SYNTHESIS AND SOLVATOCHROMIC BEHAVIOR OF STILBAZOLIUM MEROCYANINE-TYPE DYES HAVING A BENZO[c]QUINOLIZINIUM RING

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Abstract - A series of stilbazolium merocyanine-type dyes, 3-[2-(hydroxy-substituted aryl)vinyl]benzo[c]quinolizinium perchlorates, was synthesized by the aldol-type condensation of 3-methylbenzo[c]quinolizinium perchlorate with hydroxy-substituted benzaldehyde derivatives in 45-85% yields. The deprotonated form of the dyes exhibited the pronounced negative solvatochromism extended almost over the whole visible region. The negative solvatochromic character of the dyes having a benzo[c]quinolizinium ring was more striking than that of the isomeric dyes having a benzo[a]quinolizinium ring.

Cyanine dyes have been widely applied in various areas associated with nonlinear optics, photochromism, light energy transformation and so on.[1] Especially, the cyanine dyes, in which an electron-accepting group is connected to a hydroxy-substituted moiety, have attracted much attention because of their solvatochromic properties.[2, 3] Recently we reported the synthesis of new stilbazolium betaine-type dyes (1).[4] The long wavelength absorption bands of 1 underwent a remarkable hypsochromic shift as the solvent polarity increased. For example, solutions of the dye (1b) are red-colored (λmax 520 nm) in methanol, violet (553 nm) in ethanol, blue (588 nm) in 3-methylbutan-1-ol, and green (641 nm) in acetone. This solvatochromism is comparable to that of Dimroth and Reichardt's pyridinium N-phenoxide betaine dye (2),[5] which exhibits one of the largest solvatochromic shifts (515 nm in methanol and 677 nm in acetone).
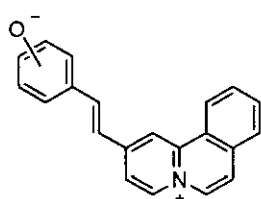

1a: ortho-O⁻
1b: para-O⁻
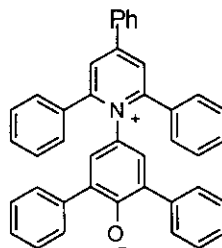
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These results prompted us to extend our studies to new merocyanine-type dyes having a benzo[c]quinolizinium ring, which is a structural isomer of benzo[a]quinolizinium ring. This paper will describe the synthesis and the solvatochromic behavior of new stilbazolium merocyanine-type dyes (**6b-g**) having a benzo[c]quinolizinium ring moiety.

RESULTS AND DISCUSSION

Synthesis.   Recently we developed the convenient synthesis of 3-methylbenzo[c]quinolizinium perchlorate (**4**) using thermal or photo-induced intramolecular quaternization.[6] The condensation of 2,4-lutidine with *o*-chlorobenzaldehyde afforded *trans*-2-[2-(2-chlorophenyl)vinyl]-4-methylpyridine (*trans*-**3**).   The *cis*-**3** prepared by the photoisomerization of *trans*-**3** was thermally cyclized at 170°C to give 3-methyl derivative (**4**). The compound (**4**) was also obtained by the photocyclization of *trans*-**3** in acetonitrile. The aldol-type condensation of **4** with *p*-methoxybenzaldehyde afforded *trans*-3-styryl derivative (**5a**) in 90 % yield.[6] This method was applied to the synthesis of new stilbazolium merocyanine-type dyes having a benzo[c]quinolizinium ring moiety (Scheme 1).
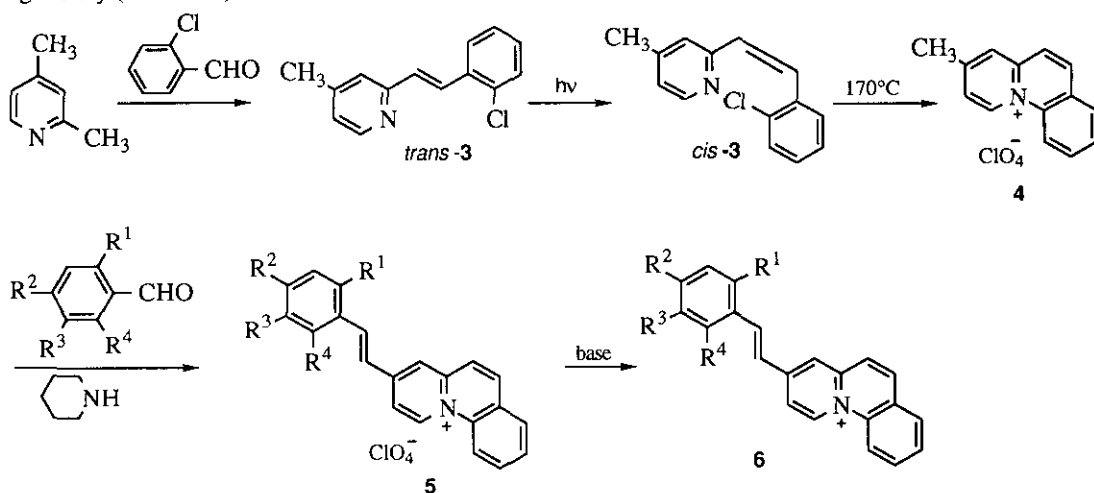
Compound	R^1	R^2	R^3	R^4
5a	H	OCH_3	H	H
5b	H	OH	H	H
5c	OH	H	NO_2	H
5d	OH	H	Br	H
5e	OH	H	H	H
5f	OH	H	OCH_3	H
5g	OH	H	$-(CH=CH)_2-$	

