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Synthesis of Some New Thiapyrylium and Pyrylium Laser Dyes

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ABSTRACT

Several new heptamethine thiapyrylium and pyrylium dyes have been synthesized by a simple and efficient procedure starting from enaminium and heterocyclic salts. The structure of the compounds was confirmed by elemental analysis, mass spectrometry and ^1H *NMR.*

1 INTRODUCTION

During recent years, an increasing number of pyrylium or thiapyrylium dyes[1,2] and selenopyrylium dyes[3] which absorb in the IR region have been synthesized. A particularly favourable route to IR absorbing dyes has taken advantage of the fact that the pyrylium and thiapyrylium nuclei, compared with other heterocyclic nuclei, give large bathochromic shifts.[4] It has also been shown that some of these dyes have high photostability, and can be used for IR mode-locking laser systems and IR laser dyes.[5–8] Most of the previously described dyes contain an electron withdrawing group, i.e. a halogen atom, on their *meso* carbon atom in the polymethine chain, but these dyes usually have a low lasing energy conversion efficiency. With respect to the design of a good organic laser dye having both high photostability and lasing energy conversion efficiency, it was thought to be useful to consider the effect of an electron-donor substituent in the polymethine chain.

We report here the preparation of a series of pyrylium and thia-

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pyrylium heptamethine dyes which contain a disubstituted amino group on the *meso* carbon atom in their bridging polymethine chain. Data on optical absorption, photostability and lasing characteristics of these dyes will be reported later.

2 RESULTS AND DISCUSSION

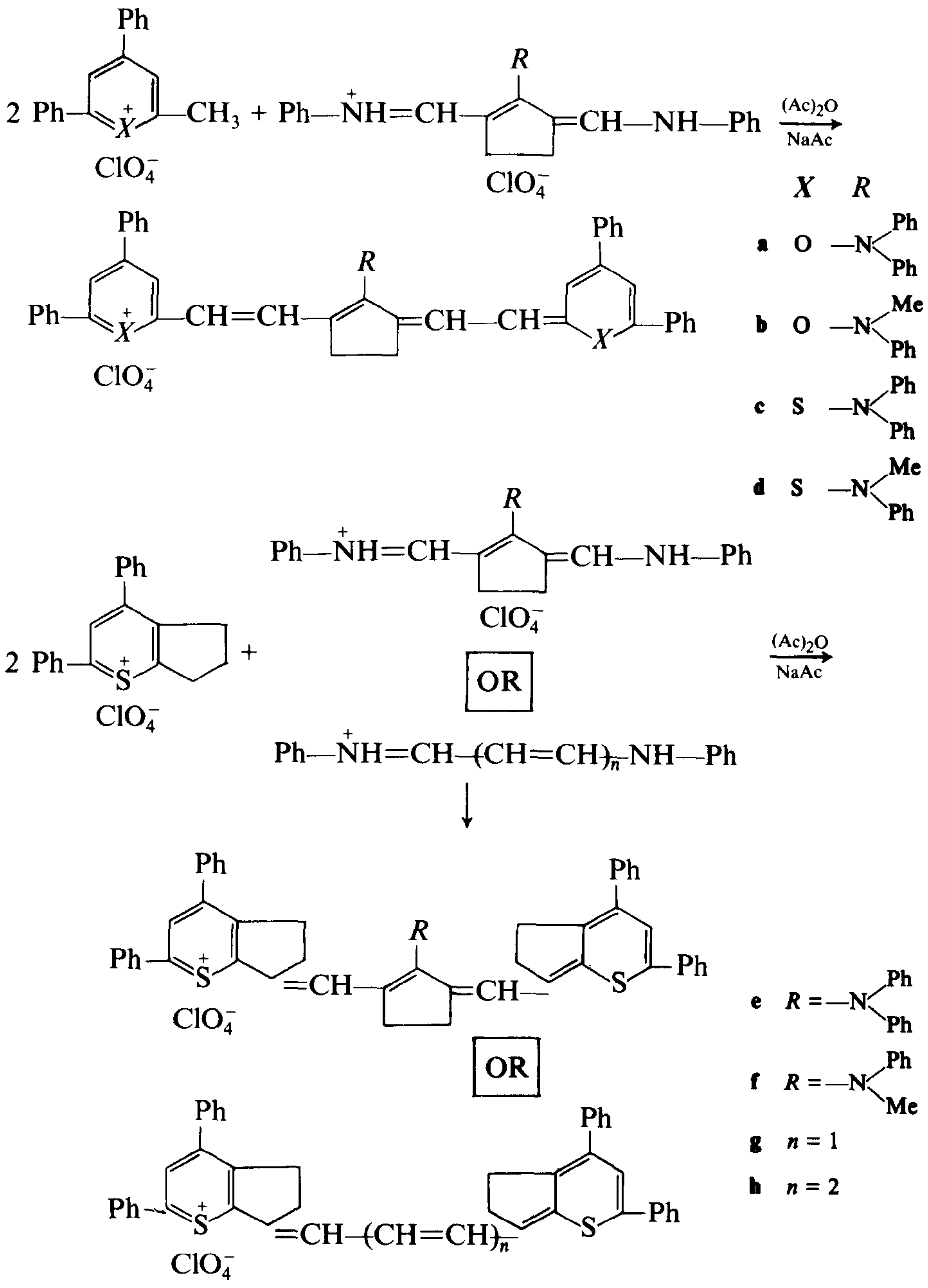
The pyrylium and thiapyrylium heptamethine dyes were prepared by condensing a pyrylium or a thiapyrylium salt with a appropriate enaminium salt, e.g. 1-anilino-3-phenylimino-1-trienehydrochloride and 1-anilino-5-phenylimino-1,3-pentadienehydrochloride. The general reaction is represented in Scheme 1.

