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CARBOCYANINES – DERIVATIVES OF NITROGEN–CONTAINING HETEROCYCLES WITH BRIDGING GROUPS IN THE CHROMOPHORE

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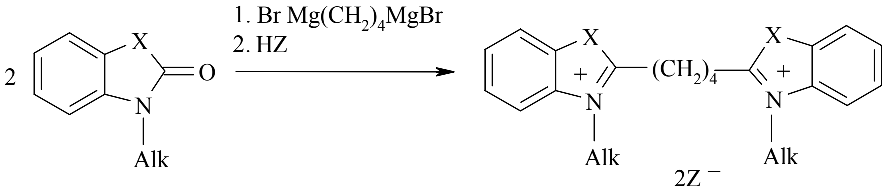
Tetramethylene-2,2'-bis(1,3,3-trimethyl-(3H)-indolium), -3-ethylbenzothiazolium, -1-methyl- quinolinium, and -1-methyl- and -1-butylbenz[c,d]indolium salts were synthesized starting from them trimethinecyanines containing an ethylene bridging group in the α,α'-positions of the chromophore have been prepared. These compounds are converted to their analogs containing a vinylene group by the action of benzoquinones. In the case of thiacarbocyanines the effect of the indicated bridging groups on the conformation and protonation route of the carbocyanines has been studied. The chromaticity of the dyes has been investigated.

Keywords: bis-salt, carbocyanine, bridging group, absorption band, chromophore.

Efficient sensitizers of silver halide light-sensitive materials [1] and dyes for the detection of biopolymers [2] have been discovered amongst carbocyanines with ethylene and vinylene bridging groups in the α,α'-position of the chromophore. In the case of benzothiazole [3] and benzoxazole [4] derivatives it has been shown that this type of dye can be synthesized from polymethylene-substituted bisquaternary nitrogen heterocycle salts by general methods used in the preparation of trimethinecyanines. However a general procedure for similar bisquaternary salts has not been reported to this time.

We have shown that such salts can be synthesized by treating oxo derivatives of the corresponding nitrogen heterocycles with the Grignard reagents prepared from α,ω-dibromoalkanes by analogy with the preparation of polymethylene bispyrilium salts [5, 6].



1-3

1 X = CMe$_2$, Alk = Me, Z = BF$_4$; **2** X= S, Alk = Et, Z = Br;
3 X = –CH=CH–, Alk = Me, Z = Br

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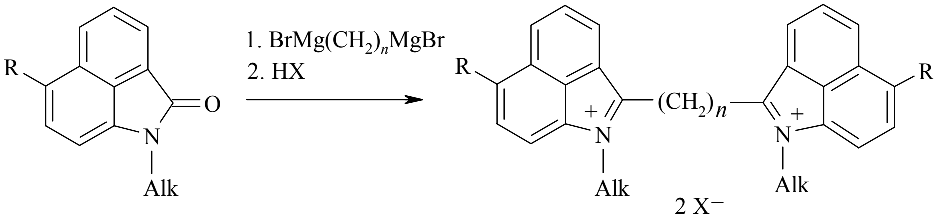
The reaction in the cases discussed is similar to that with mono magnesium bromide-substituted alkanes [7-9] but it occurs at two reactive centers. In this way the reaction of 1,3,3-trimethyloxyindole, 3-ethylbenzothiazol-2-one, 1-methylquinolin-2-one, and N-methylnaphthostyril with the Grignard reagent obtained from 1,4-dibromobutane gave the 2,2'-tetramethylenebis(3H-indolium) **1**, benzothiazolium **2**, quinolinium **3**, and benz[*c*,*d*]indolium (**4**) salts.

Use of the Grignard reagent prepared from 1,5-dibromopentane gave the bis-salt **5** in the same way.



4-6

4, 5 Alk = Me, R = H; **4** *n* = 4, X = Br; **5** *n* = 5, X = BF_4;
6 Alk = *n*-Bu, R = *n*-BuO, *n* = 4, X = ClO_4

In organic solvents the dibromide **4a** has a low solubility and it was therefore converted to the di-*p*-tolylsulfonate **4b** by fusion with excess methyl *p*-tolylsulfonate. In this way the 6-butoxy-1-butylnaphthostyril gave the bis quaternary salt **6**.

