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Novel Laser Dyes: Some Bridged Pentamethine Phosphinines

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ABSTRACT

Six novel pentamethine phosphinines were prepared and their structures were determined by ^1H NMR. Their fluorescent properties and lasing characteristics have been examined in dimethylsulfoxide (DMSO) with a nitrogen laser as the pumping source. Dyes with N,N-*diphenyl or* N-*methyl*-N-*phenyl amino groups on the* meso *position of the bridge of the polymethine chain show larger Stokes shift and higher lasing efficiency. The tunable range is 7600–8300Å and the energy conversion efficiency is 2·4–5·3% at the maximum emission wavelength.*

1 INTRODUCTION

The phosphinemethylenes or phosphorus 'ylide' have been known for many years. Of particular interest is triphenylphosphoniumcyclopentadienylide which is a non-benzenoid aromatic compound.[1] The compound is easy to couple with diazonium salts.[2] A number of phosphinines, merophosphinines and phosphocyanines have been prepared by Zhu *et al.*[3] and it has been shown that these dyes are useful as photographic sensitizers for use in color photography.[4]

No studies have been reported on the synthesis of phosphinines with a bridged chain in the polymethine residue, to enhance their photostability.

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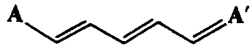
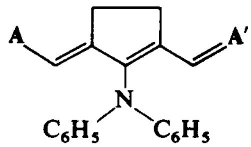
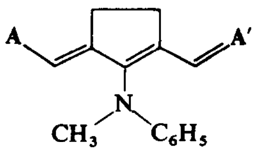
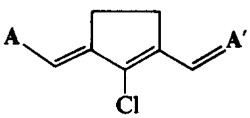
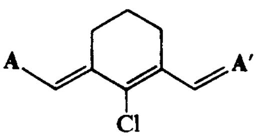
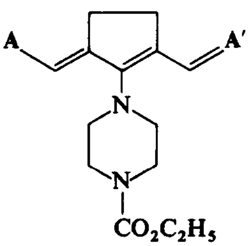
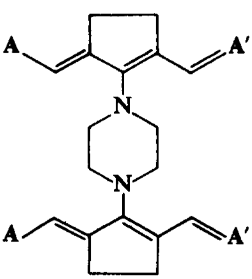
TABLE 1
Structure of the Phosphinines and their Properties

Compound number	*Structure*	λ_1[a]	ε'_{max}[b]	$\varepsilon_{337}/\varepsilon_{max}$[c]	λ_2[d]	S[e]	Y[f]	T[g]
Ph-0		6 972	0·62	0·39	7 600	628	2·4	7 570–7 880
Ph-1		7 488	2·6	0·08	8 200	712	2·7	8 100–8 300
Ph-2		7 440	2·5	0·09	8 300	860	5·3	8 150–8 300
Ph-3		7 262	1·3	0·1	—	—	—	—
Ph-4		7 432	0·81	0·4	—	—	—	—
Ph-6		6 646	1·0	0·12	7 500	854	—	—
2Ph-1		6 436	1·4	0·67	—	—	—	—

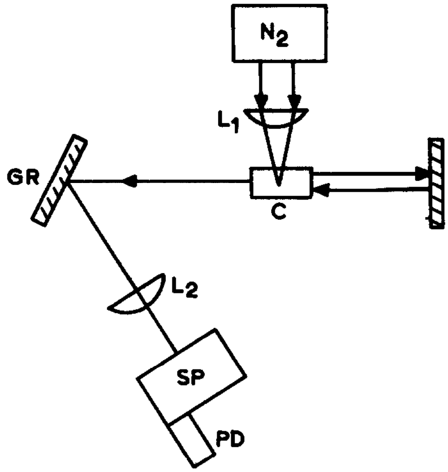


Fig. 1. Schematic of the laser system. C, dye cell; GR, grating; L1, L2, cylindrical lens; SP: monochromator, PD: photodetector, GR: grating.

This paper describes the preparation and properties of such bridged pentamethinephosphinines. Furthermore they were applied as laser dyes. Several of the dyes studied were found to have good lasing properties.

