

## SOME NOVEL HEPTAMETHINE PYRYLIUM DYES. STRUCTURE AND PHOTOSTABILITY\*

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A series of new heptamethine pyrylium dyes derived from enamine and enaminium salts has been prepared. Spectral absorptions of these dyes range from 850 nm to 1 160 nm. Relation between the structure and chromophore has been discussed and kinetic study has been made on the configuration isomerization of the dyes. Photostability has been investigated in relation to the chemical structure.

During recent years, an increasing number of pyrylium or thiopyrylium dyes<sup>1</sup>, and selenopyrylium dyes<sup>2</sup> which absorb in infrared region has been prepared. Particularly favourable route to infrared absorbing dyes has taken advantage of the fact that the pyrylium nucleus, compared to other heterocyclic nuclei, gives large bathochromic shifts due to the incorporation of two methine groups in the rings<sup>3</sup>. It was proven that some of these dyes have high photostability, and they can be used for IR mode-locking laser systems and as IR laser dyes<sup>4-6</sup>. Most of these dyes have an electron-withdrawing group, i.e. a halogen atom, on their meso carbon atom in the polymethine chain.

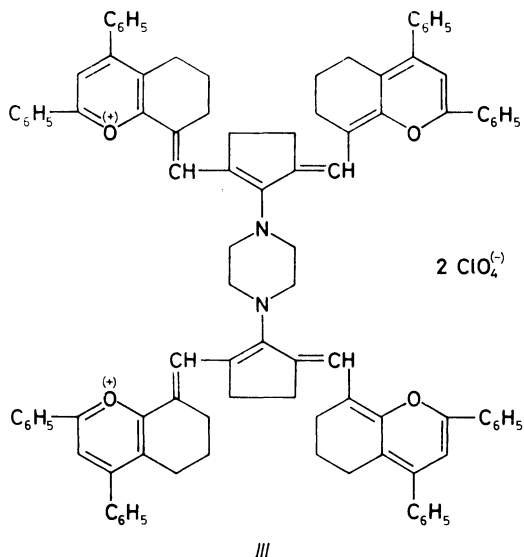
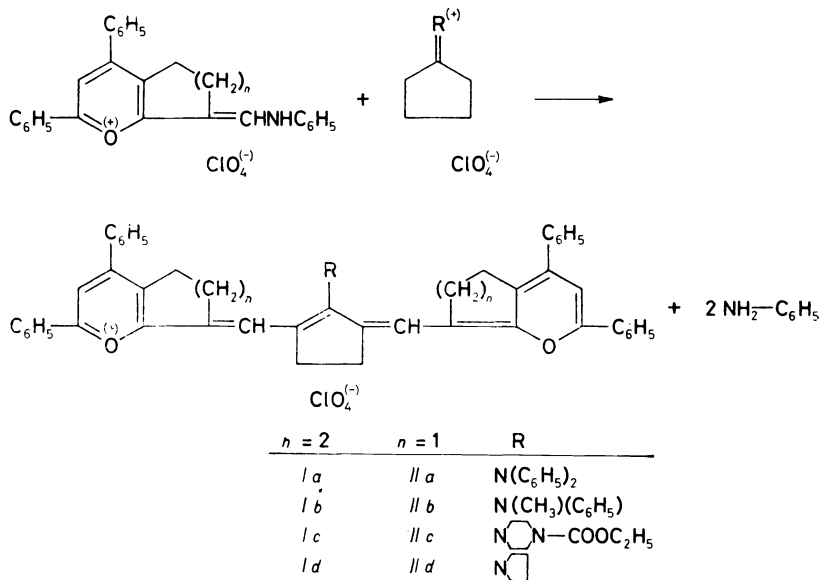
To design a good organic laser dye, it is useful to have an electron-donor substituent in the polymethine chain. The present paper describes recent work on preparation of a series of pyrylium heptamethine dyes which contain a disubstituted amino group on the meso carbon atom in their bridge polymethine chains. The optical absorption and photostability were investigated and variations substantial from molecule to molecule were observed. The isomerization of the dyes was also studied. Several of these dyes exhibited excellent lasing characteristics in 1.3  $\mu\text{m}$  to 1.5  $\mu\text{m}$ , and this part is being prepared for separate publication.

