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Azacyanine Dyes with Acridinium Terminal Groups— A New Series of Near Infrared Absorbing Dyes

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ABSTRACT

Condensation of the 9,10-dimethylacridium cation with 4-nitroso-N,N-dialkylanilines gives highly bathochromic azacyanines in good yields. In dichloromethane these show intense absorption in the near infrared (c. 720–820 nm). However, in more polar solvents, particularly water, the cations are strongly aggregated and absorb at much shorter wavelengths (c. 550–707 nm). Aggregation appears to be reduced if the arylamine has a large steric requirement. The related xanthene and thioxanthene systems are much more hypsochromic. Annelation of the acridinium dyes to give the benz[a]acridinium analogues results in a further bathochromic shift of the absorption band.

1 INTRODUCTION

As part of our continuing interest in near-infrared dyes suitable for use with i.r. diode lasers in optical recording and other electrooptical areas, we have considered ways of making relatively short chain cyanines, which because of their lower molecular weight can combine long wavelength absorption with good solubility characteristics in organic solvents.

There are three principal ways in which the absorption band of a cyanine-type dye can be displaced to longer wavelengths, namely: (a) increasing the effective electron releasing ability of the terminal group(s); (b) modifying the polymethine bridge between the termini by introducing electron withdrawing or donating groups at the appropriate positions

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indicated by perturbational MO theory; and (c) increasing the length of the polymethine bridge. From the point of view of keeping the molecular size to a minimum in order to ensure good solubility properties, approach (c) is obviously the least satisfactory. In addition, the chain length needed to shift the absorption band into the near-infrared is often associated with poor chemical and photochemical stability, unless ring systems are used to 'rigidise' the chain.

We therefore have used a combination of approaches (a) and (b) to produce a new series of near-infrared dyes utilising acridinium and benzacridinium terminal groups in combination with aza-substitution in the polymethine bridge. The related oxygen and sulphur heterocyclic systems (xanthene and thioxanthene) were also synthesised for comparison of their light absorption properties. PPP-MO theory could account satisfactorily for the absorption spectra of the various dyes prepared.

2 EXPERIMENTAL

2.1 9-Methylacridine

A mixture of diphenylamine (9·0 g) and anhydrous zinc chloride (40 g) in glacial acetic acid (10 cm^3) was heated to 220°C with stirring. After the acetic acid had evaporated, the mixture was held at 220–230°C for a further 6 h. The cooled reaction product was digested with boiling 10% sulphuric acid and then the mixture made strongly alkaline with concentrated ammonia solution, ensuring complete dissolution of the residual zinc chloride. The insoluble residue was filtered off and extracted into sulphuric acid solution. The acidic solution was neutralised with aqueous ammonia and the resultant yellow precipitate filtered off. Drying gave a crude product in 81% yield; melting point: 117–18°C (lit.[1] 118°–118·5°C) from petroleum spirit.

2.2 12-Methylbenz[a]acridine

A mixture of 2-phenylaminonaphthalene (13 g), glacial acetic acid (10 cm^3) and anhydrous zinc chloride (40 g) was heated to 230–40°C and kept at this temperature for 6 h. Treatment of the reaction mixture was the same as described for 9-methylacridine. The product was obtained in 45% yield, m.p. 144–145 (lit.,[1] 144–145°C).

2.3 9,10-Dimethylacridinium methyl sulphate[2]

9-Methylacridine (6 g) and purified dimethyl sulphate (6 g) were stirred in toluene (120 cm^3) under reflux for 6 h. The reaction mixture was cooled and the product was filtered off. Yield after washing with toluene and drying: 83%.

2.4 7,12-Dimethylbenz[a]acridinium methyl sulphate

12-Methylbenz[a]acridine (4 g) and purified dimethyl sulphate (4 g) were stirred in toluene (80 cm^3) under reflux for 6 h. The reaction mixture was cooled and the precipitated product filtered off. After washing with toluene and drying, the product was obtained in 73% yield.

