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Dyes and Pigments, Vol. 29, No. 4, pp. 263–273, 1995
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0143-7208/95 $9.50 + 0.00

0143-7208(95)00052-6

Solvatochromism of Stilbazolium Merocyanine-Type Dyes Containing a Benzoquinolizinium Ring

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(Received 28 April 1995; accepted 31 May 1995)

ABSTRACT

The UV/VIS spectra of a series of stilbazolium merocyanine-type dyes containing a benzoquinolizinium ring have been recorded in seven solvents. The dyes with a hydroxyl group showed hypsochromic shifts (less than 50 nm) on changing the solvent from 3-methylbutan-1-ol to water. On the other hand, the azonia betaine-type dyes formed by deprotonation of the hydroxy-substituted dyes exhibited a large hypsochromic shift (about 200 nm) as the solvent polarity increased. The transition energies (E_T*) of the dyes having a hydroxyl group did not correlate well with solvent polarity scales such as Brooker's* χ_R and χ_B, *Kosower's Z, and Dimroth and Reichardt's* $E_T(30)$, *while good correlations were observed between* E_T *of the azonia betaine-type dyes and the scales* χ_B, Z, *and* $E_T(30)$. *The solvatochromism was analyzed by the linear solvation energy relationship with the multiparameter proposed by the Kamlet, Abboud, and Taft group and showed excellent correlations for the azonia betaine-type dyes. The inherent wavenumber (*ν_0*) and the susceptibility of the absorption maximum (*ν_{max}*) to solvent polarity–polarizability (*π^**), to solvent hydrogen-bond donating acidity (*α*), and to solvent hydrogen-bond accepting basicity (*β*) are discussed.*

1 INTRODUCTION

Dye molecules have polarizable π-electron conjugated systems and their first absorption bands in the visible region arise from charge-transfer from an electron-donor moiety (D: auxochrome) to an electron-acceptor moiety (A: chromophore). Their absorption spectra are strongly influenced by the properties of solvents. This solvatochromic behavior depends on the structure of dyes, which can be classified into the following three types.[1]

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Type A dyes possess neutral conjugation, having a resonance system described by eqn (1):

$$[A{-}D \leftrightarrow A^{-}{-}D^{+}] \xrightarrow{h\nu} [A{-}D \leftrightarrow A^{-}{-}D^{+}] \qquad (1)$$

in which the neutral form (A—D) contributes more than the polar form (A^{-}—D^{+}) in the ground state and their contributions reverse in the excited state. This means that the polarity or the dipole moment increases by electronic transition from the ground state to the excited state. Therefore, with increasing solvent polarity the energy of the excited state is lowered more than that of the ground state, and this will result in a bathochromic (red) shift (positive solvatochromism). Typical examples of type A dyes are azo dyes and anthraquinone dyes.

Type B dyes possess an ionic conjugation in which the electron-acceptor moiety (A) is cationic, as shown in eqn (2):

$$[A^{+}{-}D \leftrightarrow A{-}D^{+}] \xrightarrow{h\nu} [A^{+}{-}D \leftrightarrow A{-}D^{+}] \qquad (2)$$

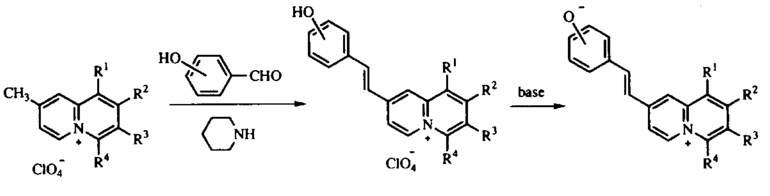
Since these dyes are ionic in both their ground and excited states, the polarity changes little with an electronic transition. Hence, only a slight solvatochromic shift will be observed with increasing solvent polarity. Dyes such as cyanines and triphenylmethyl cationic dyes are of type B.