4,6-Diphenyl-2-methylpyrylium perchlorate was prepared by interaction of acetic anhydride, acetophenone and sodium perchlorate;[9] further reaction of this with sodium hydrogen sulfide[10] gave 4,6-diphenyl-

TABLE 1
Yields, Melting Points and Elemental Analyses for **a**–**h**

Dye	*Yield (%)*	*M.p. (°C)*[a]	*Molecular formula*	*Analysis (found/calculated) (%)*		
				C	*H*	*N*
a	22	207–209	$C_{55}H_{42}ClO_6N$	77·84	5·18	1·38
			(847·5)	77·89	5·62	1·65
b	18	280–281	$C_{50}H_{40}ClO_6N$	76·39	4·61	1·64
			(785·5)	76·58	5·11	1·79
c	19	263–264	$C_{55}H_{42}ClO_4S_2N$	75·11	4·78	1·79
			(879·5)	75·03	4·77	1·59
d	20	220–221	$C_{50}H_{40}ClO_4S_2N$	73·20	5·21	1·78
			(817·5)	73·39	4·89	1·71
e	28	202–204	$C_{59}H_{46}ClO_4S_2N$	75·41	4·88	1·50
			(931·5)	75·89	4·93	1·50
f	24	218–219	$C_{54}H_{44}ClO_4S_2N$	74·25	5·20	1·59
			(869·5)	74·53	5·06	1·61
g	33	268–270	$C_{43}H_{33}ClO_4S_2$	72·00	4·80	
			(612·5)	72·37	4·63	
h	31	251–252	$C_{45}H_{35}ClO_4S_2$	73·13	4·95	
			(738·5)	73·07	4·74	

[a] Recrystallization solvent: 1,2-dichloroethane.


