DOI: 10.1002/chem.201000366

Studies of 2-Azaazulenium Derivatives: Unsymmetrical Trimethine Cyanine Dyes Bearing a 2-Azaazulenium Moiety as One of the Terminal Groups

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Abstract: We report here the synthesis of a series of symmetrical and unsymmetrical trimethine cyanine dyes derived from 2-azaazulene, combined spectral and quantum-chemical investigations of their molecular geometry and electron structure, as well as the nature of the lowest electron transitions. Based on the analysis of both calculations and experimental data obtained from absorption and ^{13}C NMR spectra, it was concluded that the 2-azaazulene residue can be treated as a weakly basic terminal group; its donor properties are provided with the participation of the HOMO−1, in contrast to the typical Brooker's terminal residues with their donor HOMOs. The new classification of the terminal groups of cyanine dyes, and hence the classification of types of unsymmetrical cyanines, is proposed. It is shown that the nature of the higher electron transitions (delocalized or local) in the cyanine dyes depends on their type. In the unsymmetrical trimethine cyanine of the mixed type, negative deviations are observed in their absorption spectra.

Keywords: absorption · azaazulenes · cyanines · density functional calculations · dyes/pigments · NMR spectroscopy

Introduction

Cyanine dyes, with their simple chromophores, represent suitable substrates for the testing of new theoretical concepts, beginning from the Hückel model[1–4] to the theory of solitonic charge waves.[5–8] One of the most important problems of the color theory of cyanine dyes is the investigation of charge distribution and the dependency of electronic transitions upon the degree of electron asymmetry. It was found both experimentally and theoretically[2, 9–13] that going from symmetrical dyes to chemically unsymmetrical cyanines affects considerably the electron distribution and spectral properties of the latter. In order to estimate quantitatively the degree of electron asymmetry, the parameter deviation D is traditionally used, so that the value of D can be calculated in the following way: $D=(\lambda_1+\lambda_2)/2-\lambda_{as}$, in which λ_{as} is the absorption maximum of the unsymmetrical dye, and λ_1 and λ_2 are maxima of the corresponding symmetrical parent molecules.[9] It was found that usually for unsymmetrical cyanines $D>0$, that is, the position of the absorption maximum for the unsymmetrical dye λ_{as} is shifted towards short wavelengths as compared to the arithmetic mean value from the maxima of the parent dyes. This spectral feature was related to the alternation of the C−C bond length along the polymethine chain (PC) if the terminal groups are non-equivalent.[2,9] At the same time, it was found that some unsymmetrical cyanines containing pyrylium residues or its heteroanalogues and benz[*c*,*d*]indolium derivatives demonstrate negative deviations,[14] which cannot be reasonably explained in the framework of the traditional concept of the deviations. One could expect this abnormal spectral effect to be connected with the peculiarities of the generation of the frontier molecular orbitals in cyanines containing terminal groups with their own extended conjugated systems.

In our previous paper,[15] devoted to the properties of symmetrical and unsymmetrical monomethine cyanine derivatives of 2-azaazulene, we discussed special features of the generation of the frontier MOs in the 2-azaazulene salt and dyes derived from it. However, the study of the regularities of the asymmetry influence was difficult due to the existence of considerable sterical hindrances in monomethine cyanines. For this purpose, a series of symmetrical (**1**) and unsymmetrical (**2**) trimethine cyanines was synthesized (in which Het represents the second terminal group, see

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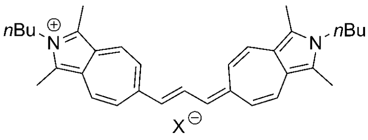

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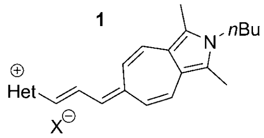

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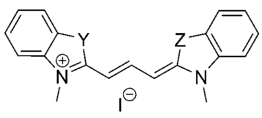
Table 1), because, clearly, dyes with longer polymethine chains should be more suitable.

Symmetrical indotrimethine (Ind) cyanine **3a**, benzimidazolo (BIm) trimethine cyanine **3b**, and the unsymmetrical dye **4** have also been investigated in order to be able to compare the effect of asymmetry in different types of cyanine dyes ($Y=Z=C(CH_3)_2$ (**3a**); $Y=Z=NCH_3$ (**3b**); $Y=NCH_3$, $Z=C(CH_2)_2$ (**4**)).



3a-b, 4

This paper presents the results of combined quantum-chemical and NMR (^{13}C) spectral studies of charge distribution in the ground state of some novel trimethine dyes, as well as the nature of the lowest electron transitions responsible for the long wavelength absorption.

Results and Discussion

Synthesis of trimethine cyanine dyes: The symmetrical trimethine cyanine (**1**) has traditionally been synthesized by the reaction of 2-butyl-1,3,6-trimethylcyclohepta[*c*]pyrrolium tetrafluoroborate (**5**) with triethyl orthoformate in acetic anhydride in the presence of anhydrous sodium acetate.

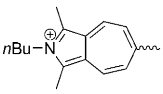
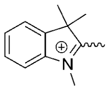
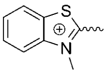
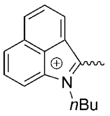
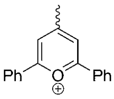
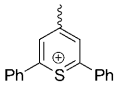
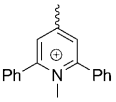
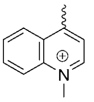
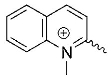
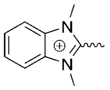
The general approach to the synthesis of unsymmetrical dyes **2** was described earlier.[16] This approach involves heating a mixture of compound **5** and a corresponding heterocyclic base **8**, containing a =CH−CHO group, in acetic anhydride. With the use 6-(2-anilinovinyl)-2-butyl-1,3-dimethylcyclohepta[*c*]-pyrrolium tetrafluoroborate (**6**), that is, the reaction product of salt **5** with *N*-ethoxymethylideaniline **7**, it was possible to synthesize the unsymmetrical trimethine cyanine dyes containing 2-quinolinium, 4-quinolinium, 2-benzimidazolium, and 2,6-diphenylthiopyrylium residues (Scheme 1).

Dye **2f** containing the 4-(2,6-diphenylpyridinium) terminal group was synthesized by the reaction of pyrylocyanine **2d** with methylamine in acetonitrile, as described previously[17] (Scheme 2).

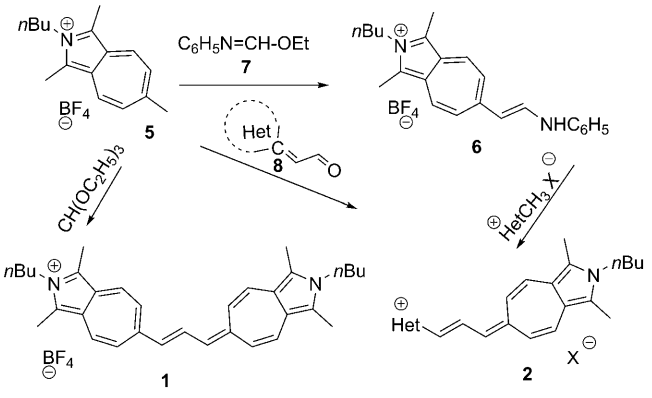
The spectral properties of the new dyes are presented in Table 1. The synthesis of trimethine cyanines **3a**,**b** have been reported previously,[18,19] and their spectral properties are collected in Table 2.

Optimized molecular geometry in the ground state: The calculations (by the DFT method)

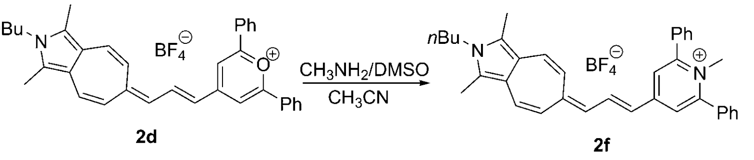
Table 1. Spectral properties of trimethine cyanine dyes **1**, **2a–k**.

Dye	Het^+ (X)	Abbreviation	λ_{max} [nm] ($\varepsilon \cdot 10^{-4}$ [$M^{-1}cm^{-1}$])		$\Delta\nu_{1/2}$ [cm^{-1}]		D [nm]
			CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	(CH_2Cl_2)[a]
1		AA	814 (23.84)	825 (25.26)	712.3	401.8	
2a		Ind	687 (11.03)	696 (11.82)	1728.4	853.37	−8.5
2b		BT	682 (9.31)	697 (15.09)	2766.98	853.24	−3
2c		BIn	788 (20.68)	798 (22.8)	696.04	531.98	−1
2d		OPy	747 (18.04)	758 (23.01)	766.95	641.90	−2.5
2e		SPy	782 (12.54)	794 (17.01)	1472.23	885.70	−0.5
2f		NPy	589 (4.29)	662 (4.81)	4082.76	3063.58	79.5
2g		4-Qu	659 (5.07)	744 (9.66)	3715.76	2041.01	27.5
2h		2-Qu	652 (6.69)	701 (12.84)	3544.72	1839.60	15.75
2k		BIm	509 (4.48)	560.0 (4.00)	5251.20	4630.4	96

[a] Absorption maxima for the corresponding symmetrical trimethine cyanines: In 550.5 nm; BT 563 nm; BIn 769 nm; 4-OPy 686 nm; 4-SPy 762 nm; 4-NPy 644 nm; 4-Q 718 nm; 2-Q 610.5 nm; BI 487 nm



Scheme 1. Synthesis of symmetrical and unsymmetrical trimethine cyanines.



