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Conformational analysis of polymethine dyes derived from the 2-azaazulene

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ABSTRACT

A systematic investigation of the conformational structure was performed for the series of symmetrical and unsymmetrical mono-, tri-, pentamethine cyanines, and styryl dyes bearing 2-azaazulenium terminal group. The rotation energy barriers of terminal groups were determined *via* the dynamic variable temperature NMR experiments. The conformational transformation energy was calculated by quantum chemical methods (B3LYP and M05-2X) both for the cases of considering the solvent influence and not tacking it into account. Based on the comparison of theoretical and experimental data, relative electron-donating abilities and geometrical features of the heterocyclic terminal groups in 2-azaazulenium dyes were estimated. The arrangement of certain heterocyclic nuclei in order of basicity by considering the results of the dynamic NMR investigations was proposed. Influence of the conjugated chain length and the solvent nature on the conformational lability of the investigated dye molecules was discussed.

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1. Introduction

Considerable attention is paid to the investigation of cyanine dyes due to their usefulness in different fields of science and industry [1,2]. These compounds have found numerous applications such as photographic sensitizers [3], nonlinear optical materials [4], fluorescent probes for the biomolecular labelling [5]. They are able to interact with biomolecules via the covalent and noncovalent coupling. Thus, suitable fluorophores can be bound to the double-stranded DNA molecules, resulting in the significant enhancement of the fluorescence properties of the latter [6]. To study interactions and structure of the complexes, different physicochemical methods of analysis including X-ray, NMR, and FRET were applied [7]. Depending on the structure, terminal groups and the length of the polymethine chain the dye can bind DNA in several ways [8]. Sterical effects of the terminal groups are very important for the *I*-aggregation of symmetrical cyanines with DNA [9.10].

The molecular structure of the cyanine dye and the asymmetry of its electronic structure (the differences in the electron-donating properties of the terminal groups) are crucial for the process of interaction with biomolecules (DNA), and hence for the spectral properties of the formed complexes [11]. Therefore, study of the peculiarities of the structure and physicochemical properties of the cyanines is important for the prediction and analysis of their bimolecular labelling properties.

The dependence of the dye spectral properties on the electronic nature of terminal groups was examined for an extensive series of symmetrical and asymmetrical cyanines in the middle of the 20th century by Brooker [12]. The concept of the absorption maximum "deviation" and the corresponding scale of basicity were introduced. The dependence of the positions of the absorption maxima in the UV spectra on the differences of the electron-donating properties (basicity) of terminal groups was reported in [13]. Quantumchemical analysis method of terminal heterocyclic groups' basicity was developed by Dyadusha and Kachkovskii [14]. On the basis of these studies one can draw conclusions regarding the influence of the asymmetry of the polymethines electronic structure on their physical properties.

However, optical methods are not the only option for the estimation of the electronic asymmetry of the cyanines. NMR spectroscopy is found to be one of the most useful instruments for the investigation of the molecular electronic structure and conformations of the cyanine dye molecules [15,16]. Influence of the sterical hindrance from the terminal groups on the trimethine cyanines conformations was investigated [17]. The dependence of the conformational transformations energy barriers (*cis-trans*-isomerization) on the terminal groups and the chromophore chain length was determined experimentally by means of dynamic NMR [18].

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Detailed data on the variable-temperature ¹H NMR conformational analysis for the series of trimethine cyanines derivatives of benzoxazole, benzothiazole, etc. is presented in the literature [19]. This method was also successfully applied to the study of the photoisomerization of trimethine cyanines [20].

According to the X-ray diffraction data and the quantum-chemical analysis of the constitution of polymethine cyanines, in the absence of the sterical hindrance dye chromophores adopt all-trans conformation [18]. Quantum-chemical calculations within the AM1 approximation were applied to determine the conformational transformations energy barriers for the cyanines and other linear conjugated systems [21].

Earlier we have synthesized the series of monomethine [22] and trimethine [23] cyanines bearing 2-azaazulenium moiety and studied it using spectral and guantum-chemical methods. In our previous paper [24] we presented the investigation results of the conformational features of the unsymmetrical monomethine cyanine dye 2-[(2-butyl-1,3-dimethylcyclohepta[c]pyrrol-6(2H)-ylidene)methyl]-3-ethyl-1,3-benzothiazol-3-ium perchlorate. It was studied both in solution by means of NMR spectroscopy and in the solid state by X-ray diffraction. Due to the data obtained, it was proved that the dye molecule is practically planar in crystalline state. We described the effect of the intramorotation of molecular fragments around lecular the Cheterocycle—C_{methine} bond, which is slow on the NMR time scale. Both the bond order of the cyanine dye, around which rotation occurs, and the energy barrier of this process were assumed to depend on the electron-donating nature of the terminal groups. The results of the quantum-chemical calculations supported the experimental data. In the work presented below we show that this approach can be used to draw a certain scale of the electron-donating properties of different terminal groups on the basis of the rotation energy derived by the dynamic NMR experiments. Thus, we studied the dependence of the conformational transformations energy barriers on the nature of the terminal groups and on the chromophore chain length for the polymethine dyes derivatives of the 2-azaazulenium.

2. Experimental

2.1. General methods

All starting materials and solvents for the synthesis and spectroscopic measurements were supplied by Aldrich Chemical Co. and were used as received without further purification. UV/Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The melting points were measured with a melting point apparatus (Kleinfeld GmbH) and are uncorrected.

We chose representatives of the following groups of 2-azaazulene derivatives as objects of our research: unsymmetrical mono-, tri-, and pentamethine cyanines AAz-n-Het (Het is second terminal group, see Table 1) and styryl (methoxystyryl) dyes AAz-St.

We also investigated styryl/methoxystyryl dyes derivatives of 2,6-di(terbutyl)-pyrylium **OPy-St(R)**:



2.2. Synthesis

The synthesis, UV/Vis spectral characteristics, ¹H and ¹³C NMR data of 2-azaazulene monomethine cyanines AAz-0-AAz, AAz-0-BIn, AAz-0-BO, AAz-0-BT, AAz-0-4Q have been described in [22], the synthesis and properties of the corresponding trimethine cyanines - AAz-1-AAz, AAz-1-BIn, AAz-1-In, AAz-1-BT, AAz-1-4Q, AAz-1-2Q, AAz-1-BIm, AAz-1-NPy - in [23]. The corresponding new monomethine AAz-0-OPy and trimethines AAz-1-OPy and AAz-1-BO have been synthesized in a similar way. The symmetrical (AAz-2-AAz) and asymmetrical (AAz-2-OPy) pentamethine cyanines as well as styryl dyes (AAz-St(R) and OPy-St(R)) were synthesized according to the general approaches described in [25]. All compounds were purified by column chromatography and/or recrystallized before use, and their structures were confirmed by NMR.