Pyrylium heptamethine dyes described in this paper were prepared by condensing a pyrylium salt with an appropriate enaminium salt. The general reaction is represented by Scheme 1.

The dyes were dissolved in 1,2-dichloroethane at a concentration of approximately  $10^{-6}$  mol l<sup>-1</sup>. Absorption spectra of the dyes *Ia*, *Iic* and *IId* are given in Fig. 1 as

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an example. Positions of the absorption maximum of the investigated dyes are listed in Table I together with the extinction coefficient ratios at 1.06  $\mu\text{m}$  to that at the absorption peak,  $\epsilon_{(1.06\mu\text{m})}/\epsilon_{\text{max}}$ .



SCHEME 1

Photostability of the dyes was determined by irradiating the sample with a high pressure Xenox Lamp made by Shanghai Lamp Co. The shorter wavelength below 750 nm was eliminated by an appropriate filter. The absorption spectra were recorded after 60 min illumination with each light. The irreversible bleaching of the dye at the absorption peak was monitored as a function of time, then the linear relation was found between the decrease of peak absorbance of dye solution and the length of illumination. The slope for the dyes prepared as described in this paper was compared with that of the commercial dye Kodak 9740 under the same conditions.

TABLE I

Absorption maxima, extinction coefficients at 1.06  $\mu\text{m}$  relative to that at absorption maximum and photostabilities of the studied dyes in 1,2-dichloroethane

Compound	$\lambda_{\text{max}}$ nm	$\epsilon_{\text{max}} \cdot 10^{-3}$	$\epsilon_{(1.06)}/\epsilon_{\text{max}}$	Relative photostability to Kodak 9740
Kodak 9740	1 055	125	0.97	1
<i>Ia</i>	1 145	108	0.57	35
<i>Ib</i>	1 150	140	0.60	>100
<i>Ic</i>	940	36	0.33	12
<i>Id</i>	870	28	0.13	22
<i>IIa</i>	1 160	126	0.48	80
<i>IIb</i>	1 162	138	0.44	50
<i>IIc</i>	870	68	0.37	15
<i>IIId</i>	900	37	0.54	20
<i>III</i>	850	12	0	

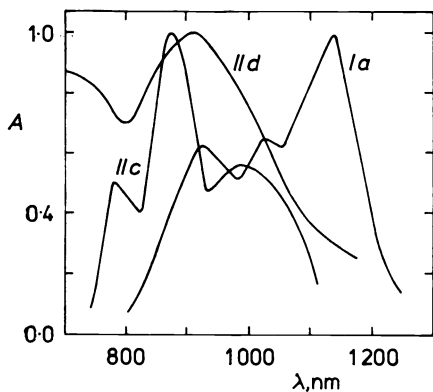
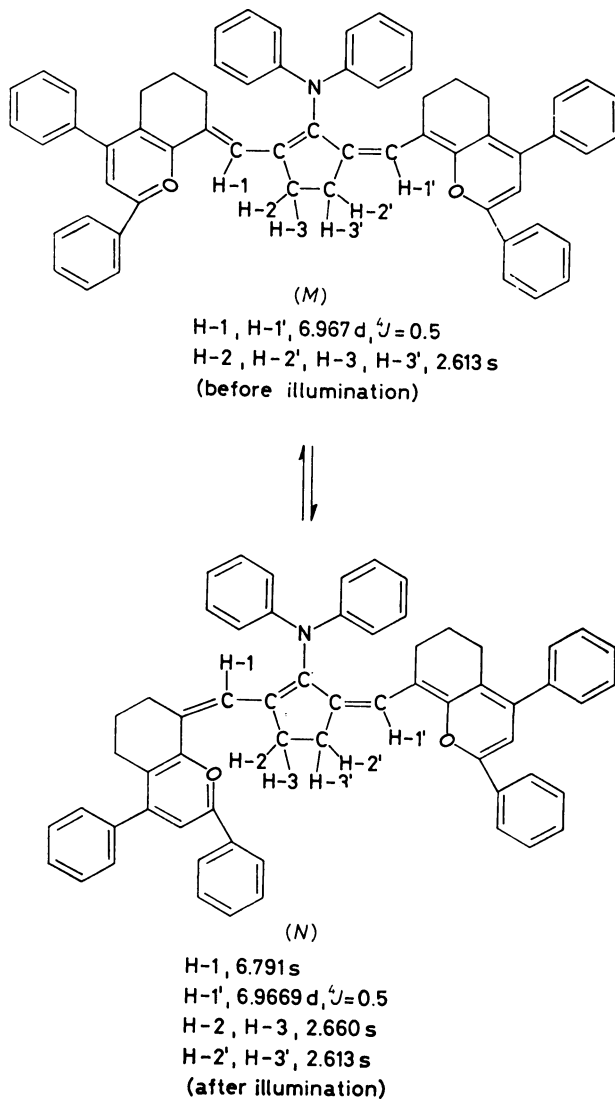


