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# Near-Infrared Absorbing Pyrylium Trimethinecyanine Dyes

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## ABSTRACT

*The synthesis of some new xanthene intermediates and derived near-infrared absorbing pyrylium trimethinecyanine dyes is described. The dyes absorb in the region from 700 to 860 nm. The structure of the compounds was confirmed by elemental analysis, electronic absorbtion spectra and in some cases by IR and* $^1$*H-NMR spectroscopy.*

## 1 INTRODUCTION

Extensive investigations in the field of pyrilium cyanine dyes absorbing in the near-IR region have been carried out in recent years. Particularly important aspects of these studies are related to applications in dye lasers for the near-IR region,[1–7] for optical recording using a diode laser on a dye–polymer medium comprising a dye absorbing in the 750–880 nm region[8–17] and for laser-beam addressed displays with liquid crystal cells doped with IR dyes.[18–21]

Novel pyrylium trimethinecyanine dyes which absorb in the region 700–860 nm are described in this present paper.

## 2 RESULTS AND DISCUSSION

1-Formyl-2-chloro-3-hydroxymethylenecyclohexene is an easily accessible product[5,22] and it has been used as an intermediate in the synthesis of

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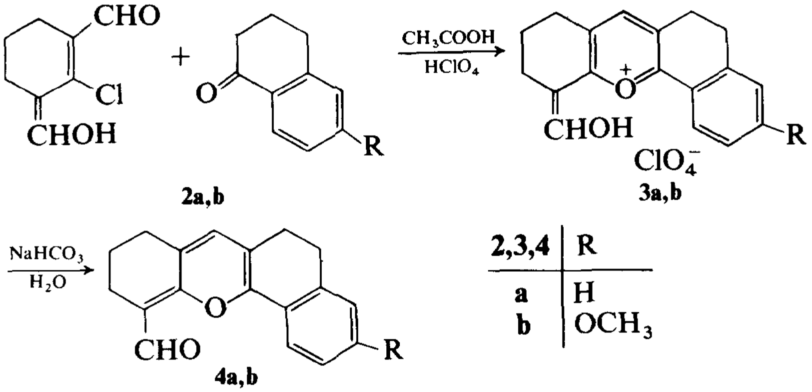
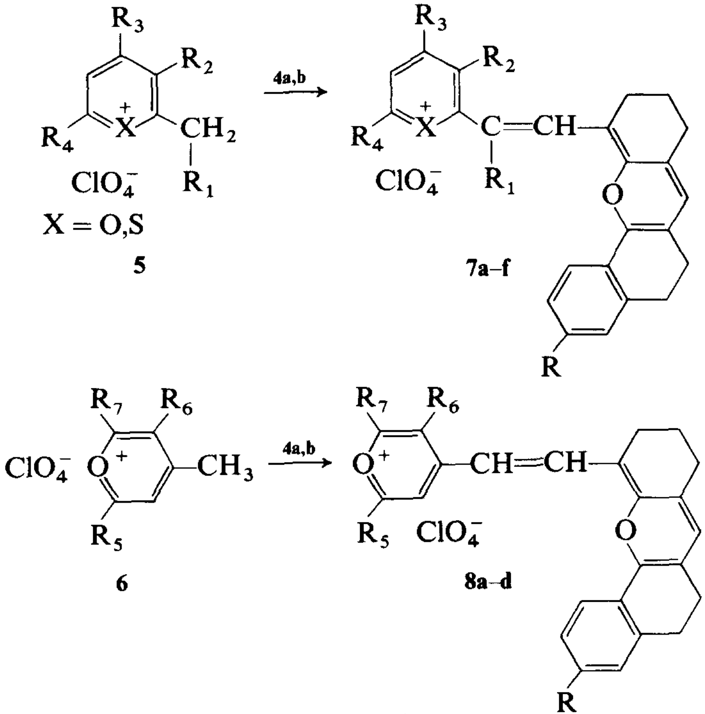


| 2,3,4 | R |
|---|---|
| a | H |
| b | $OCH_3$ |

Scheme 1

pyrylium dyes having enhanced photostability.[5] By interaction with 1-tetralones, the xanthene derivatives **4a**, **4b** containing a formyl moiety were obtained (Scheme 1).

Using a similar reaction, pyrylium salts are obtained from $\beta$-chlorovinylaldehydes and ketones.[23-26] The presence of a formyl group provides a possibility for condensation with pyrylium salts containing an active methylene or methyl group (Scheme 2).



Scheme 2

TABLE 1
Substituents in the Dyes **7a**–**7f**

| *Dye* | *X* | *R* | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|---|---|
| **7a** | O | H | H | H | $C_6H_4OCH_3$—4 | $C_6H_4OCH_3$—4 |
| **7b** | S | H | H | H | $C_6H_5$ | $C_6H_5$ |
| **7c** | O | H | —$(CH_2)_2$— | | $C_6H_5$ | $C_6H_5$ |
| **7d** | O | H | H | H | $C_6H_5$ | $C_6H_5$ |
| **7e** | O | $OCH_3$ | H | H | $C_6H_4CH_3$—4 | $C_6H_4CH_3$—4 |
| **7f** | O | $OCH_3$ | H | H | $C_6H_4OCH_3$—4 | $C_6H_4OCH_3$—4 |

The dyes thus obtained (**7a**–**7f**, **8a**–**8d**) are listed in Tables 1 and 2 and relevant data on yields, melting points and elemental analysis of the intermediates and dyes are given in Table 3.