In the electronic spectra of the synthesized bis quaternary salts **1-6** the absorption bands were close in position and double the intensity when compared with the absorption bands of the corresponding 2-methyl-substituted monocations (Table 1). The ^1H NMR spectra of these salts (Table 2) showed both the signals for the aromatic protons and the characteristic signals for the protons of the polymethylene chains, the signals for the protons of the methylene groups in the α,α'-positions being to low field of those in the β,β'-positions. The accuracy of such an assignment was confirmed by determining the spectrum of compound **4** in CD_3OD solution where the signal for the α,α'-CH_2 groups disappears due to deuterium exchange. In the bis(N-methylbenz[*c*,*d*]indolium) salt of structure **5**, which contains a pentamethylene bridge, the signals for the γ-group protons occur at highest field (α-CH_2 3.40, β-CH_2 1.98, and γ-CH_2 1.79 ppm respectively).

The carbocyanines with a bridging ethylene in the chromophore **7-11** (Table 3) were prepared from the salts **1-6**. Indocarbocyanine **7** was synthesized by condensation of salt **1** with di(ethoxymethyl)acetate in a mixture of acetic anhydride and pyridine. In the preparation of the carbocyanines **8, 9** (derivatives of benz[*c*,*d*]indole) N-phenylethoxymethaneimine or DMF in acetic anhydride were used as electrophilic agents and for the quinocyanine **10** and thiacyanine **11**, obtained as in [4], the N-phenylethoxymethaneimine was employed in pyridine medium.

TABLE 1. Electronic Absorption Spectra of Compounds **1-6** in Acetonitrile

Compound	λ_{max}, nm (log ε)	λ_{max}, nm (log ε) of monocation
1	281 (4.58)	280 (3.85)
2	280 (4.29)	275 (3.91)
3	323 (4.33)	320 (3.94)
4	330 (4.30), 374 (4.34)	330 (3.97), 371 (3.94)
5	330 (4.24), 371 (4.23)	330 (3.97), 371 (3.94)
6	268 (4.47), 324 (4.40), 385 (4.24), 449 (4.29)	271 (3.08), 324 (3.02), 384 (2.82), 441 (2.85)

TABLE 2. ^{1}H NMR Spectroscopic Characteristics for Compounds **1-10**, **12-14**, **16, 17**

