# Near IR Sensitive Unsymmetrical Squaraines†

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A class of novel, unsymmetrical squaraines, which were designed to photorespond from the visible to the near IR (400—800 nm) in organic photoconductive devices, have been synthesized without using squaric acid, by a cycloaddition–condensation sequence.

Bis(4-dimethylaminophenyl)squaraine and its derivatives are organic photoconductors that are photosensitive in the near IR where solid-state diode lasers emit (780 nm). The traditional synthesis, which involves condensing of squaric acid and an $N,N$-dialkylaniline in an azeotropic solvent,[1] often produces squaraines that exhibit low charge-accepting properties and high dark-conductivity in layered xerographic devices.[2]‡ Two modified procedures, using the mono- and the

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† 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; we find the Schmidt nomenclature system useful 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, followed by 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.

**Table 1.** Synthesis and optical properties of unsymmetrical squaraines (3)—(12).[a]

| Squaraine | Ar¹ | X in Ar² (4-Me₂NC₆H₃X–) | % Isolated yield | $\lambda_{max.}$[b] /nm | log ε /cm⁻¹ dm³ mol⁻¹ |
|---|---|---|---|---|---|
| (3) | 4-MeOC₆H₄ | H | 67 | 578.8 | 5.37 |
| (4) | 4-MeOC₆H₄ | 2-OH | 86 | 563.6 | 5.20 |
| (5) | 4-MeOC₆H₄ | 2-Me | 73 | 583.5 | 5.32 |
| (6) | 4-MeOC₆H₄ | 2-F | 32 | 581.1 | 5.40 |
| (7) | 4-MeOC₆H₄ | 2-OMe | 43 | 583.6 | 5.23 |
| (8) | 3,4-(MeO)₂C₆H₃ | H | 77 | 587.0 | 5.34 |
| (9) | 3,4-(MeO)₂C₆H₃ | 2-OH | 87 | 572.1 | 5.20 |
| (10) | 3,4-(MeO)₂C₆H₃ | 2-Me | 83 | 592.4 | 5.35 |
| (11) | 3,4-(MeO)₂C₆H₃ | 2-F | 59 | 590.4 | 5.32 |
| (12) | 3,4-(MeO)₂C₆H₃ | 2-OMe | 52 | 582.4 | 5.08 |

[a] Satisfactory elemental analyses and spectroscopic data were obtained for all unsymmetrical squaraines. [b] In CHCl₃.
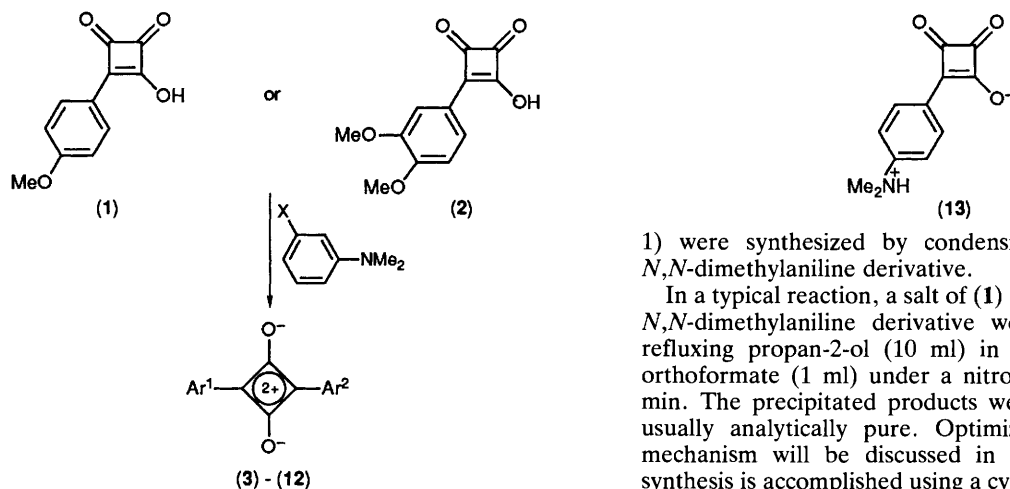


**Scheme 1.** *Reagent:* (BuO)₃CH in Pr'OH, reflux.

di-alkyl esters of squaric acid as precursors, have recently been developed to circumvent the performance problem.[3] The common starting material for these procedures is squaric acid, which by itself has to be prepared by a multi-step low-yield reaction.[4] Procedures to simplify squaraine synthesis are highly desirable.

