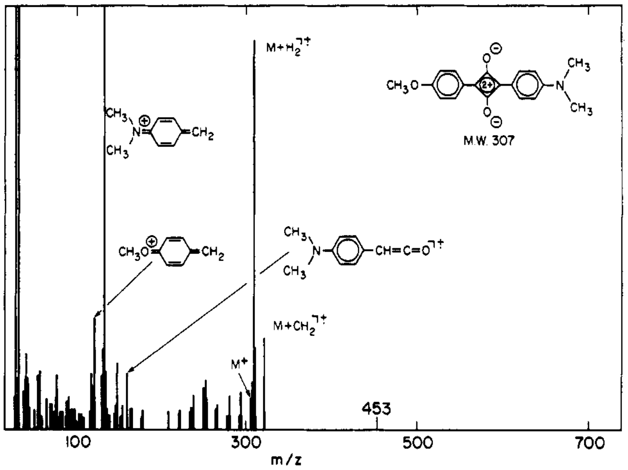
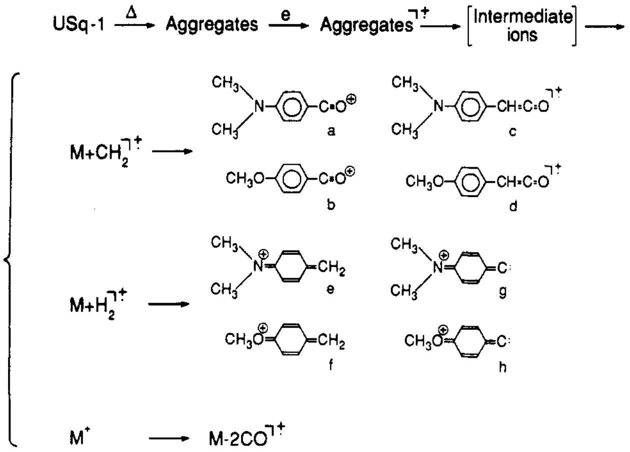


Figure 1. EI mass spectrum of **USq-1**.

Scheme V. Mass Spectral Reactions of USq-1

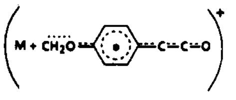


The key difference in the mass spectral data in Table IV as compared to those of *N*-alkyl squaraines and *N*-benzyl squaraines is the relatively high intensity of the M^+ ions observed. Due to the limited spectral data, it is uncertain that the high intensity is a result of the change in vaporizing mechanism or the change in fragmentation pattern of the aggregates in the vapor phase. In any event, we believe that the change is associated with the anisole group because an identical results was observed in the mass spectrum of compound **1**.[45] In the case of **1**, the major fragment ion associated with M^+ is the decarbonylated product $M - 2\,CO^{\bullet+}$ and similar decarbonylation products are observed in the mass spectra of **USq-1–13** (see Table IV).

d. Optical Properties. The visible absorption spectral data of **USq-1–13** are summarized in Table V. The absorption maxima (λ_{max}) vary from 562 to 592 nm depending on the substitution in the anisole ring and in the aniline ring. The absorption coefficients are in the range of 1.2–2.6 × 10^5 cm^{-1} M^{-1}. Since both the ground state and the excited state of squaraines are shown to be intramolecular

---

(44) As seen in the mass spectrum of USq-1 in Figure 1, a fragment ion at m/z 453, which can be assigned to intermediate ion of



according to ref 20. Its occurrence signals that mass spectral reactions of unsymmetrical squaraines are no different from those studied earlier in our laboratory.