2.5 General procedure for condensation of 9,10-dimethylacridinium methyl sulphate, or 7,12-dimethylbenz[a]acridinium methyl sulphate with 4-nitroso-*N*,*N*-dialkylanilines

A solution of the acridinium salt (1 mmol) and the appropriate nitroso compound (1 mmol) in acetic anhydride was stirred at room temperature until reaction was complete. (Reaction times and volumes of acetic anhydride are summarised in Table 1). Three different isolation procedures were employed (Table 1).

Method A
The precipitated dye was filtered off, washed successively with a small amount of ethanol and diethyl ether and dried.

Method B
Diethyl ether was added in large excess to the reaction mixture to precipitate the dye. The dye was filtered off, washed with ether and dried.

Method C
The acetic anhydride solution was added directly to a column of silica gel and eluted with a solvent mixture of dichloromethane : methanol (9 : 1). The eluted dye solution was evaporated to dryness under vacuum and the residue triturated with tetrahydrofuran. The solid was filtered off, washed with diethyl ether and dried.

Dyes were recrystallised from the solvents indicated in Table 1 and were characterised by microanalysis (Table 1).

2.6 Synthesis of the xanthene dye 11

A mixture of 9-methylxanthenium perchlorate[3] (1 mmol) and 7-acetylamino-1-ethyl-6-nitroso-2,2,4-trimethyltetrahydroquinoline (1 mmol) in acetic anhydride (5 cm^3) was stirred at room temperature for 17 h. The product was filtered off, washed with diethyl ether and dried (yield 48%). Purifica-

TABLE 1
Synthesis and Microanalytical Characterisation Data for Dyes **4–10**, **13**, **14**

Dye	*Reaction media*[a]	*Reaction time (h)*	*Isolation method*[b]	*Yield (%)*	*Recrystall. solvent*		*Microanalysis*		
							%C	*%H*	*%N*
4	1/20	24	A	35·4	CH_3CN	Calc.	63·86	5·54	9·31
						Found.	63·85	5·50	9·65
5	1/20	22	A	77·0	CH_3CN	Calc.	61·06	5·68	8·22
						Found.	60·70	5·60	8·20
6	1/6·5	21	C	33·8	THF/	Calc.[c]	66·65	6·76	7·28
					CH_2Cl_2	Found.	66·20	7·10	7·45
7	1/6·5	19	A	45·7	CH_3CN	Calc.	64·49	5·95	8·06
						Found.	63·05	6·00	8·80
8	1/20	16	A	68·5	CH_3CN	Calc.	64·52	5·81	9·03
						Found.	64·35	5·65	9·00
9	1/20	24	A	47·0	CH_3CN	Calc.[c]	60·65	6·14	10·10
						Found.	61·05	5·90	10·15
10	1/6·5	21	A	35·8	CH_3CN	Calc.[c]	63·66	6·75	9·00
					/ET_2O	Found.	64·30	6·65	8·85
13	1/8	35	B	41·2	THF/	Calc.[c]	66·07	6·54	8·33
					CH_2Cl_2	Found.	65·15	6·25	8·05
14	1/8	35	A	59·6	CH_3CN	Calc.[c]	63·58	5·96	9·27
						Found.	63·85	5·60	9·20

[a] Ratio of acridinium salt (g) to acetic anhydride (cm^3).
[b] See text.
[c] Assuming one molecule of water of crystallisation.

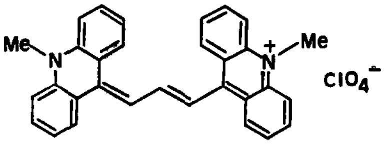
tion was effected by recrystallisation from acetonitrile. (Found: C, 64·0; H, 5·9; N, 7·3%. $C_{30}H_{32}ClN_3O_6$ requires: C, 63·7; H, 5·7; N, 7·4%.)

