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Self-assembly involving hydrogen bonds. Spectral properties and structure of supramolecular complexes of bis-aza-18-crown-6-containing dienones with alkanediammonium salts

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ABSTRACT

Dienones (ketocyanine dyes) containing two aza-18-crown-6 ether residues were synthesized. The complex formation of these dyes with the EtNH $_3^+$ and $^+H_3N(CH_2)_nNH_3^+$ ions (n = 2-10, 12) in MeCN was studied by electronic and ¹H NMR spectroscopy, including spectrophotometric and ¹H NMR titration. It was found that homoditopic bis-azacrown dienones and alkanediammonium ions with a short polymethylene chain form 1:1, 2:2, and 1:2 complexes, whereas alkanediammonium ions with a long polymethylene chain form only pseudocyclic 1:1 complexes. The stability constants of the resulting complexes were determined $(log K_{1:1})$ varies in the range from 2.74 to 5.62 [M^{-1}], log $K_{2:2} = 2.1$ [M^{-1}], and log $K_{1:2}$ varies in the range from 2.03 to 2.96 [M^{-1}]). The most stable complexes are formed by diammonium ions with a long polymethylene chain owing to simultaneous binding of both NH₃⁺ groups to the azacrown ether residues of the dye. The structure of supramolecular complexes was confirmed by quantum chemical calculations.

1. Introduction

The formation of supramolecular systems involving hydrogen bonds is considered to be one of the most efficient ways of self-assembly of biomolecules in the living nature and organic molecules in solution [1]. Organic ammonium salts are widespread in biological systems, and diammonium cations play an important role in the cell biology and pharmacy. The development of synthetic receptors for their molecular recognition and analytical determination in medical and biological studies gains much attention. Of particular interest is the design of receptor molecules that recognize primary ammonium ions and related substrates [2]. Crown ethers are typical receptors for ammonium cations. Crown ethers can bind primary ammonium ions via the formation of three hydrogen bonds with the NH₃⁺ groups [1]. Biscrown ethers are of particular interest as molecular sensors for diammonium cations, because they can efficiently bind them if the crown ether moieties are geometrically preorganized for complexation with both ammonium groups simultaneously.

The strategy we are developing for the self-assembly of photoactive supramolecular systems based on biscrown-containing unsaturated compounds (donors, D) and di(ammonioalkyl) organic derivatives (acceptors, A) allows the forced assembly of components as a result of cooperative effect of numerous weak interactions (hydrogen bonds) [3-7] and study of their unusual photochemical and photophysical properties. It is noteworthy that this strategy can be employed to obtain very strong D-A complexes even with weak acceptors. For example, bis (18-crown-6)stilbene and weak acceptors form highly stable 1:1 complexes in which ground-state charge transfer takes place, because of the proximity of the donor and acceptor moieties, giving rise to absorption in the visible range upon the formation of charge transfer complex and change in the redox potentials of both components [8,9]. It was shown that complex formation of this biscrown derivative with alkanediammonium ions promotes the formation of exotic bis-pseudosandwich complexes in which the ethylene bonds of two

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stilbenes are proximate in space and pre-organized for stereoselective [2 + 2] photocycloaddition reaction giving cyclobutane derivatives [4, 5].

Bis-aza-15-crown-5-containing dienones (ketocyanine dyes) with two identical binding sites directly connected to symmetrical crossconjugated chromophores are attractive objects for the study of selfassembly [10,11]. The interaction of these dyes with alkali and alkaline earth metal cations was studied in detail [10,12,13]. Meanwhile, the potential of bis-aza-18-crown-6-containing dienones, capable of complex formation with primary ammonium ions, as components of photoactive supramolecular assemblies consisting of several organic molecules remains unimplemented.

In this paper, we first present a ditopic receptor for diammonium salts based on azacrown-containing ketocyanine dyes. We describe the synthesis of symmetrical bis-aza-18-crown-6 dienones **1a**,**b** and study their complex formation with a series of $1,\omega$ -alkanediammonium salts ⁺H₃N(CH₂)_nNH₃⁺ 2ClO₄ (**2**, where n = 2-10, 12, respectively) and ethylammonium perchlorate by ¹H NMR and electronic spectroscopy and by quantum chemical calculations. We also compare the complexation capacity of azacrown-containing dienones with that of a model dienone **3a** with two NEt₂ groups. The effect of the chain length of the 1, ω -alkanediammonium salts on the composition, spatial structure, and stability of supramolecular complexes with bis-aza-18-crown-6 dienones **1a**,**b** was studied. The structures of the compounds are shown in Fig. 1.