Compound	R^1	R^2	R^3	R^4
6b	H	O^-	H	H
6c	O^-	H	NO_2	H
6d	O^-	H	Br	H
6e	O^-	H	H	H
6f	O^-	H	OCH_3	H
6g	O^-	H	$-(CH=CH)_2-$	

Scheme 1

Table 1. Reaction of Compound (4) with Benzaldehyde Derivatives

Compounds	Time h	Yield %	mp °C	Formula	Ms m/z (M - ClO$_4$)	Analysis/% (Required)		
						C	H	N
5b	9.5	45	246-248	$C_{21}H_{16}NO_5Cl$	298	63.51 (63.40)	3.87 (4.05)	3.64 (3.52)
6c	3	85	> 300	$C_{21}H_{14}N_2O_3$	343[a]	73.45 (73.67)	4.10 (4.12)	8.92 (8.18)
5d	7	52	241-243	$C_{21}H_{15}NO_5BrCl$	376, 378	53.11 (52.91)	3.05 (3.17)	2.77 (2.94)
5e	2	69	235-237	$C_{21}H_{16}NO_5Cl$	298	63.44 (63.40)	4.21 (4.05)	3.59 (3.52)
5f	3	52	235-236	$C_{22}H_{18}NO_6Cl$	328	61.90 (61.76)	4.37 (4.24)	3.03 (3.27)
5g	7	62	182-183	$C_{25}H_{18}NO_5Cl$	348	66.89 (67.04)	4.12 (4.05)	3.36 (3.13)

a: M+1 - ClO$_4$

The 3-methyl derivative (4) reacted with hydroxy-substituted benzaldehyde derivatives in the presence of piperidine to give the corresponding *trans*-3-(2-arylvinyl)benzo[c]quinolizinium salts (5b-g) in 45-85% yields (Table 1).

The solutions of the dyes (5b and 5d-g) were mostly yellow to orange in ethanol except for the red ethanol solution of nitro derivative. The uv and visible spectrum of the nitro derivative remained unchanged by the addition of a drop of piperidine to the ethanol solution. However, on addition of a drop of hydrochloric acid the color of the solution changed to yellow. The ir spectrum of the nitro derivative showed no absorption bands corresponding to perchlorate ion. These results and analytical data indicated that the nitro derivative was not 5c but a betaine form (6c). This would be due to the electron-withdrawing effect of nitro group *para* to hydroxy group.

Solvatochromism.   By an addition of piperidine to an ethanol solution of 5b the absorption maximum was bathochromically shifted from 441 to 571 nm, because of the formation of the betaine form (6b). The solvatochromic data in Table 2, except for the betaine (6c), were obtained by the generation of the betaine forms *in situ* from the corresponding salts (5b and 5d-g) and piperidine. The longest wavelength intramolecular charge-transfer absorption bands of the azonia betaine-type dyes (6b-g) underwent a remarkable hypsochromic shift as the solvent polarity increased, and the pronounced negative solvatochromism extended almost over the whole visible region.

