

On the Dependence of Spectra of NIR Polymethine Dyes on the Central Chromophore Ring

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The trends in spectral data of two series of dyes containing either two benzothiazole or four dimethylaminophenyl side chromophores connected by a 7-membered aliphatic chain in the central chromophore implemented by cyclohexene, furanone or cyclopentene ring are compared. In both series, the effect of the central chromophore ring variation on the maximum wavelength λ_{\max} is studied using the statistical treatment of the chromophores data obtained by quantum-chemical calculations. The significance of the factors influencing λ_{\max} is arranged in the order: the chromophore planarity; mutual angles of individual chromophore planes; the similarity of individual chromophores in the dye; substituents on individual chromophores.

In recent years, with the rapid development of data recording, laser diodes, photography, analytical tools for environmental and process monitoring, sensors techniques, and medical diagnostics, increasing attention is paid to the application of some near infrared (NIR) absorbing cyanine dyes. These dyes are cheap, easy to synthesize, and exhibit very good optical properties.

In our previous papers, a series of NIR dyes based on tris(4-dimethylaminophenyl)divinylenes [1] and tetrakis(4-dimethylaminophenyl)hexadienes [2] has been studied. The visible-NIR absorption spectra of the synthesized dyes have been measured and then interpreted on the basis of mutual chromophores interaction and its relationship to the geometry and electron structure. For this purpose, the bond lengths, atomic charges, and bond orders over the carbon skeleton of individual chromophores (phenyl rings as well as the aliphatic chains between them) were compared in terms of statistical characteristics such as arithmetic mean values and root mean square deviations (σ). The planarity of individual chromophores and their mutual angles (in terms of dihedral angles) have been studied, too. The planarity of π -bond framework of chromophores is crucial for the intensity and position of the absorption maximum, λ_{\max} . The highest λ_{\max} are obtained for the dyes with coplanar chromophores. On the other hand, protonation has an undesirable effect on λ_{\max} and usually is connected with the perturbation of planarity. In the above-mentioned dyes [1, 2], the problems with planarity of the central aliphatic

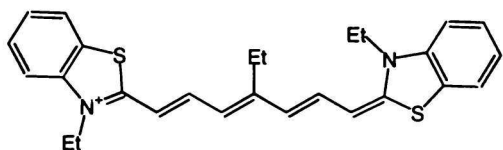
chain chromophore arise. However, the planarity could be kept by introducing a planar ring into this chromophore. The spectral data on a series of dyes containing two benzothiazole side chromophores connected by a 7-membered central chromophore aliphatic chain [3] alternatively implemented by cyclohexene [4], furanone [5] or cyclopentene [6, 7] ring (see Formula 1, dyes A1—A4) have been compared (Table 1). The benzothiazoles (side chromophores) may be substituted by pairs of 4-dimethylaminophenyls (see Formula 1, dyes B2—B4) analogously to the dyes in our previous studies [1, 2]. In both series, the effect of the central chromophore ring variation on λ_{\max} can be studied using statistical treatment of the chromophores data obtained by quantum-chemical calculations similarly as in [1, 2]. Also the effect of protonation is investigated.

QUANTUM-CHEMICAL CALCULATIONS

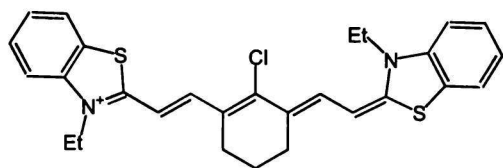
The standard semiempirical AM1 method of quantum chemistry (AMPAC program package) [8, 9] was used to find the optimal geometries of the cation parts of the dyes presented in Table 1 and Formula 1. All calculations were performed in higher precision (keyword PRECISE) using the Davidson—Fletcher—Powell optimization procedure [10, 11]. The electronic structure characteristics were evaluated in terms of charges of individual atoms and bond indices of individual bonds [12]. The electron spectra lines of the systems under study were calcu-

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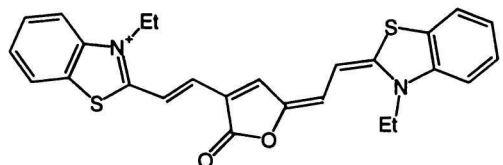
NIR POLYMETHINE DYES