2. Experimental

2.1. Materials

EtNH₃ClO₄, 1,ω-alkanediammonium diperchlorates 2 [3,4], (2E,

5*E*)-2,5-bis[4-(diethylamino)benzylidene]cyclopentanone (**3a**), (2*E*, 5*E*)-2,5-dibenzylidenecyclopentanone (**3b**) [14], and 4-(1,4,7,10, 13-pentaoxa-16-azacyclooctadecan-16-yl)benzaldehyde (**4**) [15–17] were prepared by known procedures. Bu₄NClO₄ (Fluka), cyclopentanone and cyclohexanone (**5a,b**) (Sigma–Aldrich) were used as received. MeCN (extra high purity, water content < 0.3%, Cryochrom) was used to prepare solutions.

2.1.1. (2E,5E)-2,5-Bis[4-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)benzylidene]cyclopentanone (1a)

A solution of cyclopentanone (2.1 mg, 0.025 mmol) in ethanol (0.3 mL) is added to 4'-formylphenylaza-18-crown-6 ether 4 (20 mg, 0.055 mmol), then a 40% aqueous solution of KOH (120 µL) is added dropwise with stirring. The reaction mixture is kept for 1.5 h at room temperature (TLC monitoring), acidified with 1 *M* HCl to pH = 6-7, diluted with water (5 mL), and extracted with benzene (5 \times 4 mL). The extracts are evaporated in vacuo, and the residues are purified by column chromatography on alumina (Type T, Basic, 0.063–0.200 mm, Merck), using successively benzene and benzene-ethyl acetate gradient solvent (up to 80% ethyl acetate) as eluents to give 17 mg (87% yield) of bis-aza-18-crown-6 dienone 1a as a light-red oil. Rf 0.67 (EtOH-EtOAc, 1:10 (v/ v), DC-Alufolien Aluminiumoxid 60 F254 neutral, Merck). UV-vis (MeCN) λ_{max} 275 nm ($\varepsilon = 18700 \text{ M}^{-1} \text{ cm}^{-1}$), 466 nm ($\varepsilon = 66300$ M^{-1} cm⁻¹); fluorescence (MeCN, λ_{ex} 460 nm) λ_{max}^{fl} 562 nm. IR (mineral oil, ν): 1678 cm⁻¹ (C = O). HRMS (ESI+) m/z calcd. for C₄₃H₆₂N₂O₁₁ $[M+H]^+$: 783.4432. Found: 783.4426. Anal. calcd. C43H62N2O11.0.5H2O: C, 65.21; H, 8.02; N, 3.54. Found: C, 65.45; H, 8.24; N, 3.43. ¹H NMR (500 MHz, MeCN-*d*₃, 27 °C) δ: 3.03 (br s, 4H, 3-CH2, 4-CH2), 3.59 (m, 32H, 16 CH2O), 3.66 (m, 16H, 4 CH2CH2N), 6.79 (d, 4H, J =9.2 Hz, 2 3'-H, 2 5'-H), 7.34 (s, 2H, 2 α-H), 7.51 (d, 4H, J



⁺H₃N(CH₂)_nNH₃⁺ 2ClO₄⁻

2, *n* = 2-10, 12; respectively



3: R = NEt₂ (**a**), H (**b**)

Fig. 1. Structure of compounds 1-3.

=9.2 Hz, 2 2'-H, 2 6'-H). ¹³C NMR (125 MHz, MeCN- d_3 , 30 °C) δ : 27.22 (3-C, 4-C), 51.85 (4 CH₂N), 69.10 (4 CH₂CH₂N), 71.16, 71.21, 71.31, and 71.36 (16 CH₂O), 112.63 (2 3'-C, 2 5'-C), 124.52 (2 α -C), 133.27 (2 1'-C), 133.55 (2 2'-C, 2 6'-C), 134.43 (2-C, 5-C), 149.90 (2 4'-C), 195.86 (C = O).

