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Short Communication

Near-Infrared Absorbing Asymmetrical Trimethinecyanine Dyes

ABSTRACT

The synthesis of some novel asymmetrical trimethinecyanine dyes containing pyrylium and heterocyclic rings as end groups is described. The absorption maxima of the dyes is within the range 687–793 nm.

INTRODUCTION

Dyes absorbing in the near-infrared region are of importance in modern electro-optical applications.[1,2] They find application as photoreceptors in diode laser printers[3] and developments in this field,[4] dye lasers emitting in the near-infrared region[5] and in security systems and documentation data storage.[6] Several investigations have been reported on the synthesis of IR dyes suitable for optical information recording systems using semiconductor lasers.[7-12]

Some novel asymmetrical trimethinecyanine dyes absorbing in the near-IR spectral region are described in this present paper. They contain a heterocyclic and a pyrylium ring as end groups.

RESULTS AND DISCUSSION

We have recently reported the synthesis and electronic spectra characteristics of some IR-absorbing trimethinecyanine dyes containing pyrylium

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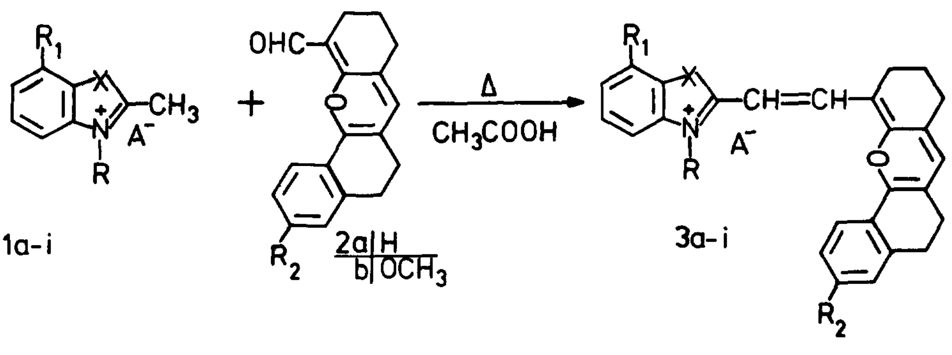
TABLE 1
Substituents in Dyes **3a**–**3i**

Dye	*R*	R^1	*X*	R^2	*A*
3a	C_2H_5	H	O	H	ClO_4
3b	CH_3	H	S	H	ClO_4
3c	$CH_2CH{=}CH_2$	H	S	H	Br
3d	C_2H_4OH	H	S	H	ClO_4
3e	CH_3	H	CH=CH	H	ClO_4
3f	C_2H_4OH	H	CH=CH	H	ClO_4
3g	CH_3	H	$C(CH_3)_2$	H	ClO_4
3h	CH_3	H	$C(CH_3)_2$	OCH_3	ClO_4
3i	C_2H_5		CH=CH—CH=C	H	I

heterocycles.[13] These dyes were found to absorb in the range 715–785 nm. As a continuation of this work we have now synthesized trimethinecyanine dyes which have a nitrogen-containing heterocycle as one of their end groups. The compounds (Table 1) were synthesized by condensation of the aldehydes **2a** and **2b** with 2-methyl heterocyclic quaternary salts **1a**–**i** (Scheme 1) in acetic acid medium at elevated temperature.

