Near-infrared-absorbing Squaraine Dyes containing 2,3-Dihydroperimidine Terminal Groups

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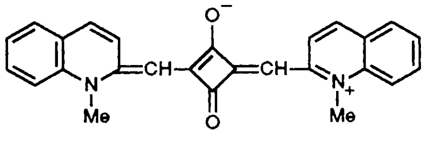
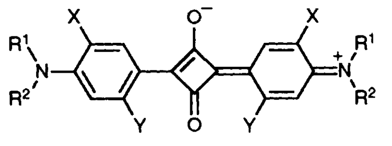
Condensation of 2,3-dihydroperimidines with squaric acid under conditions of azeotropic removal of water affords a new class of diarylsquaraine dyes with intense absorption bands at *ca.* 800 nm.

Squaraine dyes are characterised by intense, narrow absorption bands at relatively long wavelengths, and thus are of interest for the development of new near-infrared dyes for use with diode lasers (*i.e.* wavelengths *ca.* 750–850 nm). Near-infrared absorption can be achieved with certain heterocyclic terminal groups if there is a five-carbon chain between the terminal rings, *e.g.* **1**,[1,2] and such dyes are analogues of the pentamethine cyanines. The related diarylsquaraine dyes **2** contain two fewer carbon atoms in the chromophoric chain, and are generally more stable and soluble than types **1**, with

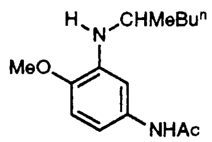


1



2

a; $R^1 = R^2$ = Et, X = Y = H
b; $R^1 = R^2$ = Et, X = H, Y = OH
c; $R^1 = R^2$ = Et, X = H, Y = NHAc
d; R^1 = H, R^2 = CHMeBu^n, X = OMe, Y = NHAc



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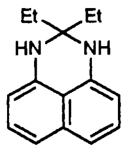

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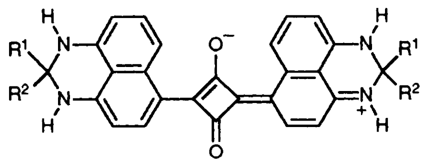


5

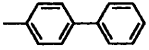
a; $R^1 = R^2$ = Et
b; R^1 = Me, R^2 = $CH_2CH_2CO_2Bu^n$
c; R^1 = Ph, R^2 = COPh
d; R^1 = Me, R^2 = 

Table 1 Yields and electronic absorption spectra of squaraine dyes **2** and **5**

Dye	Isolated yield (%)	λ_{max} (CH_2Cl_2)/ nm	ε_{max} (CH_2Cl_2)/ l mol^{-1} cm^{-1}
2a	62	640	326 000
2b	83	648	350 000
2c	71	682	350 000
2d	50	708	302 000
5a	80	808	155 000
5b	81	800	189 000
5c	33	809	135 000
5d	41	805	148 000

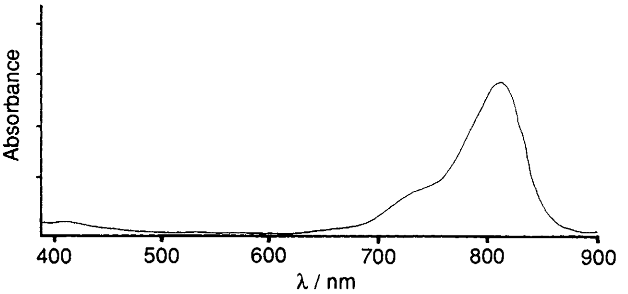


Fig. 1 Absorption spectrum of **5a** in dichloromethane

similarly high molar absorption coefficients (*ca.* 3 × 10^5 l mol^{-1} cm^{-1}) and narrow bandwidths.[2,3] However, they are less bathochromic than **1** and no derivatives are known which absorb beyond *ca.* 680 nm. Recently, Hartmann and co-workers described dyes related to **2** containing terminal aminothiophene residues, but, although these were more bathochromic than their phenyl counterparts, the maximum absorption wavelength that could be achieved was 704 nm.[4] Three-carbon-bridged squaraine dyes with azulenyl terminal groups are known which absorb up to *ca.* 770 nm,[5] but these have relatively poor stability and the starting materials for their synthesis are not readily accessible. We now describe a new class of squaraine dye with diaminonaphthyl terminal rings which absorb intensely near 800 nm and which are readily prepared in good to moderate yields.