Type C dyes have a dipolar conjugation, in which the electron-acceptor moiety (A) is cationic and the electron-donor moiety (D) is anionic, as shown in eqn (3):

$$[A^{+}{-}D^{-} \leftrightarrow A{-}D] \xrightarrow{h\nu} [A^{+}{-}D^{-} \leftrightarrow A{-}D] \qquad (3)$$

The dipolar resonance structure contributes more than the neutral one in the ground state, while the contribution reverses in the excited state. Therefore, these dyes are more dipolar in the ground state than in the excited state, and a hypsochromic (blue) shift will be observed with increasing solvent polarity (negative solvatochromism). Conjugated betaine dyes are also classified as type C dyes; a typical example is Dimroth and Reichardt's pyridinium *N*-phenoxide betaine dye.[2]

Azonia aromatic compounds are polycyclic aromatic conjugate systems having a quaternary nitrogen at the bridgehead position and they behave as π-conjugation systems with electron-accepting character.[3,4] By connecting it with an electron-donating group at the appropriate position, these azonia aromatic systems can absorb light in the visible region. Recently we have reported the synthesis of new stilbazolium merocyanine-type dyes **3a** and **3c** having benzo[*a*]- and benzo[*c*]quinolizinium rings, respectively (Scheme 1).[5,6] Dyes **3a** and **3c**, which contain a hydroxy group at the *ortho*- or *para*-position to the vinyl group in the phenyl moiety have cationic conjugation



1, 2 3a, c: *ortho-* or *para*-OH 4a, c: *ortho-* or *para*-O$^-$

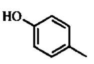
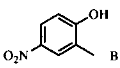
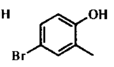
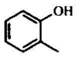
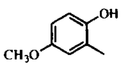
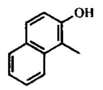
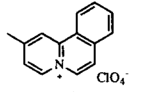
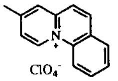
	R^1 R^2	R^3	R^4
1, 3a, 4a	$-(CH{=}CH)_2-$	H	H
2, 3c, 4c	H H	$-(CH{=}CH)_2-$	

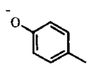
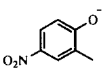
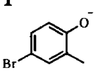
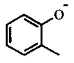
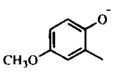
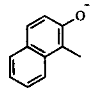
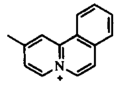
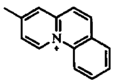
Scheme 1

and are classifed as type B dyes. The azonia betaine-type dyes **4a** and **4c**, in which the oxygen atom carries a negative charge, are classified as type C dyes. We found that the azonia betaine-type dyes **4a** and **4c** underwent a remarkable hypsochromic shift as the solvent polarity increased, and the pronounced negative solvatochromism extended almost over the whole visible region.[5,6] In this paper we discuss the solvatochromic character of stilbazolium merocyanine-type dyes of the type *X*—CH=CH—*Y*, in which *X* corresponds to benzo[*a*]quinolizinium and benzo[*c*]quinolizinium moieties, and *Y* is a substituted aryl group (Chart I).

Chart I

X-CH=CH-Y

X	Y					
						
	**5Ha**	**6Ha**	**7Ha**	**8Ha**	**9Ha**	**10Ha**
	**5Hc**	**6Hc**	**7Hc**	**8Hc**	**9Hc**	**10Hc**

X	Y					
						
	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
	**5c**	**6c**	**7c**	**8c**	**9c**	**10c**

2 EXPERIMENTAL

The stilbazolium merocyanine-type dyes were synthesized and purified according to our previous papers.[5,6] The hydroxy derivatives (**5Ha**, **7Ha–10Ha**, **5Hc**, and **7Hc–10Hc**) were prepared by the reaction of 2-methylbenzo[*a*]quinolizinium perchlorate (**1**) or 3-methylbenzo[*c*]quinolizinium perchlorate (**2**) with hydroxy-substituted benzaldehyde derivatives in the presence of piperidine as shown in Scheme 1. In the reaction with 5-nitrosalicylaldehyde the betaine dyes **6a** and **6c** were obtained. The azonia betaine-type dyes (**5a**, **7a–10a**, **5c**, and **7c–10c**) were produced *in situ* by the addition of piperidine (0·05 ml) into solutions (4 ml; *c*. 0·02 mM) of the hydroxy-substituted derivatives (**5Ha**, **7Ha–10Ha**, **5Hc**, and **7Hc–10Hc**) and subjected to UV/VIS spectral measurement. In order to avoid *trans-cis* photoisomerization, the solutions were handled in the dark. The UV/VIS spectra were recorded on a Hitachi 220A spectrophotometer. All solvents were purified and dried according to the literature procedure.[7]