FIG. 1  
Absorption spectra of dyes *Ia*, *IIc*, and *IIId*  
( $5 \cdot 10^{-6} \text{ mol l}^{-1}$  in 1,2-dichloroethane); *A*  
the normalized absorbance of dye solution

The ratio to Kodak 9740 was defined as the relative photostability. In Table I the relative photostability of the different dyes is listed.

Isomerization of the configuration<sup>7</sup> was observed in dye solutions in  $\text{CDCl}_3$  when the samples were illuminated by strong light of 500–750 nm.  $^1\text{H}$  NMR measurement at 298 K indicates that an equilibrium of isomerization during illumination exists in *Ia*, *Ib*, and *Ila*. An example of the isomerization of *Ia* is given in Scheme 2.



SCHEME 2

Relative chemical shifts of H-1, H-2, H-3 and H-1', H-2', H-3' show clearly the different modes of coupling of H-1 with H-2 and H-3. A dynamic equilibrium of isomerization has been reached in  $\text{CDCl}_3$  solution under illumination. Fig. 2 shows the kinetic curve for the isomerization under illumination of *Ia*. Mode *N* dominated and reached equilibrium after 6 h illumination.

For the equilibrium of *Ia* we have found the following values:

$$K = I_N/I_M = 10.5 \quad (1)$$

$$\Delta G_{298}^\circ = -RT \ln K = -5.83 \text{ kJ mol}^{-1}, \quad (2)$$

where  $K$  is the equilibrium constant.  $I_M$  and  $I_N$  represent the integral intensity of H-1 in modes *M* and *N* after reaching an equilibrium, respectively.  $\Delta G_{298}^\circ$  is the value of standard free energy. The calculated values of standard free energy for *Ib* and *IIa* were  $-1.92 \text{ kJ mol}^{-1}$  and  $-2.53 \text{ kJ mol}^{-1}$ , respectively. However, similar isomerization is not obvious in other dyes.

According to Table I, the absorption peak, extinction coefficient and photostability vary substantially among the dyes investigated. The absorption of several dyes is strong at  $1.06 \mu\text{m}$  and these are readily pumped for laser action. In general, the absorption is characterized by one strong maximum at long wavelengths followed by smaller vibronic side bands. The effect of chain substituents on the absorption of polymethine dyes can be seen from Table I. An aromatic disubstituted amino group at the meso position of the polymethine chain, e.g. N,N-diphenylamino group, results in a large shift to longer wavelengths, however, an aliphatic disubstituted amino group, e.g. 4-ethoxycarbonylpiperazine group, results in a large shift to shorter wavelengths. Evidently, the dyes with an aliphatic amino group on the