Com-pound	Chemical shifts δ, ppm (*J*, Hz)
1	1.65 (12H, s, $C(CH_3)_2$); 1.97 (4H, br. s, β-CH_2); 3.24 (4H, br. s, α-CH_2); 4.12 (6H, s, N–CH_3); 7.69 (4H, m, H-5,5' + H-6,6'); 7.88 (2H, m, H-7,7'); 7.97 (2H, m, H-4,4')
2	1.41 (6H, t, *J* = 7.2, N–$CH_2C\underline{H}_3$); 2.03 (4H, br. s, β-CH_2); 3.57 (4H, br. s, α-CH_2); 4.72 (4H, q, *J* = 7.2, N–CH_2); 7.76 (2H, t, *J* = 7.5, H-5,5'); 7.86 (2H, t, *J* = 7.5, H-6,6'); 8.27 (2H, d, *J* = 8.1, H-7,7'); 8.40 (2H, d, *J* = 8.1, H-4,4')
3	2.01 (4H, br. s, β-CH_2); 3.57 (4H, br. s, α-CH_2); 4.60 (6H, s, N–CH_3); 8.07 (2H, t, *J* = 6.8, H-6,6'); 8.24 (2H, d, *J* = 8.7, H-5,5'); 8.31 (2H, t, *J* = 6.8, H-7,7'); 8.47 (2H, d, *J* = 8.7, H-8,8'); 8.67 (2H, d, *J* = 9.5, H-3,3'); 9.21 (2H, d, *J* = 9.5, H-4,4')
4*	2.25 (4H, br. s, β-CH_2); 3.52 (4H, br. s, α-CH_2); 4.12 (6H, s, N–CH_3); 7.73 (2H, t, *J* = 6.6, H-7,7'); 7.87 (2H, t, *J* = 7.2, H-4,4'); 7.95 (2H, d, *J* = 6.6, H-6,6'); 8.11 (2H, d, *J* = 7.2, H-8,8'); 8.41 (2H, d, *J* = 7.8, H-5,5'); 8.57 (2H, d, *J* = 7.8, H-3,3')
5*	1.79 (2H, m, γ-CH_2); 1.98 (4H, m, β-CH_2); 3.40 (4H, m, α-CH_2); 4.02 (6H, s, N–CH_3); 7.71 (2H, t, *J* = 6.6, H-7,7'); 7.86 (2H, t, *J* = 7.5, H-4,4'); 7.93 (2H, d, *J* = 6.6, H-6,6'); 8.09 (2H, d, *J* = 7.5, H-5,5'); 8.39 (2H, d, *J* = 7.5, H-8,8'); 8.51 (2H, d, *J* = 7.5, H-3,3')
6	0.88 (6H, t, *J* = 7.5, N–C_3H_6–$C\underline{H}_3$); 1.00 (6H, t, *J* = 7.8, $OC_3H_6C\underline{H}_3$); 1.41 (4H, hex, *J* = 7.5, N–C_2H_4–$C\underline{H}_2$); 1.55 (4H, hex, *J* = 7.5, N–CH_2–$C\underline{H}_2$); 1.88 (8H, m, O–CH_2–$(C\underline{H}_2)_2$); 2.16 (4H, br. s, β-CH_2); 3.61 (4H, br. s, α-CH_2); 4.41 (4H, t, *J* = 6.0, N–CH_2); 4.66 (4H, t, *J* = 7.5, O–CH_2); 7.37 (2H, d, *J* = 8.4, H-8,8'); 8.07 (2H, t, *J* = 8.1, H-4,4'); 8.49 (2H, d, *J* = 8.1, H-5,5'); 8.75 (2H, d, *J* = 7.8, H-7,7'); 8.95 (2H, d, *J* = 6.9, H-3,3')
7	1.69 (12H, s, $C(CH_3)_2$); 3.33 (4H, s, CH_2); 3.90 (6H, s, N–CH_3); 7.32 (2H, m, H-5,5'); 7.36-7.50 (4H, m, H-6,6' + H-7,7'); 7.62 (2H, m, H-4,4'); 8.34 (1H, s, *meso*-H)
8	2.22 (3H, s, Tos-CH_3); 3.22 (4H, s, CH_2); 4.01 (6H, s, N–CH_3); 7.05 (2H, d, *J* = 7. 0, β-Tos-H); 7.45 (2H, d, *J* = 7.0, α-Tos-H); 7.52 (6H, m, H-8,8' + H-7,7' + H-6,6'); 7.83–8.27 (6H, m, H-3,3' + H-4,4' + H-5,5'); 8.52 (1H, s, *meso*-H)
9	0.98 (12H, m, N–C_3H_6–$C\underline{H}_3$, O–$C_3H_6C\underline{H}_3$); 1.48 (8H, m, *J* = 7.5, N–CH_2–$(C\underline{H}_2)_2$); 1.81 (8H, m, O–CH_2–$(C\underline{H}_2)_2$); 3.22 (4H, s, CH_2); 4.16 (4H, t, *J* = 6.0, N–CH_2); 4.48 (4H, t, *J* = 7.5 , O–CH_2); 7.09 (2H, m, H-8,8'); 7.63 (2H, m, H-7,7'); 7.88 (2H, t, *J* = 8.1 , H-4,4'); 8.25 (4H, m, H-5,5' + H-3,3'); 8.31 (1H, s, *meso*-H)
10	2.28 (3H, s, Tos-CH_3); 3.15 (4H, s, CH_2–CH_2); 4.07 (6H, s, N–CH_3); 7.16 (2H, d, *J* = 8.0, β-Tos-H); 7.50 (2H, m, H-3,3′ + 2H, α-Tos-H); 7.65 (2H, d, *J* = 9.0, H-5,5'); 7.78–7.90 (6H, m, H-6,6' + H-7,7' + H-8,8'); 7.94 (2H, d, *J* = 9.0, H-4,4'); 8.15 (1H, s, *meso*-H)
12	1.70 (12H, s, $C(CH_3)_2$); 4.04 (6H, s, N–CH_3); 7.18 (2H, s, CH=CH); 7.36-7.43 (2H, m, H-5,5'); 7.46–7.54 (2H, m, H-6,6'); 7.65–7.73 (4H, m, H-7,7'+ H-4,4'); 7.95 (1H, s, *meso*-H)
13	4.41 (6H, s, N–CH_3); 6.88 (2H, s, CH=CH); 7.66 (2H, d, *J* = 8.5, H-3,3'); 7.85-8.31 (8H, m, Ar–H); 8.45 (2H, d, *J* = 8.5, H-4,4'); 8.50 (1H, s, *meso*-H)
14	1.56 (6H, t, *J* = 7.0, N–$CH_2\underline{CH_3}$); 4.73 (4H, q, *J* = 7.0, N–CH_2); 6.85 (2H, s, CH=CH); 7.39 (1H, s, *meso*-H); 7.55 (2H, t, *J* = 8.0, H-6,6'); 7.68 (2H, t, *J* = 8.0, H-5,5'); 8.06 (2H, d, *J* = 8.0, H-7,7'); 8.16 (2H, d, *J* = 8.0, H-4,4')
16	4.20 (6H, s, N–CH_3); 6,86 (2H, s, CH=CH); 7.39 (1H, s, *meso*-H); 7.55 (2H, t, *J* = 8.0, H-6,6'); 7.66 (2H, t, *J* = 8.0, H-5,5'); 8.02 (2H, d, *J* = 8.0, H-7,7'); 8.13 (2H, d, *J* = 8.0, H-4,4')
17*	4.32 (6H, s, N–CH_3); 4.55 (2H,s, *meso*-H); 7.81 (2H, t, *J* = 9.0, H-6,6'); 7.88-7.97 (2H, m, H-5,5' + 2H, CH=CH); 8.13 (2H, d, *J* = 9.0, H-7,7'); 8.26 (2H, d, *J* = 9.0, H-4,4')