2 EXPERIMENTAL

Absorption spectra were recorded with a Shimadzu-UV-260 spectrophotometer, and ^1H NMR spectra on a JEOL-90 with TMS as the internal standard. Field-desorption mass spectra were recorded on a Hitachi M-80. The fluorescence emission spectra and lasing spectra were obtained using a

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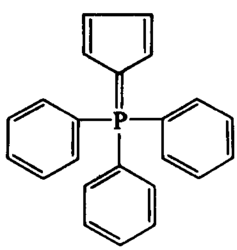
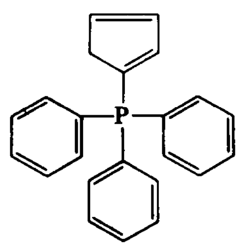
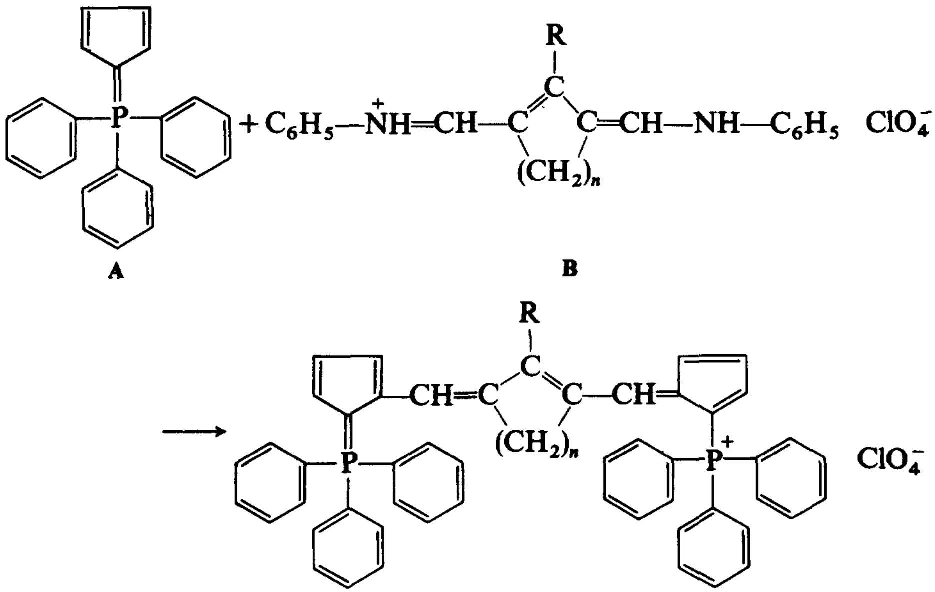
A  A′  ClO_4^-

[a] λ_1, absorption maximum (Å) in DMSO.
[b] ε'_{max}, $\varepsilon_{max} \times 10^{-5}$ (cm^{-1} M^{-1}) in DMSO.
[c] $\varepsilon_{337}/\varepsilon_{max}$, the ratio of extinction coefficient at 337 to that at maximum absorption.
[d] λ_2, fluorescence maximum (Å) in DMSO.
[e] *S*, Stokes shift (Å).
[f] *Y*, lasing efficiency of the dye at maximum lasing wavelength.
[g] tuning range (Å).

nitrogen laser. Pulse widths were 10 ns. The peak output of the nitrogen laser was about 500 kw and pulse repetition rate was 8 Hz. The experimental set-up is shown in Fig. 1. The investigation was carried out in dye solutions of concentration 2×10^{-3} M in DMSO.

The phosphonines were prepared as follows:



where $n = 0, 2, 3$; and R = hydrogen, diphenylamino, N-methylphenylamino, piperazino, 4-ethoxycarbonyl-piperazino, chloro.

The general procedure for the synthesis of the dyes (compounds A[3] and B[5] were prepared as previously described) was as follows. Firstly, 2 mmol A and 1 mmol B were dissolved in about 15 ml of chloroform and heated to 45–50°C for 100 min. After cooling, the reaction mixture was poured into

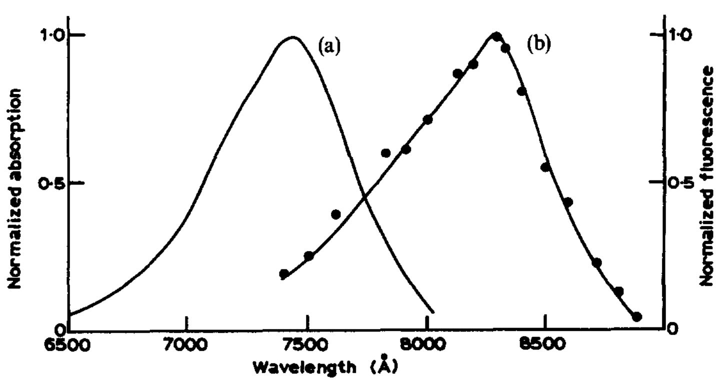


Fig. 2. (a) Absorption spectrum of **Ph-2**, 8×10^{-6} M in DMSO; (b) fluorescence spectrum of **Ph-2**, 2×10^{-3} M in DMSO.