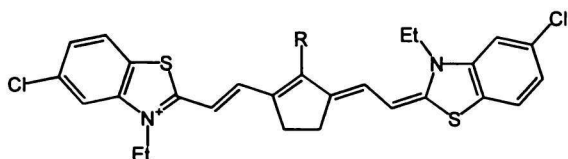
A1, 3-ethyl-2-[4-ethyl-7-(3-ethyl-3*H*-benzothiazol-2-ylidene)hepta-1,3,5-trienyl]benzothiazol-3-ium cation



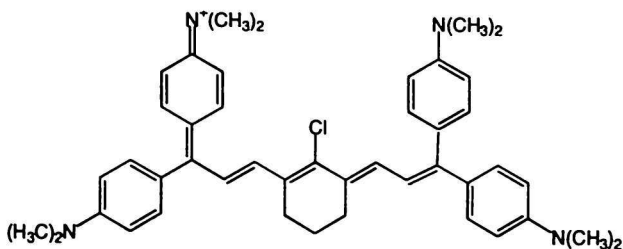
A2, 3-ethyl-2-(2-{2-chloro-3-[2-(3-ethyl-3*H*-benzothiazol-2-ylidene)ethylidene]cyclohexen-1-yl}vinyl)benzothiazol-3-ium cation



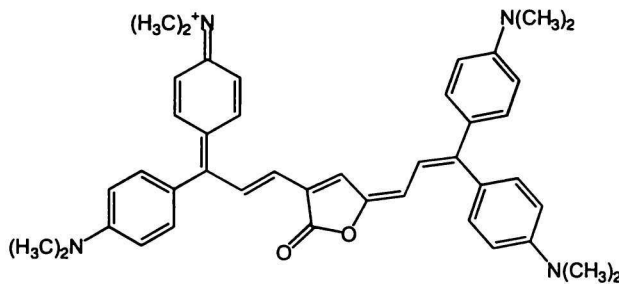
A3, 3-ethyl-2-(2-{4-[2-(3-ethyl-3*H*-benzothiazol-2-ylidene)ethylidene]-2-oxo-2,5-dihydrofuran-3-yl}vinyl)benzothiazol-3-ium cation



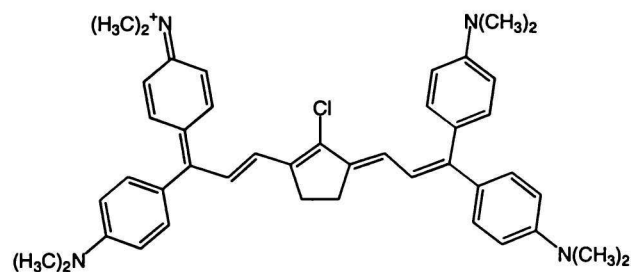
A4, 3-ethyl-5-chloro-2-{2-[2-R-3-(5-chloro-3-ethyl-3*H*-benzothiazol-2-ylidene)ethylidene]cyclopenten-1-yl}vinyl}benzothiazol-3-ium cation
A4a: R = N(Ph)₂ A4b: R = Cl



B2, {4-[3-{3-[3,3-bis(4-dimethylaminophenyl)allylidene]-2-chlorocyclohexen-1-yl}-1-(4-dimethylaminophenyl)allylidene]-cyclohexa-2,5-dienylidene}dimethyliminium cation



B3, {4-[3-{5-[3,3-bis(4-dimethylaminophenyl)allylidene]-2-oxo-2,5-dihydrofuran-3-yl}-1-(4-dimethylaminophenyl)allylidene]cyclohexa-2,5-dienylidene}dimethyliminium cation



B4, {4-[3-{3-[3,3-bis(4-dimethylaminophenyl)allylidene]-2-chlorocyclopenten-1-yl}-1-(4-dimethylaminophenyl)allylidene]-cyclohexa-2,5-dienylidene}dimethyliminium cation

Formula 1

lated using the single excited configuration interaction method with 163 configurations [13]. For comparison, the electron spectra calculated by standard ZINDO/S method [14] are presented for the compounds containing no Cl atoms (due to missing parametrization). Analogously to our previous papers on tris(4-dimethylaminophenyl)divinylenes [1] and tetrakis(4-dimethylaminophenyl)hexadienes [2] the systems under study are described by arithmetic mean values and root mean square deviations (σ) of the bond distances, atomic charges, and bond indices over the carbon skeleton of individual chromophores. The perturbations of the planar π -bond framework are described by the deviations from planarity (dihedral angles).

