A New Spiro{2*H*-naphtho[2,1-*b*]pyran-2,2′-2′*H*-1′-benzothiopyran} giving a Near-IR Absorption Band on UV Irradiation

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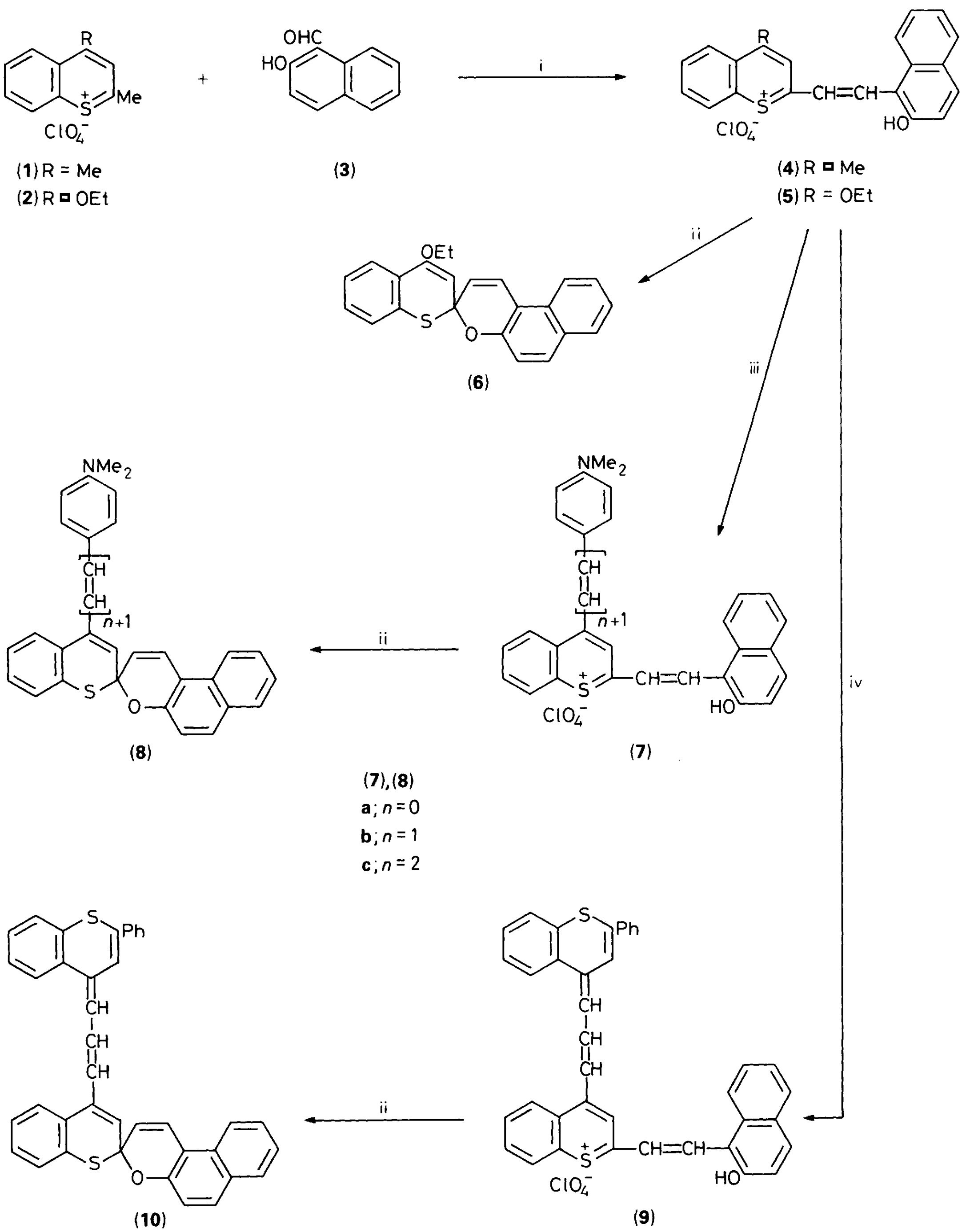
Novel 4′-styryl spiro{2*H*-naphtho[2,1-*b*]pyran-2,2′-2′*H*-1′-benzothiopyrans} have been prepared by condensation of 2,4-dimethyl-1-benzothiopyrylium perchlorate (**1**) with 2-hydroxy-1-naphthaldehyde (**3**) followed by deprotonation with piperidine which gave the coloured form having an absorption band in the near-IR region on UV irradiation.

