New Solvatochromic Cyanine Dyes derived from 2-Methylbenzo[*a*]quinolizinium Perchlorate

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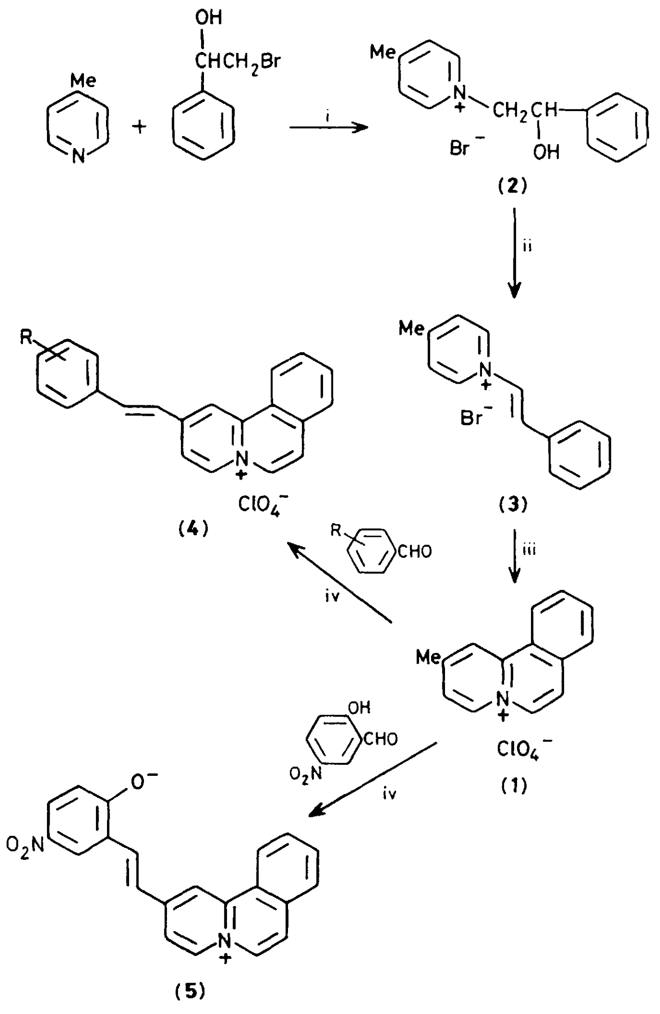
New solvatochromic cyanine dyes were obtained by the reaction between 2-methylbenzo[*a*]quinolizinium perchlorate and hydroxy substituted benzaldehydes in the presence of piperidine.

During our studies on azonia aromatic compounds, it was found that hydroxyquinolizinium salts are strong acids (pK_a 4—5) and the pK_a values correlate with the effective π-electron density.[1] These results prompted us to examine the reactivities of methyl substituted azonia aromatic compounds. The methyl group was expected to be activated by the quaternary azonia nitrogen. We now report on the synthesis of the as yet unknown compound 2-methylbenzo[*a*]quinolizinium perchlorate (**1**) which has a reactive methyl group, and its derivatization to give new solvatochromic cyanine dyes.

Compound (**1**) was synthesised as follows (Scheme 1). The γ-picolinium bromide (**2**), formed by the reaction of γ-picoline with styrenebromohydrin at 90 °C (77% yield) was treated with phosphorus tribromide at 150 °C for 3 h to afford *trans-N*-styryl-γ-picolinium bromide (**3**) (42.5% yield; m.p. 253.0—254.4 °C, from water). Compound (**1**) was obtained by the photocyclization of (**3**) in the presence of iodine using a high pressure mercury lamp, followed by the addition of 60% aqueous perchloric acid [79% yield; m.p. 254.0—254.5 °C, from methanol; ^{1}H n.m.r. (CF_3CO_2H) δ 2.92 (3H, s, CH_3) and 7.9—9.2 (9H, m, aromatic); λ_{max}(EtOH) 353 (log ϵ 4.16), 337 (4.05), and 322 nm (3.72)].



Scheme 1. Conditions: i, 90 °C, 6 h; ii, PBr_3, 150 °C, 3 h; iii, *hν*; iv, methanol, reflux.

When (**1**) was refluxed with various benzaldehyde derivatives in the presence of piperidine in methanol, *trans*-2-styryl derivatives (**4**)† were obtained in good yields (Table 1). These results show that the methyl group of (**1**) is activated by the quarternary azonia nitrogen and the proton of the methyl group is sufficiently acidic to yield a carbanion when treated with a base.‡ Table 1 shows that the first absorption band of the product is shifted to a longer wavelength with increasing electron-donating strength of *para*-substituents. The product (**4**; R = *p*-NMe_2) is a new cyanine dye. In methanol the yellow merocyanine dyes (**4**; R = *p*-OH and *o*-OH) gave red solutions, which were unaltered by the addition of base. This result shows that the hydroxy group of (**4**; R = OH) was

Table 1. Reaction of (**1**) with benzaldehyde derivatives.

RC_6H_4CHO	Time/h	Yield/%	λ_{max}(EtOH)/nm
p-NO_2	2	71.1	386
H	10	85.3	401
p-Me	5	74.1	407
p-OMe	5	98.8	420
p-OH	3	51.7	430
o-OH	3	57.7	417
p-NMe_2	3	61.9	538

Table 2. Solvatochromism of cyanine dyes.[a]

		λ_{max}/nm	
Solvent	(**4**; R = *p*-O^-)	(**4**; R = *o*-O^-)	(**5**)
H_2O	472	471	—[b]
MeOH	520	516	485
EtOH	553	546	503
$Me_2CHCH_2CH_2OH$	588	571	520
$MeCH_2CMe_2OH$	648	638	—[b]
MeCN	622	626	537
Me_2NCHO	637	642	545
Me_2CO	641	649	556

[a] The u.v. spectra were measured following addition of 0.05 ml of piperidine into 4 ml of sample solution (about 2 × 10^{-5} mol dm^{-3}).
[b] The u.v. spectra could not be measured because of low solubility.

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† All new compounds gave satisfactory spectroscopic and analytical data.

‡ Among six methylbenzo[*a*]quinolizinium salts examined, the methyl group of (**1**) was the most reactive. More detailed results on the properties of the methyl group will be described elsewhere on the basis of n.m.r. studies.

partly deprotonated in methanol even in the absence of base. In ethanol these dyes turned violet only on addition of base. A pronounced negative solvatochromism, which extended over the whole visible spectrum, was observed (Table 2). In the reaction with 2-hydroxy-5-nitrobenzaldehyde, a red betaine (**5**) was obtained (82.5% yield). Table 2 shows that the solvent effect on the betaine (**5**) is smaller than that on the compound (**4**; R = *o*-O^-).

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Reference

1 M. Hida and S. Kawakami, *Nippon Kagaku Kaishi*, 1978, 1249.