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Near-Infrared Absorbing Squarylium Dyes

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ABSTRACT

Squarylium dyes have been prepared by condensation of squaric acid and arylamines. The absorption maxima of the dyes show a progressive shift to longer wavelength as the electron-donating properties of the arylamines are increased. The light absorption characteristics of representative examples are well accounted for by PPP–MO calculations. The dyes have high molar absorption coefficients, and wavelength maxima up to 708 nm have been achieved. The high molar absorption coefficients are due to the narrower absorption bands, rather than to intrinsically high absorption intensities. Copyright © 1996 Published by Elsevier Science Ltd

1 INTRODUCTION

There is considerable technical interest in dyes with absorption maxima in the near-infrared region, principally because of their potential application in areas such as laser and optical data storage technology.[1] We have previously reported syntheses of the first recorded examples of monoazo dyes absorbing in the near-infrared, and on the syntheses of near-infrared methine dyes based on dicyanovinyl derivatives of indane-1,3-dione.[2,3] Infrared squarylium dyes with pyrylium and thiopyrilium end groups have been documented.[4–7] One report have an investigation of some arylamine-squarylium dyes with a view to examining the colour and constitution relationships and thence to examine the possibility of producing near-infrared-absorbing dyes of this type.

2 RESULTS AND DISCUSSION

2.1 Visible absorption spectroscopic properties of the dyes

Visible absorption data for the dyes are summarised in Table 1. Absorption maxima in toluene and dichloromethane are given, with their molar absorption coefficients measured in dichloromethane. In the event of the dye being insoluble in dichloromethane, chloroform or other suitable solvent was employed.

As can be seen from Table 1, the molar absorption coefficients of all the squarylium dyes derived from arylamines are very high, ranging from 300 × 10^3 to 382 × 10^3 litre mol^{-1} cm^{-1}. The results indicate that the greater the electron-donating ability of the amino donor group, the larger the bathochromic shift compared to the parent dye (**1a**) derived from *N*,*N*-dimethylaniline. The electron transition in these compounds involves a general migration of electron density from the amino arylamine group into the rest of the chromophore system, and thus the greater the electron density that can be made available to the acceptor group, the greater is the bathochromic shift that results.

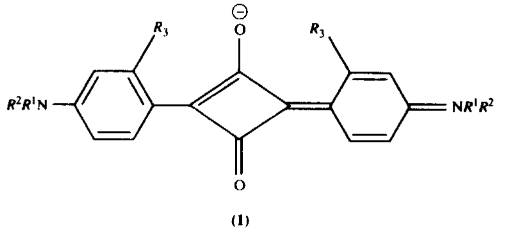
The *N*,*N*-dimethylaniline dye **1a** absorbs at 628 nm in chloroform with a half-bandwidth of 37 nm. The electron-donating effect of the hydroxy-group in dye **1b** results in a bathochromic shift of 10 mn (λ_{max} 638 nm); this hydroxy group also causes a slight increase in the molar absorption coefficient, and the visible absorption band is also sharpened, as indicated by the narrower half-bandwidth, (31 nm) and 37 nm for dyes **1a** and **1b**, respectively. The slight increase in the absorption wavelength and the intensity of this dye is presumably due to the ability of the hydroxy group in **1b** to hydrogen bond with the carbonyl oxygen atom in the squarylium acceptor.

Increasing the electron-donating ability of the donor group by replacing the methyl groups in **1a** by ethyl groups (dye **1c**) also gave a bathochromic

TABLE 1
Visible Absorption Spectroscopic Data for the Dyes

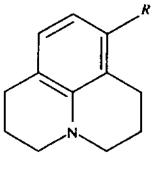
Dye	λ_{max} *(CH_2Cl_2) (nm)*	ϵ_{max}*litre* mol^{-1} cm^{-1}	λ_{max} *(toluene) (nm)*	$\frac{1}{2}^{a}$*(nm)*
1a	630		—	37
	(628)[b]	(278 100)[b]		
1b	638		—	31
	(638)[b]	(2 893 000)[b]		
1c	640	326 400	632	32
1d	648	350 400	644	30
1e	649	340 000	644	40
1f	682	349 500	680	30
1g	682	381 100	681	30
3a	670	357 600	658	33
3b	674	370 500	669	30
5	700	358 800	700	35
6	708	302 010	710	34

[a] Bandwidth at half peak height.
[b] In chloroform (solubility too low for accurate determination).