2.2.1. 2-Butyl-6-[(2,6-di-tert-butyl-4H-pyran-4-ylidene)methyl]-1, 3-dimethylcyclohepta[c]pyrrolium tetrafluoroborate AAz-0-OPy

Triethylamine (0.1 mL) was added to the solution of 2-butyl-1, 3-dimethyl-6-(methylthio)cyclohepta[c]pyrrolium iodide (0.175 g, 0.5 mmol) and 2,6-di-tert-butyl-4-methylpyrylium tetrafluoroborate (0.147 g, 0.5 mmol). The solution was refluxed for 5 min, and was then allowed to cool to room temperature. After adding of diethyl ether the dye was precipitated, filtered off, and purified by chromatography on silica gel column eluting with a mixture chloroform: methanol (50:1). Yield 0.1 g (39.6%); mp 225 °C (decomposition). λ_{max} = 580 nm, ε = 63,400 M⁻¹ cm⁻¹ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ: 7.86 (d, J = 11.3 Hz, 2H, 4-H 8-H AAz), 7.05 (d, J = 11.3 Hz, 2H, 5-H 7-H AAz), 6.86–6.81 (br. s, 2H, Ar OPy), 6.23 (s, 1H, CAAZ-CH), 4.17-4.06 (m, 2H, NCH2), 2.58 (s, 6H, AAZ-CH3), 1.82-1.54 (m, 2H, NCH₂CH₂), 1.48-1.45 (m, 2H, CH₂CH₃), 1.31 (s, 18H, *t*-Bu), 0.92 (t, *J* = 7.3 Hz, 3H, CH₂CH₃). Calcd. for C₂₉H₄₀BF₄NO (505.44): C 68.91, H 7.98, N 2.77%; found: C 68.73; H 7.71; N 2.85%.

2.2.2. 2-Butyl-6-[3-(2,6-di-tert-butyl-4H-pyran-4-ylidene)prop-1-en-1-yl]-1,3-dimethylcyclohepta[c]pyrrolium tetrafluoroborate AAz-1-OPy

Triethylamine (0.1 mL) was added to a solution of 6-(2-anilinovinyl)-2-butyl-1,3-dimethylcyclohepta[c]pyrrolium tetrafluoroborate (0.160 g, 0.38 mmol) and 2,6-di-tert-butyl-4-methylpyrylium



n=0,1,2 AAz-n-Het

AAz-St(R)





tetrafluoroborate (0.113 g, 0.5 mmol) in acetic anhydride (3 mL). The solution was heated at 60 °C for 5 min, and was then allowed to cool to room temperature. The reaction mixture was diluted with diethyl ether (10 mL). The precipitate was filtered off, washed with diethyl ether, dried, and purified by recrystallization from acetonitrile. Yield 0.145 g (72%), mp 219–221 °C. $\lambda_{max} = 705$ nm, $\varepsilon = 63,400 \text{ M}^{-1} \text{ cm}^{-1}$ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ : 8.41 (deg. t, J = 13.2 Hz, 1H, C_{AAz} —CH=CH), 7.61 (br. d, $J \sim 11.2 \text{ Hz}$, 2H, 4-H 8-H AAz), 7.19 (br. s, 1H, Ar OPy), 6.60–7.20 (very br. signal, 1H, 5-H 7-H AAz), 6.36 (br. s, 1H, Ar OPy), 6.33 (d, J = 13.5 Hz, 1H, C_{AAz} —CH), 6.10 (d, J = 12.9 Hz, 1H, C_{OPy} —CH), 4.10–3.97 (m, 2H, NCH₂), 2.49 (s, 6H, AAz—CH₃), 1.25–1.48 (m, 2H, *CH*₂CH₃ *t*-Bu), 0.96 (t, J = 7.3 Hz, 3H, *CH*₂*CH*₃). Calcd. for C₃₁H₄₂BF₄NO (531.48): C 70.06, H 7.97, N 2.64%; found: C 69.85; H 7.82; N 2.78%.

2.2.3. 2-Butyl-6-[(1E,3E)-5-(2,6-di-tert-butyl-4H-pyran-4ylidene)penta-1,3-dien-1-yl]-1,3-dimethylcyclohepta[c]pyrrolium tetrafluoroborate **AAz-2-OPy**

A mixture of 4-(2,6-di-tert-butyl-4H-pyran-4-ylidene)but-2enal (0.052 g, 0.2 mmol) and 2-butyl-1,3,6-trimethyl-cyclohepta[c]pyrrolium tetrafluoroborate (0.064 g, 0.2 mmol) and acetic anhydride (1.5 mL) was heated for 3 min at 100 °C. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (10 mL). The precipitate was filtered off, washed with diethyl ether, dried, and purified by recrystallization from acetonitrile. Yield 0.05 g (45%), mp 180–182 °C; λ_{max} = 809 nm (in acetonitrile); ¹H NMR (CDCl₃, 400 MHz) δ : 8.24 (deg. t, J = 13.0 Hz, 1H, C_{AAz}—CH=CH), 8.17 (deg. t, *J* = 13.0 Hz, 1H, C_{OPy}—CH=CH), 7.50 (d, J = 11.4 Hz, 2H, 4-H 8-H AAz), 6.99 (very br. d, 2H, 5-H 5-H AAz), 6.49 (deg. t, J = 12.5 Hz, 1H, C_{AAz}—CH=CH—CH), 6.31 (d, *J* = 13.7 Hz, 1H, C_{OPy}—CH), 6.03 (br. d, *J* = 13.5 Hz, 1H, C_{AAz}—CH), 4.07-3.96 (m, 2H, NCH₂), 2.50 (s, 6H, AAz-CH₃), 1.72-1.60 (m, 2H, NCH₂CH₂), 1.47–1.35 (m, 2H, CH₂CH₃), 1.43–1.25 (br. s, 18H, *t*-Bu), 0.99 (t, J = 7.3 Hz, 3H, CH₂CH₃). Calcd. for C₃₃H₄₄BF₄NO (557.51): C 71.09, H 7.95, N 2.51%; found: C 69.80, H 7.89, N 2.62%.

2.2.4. 2-Butyl-6-[(1E,3E)-3-(3-ethyl-1,3-benzoxazol-2(3H)-

ylidene)prop-1-en-1-yl]-1,3-dimethylcyclohepta[c]pyrrolium iodide AAz-1-BO

Triethylamine (0.05 mL) was added to a solution of 6-(2-an ilinovinyl)-2-butyl-1,3-dimethylcyclohepta[c]pyrrolium tetrafluo-roborate (0.173 g, 0.41 mmol) and 3-ethyl-2-methyl-1,3-benzoxa

zol-3-ium iodide (0.119 g, 0.41 mmol) in acetic anhydride (2 mL). The solution was heated at 60 °C for 5 min, and was then allowed to cool to room temperature. The precipitate was filtered off, washed with diethyl ether, dried, and purified by recrystallization from acetonitrile. Yield 0.120 g (55.6%), mp 219-221 °C. $\lambda_{\text{max}} = 645 \text{ nm}$ (in acetonitrile); ¹H NMR (CD₃CN, 400 MHz) δ : 8.38 (deg. t, J = 13.4 Hz, 1H, C_{AAz}-CH=CH), 7.67-7.62 (m, 1H, Ar BO), 7.61-7.55 (m, 1H, Ar BO), 7.55-7.47 (m, 2H, Ar BO), 7.18 (d, J = 11.5 Hz, 1H, Ar AAz), 7.08 (d, J = 11.5 Hz, 1H, 5-H AAz), 6.98 (d, J = 11.5 Hz, 1H, Ar AAz), 6.34–6.25 (m, 3H, 7-H AAz C_{AAz} —*CH*=*CH*—*CH*), 4.26 (q, *J* = 7.3 Hz, 2H, N*CH*₂*CH*₃), 3.97–3.88 (m, 2H, NCH₂CH₂), 2.38 (br. s, 3H, AAz-CH₃), 2.35 (br. s, 3H, AAz-CH₃), 1.67-1.57 (m, 2H, NCH₂CH₂), 1.44 (t, *J* = 7.3 Hz, 3H, NCH₂CH₃), 1.44–1.33 (m, 2H, CH₂CH₃), 0.96 (t, I = 7.3 Hz, 3H, CH₂CH₃). Calcd. for C₂₇H₃₁IN₂O (531.48): C 61.60, H 5.94, I 24.11%; found: C 61.45, H 5.72, I 24.38%.