2.1.2. (2E,6E)-2,6-Bis[4-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)benzylidene]cyclohexanone (1b)

A solution of cyclohexanone (4.9 mg, 0.05 mmol) in ethanol (0.2 mL) is added to 4'-formylphenylaza-18-crown-6 ether 4 (44.8 mg, 0.12 mmol), then a 5% NaOH solution in an ethanol-water mixture (2:1, v/v) (0.25 mL) is added dropwise with stirring. The reaction mixture is refluxed for 4 h (TLC monitoring), acidified with 0.5 M HCl to pH = 6–7, diluted with water (5 mL), and extracted with benzene $(3 \times 4 \text{ mL})$ and ethyl acetate (3×4 mL). The extracts are evaporated *in vacuo*, and the residues are purified by column chromatography on alumina (Type T, Basic, 0.063–0.200 mm, Merck), using benzene and then benzene-ethyl acetate gradient solvent (up to 9% ethyl acetate) as eluents to give 28 mg (70% yield) of bis-aza-18-crown-6 dienone 1b as a brown-red oil. $R_f 0.73$ (EtOH-EtOAc, 1:10 (v/v), DC-Alufolien Aluminiumoxid 60 F254 neutral, Merck). UV–vis (MeCN) λ_{max} 272 nm ($\varepsilon = 19900 \text{ M}^{-1} \text{ cm}^{-1}$), 439 nm (ε = 48900 M⁻¹ cm⁻¹); fluorescence (MeCN, λ_{ex} 435 nm) λ_{max}^{fl} 563 nm. IR (mineral oil, ν): 1651 cm⁻¹ (C=O). HRMS (ESI+) m/z calcd. for C44H64N2O11 [M+H]+: 797.4588. Found: 797.4583. Anal. calcd. for C44H64N2O11: C, 66.31; H, 8.09; N, 3.51. Found: C, 66.41; H, 8.11; N, 3.51. ¹H NMR (500 MHz, MeCN-*d*₃, 27 °C) δ: 1.80 (m, 2H, 4-CH₂), 2.92 (m, 4H, 3-CH₂, 5-CH₂), 3.58 (m, 32H, 16 CH₂O), 3.65 (m, 16H, 4 CH₂CH₂N), 6.77 (d, 4H, J =8.9 Hz, 2 3'-H, 2 5'-H), 7.43 (d, 4H, J =8.9 Hz, 2 2'-H, 2 6'-H), 7.60 (s, 2H, 2 α-H). ¹³C NMR (125 MHz, MeCNd₃, 30 °C) δ: 23.95 (4-C), 29.47 (3-C, 5-C), 51.89 (4 CH₂N), 69.19 (4 CH₂CH₂N), 71.23, 71.28, 71.37, and 71.41 (16 CH₂O), 112.36 (2 3'-C, 2 5'-C), 124.50 (2 α-C), 133.32 (2 1'-C), 133.50 (2 2'-C, 2 6'-C), 136.94 (2-C, 6-C), 149.49 (2 4'-C), 189.45 (C = O).

2.2. Methods

IR spectra in KBr pellets were recorded on a Bruker IFS-113v FTIR spectrometer in the range of $4000-400 \text{ cm}^{-1}$. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI) [18]. The measurements were done in a positive ion mode (interface capillary voltage of -4500 V); mass range from m/z 50–3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in MeCN (flow rate of 3 mL min⁻¹). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. IR and high resolution mass spectra were recorded at the Department of Structural Studies of N. D. Zelinsky Institute of Organic Chemistry (Russian Academy of Sciences, Moscow, Russian Federation). Elemental analysis was carried out at the Microanalytical Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences, Moscow, Russian Federation). The samples for elemental analysis were dried at 80 °C in vacuo.