Photochromic spiropyrans have attracted a great deal of interest from the applications viewpoint, especially as potential erasable optical recording media for information storage. In practical systems, the coloured form of photochromic spiropyran compounds should absorb near-IR light as diode lasers (oscillator wavelength 780—830 nm) are used as the light source for recording and reproducing the information.[1] However, there are few examples of photochromic spiropyrans whose coloured form gives an absorption band in the near-IR region.[2] We now report for the first time the synthesis and properties of spiropyrans which give a coloured form having an absorption maximum beyond 780 nm.

Generally, coloured forms of common photochromic spiropyrans have an absorption band in the visible region.[3] The photochromic spiropyran (**6**), which was prepared by the reaction of 4-ethoxy-2-methyl-1-benzothiopyrylium perchlorate (**2**)[4] with 2-hydroxy-1-naphthaldehyde (**3**), also gave the blue coloured form ($\lambda_{max.}$ 629 nm in $CHCl_3$). An approach to a system absorbing beyond 780 nm is to make use of the bathochromic effect of extend conjugation at the 4-position of the 1-benzothiopyrylium ring in the coloured form of the photochromic spiropyran.

Thus, 2,4-dimethyl-1-benzothiopyrylium perchlorate (**1**),[5] a key compound having two active methyl groups, reacted with



Scheme 1. *Reagents and conditions*: i, EtOH, 0 °C; ii, piperidine, Me_2CO, room temp.; iii, $OHC[CH{=}]_nC_6H_4NMe_2$, EtOH, reflux; iv, 2-phenyl-4*H*-1-benzothiopyran-4-ylideneacetaldehyde, EtOH, reflux.

(**3**) in ethanol at 0 °C for 24 h to give the 2-condensed compound (**4**) in 75% yield ($\lambda_{max.}$ 616 nm, ε 1.85 × 10^4 dm^3 mol^{-1} cm^{-1} in $CHCl_3$). Further reaction of (**4**) with *p*-(dimethylamino)benzaldehyde or vinylogous aldehydes in refluxing ethanol readily proceeded to give compounds (**7a**—**c**) with a styryl component in good yield [(**7a**), 76%, $\lambda_{max.}$ 704 nm (ε 2.69 × 10^4 dm^3 mol^{-1} cm^{-1}); (**7b**) 76%, $\lambda_{max.}$ 787 nm (ε 2.79 × 10^4); (**7c**) 62%, $\lambda_{max.}$ 862 nm (ε 1.54 × 10^4) in $CHCl_3$]. Compound (**9**) with a cyanine component (75%, $\lambda_{max.}$ 790 nm, ε 5.14 × 10^4 in $CHCl_3$) was similarly obtained by the reaction of (**4**) with 2-phenyl-4*H*-1-benzothiopyran-4-ylideneacetaldehyde. These compounds were easily deprotonated with piperidine in acetone at room temperature to give the corresponding spiropyrans (**8a**—**c**) and (**10**)† in 44 and 9% yields, respectively.

Upon UV irradiation, the spiropyran (**8a**) gave an absorption band in the near-IR region at 692 nm (Scheme 2). Further pronounced bathochromic shift in the chromophoric system

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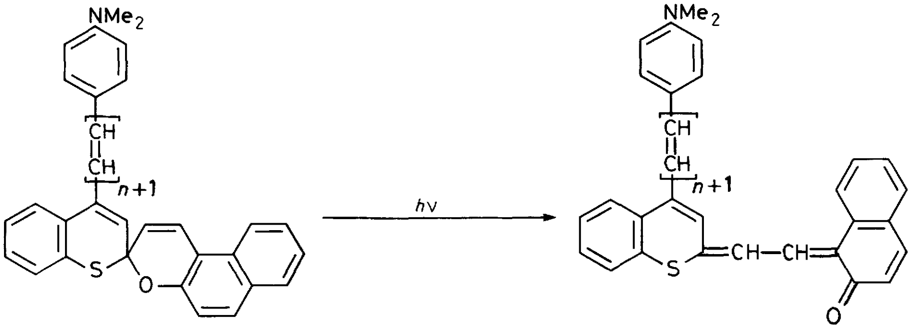
† All new spiropyran compounds and dyes (**4**)—(**10**) described here gave satisfactory elemental analysis.