2.7 Synthesis of the thioxanthene dye 12

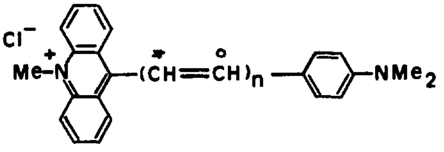
A similar procedure to that described for dye **11** was followed, using 9-methylthioxanthenium perchlorate.[3] The dye was obtained in 42% yield before recrystallisation. An analytical sample was obtained by recrystallisation from acetonitrile. (Found: C, 62·4; H, 5·8; N, 7·2%. $C_{30}H_{32}ClN_3O_5S$ requires: C, 61·9; H, 5·5; N, 7·2%.)

3 RESULTS AND DISCUSSION

It is known that the *N*-alkylacridine residue has a powerful electron releasing effect in cyanine dyes. For example, the symmetrical trimethine cyanine dye **1** absorbs at 822 nm in dichloromethane,[4] whereas the more



1



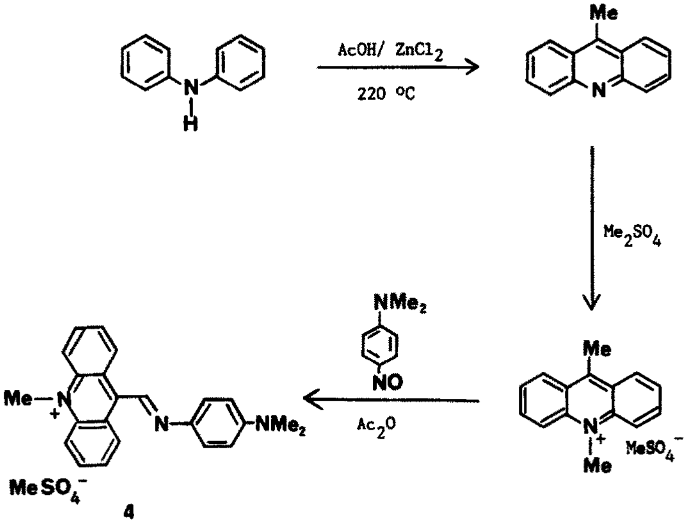
2 ; n = 1
3 ; n = 2

commonly encountered trimethine dyes with, for example, indole, benzthiazole, quinoline, etc., terminal groups absorb in the range 600–700 nm.

Unsymmetrical cyanine dyes with an acridinium group combined with a 4-*N*,*N*-dialkylaminophenyl terminal group also absorb at exceptionally long wavelengths and for example **2** absorbs at 680 nm in dichloromethane. Lengthening the bridge by one vinyl group results in a bathochromic shift of 58 nm and **3** has λ_{max} 738 nm in the same solvent.

Dyes such as **2** and **3** offer more potential than **1** for the development of i.r. dyes as the terminal arylamino group can be modified much more readily than the acridinium group. However, although **3** has an absorption maximum approaching the wavelengths of the near i.r. diode lasers, the increased chain length of the chromophore results in decreased solubility in organic solvents and polymers and also renders the system less stable. To overcome these problems, the shorter chain system of **2** was retained and the requisite bathochromic shift achieved by aza substitution in the ethylene bridge. According to perturbational MO theory, replacement of CH by N at the 'inactive' positions marked (o) of the molecules **2** and **3** should produce a bathochromic shift of the longest wavelength absorption band.[5] To test this prediction, dye **4** was synthesised according to the method shown in Scheme 1. The resultant dye had an absorption maximum at 728 nm in dichloromethane, showing that the bathochromic shift due to aza substitution is similar to that produced by one additional vinyl group.

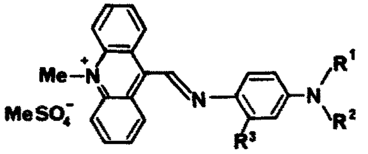
The simplicity of the synthesis of the 9,10-dimethylacridium salt (Scheme 1) and the efficiency of its condensation reaction with 4-nitrosoarylamines offer distinct advantages for the synthesis of azacyanine dyes as near-infrared absorbers. Thus attempts were made to extend the absorption of **4** further into the near-infrared by structural modification. Thus nitroso