2.2.5. 2-Butyl-6-[5-(2-butyl-1,3-dimethylcyclohepta[c]pyrrol-6(2H)ylidene)penta-1,3-dien-1-yl]-1,3-dimethylcyclohepta[c]pyrrolium tetrafluoroborate **AAz-2-AAz**

A solution of 2-butyl-1,3,6-trimethyl-cyclohepta[c]pyrrolium tetrafluoroborate (0.315 g, 1 mmol), N-(3-anilinoprop-2-en-1-ylidene)benzenaminium chloride (0.130 g, 0.5 mmol), and anhydrous sodium acetate (0.1 g) in acetic anhydride (7 mL) was heated under stirring at 40 °C for 3 h. After cooling to room temperature the precipitated dye was filtered off and washed with acetic anhydride (1 mL) and dry diethyl ether (10 mL). For purification the solution of dye in methylene chloride (20 mL) was filtered, and filtrate was evaporated in vacuum. Yield 0.140 g (24%), mp 175-177° (decomposition); $\lambda_{\text{max}} = 924 \text{ nm}, \varepsilon = 212,000 \text{ M}^{-1} \text{ cm}^{-1}$ (in acetonitrile). ¹H NMR (acetone- d_6 + CD₃CN, 400 MHz) δ : 7.68 (t, J = 12.9 Hz, 2H, C_{AAz}—CH=CH), 7.39 (d, J = 11.5 Hz, 4H, 4-H 8-H AAz), 6.77 (d, J = 11.5 Hz, 4H, 5-H 7-H AAz), 6.58 (t, J = 12.2 Hz, 1H, C_{AAz}—CH=CH—CH), 6.40 (d, J = 13.6 Hz, 2H, C_{AAz}—CH), 4.11–3.88 (m, 4H, NCH₂), 2.46 (s, 12H, AAz–CH₃), 1.59–1.71 (m, 4H, NCH₂CH₂), 1.33–1.45 (m, 4H, CH₂CH₃), 0.95 (t, J = 7.1 Hz, 6H, CH₂CH₃). Calcd. for C₃₅H₄₃BF₄N₂ (578.53): C 72.66, H 4.79, N 4.84%; found: C 72.52, H 5.02, N 4.99%.

2.2.6. Preparation of AAz styryl dyes (general procedure)

A solution of 1 mmol of 2-butyl-1,3,6-trimethyl-cyclohepta[*c*]pyrrolium tetrafluoroborate and 1.5 mmol of p-dimethylaminobenzaldehyde or p-anisaldehyde in dimethylsulfoxide (2 mL) was heated at 50 °C for 15–20 min. The solvent was evaporated in vacuum. The residue was triturated with diethyl ether (5×5 mL), and dissolved in ethanol (2 mL). After cooling to room temperature the precipitated dye was filtered off and crystallized from ethanol.

2.2.7. 2-Butyl-6-{2-[4-(dimethylamino)phenyl]vinyl}-1,3dimethylcyclohepta[c]pyrrolium tetrafluoroborate **AAz-St(NMe₂)**

Yield 32%, mp >250 °C; $\lambda_{max} = 680$ nm, $\varepsilon = 48,200 M^{-1} cm^{-1}$ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ : 8.17 (d, *J* = 11.0 Hz, 2H, 4-H 8-H AAz), 7.80 (d, *J* = 15.3 Hz, 1H, C_{St}—CH), 7.62 (d, *J* = 8.6 Hz, 2H, 3-H 5-H St), 7.44 (d, *J* = 11.0 Hz, 2H, 5-H 7-H AAz), 6.95 (d, *J* = 15.3 Hz, 1H, C_{AAz}—CH), 6.70 (d, *J* = 8.6 Hz, 2H, 2-H 6-H St), 4.20–4.11 (m, 2H, NCH₂), 3.13 (s, 6H, N(CH₃)₂), 2.65 (s, 6H, AAz—CH₃), 1.70–1.57 (m, 2H, NCH₂CH₂), 1.47–1.36 (m, 2H, CH₂CH₃), 0.97 (t, *J* = 7.2 Hz, 3H, CH₂CH₃). Calcd. for C₂₅H₃₁BF₄N₂ (446.33): C 67.27, H 7.00, N 6.28%; found: C 67.07, H 6.88, N 6.35%.

2.2.8. 2-Butyl-6-[2-(4-methoxyphenyl)vinyl]-1,3dimethylcyclohepta[c]pyrrolium tetrafluoroborate **AAz-St(OMe**)

Yield 29%, mp 142–143 °C; $\lambda_{max} = 498$ nm, $\varepsilon = 23,900$ M⁻¹ cm⁻¹ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ : 8.42 (d, *J* = 10.8 Hz, 2H, 4-H 8-H AAz), 7.66 (d, *J* = 16.0 Hz, 1H, C_{St}—CH), 7.57 (d, *J* = 8.6 Hz, 2H, 3-H 5-H St), 7.56 (d, *J* = 10.8 Hz, 2H, 5-H 7-H AAz), 6.99 (d, *J* = 16.0 Hz, 1H, C_{AAz}—CH), 6.90 (d, *J* = 10.8 Hz, 2H, 2-H 6-H St), 4.27–4.18 (m, 2H, NCH₂), 3.87 (s, 3H, OCH₃), 2.70 (s, 6H, AAz—CH₃), 1.75–7.65 (m, 2H, NCH₂CH₂), 1.50–1.35 (m, 2H, *CH*₂CH₃), 0.98 (t, *J* = 7.3 Hz, 3H, CH₂CH₃). Calcd. for C₂₄H₂₈BF₄NO (433.29): C 66.53, H 6.51, N 3.23%; found: C 66.32, H 6.34, N 3.45%.

2.2.9. Preparation of **OPy** styryl dyes (general procedure)

A solution of 2,6-di-*tert*-butyl-4-methylpyrylium perchlorate (1 mmol) and p-dimethylamino-benzaldehyde or p-anisaldehyde (1.1 mmol) in acetanhydride (2 mL) was heated for 1 h at 130 °C. After cooling, the reaction mixture was triturated with diethyl ether (50 mL) and the obtained solid was filtered and crystallized from the mixture of ethanol–diethyl ether (1:2).