A molecular orbital study of the chromophore **2** showed that the longest wavelength transition involves electron density transfer from the terminal amino groups into the central four-membered ring, and that enhancement of the electron donating ability of the aryl rings causes a bathochromic shift of the absorption band. We were able to demonstrate this with dyes **2a–c**, where λ_{max} (in dichloromethane) is displaced from 640 to 682 nm as the electron-releasing effect of the 2-substituent in the 4-*N*,*N*-diethylaminophenyl ring is increased (Table 1).

The maximum electron-releasing effect that can be achieved with a poly-substituted phenyl ring is limited by steric interactions between *ortho* substituents, which can drastically reduce the +*M* effect of electron-donor groups. It is generally accepted that for charge-transfer transitions in many dye types, the 4-*N*-alkylamino-3-alkoxy-6-acylamino residue (*e.g.* **3**) approximates to the maximum electron-donating effect that can be achieved from a poly-substituted phenyl ring. Condensation of squaric acid with primary and secondary arylamines normally affords *N*-condensed products which are yellow in colour.[6] However, we examined the reaction between the secondary amine **3** and squaric acid, and contrary to expectation this afforded exclusively the *C*-condensed dye **2d**, which had λ_{max} 708 nm in dichloromethane. Thus, it is a reasonable assumption that absorption bands approaching 800 nm cannot be achieved by simple poly-substitution of a diphenylsquaraine system.

The observation that secondary arylamines such as **3** will condense with squaric acid efficiently at aryl carbon rather than at nitrogen suggested use of the 2,3-dihydroperimidine system **4** for condensation with this species. It is known that the 2,3-dihydroperimidine residue is exceptionally bathochromic in donor–acceptor dye chromophores. Moreover molecular orbital calculations (PPP SCF-CI) suggested that squaraine dyes of type **5** would absorb at significantly longer wavelengths than even dye **2d**.

To examine this possibility, the dihydroperimidine **4** was heated with squaric acid (0.5 equiv.) in a mixture of toluene and n-butanol with azeotropic removal of water. A green colour rapidly developed and the dye **5a** was deposited as a black solid in 80% yield. The structure was confirmed by elemental analysis, mass spectrometry and ^{1}H NMR spectroscopy. The chemical shifts of the NH protons were particularly noteworthy. Thus, the protons on nitrogen directly conjugated to the squarylium ring showed a large downfield shift (δ 10.7), consistent with the partial positive character of nitrogen. The remaining NH protons showed a broad peak at δ 4.3.

The electronic absorption spectrum of **5a** (Table 1) showed that the 2,3-dihydroperimidine system did indeed produce a remarkable bathochromic shift of the absorption band, and the dye had λ_{max} 808 nm in dichloromethane (ε_{max} 155 000 l mol^{-1} cm^{-1}) (Fig. 1). Of particular note was the minimal absorption of light by the dye over the range 400–700 nm, which meant that dye solutions could be prepared which were virtually colourless but which absorbed *ca.* 95% of the light at 800 nm. Thus, the dye chromophore has ideal absorption characteristics for use with diode lasers, and the minimal visible colour offers other advantages in areas such as optical data recording, imaging, and security printing.

The dihydroperimidine terminal groups of **5a** lend themselves readily to further structural modification. Thus a wide range of side chains can be introduced into the 2-position of the dihydroperimidine starting material by condensing 1,8-diaminonaphthalene with substituted ketones and aldehydes under acid-catalysed conditions.[7] In this way the derivatives **5b–d** were prepared, and as might be expected, these showed very similar light absorption characteristics (Table 1). Variation of the 2-substituents thus permits the facile synthesis of dyes with optimised solubility properties for specific applications.

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