Scheme 1

derivatives of various *N*,*N*-dialkylanilines were used and the dyes **5–10** prepared in good yields (Table 1). The dyes, isolated as their methyl sulphate salts, were characterised by microanalysis. Their absorption spectra were measured in various solvents and the results are summarised in Table 2. In dichloromethane, the absorption spectra of the dyes show the expected variations with structure, with λ_{max} ranging from 823 nm for dye **10** to 720 nm for dye **5**, consistent with the electron releasing effect of the arylamine residue. Absorption intensities were in the range ε_{max} 31 000–48 000 l mol^{-1} cm^{-1} for all the dyes except **9** and **10**, which had the higher values of 79 300 and 73 400 l mol^{-1} cm^{-1} respectively, values more consistent with those normally expected for cyanine dyes.

This variation in extinction coefficient was related to absorption bandwidth, and it can be seen from Table 2 that half-bandwidths are



4; $R^1 = R^2 = Me$, $R^3 = H$
5; $R^1 = R^2 = CH_2CH_2OH$, $R^3 = H$
6; $R^1 = R^2 = n\text{-}Bu$, $R^3 = H$
7; $R^1 = Et$, $R^2 = CH_2CH_2OH$, $R^3 = H$
8; $R^1 = R^2 = R^3 = Me$
9; $R^1 = R^2 = Et$, $R^3 = NHAc$

TABLE 2
Characteristics of the Longest Wavelength Absorption Band of Dyes **4**–**10** in Various Solvents

Dye		*Solvent*					
		CH_2Cl_2	*MeOH*	*DMF*	*AcMe*	*MeCN*	*H_2O*
4	λ_{max} (nm)	728	661	655	650	643	552
	$\varepsilon_{max} \times 10^{-4}$	1·89[a]	0·13	0·27	1·15	0·70	0·63
	$\Delta\lambda_{1/2}$ (nm)	170	200	219	191	196	—
5	λ_{max} (nm)	720	652	677	667	649	575
	$\varepsilon_{max} \times 10^{-4}$	4·03	1·72	1·58	2·13	1·68	1·24
	$\Delta\lambda_{1/2}$ (nm)	191	196	208	197	193	197
6	λ_{max} (nm)	790	727	724	722	720	674
	$\varepsilon_{max} \times 10^{-4}$	4·84	2·13	2·11	2·71	2·54	0·92
	$\Delta\lambda_{1/2}$ (nm)	141	187	202	196	197	227
7	λ_{max} (nm)	742[b]	667	680	677	666	592
	$\varepsilon_{max} \times 10^{-4}$	3·13	1·35	1·55	1·91	1·65	1·05
	$\Delta\lambda_{1/2}$ (nm)	178	199	197	196	197	205
8	λ_{max} (nm)	761	696	691	689	649	610
	$\varepsilon_{max} \times 10^{-4}$	3·65	0·74	0·91	1·60	1·36	0·49
	$\Delta\lambda_{1/2}$ (nm)	160	207	218	200	207	—
9	λ_{max} (nm)	797	727	737	739	733	610
	$\varepsilon_{max} \times 10^{-4}$	7·93	2·69	2·54	2·41	3·73	0·49
	$\Delta\lambda_{1/2}$ (nm)	110	179	170	200	175	203
10	λ_{max} (nm)	823	788	787	802	798	707
	$\varepsilon_{max} \times 10^{-4}$	7·34	1·14	1·61	3·35	3·29	3·06
	$\Delta\lambda_{1/2}$ (nm)	97	169	155	144	150	132

[a] Dye solution unstable.
[b] Containing 1% DMF.

c. 140–180 nm for the low intensity dyes but are much narrower (97–110 nm) for dyes **9** and **10**. These observations suggest that aggregation occurs readily in this azacyanine system, causing a displacement of the absorption band to shorter wavelengths. The overlap of monomer and aggregate absorption bands causes band broadening and a lowering of ε_{max}. The lower propensity for **9** and **10** to aggregate may be due to the higher degree of substitution of the aryl ring and the resultant increased steric requirement. This is particularly true in the case of the 2,2,4-trimethyltetrahydroquinoline dye **10**.