2.2.1. NMR spectroscopy measurements and titration

¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 instrument in MeCN- d_3 at 25–30 °C with the MeCN- d_2 signal as the internal standard ($\delta_{\rm H}$ 1.96, $\delta_{\rm C}$ 116.70). 2D homonuclear ¹H–¹H COSY and NOESY spectra and heteronuclear ¹H–¹³C COSY spectra (HSQC and HMBC) were used to assign the proton and carbon signals. In ¹H NMR titration, the compositions and stability constants for complexes of dye **1a** with alkanediammonium ions (⁺H₃N(CH₂)_nNH₃⁺, n = 2, 12) or EtNH₃⁺ and complexes of dye **3a** with EtNH₃⁺ ions were determined by analyzing the changes in the positions of proton signals ($\Delta\delta_{\rm H}$) of the dye depending on the concentration ratio of alkanediammonium ions or EtNH₃⁺ and the dye. The concentration of EtNH₃⁺ ions was varied in the range from 0 to 5.1×10^{-2} M, while the overall concentration of dyes **1a**, **3a** did not change, being equal to ${\sim}1\times10^{-3}$ and ${\sim}2.5\times10^{-3}$ M for 1a and 3a, respectively. The concentration of ${}^+\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3^+$ ions was varied in the range from 0 to 1.17×10^{-2} M, while the overall concentration of dye 1a did not change, being equal to ${\sim}6\times10^{-4}$ M. The concentration of ${}^+\text{H}_3\text{N}(\text{CH}_2)_{12}\text{NH}_3^+$ ions was varied in the range from 0 to 1.76×10^{-2} M, while the overall concentration of dye 1a did not change, being equal to ${\sim}3\times10^{-3}$ M. The $\Delta\delta_{\rm H}$ values were measured to an accuracy of 0.001 ppm with correction for MeCN-d_2 signal shift. The stability constants of the complexes were calculated using the HYPNMR program [19].

2.2.2. Optical spectroscopy measurements and titrations

The absorption spectra were recorded on a Cary 4000 (Agilent) spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC spectrofluorimeter. All the spectra were recorded in MeCN at room temperature. The spectrophotometric titrations were performed in MeCN at room temperature. The composition and thermodynamic stability of the complexes were determined from the dependence of the absorption spectrum of a MeCN solution of the dye 1a,b on the overall concentration (C_A) of the EtNH₃⁺ or ⁺H₃N(CH₂)_nNH₃⁺ (n = 2-10, 12) ions. The C_A value was varied in the range from 0 to 4.3×10^{-3} M, while the overall concentration of dye ($C_{\rm I}$) was 1×10^{-5} M. The overall concentration of the ClO₄ counter-ions (0.01 M) in all experiments was maintained by a supporting electrolyte, Bu₄NClO₄, since the ionic strength is known to affect the stability constant of supramolecular complexes built of charged components. For spectrophotometric titration, the working range of the reagent concentrations $(10^{-5}-10^{-3} \text{ M})$ allowed for much higher concentrations of the supporting electrolyte maintaining a constant ionic strength. In the case of NMR titration, the working range of the reagent concentrations was much higher, 10^{-3} – 10^{-2} M, and it was impossible to use higher concentration of the supporting electrolyte due to salting out. Thus, NMR titration gave only effective stability constants, which, as a rule, are comparable, but somewhat lower than those given by the methods using supporting electrolyte. All manipulations with dye solutions were carried out in a dark room with a red light to prevent E-Z isomerization of the dyes. The stoichiometry and stability constants of complexes were calculated using HypSpec software (Hyperquad program package) [20].

2.2.3. Quantum chemical modeling

The geometries of 1a, b and their complexes with ammonium salts were optimized by the density functional theory (DFT) with PBE functional [21] and triple-zeta quality basis set 3z using Priroda program package [22,23]. The absorption spectra were calculated by the time-dependent density functional theory (TDDFT) with PBE0 functional and 6–31 G(d,p) basis set using FireFly program [24] partially based on GAMESS code [24]. The solvent (MeCN) effects for the absorption spectra were taken into account using Dielectric Polarizable Continuum model (D-PCM) [25].

3. Results and discussion

3.1. Synthesis of dyes 1a,b

With the goal to design photoactive supramolecular systems based on bis-aza-18-crown-6 dienones and $1,\omega$ -alkanediammonium salts and to study the effect of the salt chain length on the properties of supramolecular complexes, we synthesized dienones **1a,b** based on cyclopentanone and cyclohexanone, respectively. Azacrown-containing dienones **1a,b** were obtained by the alkaline aldol-crotonic condensation of aza-18-crown-6 aldehyde **4** with cyclic ketones **5a,b** in the presence of a base (Claisen–Schmidt reaction) (Scheme 1). The yields of **1a,b** were 87% and 70%, respectively.



Scheme 1. Synthesis of dienones 1a,b.