Scheme 2. Synthesis of unsymmetrical trimethine cyanine bearing a 4-(2,6-diphenylpyridinium) terminal group.

Table 2. Spectral properties of trimethine cyanine dyes **3**, **4**.

Dye	Absorption spectra λ_{max} [nm] ($\varepsilon \cdot 10^{-4}$ [$M^{-1}cm^{-1}$]) CH$_3$CN	CH$_2$Cl$_2$	$\Delta\nu_{1/2}$ [cm^{-1}] CH$_3$CN	CH$_2$Cl$_2$
3a	541 (12.5)	550.5 (13.8)	1853.97	1803.52
3b	488 (13.4)	493 (12.6)	1819.73	1733.77
4	440 (2.8)	461 (3.9)	4499.32	4234.08

have shown that all investigated molecules **1–4** are practically planar (in accordance with B3LYP 3-21G**), which is typical for conjugated systems. It is only dyes **3b** and **4** that are slightly twisted due to the steric influence of methyl substituents. Both phenyl substituents in the trimethine **2f** also lie out of the plane of the heterocycle because of steric hindrance from the *N*-methyl group of the pyridinium ring.

Generally, there is no steric hindrance in the trimethine dye molecules that could disturb the effect of asymmetry, in contrast to the monomethine cyanines investigated in our previous paper.[15]

The calculated lengths of carbon–carbon bonds and valence angles in the PC of the symmetrical trimethine **1** as well as in the Ind (**3a**) and BIm (**3b**) trimethine cyanines are practically equalized, and are similar to the bond lengths in a usual polymethine chromophore, about 1.4 Å.[12] Also, the equalizing of the bond lengths results from the calculations for the C–C bonds within the terminal (AA) heterocycle, similarly to the initial AA salt, as described in reference [15].

At the same time, in spite of such important equalizing of the bond lengths in the open PC, their appreciable alternation from the center to each terminal group could arise. This was found to be dependent on the basicity of the terminal groups.[20] The values of the alternation of the bond lengths in the open PC of symmetrical dyes are calculated with Equation (1), in which l_ν is the length of the ν-th bond in the open PC. These values are presented in Figure 1 (top).

$$\Delta l_\nu = l_{\nu+1} - l_\nu \qquad (1)$$

One can see that the difference in the lengths of each central bond and the neighboring bonds (nearest to the corresponding terminal groups) decreases upon going from imidotrimethine **3a** to indotrimethine **3b**.

According to Brooker's concept of the basicity,[9] the BIm residue is treated as a highly basic terminal group, whereas the In nucleus is treated as a weakly basic terminal residue, which agrees with the decreasing of the degree of bond length alternation (BLA) in the symmetrical indocyanine **3a** in comparison with the BIm dye **3b**. In the case of dye **1**, the BLA Δl_ν is higher than this parameter even for the dye **3b** with highly basic terminal groups. More detailed analysis shows that the lengths of both bonds in the chain ends are 1.418 Å. The corresponding values for the other symmetrical dyes are 1.394 (**3a**) and

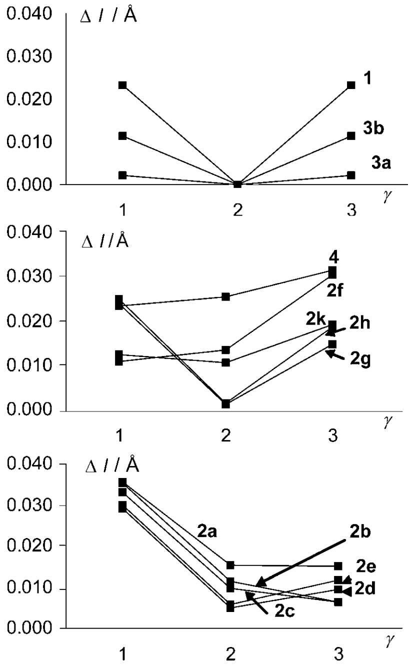


Figure 1. Alternation of the bond lengths in the open PC for symmetrical dyes **1** and **3a**,**b** (top); for unsymmetrical dyes **2g–k** and **4**, containing the highly basic residues (middle); for unsymmetrical dyes **2a–d**, containing more weakly basic terminal groups (bottom); γ is the number of the bond pair in the open PC.

1.406 Å (**3b**), whereas the lengths of the central bonds are close to the corresponding bonds in the imidotrimethine: 1.393 (**1**), 1.394 (**3b**), and 1.396 Å (**3a**). However, based only on the change of the parameter Δl_{ν} for the same bond in the symmetrical dye **1**, we could not interpret unambiguously the basicity of the AA residue.

It was postulated that upon proceeding from symmetrical polymethines to unsymmetrical dyes one could observe the appearance of an additional BLA along with the PC, from the terminal group with the higher basicity to the other, more weakly basic residue, with the degree of the alternation being proportional to the difference in donor strength of both terminal groups.[2,9,10,12] Thus, as we can see from Figure 1 (middle), in unsymmetrical dyes **2f–k** containing highly basic residues (NPy, BIm, 2-Qu, 4-Qu) as the second terminal group, the AA residue could be treated as a more weakly basic terminal group. The difference in the central bond lengths in the unsymmetrical dyes **2** should change upon increasing the degree of electron asymmetry. One can see from Figure 1 (middle) that the parameter Δl_{ν} for this pair of bonds decreases in the series: $\Delta l = 0.0253$ (**4**), 0.0134 (**2f**), 0.0104 (**2k**), 0.0014 (**2h**), 0.0011 Å (**2g-**). Thus, the asymmetry estimated with the BLA for central bonds in unsymmetrical dye derivatives of AA is lower than the asymmetry in the typical Brooker's unsymmetrical cyanine **4**.

As can also be seen from Figure 1 (middle), the alternation of lengths for the next pair of bonds in the open chain is half as high as that for the unsymmetrical cyanine molecule **2**, which is connected with the weakly basic AA residue, similarly to the unsymmetrical Ind–BIm trimethine cyanine **4**.

The calculated values Δl_{ν} for the other unsymmetrical dyes **2** containing weakly basic residues as the second terminal groups are presented in Figure 1, bottom. In contrast to the above-mentioned unsymmetrical dyes, the maximum of the BLA is reached for the bonds adjacent to the AA terminal group (compared with Figure 1, middle). The maximum difference in the central bond lengths is obtained for the dye **2a**: $\Delta l_{\nu} = 0.0153$ Å. This fact could be interpreted by the basicity of the AA terminal group exceeding the basicity of the weakly basic Ind residue. With regard to the other unsymmetrical cyanines **2a–e**, the parameter Δl_{ν} for the central bonds decreases in the dye series: **2a** > **2b** > **2c** > **2e** > **2d**.

The calculations reveal the minimum value for Δl_{ν} for the unsymmetrical dyes **2e** and **2d** containing SPy and OPy residues. Consequently, the donor strengths of these second terminal groups appear to be closer to the donor strength of the AA residue.

Charge distribution and ^{13}C NMR signals: It was established[15] that the considerable cyanine-like alternation of the charges at neighboring carbon atoms is observed for AA salt and AA terminal groups for monomethine cyanines, which was confirmed experimentally by NMR spectroscopy: the ^{13}C chemical shifts (δ_{μ}) are correlated with the calculated electron density values (q_{μ}) in the carbon atoms.

The same alternations of both atomic charges (q_{μ}) and the corresponding NMR signals (δ) are obtained for the AA residue as well as for the carbon atoms in the open chain of trimethine dyes **1** and **2**. The investigated calculated charges and measured chemical shifts of the dyes are collected in Table 3, and the alternation of the values Δq_{μ} and $\Delta\delta_{\mu}$ (μ = the number of the corresponding carbon atom in the open trimethine chain) calculated by Equations (2) and (3) for the open chain are depicted in Figure 2.

$$\Delta q_{\mu} = (-1)^{\mu}(q_{\mu} - q_{\mu+1}) \tag{2}$$

$$\Delta\delta_{\mu} = (-1)^{\mu}(\delta_{\mu} - \delta_{\mu+1}) \tag{3}$$

Experimental values $\delta_{\mu}(^{13}\text{C})$ show a significant alternation in the magnitude of the chemical shifts of the neighboring carbon atoms along with the whole chromophore of dye **1**, which is in good agreement with the corresponding calculated atomic charges.

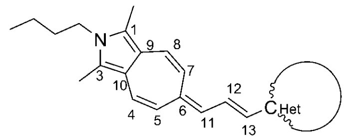
Figure 2 (top) shows a well-defined increase in the alternation of charges and chemical shifts for both pairs of central carbon atoms in the symmetrical dyes upon increasing the donor strength of the terminal groups: $\Delta q_{\mu} = 0.093$ (AA), 0.242 (Ind), 0.252 (BIm) for **1**, **3a** and **3b**, respectively, and $\Delta\delta_{\mu} = 11.14$ (AA), 46.85 (Ind), and 60.07 (BIm), for **1**, **3a** and **3b**, respectively.

Similarly to the BLA, we can use both calculated Δq_{μ} and experimental values $\Delta\delta_{\mu}$ to enable the estimation of the basicity of the terminal groups. Thus, we confirm the conclusion that azaazulenium residue should be considered as the weakly basic terminal group in the cationic cyanine dyes.