(45) The mass spectral data of 1 are as follows: m/z 441 (0.5, 1.5 $M^{\bullet+}$); 308 (1.5, M + $CH_2^{\bullet+}$); 296 (15, M + $H_2^{\bullet+}$); 294 (100 M^+); 238 (37, (M − $2CO^{\bullet+}$); and 223 (22, (238 − CH_3). The base peak is at m/z 294, which corresponds to M^+; the major fragmentation of M+ is decarbonylation reaction. Although intermediate ion at 441, alkylated ion at 308, and hydrogenated ion at 296 were observed, their intensities are low as compared to those seen in Table IV. The change in fragmentation pattern in 1 is attributable to the change in electronic structure in 1 due to the methoxy groups.

(46) Farnum, D. G.; Webster, B.; Wolf, A. D. *Tetrahedron Lett.* **1968**, 5003.

(47) Law, K. Y. *Chem. Phys. Lett.* **1988**, *150*, 357.

Table IV. Mass Spectral Data of Unsymmetrical Squaraines

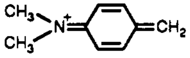
	ion peak, m/z (rel. intensity)								
				a	c		e	g	
squaraine	M^+	$M - 2CO^{\bullet+}$	$M + CHR^{\bullet+}$	b	d	$M + H_2^{\bullet+}$	f	h	base peak
USq-1	307 (7.7)	251 (6.20)	321 (22)	148 (15)	161 (13)	309 (98)	134 (100)	132 (19)	
				135 (13)	148 (15)		121 (26)		
USq-2	323 (100)	267 (60)	337 (2.9)	164 (7.0)	176 (13)	325 (14)	150 (5.0)	148 (26)	M^+
				135 (4.3)	148 (26)		121 (16)	119 (7.0)	
USq-3	321 (41)	265 (52)				323 (100)			$M + H_2^{\bullet+}$
					148 (65)				
USq-4	325 (35)	269 (66)	339 (52)	166 (27)		327 (100)	152 (99)		$M + H_2^{\bullet+}$
							121 (34)		
USq-5	337 (21)		351 (100)	178 (18)	191 (30)	339 (35)	164 (27)	162 (31)	$M + CH_2^{\bullet+}$
					148 (18)		121 (27)		
USq-6	383 (15)		397 (16)			385 (7.0)	210 (14)		$C_7H_7^+$
			473 (57)						
USq-7	337 (56)	281 (36)	351 (43)	148 (10)	161 (15)	339 (100)	134 (75)	132 (33)	$M + H_2^{\bullet+}$
				165 (7.6)			151 (14)		
USq-8	353 (100)	297 (21)			176 (36)	355 (40)	150 (14)	148 (27)	M^+
					178 (20)		151 (35)	149 (9.5)	
USq-9	351 (83)	294 (100)	365 (35)	162 (13)	175 (10)	353 (85)	148 (34)	146 (29)	$M - 2CO^{\bullet+}$
				165 (13)	178 (7.8)		151 (18)	149 (12)	
USq-10	355 (30)	299 (50)	369 (42)	166 (15)		357 (100)	152 (80)		$M + H_2^{\bullet+}$
							151 (11)		
USq-11	337 (37)	281 (100)		178 (11)					$M - 2CH^{\bullet+}$
					178 (11)				
USq-12	367 (16)	311 (9.6)	381 (12)	148 (4.1)			134 (25)	132 (6.8)	CH_3O^+
						369 (16)			
USq-13	383 (4.2)				176 (2.7)	385 (2.9)			CO^+
					208 (3.3)		181 (3.2)	179 (1.9)	

Table V. Absorption Spectral Data of Unsymmetrical Squaraines in Chloroform

squaraine	λ_{max} (nm)	log ϵ (cm^{-1} M^{-1})
USq-1	578.8	5.37
USq-2	563.6	5.20
USq-3	583.5	5.32
USq-4	581.1	5.40
USq-5	583.6	5.23
USq-6	581.1	5.41
USq-7	587.0	5.34
USq-8	572.1	5.20
USq-3	592.4	5.35
USq-10	590.6	5.32
USq-11	582.4	5.08
USq-12	583.1	5.39
USq-13	562.4	5.12
1[a]	536	5.15
2[b]	624	5.48

[a] Reference 46. [b] Reference 47.

donor–acceptor–donor charge-transfer states,[5,30] replacement of the dimethylamino group by a methoxy group in squaraine is expected to produce a hypsochromic effect on the λ_{max}.[31] This is indeed observed experimentally because the range of absorption for **USq-1** to **USq-13** lies exactly between those of **1** and **2** (Table V). The spectral data in Table V further shows that there is a structural effect on λ_{max}, and we plan to address this effect along with the fluorescence spectral data of these compounds in a forthcoming report.