Scheme 2

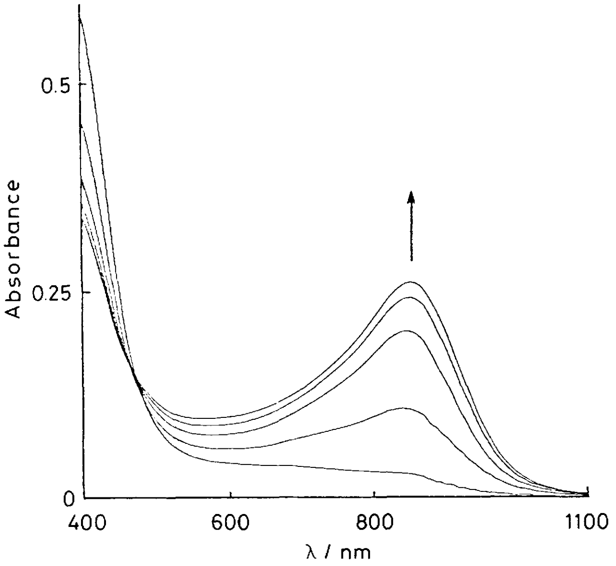


Figure 1. Absorption spectral change of a solution of (**8c**) in $CHCl_3$ (1×10^{-4} mol dm^{-3}) at 20 °C on UV irradiation.

was attainable by increasing the number of vinyl groups in the conjugated chain (*ca.* 80 nm per vinyl group). The coloured forms of the spiropyrans (**8b** and **c**) showed absorption bands at 786 and 858 nm, respectively (Table 1). The change in the spectra of (**8c**) by a UV irradiation is shown in Figure 1. An isobestic point was observed at 468 nm. Under the same conditions the spiropyran (**10**) also gave a sharp absorption band at 800 nm.

The photochemical transformation of the spiropyrans (**8**) and (**10**) to the coloured form obeyed good first-order kinetics. The colouration rate constant for (**8**), which includes a styryl component, increased with increasing length of the polymethine chain. The colouration rate of the spiropyran (**10**), including a cyanine component, was faster than that of the styryl-substituted (**8**). Activation energies for the colouration of (**8**) and (**10**) are significantly smaller than those of common indolinospiropyrans (E_a 15 kcal mol^{-1}).[6]

Table 1. Kinetic data for photochemical colouration of spiropyrans (**8**) and (**10**).

Compound	Yield/%[a]	$\lambda_{max.}$/nm[b]	$k\,(\times 10^2)/s^{-1}$[c]	E_a/kcal mol^{-1}[d]
(**8a**)	44	692	2.68	1.39
(**8b**)	44	786	3.44	1.47
(**8c**)	45	858	4.71	1.83
(**10**)	9	800	6.85	1.67

[a] Isolated yield. [b] Absorption maximum of the coloured form in $CHCl_3$. [c] The colouration rate was observed for a solution of the spiropyrans (1×10^{-4} mol dm^{-3}) in $CHCl_3$ at 20 °C, with a 100 W high-pressure mercury lamp through a Toshiba glass filter (UV-D33S), 20 cm from the samples. [d] Activation for colouration; 1 cal = 4.184 J.

The photoreactions of these spiropyrans depended markedly on the solvent. In CH_2Cl_2, $CHCl_3$, CCl_4, and $CHCl_2CHCl_2$ they gave the coloured form, but in ethanol, which would be expected to favour formation of the coloured form, no colour species was observed.

The present system is expected to provide a useful material for use in erasable optical recording media. However, the photocolouration mechanism of these novel spiropyrans may be different from that of normal indolinospiropyrans, as their colouration rates are too large and their activation energies too small to be explained by this mechanism. Further investigation of the photocolouration mechanism, as well as studies of the decolouration reaction, are in progress.

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