In the case of unsymmetrical dyes **2**, the carbon atoms in the α and α′ positions of the open chain become non-equivalent, and hence, both parameters Δq_{μ} and $\Delta\delta_{\mu}$ are different, the value of the charge and/or chemical shift alternation being larger for the pair of atoms positioned closer to the terminal group with the higher basicity, as one can see from Figure 2. Thus, the analysis of the charge distribution and chemical shifts, $\delta_{\mu}(^{13}\text{C})$, reveals unambiguously that the AA residue in the symmetrical and unsymmetrical cyanines, **1** and **2**, manifests itself as the terminal group with comparatively low donor properties. Such low basicity could be correctly interpreted by taking into consideration only the mutual arrangement of the donor and local orbitals of both the AA heterocycle and the corresponding cyanine dyes.

Two approaches for the generation of HOMOs in symmetrical trimethine cyanines: As established earlier,[21] terminal groups with their own highly localized orbitals can make the main contributions to the highly occupied MOs of cyanine dyes with comparatively short PCs. Taking into account that the positive charge in the cationic polymethine dye is localized practically in the external PC, symmetrical dyes **1** or **3** can be presented as the following system: D–π(+)–D or D–A–D, in which the acceptor A is a PC, and D is a donor residue. Due to the additional electrons contributed by terminal donor groups, such a conjugated system becomes a charge-

Table 3. The experimental chemical shifts of the ^{13}C NMR signals from the carbon atoms and corresponding calculated charges for trimethines **1** and **2a–k**.



Carbon atom number	δ [ppm]; (experimental) / *q* [a.u.] (B3LYP/6-31G**; NBO)				
	1[a]	**2a**[a]	**2b**[a]	**2c**[a]	**2d**[b]
1	131.98/0.222	131.69/0.221	130.77/0.221	132.25/0.220	130.00/0.219
3	131.98/0.225	131.69/0.223	130.77/0.223	132.25/0.223	130.00/0.221
9	121.53/−0.111	120.87/−0.108	–/−0.108	122.15/−0.108	121.57/−0.108
10	121.53/−0.108	120.87/−0.106	–/−0.106	122.15/−0.106	121.57/−0.106
4	135.37/−0.135	134.90/−0.135	132.34/−0.136	136.98/−0.138	128.80/−0.139
8	135.37/−0.134	134.90/−0.135	132.34/−0.135	136.98/−0.137	128.80/−0.139
5	123.80/−0.245	–/−0.240	119.80/−0.240	123.80/−0.238	127.00/−0.238
7	123.80/−0.252	–/−0.245	118.21/−0.244	123.80/−0.243	127.00/−0.243
6	156.98/0.004	157.51/0.022	153.94/0.021	158.94/0.015	149.99/0.014
11	130.95/−0.258	127.07/−0.267	125.24/−0.266	130.64/−0.256	126.90/−0.255
12	142.09/−0.165	146.05/−0.135	144.25/−0.141	143.74/−0.143	144.68/−0.149
13	130.95/−0.258	106.92/−0.339	108.26/−0.356	110.00/−0.304	123.69/−0.268
C$_{Het}$	156.98/0.004	174.74/0.310	167.74/0.081	153.20/0.263	160.94/0.013

Carbon atom number	δ [ppm]; (experimental) / *q* [a.u.] (B3LYP/6-31G**; NBO)				
	2e[a]	**2f**[b]	**2g**[a]	**2h**[a]	**2k**[a]
1	131.80/0.218	130.45/0.214	129.34/0.218	129.98/0.219	129.19/0.217
3	131.80/0.222	130.80/0.216	129.53/0.220	130.05/0.221	129.51/0.219
9	–/−0.108	120.25/−0.112	118.95/−0.109	119.42/−0.110	118.54/−0.112
10	–/−0.106	119.98/−0.109	118.70/−0.107	119.18/−0.108	118.34/−0.110
4	126.50/−0.139	128.93/−0.151	128.74/−0.143	130.58/−0.141	127.97/−0.146
8	126.50/−0.139	128.67/−0.149	128.06/−0.142	129.98/−0.140	127.76/−0.144
5	126.80/−0.237	127.47/−0.238	128.28/−0.238	126.34/−0.240	125.82/−0.242
7	126.80/−0.242	118.91/−0.244	118.11/−0.243	118.34/−0.245	117.47/−0.249
6	148.00/0.013	150.00/0.005	149.29/0.012	151.90/0.015	148.52/0.012
11	126.30/−0.251	126.72/−0.262	126.97/−0.257	126.65/−0.265	124.47/−0.278
12	138.29/−0.154	139.84/−0.153	139.97/−0.147	143.89/−0.144	141.71/−0.155
13	122.89/−0.258	122.35/−0.280	117.93/−0.270	115.39/−0.328	103.94/−0.379
C$_{Het}$	–/0.004	154.10/0.005	151.29/0.027	154.64/0.236	148.25/0.459

[a] Recorded in [D$_6$]DMSO. [b] Recorded in CD$_3$CN.

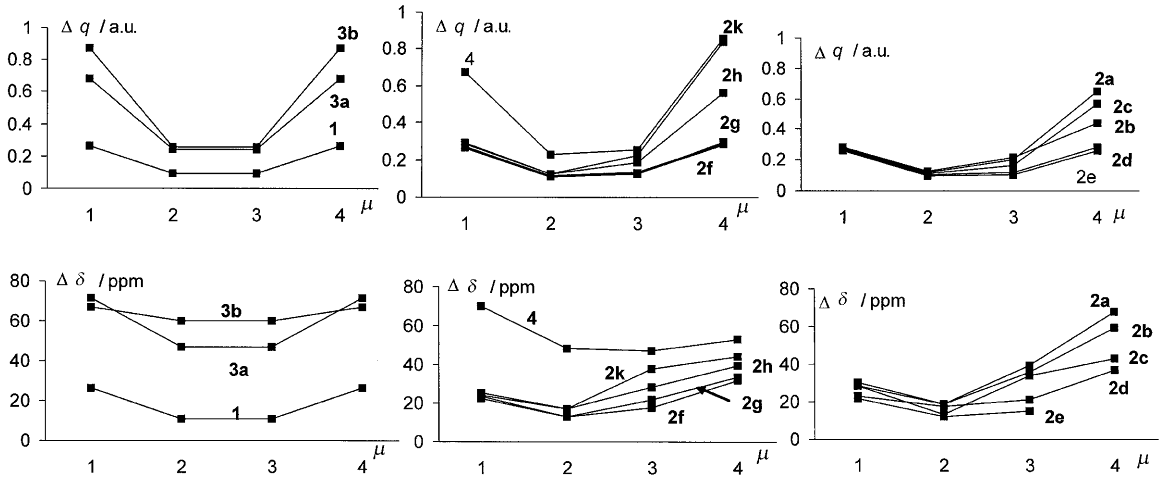
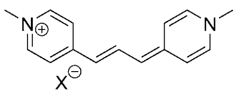


Figure 2. Alternation of calculated charge distribution (B3LYP/3-21G** NBO) (top) and experimental ^{13}C NMR shifts (CDCl$_3$) (bottom) for compounds **1**, **2a–k**, **3a**,**b**, and **4**.

excessive one whilst keeping the same total charge. As a result, the highest occupied MOs (HOMO) are formed by interaction of the initial orbitals of both terminal conjugated residues, especially in the case of dyes with short PC.



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There are two main ways of generating the HOMO in the symmetrical polymethine dyes D–A–D. For convenience of interpretation, we will consider the trimethine cyanines containing the symmetrical terminal groups (model pyrido carbocyanine **9** and AA dye **1**). In these cases, the unsymmetrical local MOs of the terminal groups have their nodes at reference atoms which are connected with the PC.

It should be mentioned that for simplicity we consider here a dye structure **9** that is unsubstituted in the 2- and 6-positions of the pyridinium ring, instead of the 2,6-diphenyl substituted molecule **3b**. These changes do not affect the main characteristics discussed.

From Figure 3a one can see that the HOMO of the initial salt 1,4-dimethylpyridinium cation has no nodes at the 4-position. This HOMO could be treated as a donor orbital. Hence, in the symmetrical dye **9**, HOMOs (as donor orbitals) of both pyridinium residues are conjugated with the PC as well as with each other, as presented in Figure 3b. As shown earlier,[21] their interaction leads to the splitting of donor orbitals, resulting in two new MOs which, in the first approximation, could be presented by the symmetrical and unsymmetrical linear combination of the HOMOs of each of the two terminal groups $\phi(\mathrm{D}_1)$ and $\phi(\mathrm{D}_2)$, as given in Equations (4) and (5), that is, the corresponding two levels could be interpreted as two split donor ones, as the chain is considered to be a common external conjugated substituent for each donor D.

$$\phi_1 = (2)^{1/2}\{\phi(\mathrm{D}_1) + \phi(\mathrm{D}_2)\} \tag{4}$$

$$\phi_2 = (2)^{-1/2}\{\phi(\mathrm{D}_1) - \phi(\mathrm{D}_2)\} \tag{5}$$

It should be mentioned that the considerable interaction of the initial orbitals of terminal groups, and, hence, their splitting, causes the comparatively deep color of cyanine dyes.[21]

In contrast to the HOMO of the terminal pyridinium residue, the previous occupied orbital, HOMO−1 (see Figure 3a) has its node at a carbon atom connected with the chain, hence it cannot conjugate with the rest of the molecule and remains as a "pure" local MO. As a result, two local orbitals of both terminal groups produce two degenerate occupied MOs in the symmetrical pyrido trimethine cyanine **9** (Figure 3b). This approach to the generation of the two highest occupied orbitals is the same for the traditional cyanines with, for example, 2-Qu, 4-Qu, Ind, BIm, and BT residues as terminal groups.