RESULTS AND DISCUSSION

Experimental data on absorption maxima λ_{\max} of A series of dyes (Table 1, Formula 1) are in a reasonable agreement with AM1 results despite the fact that the optimal geometries of molecular ions *in vacuo* have been used for electron spectra calculations. The systematic λ_{\max} underestimation may be ascribed to the interactions with solvent molecules (especially for A4a dye with the large R substituent). According to our results, the B series of hypothetical compounds are not suitable as NIR dyes due to lower λ_{\max} value and the intensity split into several bands (see Table 1). This might be related to an improper chain length of

Table 1. Values of λ_{\max} Wavelengths of the Most Intense Peaks in Visible-NIR Spectra (Oscillator Strength Values in Parentheses)

Dye ^a	Charge	λ_{\max}/nm		
		AM1	ZINDO/S	exp.
A1	1	737(1.8)	596(2.2)	785 ^c
A2	1	764(1.7)	–	810 ^d
A3	1	734(1.8)	620(2.2)	716 ^e
A3h ^b	2	461(1.5)	487(1.8)	–
A4a	1	633(1.7)	–	809 ^f
A4b	1	772(1.8)	–	–
B2	1	579(1.2), 468(1.1)	–	–
B3	1	605(0.9), 482(1.1)	628(1.1), 447(0.9)	–
B3h ^b	2	897(0.4), 541(1.2), 476(0.6)	999(0.2), 526(0.5), 521(0.6), 426(0.6), 413(0.8)	–
B4	1	659(1.5), 454(0.7)	–	–

a) See Formula 1; b) A3 or B3 with H⁺ bonded to O of C=O; c) Ref. [3]; d) Ref. [4]; e) Ref. [5]; f) Ref. [6].

the central chromophore. However, the chain lengths optimization is outside the scope of this paper.

In accordance with our previous results [1, 2], the importance of chromophore planarity for λ_{\max} position is confirmed (Table 2). Whereas the protonation of A3 dye causes the nonplanarity of the central chro-

mophore with lower λ_{\max} in A3h, the protonation of this improves the central chromophore planarity in B3h which leads to a higher λ_{\max} (despite higher interchromophore deviations).

Despite that our study is restricted to carbon atoms in the dyes skeleton only, the importance of maximal similarity of bond lengths, atomic charges, and bond indices between the central and side chromophores (including interchromophore bonds) is confirmed (Table 3) in agreement with our previous papers [1, 2]. Mutual comparison of both the series is not reasonable due to heteroatoms in the skeleton of the A series of dyes. Both series indicate a significant λ_{\max} variation for the dyes with various rings implemented into the central chromophore. These variations are substantially larger than in our previous studies [1, 2] on the dyes with varying substituents on the same chromophores skeleton. The best results are obtained for cyclopentene ring implementation (A4b and B4 dyes) whereas the highest nonplanarity is related to cyclopentene ring (A2 and B2 dyes). This planarity may be influenced by large substituents, too (*cf.* A4a and A4b dyes). Moreover, the sterical effect of four large side chromophores undesirably affects the central chromophore planarity.

Our results (Tables 2–4) as well as the results of our previous studies [1, 2] confirmed the significance of λ_{\max} -influencing factors in the following order: the chromophore planarity – mutual angles of individual chromophore planes – the similarity (*e.g.* statistical characteristics) of individual chromophores in the dye – substituents on individual chromophores.