This aggregation effect was clearly enhanced in more polar solvents and from dichloromethane to chloroform band broadening was observed, which could be demonstrated to be concentration dependent. Thus, dye **9** in chloroform at a concentration of $7{\cdot}4 \times 10^{-5}$ M shows $\lambda_{max} = 754$ nm, with a shoulder at *c.* 790 nm, but at a concentration of $1{\cdot}8 \times 10^{-6}$, the

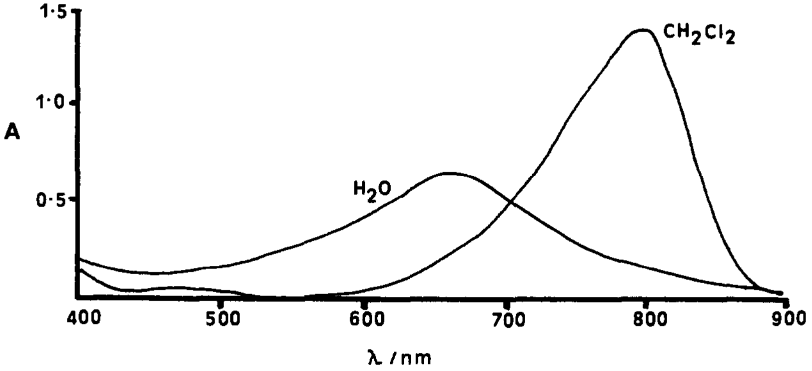


Fig. 1. Absorption spectrum of dye **9** in dichloromethane and in water (approximate concentration $1 \cdot 7 \times 10^{-5}$ M).

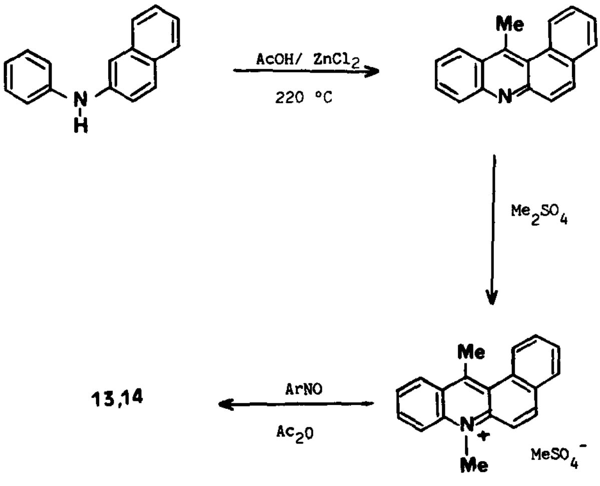
shape of the spectrum is reversed, with λ_{max} = 800 nm and a shoulder at *c.* 755 nm. Such concentration effects were shown most clearly in chloroform, as in more polar solvents, such as acetonitrile, acetone, methanol and water, aggregation was so pronounced that only at very high dilutions could one see emergence of the monomer peak from the strongly blue-shifted aggregate peak. Thus, absorption bands for dyes **4–10** in these solvents were particularly broad and the effect was most extreme in water (Table 2). This remarkable solvent effect is shown in Fig. 1 for dye **9**, which is almost colourless in dichloromethane (λ_{max} 797 nm), but is intense blue in water (λ_{max} 610 nm). It can be concluded that dyes of this class are only useful near-i.r. absorbers in media which minimise their tendency to aggregate. The reduced tendency of dye **10** to aggregate however, does suggest that by suitable design of the dye molecule the problem could be minimised.

To examine further the role of the acridine residue on the chromophoric properties of these dyes, the related oxygen- and sulphur-containing terminal groups were considered. The absorption spectroscopic properties of dye **10** are compared in Table 3 with those of the xanthene and thioxanthene analogues, **11** and **12** respectively. It is clear that the reduced electron releasing effect of the terminal oxygen and sulphur moieties leads to a large hypsochromic shift, and **11** and **12** in dichloromethane are intense cyan and green in colour respectively. (The green colour of **12** is indicative of both the stronger bathochromic effect of sulphur relative to oxygen (λ_{max} 680 nm versus 662 nm in dichloromethane) and also the presence of a second absorption band present in **12** (478 nm), not observed in the spectrum of **11**.) As well as being much more hypsochromic than the acridines, **11** and **12** also show a tendency to aggregate and consequently exhibit large half-bandwidths. It can be concluded that these systems have little potential as sources of near-i.r. absorbing dyes.