It has to be noted that the donor strength of the terminal group is determined by the position of the highest occupied level in this residue, which produces the HOMOs of the symmetrical cyanine dyes. We will call these heterocycles the terminal groups of "Brooker's cyanine type" (BC-type).

A fundamentally different way to generate the HOMO can be realized in the dye **1**, bearing the AA residues as the terminal groups. As seen in Figure 3c, the HOMO of the initial salt **5** has its node at the carbon atom connected with the PC. Thus, two local MOs give two degenerate orbitals in the dye **1**: HOMO−1 and HOMO−2, as shown in Figure 3d. Meanwhile, the next MO of the salt can interact

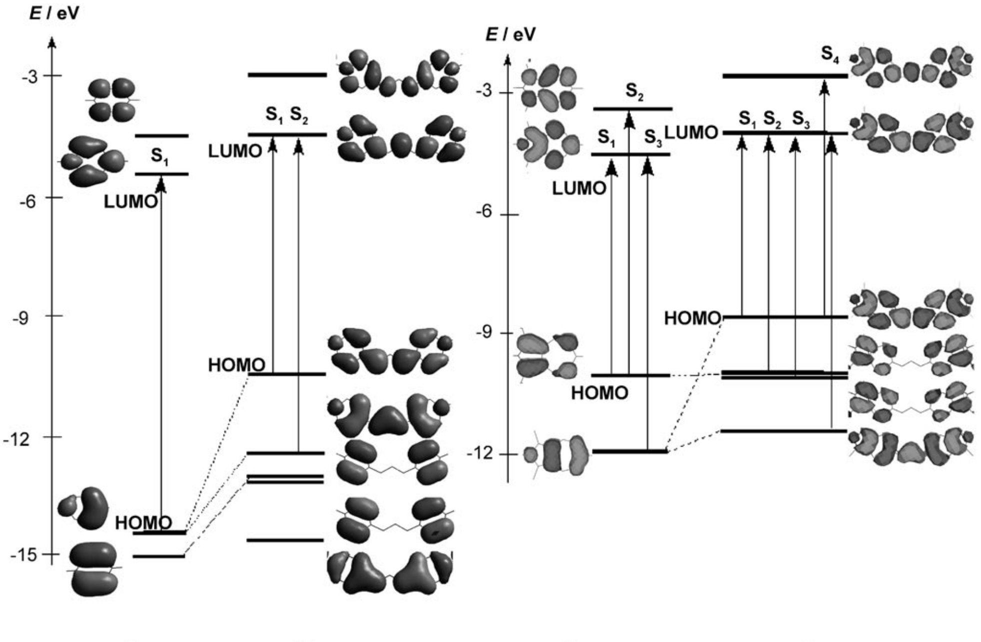

Figure 3. Two approaches for the generation of molecular orbitals. Left: in pyrido trimethine (b) from HOMO of its salt (a); right: in AA trimethine cyanine (d) from HOMO−1 of its salt (c).

with the chain and, hence, with the corresponding MO of the second terminal group, because of the absence of the molecular node at the 7-position, resulting in two splitting MOs: HOMO and HOMO−3, so that the local MOs prove to be situated between the splitting orbitals (see Figure 3d). To distinguish such heterocycles (OPy, SPy, BIn) from residues of the BC-type, we will call them terminal groups of azaazulene type (AAz-type).

It should be noted that electron transitions from the four highest occupied MOs to the LUMO and LUMO+1 are responsible for the absorption spectra in the visible region.

Three approaches to generate HOMOs in unsymmetrical trimethine cyanines: On the grounds of the known investigations of Brooker[9,22], unsymmetrical cyanine dyes could be considered as derivatives constructed from the corresponding parent symmetrical cyanines. Taking into account the difference in the generation of the HOMOs in the symmetrical dyes containing the terminal groups of the two types mentioned above (BC- and AAz-type), we can assume that there are three possible ways to generate the highest occupied molecular orbital (HOMO) in the unsymmetrical dyes and, hence, three types of unsymmetrical cyanines exist:

BC–BC-type (or "pure" BC-type): The unsymmetrical cyanine is made up from symmetrical dyes of the first type (BC), for example, the IndBIm-trimethine cyanine **4**. In both parent symmetrical dyes, Ind- and BIm-trimethines, the splitting donor HOMO and HOMO−1 are formed from the HOMOs of the terminal groups, similarly to the pyrido trimethine **6** (Figure 3a). The shapes of the frontier and the nearest MOs are presented in Figure 4a. One can see that both the HOMO and HOMO−1 are similar to the two highest occupied orbitals in the symmetrical cyanine of the BC-type, so we can also treat these MOs as donor orbitals. At the same time, the LUMO is shifted to the BIm residue, which is connected with the higher basicity of this terminal group (as compared with the In residue), and, hence, with the corresponding shifting of the positive charge in the PC. Vice versa, the HOMO is shifted to the Ind residue, and the HOMO−1 is delocalized uniformly along the whole chromophore.

BC–AAz- or AAz-BC-type (mixed type): An unsymmetrical cyanine is constructed from the symmetrical dyes of different types, for example, dye **2a**. As seen from Figure 3b, one initial symmetrical parent AA cyanine **1** is the AAz-type dye, whereas the corresponding Ind cyanine **3a** is the BC-type dye. The main feature of this type is the disposition of the local level, HOMO−1, of the AA residue between the splitting levels: HOMO and HOMO−2. Comparison of Figure 3b and Figure 4b shows that the positions of the local levels in the symmetrical dye **1** and unsymmetrical cyanine practically coincide, which is explained by the absence of the interaction of the local MOs of the terminal groups, because of the molecular node at the carbon atom connecting the heterocycle with the polymethine chain. One of the splitting orbitals, HOMO, is delocalized relatively uniformly along with the whole chromophore, including the chain and both terminal groups, whereas the second splitting orbital, HOMO−2, is shifted to the Ind residue. At the same time, the LUMO is delocalized along the whole chain and branched π-system of the AA residue, which could be treated as lengthening of the chromophore.

AAz–AAz-type ("pure" AAz-type): The unsymmetrical cyanine is made up from the symmetrical dyes of the AAz-type, for example, the dye **2d**, containing AA- and 4-OPy terminal groups. Figure 4c shows that two local MOs are disposed between the splitting orbitals, HOMO and HOMO−3; one orbital is located totally at the AA residue, and the second local orbital is localized at atoms of the 2,6-diphenylpyrilium residue.

Absorption spectra and electron transitions: Figure 5 (top) shows UV/Vis absorption spectra of the symmetrical trimethine cyanines containing heterocyclic residues of different basicity: AA (**1**), In (**3a**), and BIm (**3b**) in polar acetonitrile and in nonpolar CH_2Cl_2. The spectra of the unsymmetrical dyes are presented in Figure 5 middle (all combinations of the terminal groups mentioned

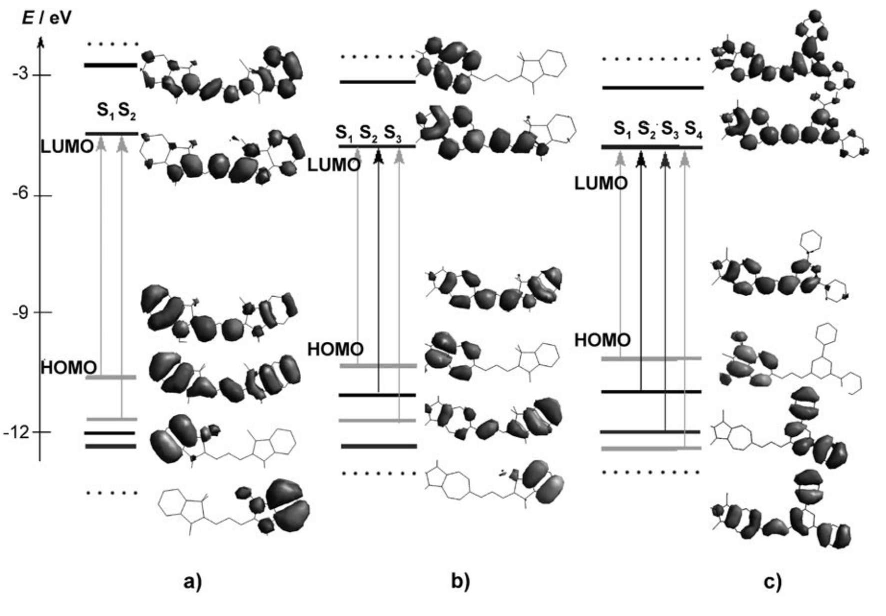

Figure 4. Molecular orbitals and electron transitions in unsymmetrical trimethine cyanines of **BC**-type (a), **AAz-BC**-type (b), **AAz**-type (c).