3.2. ¹H NMR spectroscopy

The complex formation between dienone **1a** and EtNH_3^+ ClO_4^- or $^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$ 2ClO_4^- (n = 2, 12) and between model compound **3a** and EtNH_3^+ ClO_4^- was studied by ^1H NMR spectroscopy. Dienone **3a**, the chromogen of which is fully identical to that of dye **1a**, was chosen as the reference compound for studying the complexation. The structures of dienones **1a** and **3a** and atom numbering are depicted in Fig. 1.

The complex structures were determined on the basis of simultaneous analysis of both qualitative and quantitative data of 1 H NMR and spectrophotometric titration and quantum-chemical calculations (see below).

The formation of supramolecular complexes results in substantial changes in the ¹H NMR spectra of host molecule **1a**.

The addition of $EtNH_3^+$ ClO_4^- to a solution containing dienone **1a** induces monotonic downfield shifts of the signals of most protons of 1a, which is caused by the effect of the positively charged $EtNH_3^+$ ion complexed with the azacrown ether residue. This behaviour is characteristic of complexes in which the primary ammonium ion is hydrogenbonded to the macrocycle heteroatom, which induces electron density shift from the electron-donating ligand heteroatoms to the cation (electron-withdrawing effect of the cation) [4,26,27]. The most pronounced changes are observed for the 3'-H and 5'-H protons of the benzene rings, whereas the signals of more remote aromatic protons, α -H protons, and methylene protons of the cyclopentanone moiety shift to a lesser extent; furthermore, some of the methylene proton signals of the azacrown ether moiety shift upfield (Fig. 2a and Table 1). This abnormal behaviour of the azacrown methylene protons is apparently attributable to a change in the nitrogen atom geometry (hybridization) and conformational rearrangement of the macrocycle upon binding of the $EtNH_3^+$ ion [26,27]. Reorientation of the lone pairs (LPs) of all heteroatoms towards the macrocycle cavity accommodating the EtNH₃⁺ ion decreases the conjugation of the nitrogen LP with the benzene ring.

Since the stabilities of complexes formed by **1a** with the studied ammonium ions are substantially different, for correct comparison, Table 1 shows the changes in the chemical shifts ($\Delta \delta_{\rm H}$) of chromogen protons of dienone **1a** induced by its complex formation with EtNH₃⁺, 1,2-ethanediammonium, and 1,12-dodecanediammonium ions at $C_{\rm A}/C_{\rm 1a} \approx 2$.

Considering the $\Delta \delta_{\rm H}$ values found for various protons of dienone 1a and $^1{\rm H}$ NMR titration data (see below), it is possible to propose the most likely structure for complex 1a (EtNH_3^+)_2, with the EtNH_3^+ ions being bound to heteroatoms of two azacrown ether residues of dienone 1a.

Mixing of dienone 1a with ${}^{+}H_3N(CH_2)_2NH_3^+$ resulted in similar

changes in the ¹H NMR spectra (Fig. 2*b* and Table 1), which may be indicative of the formation of similar supramolecular complexes. However, the observed changes in the proton chemical shifts of dienone **1a** are markedly greater in magnitude, which is attributable to the formation of a more stable complex with the $^+H_3N(CH_2)_2NH_3^+$ dication and a 2:2 complex.

In this case, a pseudocyclic structure, which is in line with this spectral behaviour and ¹H NMR titration data (see below), is the most likely structure for the 2:2 complex $(1a)_2 \cdot (^+H_3N(CH_2)_2NH_3^+)_2$. The two ethanediammonium ions are linked to two molecules of dienone 1a; the formation of twelve hydrogen bonds substantially increases the stability of the complex. The absence of upfield shifts for the protons of double bonds and benzene rings implies that this complex does not, apparently, have an eclipsed configuration (Fig. 3a).

The ¹H NMR spectrum of a $1a/^{+}H_3N(CH_2)_{12}NH_3^+$ mixture exhibited analogous shifts of the proton signals of dienone 1a (Fig. 2c and Table 1). In this case, the shifts of the proton signals of dienone 1a are much greater in magnitude than those for $1a/EtNH_3^+$, which also attests to the formation of a more stable complex. However, shifts of the proton signals of the methylene groups at nitrogen atoms are smaller in magnitude than those for $1a/EtNH_3^+$ or $1a/^+H_3N(CH_2)_2NH_3^+$, which attests to a higher degree of conjugation of the nitrogen LP with benzene rings. The $\Delta\delta_H$ values found for various protons of dienone 1a and the geometric match between the extended diammonium ion and 1a suggest a pseudocyclic structure for the complex $1a\cdot^+H_3N(CH_2)_{12}NH_3^+$. The complex stability is caused by the formation of six hydrogen bonds between the protons of both ammonium groups of the 1,12-dodecanediammonium ion and heteroatoms of the two azacrown ether residues of 1a as a result of ditopic interaction.