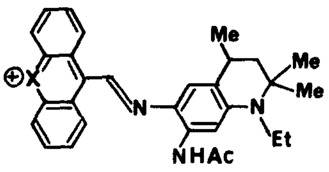
TABLE 3
Comparison of the Absorption Spectroscopic Properties of Dyes **10**, **11–14** in Dichloromethane

Dye	λ_{max} *(nm)*	$\varepsilon_{max} \times 10^{-4}$ *(litre mol^{-1} cm^{-1})*	$\Delta\lambda_{1/2}$ *(nm)*
10	823	7·34	97
11	662	5·72	135
12	680	2·94	138
13	835	10·82	96
14	816	6·19	125

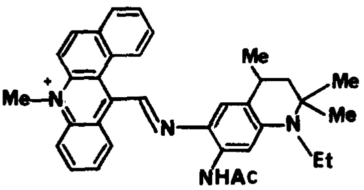
Benzannelation of the acridinium dyes was also examined as a means of inducing further bathochromic shifts and the benz[a]acridine dyes **13** and **14** were synthesised as shown in Scheme 2. (Attempts to prepare the benz[c]acridine analogues from *N*-phenyl-1-naphthylamine were unsuccessful due to difficulty in methylating the intermediate 7-methylbenz[c]acridine.) The visible absorption spectroscopic properties of **13** and **14** are summarised in Table 3. As expected **13** and **14** absorb at longer wavelengths than analogues **10** and **9**, and **13** has a particularly high molar absorption coefficient in dichloromethane (108 200 1 mol^{-1} cm^{-1}). The narrow half-bandwidth (96 nm) indicates that, like **10**, the dye has a low tendency to aggregate in dichloromethane. The 835 nm absorption band of **13** in this solvent is shifted to 713 nm in water and the half-bandwidth increases to 139 nm. The influence of dilution on the spectrum of **14** in chloroform is shown in Fig. 2. Similar disaggregation effects can be achieved in more polar solvents by the addition of surfactants, e.g. cetyltrimethylammonium bromide.



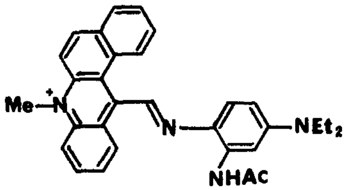
Scheme 2



10; X = NMe
11; X = O
12; X = S



13



14

The light absorption properties of the various dyes synthesised were examined by the PPP-MO method. Difficulties are always encountered with this semi-empirical technique when applied to the cationic cyanine-type dyes, because of uncertainty about the parameters for the terminal nitrogen atoms, which carry a significant amount of positive charge and are as a consequence fully sp^2 hybridised. Within the simple non-variable β approach this problem has been overcome satisfactorily in the di- and triarylmethane cationic dyes series by setting much reduced ionisation potential and electron repulsion integrals for the nitrogen atoms.[6] Application of these parameters to the acridine dyes (**4–10**, **13**, **14**) was not entirely satisfactory and thus an empirical re-parameterisation was carried out. Suitable nitrogen values found were: acridine, VSIP = 10·5 eV, EA = 6·6 eV; Me_2N, VSIP = 14·0 eV, EA = 5·5 eV; Et_2N, VSIP = 11·0 eV, EA = 5·5 eV; tetrahydroquinoline; VSIP = 10·0 eV, EA = 5·5 eV. Parameters for the heterocyclic oxygen and sulphur atoms in dyes **11** and **12** were assumed to be the same as those for five-membered ring heterocycles.[7,8] Resonance integrals and other parameters were as described elsewhere.[7] Fully planar systems were assumed for convenience for all dyes except **13** and **14**.