The dyes were crystalline salts and contained in some cases molecules of the crystallization solvent. Characterization data for the dyes are shown in Table 2. Several maxima are observed (Table 3) in the spectra of the dyes; the longer-wavelength adsorption (designated λ_{max} in Table 3) was in the range 687–793 nm. This absorption was not, however, always the most intense. In dyes **3a**–**3f**, a donor wavelength absorption (λ_3) was the most intense absorption whilst with dyes **3g**–**3i** λ_{max} was the most intense although these dyes did not show the lower-wavelength absorption in the 600–680 nm



Scheme 1

TABLE 2
Melting Points, Yields, Reaction Time and Analysis of Dyes **3a**–**3i**

Dye	*Molecular formula*	*Yield* (%)	*Reaction time* (*min*)	*M.p.* (°*C*) [*Solvent*]	*Analysis* (%) *Calcd*/*Found*		
					C	*H*	*N*
3a	$C_{28}H_{26}ClNO_6 . C_2H_5OH$	98·8	30	245–247	65·0	5·8	2·5
				[C_2H_5OH]	65·2	5·85	2·6
3b	$C_{27}H_{24}ClNO_5S . 0{\cdot}75CH_3CN$	90·5	5	300–301	63·3	4·9	4·5
				[CH_3CN]	63·4	4·9	4·45
3c	$C_{29}H_{26}BrNOS$	93·0	5	243–244	67·4	5·0	2·7
				[CH_3CN]	67·1	5·0	2·9
3d	$C_{28}H_{26}ClNO_6S$	89·0	30	250–252	62·3	4·8	2·6
				[CH_3CN]	62·0	4·6	2·6
3e	$C_{29}H_{26}ClNO_5 . 0{\cdot}5CH_3CN$	83·4	20	287–289	68·7	5·25	4·0
				[CH_3CN]	68·8	5·1	4·3
3f	$C_{30}H_{28}ClNO_6$	81·0	25	249–251	67·5	5·25	2·6
				[CH_3CN]	67·3	5·1	2·9
3g	$C_{30}H_{30}ClNO_5$	98·0	5	260–262	69·3	5·8	2·7
				[C_2H_5OH]	69·8	5·7	2·45
3h	$C_{31}H_{32}ClNO_3$	94·9	5	262–264	68·7	5·8	2·55
				[C_2H_5OH/ CH_3CN]	68·4	5·7	2·4
3i	$C_{32}H_{28}INO$	82·5	5	268–270	67·5	4·9	2·5
				[CH_3CN]	67·1	5·1	2·6

TABLE 3
Absorption Maxima of Dyes **3a**–**3i**

Dye	λ_1 (*nm*)	E_1	λ_2 (*nm*)	E_2	λ_3 (*nm*)	E_3	λ_{max} (*nm*)	E_{max}
3a	444	12 700	602	36 600	648	46 300	702	27 800
3b	462	10 400	625	31 300	677	44 000	732	31 300
3c	463	10 900	631	32 300	677	50 000	734	37 700
3d	463	10 000	634	30 100	679	46 700	734	35 200
3e	486	8 800	631	36 500	679	49 000	736	34 900
3f	488	8 500	637	34 500	682	49 200	740	38 400
3g	454	10 500	—	—	—	—	687	29 200
3h	445	9 100	—	—	—	—	714	32 500
3i	398	17 100	—	—	—	—	793	75 900

region. Dye **3i** was of particular interest in view of its almost complete lack of visible absorption.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. Electronic absorption spectra were recorded on Specord UV/VIS and Carl Zeiss 40M spectrophotometers in CH_3CN at a concentration of 2×10^{-5} mol litre^{-1}.

General procedure for the preparation of dyes 3a–3i[14]

A solution of 0·005 M of the appropriate 2-methyl heterocyclic quaternary salt and 0·005 M of 5,6,9,10-tetrahydro-8*H*-benzo[*c*]xanthen-11-carboxaldehyde or 3-methoxy-5,6,9,10-tetrahydro-8*H*-benzo[*c*]xanthene-11-carboxaldehyde in acetic acid (5 ml) was refluxed for 5–30 min (Table 2). In the case of dyes **3g** and **3h** the dyes were obtained after addition of 2–3 ml of acetic anhydride. On cooling the reaction mixture, in some cases after dilution with an equal volume of diethyl ether the products were filtered. Yields and melting points of the products are shown in Table 2. The aldehydes used in the above syntheses were prepared as previously described.[13]

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