Table 2. Solvatochromism of Azonia Betaine-Type Dyes (6b-g) (nm)

Solvents	6b	6c	6d	6e	6f	6g	1b[a]	2[b]
H_2O	482	c	d	481	511	556	472	453
CH_3OH	537	494	529	529	572	603	520	515
C_2H_5OH	571	515	561	562	612	630	553	550
$(CH_3)_2CHCH_2CH_2OH$	604	538	591	592	644	649	588	583
CH_3CN	641	550	638	650	700	663	622	622
$(CH_3)_2NCHO$	655	558	654	669	727	675	637	652
$(CH_3)_2CO$	660	571	666	678	720	681	641	677
$CH_3CH_2C(CH_3)_2OH$	663	578	653	657	710	679	648	695

[a]Reference 4   [b]Reference 5   [c]Insoluble   [d]Rather unstable

The dyes (6b-g) can be described by two resonance structures: one is the polar zwitterionic form e.g. 6b; the other is the nonpolar quinoidal form e.g. 7b (Scheme 2). The negative solvatochromism would be explained in terms of large polarity change on excitation from more polar ground state to less polar excited state. Thus, with increasing solvent polarity, the energy of the ground state is lowered more than that of the excited state, and this produces a hypsochromic shift. The azonia betaine-type dyes (6b and 6e) showed a large bathochromic shift compared with simple analogue stilbazolium betaines (8) (8a λmax 520 nm and 8b 515 nm in ethanol).[7] Table 2 also shows that the absorption maxima of the azonia betaine-type dyes (6c-f) are hypsochromically shifted with increasing the electron-withdrawing ability of the substituents para to the phenoxide oxygen. This implies that the electron-withdrawing group stabilizes the ground state compared with the excited state.
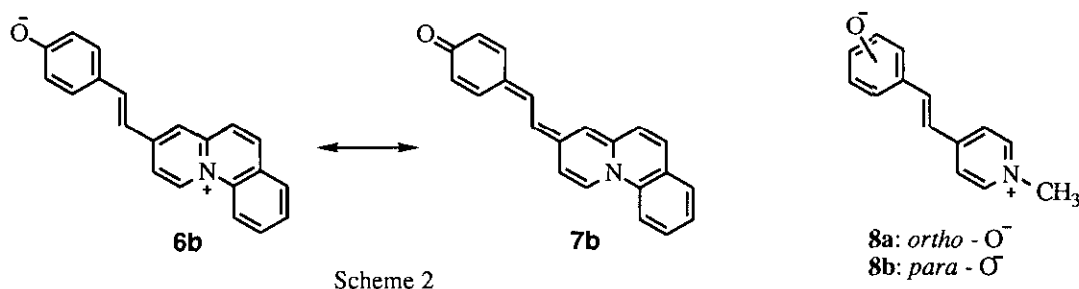

6b   7b   8a: ortho - O⁻
                                           8b: para - O⁻

Scheme 2

Table 2 compares the solvatochromism of the dye (6b) with that of the dye (1b) having a benzo[a]quinolizinium ring. The absorption band of the dye (6b) is bathochromically shifted about 10-19 nm compared with that of the dye (1b) in all of the solvents used. The hypsochromic shift of 178 nm of the dye (6b) from water to acetone is larger than that of 169 nm of 1b.

Plots of the transition energy for azonia betaine-dyes (1b and 6b) against polarity parameter E_T(30) are linear as shown in Figure 1. Therefore, azonia betaine-dyes can be used as an indicator of solvent polarity.
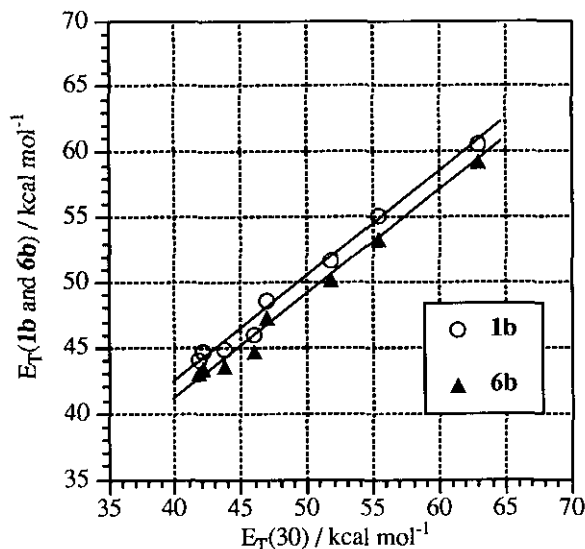
Figure 1. Correlation between $E_T(30)$ and the transition energy of the azonia betaine-type dyes (**1b** and **6b**)

Further studies on the solvatochromic behavior are in progress and will be discussed elsewhere.