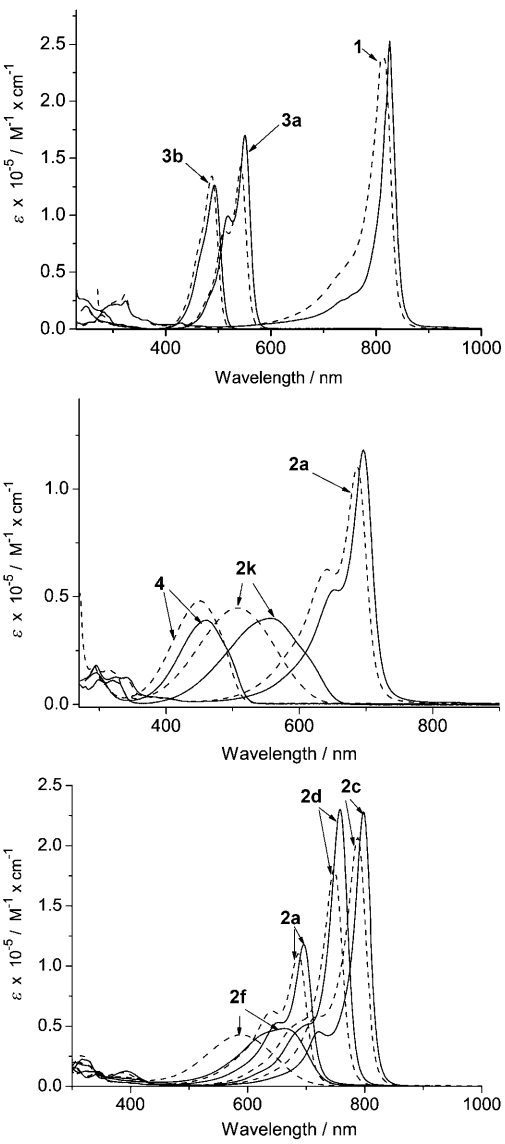

Figure 5. Absorption spectra of trimethines in methylene chloride (solid line) and acetonitrile (dashed line). Top: the symmetrical trimethine cyanines containing the heterocyclic residues of different basicity. Middle: unsymmetrical trimethines (combinations of the terminal groups In, AA, BIm). Bottom: comparison of unsymmetrical AA dyes bearing the second terminal group characterized by different basicity.

above) and bottom (combinations of the azaazulene residue and some other heterocycles).

One can see that, typically for cyanines, highly intense and highly selective spectral bands are observed for all symmetrical dyes. The absorption of the AA-trimethincyanine **1** is considerably red shifted to 825 nm (CH_2Cl_2), compared to the position of the long-wavelength spectral bands of the known "Brooker's" cyanine dyes **3a** and **3b**. In our previous paper,[15] we have shown that this effect is connected with the comparatively large effective length, L, of the azaazulene as an aza analogue of the non-alternate bicyclic hydrocarbone. The parameter L corresponds to the effective lengthening of the chromophore by including of the π-electrons of the terminal residue to the total conjugated system, and can be calculated from the equation: $\lambda_n = V(n+L)$, in which V is the vinylene shift in a vinylogous series of symmetric dyes with a specific terminal group, and n is the number of vinylene groups in the PC. Thus, the parameter L can be estimated experimentally by the following expression: $L^{\text{eff}} = (\lambda_{\max} - nV)/V$. The effective length can be also calculated in the approximation of the polymethine with a long chain.[23]

Taking into consideration that the vinylene shifts for each out of three vinylogous series of dyes bearing AA-, In-, and BIm- terminal groups are approximately equal ($V \approx 100$ nm), we have obtained for these heterocycles the following rough values of effective lengths: $L^{\text{eff}} = 4.13$ (BIm); 4.48 (Ind); 7.14 (AA). In other words, in the trimethine cyanine dyes, the replacement of the typical "Brooker's" terminal groups by the nitrogenic analogue of the non-alternate hydrocarbon (AA residue) is accompanied by a significant increase in the magnitude of effective length, and hence by a considerable bathochromic shift of the absorption band (see Figure 5, top).

According to quantum-chemical calculations (AM1 and ZINDO/S) of cyanine dye characteristics in ground and excited states, the first electron transition is described by a practically "pure" configuration with the single occupied HOMO and LUMO (see data in Table 2). The principal difference between the nature of the lowest electron transition in the initial AA salt and cationic cyanines based on this heterocycle was discussed earlier in detail;[15] here it was established that both frontier MOs are totally delocalized along the whole chromophore. As a result, the typical cyanine-like lowest electron transition is responsible for the principal cyanine-like spectral properties: a high intense and selective spectral band with its vinylene shift of ≈100 nm. This transition is accompanied by electron-density transfer from the carbon atoms in even positions to the atoms in odd positions, that is, to the neighboring atoms, along the total chromophore, including the open chain and both terminal groups, just in the same way as observed in the monomethine cyanine.[15] Also, similarly to the monomethine cyanine, the next two electron transitions in the symmetrical trimethine cyanine **1** containing AA terminal residues involve one local MO and the LUMO. Consequently, they can be treated as local electron transitions. By definition, both local transitions are initially degenerate. The interaction between them leads to the splitting and hence to the creation of two new local states, which are the sum and difference of both initial local orbitals: Loc(+) and Loc(−).

The analysis of the diagrams of the electron density redistribution reveals that both local transitions are localized in AA terminal groups and are practically equal to those of azaazulenium salt **5**, similarly to the dyes with shorter PC.[15] Additionally, local transitions also include an atom in the chain center that is in vinylogous position relative to the atom of AA (or Py) connected with PC. One can see that the $S_0 \rightarrow S_1$ transition in unsymmetrical cyanines of both AAz-BC- and AAz-types is not the same as the one in the unsymmetrical cyanine of BC-type. Besides, two different local transitions appear in the unsymmetrical dye of AAz type: $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$, located in the AA and Py residues, respectively.

Now, let us discuss the absorption spectra and electron transitions of unsymmetrical dyes. First of all, one can see from Figure 4 that the HOMOs in the dyes of all three different types considered above are of the same nature as one of the splitting donor MOs, whereas the LUMOs could be treated as the levels of the positive charge.

Consequently, the nature of the first electron transitions in all unsymmetrical cyanines investigated here is the same. Figure 6 shows that the asymmetry causes only a slight distortion of the usual transfer of the electron density between neighboring atoms. This conclusion is in good agreement with the similar intensity and shapes of the long-wavelength bands in the absorption spectra presented in Figure 5. It should be mentioned that the absorption band half-width ($\Delta\nu_{1/2}$) and molecular extinction coefficients of the unsymmetrical dyes of the AAz type (**2c** and **2d**, see Table 1, Figure 5, bottom) are practically the same as the ones in the symmetrical trimethine cyanine **1**. Also, these dyes are moderately sensitive to solvent polarity, analogously to the symmetrical dye **1**. Similarly, the shape and sensitivity of the spectral band of the Brooker's type unsymmetrical dye Ind-BIm **4** to the nature of solvents differ only slightly from the spectral characteristics of the corresponding symmetrical dyes; thus, the band half-width $\Delta\nu_{1/2} = 1198\ \mathrm{cm}^{-1}$ is close to this parameter for the "parent" indotrimethine cyanine ($1051\ \mathrm{cm}^{-1}$ in ethanol).

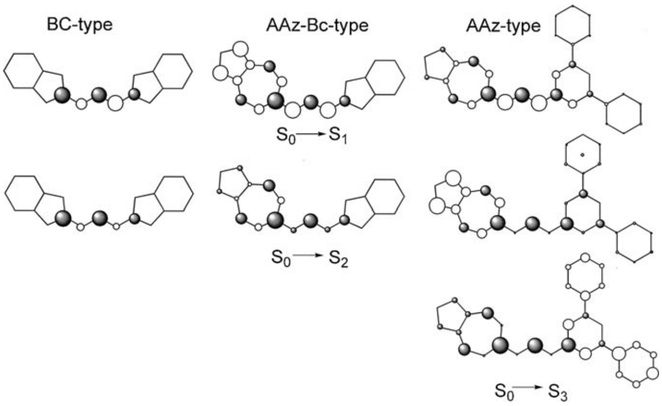

Figure 6. Redistribution of the electron density upon excitation for unsymmetrical trimethines of different types: empty circle: electron density decreases; full circle: electron density increases.

In contrast, the effect of asymmetry is much more pronounced in the unsymmetrical dyes of the mixed type: BC–AAz. From Table 1 one can see that the magnitudes of band half-widths $\Delta\nu_{1/2}$ of the dyes AA-NPy (**2f**), AA-Qu-2 (**2h**), AA-Qu-4 (**2g**) are much larger in comparison with the AAz dyes considered above. On the other hand, an increase in solvent polarity leads to the essential blue shift of the long-wavelength band in the spectra of unsymmetrical dyes containing highly basic pyridinium and quinolinium residues as a second variable terminal group.

To estimate quantitatively the degree of asymmetry of unsymmetrical cyanines by their absorption spectra, we used a parameter deviation D proposed by Brooker.[9] This parameter is calculated according to Equation (6), in which λ_{as} is the absorption maximum of the unsymmetrical dye, and λ_1 and λ_2 are maxima of the corresponding symmetrical parent molecules.

$$D = (\lambda_1 + \lambda_2)/2 - \lambda_{as} \tag{6}$$

It was found[2,9,11,12] that for typical unsymmetrical cyanines that $D > 0$, that is, the positions of the maxima for unsymmetrical dyes λ_{as} are shifted in the direction of shorter wavelengths as compared to the arithmetic mean value from the maxima of the parent dyes.

The calculated magnitudes of deviations for unsymmetrical cyanines **2** are collected in Table 1. One can see that the values of D are negligible for unsymmetrical cyanines of AAz-type with both weakly basic terminal groups ($D_{\mathbf{2c}} = -1$, $D_{\mathbf{2d}} = -2.5$, $D_{\mathbf{2e}} = -0.5$), in contrast to the appreciable magnitude of D for unsymmetrical dyes of mixed type, but with highly basic terminal groups. The increase in basicity of the variable terminal residue in the series: Qu-2, Qu-4, and NPy leads to the regular increase of the deviation for the corresponding dyes: $D_{\mathbf{2h}} = 15.75$, $D_{\mathbf{2g}} = 27.5$, $D_{\mathbf{2f}} = 79.5$.