Solid-State Properties. One of the objectives of the present work is to synthesize photoconductive squaraines with improved spectral response in the visible region in xerographic devices. Since both the photoconductivity and the spectral response of squaraine are governed by the aggregated form of squaraine in the solid state,[32] we have examined the aggregation of **USq-1–13** in solid by absorption spectroscopy and X-ray powder diffraction technique. Preliminary data on the absorption and the X-ray diffraction pattern of **USq-1** are depicted in Figures 2 and 3, respectively. By comparison of the data of **USq-1** to those of model squaraine **2**, we conclude that the aggregated form of **USq-1** in solid is identical to that of **2**, implying that **USq-1** would be sensitive in a photoconductive device. This is in fact observed.[48] More importantly, the hypsochromic shift on the solution λ_{max} has led to a similar hypsochromic shift on the entire solid-state absorption, resulting in an increase in absorptivity at 400–500 nm and an improvement in spectral responses in the visible region.

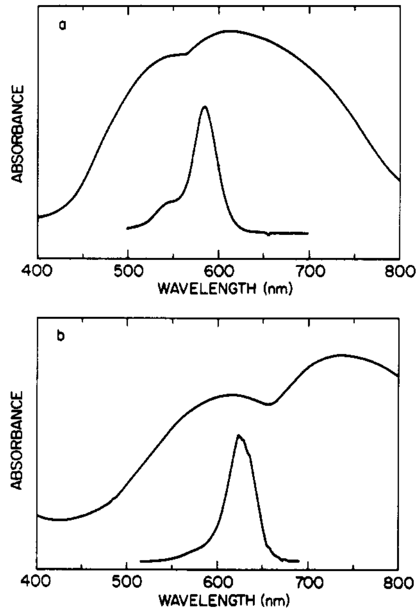


Figure 2. Solid-state absorption spectra of (a) **USq-1** and (b) model squaraine **2** in KBr pellet (inset: solution absorption spectra in $CHCl_3$).

Concluding Remarks

This work reports our investigtion on the synthesis of photoconductive squaraines with improved spectral response in the visible region in xerographic devices. Con-

---

(48) Law, K. Y. *J. Imaging Sci. Technol.* Submitted for publication.

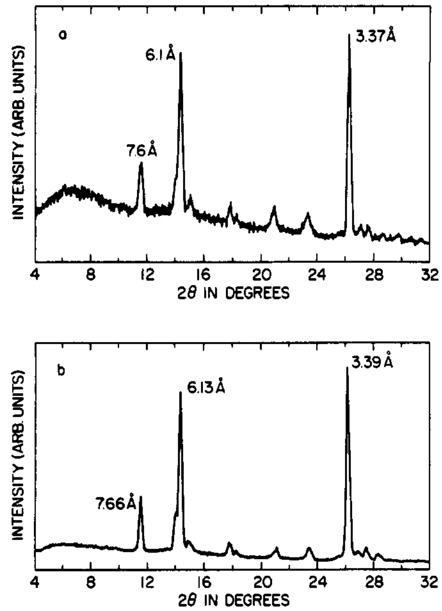


Figure 3. X-ray powder diffraction patterns of (a) **USq-1** and (b) model squaraine **2**.