3 RESULTS AND DISCUSSION

The electronic spectral data of ten stilbazolium merocyanine-type dyes (**5Ha**, **7Ha–10Ha**, **5Hc**, and **7Hc–10Hc**) are compared in Table 1. The solvatochromism of these dyes is rather small, as predicted by considering that they are conjugated cations (type B dyes): the hypsochromic shifts are generally less than 50 nm with change of solvent from 3-methylbutan-1-ol to water. On the other hand, the azonia betaine-type dyes (**5a–10a** and **5c–10c**) of type C show a large hypsochromic shift with increasing solvent polarity (Table 2). The intramolecular charge-transfer absorption band of dye **9c** shifted by 209 nm on going from acetone (λ_{max} = 720 nm) to water (λ_{max} = 511 nm). This solvatochromism is comparable to that of Dimroth and Reichardt's pyridinium *N*-phenoxide betaine dye (677 nm in acetone and 453 nm in water).[2] These results indicate that the azonia betaine-type dyes (**5a–10a** and **5c–10c**) can be used as indicators of solvent polarity, similarly to Dimroth and Reichardt's dye.

Brooker and co-workers introduced the empirical parameters of solvent polarity, χ_R and χ_B scales based on the π–π^* transition energies of a positive solvatochromic merocyanine dye and those of a negative solvatochromic merocyanine dye, respectively.[8] Kosower developed *Z*-values, which were obtained from the solvent-dependent intermolecular charge-transfer absorption band of 1-ethyl-4-methoxycarbonylpyridinium iodide.[9] The $E_T(30)$-values were proposed by Reichardt, *et al.*[10,11] They used the longest-wavelength intramolecular charge-transfer absorption of 4-(2,4,6-triphenyl-

TABLE 1
Electronic Spectral Data of Azonia Dyes

Solvent	*5Ha*		*5Hc*		*7Ha*		*7Hc*		*8Ha*		*8Hc*		*9Ha*		*9Hc*		*10Ha*		*10Hc*	
	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*	λ_{max} *(nm)*	ν_{max} *(10^3 cm^{-1})*
H_2O	405	24·69	415	24·10	398	25·13	411	24·33	399	25·06	411	24·33	406	24·63	415	24·10	418	23·92	432	23·15
CH_3OH	423	23·64	432	23·15	408	24·51	420	23·81	413	24·21	422	23·70	432	23·15	439	22·78	442	22·62	462	21·65
C_2H_5OH	430	23·26	441	22·68	414	24·16	425	23·53	417	23·98	429	23·31	440	22·73	450	22·22	450	22·22	470	21·28
CH_3CN	416	24·04	427	23·42	403	24·81	416	24·04	406	24·63	417	23·98	422	23·70	430	23·36	432	23·15	449	22·27
$(CH_3)_2NCHO$	425	23·53	434	23·04	409	24·45	420	23·81	413	24·21	424	23·59	432	23·15	441	22·68	439	22·78	460	21·74
$(CH_3)_2CO$	420	23·81	431	23·20	407	24·57	420	23·81	409	24·45	421	23·75	428	23·36	434	23·04	436	22·94	454	22·03

TABLE 2
Electronic Spectral Data of Azonia Betaine-Type Dyes

Solvent	**5a**		**5c**		**6a**		**6c**		**7a**		**7c**		**8a**		**8c**		**9a**		**9c**		**10a**		**10c**	
	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})	λ_{max} (nm)	ν_{max} (10^3 cm^{-1})
H_2O	472	21·19	482	20·75	—[a]	—[a]	—[a]	—[a]	—[b]	—[b]	—[b]	—[b]	471	21·23	481	20·79	501	19·96	511	19·57	520	19·23	556	17·99
CH_3OH	520	19·23	537	18·62	485	20·62	494	20·24	516	19·38	529	18·90	516	19·38	529	18·90	558	17·92	572	17·48	582	17·18	603	16·58
C_2H_5OH	553	18·08	571	17·51	503	19·88	515	19·42	545	18·35	561	17·83	546	18·32	562	17·79	594	16·84	612	16·34	609	16·42	630	15·87
CH_3CN	622	16·08	641	15·60	537	18·62	550	18·18	616	16·23	638	15·67	626	15·97	650	15·39	688	14·54	700	14·29	648	15·43	663	15·08
$(CH_3)_2NCHO$	637	15·70	655	15·27	545	18·35	558	17·92	630	15·87	654	15·29	642	15·58	669	14·95	702	14·25	727	13·76	659	15·18	675	14·82
$(CH_3)_2CO$	641	15·60	660	15·15	556	17·99	571	17·51	640	15·63	666	15·02	649	15·41	678	14·75	701	14·27	720	13·89	665	15·04	681	14·68