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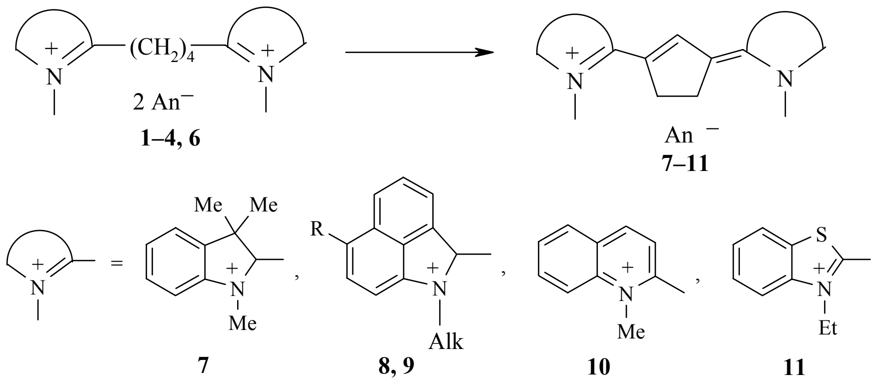
* Spectra recorded in DMSO-d$_6$ (compounds **1-3, 6-14, 16**), deutero-trifluoroacetic acid (compounds **4, 5**) or in deuteroacetonitrile (compound **17**).