Earlier,[2,9,11,12] this spectral effect was explained to be connected with the appearance of alternation of C–C bond lengths along the PC, if the terminal groups are non-equivalent. However, according to the results of our calculations discussed above (see Figure 1), there is no regular alternation of the bond lengths along the chain from one terminal group to another in the investigated unsymmetrical cyanines **2**. A similar phenomenon was described by Tolmachev et al.[14] by the example of unsymmetrical indopyrilo tri- and pentamethines, with $D = 117$ and 150 nm, respectively. This spectral effect cannot be explained by the existence of any "specific" BLA.

We assume that the deviation is connected with the distinction in the generation of initial donor orbitals, and, therefore, with the appearance of the distance between them in unsymmetrical dyes containing non-equivalent terminal groups, in contrast to the degeneracy of donor levels in symmetrical dyes. Taking into account the fact that the dispositions of the initial orbitals of each terminal group are different, we should consider the interaction between initial donor MOs. Hence, the values of splitting energy are lower, compared with the corresponding symmetrical parent cyanines with their degenerate initial MOs, according to Equation (7), in which $C^2_{i\mu}$ and $C^2_{j\nu}$ are MO coefficients at atoms μ and ν (i and j represent the orbital numbers), and $\beta_{\mu\nu}$ is a resonance integral. This equation shows that the splitting energy, ΔE_{spl}, is inversely proportional to the distance between interacting levels with their energies, ε_i and ε_j.[24]

$$\Delta E_{spl} = C^2_{i\mu} C^2_{j\nu} \beta_{\mu\nu} / (\varepsilon_i - \varepsilon_j) \tag{7}$$

Such a decrease of the interaction between initial donor levels in unsymmetrical cyanine dyes should result in an increase of transition energy, that is, the spectral band maximum λ_{un} related to the first electron transition should be shifted to the blue region of spectrum.

Thus, in our opinion, a possible reason for the phenomenon deviation, *D*, could be the decrease of interaction between the initial donor levels and the splitting energy in unsymmetrical dyes, whereas the appearance of the alternation of the C−C bond lengths in the PC seems to be a secondary effect.

Conclusion

A combined quantum-chemical and spectral investigation of the symmetrical and unsymmetrical trimethine cyanines bearing a 2-azaazulenium moiety has shown that the AA residue can be treated as a weakly basic terminal group. Its donor properties are provided by participation with HOMO−1, in contrast to the typical Brooker's terminal residues with their donor HOMOs. This enables us to propose a new classification of terminal groups of cyanine dyes and, hence, the classification of unsymmetrical cyanine types. It is shown that the nature of the higher electron transitions (delocalized or local) in cyanine dyes depends on their type. In the unsymmetrical trimethine cyanines of mixed type, negative deviations are observed in their absorption spectra.

Experimental Section

UV/Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

All NMR measurements were carried out on a Varian GEMINI 2000 spectrometer with ^{1}H and ^{13}C frequencies of 400.07 and 100.61 MHz, respectively, at 293 K. Tetramethylsilane was used as a standard for δ scale calibrating. ^{1}H NMR spectra were recorded with spectral width 8000 Hz and numbers of points 32000; ^{13}C NMR spectra were recorded with spectral width 30000 Hz and numbers of points 128000. ^{1}H-^{1}H COSY[25] spectra were acquired into a 2048 (F_2) and 512 (F_1) time-domain data matrix and 2048 (F_2)×2048 (F_1) frequency-domain matrix after zero-filling. NOESY[26] spectra were acquired, if necessary, with parameters similar to COSY spectra. Mixing times were determined preliminarily from T_1-measurement experiments for each sample by the conventional inversion–recovery method. Heteronuclear chemical shift correlation (HETCOR)[27] was used to determine ^{1}H-^{13}C attachment with the 2048 (F_2)×256 (F_1) time-domain matrix and 2048 (F_2)×1024 (F_1) frequency-domain matrix after zero-filling. The average value of one bond constant J_{CH} was set to 140 Hz. HETCOR for determination of long range correlation had very similar parameters, and the average value of the multibond C−H coupling constant was set to 8 Hz.

Quantum-chemical calculations were carried out to study the dependence of the electron structure and electron transitions on molecular constitution. The equilibrium geometry of dye molecules in the ground state was optimized using the Gaussian 98[28] program set within the DFT approximation. A functional B3LYP[29] was chosen, in combination with the standard 3-21G** basis sets. If needed, for some structures a conformational analysis was carried out by scanning the potential energy surface to search for the optimal conformation with the energy minimum. For the optimized geometry the calculation of force constants and the resulting vibrational frequencies was performed. Charge distributions in atoms were calculated using the B3LYP 6-31G** method and the theory of Natural Bond Orbital analysis (NBO).[30] The electron transition characteristics were calculated in the program package HyperChem 6.0[31] by the ZINDO/S method using, as a rule, all the π-electron single excited configurations; the empirical parameter OWF (overlap weight factor) was varied to achieve the best agreement between the calculated and spectral energy of the first electron transition. Then, we could analyze the shape of the molecular orbital as well as the nature of the lowest and high electron transitions.

Starting materials and solvents for the synthesis and spectroscopic measurements were purchased from Aldrich.

2-Butyl-6-[(1*E*)-3-(2-butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-1,3-dimethylcyclohepta[*c*]pyrrolium tetrafluoroborate (1): A mixture of compound **5**[15] (0.315 g, 1 mmol), triethyl orthoformate (1.12 g, 7.5 mmol), and anhydrous sodium acetate (0.08 g) was heated in acetic anhydride (3 mL) at 80 °C for 20 min. After cooling to room temperature the precipitated dye was filtered off, washed with acetic anhydride (1 mL) and dry diethyl ether (10 mL). Purification was by recrystallization from acetonitrile. Yield 0.1 g (36.2 %); m.p. 225–227 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=8.41 (t, ^3J(H,H)=12.7 Hz, 1H; 12-H), 7.54 (d, ^3J(H,H)=7.5 Hz, 4H; 4-H 8-H AA), 7.01 (brs, 4H; 5-H 7-H A), 6.54 (d, ^3J(H,H)=12.7 Hz, 2H; 11-H 13-H), 4.08 (t, ^3J(H,H)=6.6 Hz, 4H; NCH$_2$), 2.52 (s, 12H; C1-CH3 C3-CH3), 1.68–1.56 (m, 4H; NCH$_2$CH$_2$), 1.42–1.30 (m, 4H; CH$_3$CH$_2$), 0.94 ppm (t, ^3J(H,H)=7.1 Hz, 6H; CH$_3$CH$_2$); elemental analysis calcd (%) for $C_{33}H_{41}BF_4N_2$: C 71.74, H 7.48, N 5.07; found: C 71.54, H 7.62, N 5.23.

6-(2-Anilinovinyl)-2-butyl-1,3-dimethylcyclohepta[*c*]pyrrolium tetrafluoroborate (6): A solution of compounds **5** (0.945 g, 3 mmol) and **7** (1.34 g, 9 mmol) in acetonitrile (5 mL) was heated at 100 °C for 30 min and then allowed to cool to room temperature. The resulting precipitate was filtered off, washed with acetonitrile (2 mL) and diethyl ether (2×10 mL), and recrystallized from acetonitrile. Yield 0.48 g (38.4 %); m.p. 242–245 °C; elemental analysis calcd (%) for $C_{23}H_{27}BF_4N_2$: C 66.04, H 6.51, N 6.70; found: C 65.92, H 6.45, N 6.87.

(1-Butylbenzo[*c*,*d*]indol-2(1*H*)-ylidene)acetaldehyde: This compound was synthesized similarly to (1-ethylbenzo[*c*,*d*]indol-2(1*H*)-ylidene)acetaldehyde:[32] m.p. 107–109 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=10.29 (d, ^3J(H,H)=7.6 Hz, 1H; CHO), 8.54 (d, ^3J(H,H)=7.6 Hz, 1H; Ar), 8.00 (d, ^3J(H,H)=8.4 Hz, Ar), 7.69 (degen. t, ^3J(H,H)=7.6 Hz, 1H; Ar), 7.48–7.41 (m, 2H; Ar), 7.07–7.00 (m, 1H; Ar), 5.76 (d, ^3J(H,H)=7.6 Hz, CHCHO), 3.98–3.91 (m, 2H; NCH$_2$), 1.73–1.62 (m, 2H; NCH$_2$CH$_2$), 1.47–1.36 (m, 2H; CH$_2$CH$_3$), 0.94 ppm (t, ^3J(H,H)=7.4 Hz, 3H; CH$_3$); elemental analysis calcd (%) for $C_{17}H_{17}NO$: C 81.24, H 6.82, N 5.57; found: C 81.12, H 6.78, N 5.62.

Unsymmetrical trimethine cyanines (general procedure for dyes 2a–d): A mixture of compound **5** (1 mmol) and the corresponding unsaturated aldehyde **8** (1 mmol) was dissolved in acetic anhydride (3 mL) at 40 °C, and was then allowed to cool to room temperature and to stand for 5 h. The reaction mixture was diluted with diethyl ether (5 mL). The solid was filtered off, washed with diethyl ether (2×10 mL), dried, and purified by recrystallization from an appropriate solvent.