2.2.10. 2,6-di-tert-Butyl-4-{-2-[4-

(dimethylamino)phenyl]vinyl]pyrylium perchlorate, **OPy-St(NMe₂)**

Yield 71%, mp 192–194 °C; $\lambda_{max} = 577$ nm, $\varepsilon = 78,400$ M⁻¹ cm⁻¹ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ : 8.26 (d, *J* = 15.3 Hz, 2H, C_{St}—CH), 7.89 (d, *J* = 9.0 Hz, 2H, 3-H 5-H St), 7.44 (s, 2H, Ar OPy), 7.13 (d, *J* = 15.3 Hz, 1H, C_{OPy}—CH), 6.72 (d, *J* = 9.0 Hz, 2-H 6-H St), 3.15 (s, 6H, N(CH₃)₂), 1.45 (s, 18H, *t*-Bu). Calcd. for C₂₃H₃₂ClNO₅ (437.96): C 63.08, H 7.36, Cl 8.10%; found: C 62.84, H 7.21, Cl 8.24%.

2.2.11. 2,6-di-tert-Butyl-4-[2-(4-methoxyphenyl)vinyl]pyrylium perchlorate **OPy-St(OMe)**

Yield 56%, mp 261–263 °C; $\lambda_{max} = 446$ nm, $\varepsilon = 37,800$ M⁻¹ cm⁻¹ (in acetonitrile). ¹H NMR (CDCl₃, 400 MHz) δ : 8.34 (d, *J* = 15.8 Hz, 1H, C_{St}—CH), 7.89 (d, *J* = 8.8 Hz, 3-H 5-H St), 7.80 (s, 2H, Ar OPy), 7.73 (d, *J* = 15.8 Hz, 1H, C_{OPy}—CH), 6.90 (d, *J* = 8.8 Hz, 2-H 6-H St), 3.85 (s, 3H, OCH₃), 1.50 (s, 18H, t-Bu). Calcd. for C₂₂H₂₉ClO₆ (424.92): C 62.19, H 6.88, Cl 8.34%; found: C 62.26, H 6.65, Cl 8.52%.

2.3. DFT calculation

The geometries of the ground and transition states were optimized using the GAUSSIAN03 program set [26] within the DFT approximation. A functional M05-2X [27] was chosen as the most recommended for the determination of the kinetic and thermodynamic parameters as well as B3LYP [28] method in combination with 6-311G(d,p) basis sets [29] for the geometry optimization. For the ground and transition states the vibration analysis was \performed which yielded vibration frequencies (no imaginary vibration for the ground state and one imaginary vibration for the transition state) and zero point corrected energies. The rotation energy barriers around methine bonds were defined as the difference between the energies of the transition and ground states (1):

$$\Delta E = E_{\text{t.s.}} - E_{\text{g.s.}} \tag{1}$$

Wiberg bond indexes [30] were determined using the Natural Bond Orbital analysis [31]. Quantum-chemical calculations were performed for the isolated cation. In some cases the influence of the solvent was also taken into account. Geometry optimization and calculation of the energy and vibration frequencies for the ground and transition states were performed under the following algorithms. We used parameters obtained for vacuum as the starting geometry. The geometry optimization and calculation of the vibrational frequencies were carried out using the Onsager model [32]. Then we performed the geometry optimization by means of the CPCM polarizable conductor calculation model [33]. The total energy was defined as the sum of the electronic (PCM) and zeropoint (Onsager) energies. In our calculations the counter ions were neglected due to the assumption that in the diluted solutions the counter-ion has only weak influence on the cation conformation. We assumed also that aggregation of the molecules does not take place.

2.4. NMR experiments

All NMR experiments were carried out on Varian GEMINI 2000 spectrometer with 1H and 13C frequencies of 400.07 and 100.61 MHz, respectively. Tetramethylsilane was used as a standard for the δ scale calibration. We used DMSO- d_6 , CD₃CN, CDCl₃, acetone- d_6 , CD₂Cl₂ and some mixtures (see below) as solvents. Concentrations of the solutions constituted from 5 to 20 mmol L⁻¹. One of the main problems of the NMR experiments was to achieve the concentrations necessary for the accumulation of the acceptable spectra. Therefore, choosing a solvent we considered first of all the solubility of the substances. The crystallization and boiling points of the solvents were also important because in certain cases it was necessary to cool or heat the solution intensively in order to achieve the definite values of reaction rate constants it was necessary to cool or to heat the solution strongly.

The temperature of the experiments was determined accurate to 0.5 K. The errors of the parameters calculation could be attributed to the temperature determination accuracy upon the thermostating and to the precision of the line shape analysis.

2.5. Dynamic NMR calculations

The rate constants were determined by the visual comparison of the theoretical and experimental spectra. It was realized by means of WINDNMR 7.1 program [34], which afforded the simulation of the theoretical spectra using the modified Bloch equation. Upon the variation of the spectral parameters such as chemical shifts, coupling constants, line widths and rate constants it was possible to get the exact fitting of the theoretical and experimental spectra. Thus, it was possible to determine the rate constant of the isomerization process from the experimental spectra recorded at different temperatures based on the signal widths of protons participating in the exchange processes (for details see [34,35]). We chose "dddd" (for aromatic AAz protons), "AB Coupl" (for aromatic OPy protons) or "2-spin" (for CH3 and tert-Bu groups) with the two equal population (%a = %b = 50) as simulation patterns in WIND-NMR program, as at the first approximation these spectra can be regarded as a first-order system. Thermodynamic parameters of the isomerization process were determined by means of Eyring eq. (2) [35]:

$$k_{T} = \frac{k_{\rm B}T}{h} \exp\left(\frac{-\Delta G_{T}^{\neq}}{RT}\right) \tag{2}$$

where k_T is the rate constant, h is the Plank constant, k_B is the Boltzmann constant, and R is the gas constant. Enthalpy ΔH^{\neq} and entropy of activation ΔS^{\neq} were calculated from the eq. (3):

$$\ln\frac{k}{T} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + 23.76 \tag{3}$$

Thermodynamic parameters were determined by the leastsquares method adjusted from the linear relationship between the ln(*k*/*T*) and the inverse value of temperature 1/(*RT*). The absolute errors of the parameter values were determined by the leastsquares method. Free energy of activation ΔG_T^{\neq} was calculated as $\Delta G_T^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$.

3. Results and discussion

3.1. Molecular geometry and the analysis of NMR spectra

It is possible to present the electronic structure of investigated dyes simplistically from a position of the mesomerism theory as a hybrid of two canonical structures (rotations around of the C-C bonds 1 and 2n + 2 are shown by arrows), n – number of vinylene groups:



The contribution of each boundary forms to the molecular structure of a dye depends on the differences in the electron-donating properties of both terminal groups AAz and Het. The bond populations (bond orders) of the polymethine chain (PC), the rotation energy and the bond lengths change upon the variation of an electron-donating ability of the Het groups. For the given family of dyes energy of the rotation around methine bonds equals to the value of the energy barrier, which corresponds to the difference of energies between the transition state (perpendicular conformation, Fig. 1b) and the ground state (planar conformation, Fig. 1a).

Upon the rotation of the terminal group for 180° the degenerated isomer is formed. Thus, such a rotation process can be referred to as a pseudo-isomerization. The bond population and the rotation energy is a function of the electron-donating ability of the terminal Het group.