The photoconductivity and the optical absorption of squaraine layered xerographic devices are controlled by the state of aggregation of squaraine in the microcrystalline state.[5] The spectral response of such a device, which images the absorption spectrum, is flat from 500 to 900 nm; a decrease in photosensitivity from 400 to 500 nm is observed due to the decrease in light absorption. As a result, squaraine is not considered to be useful in copier and multi-functional copier–printer applications. Our research goal is to develop new synthetic procedures, from which highly sensitive squaraines with improved response at 400—500 nm can be synthesized. We report here the synthesis of a class of unsymmetrical squaraines, which have been shown to meet our spectral and sensitivity requirements.

The precursors for the squaraine synthesis, (1) and (2), were prepared by a [2 + 2] cycloaddition reaction in 57 and 40% yield, respectively, using a procedure similar to that developed by Bellus,[6] between 4-methoxyphenylketene or 3,4-dimethoxyphenylketene, and tetraethoxyethylene in n-hexane followed by acid hydrolysis of the cycloadduct mixtures. The overall isolated yields of (1) and (2) were 57 and 40%, respectively. The unsymmetrical squaraines (3)—(12) (Table

1) were synthesized by condensing (1) or (2) with an N,N-dimethylaniline derivative.

In a typical reaction, a salt of (1) or (2) (1.25 mmol) and an N,N-dimethylaniline derivative were allowed to react in refluxing propan-2-ol (10 ml) in the presence of tributyl orthoformate (1 ml) under a nitrogen atmosphere for ~90 min. The precipitated products were filtered off and were usually analytically pure. Optimization and the reaction mechanism will be discussed in a full report. Since the synthesis is accomplished using a cycloaddition–condensation reaction sequence, it represents a new approach for squaraines, where the use of squaric acid is avoided.

The absorption maxima ($\lambda_{max.}$) of the unsymmetrical squaraines (3)—(12) vary from 562 to 592 nm, depending on the substituent in the anisole ring and the phenyl ring. Their absorption coefficients are of the order of 10⁵ cm⁻¹ dm³ mol⁻¹.[7] The range of absorption lies between those of bis(4-dimethylaminophenyl)squaraine and bis(4-methoxyphenyl)squaraine, $\lambda_{max.}$ 624 and 536 nm, respectively, in chloroform. The observed hypsochromic shift, from the $\lambda_{max.}$ of bis(4-dimethylaminophenyl)squaraine, is consistent with the intramolecular charge-transfer character of the ground and the excited state of squaraine.[7,8]

As noted earlier, both the photoconductivity and the absorption of squaraine are governed by squaraine aggregates. We have examined the aggregation of (3)—(12) in the solid state by X-ray diffraction and absorption spectroscopy. Preliminary findings reveal that their aggregation is similar to that of bis(4-dimethylaminophenyl)squaraine, implying that they should be sensitive in layered xerographic devices. This surmise has recently been verified.[9] The significance of the achievement lies not only in the synthesis of a highly photosensitive squaraine (without using squaric acid), but also in the improvement of photoresponse at 400—500 nm, owing to the hypsochromic effect produced by the methoxy groups. For example, a device using (11) has been shown to have a high and flat response in the range 400—650 nm and a peak photoresponse at 780 nm.[9] This enables the photoconductive device to be usable in diode laser printers, copiers, and multi-functional copier–printers.

Finally, we have recently extended the same synthetic

method to synthesize (13) from which bis(4-dimethylamino-phenyl)squaraine and its unsymmetrical derivatives can be synthesized. The results of that study will be reported in due course.

## References

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