Triphenylmethane Dye Ethynologues with Absorption Bands in the Near I.R.[1]

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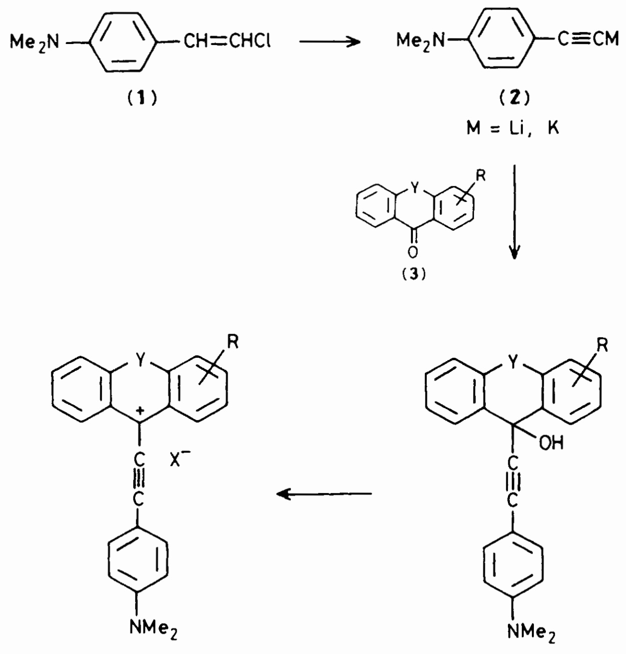
The first examples of triphenylmethane dye ethynologues (*i.e.*, *p*-dimethylaminophenylethynylxanthenylium, thioxanthenylium, and selenoxanthenylium perchlorates) absorbing in the near i.r. (up to 802 nm in CH_2Cl_2) have been synthesized by treatment of the corresponding alcohols with acids.

In recent years, near i.r. dyes showing absorption maxima beyond *ca.* 700 nm have been of interest for applications in such areas as optical and laser data storage technology.[2] It was observed that the introduction of an acetylenic bond into the resonating system of triphenylmethane dyes makes the cation part coplanar by releasing steric congestion between *ortho*-hydrogen atoms of phenyl groups in the dyes and induces a strong bathochromic effect on the peak in the visible region of the spectra.[1,3] Accordingly, it was anticipated that for the dye ethynologues a larger delocalization of the positive charge would be caused by a replacement of the diphenylmethyl part with a xanthene, thioxanthene, or selenoxanthene nucleus, and that such modification will give light absorption in the near i.r.

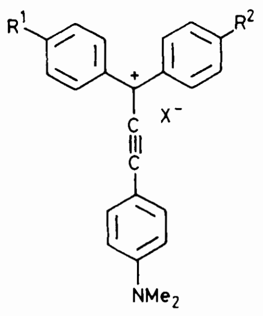
The precursors (**4**) were prepared by the reaction of xanthones (**3**) with the metallated *p*-dimethylaminophenylacetylides (**2**) derived from *p*-dimethylamino-β-chlorostyrene (**1**).[4] The isolated alcohols (**4**) were treated with the acid (perchloric acid, fluoroboric acid, or picric acid) to give the dyes (**5**) as crystals [m.p. (°C): (**5a**), 184—185; (**5b**), >195; (**5c**), >300; (**5d**), 148—150; (**5e**), >230; (**5f**), 170; (**5g**), 183—185; (**5h**), >178; (**5i**), 208—210]. The absorption spectral data are summarized in Table 1. The remarkable bathochromic shifts of the dye systems can be seen by comparing (**5a**—**i**) with bis(*p*-substituted phenyl)(*p*-dimethylaminophenylethynyl) carbonium ions (**6a**—**c**) [$\lambda_{max.}$ (CH_2Cl_2): (**6a**), 705; (**6b**), 663; (**6c**), 727].[1,3] In the series of (**5a**), (**5b**), and (**5h**), pronounced red shifts were clearly observed with decrease in electronegativity (O > S > Se).

It is interesting to note that the dyes have large molar



(5) (4)

	Y	R	X$^-$
a;	O	H	ClO_4^-
b;	S	H	ClO_4^-
c;	S	H	BF_4^-
d;	S	H	Picrate
e;	S	3-OMe	ClO_4^-
f;	S	2,4-Et$_2$	ClO_4^-
g;	S	2-Cl	ClO_4^-
h;	Se	H	ClO_4^-
i;	Se	3-OMe	ClO_4^-



(6)

	R^1	R^2	X$^-$
a;	H	H	$CF_3CO_2^-$
b;	H	NMe$_2$	ClO_4^-
c;	NMe$_2$	NMe$_2$	ClO_4^-

Table 1. Light absorption properties of dyes (**5**).[a]

Dye	$\lambda_{max.}$/nm (CH_2Cl_2)	log ε/dm^3 mol^{-1} cm^{-1}
(**5a**)	737	4.86
(**5e**)	745	4.74
(**5i**)	755	4.85
(**5f**)	762	4.91
(**5b**)	775	4.94
(**5c**)	775	4.92
(**5d**)	775	4.82
(**5h**)	802	4.93
(**5g**)	802	4.89

[a] All new compounds gave satisfactory microanalytical data.

absorption coefficients and that there are clear substituent effects on the thio- and seleno-xanthenyl nuclei. The chloro-dye (**5g**) shows the progressive shift to longer wavelength (802 nm), while the dyes (**5e**), (**5f**), and (**5i**) give blue shifts based on the corresponding parent compounds. The absorption wavelengths of (**5b—d**) were independent of the counter ion.

The new near i.r. absorbing dyes (**5**) are fairly stable and are now being examined for applications in diode-laser high density recording. The experimental details will be published elsewhere.

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