As an example, let us consider the constitution of pentamethine cyanine **AAz-2-OPy**, bearing 2-azaazulene and 2,6-di(*tert*-

butyl)pyrylium groups. We used Wiberg bond indexes (WBI) from the NBO theory as analogs of the bond orders. Traditionally, upon a study of the linear conjugated systems, the values of bond lengths in the conjugated chain are analyzed [36]. Fig. 2 demonstrates the values of the bond lengths, WBI, and rotation energy values for each bond of the PC for **AAz-2-OPy**:

The alternation of the bond lengths and bond orders is observed along the PC. The length of the bond 1 (C_{AAz} — $C_{methine}$) is maximal and its order is minimal due to the considerable contribution of the boundary structure **1.b**. For the bonds with the higher population the larger values of the rotation energies are observed.

As follows from the analysis of ¹H NMR spectra of monomethine cyanines **AAz-0-Het**, in the case of Het = 4Q, BT, BO, BIm (relatively strong electron donors – highly basic terminal groups) the signals of aromatic protons of AAz fragment appear as four broad non-equivalent doublets. For example, for **AAz-0-4Q** we observe them at 7.03 ppm (H8) and 6.86 ppm (H4), 6.90 ppm (H7) and 6.35 ppm (H5). In the case of relatively weakly basic terminal groups Het two doublets of the corresponding two pairs of AAz protons are observed: at 7.61 and 7.04 ppm for the symmetrical cyanine **AAz-0-AAz** [22] and at 7.86 and 7.05 ppm for **AAz-0-OPy**.

NOESY experiments on the dye **AAz-0-BO** revealed that "through space correlation" between the methine proton (6.42 ppm) and AAz—H5 (7.13 ppm) takes place, and not between the methine proton and AAz—H7 (7.69 ppm). This phenomenon can be explained by the hindered intramolecular rotation for some cyanines. The activation energy of this process depends mainly on the electron-donating abilities of the terminal groups and on their spatial properties, and can be estimated qualitatively from the simple ¹H NMR spectra. More accurate information can be obtained *via* the variable temperature NMR experiments.

It should be mentioned that in our case the dynamic NMR investigations are possible due to the fact that AAz fragment has the $C_{2\nu}$ symmetry and thus the both corresponding conformers are equivalent. In a similar way, it is possible to determine the rotation energy barriers for other terminal groups with the same symmetry, *e.g.* for OPy and BIm (bond 2 in structure **1.a**), and with the proper values of the activation energies. In the case of the terminal groups with low symmetry (C_s) rotation conformers have different energies. Therefore, most probably their relative populations will be considerably different. For such compounds the population of the energetically less favorable conformer is so poor that usually it cannot be detected by ¹H NMR.

To prove the possibility to detect the dynamic processes for the other then AAz groups with $C_{2\nu}$ symmetry group we synthesized and investigated three vinylogs **AAz-n-OPy** (n = 0, 1, 2), bearing 2,6-di(*tert*-butyl) residue. Indeed, at room temperature the signals of aromatic protons of the OPy moiety were significantly broadened; they appeared at ~6.83 ppm for **AAz-0-OPy** (in CDCl₃ at room temperature). At the same time, the signals of AAz protons were observed as two doublets (*vide supra*).

Cooling of the sample to low temperature resulted in the appearance of four separate doublets of AAz protons (7.89, 7.66,



Fig. 1. The spatial structure of two conformations of the dye AAz-1-OPy according to M05-2X/6-311G(d,p). The ground state (planar conformation, (a)) and the transition state (perpendicular conformation, (b)) are indicated.



Fig. 2. The bond lengths (a), Wiberg bond indexes (b), and the rotation energies (c) for the PC bonds of pentamethine cyanine **AAz-2-OPy** (n = 2) according to M05-2X/ 6-311G(d,p). "Bond" – means the number of bond in PC, see **1.a**.

7.25 and 7.71 ppm at -74 °C) and two signals of OPy protons (7.17 and 6.46 ppm with the *meta*-spin-spin coupling constants ${}^{4}J_{HH}$ < 1 Hz at -74 °C) in the spectra. Also we observed two separate signals of two methyl groups of the AAz fragment (at 2.61 and 2.56 ppm) and two singlets of *tert*-Bu substituents (at 1.32 and 1.28 ppm). Thus, here we detected two parallel dynamic processes for a single molecule. For tri-, and pentamethine cyanines **AAz-n-OPy**, and for the styryl dyes we observed the same phenomenon.

3.2. Calculation model influence and solvent effects

The thermodynamic parameters of the C_{Het} — $C_{methine}$ bond, which were determined both theoretically and experimentally, are presented in Table 2.

To search the regularities for correct analysis of received data it would be reasonable to compare the calculated values of rotation energy ΔE and experimental values of free energy ΔG^{\neq} [37]. But calculated magnitudes ΔE and the corresponding experimental parameters ΔG^{\neq} determined for the same dyes are different. The values of energy calculated for system in vacuum practically in each case predict the greater values of energy, than experimental values for a solution. Such difference is more pronounced for weakly basic terminal groups, then for highly basic one, and runs up to >30 kJ mol⁻¹. This fact could be explained by that in calculation the influence of solvent is not considered. Some influence of anion on the experimental result is also possible.

In order to try to explain this discrepancy and also to prove the correctness of our assumptions regarding the isomerization process, geometries of some dyes have been optimized by means of different quantum-chemical methods (we used functionals M05-2X and B3LYP) taking into account the influence of the medium. Functional B3LYP regularly underestimate the total energy of a molecule in comparison with M05-2X, especially it concerns to the energy of the ground state. It results in increase of the calculated value of an energy barrier. The rotation energy values for monomethine **AAz-0-OPy** obtained by methods M05-2X and B3LYP and 6-311G(d,p) basis set are equal correspondingly 55.2 and $61.8 \text{ kJ} \text{ mol}^{-1}$; for dye **AAz-0-BT** – 69.7 and 71.7 kJ mol⁻¹ [24]; for trimethine **AAz-1-BT**: 74.0 and 82.3 kJ mol⁻¹.

For some cyanines and styryl dyes AAz-St the calculations of rotation energy were performed taking into account the solvent influence (Table 2). It was possible to get the required structural regularities by the calculations of the most interesting cases which have been mentioned in the Table 2. The calculations have been performed not for all compounds because such procedures usually are labor-intensive and time-consuming process. Geometry optimization of the ground and transition states when taking into account the solvent influence, predicts some decreasing of the full molecule energy due to the solvation effect, where for the transition state such stabilizing is more pronounced then for the ground state. It means that upon solvation, the decreasing of the rotation energy takes place. For example, for symmetrical monomethine cyanine AAz-0-AAz, stabilizing energies for the ground and transition states are equal 139.9 and 161.4 kJ mol⁻¹ correspondingly. It resulted in decreasing of the value of rotation energy on 21.5 kJ mol⁻¹.

For some dyes we performed the measurements in different solvents using polar DMSO (dielectric constant ε = 46.7) and acetonitrile (ε = 36.6) as well non-polar chloroform (ε = 4.9) and methylene chloride (ε = 8.9) in order to fix the possible differences that could appear for media of different polarity. But minor differences are observed between the corresponding values in different solvents (ΔG^{\neq} is not more than 1–2 kJ mol⁻¹, see Table 2.). Thus we can make a conclusion regarding a relatively slight influence of medium polarity on the conformational behavior of dye molecules. The calculations of rotation energy with regard to the solvent polarity influence predict larger range of difference in values (ΔE : 7–10 kJ mol⁻¹) than it follows from experiment.

