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Solvatochromism of 1-(*p*-Aminostyryl)pyridinium Salts

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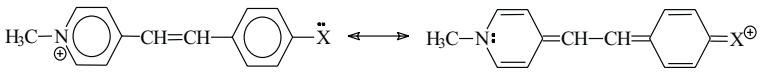
Solvatochromism of eighteen 1-methyl-(*p*-aminostyryl)pyridinium perchlorates was studied. For each solvent the $\tilde{\nu}_{max}$ values follow the σ_R^o substituent constants of the amino groups present in the molecule. The $\tilde{\nu}_{max}$ values for compounds are usually highest and lowest in water and in methylene chloride, respectively. The substituent bathochromic shifts in some solvents are as large as 5700 cm–1. No inverted solvatochromism is observed. Analysis of the spectra do not confirm also this effect to be negative. Dependence between the band position and solvent polarity, hydrogen bond donor acidity and hydrogen bond acceptor basicity is of low quality. There is no simple relationship between the $\tilde{\nu}_{max}$ values and the solvent dielectric constants.

Key words: 1-methyl-(*p*-aminostyryl)pyridinium salts, solvatochromism, substituent effect

Brooker's merocyanine [1-(4-aza-4-methylphenyl)-2-*trans*-(4-oxyphenyl)ethene, *trans*-4-[(1-methyl-4(1*H*)-pyridinylidene]-2,5-cyclohexadien-1-one], (X = O^-), [1,2] is a typical compound that exhibits an inverted solvatochromism [3]. This means that the shift of the long-wavelength $\pi \rightarrow \pi^*$ absorption band change from batho- to hypsochromic as the solvent polarity increases. Brooker's merocyanine and 1-methyl-(*p*-aminostyryl)pyridinium cations are isoconjugated systems. These compounds reveal inverted and negative solvatochromism, respectively [3,4]. Effect of the electron-donor strength of different amino groups present in their molecules on electron absorption spectra of these compounds is not known. This prompted us to study the solvatochromism of 1-methyl-2- and -4-(*p*-aminostyryl)pyridinium perchlorates:

Scheme 1



B **Q**

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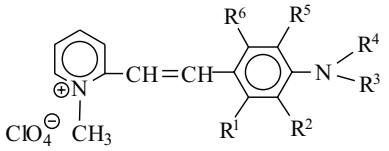
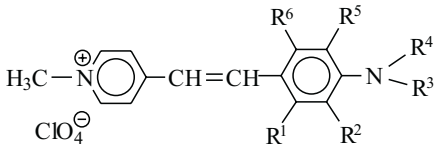
Scheme 2



1



2

	R^1	R^2	R^3	R^4	R^5	R^6
a	H	H	H	H	H	H
b	H	H	H	CH_3	H	H
c	H	H	CH_3	CH_3	H	H
d	H	H	CH_3	C_2H_5	H	H
e	H	H	C_2H_5	C_2H_5	H	H
f	CH_3	H	CH_3	CH_3	H	H
g	CH_3	H	CH_3	CH_3	H	CH_3
h	H	CH_3	CH_3	CH_3	H	H
i	H	CH_3	CH_3	CH_3	CH_3	H
j	H	H	$(CH_2)_4$		H	H
k	H	H	$(CH_2)_5$		H	H
l	H	H	$(CH_2)_6$		H	H
m	H	$(CH_2)_2$		CH_3	H	H
n	H	$(CH_2)_3$		H	H	H
o	H	$(CH_2)_3$		CH_3	H	H
p	H	$(CH_2)_4$		CH_3	H	H
q	H	$(CH_2)_2$		$(CH_2)_3$		H
r	H	$(CH_2)_3$		$(CH_2)_3$		H

In general, electron properties of different amino groups are affected by other substituents and bridges (rings) present in the molecule [5]. The optimum conformation of aromatic amines is a compromise between the tendency of the nitrogen atom to be pyramidal and its tendency to assume planar configuration, in order to maximize the resonance inter-action with the aromatic part of the molecule. Styrylpyridinium salts have interesting physical properties [6–12] that enable them to be applied in non-linear optics and in physiology/biochemistry areas [13–16]. 1-Methyl-2-(*p*-dimethylaminostyryl)pyridinium iodide is a powerful sensitizer for green light [17]. These compounds also show other very interesting properties, namely they become fluorescent upon infrared excitation [18,19]. Hemicyanine dyes, as exemplified by some stilbazolepyridinium salts, have been used as laser dyes [18,19].