ventional photoconductive squaraines exhibit flat photoresponses between 500 and ~900 nm, but the photoresponses at 400–500 nm are rather poor due to the low absorptivity. Since the output of the diode laser used in laser-addressed technologies is at ~780 nm and photoresponses beyond that are unused anyway, our approach to improve the spectral response is to engineer a 50–100 nm hypsochromic shift in the solid-state absorption of squaraine. This will enable the resulting xerographic device to have flat photoresponses from 400 to ~800 nm. On the basis of recent spectroscopic and theoretical studies, we launched an effort to synthesize unsymmetrical squaraines, **USq-1–13** where the dimethylamino group in squaraine is replaced by a less powerful, electron-releasing methoxy group. Hypsochromic shifts on both solution- and solid-state absorption are indeed obtained. Preliminary measurements on the photoconductivity of these compounds already revealed the expected improvement at 400–500 nm.

The unsymmetrical photoconductive squaraines synthesized in this work were prepared by a cycloaddition–condensation reaction sequence. By using a secondary alcohol as reaction solvent and tributyl orthoformate as an in situ homogeneous drying reagent, we have been able to suppress both secondary and side reactions, enabling these compounds to be synthesized in high chemical yields in a very short reaction time. The synthesis represents *the first general synthesis of photoconductive squaraine without using squaric acid as a precursor.* Our current effort is to extend our synthetic concept to synthesize symmetrical and unsymmetrical photoconductive squaraines with dimethylamino groups using a similar cycloaddition–condensation reaction sequence. Preliminary results are encouraging.[49]

---

[49] Law, K. Y.; Bailey, F. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1156.

Crystal and Molecular Structure of 10-Substituted 9-Anthracenones. Substituent Size as the Controlling Factor for the Nonplanarity of the Central Ring

Andrzej Sygula,* Renata Sygula, Frank R. Fronczek, and Peter W. Rabideau*

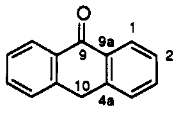
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received January 22, 1992

MM2 calculations for a series of 10-*R*-9-anthracenones demonstrate an increase of the folding of the central ring with increasing size of the substituent. All the substituents considered prefer the pseudoaxial position except fluorine, which prefers the pseudoequatorial orientation. The anthracenone moiety approaches planarity when the size of the substituents approaches the size of the hydrogen atom. The planar conformation for 9-anthracenone is also shown by vibrational frequency calculations to be a true potential energy minimum at the ab initio 3-21G level. X-ray structure determination shows that 10-R-9-anthracenones (R = Me, iPr, tBu, Ph, and Br) generally exhibit the structural features predicted by MM2 calculations for the isolated molecules. However, 10-Me and 10-Ph-9-anthracenones are found to be significantly less folded than calculated by MM2, the discrepancy being attributed to the crystal packing forces. Consideration of the theoretical as well as the experimental results leads to the conclusion that the parent 9-anthracenone is expected to be planar in the crystal state.

Introduction

The structure of 9-anthracenone (9-anthrone) derivatives is of interest since some of them are biologically active. However, the structure of the parent 9-anthracenone (**1**) is controversial; **1** displays structural disorder in the crystal, so the details of its crystal structure are not known.[1,2] Also, a large independent out-of-plane vibration of the oxygen atom precludes determination of whether **1** is planar or folded in the crystal.[1] The ^{1}HNMR analysis of **1** suggested an inverting nonplanar molecule in solution based on the interpretation of the long-range, spin–spin coupling constants.[3] On the other hand, earlier solution studies based on dipole moment and the Kerr constant



1

---

[1] Flack, H. D. *Philos. Trans. R. Soc. London, Ser. A* **1970**, *266*, 561.

[2] Srivastava, S. N. *Ind. J. Phys.* **1972**, *46*, 56.

[3] Schaefer, T.; Sebastian, R.; Wildman, T. A.; Dettman, H. *Can. J. Chem.* **1982**, *60*, 2274.

0022-3263/92/1957-3286$03.00/0