

New Synthetic Approach to Squarylium Near Infrared Dyes

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Abstract: The 1,3-bis(4-aminoaryl)squaraines showed colour change behaviour, they were found to undergo reduction with sodium borohydride in solution to give colourless leuco compounds, which oxidised readily in air back to the coloured squaraine dye. We have shown that oxidation of the parent *leuco*-squaraines gives the neutral squaraine system. Initial observations indicated that the derivatives gave new long-wavelength absorbing chromophores, and it is interesting to note that the oxidation of the leuco squaraines did initially produce a species absorbing at longer wavelengths than the parent squaraine dye. This colour-change redox behaviour has potential in the area of peroxidase-based bioassays and artificial camouflage.

Introduction

Squarylium, or squaraine, dyes are derived from 1,2-dihydroxycyclobuten-3,4-dione, otherwise known as *squaric acid* (a). They are of two principal types (Fig. 1): the 1,2-bis-donor substituted derivatives (b), and the 1,3-bis-donor substituted derivatives (c). The former is essentially merocyanines which have no distinctive properties, whereas the latter represent a unique type of chromophore, which is neither a merocyanines nor a cyanine, and has exceptional light absorption characteristics. In this respect, types (c) can be classified along with the H-chromophores as special cross-conjugated π -electron systems. They have many functional applications based on their special properties.

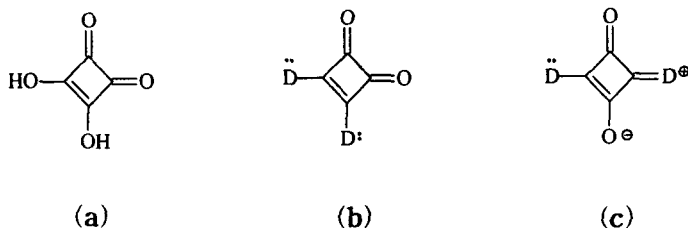


Figure 1. Squarylium or squaraine chromophores.

Experimental

These symmetrical structures were prepared from squaric acid and the appropriate *N,N*-dialkylanilines. The now standard technique involves heating squaric acid in a mixture of toluene and *n*-butanol under azeotropic conditions, so that the mono-*n*-butyl squarate ester is formed. This then undergoes *in situ* nucleophilic substitution by the arylamine, giving the half-condensate. A second condensation reaction then gives the 1,3-bis(4-aminoaryl) squaraine.

Preliminary experiments showed that the 1,3-bis(4-aminoaryl)squaraines were readily decolourised by a variety of reducing agents, and the colour could be regenerated by leaving the solutions in air, or by adding oxidising agents such as ferric chloride. The most convenient method of reduction involved using excess sodium borohydride in a mixture of a dichloromethane and methanol at room temperature, most of the squaraine dyes being soluble in this medium. A reaction time of 2 hours was sufficient to effect complete reduction. Isolation of the *leuco* dye could be achieved by removal of the solvent on a rotary evaporator, adding water and acetic acid to the residue, and filtering off the precipitate.

Results and Discussion

The 1-alkylamino *leuco* squaraines after oxidation should give the alkylamino cationic dye system which may then undergo deprotonation to give the neutral 1-amino squaraine system, which is iso-electronic with the parent squaraine system. Dyes of the type (1d-f) and (2d-f) are unknown. Oxidation of the 1-alkylamino *leuco* squaraines could be effected with ferric chloride, chloranil or lead dioxide, and gave cationic dyes.

These were confirmed to be cationic by their very low *R_f* values on t.l.c. compared to

neutral squaraine dyes. As predicted by Dewars rules, these cationic dyes absorbed at even longer wavelengths than their methoxy counterparts, and furthermore the bathochromic shift increased with increasing electron donating strength of the alkylamine. Thus in the NN-diethylamino series (**1d-f**), the max values were 688, 690 and 693 nm for the methylamino, ethylamino and n-butyamino derivatives respectively. For the NN-dbutylamino series (**2d-f**) the corresponding max values were 693, 696 and 697 nm.

A typical absorption spectrum of an oxidised amino leuco squaraine dye solution compared to the parent squaraine dye is shown in Figure 2.

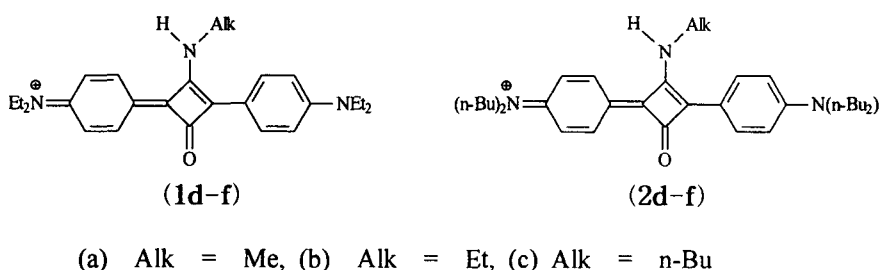


Figure 2. The cationic chromophore of leuco squaraines.

Conclusions

The bis(4-aminoaryl)squaraines showed that they were found to undergo reduction with sodium borohydride in solution to give colourless leuco compounds, which oxidised readily in air back to the coloured squaraine dye. This colour-change redox behaviour has potential in the area of bio- and military.

The discovery of the facile synthesis of the leuco squaraine system and the demonstration that the leuco compounds can undergo a wide range of chemical inter-conversions and then be oxidised back to a squaraine system, opens up many possibilities for synthesising new types of squaraine dye not accessible by existing chemical routes.