EXPERIMENTAL

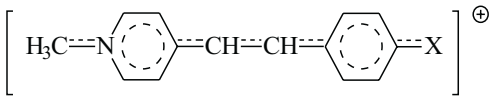
Syntheses of compounds **1** and **2** as well as conditions for recording the UV-VIS spectra (room temperature) were described earlier [20]. Spectral grade solvents were either commercially available or were prepared by standard methods.

NMR experiments were run with a Bruker Avance DRX 500 spectrometer equipped with an inverse 5 mm diameter probehead with a *z*-gradient for 0.1–0.2 M DMSO-d_6 solutions at 303 K. Acquisition and processing parameters of the NMR experiments are those reported earlier [21]. 2 D *z*-pulsed field gradient (PFG) selected ^{1}H, ^{13}C HMQC and ^{1}H, ^{13}C HMBC experiments were run to assign reliably the ^{13}C NMR spectra [21]. ^{15}N NMR chemical shifts (referenced to an external neat ^{15}N-enriched nitromethane, $\delta = 0.0$) are these obtained with the *z*-PFG ^{1}H, ^{15}N HMBC experiments [21].

RESULTS AND DISCUSSION

Inverted solvatochromism is observed when the increase in solvent polarity causes that the ground state of the compound changes from quinoid (**Q**) to benzenoid one (**B**). Contribution of each resonance form depends (Scheme 1) on the solvent used. The extreme bathochromic shift of the absorption band is observed when the charge is efficiently delocalized [3]:

Scheme 3



This usually happens in the chloroform-like solvents. Theoretical calculations show that the solvent affects markedly the molecular geometry of Brooker's merocyanine. Both polar and non-polar solvents stabilize the highly polar ground-state structures (**B** and **Q**), which differ from each other [3]. ^{1}H and ^{13}C NMR spectra evidence that Brooker's merocyanine exists as a resonance hybrid, which is weighed towards the zwitterion (**B**) even in solvents of low dielectric constants [22]. PM3 calculations show that large shifts observed in the UV-VIS spectra of these compounds are the results of much greater stabilizing effect of solvents with large dielectric constants on the more polar ground state of the merocyanine than they do on the first excited state [22].

Parameters of the UV-VIS spectra of compounds **1** and **2** are collected in Tables 1 and 2. No band intensities are available for these salts, which are not soluble in weakly polar solvents and insufficiently soluble in other solvents.

Compounds **1i** and **2i** seem to be unique. Due to the steric influence of two *ortho* methyl groups, the dimethylamino substituent is a very weak electron donor [5]. Steric influence of two methyl groups, neighbouring the ethylene bond in compounds **1g** and **2g**, is responsible for lowering of the band intensities in their spectra. In general, for each solvent the $\tilde{\nu}_{max}$ values follow the σ_R^o substituent constants [5] of the amino groups present in the molecule. Thus, the more strong electron-donor is the

substituent, the more bathochromically is shifted the $\pi \rightarrow \pi^*$ absorption band in its spectrum. This shows that the band position is strongly dependent on ability of the amino group to donate electrons. In such a case, contribution of the **Q** form is increased. It should be mentioned, however, that σ_R^o values are based on the ^{13}C NMR chemical shifts of *p*-amino-benzaldoximes in acetone solutions and cannot be treated as universal ones, due to peculiar influence of the solvent (*e.g.* due to possibility of formation of hydrogen bonds between the solvent and the amino group). This is why the linear dependence between the band position and substituent constant is of low quality.

Table 1. UV-VIS spectra of compounds **1** in different solvents; $\tilde{\nu}_{max}$ [kK] (first row), ε_{max} [M^{-1} cm^{-1}] (second row)[a].