It is possible to assume the rotation barrier values to be dependent on the solution concentration since dye molecules could form aggregates. But we did not perform the special experiments aiming the investigation of the concentration dependence of the rotation barriers due to the insufficient solubility of azaazulenium dyes. At the same time, the experiments in the different solvents proved the low solvent dependence of ΔG^{\neq} values. It allows us to assume the corresponding low dependence of ΔG^{\neq} on the concentration factor.

3.3. Monomethine cyanines

The symmetrical monomethine cyanine AAz-O-AAz has the lowest value of the rotation energy barrier. Using a mixture of acetone- d_6 and CDCl₃ (approx. 5:1 v/v) as a solvent (because the solubility of this dye in the pure acetone is too low) it was still impossible to attain the complete resolution of the signals of the corresponding pairs of AAz moiety protons even at -70 °C. The same situation took place in the case of the unsymmetrical dye AAz-0-BIn. Here the measurements were complicated due to the limited dye solubility at low temperatures. For the monomethine cvanine containing less basic terminal BO group four non-equivalent doublets of AAz protons are observed (7.68, 7.58, 7.50, and 6.74 ppm), which are slightly broadened due to the dynamic process at room temperature in DMSO-d₆. Only upon heating of the sample to 100 °C we detected the coalescence of the aromatic protons. In this same as in many other cases of AAz cyanine dyes the difference of the chemical shifts for the H5 and H7 proton pair can exceed 300 Hz at 400 MHz ¹H frequency (in the case of **AAz-0-BO** it constituted 373 Hz in DMSO- d_6). Evidently, this fact could be

Table 2

Calculated values of the rotation energy around the C_{Het} - $C_{methine}$ bond (ΔE) (M05-2X/6-311G(d,p)), calculated energy values with the consideration of the solvent influence (M05-2X/6-311G(d,p) CPCM (ΔE (CPCM)), and experimental thermodynamic activation parameters.

| Dye (Het) ^a | Solvent | ΔE | ΔE (CPCM) | $\Delta H^{ eq}$ | ΔS^{\neq} | ΔG^{\neq}_{298} |
|------------------------|-------------------------------------|------------|-------------------|---------------------|-------------------|-------------------------|
| AAz-0-AAz | Acetone- d_6 + CDCl ₃ | 57.4 | 35.8 | 30.5 ^b | -26.3 | 38.3 |
| AAz-1-AAz | Acetone- d_6 + CDCl ₃ | 77.5 | 55.3 | 52.2 ± 0.9 | 8.0 ± 3.4 | 49.8 |
| AAz-2-AAz | Acetone- d_6 + CD ₃ CN | 78.5 | 36.6 | 43.6 ± 0.8 | -3.4 ± 0.1 | 44.6 |
| AAz-0-OPy | CDCl ₃ | 55.2 | 42.6 | 44.4 ± 2.5 | 5.0 ± 0.3 | 42.9 |
| AAz-0-OPy (OPy) | CDCl ₃ | 64.2 | 51.9 | 50.5 ± 1.3 | -6.4 ± 0.1 | 52.4 |
| AAz-1-OPy | CDCl ₃ | 69.6 | 57.7 | 51.3 ± 0.5 | 7.3 ± 2.0 | 49.1 |
| AAz-1-OPy (OPy) | CDCl ₃ | 85.1 | 68.4 | 67.8 ± 1.9 | 26.9 ± 6.5 | 59.8 |
| AAz-1-OPy | CD ₃ CN | 69.6 | 50.3 | 50.1 ± 0.6 | -5.8 ± 2.1 | 51.8 |
| AAz-1-OPy (OPy) | CD ₃ CN | 85.1 | 58.5 | 53.6 ± 0.8 | -14.5 ± 2.7 | 57.9 |
| AAz-2-OPy | CDCl ₃ | 75.3 | 53.6 | 43.0 ± 0.8 | -23.8 ± 2.8 | 50.1 |
| AAz-2-OPy (OPy) | CDCl ₃ | 96.5 | 62.2 | 56.7 ± 0.8 | -1.7 ± 1.1 | 57.2 |
| AAz-2-OPy | CD_3CN | 75.3 | 38.4 | 42.5 ± 0.8 | -17.5 ± 2.8 | 47.7 |
| AAz-2-OPy (OPy) | CD_3CN | 96.5 | 44.6 | 47.4 ± 0.8 | -16.7 ± 2.8 | 52.4 |
| AAz-0-BIn | CDCl ₃ | 48.5 | - | 36.4 | -11.5 | 39.8 |
| AAz-1-BIn | CD_3CN | 71.1 | - | 63.6 ± 0.9 | 40.7 ± 3.4 | 51.4 |
| AAz-1-In | CD ₃ CN | 70.0 | - | 60.5 ± 0.6 | 11.4 ± 2.0 | 57.1 |
| AAz-0-BO | DMSO | 77.6 | - | 84.2 ± 3.2 | 37.5 ± 9.6 | 73.0 |
| AAz-0-BO | CDCl ₃ | 77.6 | - | 79.1 ± 3.4 | 22.3 ± 10.6 | 72.4 |
| AAz-1-BO | CD ₃ CN | 77.7 | - | 62.9 ± 0.6 | -9.1 ± 2.0 | 65.6 |
| AAz-0-BT | CD ₃ CN | 69.7 | - | 61.1 ± 0.8 | -8.9 ± 2.5 | 63.7 |
| AAz-0-BT | DMSO | 69.7 | - | 59.1 ± 0.5 | -19.5 ± 1.6 | 64.9 |
| AAz-1-BT | CD ₃ CN | 74.0 | - | 79.3 ± 1.1 | 50.8 ± 3.5 | 64.2 |
| AAz-1-BT | DMSO | 74.0 | - | 72.8 ± 3.4 | 26.1 ± 10.1 | 65.0 |
| AAz-1-BT | CD_2Cl_2 | 74.0 | - | 84.4 | 69.8 | 63.6 |
| AAz-0-4Q | CDCl ₃ | 63.0 | 59.0 | 71.0 ± 1.3 | 25.7 ± 4.4 | 63.3 |
| AAz-1-4Q | DMSO | 78.3 | 65.9 | 90.1 ± 2.9 | 52.5 ± 8.2 | 72.6 |
| AAz-1-2Q | DMSO | 82.1 | - | 74.7 ± 1.0 | 2.9 ± 3.0 | 73.9 |
| AAz-1-BIm | DMSO | 97.6 | - | 110 °C ^c | - | - |
| AAz-1-NPy | DMSO | 100.1 | - | 78 °C | - | - |
| AAz-St(NMe2) | CDCl ₃ | 50.4 | 40.9 | −70 °C | - | - |
| AAz-St(NMe2) (St) | CDCl ₃ | 52.3 | - | −70 °C | - | - |
| AAz-St(OMe) | CDCl ₃ | 38.8 | 31.1 | −63 °C | - | - |
| AAz-St(OMe) (St) | CDCl ₃ | 36.8 | | −63 °C | - | - |
| Py-St(NMe2) (OPy) | CDCl ₃ | 65.3 | - | 43.8 ± 0.5 | -14.5 ± 2.3 | 48.1 |
| Py-St(NMe2) (St) | CDCl ₃ | 62.7 | - | 48.2 ± 0.8 | 8.9 ± 5.7 | 45.6 |
| Py-St(OMe) (OPy) | CDCl ₃ | 52.6 | - | 36.5 ± 0.3 | 0.3 ± 1.7 | 36.4 |
| Py-St(OMe) (St) | CDCl ₃ | 44.2 | - | −92 °C | - | _ |

^a On default, one means the rotation energy around bond 1 (formulae **1.a**) Het = AAz. In parentheses we placed terminal groups different from AAz for which the values of rotation energy around the bond 2 (**1.a**) was determined.