	R^1	R^2	R^3
a	Me	Me	H
b	Me	Me	OH
c	Et	Et	H
d	Et	Et	OH
e	*n*-Bu	*n*-Bu	H
f	Et	Et	NHAc
g	*n*-Pr	*n*-Pr	NHAc

(1)



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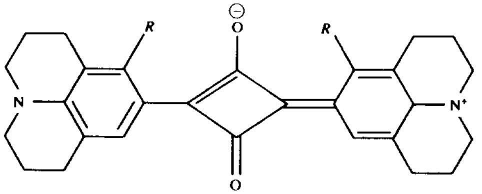
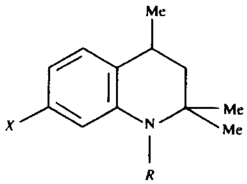


a $R = H$
b $R = OH$

(3)



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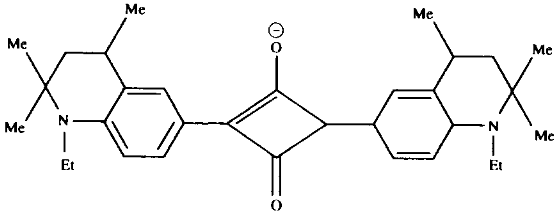

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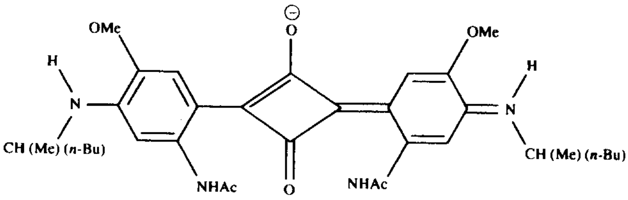


(6)

shift of 10 nm, and an additional shift of 8 nm was also obtained when a hydroxy group was introduced *ortho* to the cyclobutane ring, as in **1d**. Of the derivatives containing a single amino donor group, the *N*,*N*-di-*n*-butylamino derivative **1e** proved to be the most bathochromic, absorbing at 649 nm, in dichloromethane.

Dye **1f** possesses an additional electron-donating acetamido group *ortho* to the cyclobutane ring, and shows a bathochromic shift of 42 nm relative to the *N*,*N*-diethylamino analogue **1c** (λ_{max} 682 nm and 640 nm, respectively in dichloromethane). The acetylamino group may also hydrogen bond with the carbonyl group of the four-membered ring, thus causing a narrowing of the absorption band (half-bandwidth = 30 nm). This effect also accounts for the higher intensity of such dyes compared to those lacking such hydrogen bonding. Replacement of the ethyl groups in **1f** by *n*-propyl (dye **1g**) was also expected to cause a small additional bathochromic shift. However, the two dyes absorbed at the same wavelength (682 nm) but the intensity of the latter was greater (molar absorption coefficients 349 500 and 381 100 litre mol^{-1} cm^{-1}, respectively).

Dye **6** demonstrates clearly how increasing the number of electron-donating groups in the arylamine ring can cause a pronounced bathochromic shift of the absorption band. This dye absorbs at 708 nm in dichloromethane, compared to 640 nm for **1c** in the same solvent. This large shift is due to the presence of two electron-donating groups at position 2, 5 relative to the electron acceptor ring. This is the first recorded arylamino squarylium dye absorbing beyond 700 nm.

When the lone pair orbital of the amino donor group is forced into greater overlap with the rest of the chromogen, as in the julolidine dye **3a**, the absorption maximum is also shifted to longer wavelength, Thus dye **3a** absorbs at 670 nm in dichloromethane, whereas the parent dye **1c** absorbs at 640 nm, a bathochromic shift of 30 nm. Further introduction of a hydroxy group *ortho* to the cyclobutane ring, as in **3b**, causes an additional bathochromic shift of 4 nm with an increase in the molar absorption coefficient. Dyes **3**, however, are not as bathochromic as **1f** and **1g**, which indicates that the julolidine and 3-hydroxy julolidine moieties are weaker electron-donor systems than those based on *meta* acetylamino dialkylanilines, but are stronger than simple *N*,*N*-dialkylanilines. On the other hand, in dye **5**, there is enhanced overlap between the lone pair orbital on nitrogen and the π-electron system of the molecule, and also an acylamino group. This results in **5** absorbing at 700 nm in dichloromethane, i.e. a bathochromic shift of about 30 nm compared to dye **3a**. These results also show that tetrahydroquinoline residue is only about as effective as the 5-methoxy coupler system in dye **6** in terms of its electron-donating properties.

The light absorption characteristics of the dyes were examined by carrying out PPP–MO calculations on representative examples using the parameters described elsewhere.[8] By using slightly modified carbonyl parameters, it was found that reasonable agreement between experimental and calculated λ_{max} values could be obtained. The electron affinity of the carbonyl oxygen atom was changed from 2·5 eV to 3·8 eV, and the normal valence state ionisation potential (VSIP) of 18·00 eV was retained. It was then found that reasonable calculated results could be obtained using an approximate geometry, in

TABLE 2

Comparison of Calculated (PPP) and Experimental (Cyclohexane) λ_{max} Values for the Dyes

Dye	λ_{max} *(C_6H_{12})(nm)*	λ_{max}*(calc.)(nm)*	*f(calc.)*[a]
1a	(628)[b]	635	1·76
1b	635	627	1·80
1c	620	640	1·88
1d	635	629	1·88
1e	630	643	1·95
1f	670	655	2·03
6	703	700	1·39

[a] Oscillator strength.