[a] Insoluble.

[b] Rather unstable.

pyridinium)-2,6-diphenylphenoxide to probe solvent polarities. The scales Walther's E_K,[12] Knauer and Napier's A_N,[13] and Dubois and Bienvenüe's ϕ[14] have also been proposed. Correlations between the transition energies (E_T) of the azonia dyes in six solvents and the above solvent polarity scales were examined. In the case of the hydroxy-substituted dyes (**5Ha**, **7Ha–10Ha**, **5Hc**, and **7Hc–10Hc**) no linear correlations were obtained, while E_T of the azonia betaine-type dyes (**5a–10a** and **5c–10c**) correlated well. The correlation coefficients (r) with the dye (**5a**) were 0·993 for Z, 0·997 for $E_T(30)$, 0·965 for A_N, and 0·960 for ϕ. χ_B also correlates well (r = 0·994), while no correlations with χ_R and E_K were obtained. These results suggest that the solvent polarity scales based on the spectral data of a single indicator dye can be applied only if solute–solvent interactions of the examined solute dye are close to those of the reference indicator dye.[1,15] Consequently, correlations with the solvent polarity scales based on multiple parameters were examined.

The Kamlet, Abboud and Taft group proposed the linear solvation energy relationships (LSER) with a multiparameter.[16] Solvent effects on absorption spectra are caused not only by solvent polarity and polarizability, but also by solvent hydrogen-bond-donating (HBD) and -accepting (HBA) characters. The absorption maximum (ν_{max}: 10^3 cm^{-1}) in a given solvent is expressed by eqn (4), where the parameter π^* is a measure of solvent polarity–polarizability, α a measure of solvent hydrogen-bond donor acidities, and β a measure of solvent hydrogen-bond acceptor basicities. The coefficients (s, a, and b) measure the relative susceptibilities of ν_{max} to the indicated solvent property scales.

$$\nu_{max} = s\pi^* + a\alpha + b\beta + \nu_0 \ (10^3 \text{ cm}^{-1}) \qquad (4)$$

The parameter ν_0 (10^3 cm^{-1}) corresponds to the wavenumber in a nonpolar solvent without hydrogen bonding character, such as cyclohexane. It can be considered to be the inherent wavenumber of the dye. The data listed in Tables 1 and 2, except for those in water, were analysed by multiparameter regression according to eqn (4), because dyes **6a** and **6c** are insoluble in water. The multiple linear-regression analysis shows good correlation, as summarized in Tables 3 and 4. The calculated wavenumbers (ν_{max}^{calcd}) correlate excellently with the observed values (ν_{max}^{obsd}), as shown in eqn (5).

$$\nu_{max}^{calcd} = 0{\cdot}9991\ \nu_{max}^{obsd} + 0{\cdot}0169\ (n = 110,\ r = 0{\cdot}9995) \qquad (5)$$

The azonia betaine-type dyes (**5a–10a** and **5c–10c**) have positive susceptibilities 's' and 'a' (Table 4). The results could be rationalized in terms of both the decrease in the dipole moment and the enhanced charge delocalization of the phenolate oxygen by excitation. Table 4 also shows that dyes

TABLE 3
Solvatochromic Parameters of Azonia Dyes

Parameters	*Compounds*									
	5Ha	*5Hc*	*7Ha*	*7Hc*	*8Ha*	*8Hc*	*9Ha*	*9Hc*	*10Ha*	*10Hc*
s	0·21	0·39	0·37	0·48	0·32	0·25	0·65	0·46	1·06	0·80
$-b$	1·49	1·21	1·07	0·67	1·21	1·17	1·59	1·85	1·27	1·64
ν_0	24·36	23·51	24·84	23·84	24·76	24·16	23·67	23·53	22·71	22·16
r	0·981	0·932	0·962	0·939	0·994	0·955	0·989	0·963	0·978	0·989

6a and **6c** have greater solvatochromic sensitivity for solvent polarity and polarizability compared to dyes **7a, c–9a, c**.