The long-wavelength absorption maxima of the dyes are in the region 700–860 nm (Table 4).

The dyes derived from the 4-methylpyrylium salts (**8a**–**8d**) show three transitions, the longest-wavelength one (except for **8c**) being the most intense. The presence of a methoxy group results in a clearly defined hypochromic effect (cf. **8a** and **8c**; **8b** and **8d**) without significant hypsochromic or bathochromic effects.

The dyes derived from 2-methyl- or 2-methylene-pyrylium salts (**7a**–**7f**) also show three transitions. In these dyes the methoxy group gives a noticeable (20 nm) bathochromic shift, and the absorbtion intensity remains unaffected (cf. **7a** and **7f**).

In the IR-spectra of **3a** and **3b**, skeleton vibrations of the pyrylium ring are observed in the range 1650–1640 cm$^{-1}$. A broad absorption, having a local maximum at 3190 cm$^{-1}$, is observed in the range of 3500–2700 cm$^{-1}$ and this is caused by valence vibrations of associated hydroxy groups.

An intense band in the range of 1625–1610 cm$^{-1}$ is present in the IR spectra of compounds **4a**, **4b**, caused by stretching vibrations of the aldehyde carbonyl group. The extremely low frequency of the carbonyl band could be

TABLE 2
Substituents in the Dyes **8a**–**8d**

| *Dye* | *R* | $R_5$ | $R_6$ | $R_7$ |
|---|---|---|---|---|
| **8a** | H | $C_6H_5$ | H | $C_6H_5$ |
| **8b** | H | $C_6H_5$ | —$(CH{=}CH)_2$— | |
| **8c** | $OCH_3$ | $C_6H_5$ | H | $C_6H_5$ |
| **8d** | $OCH_3$ | $C_6H_5$ | —$(CH{=}CH)_2$— | |

TABLE 3
Melting Points,[a] Yields and Elemental Analysis Data for **4a** and **4b**, **7a**–**7f** and **8a**–**8d**

| *Compound* | *M.p.°C* | *Yield (%)* | *Molecular formula* | *Analysis (%) Found/Calculated* | |
|---|---|---|---|---|---|
| | | | | *C* | *H* |
| **4a** | 171–172 | 100 | $C_{18}H_{16}O_2$ | 81·35/81·8 | 6·03/6·06 |
| **4b** | 126–128 | 100 | $C_{19}H_{18}O_3$ | 78·0/77·55 | 6·3/6·1 |
| **7a** | 265–267 | 65 | $C_{38}H_{33}ClO_8$ | 70·0/69·9 | 5·1/5·1 |
| **7b** | 258–260 | 82 | $C_{36}H_{29}ClO_5S$ | 71·3/71·0 | 5·1/4·8 |
| **7c** | 260–262 | 40 | $C_{38}H_{31}ClO_6$ | 74·2/73·7 | 5·1/5·0 |
| **7d** | 267–269 | 61 | $C_{36}H_{29}ClO_6$ | 72·6/72·9 | 4·9/4·9 |
| **7e** | 248–250 | 80 | $C_{39}H_{35}ClO_7$ | 72·2/71·9 | 5·1/5·4 |
| **7f** | 261–263 | 74 | $C_{39}H_{35}ClO_9$ | 68·55/68·6 | 5·1/5·1 |
| **8a** | 260–262 | 83 | $C_{36}H_{29}ClO_6$ | 73·2/72·9 | 5·2/4·9 |
| **8b** | 327–328 | 88 | $C_{34}H_{27}ClO_6$ | 71·2/71·55 | 4·9/4·85 |
| **8c** | 272–274 | 81 | $C_{37}H_{31}ClO_7$ | 71·25/71·3 | 4·9/5·0 |
| **8d** | 274–276 | 92 | $C_{35}H_{29}ClO_7$ | 70·7/70·4 | 4·75/4·9 |

[a] **4a**, **4b** recrystallised from $EtOH/H_2O$, 2:1; **7a**–**7f** and **8a**–**8d** from $CH_3CN$.

attributed to a very strong conjugation effect through the double bond with the aromatic ring. Absorption bands in the region of the OH vibrations are not observed.