[b] In chloroform.

which all C—C bond lengths were given an averaged resonance integral of −2·7 eV rather than −2·46 eV. Experimental λ_{max} values in cyclohexane are compared with the calculated values for the seven dyes in Table 2.

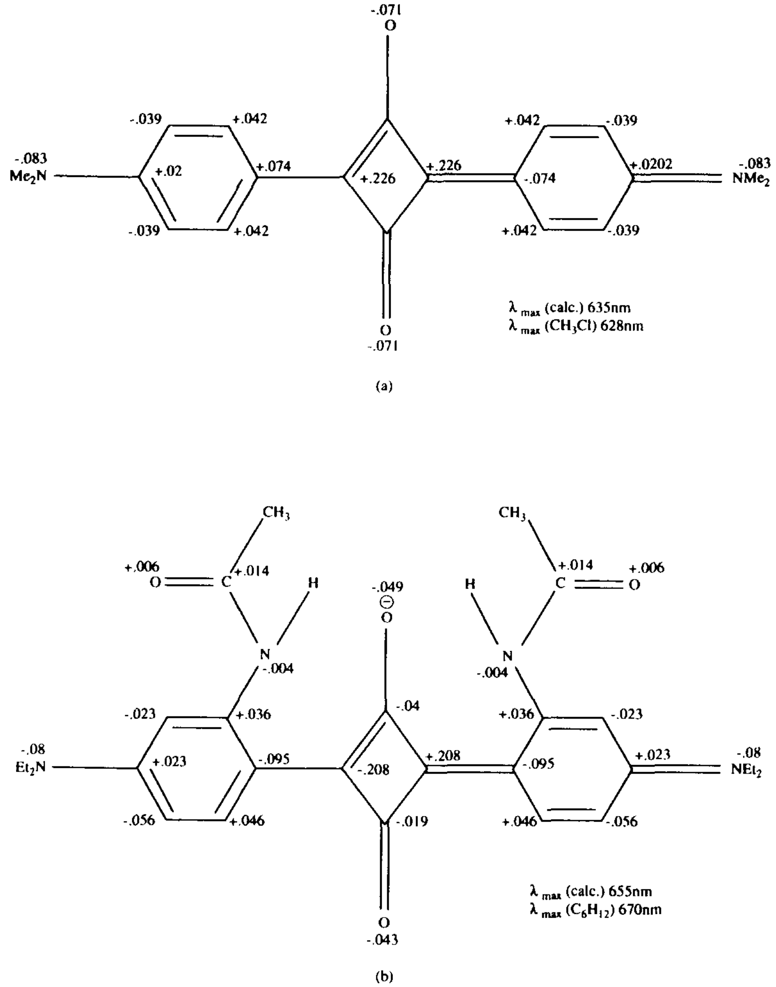
The MO calculations predict a progressive bathochromic shift as the electron-donating ability of the arylamines is increased, exactly the same as was observed experimentally. More importantly, the theoretical approach confirms the highly bathochromic character of the squarylium dyes and their exceptionally high absorption intensities. The calculation also predict correctly the strong bathochromic effect of the 2-acylamino-4-amino-5-methoxy electron donor system, as noted for dye **6**.

Consideration of the π-electron density changes accompanying light absorption in the visible band for the dyes in Table 2 shows the typical donor–acceptor character of these chromophores, with excitation casing a pronounced migration of electron density from the terminal amino nitrogen atoms into the squarylium ring, particularly into the central bridging carbon atom and the terminal carbonyl group, The electron density changes for dyes **1a** and **1f** are shown in Fig. 1.

2.2 Stability properties

The stability properties of the squarylium dyes were assessed using the procedures previously described[9] and the results obtained are summarised in Table 3, together with comparative data for a reference standard.

The stability properties of dye **1c** derived from *N*,*N*-diethylaniline were poor and were inferior to those of the reference dye. When a hydroxy group is introduced *ortho* to the cyclobutane ring (dye **1d**) the thermal stability is significantly improved. In fact **1d** shows better thermal stability than the reference dye. On the other hand the lightfastness properties were



(a)

(b)

Fig. 1. Electron density changes for the visible absorption transition for (a) dye **1a** and (b) dye **1f**.

not as good as those of the reference dye, but there was still a slight improvement in lightfastness when compared with the parent dye **1c**.