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Table 2. Deviations from Planarity (Dihedral Angles δ) in the Central Chromophore as well as between the Central and Side Chromophores of the Dyes under Study

Dye	$\delta/^\circ$		
	(C—C—C—C) _{centr}	(C—C—C) _{centr} —C _{side}	(C—C) _{centr} —(C—X) _{side}
X = N			
A1	0,0,0,0	0,0	0,0
A2	5,4,4,5	1,1	4,2
A3	0,0,0,0	0,0	0,0
A3h	1,0,0,1	1,1	24,10
A4a	2,6,7,3	4,4	1,1
A4b	0,0,0,0	0,0	0,0
X = C			
B2	6,12,2,28	6,5,42,38	64,33,30,25
B3	2,5,4,6	10,7,26,28	43,33,29,28
B3h	1,1,5,9	9,12,61,65	25,43,19,25
B4	3,7,2,2	4,4,28,25	82,25,42,23

Table 3. Statistical Characteristics of the Carbon Part of the Side-Chromophores Rings in the Dyes under Study

Dye	Interatomic distances		Atomic charges		Bond indices	
	Mean/ 10^{-10} m	$\sigma/10^{-10}$ m	Mean	σ	Mean	σ
A1	1.401	0.014	-0.109	0.110	1.379	0.052
	1.402	0.015	-0.110	0.111	1.377	0.057
A2	1.401	0.014	-0.111	0.111	1.377	0.059
	1.401	0.013	-0.108	0.106	1.378	0.056
A3	1.402	0.015	-0.113	0.111	1.375	0.068
	1.402	0.015	-0.110	0.111	1.377	0.060
A3h	1.403	0.015	-0.120	0.111	1.367	0.088
	1.403	0.015	-0.119	0.109	1.369	0.085
A4a	1.402	0.014	-0.098	0.119	1.370	0.048
	1.402	0.014	-0.098	0.119	1.370	0.048
A4b	1.402	0.014	-0.099	0.121	1.368	0.056
	1.402	0.014	-0.098	0.119	1.368	0.056
B2	1.408	0.024	-0.084	0.162	1.338	0.152
	1.407	0.022	-0.089	0.156	1.344	0.133
	1.403	0.014	-0.091	0.117	1.372	0.068
	1.402	0.013	-0.098	0.103	1.379	0.053
B3	1.407	0.022	-0.086	0.157	1.343	0.137
	1.409	0.025	-0.078	0.163	1.336	0.155
	1.404	0.015	-0.091	0.125	1.368	0.075
	1.397	0.025	-0.092	0.118	1.372	0.067
B3h	1.411	0.029	-0.075	0.162	1.318	0.223
	1.413	0.034	-0.083	0.160	1.328	0.188
	1.404	0.017	-0.087	0.149	1.348	0.128
	1.407	0.022	-0.103	0.129	1.365	0.084
B4	1.408	0.023	-0.085	0.158	1.342	0.139
	1.406	0.019	-0.094	0.145	1.355	0.105
	1.405	0.017	-0.088	0.136	1.361	0.091
	1.403	0.014	-0.100	0.114	1.377	0.059

Table 4. Statistical Characteristics of the Central Chromophore Chains in the Systems under Study (Values in Parentheses Correspond to Extended Chains Including Interchromophore Bonds)

Dye	Interatomic distances		Atomic charges		Bond indices	
	Mean/ 10^{-10} m	$\sigma/10^{-10}$ m	Mean	σ	Mean	σ
A1	1.397	0.014	-0.130	0.197	1.358	0.083
	(1.396)	(0.013)			(1.356)	(0.077)
A2	1.398	0.007	-0.111	0.176	1.350	0.025
	(1.399)	(0.006)			(1.342)	(0.026)
A3	1.395	0.016	-0.114	0.166	1.363	0.100
	(1.398)	(0.015)			(1.337)	(0.100)
A3h	1.398	0.037	-0.095	0.097	1.405	0.297
	(1.409)	(0.037)			(1.321)	(0.296)
A4a	1.410	0.033	-0.101	0.214	1.308	0.161
	(1.402)	(0.031)			(1.341)	(0.151)
A4b	1.397	0.013	-0.114	0.175	1.347	0.039
	(1.397)	(0.012)			(1.344)	(0.034)
B2	1.403	0.036	-0.014	0.204	1.386	0.271
	(1.420)	(0.037)			(1.269)	(0.260)
B3	1.402	0.039	-0.012	0.213	1.376	0.275
	(1.419)	(0.038)			(1.270)	(0.255)
B3h	1.406	0.043	-0.012	0.172	1.342	0.280
	(1.416)	(0.038)			(1.280)	(0.242)
B4	1.400	0.024	-0.010	0.214	1.372	0.172
	(1.420)	(0.032)			(1.254)	(0.201)

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