^b By italics the values determined with lowered accuracy are shown.

^c For compounds, for which it was not possible to determine the thermodynamic parameters owing to very great (or small) energy values, the temperature, to which the solution was heated up (or the solution was cooled) are specified.

explained by the magnetic shielding of the H7 proton by the conjugated system. The signals of the AAz H7 proton are usually shifted upfield (in the case of **AAz-0-BO** it appears at 6.76 ppm). It results in the observed wide temperature range (>100°) where the dynamic process can be detected by NMR, allowing accurate line shape analysis. It is worth mentioning that the 2-azaazulenium unit has one distinctive feature: due to its electron-donating properties and symmetry it yields such values of the rotation energy barriers that they are the most suitable for running DNMR investigations. Fig. 3 demonstrates the experimental and calculated values of the rotation energy barriers for the series of monomethine cyanines.

In the series of monomethine dyes **AAz-0-Het** changes from OPy to 4Q lead to the increase of the C_{AAz} — $C_{methine}$ bond order values, indicating the increase of the boundary structure **1.a** contribution.

According to the quantum-chemical calculations (M05-2X/6-311G(d,p) as well as B3LYP [22]), monomethine cyanine cations are nonplanar due to the considerable steric hindrance between the heterocyclic terminal groups, with the exception of **AAz-0-BO**, which is practically planar due to the small size of the oxazole cycle. Therefore, aiming to reduce the influence of the steric factors on the result of the analysis to get a clear insight in the effects of the electron-donating properties of the terminal groups we have to consider trimethine dye molecules.

3.4. Trimethine cyanines

Fig. 4 demonstrates graphically the values of Wiberg indexes for the C_{AAz} — $C_{methine}$ bond (bond 1 – **1.a**) in molecules of trimethine cyanines, rotation around which was investigated by the dynamic NMR.

For trimethine **AAz-1-Het**, where Het = OPy, In, Bin, as well as for the symmetrical trimethine cyanine (Het = AAz), ¹H NMR signals of the AAz H4 and H8 protons appear as broad doublets (for Het = OPy at 7.60 ppm in CDCl₃ at 20 °C) and signals of the H5 and H7 appear as considerably broadened peaks (for Het = OPy at 7.08 ppm in CDCl₃) due to the fast rotation of the AAz fragment at room temperature. To attain the conditions of slow exchange we cooled the solution nearly to the crystallization point. Indeed,



Fig. 3. Values of the rotation energy around C_{AA2} — $C_{methine}$ bond of the monomethine **AA2-0-Het** dyes according to the quantum chemical calculations M05-2X/6-311G(d,p) (DFT), ΔE , and experimental measurements (DNMR), $\Delta G_{298}^{=}$.



Fig. 4. Wiberg bond indexes for the $C_{AAz}-C_{methine}$ bond (bond 1 in structure 1.a) for the trimethine cyanines AAz-1-Het.

upon cooling two doublets divided into four separate doublets (for Het = OPy at 7.70, 7.54, 7.44, 6.52 ppm in CDCl₃ at -69 °C). In the case of more basic terminal groups (BT, BO, 4Q, 2Q) we observed the signals of the AAz protons as four non-broadened doublets even at room temperature. Upon heating the broadening of doublets followed by the coalescence was detected. For the most basic terminal groups the activation energy is so high that we did not manage to detect any appreciable broadening of the signals even at temperatures above 100 °C and thus we could not measure the rotation barriers experimentally. Such increase of the activation energy is confirmed by the quantum-chemical calculations, which predict its value in the range of 97–100 kJ mol⁻¹ for NPy and BIm (Table 2).

The dyes **AAz-***n***-OPy** are among the few cyanines for which both dynamic processes were detected. Fig. 5 shows the series of the variable temperature ¹H NMR spectra recorded in CD₃CN in the temperature range from the crystallization to the boiling point of the solvent.

At temperatures below $-40 \,^{\circ}\text{C}$ the intramolecular rotation around both C_{AAz} — $C_{methine}$ and C_{OPy} — $C_{methine}$ bonds became slow on the NMR time scale, and we observed the signals of all groups of protons, marked as H4—H12, separately. At higher temperatures we detected the coalescence of the corresponding pairs of signals. At $-36 \,^{\circ}\text{C}$ the coalescence of the proton signals of two methyl groups of AAz moiety was observed. At 2 °C the coalescence of *tert*-Bu group signals took place. At temperatures above 60 °C the intramolecular rotation rate increases to such an extend that the entire corresponding proton pairs become equivalent. Besides that, the shift of peaks positions was detected upon the temperature variation. The same pattern was observed for all the other dyes.

Temperature variations did not induce any irregular changes in the spectra *e.g.* appearance of additional signals or shifts of the signals, which were not connected with the temperature influence. From our point of view, it indicates the absence of the dye molecules aggregation. The similarity of the spectra, which were recorded in the solvents with different polarities, also proves this conclusion.

It should be noted that rotation energies of the exocyclic C_{OPy} — $C_{methine}$ bonds were estimated earlier for the series of hetero-fulvenes and fell in the range of 58–92 kJ mol⁻¹ [38].

The calculated values of the rotation energies (see Fig. 6) are in good agreement with the bond orders: upon the increase of the bond order the rotation energy value also increased. However, in some cases experimental data differ from the theoretical both in the absolute value and in the relative one.



Observed differences could be explained by the solvent influence, which would be discussed below, as well as by the peculiarities of the calculation model. Despite these distinctions, the general tendencies in the basicity variations upon the terminal Het group changes are clearly visible.

It is important to note that when Het is more basic than AAz the value of the rotation barrier around the C_{AAz} — $C_{methine}$ bond increases while the rotation barrier around the C_{Het} — $C_{methine}$ bond decreases upon the increase in difference of the terminal groups



Fig. 5. Variable temperature ¹H NMR spectra of AAz-1-OPy in CD₃CN. Coalescences of different signals at the corresponding temperatures are marked as "*T* coal". For the pairs of H5–H7 and H12–H13 signals the significant difference of chemical shifts is observed, and in the region of their coalescence temperatures these peaks are "smeared".

basicity. Thus, in the case of the most basic 2Q and 4Q groups the largest values of the rotation barrier around the $C_{AAz}-C_{methine}$ bond are observed. We also confirm again our conclusion regarding the low basicity of the 2-azaazulenium terminal group. On the basis of results of the dynamic NMR investigations we obtained the following basicity order (electron donor ability) for the heterocyclic terminal groups:

$$OPy < AAz < BIn < In < BT < BO < 4Q < 2Q < BIm, NPy$$

This sequence is analogous to the one presented by Brooker, who arranged heterocyclic nuclei in order of basicity considering the deviations in absorption maxima of *para*-dimethylaminostyryl dyes [12]. There are only two exceptions in these sequences, namely, according to [12] 4Q is more basic than 2Q, and BT is more basic than BO.