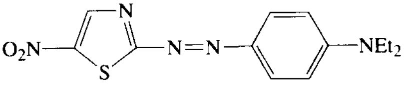
Increasing the length of the alkyl chain in **1c** did not give any significant improvement in thermal stability, although there was a slight improvement in the case of dye **1e**. This dye was still very inferior to the reference dye, and the photochemical stability was exceptionally bad.

When an acetylamino group is introduced into **1c**, the resulting dye **1f** has very good thermal stability, on a par with that of the reference dye. The lightfastness of this dye was also reasonable. There was a significant further improvement when the ethyl groups in **1f** were replaced by *n*-propyl, the

TABLE 3
Stability Properties of the Dyes

Dye	*Thermal stability Dye decomposed (%)*	*Photochemical stability Dye faded(%)*
Reference dye	10·1	5·3
1c	66·9	45·5
1d	2·1	25·0
1e	49·0	54·0
1f	10·9	15·3
1g	3·8	14·6
3a	91·0	89·9
3b	80·0	82·3
5	16·0	17·9
6	30·55	43·0

Reference dye:



thermal stability of this dye **1g** being even better than that of the reference, and thus equal to that of the hydroxy dye **1d**. The lightfastness of this dye was slightly lower than that of the reference dye.

Dyes **3a** and **3b** derived from julolidine were very inferior. Their lightfastness properties were disappointing and even the introduction of a hydroxy group gave no significant improvement in either their thermal or their photochemical stability. Dye **5**, with a tetrahydroquinoline residue, showed moderate thermal stability relative to the reference dye, but its thermal stability was not as good as that of **1g** derived from 3-acetamido-*N*,*N*-di-*n*-propylaniline. The stability property of **6** was poor relative to the reference dye, and its photochemical stability was also very poor.

In general, it can be seen from the data in Table 3 that the introduction of a hydroxy group *ortho* to the squarylium residue in the arylamine series tends to give dyes with good stability. This may be due to the intramolecular hydrogen bond formed between the hydroxy group and the carbonyl oxygen atom of the squarylium ring. An acetylamino group *ortho* to the cyclobutane ring also exerts a useful stabilising effect, presumably for the same reason.

3 EXPERIMENTAL

Squaric acid (2 mmole) and the appropriate arylamine (4 mmole) were refluxed with stirring in a mixture of *n*-butanol (40 cm^3) and toluene (20

TABLE 4
Yields and Characterisation Data for the Dyes

Dye	*Yield* (%)	*m.p.*[a] (°C)	*Formula*	*Found* (%)			*Required* (%)		
				C	*H*	*N*	*C*	*H*	*N*
1a	62	288	$C_{20}H_{20}N_2O_2$	75·0	6·25	8·25	75·0	6·25	8·75
1b	90	339	$C_{20}H_{20}N_2O_4$	68·10	5·75	7·9	68·18	5·68	7·95
1c	62	207	$C_{24}H_{28}N_2O_2$	76·65	7·55	7·2	76·59	7·44	7·44
1d	83	257	$C_{24}H_{28}N_2O_4$	70·45	6·85	6·4	70·58	6·86	6·86
1e	32	172	$C_{32}H_{44}N_2O_2$	78·40	9·20	5·6	78·68	9·02	5·73
1f	71	255	$C_{28}H_{34}N_4O_4$	68·40	7·10	11·2	68·57	6·94	11·42
1g	74	242	$C_{32}H_{42}N_4O_4$	70·0	7·70	10·0	70·32	7·79	10·25
3a	45	242	$C_{28}H_{28}N_2O_2$	79·15	6·70	6·65	79·24	6·60	6·60
3b	88	247	$C_{28}H_{28}N_2O_4$	73·50	6·15	6·00	73·68	6·14	6·14
5	65	316–318	$C_{38}H_{50}N_4O_4$	73·80	7·8	8·75	73·31	7·40	9·00
6	50	244	$C_{34}H_{46}N_4O_6$	67·5	7·55	9·25	67·33	7·59	9·24

[a] By differential scanning calorimetry.

cm^3) for 4 h and the water formed was removed by azeotropic distillation. The mixture was cooled and the precipitated dye was filtered off, washed with ethanol and recrystallised from the appropriate solvent. Yields, m.p. and microanalytical data are summarised in Table 4.

4 CONCLUSION

Condensation of squaric acid with arylamines proceeds smoothly to give the corresponding squarylium dyes. The chromophores show typical donor–acceptor characteristics, with increasing bathochromic shifts as the electron donating properties of the arylamines is increased. The largest bathochromic shift was observed with the *ortho* anisidine based dye **6**, which was green in colour with a λ_{max} value in the infrared region. The dyes have high molar absorption coefficients, and intense and narrow absorption bands. The introduction of a hydroxy group *ortho* to the cyclobutane ring improved the stability properties of the dyes on cellulose acetate film.

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