EXPERIMENTAL

General.   Melting points were obtained on a Yamato melting point apparatus MP-21 and are uncorrected. The ^{1}H nmr spectra were obtained using a JEOL FX90Q (90 MHz) spectrometer as solutions in DMSO-d_6. Chemical shifts are reported in ppm from TMS as an internal standard. The ir spectra were measured on a JASCO IRA-1 spectrophotometer.   The uv and visible spectra were obtained with a Hitachi 220A spectrophotometer. The fast-atom bombardment (FAB) mass spectra were recorded with a JEOL JMS-DX 300 spectrometer with m-nitrobenzyl alcohol as matrix. Microanalyses were performed by Mr. Hirokatsu Suzuki at Department of Chemistry, Tokyo Metropolitan University. All commercial compounds of reagent grade were used without further purification. All solvents were purified according to the literature procedure.[8] 3-Methylbenzo[c]quinolizinium perchlorate (**4**) was prepared by thermal cyclization of cis-2-[2-(2-chlorophenyl)vinyl]-4-methypyridine (**3**) as described in our previous paper.[6]

General procedure for the synthesis of the stilbazolium merocyanine-type dyes (**5**).   To a solution of 0.5 mmol of compound (**4**) and 0.6 mmol of aldehyde in methanol (20 ml) was added three drops of piperidine and the mixture was heated under reflux. The progress of the reaction was monitored by UV and visible spectra. After being cooled to room temperature, the solvent was evaporated in vacuo. This crude mixture was recrystallized from methanol. Reaction of compound (**4**) with 2-hydroxy-5-nitrobenzaldehyde afforded a dark violet solid, which was filtered off, washed with methanol, and recrystallized from N,N-dimethylformamide to give compound (**6c**). The physical properties and analytical data of the stilbazolium merocyanine-type dyes (**5**) are listed in Tables 1 and 3.

Uv-visible spectral measurement of the dyes.   In order to avoid *trans-cis* photoisomerization, the solutions were handled in the dark. The uv and visible spectra of the dyes (6) were recored by the addition of piperidine (0.05 ml) to the dyes (5) solution (4 ml; *ca* 0.02 mM)

Table 3. Spectroscopic Properties of Compounds (5b, 6c, and 5d-5g)

Compound	Uv/λmax [a] nm	^{1}H Nmr (DMSO-d_6)	Ir (KBr) $\bar{\nu}$ / cm^{-1}
5b	441	6.8-10.3 (14H, m, ArH and olefin-H) 7.38 (1H, d, J=16.5 Hz, olefin-H) 10.0 (1H, br s, OH)	3425,1642, 1597 1451, 1263, 1172 1124, 820
6c	515	6.14 (1H, d, J=9.9 Hz, ArH) 7.7-10.0 (13H, m, ArH and olefin-H)	1640, 1590,1520 1554, 1375, 1275 822
5d	425	6.9-10.3 (13H, m, ArH and olefin-H) 7.68 (1H, d, J=16.5 Hz, olefin-H) 10.88 (1H, s, OH)	3425, 1642, 1612 1452, 1345, 1174 1125, 822
5e	429	6.9-10.2 (15H, m, ArH and olefin-H) 10.41 (1H, s, OH)	3400, 1643, 1610 1452, 1350, 1251 1112, 722
5f	450	3.77 (3H, s, CH$_3$) 6.9-10.2 (13H, m, ArH and olefin-H) 7.65 (1H, d, J=16.5 Hz, olefin-H) 9.77 (1H, s, OH)	3400, 1642, 1605 1452, 1350, 1262 1112, 820
5g	470	7.2-10.3 (17H, m, ArH and olefin-H) 10.90 (1H, br s, OH)	3425, 1641, 1608 1452, 1340, 1272 1124, 818

a: the first absorption band in C$_2$H$_5$OH

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