	H_2O A	DMSO B	MeCN C	DMF D	MeOH E	EtOH F	AcMe G	CH_2Cl_2 H	THF I	AcOEt J
1a	25.25	22.37	23.70	23.70	22.99	22.62	23.15	22.87	22.08	23.64
	–	37300	31800	34500	29370	23900	33200	–	–	–
1b	24.04	21.83	22.52	21.83	21.93	21.69	22.22	21.01	21.98	22.78
	–	40400	40800	33900	40600	34400	37900	21000	–	–
1c	23.09	21.93	21.79	21.83	21.64	21.55	21.28	20.08	21.74	22.37
	–	37200	41100	37500	38800	35700	36300	19800	–	–
1d	22.47	21.60	21.65	21.55	21.41	21.32	21.65	19.76	21.55	22.08
	–	49800	47200	39500	41700	39100	42500	16000	–	–
1e	21.83	21.23	21.41	21.32	21.10	21.05	21.79	19.49	21.14	21.83
	–	33300	48000	39300	49900	39100	47200	11500	–	–
1f	23.09	21.69	21.65	21.60	21.46	21.31	21.41	19.69	21.51	22.03
	–	26200	28800	26700	24000	22300	30200	15300	–	–
1g	29.50	29.33	29.07	28.90	31.65	28.65	28.96	32.05	36.23	22.27
	–	14000	14400	15100	14900	11300	13900	–	–	–
1h	26.88	24.81	24.63	24.57	24.57	24.63	24.57	21.79	24.45	23.13
	–	28200	25300	21700	24200	21300	23500	7000	–	–
1i	27.40	24.75	24.81	24.87	25.32	25.19	24.57	29.76	25.19	26.22
	–	19900	18900	16700	17700	17000	16800	16600	–	–
1j	21.98	21.32	21.37	21.28	21.10	21.01	21.23	19.49	21.14	21.69
	–	41200	45900	40800	39500	36000	43600	34700	–	–
1k	25.32	22.22	22.32	20.96	21.93	21.83	22.17	20.58	21.83	22.78
	–	35100	32400	36000	33500	29200	35200	4600	–	–
1l	21.83	21.19	21.28	21.19	21.01	20.96	21.19	19.46	21.14	27.70
	–	48000	45800	43700	47400	41200	49200	41700	–	–

Table 1 (continuation)

1m	23.87	21.37	21.55	21.46	21.28	21.32	21.41	19.27	21.23	21.93
	–	30300	34600	31000	32600	27500	31700	20900	–	–
1n	28.25	21.10	21.51	21.19	21.10	20.79	21.37	26.11	21.14	27.40
	–	1900	2300	1800	2300	2000	1900	–	–	–
	–	27.47	27.55	27.55	27.86	27.55	26.95	–	27.32	b
	–	10200	14500	11900	11700	11500	15700	–	–	b
1o	21.98	20.96	21.01	20.96	20.83	20.70	20.96	19.12	20.88	21.37
	–	39300	41600	36100	39900	28000	39400	26300	–	–
1p	25.97	23.36	23.31	23.31	23.15	23.09	23.20	21.37	23.31	23.75
	–	26600	25300	24500	26100	22200	24700	4700	–	–
1q	23.87	20.58	20.53	20.62	20.33	20.24	20.49	18.25	20.24	19.96
	–	32600	34800	32900	34500	31800	33000	25000	–	–
1r	21.01	20.12	20.08	20.12	19.84	19.80	20.08	18.32	19.88	20.75
	–	43300	44600	40100	41000	39500	43200	45200	–	–

[a]Some intensities are missing due to low solubility of the compound.
[b]There is a very weak and very wide absorption band above 400 nm.

Table 2. UV-VIS spectra of compounds **2** in different solvents; $\tilde{\nu}_{max}$ [kK] (first row), ε_{max} [M^{-1} cm^{-1}] (second row)[a].

	H_2O A	DMSO B	MeCN C	DMF D	MeOH E	EtOH F	AcMe G	CH_2Cl_2 H	THF I	AcOEt J
2a	24.81	21.98	23.04	22.03	22.22	21.98	22.37	21.46	21.79	22.83
	–	41700	39600	40800	50600	24600	41700	–	–	–
2b	23.42	21.41	23.81	21.37	21.23	21.05	21.55	20.12	21.51	22.08
	–	30400	32035	42700	42900	36300	43852	42700	–	–
2c	22.22	21.32	21.28	21.23	21.05	20.96	21.19	19.12	21.14	21.74
	–	44700	44200	42600	40900	45900	43700	55100	–	–
2d	21.79	21.05	21.05	21.01	20.75	20.70	20.92	18.87	21.01	21.51
	–	44600	46900	46200	47200	44400	49300	55400	–	–
2e	21.19	20.70	20.70	20.75	20.45	20.45	20.66	18.66	20.79	21.19
	–	48200	54900	50600	49500	48700	51400	58400	–	–
2f	22.22	20.96	20.96	20.96	20.70	20.58	20.92	18.73	20.88	21.28
	–	30200	32500	30900	33600	33100	37300	38700	–	–
2g	23.09	21.19	21.10	21.14	20.83	20.79	20.96	18.80	21.05	21.55
	–	40400	37500	38300	34600	23100	35800	46200	–	–