TABLE 2
Analysis Data on the Prepared Dyes

Compound	*Molecular formula*	*Elemental analysis*						*FDMS m/e*
		Calculated			*Found*			
		C	*H*	*N*	*C*	*H*	*N*	
Ph-0	$C_{51}H_{42}ClO_4P_2$	75·3	5·1	—	75·6	5·1	—	716
Ph-1	$C_{65}H_{53}ClNO_4P_2$	77·3	5·3	1·4	77·6	5·5	1·6	909
Ph-2	$C_{60}H_{51}ClNO_4P_2$	76·1	5·3	1·5	75·8	5·3	1·8	847
Ph-3	$C_{53}H_{43}Cl_2O_4P_2$	72·8	5·0	—	73·1	5·2	—	776
Ph-4	$C_{54}H_{45}Cl_2O_4P_2$	73·0	5·1	—	73·4	5·5	—	790
Ph-6	$C_{60}H_{56}ClN_2O_6P_2$	72·1	5·6	2·8	71·7	5·4	2·5	898
2Ph-1	$C_{110}H_{94}Cl_2N_2O_8P_4$	74·7	5·3	1·6	74·6	5·6	1·3	784

^{1}H NMR (Deuteriochloroform/TMS)

Compound	*[NMR data]*
Ph-0	1·94 (s, 2), 6·38 (d, 1), 6·58 (d, 1), 6·72 (d, 1), 6·84 (d, 1), 7·56–7·64 (t, 15).
Ph-1	1·59 (s, 2), 3·02 (s, 2), 6·38 (d, 1), 6·46 (d, 1), 6·70 (d, 1), 7·16 (s, 5), 7·52–7·65 (t, 15).
Ph-2	1·61 (s, 2), 3·03 (s, 2), 3·38 (t, 3), 6·40 (d, 1), 6·45 (d, 1), 6·62 (d, 1), 6·84 (d, 1), 7·20 (s, 5), 7·54–7·66 (t, 15).
Ph-3	1·72 (s, 2), 3·02 (s, 2), 6·47 (d, 1), 6·50 (d, 1), 6·76 (d, 1), 6·82 (d, 1), 7·55–7·69 (t, 15).
Ph-4	1·24 (t, 3), 1·50 (s, 2), 3·72 (g, 2), 6·52 (d, 1), 6·54 (d, 1), 6·67 (d, 1), 6·82 (d, 1), 7·58–7·70 (t, 15).
Ph-6	1·23 (t, 3), 1·61 (s, 2), 2·94 (s, 2), 3·72 (d, 2), 4·08 (q, 2), 6·40 (d, 1), 6·46 (d, 1), 6·62 (d, 1), 6·72 (d, 1), 7·52–7·64 (t, 15).
2Ph-1	1·63 (s, 2), 2·86 (s, 2), 3·96 (d, 2), 6·38 (d, 1), 6·42 (d, 1), 6·64 (t, 2), 7·52–7·62 (t, 15).

50 ml of ether with ice cooling. The products were filtered, washed with ethanol and recrystallized from a mixture of 1,2-dichloroethane and ethanol. The dye structures are shown in Table 1 and analysis data in Table 2.

3 RESULTS AND DISCUSSION

The absorption and fluorescence properties and the corresponding lasing characteristics of the dyes are shown in Table 1. The elemental analyses and spectroscopic data are tabulated in Table 2. An example of the spectra for absorption, fluorescence and stimulated emission are shown in Figs 2 and 3 respectively.

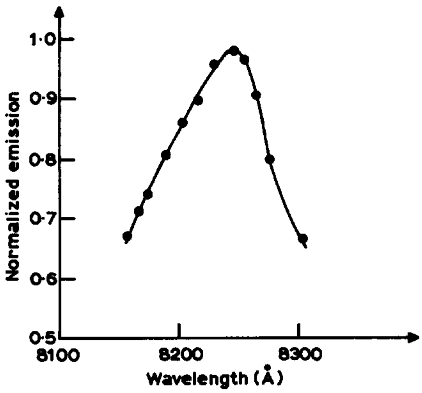


Fig. 3. Spectrum of stimulated emission of **Ph-2**, 2×10^{-3} M in DMSO.

It can be seen from Table 1 that a dye with an electron-donor group on the *meso* position of the polymethine chain causes a red shift and larger extinction coefficient, and its Stokes shift is consistently larger. The larger Stokes shift will favour an increased lasing efficiency because of the decrease in overlap between the absorption and emission spectra. On the contrary, a dye with an electron-acceptor group, e.g. chloro atom in the chain, gives no fluorescence.

4 CONCLUSION

Six novel pentamethine phosphinines with a bridged ring across the pentamethine chain were prepared. These dyes are shown to have good lasing properties with a tunable range of 7600–8300Å and energy conversion efficiency. 2·4–5·3% at maximum emission wavelength, especially when a disubstituted aromatic amino group is situated in the *meso* position of the pentamethine chain. It is also found that they have unique photostability, which is very important in its application as a laser dye.

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