2-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-1,3,3-trimethyl-3*H*-indolium tetrafluoroborate (2a): Compound **2a** was obtained from **5** and (1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)acetaldehyde (CAS 84-83-3). Purification was by recrystallization from ethanol. Yield 0.22 g (44 %); m.p. 213–215 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): δ=8.28 (t, ^3J(H,H)=13.4 Hz, 1H; 12-H), 7.68 (d, ^3J(H,H)=7.2 Hz, 1H; 4-H In), 7.59–7.39 (m, 4H; 6-H 7-H In 4-H 8-H), 7.36 (t, ^3J(H,H)=7.2 Hz, 1H; 5-H In), 7.32 (brs, 1H; AA), 6.59 (d, ^3J(H,H)=13.4 Hz, 1H; 13-H), 6.52 (d, ^3J(H,H)=13.4 Hz, 1H; 11-H), 6.5 (brs, 1H; AA), 4.17–3.98 (m, 2H; NCH$_2$), 3.71 (s, 3H; NCH$_3$), 2.49 (s, 6H; C1-CH$_3$ C3-CH$_3$), 1.68 (s, 6H; 2×CH$_3$ In), 1.80–1.52 (m, 2H; NCH$_2$CH$_2$), 1.43–1.27 (m, 2H; CH$_3$CH$_2$), 0.94 ppm (t, ^3J(H,H)=7.2 Hz, 3H; CH$_3$CH$_2$); elemental analysis calcd (%) for $C_{29}H_{35}BF_4N_2$: C 69.88, H 7.08, N 6.62; found: C 69.76, H 7.00, N 6.80.

2-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2H)-ylidene)prop-1-en-1-yl]-3-methyl-1,3-benzothiazol-3-ium tetrafluoroborate (2b): Compound **2b** was obtained from **5** and (3-methyl-1,3-benzothiazol-2(3*H*)-ylidene)-

acetaldehyde.[33] Purification was by recrystallization from acetonitrile. Yield 0.15 g (30.7%); m.p. 219–222°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C, TMS): δ=8.15 (d, ^3JJ(H,H)=7.2 Hz, 1H; 7-H BT), 8.13 (t, ^3J(H,H)=13.5 Hz, 1H; 13-H), 7.92 (d, ^3J(H,H)=7.6 Hz, 1H; 4-H BT), 7.69 (t, ^3J(H,H)=7.6 Hz, 1H; 5-H BT), 7.56 (t, ^3J(H,H)=7.6 Hz, 6-H BT), 7.18–7.00 (m, 3H; 4-H 7-H 8-H AA), 6.97 (d, ^3J(H,H)=13.5 Hz, 1H; 13-H), 6.35 (d, ^3J(H,H)=12.6 Hz, 1H. 11-H), 6.27 (brd, ^3J(H,H) ≈ 10 Hz, 1H; 5-H), 3.99 (s, 3H; NCH$_3$), 3.98–3.81 (m, 2H; NCH$_2$), 2.39 2.37 (2s, each 3H; C1-CH$_3$ C3-CH$_3$), 1.66–1.47 (m, 2H; NCH$_2$CH$_2$), 1.42–1.22 (m, 2H; CH$_3$CH$_2$), 0.93 ppm (t, ^3J(H,H)=7.2 Hz, 3H; CH$_3$CH$_2$); elemental analysis calcd (%) for $C_{26}H_{29}BF_4N_2S$: C 63.94, H 5.99, N 5.74; found: C 63.82, H 6.14, N 5.86.

1-Butyl-2-[3-(2-butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)-prop-1-en-1-yl]benzo[*c*,*d*]indolium tetrafluoroborate (2c): Compound **2c** was obtained from **5** and (1-butylbenzo[*c*,*d*]indol-2(1*H*)-ylidene)acetaldehyde. Purification was by recrystallization from acetonitrile. Yield 0.128 g (46.7%); m.p. 254–256°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C, TMS): δ=8.78–8.59 (m, 2H; 3-H BIn 12-H), 8.19 (d, ^3J(H,H)=8.0 Hz, 1H; 5-H BIn), 7.86 (t, ^3J(H,H)=7.5 Hz, 1H; 4-H BIn), 7.73–7.52 (m, 4H; 4-H 8-H A 6-H 7-H BIn), 7.46 (d, ^3J(H,H)=7.4 Hz, 1H; 8-H BIn), 7.10 (brs, 2H; 5-H 7-H A), 6.84–6.67 (m, 2H; 11-H 13-H), 4.27–4.12 (m, 2H; NCH$_2$ BIn), 4.13–3.96 (m, 2H; NCH$_2$ A), 2.50 (s, 6H; C1-CH$_3$ C3-CH$_3$), 1.82–1.53 (m, 4H; 2×CH$_2$), 1.52–1.27 (m, 4H; 2×CH$_2$), 1.00–0.86 ppm (m, 6H; 2×CH$_3$); elemental analysis calcd (%) for $C_{33}H_{37}BF_4$N2: C 72.27, H 6.80, N 5.11; found: C 72.21, H 6.92, N 5.15.

4-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-2,6-diphenylpyrylium tetrafluoroborate (2d): Compound **2d** was obtained from **5** and (2,6-diphenyl-4*H*-pyran-4-ylidene)acetaldehyde.[34] Purification was by recrystallization from ethanol. Yield 0.275 g (48.1%); m.p. 182–185°C (decomp); ^{1}H NMR (400 MHz, CD$_3$CN, 25°C, TMS): δ=8.04 (degen. t, ^3J(H,H)=13.1 Hz, 1H; 12-H), 7.85 (d, ^3J(H,H)=4.6 Hz, 2H; Ar), 7.66–7.24 (m, 10H; Ar), 7.06 (d, ^3J(H,H)=10.7 Hz, 2H; 5-H 7-H AA), 6.74 (s, 2H; 3-H 5-H O-Py), 6.13 (d, ^3J(H,H)=13.2 Hz, 1H; 11-H), 5.95 (d, ^3J(H,H)=12.9 Hz, 1H; 13-H), 3.70–3.56 (m, 2H; NCH$_2$), 1.87 (s, 6H; C1-CH$_3$ C3-CH$_3$), 1.49–1.36 (m, 4H; CH$_3$*CH$_2$CH$_2$*), 0.93 ppm (t, ^3J(H,H)=7.2 Hz, *CH$_3$*CH$_2$); elemental analysis calcd (%) for $C_{35}H_{34}BF_4NO$: C 73.56, H 6.00, N 2.45; found: C 73.40, H 6.22, N 2.55.

4-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-2,6-diphenylthiopyrylium perchlorate (2e): Compound **2e** was obtained as follows: a solution of **5** (0.135 g, 0.4 mmol), 4-(2-anilinovinyl)-2,6-diphenylthiopyrylium perchlorate (0.2 g, 0.4 mmol),[14] and anhydrous sodium acetate (0.1 g) in acetic anhydride (3 mL) was heated at 60°C for 10 min, and was then allowed to cool to room temperature (2 h). The dye precipitated was filtered off, and washed with acetic anhydride (3 mL) and diethyl ether (2×10 mL). Purification was by recrystallization from acetonitrile with addition of a solution of NaClO$_4$ (0.1 g) in acetonitrile (1 mL). Yield 0.107 g (44.6%); m.p. 149–151°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C, TMS): δ=6.68 (t, ^3J(H,H)=8.6 Hz, 1H; 12-H), 8.30 (brs, 1H; Ar), 7.99–7.69 (m, 13H; Ar) 7.32 (brs, 2H; 3-H 5-H SPy), 6.62–6.54 (m, 2H; 11-H 13-H), 4.23–4.06 (m, 2H; NCH$_2$), 2.58 (s, 6H; C1-CH$_3$ C3-CH$_3$), 1.74–1.56 (m, 2H; NCH$_2$*CH$_2$*), 1.49–1.32 (m, 2H; *CH$_2$*CH$_3$), 0.97 ppm (t, ^3J(H,H)=7.3 Hz, 3H; CH$_2$*CH$_3$*); elemental analysis calcd (%) for $C_{35}H_{34}ClNO_4S$: C 70.04, H 5.71, Cl 5.91; found C 69.90, H 5.64, Cl 6.02.

4-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-1-methyl-2,6-diphenylpyridinium tetrafluoroborate (2f): Compound **2f** was obtained as follows: a 25% solution of methyl amine in DMSO (0.5 mL) was added to a solution of **2d** (0.275 g, 0.48 mmol) in acetonitrile (5 mL), and the resulting reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure. The residue was triturated with diethyl ether (2×5 mL), then with isopropanol (5 mL), yielding 0.195 g of the crude dye **2f**. Purification was by recrystallization from ethanol. Yield 0.1 g (35.7%); m.p. 158–160°C (decomp); ^{1}H NMR (400 MHz, CD$_3$CN, 25°C, TMS): δ=8.10–7.45 (m, 1H; 12-H), 7.87–7.40 (m, 12H; Ar), 6.72 (d, ^3J(H,H)=12.0 Hz, 1H; 8-H AA), 6.65 (d, ^3J(H,H)=12.0 Hz, 7-H AA), 6.61 (d, ^3J(H,H)=11.9 Hz, 1H; 4-H AA), 6.45 (d, ^3J(H,H)=14.7 Hz, 1H; 13-H), 6.07 (d, ^3J(H,H)=12.5 Hz, 1H; 11-H), 6.01 (d, ^3J(H,H)=11.9 Hz, 1H; 5-H AA), 3.86–3.71 (m, 2H; NCH$_2$), 3.52 (s, 3H; NCH$_3$), 2.25 (s, 3H; CH$_3$ AA), 2.24 (s, 3H; CH$_3$ AA), 1.63–1.50 (m, 2H; NCH$_2$*CH$_2$*), 1.44–1.24 (m, 2H; *CH$_2$*CH$_3$), 0.93 ppm (t, ^3J(H,H)=7.3 Hz, 3H; CH$_2$*CH$_3$*); elemental analysis calcd (%) for $C_{36}H_{37}BF_4N_2$: C 73.98, H 6.38, N, 4.79; found C 74.06, H 6.28, N 4.4.85.