Table 2 (continuation)

2h	26.04	23.81	24.15	24.04	23.98	23.98	23.87	21.10	23.75	24.39
	–	20800	29400	25900	27100	25100	3040	26800	–	–
2i	27.62	24.34	24.21	24.51	24.94	24.88	24.33	21.19	24.63	25.00
	–	24400	17200	18300	20500	18500	19500	16800	–	–
2j	20.70	20.62	20.70	20.79	20.49	20.41	20.62	17.45	20.70	21.19
	–	25600	52100	45800	51900	50600	51700	54900	–	–
2k	24.69	21.60	21.65	21.69	21.46	21.51	21.51	19.08	21.46	22.22
	–	35300	36400	34300	36300	32400	35100	38300	–	–
2l	21.28	20.66	20.66	20.66	20.24	20.37	20.58	18.62	20.58	21.05
	–	373000	49400	46300	45500	48700	51100	63100	–	–
2m	23.09	21.01	21.19	21.05	20.79	20.96	21.01	18.42	20.88	21.46
	–	28800	29200	30000	32300	28800	26400	–	–	–
2n	b	20.53	21.10	20.53	20.37	20.45	20.66	19.31	20.70	21.65
	b	4900	2500	3500	4100	3800	3600	–	–	–
	27.17	26.04	26.46	26.04	26.53	26.53	25.91	24.75	25.97	26.32
	–	20300	14700	15200	14200	13000	16300	–	–	b
2o	21.32	20.45	20.41	20.45	20.16	20.08	20.28	18.32	20.28	20.88
	–	41800	42900	42200	46200	40700	47100	57700	–	–
2p	25.32	22.83	22.73	22.78	22.64	22.78	22.68	19.34	22.73	23.26
	–	27000	29700	28900	28300	26600	27800	27300	–	–
2q	20.45	19.69	20.20	20.16	19.80	19.84	19.57	17.51	19.53	20.20
	–	26900	36300	28200	35100	26200	33400	48800	–	–
2r	23.64	20.49	19.57	19.69	19.31	19.31	20.00	17.48	20.16	20.75
	–	24300	29600	35600	48400	42300	26600	38900	–	–

[a]Some intensities are missing due to low solubility of the compound.
[b]There is a very weak and very wide absorption band above 400 nm.

The $\tilde{\nu}_{max}$ values for compounds **1** and **2** (Tables 1 and 2) are usually highest and lowest in water and in methylene chloride, respectively. The highest $\tilde{\nu}_{max}$ values were found for **1i** and **2i** that contain the highly strained (twisted) and weak electron-donor dimethylamino group. The $\Delta\tilde{\nu}_{max}$ values depend on solvent. The substituent bathochromic shifts in some solvents (MeOH) are as large as 5700 cm^{-1}.

Various solvents have different polarities. Moreover, they are more or less effective acids or bases and, thus, they may favour formation of the more or less strong hydrogen bonds with the solute. Nevertheless, dependences between the $\tilde{\nu}_{max}$ values for different solvents show that all of them reveal similar effects on the spectra of compounds **1** and **2**. For example, $\tilde{\nu}_{max}$ (DMF) *vs*. $\tilde{\nu}_{max}$ (MeOH) for series **2** gives the straight line (slope 0.8697, intercept 29062, R = 0.998, n = 18).

No inverted solvatochromism is observed for 1-methyl-(*p*-aminostyryl)pyridinium perchlorates studied. Analysis of the spectra do not confirm also this effect to be negative [4]. The $\tilde{\nu}_{max}$ values are not linearly dependent on E_T^N, even after rejection of weakly polar solvents (this was the case for Brooker's merocyanine [23]). Exclusion of protic solvents (H_2O, MeOH and EtOH) shows, however, that *p*-(aminostyryl)pyridinium perchlorates reveal the inverted solvatochromism. This also proves that there is the RO–H···N hydrogen bond present in solutions of **1** and **2** in these three solvents.