(Ac)2O
NaAc
X R
a O —N(Ph)Ph
b O —N(Me)Ph
c S —N(Ph)Ph
d S —N(Me)Ph
OR
e R = —N(Ph)Ph
f R = —N(Ph)Me
g n = 1
h n = 2
ClO4-

Scheme 1

TABLE 2
Characterization Data of Dyes

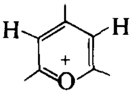
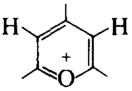
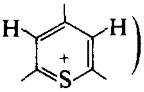
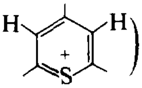
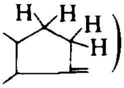
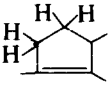
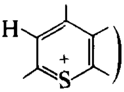
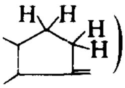
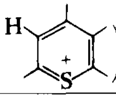
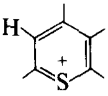
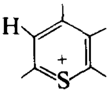
Dye	*^1H NMR* *(δ)*	*Mass spectra* *M^+, m/z*
a	δ^{TMS}_{DMSO} 3·1 (s, 4H, —CH$_2$—CH$_2$—), 7·1 (d, 4H, —CH=CH—) 7·5 (m, 10H, $-N<^{Ph}_{Ph}$), 7·6 (m, 20H, —Ph) 7·9 (s, 4H, )	748
b	δ^{TMS}_{DMSO} 2·8 (s, 4H, —CH$_2$—CH$_2$—), 3·9 (s, 3H, —$\overset{\vert}{N}$—Me) 7·0 (d, 4H, —CH=CH—), 7·3 (m, 5H, —N—Ph) 7·5 (m, 20H, —Ph), 7·7 (s, 4H, )	686
c	δ^{TMS}_{DMSO} 3·1 (s, 4H, —CH$_2$—CH$_2$—), 7·0 (d, 4H, —CH=CH—) 7·4 (m, 10H, $-N<^{Ph}_{Ph}$), 7·5 (m, 20H, —Ph) 7·8 (s, 4H, )	780
d	δ^{TMS}_{DMSO} 3·0 (s, 4H, —CH$_2$—CH$_2$—), 3·7 (s, 3H, —$\overset{\vert}{N}$—Me) 6·7 (d, 4H, —CH=CH—), 7·2 (m, 5H, —$\overset{\vert}{N}$—Ph) 7·6 (m, 20H, —Ph), 8·2 (s, 4H, )	718
e	$\delta^{TMS}_{CDCl_3}$ 3·1 (s, 4H, —CH$_2$—CH$_2$—), 3·2 (t, 4H, ) 3·3 (t, 4H, ), 7·1 (m, 2H, —CH=) 7·6 (m, 30H, —Ph), 7·8 (s, 2H, )	832
f	$\delta^{TMS}_{CD_3Cl}$ 3·1 (s, 4H, —CH$_2$—CH$_2$—), 3·2 (t, 8H, ) 3·5 (s, 3H, —N—Me), 6·9 (m, 2H, —CH=) 7·5 (m, 25H, —Ph), 7·7 (s, 2H, )	770

TABLE 2—*contd.*

Dye	^1H *NMR* (δ)	*Mass spectra* M^+, *m/z*
g	$\delta^{TMS}_{CDCl_3}$ 3·1 (t, 8H, —CH_2—CH_2—), 7·0 (m, 3H, —CH=CH—CH=) 7·6 (m, 20H, —Ph), 7·8 (s, 2H, )	612 (M^+-1)
h	$\delta^{TMS}_{CDCl_3}$ 3·0 (t, 8H, —CH_2—CH_2—) 7·0 (m, 5H, —CH=CH—CH=CH—CH=), 7·6 (m, 20H, —Ph) 7·5 (s, 2H, )	639

2-methylthiapyrylium perchlorate. Similarly, 2,4-diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]thiapyrylium perchlorate was prepared from 2,4-diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyrylium perchlorate. The enaminium salts used were obtained from cyclopentanone, ethylisoformanilide and diphenylamine hydroperchlorate or *N*-methylaniline hydroperchlorate. 1-Anilino-5-phenylimino-1,3-pentadienehydrochloride was obtained from 2,4-dinitrophenylpyridinium chloride and aniline,[11] and 1-anilino-3-phenylimino-1-trienehydrochloride was prepared from propargyl aldehyde.[12] The dyes were prepared by reaction of the pyrylium or thiapyrylium salts with the enaminium salts 1-anilino-5-phenylimino-1,3-pentadienehydrochloride or 1-anilino-3-phenylimino-1-trienehydrochloride.