General procedure for dyes 2g–k: Triethylamine (0.1 mL) was added to a solution of compound **6** (0.21 g, 0.5 mmol) and the corresponding quaternary salt of 4-Qu, 2-Qu, BI (0.75 mmol) in acetic anhydride (3 mL). This solution was heated at 60°C for 15 min, and was then allowed to cool to room temperature. The reaction mixture was diluted with diethyl ether (7 mL). The precipitate was filtered off, washed with diethyl ether (2×10 mL), dried, and purified by recrystallization from an appropriate solvent.

4-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-1-methylquinolinium perchlorate (2g): Compound **2g** was obtained from **6** and 1,4-dimethylquinolinium perchlorate.[33] Purification was by recrystallization from ethanol. Yield 0.120 g (48%); m.p. 147–149°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C, TMS): δ=8.85 (d, ^3J(H,H)=6.9 Hz, 1H; 2-H Qu), 8.65 (d, ^3J(H,H)=8.7 Hz, 1H; 5-H Qu), 8.43 (degen. t, ^3J(H,H)≈13.5 Hz, 1H; 12-H), 8.13 (d, ^3J(H,H)=6.8 Hz, 1H; 3-H Qu), 8.18 (d, ^3J(H,H)=8.7 Hz, 1H; 8-H Qu), 8.12–8.03 (m, 1H; 7-H Qu), 7.88–7.80 (m, 1H; 6-H Qu), 7.46 (d, ^3J(H,H)=14.0 Hz, 13-H), 6.96 (d, ^3J(H,H)=11.9 Hz, 1H; 7-H AA), 6.74 (d, ^3J(H,H)=11.7 Hz, 1H; 4-H AA), 6.73 (d, ^3J(H,H)=11.9 Hz, 1H; 8-H AA), 6.34 (d, ^3J(H,H)=12.2 Hz, 1H; 11-H), 6.07 (d, ^3J(H,H)=11.7 Hz, 1H; 5-H AA), 4.31 (s, 3H; NCH$_3$), 3.91–3.77 (m, 2H; NCH$_2$), 2.30 (s, 3H; CH$_3$ AA), 2.29 (s, 3H; CH$_3$ AA), 1.63–1.48 (m, 2H; NCH$_2$*CH$_2$*), 1.37–1.22 (m, 2H; *CH$_2$*CH$_3$), 0.92 ppm (t, ^3J(H,H)=7.35 Hz, 3H; CH$_2$*CH$_3$*); elemental analysis calcd (%) for $C_{28}H_{31}ClN_2O_4$: C 67.94, H 6.31, Cl 7.16; found: C 68.05, H 6.26, Cl 7.00.

2-[3-(2-Butyl-1,3-dimethylcyclohepta[*c*]pyrrol-6(2*H*)-ylidene)prop-1-en-1-yl]-1-methylquinolinium tetrafluoroborate (2h): Compound **2h** was obtained from **6** and 1,2-dimethylquinolinium iodide, and purified by recrystallization from acetonitrile with addition of *N*-benzyl-*N*,*N*,*N*-triethylammonium tetrafluoroborate (CAS 77794-93-5, 0.5 mmol) to avoid possible precipitation of the corresponding dye as a mixture of salts with different counter ions. Yield 0.130 g (54%); m.p. 167–169°C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25°C, TMS): δ=8.54 (degen. s, 2H; 3-H 4-H Qu), 8.44 (degen. t, ^3J(H,H)=12.8 Hz, 1H; 12-H), 8.16 (d, ^3J(H,H)=8.8 Hz, 1H; 8-H Qu), 8.05 (d, ^3J(H,H)=7.9 Hz, 1H; 5-H Qu), 7.99–7.91 (m, 1H; 7-H Qu), 7.76–7.66 (m, 1H; 6-H Qu), 7.03 (d, ^3J(H,H)=11.6 Hz, 1H; 7-H AA), 6.93 (d, ^3J(H,H)=13.9 Hz, 1H; 13H), 6.96–6.88 (m, 2H; 4-H 8-H AA), 6.35 (d, ^3J(H,H)=12.2 Hz, 1H; 11-H), 6.11 (d, ^3J(H,H)=11.6 Hz, 1H; 5-H AA), 4.17 (s, 3H; NCH$_3$), 3.95–3.84 (m, 2H; NCH$_2$), 2.32 (s, 3H; C1-CH$_3$), 2.26 (s, 3H; C3-CH$_3$), 1.62–1.50 (m, 2H; NCH$_2$*CH$_2$*), 1.39–1.25 (m, 2H; *CH$_2$*CH$_3$), 0.93 ppm (t, ^3J(H,H)=6.8 Hz, 3H; CH$_2$*CH$_3$*); elemental analysis calcd (%) for $C_{28}H_{31}BF_4N_2$: C 69.72, H 6.48, N 5.81; found: C 69.55, H 6.32, N 5.94.

2-[3-(2-butyl-1,3-dimethylcyclohepta[c]pyrrol-6(2H)-ylidene)prop-1-en-1-yl]-1,3-dimethyl-1H-3,1-benzimidazol-3-ium tetrafluoroborate (2k): Compound **2k** was obtained from 6 and 1,2,3-trimethyl-3H-benzoimidazol-1-ium iodide (CAS 3805-38-7). Purification was by recrystallization from methanol with addition of N-benzyl-N,N,N-triethylammonium tetrafluoroborate (CAS 77794-93-5, 0.5 mmol). Yield 0.085 g (35%); m.p. 249–251°C (decomp); 1H NMR (400 MHz, [D6]DMSO, 25°C, TMS): δ=7.99–7.85 (m, 3H; 4-H 7-H BIm 12-H), 7.64–7.52 (m, 2H; 5-H 6-H BIm), 6.64–6.54 (m, 4H; 4-H 7-H 8-H A 13-H), 6.20 (d, 3J(H,H)=11.8 Hz, 1H; 11-H), 6.03 (d, 3J(H,H)=11.6 Hz, 5-H AA), 4.04 (s, 6H; 2×NCH3), 3.89–3.75 (m, 2H; NCH2), 2.28 (s, 3H; CH3 AA), 2.26 (s, 3H; CH3 AA), 1.59–1.46 (m, 2H; NCH2CH2), 1.36–1.26 (m, 2H; CH2CH3), 0.92 ppm (t, 3J(H,H)=7.1 Hz, 3H; CH2CH3); elemental analysis calcd (%) for C27H32BF4N3: C 66.81, H 6.65, N 8.66; found: C 66.72, H 6.46, N 8.90.

2-[3-(1,3-dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene)prop-1-en-1-yl]-1,3-dimethyl-1*H*-3,1-benzimidazol-3-ium iodide (3b): Compound **3b** was synthesized according to the method described in reference [19] for 1,1′,3,3′-tetraethyl-benzimidazolocarbocyanine.

1,3-dimethyl-2-[(1*E*,3*Z*)-3-(1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)prop-1-en-1-yl]-1*H*-3,1-benzimidazol-3-ium 4 iodide (4): Piperidine (0.4 mL) was added to a solution of (1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)acetaldehyde (CAS 84-83-3, 0.2 g, 1 mmol) and 1,2,3-trimethyl-1*H*-3,1-benzimidazol-3-ium iodide in isopropanol (5 mL). This solution was heated under reflux for 10 h. Then two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added, and the heating under reflux was continued for 30 min. After cooling the precipitate was filtered off, washed with isopropanol (5 mL) and diethyl ether (2×5 mL), dried, and purified by recrystallization from ethanol (twice). Yield 0.150 g (32 %); m.p. 264–265 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 7.95–7.81$ (m, 3H; 2-H propen 5-H 6-H BIm), 7.61–7.51 (m, 2H; 4-H 7-H BIm), 7.42 (d, 1H; ^3J(H,H) = 7.3 Hz, 4-H In), 7.27 (degen. t, ^3J(H,H) = 7.7 Hz, 1H; 6-H In), 7.08 (d, ^3J(H,H) = 7.7 Hz, 1H; 7-H In), 7.02 (degen. t, ^3J(H,H) = 7.4 Hz, 1H; 5-H In), 6.43 (d, ^3J(H,H) = 14.9 Hz, 1H; 3-H propen), 5.91 (d, ^3J(H,H) = 12.2 Hz, 1H; 1-H propen), 4.01 (s, 6H; 2×NCH$_3$ BIm), 3.34 (s, 3H; NCH$_3$ In), 1.61 ppm (s, 6H; C(CH$_3$)$_2$); elemental analysis calcd (%) for $C_{23}H_{26}IN_3$: C 58.60, H 5.56, N 8.91; found: C 58.55, H 5.42, N 9.04.

Acknowledgements

The authors thank Dr. Yu. L. Slominskii and Ms Irina Lebedeva for valuable discussions.

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Received: February 10, 2010