Two separate lines were obtained for the dependence $\tilde{\nu}_{max}$ of Brooker's merocyanine *vs*. π^* solvent polarity parameter (the sovents used were: DMSO, DMF, THF, dioxane, carbon tetrachloride, diethyl ether, triethylamine and cyclohexane) [23]. There is no such relation between $\tilde{\nu}_{max}$ in the spectra of compounds **1** and **2**, and π^*.

Equation (1) was used to see the dependence between the band position and solvent

$$\tilde{\nu}_{max} = a\pi^* + b\alpha + c\beta + d \qquad (1)$$

polarity (dipolarity-polarizability, π^* parameter represents a measure of polarity without a contribution from hydrogen bonding interactions) [24,25], hydrogen bond donor acidity (α) [26] and hydrogen bond acceptor basicity (β) [27]. Unfortunately, the quality of the correlation obtained is unsatisfactory (all the solvent parameters used were those compiled in [28]).

There is no simple relationship between the $\tilde{\nu}_{max}$ values and solvent dielectric constants. Except ethyl acetate and methylene chloride $\tilde{\nu}_{max}$'s follow the $\in$ values of the solvent [29], but the quality of the linear correlation is low.

The results obtained show that there are crucial differences between Brooker's merocyanine (zwitterion or highly polarized quinone derivative) and 1-methyl-(*p*-aminostyryl)pyridinum salts (positive charge in their cations is compensated by the negative charge of the counterions). In consequence, the former compound shows an inverted solvatochromism and 1-methyl-(*p*-aminostyryl)pyridinum salts do not. NMR spectra and AM1 calculations prove that there are many different nonplanar conformers and dimers of Brooker's merocyanine in chloroform and THF solutions [30]. Some its conformers disappear in low temperatures and this causes an increase in the concentration of the aggregates (dimers). The presence of the mentioned species in solution is shown by the multiple absorption band in its UV-VIS spectrum [30]. As seen in the UV-VIS spectra of compounds **1** and **2**, except **1n** and **2n**, no similar phenomenon was observed for 1-methyl-(*p*-aminostyryl)pyridinum salts studied.

Strong electron donor substituents are expected to favourize the **Q** form (over the **B** form) for compounds **1** and **2**. Increased contribution of the quinoid form results in lowering of the C–C ethylene bond order: –CH=CH– ↔ =CH–CH=. This means that the vicinal spin-spin proton-proton coupling constants in the ^{1}H NMR spectra of compounds **1** and **2** should follow the σ_R^o substituent constants. These ^3J(H,H) values are

equal to 15.1–17.2 and 15.9–16.4 Hz for compounds **1** and **2**, respectively. It is clear from ^{1}H NMR spectra recorded that, in general, the ^{3}J(H,H) coupling constants decrease for strong electron donor amino substituents in compounds **1**. However, the narrow range of ^{3}J(H,H) in the spectra of compounds **2** enables to follow the substituent effect. Increased values of ^{3}J(H,H) for **1g** (16.4 Hz) and **2g** (17.2 Hz) are, however, noteworthy.

The ^{1}H and ^{13}C NMR spectra support the structures and high purity of compounds **1** and **2**. The respective spectral data will not be discussed in the present paper. The chemical shifts for compounds **1c** and **2c** are in agreement with the chemical shifts for the respective iodides [31]. ^{15}N chemical shifts for two selected compounds are shown in Table 3. Large negative values of the substituent nitrogen atom may suggest that significant positive charge is localized there.

Table 3. ^{15}N chemical shifts (δ, with respect to external CH_3NO_2) of **1k** and **2j** for 0.1–0.2 M solutions in DMSO-d_6 at 303 K.

	N(pyridine)	N(substituent)
1k	–190.0	–300.8
2j	–192.5	–293.2

In conclusion, it can be stated that 1-methyl-(*p*-aminostyryl)pyridinum salts show no regular solvent effect. From this point of view, they differ from isoconjugated Brooker's merocyanine. Considering possible applications of these compounds in linear optics, biochemistry (physiology), polymerization processes and other areas of science and industry, their solvatochromism deserves to be further investigated.

Acknowledgment

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