3.5. Styryl dyes

From the resonance-mesomerism theory point of view, the main feature of the styryl dyes lies in more "polyene" than "cyanine" character of their conjugated system. It is exhibited in more pronounced alternation of the bond lengths and bond orders, and less pronounced alternation of the atomic electron density for styryles. For the comparison, the magnitudes of Wiberg indexes for the bonds of the conjugated chain constitute 1.259, 1.530, 1.227 for the styryl dye AAz-St(NMe2); 1.207, 1.605, 1.170 for the methoxystyryl AAz-St(OMe); 1.337, 1.424, 1.383, 1.367 for the cyanine AAz-1-OPy. From these data it is evident that for the styryl AAz-St(NMe₂) the bond alternation is less pronounced than for the methoxystyryl AAz-St(OMe). Therefore for the styryl dyes the values of the rotation energy around CAAZ-Cmethine and C_{Ph}-C_{methine}bonds are lower then for the cyanines. The calculations support this fact (Table 2). Unfortunately, we were unable to determine experimentally the rotation barrier for the styryl AAz-St(NMe₂) due to its extremely low value, although at T < -30 °C we detected some deceleration of the molecular fragments rotation according to the NMR spectra. For the methoxystyryl, no broadening of the corresponding signals was detected even at the solvent crystallizing point at -63 °C.

The solvation effects observed for the styryles are similar to that observed for the cyanine dyes. According to the calculations, the solvent reduces the energies of the ground and the excited states as well as the rotation energy (Table 2). Di-*tert*-Bu-pyrylium terminal group is less basic then the 2-azaazulenium one. It results in the decrease of the alternations of the bond lengths and orders upon the change to styryles **OPy-St** bearing di-*tert*-Bu-pyrylium residue. We managed to measure experimentally the values of the isomerization energy for these dyes. Besides that, we registered also two parallel dynamic processes of the rotation around C_{Ph}-C_{methine} and C_{OPy}-C_{methine} bonds. However, the exact value for the first bond was not calculated, since the separation of the corresponding signals was not achieved even at -92 °C.



Fig. 6. Values of the rotation energy around the C_{AAz} — $C_{methine}$ bond for trimethines **AAz-1-Het** according to the quantum chemical calculations (M05-2X/6-311G(d,p)), ΔE , and to the experimental measurements (DNMR), $\Delta G_{298}^{=}$.

For the styryles the values of the rotation barriers for both $C_{Ph}-C_{methine}$ and $C_{AAz}(C_{OPy})-C_{methine}$ bonds are in direct proportion to the difference in basicities of the terminal groups. As could be expected, the values of the rotation energy barriers for these bonds of the styryl **OPy-St(NMe_2)** are higher than for the methoxystyryl **OPy-St(OMe)** (Table 2). The same difference in the rotation energies was also detected in the carbon NMR spectra of these compounds recorded at ambient temperature in CDCl₃. For the styryl **OPy-St(NMe_2)** signals of the carbon atoms C1 (109.94 ppm) and C6 (134.71 ppm) are appreciably broadened due to the hindered rotation around the C2–C3 and C4–C5 bonds, respectively (Fig. 7). Such an effect was not observed for the methoxystyryl molecules, which are characterized by lower rotation energies of the corresponding bonds and sharp signals of atoms C1 (112.73 ppm) and C6 (133.09 ppm).

3.6. The Influence of polymethine chain length

On the basis of the rotation energy values for the dye vinylogs we can draw certain conclusions concerning the influence of the length of polymethine chain on the characteristic features of the conjugation in the system.

Only minor changes of the C_{AAz} — $C_{methine}$ bond lengths were observed upon going from the monomethine to pentamethine cyanines. Due to the M05-2X/6-311G(d,p) calculations in the case of the symmetrical cyanines **AAz-n-AAz** these bond lengths are 1.407 Å, 1.407 Å, 1.405 Å, and in the case of the unsymmetrical **OPy-n-AAz** they are 1.408 Å, 1.410 Å, 1.409 Å respectively. However, the bond populations and rotation energies are more sensitive to the polymethine chain length. It was found that upon going from the sterically hindered monomethine cyanines to the unhindered trimethines with the same terminal groups the change of the free activation energy $\Delta \Delta G_{298}^{\neq}$, calculated by the Eq. (4) correlates with the torsion angle between the planes of the terminal groups in the monomethine molecule (Fig. 8).

$$\Delta\Delta G_{298}^{\neq} = \Delta G_{298}^{\neq} (\text{trimethine}) - \Delta G_{298}^{\neq} (\text{monomethine})$$
(4)

Among the dyes which have been investigated the minimal spatial strain was observed for the molecules of the benzoxazolium monomethine cyanine **AAz-0-BO**. It results in the stabilization of the ground state and increase of the rotation energy. The perpendicular transition state is not affected by the sterical features of the terminal groups. In the case of **AAz-n-BO** the energies rises in the row from the trimethine to the monomethine ($\Delta\Delta G^{\neq} < 0$). For the others monomethines the ground states are non-planar and therefore energetically destabilized. It reduces the rotation



ppm 132 124 116

Fig. 7. Fragments of ¹³C NMR spectra of the dyes **OPy-St** $R = N(CH_3)_2$ (a) and $R = OCH_3$ (b) in $CDCl_3$ at T = 293 K.



Fig. 8. The differences of free energy activation $\Delta \Delta G_{298}^{\neq}$ (4) as a function of dihedral (torsion) angle between the planes of the terminal groups of the monomethine cyanine **AAz-0-Het**, and linear regression (solid line) calculated by the least-squares method.



Fig. 9. The rotation energies of the C_{AAz}—C_{methine} bond for the vinylogs **AAz-n-AAz** and **AAz-n-OPy** (in CDCl₃).

energy and receds the energies in the row from the tri- to monomethine ($\Delta\Delta G^{\neq} > 0$). Thus, $\Delta\Delta G^{\neq}$ parameter can be used to draw certain conclusions on the spatial arrangement of the terminal groups.

Further lengthening of the polymethine chain in the pentamethine cyanines leads to the decrease of the activation energy in the case of the symmetrical cyanines **AAz-n-AAz**. *Vice versa*, in the case of the unsymmetrical **AAz-n-OPy** minor increase of the energy is observed (Fig. 9).

4. Conclusions

A systematic study of the conformational behavior of the symmetrical and unsymmetrical cyanine dyes bearing a 2-azaazulenium moiety in solution was carried out by means of quantumchemical and experimental methods.

The direct correlation between the barriers to conformational transformations and such parameters as electron-donating properties of the terminal groups and the polymethine chain length were established experimentally. The values of the rotation energies for the methine bonds are proportional to the difference in the electron-donating properties of the terminal groups of the unsymmetrical cyanines. Spatial hindrances of the bulky terminal groups reduce the bond rotation energy in monomethine cyanines. The styryl dyes are characterized by the minor values of the rotation energies around the corresponding bonds compared to the cyanines. The data of the quantum-chemical calculations are in agreement with those obtained experimentally.

It was proved by the calculations using the polarizable continuum model that solvation stabilizes the ground and transition states of the dyes and appreciably reduces the barrier values. The solvent polarity has relatively weak influence on the absolute energy values.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.10.003.

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