More information about the complex formed by **1a** with ${}^{+}H_{3}N$ (CH₂)₁₂NH₃⁺ can be gained by analyzing the 2D NOESY spectrum. Therefore, we recorded the NOESY spectrum of a saturated solution of **1a** in MeCN-*d*₃ in the presence of excess ${}^{+}H_{3}N(CH_{2})_{12}NH_{3}^{+}$ ions (Fig. 4).

Apart from the intense intramolecular cross-peaks, the NOESY spectrum was found to exhibit peaks corresponding to the intermolecular through-space interactions of the protons of the central part (CH₂)₈ of the polymethylene chain of the ⁺H₃N(CH₂)₁₂NH₃⁺ ion with the 3-CH₂ and 4-CH₂ methylene protons of the cyclopentanone ring; CH₂NH₃⁺ methylene protons with the azacrown ether protons (Fig. 4*a*); ethylene bond α -H protons and benzene ring 2'-H, 6'-H, 3'-H, and 5'-H protons of dienone **1a** with the protons of the central part (CH₂)₈ of the polymethylene chain of the ⁺H₃N(CH₂)₁₂NH₃⁺ ion; and benzene ring 3'-H and 5'-H protons of dienone **1a** with the CH₂NH₃⁺ ion; and benzene ring 3'-H and 5'-H protons of the cH₃N(CH₂)₁₂NH₃⁺ ion (Fig. 4*b*).

The detected interactions and ¹H NMR titration data (see below), suggest the most probable structure for the complex of dienone **1a** with 1,12-dodecanediammonium diperchlorate shown in Fig. 3b. The ammonium groups of 1,12-dodecanediammonium are bound simultaneously to both azacrown ether residues of **1a**, the polymethylene chain of the dication is located above (or near) the central moiety of dienone **1a** molecule. In other words, complex of **1a** with the 1,12-dodecanediammonium ion is a pseudocyclic structure.

For determining the stability constants of the complexes, ¹H NMR titration was carried out. At any $1a/EtNH_3^+$, $1a/^+H_3N(CH_2)_2NH_3^+$, and $1a/^+H_3N(CH_2)_{12}NH_3^+$ ratios, the spectra exhibited averaged (in some cases, broadened) proton signals for the complexes and free components, which is apparently associated with rather fast, on the ¹H NMR time scale, exchange processes. The stability constants of complexes were determined by analysis of dependences of the shifts ($\Delta\delta_H$) of proton signals of dienone **1a** on the concentrations (C_A) of the added EtNH₃⁺·ClO₄ or ⁺H₃N(CH₂)_nNH₃⁺·2ClO₄ (n = 2, 12) salt.

Since the molecule of dienone **1a** contains electron-donating centres of two types, azacrown ether residues and the carbonyl oxygen atom, we suggested that the ammonium ion in the **1a**/EtNH₃⁺ and **1a**/⁺H₃N (CH₂)_{*n*}NH₃⁺ (n = 2-10, 12) systems can also bind to the dienone C=O group, and this would also contribute to the stability constant. In order



Fig. 2. ¹H NMR spectra of **1a** and its mixtures with ammonium salts: (a) **1a** ($C_{1a} = 1.13 \times 10^{-3}$ M) (1) and a mixture of **1a** and EtNH₃⁺ ClO₄⁻ ($C_A = 1.85 \times 10^{-2}$ M) (2); (b) **1a** ($C_{1a} = 6.3 \times 10^{-4}$ M) (3) and a mixture of **1a** and ⁺H₃N(CH₂)₂NH₃⁺ 2ClO₄⁻ ($C_A = 1.7 \times 10^{-2}$ M) (4); (c) **1a** ($C_{1a} = 5.1 \times 10^{-3}$ M) (5) and a mixture of **1a** and ⁺H₃N(CH₂)₂NH₃⁺ 2ClO₄⁻ ($C_A = 1.76 \times 10^{-2}$ M) (6); MeCN- d_3 , 25 °C.