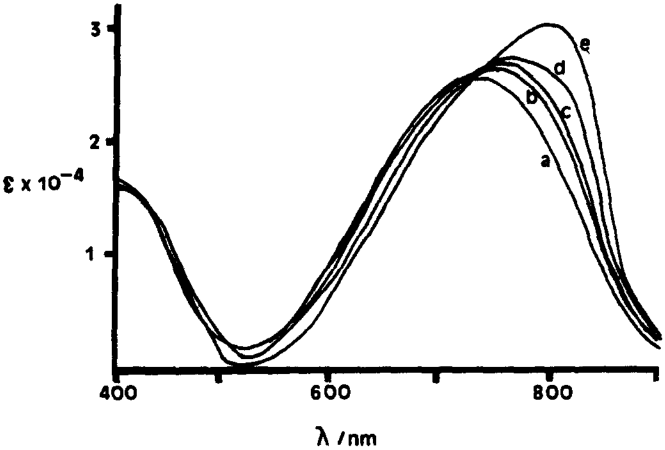


Fig. 2. Effect of concentration on the absorption spectrum of dye **14** in chloroform: (a) 9·2 × 10^{-5} M; (b) 9·2 × 10^{-6} M; (c) 4·6 × 10^{-6} M; (d) 2·3 × 10^{-6} M; (e) 9·2 × 10^{-7} M.

In the case of the benz[a]acridinium dyes **13** and **14** molecular models indicated a significant lack of planarity and thus for the purposes of the calculations rotation of the heterocyclic ring system of *c.* 30° relative to the rest of the chromophore was assumed. Thus the resonance integral for the relevant twisted-bond was decreased from the normal value of −2·4 eV to −2·0 eV, this giving satisfactory calculated spectral data. Calculated spectroscopic properties are compared with experimental data (solvent dichloromethane) in Table 4. It can be seen that the long wavelength absorption band of the acridinium dyes can be reproduced reasonably well and the bathochromic shifts accompanying benz[a]-

TABLE 4
Comparison of Experimental and PPP-MO Calculated Spectra of Representative Azacyanine Dyes

Dye	λ_{max} *(calc.)*	*f (calc.)*[a]	$\lambda_{max}^{CH_2Cl_2}$ *(nm)*	$\varepsilon_{max} \times 10^{-4}$ *(litre mol^{-1} cm^{-1})*
4	769	2·01	728	1·89
9	809	2·21	797	7·93
10	828	2·28	823	7·34
11	661	2·04	662	5·72
12	682	1·97	680	2·94
	517	0·03		
	434	0·05	478	1·24
13	839	1·79	835	10·82
14	817	1·69	816	6·19

[a] Oscillator strength.

annelation are indicated correctly. The significantly shorter wavelengths of absorption of the xanthene and thioxanthene dyes are also predicted correctly and the prediction of secondary absorptions in the range 430–520 nm for dye **12** is also consistent with the experimental observations.

Absorption intensities do not agree well with predicted oscillator strengths however, and in fact the benz[a]acridine dyes are predicted to have a lower intensity than the non-annelated analogues, which is contrary to that observed for dyes **9** and **14**. However, the problems of aggregation in the acridinium dyes makes any direct comparison of extinction coefficients very unreliable.

4 CONCLUSIONS

Relatively short-chain cationic dyes absorbing in the 720–820 nm range have been prepared by condensing the 9,10-dimethylacridinium ion with 4-nitroso-*N*,*N*-dialkylanilines. The dyes show a pronounced tendency to undergo aggregation in polar solvents with a consequent large shift of the absorption band to shorter wavelengths. Thus the value of these dyes as near-i.r. absorbers is restricted to their use in non-aggregating media. Benz[a]acridinium analogues are rather more bathochromic. The light absorption properties of the dyes and their xanthene and thioxanthene analogues can be predicted satisfactorily by the PPP-MO method by adopting suitable parameters for the terminal nitrogen atoms in these chromophores.

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