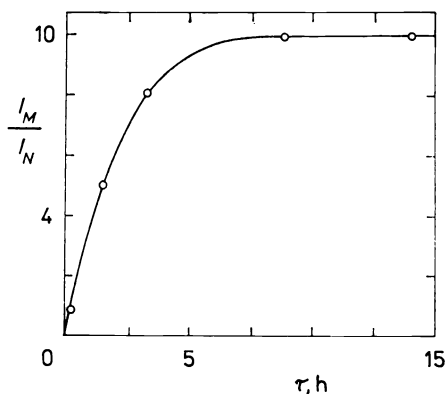


FIG. 2  
Correlation of relative integral intensity of modes *N* and *M* ( $I_M/I_N$ ) and duration of light illumination ( $\tau$ )

meso carbon of the chain are in a crowded configuration since their peak  $\epsilon$  value is only about 1/3 the value of the similar dyes with a disubstituted aromatic group on their chain, and the dyes with such crowded configuration are relatively unstable.

The dyes *Ia*, *Ib*, *IIa* and *IIb* exhibit absorption maxima at longer wavelengths and higher photostability. The configuration isomerization takes place in these dyes under illumination. On the contrary, dyes *Ic*, *Id*, *IIC*, *IId*, and *III* exhibit absorption maxima at shorter wavelengths and lower photostability. Some of these novel dyes may be useful in practice as infrared laser dyes.

### EXPERIMENTAL

The  $^1\text{H}$  NMR spectra were recorded on Spectrospin AM-400, with TMS as the internal standard. Absorption spectra were recorded on a UV-visible spectrophotometer Shimadzu-UV-365.

TABLE II  
Analytical data of the dyes

Compound	Yield %	Formula (M.w.)	Calculated/Found		
			% C	% H	% N
<i>Ia</i>	24	$\text{C}_{61}\text{H}_{50}\text{ClNO}_6$ (928.5)	78.90	5.43	1.51
			78.72	5.27	1.75
<i>Ib</i>	21	$\text{C}_{56}\text{H}_{48}\text{ClNO}_6$ (866.5)	77.62	5.58	1.62
			77.34	5.50	1.72
<i>Ic</i>	32	$\text{C}_{56}\text{H}_{53}\text{ClN}_2\text{O}_8$ (917.5)	73.24	5.82	3.05
			72.84	5.45	2.80
<i>Id</i>	12	$\text{C}_{53}\text{H}_{48}\text{ClNO}_6$ (830.4)	76.65	5.83	1.69
			76.91	5.67	1.87
<i>IIa</i>	30	$\text{C}_{59}\text{H}_{46}\text{ClNO}_6$ (900.4)	78.70	5.25	1.56
			78.44	5.60	1.95
<i>IIb</i>	17	$\text{C}_{54}\text{H}_{44}\text{ClNO}_6$ (838.4)	77.36	5.29	1.67
			77.65	5.48	1.96
<i>IIC</i>	24	$\text{C}_{54}\text{H}_{49}\text{ClN}_2\text{O}_8$ (889.4)	72.81	5.55	3.15
			72.48	5.30	3.14
<i>IId</i>	17	$\text{C}_{51}\text{H}_{44}\text{ClNO}_6$ (802.3)	76.35	5.53	1.75
			76.76	5.65	1.43
<i>III</i>	12	$\text{C}_{102}\text{H}_{88}\text{Cl}_2\text{N}_2\text{O}_{12}$ (1604.6)	76.35	5.47	1.75
			76.04	5.22	1.46