Table 1

Changes in the 1 H NMR chemical shifts upon the addition of ammonium salts to dienone **1a**.^a.

| Ammonium salt | $\Delta \delta_{ m H}{}^{ m b}$ | | | | |
|--|---|-------|----------------|----------------|--|
| | 3-CH ₂ , 4- CH ₂ | 2α-Η | 2 2'-H, 2 6'-H | 2 3'-H, 2 5'-H | |
| EtNH ₃ ⁺ ClO ₄ ⁻ | 0.024 | 0.037 | 0.049 | 0.107 | |
| $^{+}\text{H}_{3}\text{N(CH}_{2})_{2}\text{NH}_{3}^{+}\cdot 2\text{ClO}_{4}^{-}$ | 0.051 | 0.080 | 0.108 | 0.194 | |
| ⁺ H ₃ N (CH ₂) ₁₂ NH ₃ ⁺ ·2ClO ₄ ⁻ | 0.057 | 0.074 | 0.113 | 0.370 | |

^a $C_A/C_{1a} \approx 2$, MeCN- d_3 , 25 °C.

^b $\Delta \delta_{\rm H} = \delta_{\rm H} (1 {\rm a}/{\rm ammonium \ salt \ mixture}) - \delta_{\rm H} ({\rm free \ } 1 {\rm a}).$

to verify this assumption, we carried out ¹H NMR titration of model dienone **3a** with ethylammonium perchlorate. Even at the relative cation concentration $C_A/C_{3a} = 20$, no noticeable spectral changes were observed. The most pronounced downfield shift ($\Delta \delta_{\rm H} = 0.012$ ppm) took place for the α -H protons of **3a**. Treatment of the titration data leads to the conclusion that no interaction between the EtNH₃⁺ ion and dienone **3a** takes place within the scope of applicability of this method.

In other words, we can state that the EtNH₃⁺ ion and the carbonyl

group of dienone **3a** virtually do not interact; hence, in the calculation of stability constants for complexes formed by ammonium ions with **1a**, this equilibrium can be neglected.

In the case of $1a/EtNH_3^+$, the dependences $\Delta \delta_H - C_A/C_{1a}$ are adequately described by the reaction model including two equilibria (1) and (2).

$$L + A \stackrel{K_{1:1}}{\rightleftharpoons} LA,$$
 (1)

$$LA + A \stackrel{A_{1,2}}{\rightleftharpoons} LA_2, \tag{2}$$

In the case of $1a/^{+}H_{3}N(CH_{2})_{2}NH_{3}^{+}$, the dependences $\Delta\delta_{H} - C_{A}/C_{1a}$ are adequately described by the reaction model including two equilibria (1) and (3).

$$LA + LA \stackrel{A_{22}}{\rightleftharpoons} L_2 A_2, \tag{3}$$

In the case of $1a/^{+}H_3N(CH_2)_{12}NH_3^+$, the dependences $\Delta\delta_H - C_A/C_{1a}$ correspond to the reaction model including only one equilibrium (1).

The following designations are used in equilibria (1)–(3): L is dienone **1a**; A is mono- or diammonium ion; $K_{1:1}/M^{-1}$, $K_{1:2}/M^{-1}$, and $K_{2:2}/M^{-1}$ are the stability constants of 1:1 (LA), 1:2 (LA₂), and 2:2 (L₂A₂)



a



Fig. 3. Putative pseudocyclic structure of the 2:2 complex $(1a)_2 \cdot (^+H_3N(CH_2)_2NH_3^+)_2$ and spatial structure of $^+H_3N(CH_2)_2NH_3^+$ (*a*), structure of the pseudocyclic complex $1a \cdot ^+H_3N(CH_2)_{12}NH_3^+$ (*b*).



Fig. 4. Fragments of the aliphatic (*a*) and aromatic (*b*) regions of the NOESY spectrum of a mixture of compound **1a** (saturated solution, $C_{1a} = 5 \times 10^{-3}$ M) and $^{+}H_3N(CH_2)_{12}NH_3^+$ 2ClO₄⁻ ($C_A = 1.7 \times 10^{-2}$ M), MeCN- d_3 , 25 °C.

complexes, respectively.

Treatment of the ¹H NMR titration data taking account of the abovementioned equilibria resulted in determination of the effective stability constants of the complexes; the logK values are summarized in Table 2.