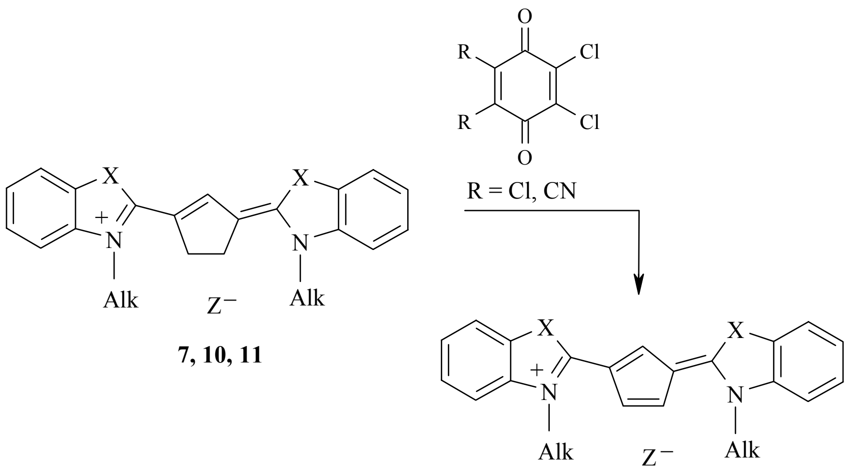
1–4, 6 **7–11**

7 **8, 9** **10** **11**

7 An$^-$ = BF_4^-, **8, 10** An$^-$ = TosO$^-$, **9** An$^-$ = ClO_4^-, **11** An$^-$ = Br$^-$

We have recently reported the possible dehydrogenation of the ethylene bridging group in thiacarbocyanine chromophores to vinylene in the presence of quinones [10]. It was found that this reaction is general to trimethinecyanines of this type containing different heterocyclic residues. The strongly basic quinocarbocyanine **10** and medium basicity thiacarbocyanine **11** were dehydrogenated using chloranil in acetonitrile to give the dyes **13** and **14** respectively. In the case of the low basicity indocarbocyanine **7** only the use of the more powerful oxidant 2,3-dichloro-5,6-dicyanobenzoquinone led to the preparation of the carbocyanine **12**.

Previously a series of carbocyanines, the trimethylene chromophore of which hides a 1,2-vinylene group, was obtained by treatment of cyclopentadiene with alkylthio- or bromo-substituted quaternary salts of nitrogen heterocycles [3, 11].

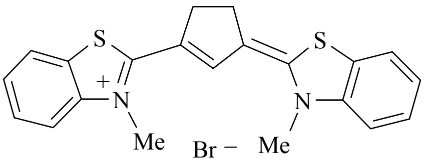


7, 10, 11

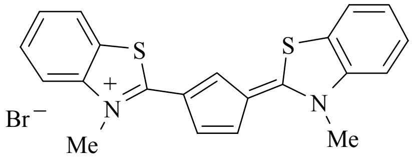
12–14

7, 12 X = CMe_2, Alk = Me; **7** Z^- = BF_4^-, **12** Z^- = ClO_4^-; **10, 13** X = –CH=CH–, Alk = Me,
10 Z^- = TosO$^-$, **13** Z^- = ClO_4^-; **11, 14** X = S, Alk = Et, Z^- = Br$^-$

With the aim of clarifying the spatial structure of the thiacarbocyanines with ethylene and vinylene bridging groups in the chromophore we have used the nuclear Overhauser effect (NOE). Because the ^{1}H NMR spectra of these compounds show signals which are well resolved and virtually nonoverlapped the interpretation of the results proved unambiguous. In the spectra of the thiacarbocyanine **15** (prepared according to [4]) a cross peak is observed corresponding to an NOE between the N-alkyl group protons and the proton in the *meso* position of the chromophore. On the other hand, in the dye with the vinylene bridge **16** a cross peak is observed between the signals for the N–CH_3 groups and the protons of the vinylene bridge. An interaction between the bridging group protons and the N-ethyl substituents is observed for thiacarbocyanines containing both ethylene and vinylene bridges and a chlorine atom or nitrile group in the *meso* position of the chromophore [10]. Hence it was shown that the introduction of only an ethylene bridge in the thiacarbocyanine is accompanied by a change in the conformation of the chromophore from *all-trans-E,E,E,E* (as found in the analog unsubstituted in the chromophore) to *Z,E,E,Z* whereas the introduction of the vinylene bridge does not change the conformation.

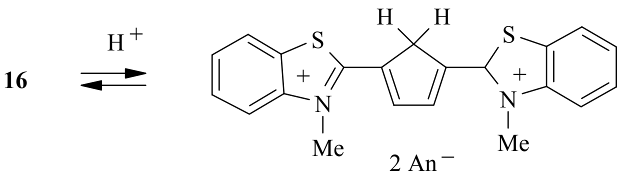


Z,E,E,Z-**15**



E,E,E,E-**16**

In the case of the thiacarbocyanine **16** it has been shown by ^{1}H NMR that, by contrast with the saturated bridging group **15**, the addition of a proton to the carbocyanines with a vinylene bridge occurs not at the usual α-position [12] but at the β-position of the chromophore to form the dications with the symmetrical type structure **17** (compound not separated). Protonation was carried out by trifluoromethane-sulfonic acid in CD_3CN solution. As a result, the signal for the vinylene bridge protons (δ = 6.85 ppm) are shifted to low field (δ = 7.40) and the signal for the CH group in the *meso* position of the chromophore (δ = 7.38 ppm) disappears. In place a signal appears at δ = 4.55 pm for the methylene group. Protonation is accompanied by a 64 nm hypsochromic shift of the electron spectrum absorption maximum. The addition of the proton to the β-position is associated with the fact that, in the dye with a vinylene bridge in this position, there is localized a partial negative π-charge equal to -0.059 (value calculated by PPP type quantum-chemical calculation). The addition of a proton to the β-position of the chromophore also preserves the chain of conjugation.



