

A New Approach to Symmetrical and Unsymmetrical Photoconductive Squaraines

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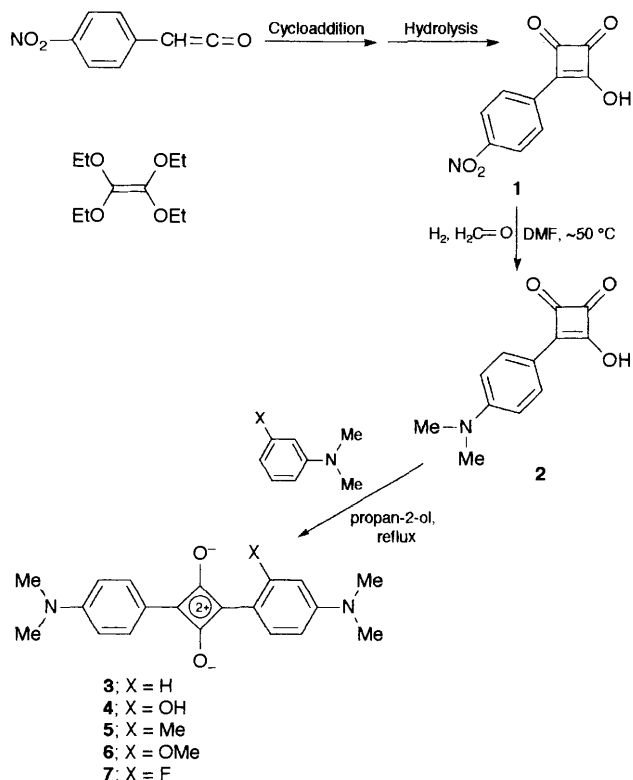
A new synthesis for symmetrical and unsymmetrical photoconductive squaraines, based on a (2 + 2) cycloaddition, reductive-alkylation and condensation reaction sequence, is described.

Bis(4-dimethylaminophenyl)squaraine **3**[†] and its derivatives are organic photoconductors known to be useful for xerographic diode laser (780 nm) printers.¹ These compounds are traditionally synthesized by condensation of squaric acid with *N,N*-dimethylaniline derivatives.² Owing to their low solubility, they are usually used as-synthesized and are often found to

exhibit low charge-acceptance and high dark-conductivity in xerographic devices.^{1‡} We have recently found that photoconductive squaraines with improved xerographic properties could be synthesized by condensing dibutyl squarate with *N,N*-dimethylaniline derivatives.³ The improvement was shown to be a purity effect, enabled by an alteration of the crystallographic and morphological properties of the micro-

[†] The nomenclature of the condensation products from squaric acid and *N,N*-dialkylanilines has not been systematic. In 1981, Schmidt proposed the name squaraine for this class of compound and we find the Schmidt nomenclature system very systematic and compounds with a variety of substitution can be named unambiguously. See A. H. Schmidt, in *Oxocarbons*, ed. R. West, Academic Press, New York, 1980.

[‡] There are four key steps in xerography, namely charging, photodischarge, image transfer and development and cleaning. In order to achieve high imaging quality, a layered xerographic device should have a high charge-acceptance and low dark-conductivity values. For discussion, see J. W. Weigl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 374.



Scheme 1

crystalline squaraine products, whereby the inclusion of impurity is minimal. While difluoro substituted squaraine is highly photoconductive, its synthetic yield is low due to the low nucleophilicity of the fluoroaniline.^{1,3} To overcome the yield-sensitivity dilemma, mixtures of halosquaraines consisting of three components, symmetrical squaraine **3**, an unsymmetrical halosquaraine and a symmetrical dihalosquaraine, were synthesized by co-reacting dibutyl squarate with a mixture of *N,N*-dimethylaniline and a 3-halo-*N,N*-dimethylaniline.⁴ High xerographic sensitivity was obtained from these mixtures. The results are considered as surprising because we intuitively expected that high purity and high crystallinity are essential for the high photoconductivity.⁵ This observation, however, suggests that unsymmetrical squaraines are promising organic photoconductive materials. Today squaraines can only be synthesized from squaric acid or dibutyl squarate. Due to the nature of the condensation reaction, pure unsymmetrical squaraines are not accessible. A general procedure to these seemingly promising materials is needed.