TABLE III  
 $^1\text{H}$  NMR data of the dyes

Com- pound	CH (pyrylium)	$\text{C}_6\text{H}_5$	$-\text{CH}_2-(\text{CH}_2)_n-$	$-\text{CH}=\text{}$	$-\text{CH}_2-\text{CH}_2-$ (cyclopentene)	R
<i>Ia</i>	8.173 s, 2 H	7.084–7.672 m, 30 H	2.767, 2.989 t, 12 H, $^3J = 9.6$	6.967 d, 2 H, $^4J = 0.5$	2.613 s, 4 H	
<i>Ib</i>	9.026 s, 2 H	7.240–7.623 m, 25 H	2.791, 3.020 t, 12 H, $^3J = 9.6$	6.902 d, 2 H, $^4J = 0.4$	2.613 s, 4 H	3.387 s, 3 H (NCH <sub>3</sub> )
<i>Ic</i>	8.397 s, 2 H	7.424–7.642 m, 20 H	3.125, 3.187 t, 12 H, $^3J = 9.6$	6.977 d, 2 H, $^4J = 0.7$	2.827 s, 4 H	1.179 t, 3 H (OCH <sub>2</sub> CH <sub>3</sub> , $^3J = 7.0$ ) 3.610, 3.765 t, 8 H (CH <sub>2</sub> of piperazine, $^3J = 7.0$ ) 4.075 q, 2 H (OCH <sub>2</sub> CH <sub>3</sub> , $^3J = 7.0$ ) 3.714 t, 8 H (N(CH <sub>2</sub> ) <sub>4</sub> , $^3J = 6.2$ )
<i>Id</i>	7.917 s, 2 H	7.422–7.633 m, 20 H	2.994, 3.054 t, 12 H, $^3J = 9.5$	6.464 d, 2 H, $^4J = 2.2$	2.774 s, 4 H	
<i>Ila</i>	8.006 s, 2 H	7.070–7.678 m, 30 H	3.217, 3.304 t, 8 H, $^3J = 9.8$	6.910 d, 2 H, $^4J = 0.2$	2.611 s, 4 H	
<i>Ilb</i>	7.936 s, 2 H	7.500–7.657 m, 25 H	3.279, 3.315 t, 8 H, $^3J = 8.0$	6.977 s, 2 H	3.250 s, 4 H	3.460 s, 3 H (NCH <sub>3</sub> )
<i>Ilc</i>	8.294 s, 2 H	7.476–7.619 m, 20 H	3.238, 3.314 t, 8 H, $^3J = 7.8$	6.922 d, 2 H, $^4J = 1.0$	3.070 s, 4 H	1.301 t, 3 H (OCH <sub>2</sub> CH <sub>3</sub> , $^3J = 7.0$ ) 3.712, 3.730 t, 8 H CH <sub>2</sub> of piperazine, $^3J = 7.0$ ) 4.215 q, 2 H (OCH <sub>2</sub> CH <sub>3</sub> , $^3J = 7.0$ )
<i>Ild</i>	8.054 s, 2 H	7.407–7.633 m, 20 H	3.037, 3.219 t, 8 H, $^3J = 9.0$	6.747 d, 4 H	2.919 s, 4 H	3.955, 4.099 t, 8 H (N(CH <sub>2</sub> ) <sub>4</sub> , $^3J = 7.1$ )
<i>III</i>	7.907 s, 4 H	7.422–7.667 m, 40 H	3.055, 3.070 t, 24 H, $^3J = 6.0$	6.656 d, 4 H, $^4J = 2.0$	2.949 s, 8 H	3.764 t, 8 H (CH <sub>2</sub> of piperazine, $^3J = 8.0$ )

### General Procedure for the Synthesis of the Dyes *I* and *II*

A mixture of 2 mmol of pyrylium salt, 1 mmol of enaminiium salt, 2 mmol of sodium acetate and 5 ml of acetic anhydride were refluxed for 10 min, and after chilling, the solid was collected, washed with acetic acid and ethanol, and then recrystallized from the mixture of 1,2-dichloroethane and ethanol. Characteristics of prepared compounds are given in Tables II and III.

### Synthesis of *III*

To a mixture of 19.4 g (100 mmol) of piperazine, 20 g (240 mmol) of cyclopentanone and 100 ml of ethanol, 30 g (200 mmol) of 72% perchloric acid was added with cooling. The mixture was then refluxed for 30 min. After chilling, the product was collected and dried; yield 15.8 g of 1,4-dicyclopentylidene-piperazinium diperchlorate, m.p.  $> 300^{\circ}\text{C}$ . Compound *III* was prepared from 4 mmol of pyrylium salt ( $n = 2$ ) and 1 mmol of 1,4-dicyclopentylidenepiperazinium diperchlorate by a procedure as described above. Its properties are also given in Tables II and III.

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