17

The spectroscopic data for the dyes synthesized (Table 4) confirms the phenomenon observed previously of a depression of the color of trimethinecyanines under the influence of an ethylene and its increase with a vinylene bridge and also the more powerful effect of the latter [10].

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Varian-300 instrument (300 MHz) using HMDS (δ 0.055) as internal standard. Electronic absorption spectra were taken on a Shimadzu UV-3100 spectrophotometer. The purity of the products was monitored by TLC on Silufol UV-254 plates with chloroform as eluent. Compounds **11** and **15** were prepared by a known method [4].

TABLE 3. Characteristics of Compounds **1**, **3-10**, **12-14**, **16**

Com-pound	Empirical formula	Found, % Calculated, % C	H	Hal	N (S)	mp, °C	Yield, %
1	$C_{26}H_{34}B_2F_8N_2$	57.20 56.96	6.45 6.25		5.16 5.11	227-228	56
3	$C_{24}H_{26}Br_2N_2$	57.29 57.38	5.36 5.22		5.43 5.58	187-188	29
4	$C_{28}H_{26}Br_2N_2$			28.74 29.03	4.92 5.06	220-221	47
5	$C_{29}H_{28}B_2F_8N_2$	59.94 60.24	4.77 4.88		4.80 4.85	201-203	30
6	$C_{42}H_{54}Cl_2N_2O_{10}$		—	7.97 8.15	3.34 3.22	199-201	39
7	$C_{27}H_{31}BF_4N_2$	68.89 68.94	6.60 6.64		6.04 5.96	217-218	66
8	$C_{36}H_{30}N_2O_3S$	75.77 75.90	5.30 4.97		4.91 5.08	218-220	81
9	$C_{43}H_{51}ClN_2O_6$	71.01 71.00	7.07 7.08		3.85 3.83	211-213	38
10	$C_{32}H_{30}N_2O_3S$	73.54 73.60	5.79 6.03		5.36 5.26	175-176	47
12	$C_{27}H_{29}ClN_2O_4$	67.42 67.27	6.08 6.04	7.37 7.22	—	190-192	82
13	$C_{25}H_{23}ClN_2O_4$	66.59 66.46	—	7.86 7.85	—	212-214	78
14	$C_{23}H_{21}BrN_2S_2$		—	17.02 16.94	(13.66) (13.49)	153-154	87
16	$C_{21}H_{17}BrN_2S_2$		—	18.11 17.90	(14.53) (14.84)	247-249	89

TABLE 4. Characteristics of the Long Wavelength Absorption Bands of the Dyes **7-14**, **16** in Methanol

Compound	λ_{max}, nm (log ε)	λ_{max}, nm (log ε)*	$\Delta\lambda_{max}$, nm	$\Delta\nu$, cm^{-1}
7	592 (5.00)	545 (5.08)	47	1456
8	814 (5.21)	755 (5.10)	59	960
9	892 (5.10)	821 (5.13)	71	969
10	716 (4.90)	605 (5.25)	111	2562
11	601 (5.20)	558	43	1282
12	482 (4.76)		–63	2398
13	533 (4.87)		-72	2232
14	472 (4.91)		-76	2885
16	469 (4.99)	554	-85	3271

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* Characteristics of the analogs unsubstituted in the chain.

Preparation of bis-quaternary salts 1-6 (General Method).

2,2'-Tetramethylenebis(1,3,3-trimethyl-3H-indolium) Ditetrafluoroborate (1). The Grignard reagent prepared from metallic magnesium (0.5 g, 20 mmol), 1,4-dibromobutane (2.16 g, 10 mmol), and absolute ether (10 ml) was added with stirring to a solution of 1,3,3-trimethyloxyindole (3.2 g, 20 mmol) in anhydrous ether (20 ml). After addition of the solution the reaction mixture was heated for 2 h at 40ºC. Solvent was evaporated at 0ºC under reduced pressure and HBF_4 (22%, 12 ml) was added. The precipitate was filtered off and washed with ether. Compound **1** was recrystallized from acetonitrile.