Here a novel procedure to synthesize unsymmetrical squaraines **4–7**, based on a cycloaddition, reductive alkylation and condensation reaction sequence, is reported. Depending on the selection of the starting compounds, symmetrical squaraines such as **3**, can be prepared as well. The precursor for the squaraine synthesis, **2**, was prepared by reductive-alkylation of 1-*p*-nitrophenyl-2-hydroxycyclobutene-3,4-dione **1** with hydrogen in *N,N*-dimethylformamide (DMF) in the presence of >2 equivalents of formaldehyde at ~50 °C inside a Parr apparatus. Compound **1** was prepared by a (2 + 2) cycloaddition reaction analogous to that reported by Bellus,⁶ between *p*-nitrophenylketene and tetraethoxyethylene, followed by an acid hydrolysis. The isolated yields for **1** and **2** are 55 and 81%, respectively. Condensation of **2** with an *N,N*-dimethylaniline derivative in refluxing propan-2-ol, in the presence of an *in situ* drying agent (tributyl orthoformate) results in symmetrical squaraine **3** and unsymmetrical squa-

Table 1 Synthesis and optical properties of squaraines

Squaraine ^a	Isolated yield (%)	λ_{\max}^b /nm	Log ϵ /dm ³ mol ⁻¹ cm ⁻¹
3	46	623.9 (lit. 624) ^c	5.43 (5.48) ^c
4	52	626.1	5.30
5	22	632.5	5.30
6	33	627.3	5.07
7	3.8	625.0	5.03

^a Satisfactory C, H, N elemental analyses and spectroscopic (IR, ¹H NMR and mass) data were obtained for these compounds. ^b In chloroform. ^c Ref. 7.

raines **4–7** (Scheme 1.) The synthetic data and the optical properties of the squaraine products are given in Table 1. A detailed discussion of our synthetic strategy, optimization of the synthesis and reaction mechanism will be given in a full report.

In a typical synthesis, a DMF solution of **2** (0.3 g in ~4 cm³ of DMF) was added in a 2 h period to a refluxing propan-2-ol solution containing 2 equivalents of an *N,N*-dimethylaniline derivative and 6 equivalents of tributyl orthoformate under a nitrogen atmosphere. The mixture was refluxed for 3 more hours after the addition was completed. The precipitated blue powder products were filtered off and were washed with methanol and diethyl ether. The present synthesis starts with a (2 + 2) cycloaddition between *p*-nitrophenylketene and tetraethoxyethylene, followed by a reductive-alkylation of the nitro intermediate and a condensation reaction. The entire squaraine synthesis is accomplished without using squaric acid as a precursor. The avoidance of squaric acid represents a significant cost saving and a probable simplification for the squaraine synthesis. Moreover, since substituents in squaraine can be introduced either through the nitrophenylketene or the *N,N*-dialkylaniline derivative, the methodology described here may provide an entrance to new symmetrical and unsymmetrical structures, which were not accessible previously.

Squaraine **3** is the only symmetrical squaraine synthesized in this work. It exhibits an absorption maximum at 623.9 nm in chloroform with an absorption coefficient of 270 000 dm³ mol⁻¹ cm⁻¹. The absorption data are identical to those reported earlier on a sample that was synthesized from squaric acid.⁷ Squaraines **4–7** are unsymmetrical. Their absorption maxima vary from 625.0 to 632.5 nm, depending on the substituent in the phenyl ring. It is known from our previous work that substituents in the phenyl ring usually induce bathochromic shifts on the λ_{\max} value. In the case of di-substituted symmetrical squaraines, the bathochromic shifts are: Me, 15.9 > OH, 8.3 > OMe, 4.2 > F, 2.4 nm.⁸ The bathochromic shifts in Table 1 are: Me, 8.6 > OMe, 3.4 > OH, 2.2 > F, 1.1 nm. Although the trend for the bathochromic shift is very similar, the magnitude of the shift for **4–7** is about half of their symmetrical, di-substituted analogues. These results are consistent with the intramolecular charge-transfer character of the ground and the excited states of squaraines^{8,9} and also suggest that the substituent effect is additive. The absorption coefficients of **4–7** are typical of squaraines, of the order of ~10⁵ dm³ mol⁻¹ cm⁻¹. By comparison with the ϵ_{\max} values of **3** and other symmetrical squaraines, the ϵ_{\max} values of **4–7** are about a factor of 1.5–2 smaller. We attribute the decrease in ϵ_{\max} to the unsymmetrical structure of these compounds.

The photoconductivity of squaraines is shown to be governed by the aggregation of squaraine molecules in the microcrystalline state.⁵ Photoconductive squaraine aggregates are characterized by the characteristic X-ray powder diffrac-

tion lines at $2\theta \sim 11.5$, ~ 14.5 and $\sim 26^\circ$, and by the intense panchromatic solid state absorption which consists of two bands at around 500–650 and ~ 700 nm. We have examined the aggregation of **3** and **4–7** by solid state absorption spectroscopy and X-ray powder diffraction. Results indicate that they form photoactive aggregates in the solid state. These squaraines should be photoconductive in xerographic devices. This anticipation has been experimentally verified and we plan to elaborate the details of these measurements elsewhere.

Finally, we have previously shown that fluoro and chloro substituents enhance the xerographic sensitivity of squaraines in devices.⁴ The isolated yields of halosquaraines are low due to the low reactivity of halo-*N,N*-dimethylanilines. However, the synthetic route here suggests that halo substituents can be introduced through the ketene precursor in the cycloaddition step. An improvement in the synthetic efficiency of halosquaraines is anticipated. Synthetic work to use this route to

improve the yields of halosquaraines and to synthesize novel unsymmetrical structures is in progress.

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