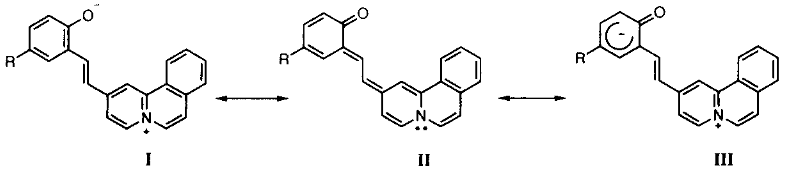
The conjugate system of the dyes can be approximately expressed as the hybrid of formulae I, II, and III as shown in Scheme 2. Formula III is a hybrid of the formulae having a negative charge on the benzene ring (IIIa–IIId), in which formula IIId should be considered only in the case of a nitro substituent (Scheme 3). The energies of these formulae can be assumed to be in the order: E(I) < E(II) < E(III). Furthermore, since formula III corresponds to a higher energy excitation of a local charge transfer in the phenolate moiety, the energy E(III) will be higher than E(I) and E(II). On the basis of these considerations the wave functions of the ground and the excited states (Φ_G and Φ_E) of the dyes would be expressed by the mixing of formula III with the in-phase (I + II) and the out-phase (I–II) hybrids, respectively.[17] Consequently, the wave function of the ground state (Φ_G) can be approximately written as follows:

$$\Phi_G = C_{IG}\Phi_I + C_{IIG}\Phi_{II} + C_{IIIG}\Phi_{III}, \qquad (6)$$

where $C_{IG} > C_{IIG} > C_{IIIG}$. On the other hand, the mixing of III with the out-phase wave function in the first excited state will be slight and consequently the wave function of the first excited state (Φ_E) will be approximated by the out-phase hybrid (I–II) as follows:

$$\Phi_E = C_{IE}\Phi_I - C_{IIE}\Phi_{II}, \qquad (7)$$

where $C_{IE} < C_{IIE}$. The squares of the developing coefficients (C) of eqns



Scheme 2

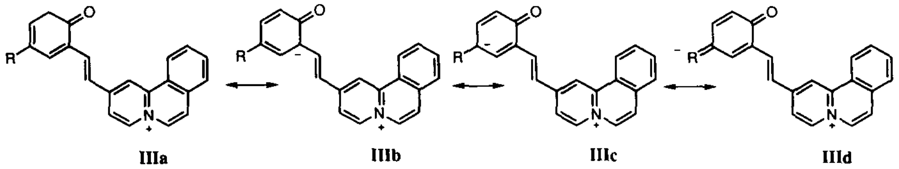
TABLE 4
Solvatochromic Parameters of Azonia Betaine-Type Dyes

Parameters	*Compounds*											
	5a	*5c*	*6a*	*6c*	*7a*	*7c*	*8a*	*8c*	*9a*	*9c*	*10a*	*10c*
s	3·21	3·13	3·66	4·07	3·60	3·89	3·27	3·61	2·11	2·41	2·66	2·63
a	4·33	4·15	3·35	3·50	4·54	4·72	4·73	4·98	4·20	4·20	2·66	2·40
ν_0	12·85	12·48	15·08	14·29	12·64	11·80	12·63	11·72	12·31	11·69	12·84	12·53
r	0·994	0·993	0·998	0·997	0·997	0·997	0·997	0·997	0·993	0·993	0·992	0·991
a/s	1·39	1·33	0·92	0·86	1·26	1·21	1·45	1·38	1·99	1·74	1·00	0·91

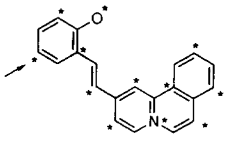
(6) and (7) denote the contributions of the respective resonance formulae. The dipole moment and the charge of the phenolate oxygen of I are larger than those of II, and consequently, the dipole moment and the charge of the oxygen should greatly decrease on a transition from the ground state to the first excited state. This consideration implies positive signs for both of the susceptibilities 's' and 'a'.