Salts 2-4 were prepared similarly but 20% HBr was added with crystallization from ethanol. In the case of salt **6** perchloric acid was used with crystallization from methanol. The Grignard reagent in the synthesis of salt **5** was prepared from 1,5-dibromopentane.

1,3,3-Trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)cyclopent-1-enyl]-3H-indolium Tetrafluoroborate (7). A mixture of salt **1** (0.23 g, 0.42 mmol), di(ethoxymethyl)acetate (0.13 g, 0.84 mmol), pyridine (0.03 g, 0.42 mmol), and acetic anhydride (2 ml) were refluxed for 7 min. The reaction mixture was cooled and treated with ether and water. The precipitate was filtered off, washed with ether, and recrystallized from 2-propanol.

1-Methyl-2-[3-(1-methyl-1,2-dihydrobenzo[*c,d*]indolylidene-2)-1-cyclopentenyl]benz[*c,d*]indolium *p*-tolylsulfonate (8). Salt **4** (0.28 g, 0.50 mmol) and methyl tosylate (1.25 g, 6.71 mmol) were fused for 1 h at 100-110ºC. The melt was treated with ether and acetone. The ditosylate salt, di(ethoxymethyl)acetate (0.15 g, 1 mmol), pyridine (0.04 g, 0.5 mmol), and acetic anhydride (2.5 ml) were refluxed for 7 min. The reaction mixture was cooled and treated with ether and water. The precipitate was filtered, washed with ether, and recrystallized from methanol.

6-Butoxy-1-butyl-2-[3-(1-butyl-6-butoxybenzo[*c,d*]indolylidene-2)-1-cyclopentenyl]benz[*c,d*]indolium Perchlorate (9). A mixture of the bis salt **6** (0.215 g, 0.25 mmol), N-phenylethoxymethaneimine (0.075 g, 0.50 mmol), pyridine (0.025 g, 0.25 mmol), and acetic anhydride (1 ml) was refluxed for 2 min in a gas flame. The product was cooled and the precipitate formed was washed with water and ether and then recrystallized from acetonitrile.

1-Methyl-2-[3-(1-methylquinolinylidene-2)-1-cyclopentenyl]quinolinium *p*-Tolylsulfonate (10) was obtained from salt **3** similarly to compound **8** but refluxed with N-phenylethoxymethaneimine in pyridine for 3 min. The carbocyanine was recrystallized from acetonitrile.

1,3,3-Trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)cyclopenta-1,4-dienyl]-3H-indolium Perchlorate (12). The carbocyanine **7** (0.20 g, 0.43 mmol) was dissolved in acetonitrile (3 ml), 2,6-dichloro-3,5-dicyanobenzoquinone (0.195 g, 0.86 mmol) added, and the product was refluxed for 3 min. The product was washed with ether, filtered, washed with toluene and ether, and chromatographed on Al_2O_3 using chloroform as eluent. The dye was converted to the perchlorate by dissolving in acetonitrile and addition of an aqueous, saturated solution of sodium perchlorate and was recrystallized from a mixture of ethanol and 2-propanol (1:1).

1-Methyl 2-[3-(1-methyl-1,2-dihydro-2-quinolinylidene)-1,4-cyclopentadienyl]quinolinium Perchlorate (13). The carbocyanine **10** (0.20 g, 0.38 mmol) was dissolved in acetonitrile (10 ml) and chloranil (0.177 g, 0.72 mmol) was added. After 30 min the precipitate was filtered off, washed with warm benzene, ether, and recrystallized from acetonitrile. The dye was converted to the perchlorate using aqueous $NaClO_4$ solution.

3-Ethyl-2-[3-(3-ethyl-2,3-dihydro-1,3-benzothiazol-2-yliden)-1,4-cyclopentadienyl]-1,3-benzothiazolium Bromide (14) was prepared similarly to cyanine **11** but heated at 100ºC for 30 min and recrystallized from acetonitrile.

3-Methyl-2-[3-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)-1,4-cyclopentadienyl]-1,3-benzothiazolium Bromide (16) was prepared similarly to compound **14** from **15**.

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