Data on yields, melting points and elemental analyses are given in Tables 1 and 2.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. Elemental analyses were obtained using a Carlo Erba 1160 R element analyser. Mass spectra were recorded on a Hitachi M-80 spectrometer and ^{1}H NMR spectra on a Bruker WP-100SY at 100 MHz.

4,6-Diphenyl-2-methylpyrylium perchlorate,[9] 2,4-diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyrylium perchlorate,[13] 1-anilino-5-phenylimino-1,3-pentadienehydrochloride[11] and 1-anilino-3-phenylimino-1-trienehydrochloride[12] were prepared by the literature procedures.

3.2 4,6-Diphenyl-2-methylthiapyrylium perchlorate and 2,4-diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]thiapyrylium perchlorate

To a stirred suspension of 4,6-diphenyl-2-methylpyrylium perchlorate (8·6 g, 25 mmol) in acetone (200 ml), an aqueous ethanolic solution (40 ml) of sodium hydrogen sulfide (25 mmol) was added. The mixture was stirred for 5 min, and then poured into 75% perchloric acid (6 ml). The precipitated product was isolated by filtration: yield 7·6 g (84%); m.p. 255–256°C (lit.[10] m.p. 257–258°C).

Analysis for $C_{18}H_{15}ClO_4S$ (362·8): calculated: C 59·6%, H 4·2%; found: 60·0%, 4·3%.

2,4-Diphenyl-6,7-dihydro-5*H*-cyclopenta[*b*]thiapyrylium perchlorate was prepared by a similar procedure: yield 55%; m.p. 215–216°C; M^+ (FD) 289.

Analysis for $C_{20}H_{17}SClO_4$ (388·5): calculated: C 61·78%, H 4·38%; found: 61·76%, 4·44%.

3.3 *N*-(2,5-Dianilinomethylenecyclopentylidene)diphenylaminiumperchlorate (i) and 3-anilinomethylene-2-(*N*-methylanilino)-1-phenyliminomethylcyclopentene perchlorate (j)

1-Cyclopentylidenediphenylaminium perchlorate (33·5 g, 0·1 mol) and ethylisoformanilide (37·3 g, 0·2 mol) were thoroughly mixed and heated at 140°C for 30 min. After cooling, the cake was crushed under methanol, the solid filtered and recrystallized from *N*,*N*-dimethylformamide: yield 43 g (92%); m.p. 181–182°C (lit.[14] m.p. 180–181°C).

Analysis for $C_{31}H_{28}N_3ClO_4$ (541·5): calculated: C 68·70%, H 5·17%; N 7·76%; found: 68·43%, 5·13%, 7·65%.

3-Anilinomethylene-2-(*N*-methylanilino)-1-phenyliminomethylcyclopentene perchlorate was similarly prepared: yield 69%; m.p. 228–229°C (lit.[14] m.p. 228–229°C).

Analysis for $C_{26}H_{26}N_3ClO_4$ (479·5): calculated: C 62·57%, H 5·42%, N 8·76%; found: 62·13%, 5·29%, 8·89%.

3.4 Preparation of dyes

A mixture of 2 mmol of the pyrylium or thiapyrylium salt, 1 mmol of the enaminium salt or **i** or **j**, 2 mmol of sodium acetate and 8 ml of acetic anhydride were refluxed for 8 min, and after chilling the solid was collected, washed with acetic acid and ethanol, and purified by column chromatography on silica gel, using 1,2-dichloromethane : acetone 15 : 1 (v/v) as eluant. Characterisation data of the products are given in Tables 1 and 2.

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