A substituent R with electron-withdrawing character will enhance the contribution of III in Φ_G due to the decrease in E(III), but will only slightly change the wave function Φ_E. The dipole moment in the excited state will be proportional to the contribution of I in Φ_E, which will only scarcely be affected by the substituent R. On the other hand, if the dipole moment of III is assumed to resemble that of I, the dipole moment in the ground state will be proportional to the sum of the contributions of I and III in Φ_G. The increase in the contribution of III by an electron-withdrawing substituent will cause an increase in the sum of the contributions of I and III in Φ_G, because the substituent decreases that of II and the total is constant. The electron-withdrawing substituent will thus cause an increase of the dipole moment in the ground state and a decrease of the dipole moment on excitation. Consequently, the values of 's' will be increased by an electron-withdrawing substituent, (R) in accord with the observations (Table 4).

Similarly the change of the charge of the phenolate oxygen by excitation will be proportional to the difference between the contributions of I in the ground and the excited states (Φ_G and Φ_E). The electron-withdrawing



Scheme 3



Scheme 4

substituent will decrease that of I in Φ_G by mixing of III, but it will only very slightly change that of I in Φ_E. Hence, an electron-withdrawing substituent will cause a slight decrease in the charge of the oxygen on excitation, and will be expected to decrease the value of the susceptibility '*a*'. This expectation is in accord with the observations, except in the case of a methoxy substituent, which decreases the susceptibility even though it has an electron-donating character. The electron-withdrawing substituent increases the value of '*s*', while it decreases that of '*a*'. Consequently, the ratio *a*/*s* will be expected to decrease with increase in the electron-withdrawing character of the substituent. This expectation is well in accord with the observations (Table 4).

The dyes (**5Ha**, **7Ha–10Ha**, **5Hc**, and **7Hc–10Hc**) have a positive and rather small value of '*s*', because the dyes are conjugated cations of type B. They also have a negative sign of '*b*' (Table 3), because solvents with hydrogen-bond-accepting character will shift the absorption band to longer wavelength due to the enhancement of the electron-donating ability of the phenolate oxygen.

Although no linear correlations between the inherent wavenumbers ν_0 and the Hammett substituent constants[18] were obtained, substituents at the 5-position of the phenyl moiety of the dyes (**8a** and **8c**) affected the position of the absorption maximum. Electron-withdrawing substituents cause a hypsochromic shift and this can be rationalized by using perturbation theory. The atoms (π-cores) of the π-electron system without an odd-membered ring are classified into two parities, the starred and the unstarred, as illustrated by Scheme 4, where the number of the starred atom is assigned in such a way that it is more than that of the unstarred atoms. When the conjugated π-system has an odd number of atoms, and the number of the electrons is one more than that of the atoms, the substituent effect on its first absorption band can be reasonably understood by Dewar's rules,[19] viz:

(i) an electron-donating group placed at the starred position will give a bathochromic effect, while an electron-withdrawing group will give a hypsochromic effect;
(ii) a substituent placed at the unstarred position will give the opposite effect.

Thus, the azonia betaine-type dyes (**6a**, **6c**, **7a** and **7c**) with an electron-withdrawing group (NO_2 and Br) placed at the starred atom give a hypsochromic shift, while dyes **9a** and **9c** having the electron-donating group OMe substituent, give a bathochromic shift in all of the solvents used.

Although the dyes (**5Hc**, **7Hc–10Hc**, and **5c–10c**) having a benzo[*c*]quinolizinium ring showed similar solvatochromic characters to the dyes (**5Ha**, **7Ha–10Ha**, and **5a–10a**) having a benzo[*a*]quinolizinium ring as described above, Tables 3 and 4 indicate that the parameters ν_0 of the former dyes are smaller than those of the latter dyes. This result can be explained on the basis that the electron-accepting character of the benzo[*c*]quinolizinium salt is larger than that of the benzo[*a*]quinolizinium salt.[20] The reduction potentials (versus SCE in acetonitrile) of benzo[*a*]quinolizinium salt and benzo[*c*]quinolizinium salt are −1·18 and −1·06 V, respectively.

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