The presence of the aldehyde group is confirmed also by $^1$H-NMR spectra. In the case of **3a** no signal for the hydroxy group proton from the hydroxymethylene moiety is observed, probably due to the low solubility of this compound. In the spectra of **3b**, however, a broad peak at 6·52 ppm for

TABLE 4
Absorption Maxima (nm) and Molar Extinction Coefficients (litre mol$^{-1}$ cm$^{-1}$) of the Dyes **7a**–**7f** and **8a**–**8d**

| *Compound* | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_3$ |
|---|---|---|---|---|---|---|
| **7a** | 424·1 | 751·9 | 829·3 | 54 495 | 61 818 | 81 263 |
| **7b** | 407·5 | 744·0 | 823·8 | 35 838 | 53 096 | 64 822 |
| **7c** | 415·6 | 772·9 | 857·7 | 37 128 | 59 096 | 89 202 |
| **7d** | 405·5 | 749·7 | 823·8 | 40 576 | 61 029 | 72 222 |
| **7e** | 422·0 | 768·1 | 846·1 | 43 776 | 61 480 | 75 102 |
| **7f** | 426·3 | 768·1 | 849·0 | 49 296 | 57 437 | 81 910 |
| **8a** | 384·9 | 682·2 | 763·4 | 62 381 | 80 000 | 85 810 |
| **8b** | 375·1 | 645·2 | 705·3 | 41 097 | 54 468 | 172 827 |
| **8c** | 401·6 | 678·5 | 765·8 | 53 990 | 88 621 | 60 493 |
| **8d** | 376·8 | 646·9 | 701·3 | 42 886 | 57 313 | 156 816 |

the proton of the hydroxyl group is seen, which in the presence of $D_2O$ disappears. The proton magnetic resonance spectra of **4a** and **4b** show singlets at 10·29 and 10·26 ppm respectively for the protons of the aldehyde groups.

## 3 EXPERIMENTAL

### 3.1 General

Melting points were determined on a Kofler apparatus and are uncorrected. $^1$H-NMR spectra were recorded on a Tesla BS 487-C at 80 MHz, absorption spectra on a Carl-Zeiss Specord M-40 ($2 \times 10^{-5}$ M in $CH_3CN$) and infrared spectra on a Perkin–Elmer 983 G (Nujol).

### 3.2 11-Hydroxymethylene-5,6,8,9,10,11-hexahydrobenzo[*c*]xanthylium perchlorate (3a) and 11-hydroxymethylene-3-methoxy-5,6,8,9,10,11-hexahydrobenzo[*c*]xanthylium perchlorate (3b)

1-Formyl-2-chloro-3-hydroxymethylenecyclohexene (0·04 mol), 1-tetralone or 6-methoxy-1-tetralone (0·04 mol), acetic acid (120 ml for **3a**, 30 ml in the case of **3b**) and perchloric acid (12 ml) were refluxed for 1 h. The precipitate which formed on cooling was collected, washed with ether and air-dried. Yields were 45% (**3a**) and 41% (**3b**). After recrystallisation from acetic acid the melting points were 228–230°C and 214–216°C respectively.

**3a**: $^1$H-NMR ($CDCl_3$–DMSO-$d_6$) (ppm): 1·92 (q, $ArCH_2$, 2H); 2·55–3·25 (m, $4CH_2$, 8H); 7·25–8·75 (m, Ar—C$\underline{H}$OH, 6H).

**3b**: 1·92 (q, $ArCH_2$, 2H); 2·75–3·13 (m, $4CH_2$, 8H); 3·90 (s, $OCH_3$, 3H); 6·52 (broad, CHO$\underline{H}$, 1H); 6·83–8·43 (m, Ar—C$\underline{H}$OH, 5H).

### 3.3 5,6,9,10-Tetrahydro-8H-benzo[*c*]xanthene-11-carbaldehyde 4a and 3-methoxy 5,6,9,10-tetrahydro-8H-benzo[*c*]xanthene-11-carbaldehyde 4b

The perchlorate salt **3a** or **3b** (5 g) was dissolved in water (100 ml) and 1 M-sodium bicarbonate aqueous solution was added with stirring until the pH was 8. The aldehyde thus obtained was collected, washed with water and dried. The yields were quantitative. Melting points and analytical data are shown in Table 3.

**4a**: $^1$H-NMR ($CDCl_3$) (ppm): 1·70 (q, $ArCH_2$, 2H); 2·35–3·05 (m, $4CH_2$, 8H); 6·30 (s, —CH=, 1H); 7·07–7·73 (m, Ar, 4H); 10·29 (s, CHO, 1H).

**4b**: 1·74 (q, $ArCH_2$, 2H); 2·38–3·00 (m, $4CH_2$, 8H); 3·80 (s, $OCH_3$, 3H); 6·30 (s, —CH=, 1H); 6·63–7·63 (m, Ar, 3H); 10·26 (s, CHO, 1H).

### 3.4 Preparation of dyes 7a–7f, 8a–8d

The aldehyde (**4a**, **4b**) (0·01 mol) and the respective pyrylium or thiopyrylium salts (**5**, **6**) (0·01 mol) were refluxed for 5–60 min in 30 ml acetic acid. The precipitate which formed on cooling was collected, washed with ether and dried. Yields, melting points and analytical data are shown in Table 3.

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