Analysis of the data of Table 2 demonstrated that the most stable complex is formed with 1,12-dodecanediammonium diperchlorate; the complex has a pseudocyclic structure. It is noteworthy that in relatively concentrated solutions, 1,2-ethanediammonium diperchlorate forms predominantly a pseudocyclic 2:2 complex, while in dilute solutions, 1:1 and 1:2 complexes are mainly formed with dienone **1a** (see below).

3.3. Optical spectroscopy measurements

The complexation of bis-azacrown dienones 1a,b with EtNH₃⁺ ClO₄ and ⁺H₃N(CH₂)_nNH₃⁺ 2ClO₄ (n = 2–10, 12) was studied by electronic spectroscopy with MeCN as the solvent.

The absorption spectra of dienones **1a,b** in MeCN exhibit two bands: intense long-wavelength absorption band (LWAB) ($\lambda_{max} = 466$ nm and $\lambda_{max} = 439$ nm, respectively), caused by $\pi \rightarrow \pi^*$ electronic transition with internal charge transfer from the electron-donating crown residue to the electron-withdrawing carbonyl group, and less intense band, caused by local $\pi \rightarrow \pi^*$ transitions ($\lambda_{max} = 275$ nm and $\lambda_{max} = 272$ nm, respectively). The weak $n \rightarrow \pi^*$ bands are superimposed by more intense long-wavelength $\pi \rightarrow \pi^*$ bands and virtually cannot be observed in the spectra [28–31].

Table 2

Effective stability constants of complexes of **1a** with $EtNH_3^+ \cdot ClO_{4^-}$, $^+H_3N(CH_2)_2NH_3^+ \cdot 2ClO_4^-$, and $^+H_3N(CH_2)_{12}NH_3^+ \cdot 2ClO_4^-$.

| Ammonium salt | $log K_{1:1}$ | $log K_{1:2}$ | log <i>K</i> _{2:2} |
|--|---------------|---------------|-----------------------------|
| $ \begin{array}{l} EtNH_3^+ \ ClO_4^- \\ {}^+H_3N(CH_2)_2NH_3^+ \cdot 2ClO_4^- \end{array} \end{array} $ | 3.2 2.9 | 2.1 | 2.1 |
| $^{+}\text{H}_{3}\text{N(CH}_{2})_{12}\text{NH}_{3}^{+}\cdot2\text{ClO}_{4}^{-}$ | > 5 | | |

^{a1}H NMR titration, MeCN- d_3 , 25 °C, the experimental error of the measurement of *K* is ±30%.

The complexation of **1a**,**b** with ethylammonium perchlorate or $1,\omega$ alkanediammonium diperchlorates is accompanied by increasing energy of the charge transfer electronic transition, since hydrogen bonding between the ammonium ion and azacrown ether considerably decreases the electron-donating properties of the latter. As a result, the LWABs undergo blue shifts, indicating the complex formation between the (di) ammonium ions and azacrown ether residues.

The obtained dependences of the absorption spectra of solutions of **1a**,**b** on the EtNH₃⁺ and ⁺H₃N(CH₂)₂NH₃⁺ concentrations are depicted in Fig. 5 (dependences of the absorption spectra of solutions of **1a**,**b** on the concentrations of ⁺H₃N(CH₂)_nNH₃⁺ (n = 3–10) are given in Figs S1–S16 of Supplementary data). The electronic absorption spectra of solutions of **1a**,**b** during titration with ethylammonium perchlorate or ethanediammonium diperchlorate exhibited considerably increased intensity of bands at 331 nm for **1a** and 320 nm for **1b** with a shift to longer wavelengths (Fig. 5a–d).

Similar changes, that is, blue shifts and intensity decrease for the LWAB maxima of dienones **1a**,**b** and red shifts and considerable intensity increase for 331 nm band for **1a** and 320 nm band for **1b**, take place in the electronic absorption spectra of solutions of **1a**,**b** during titration with **1**, ω -alkanediammonium (⁺H₃N(CH₂)_{*n*}NH₃⁺) diperchlorates with polymethylene chain length n = 3-7. We assume that in this case, the nitrogen LPs of **1a**,**b** are largely involved in hydrogen bonding with organic cations, and thus their involvement in the conjugation with the chromophore decreases. Simultaneously, the dye chromophore is a sort of shortened, and the electronic spectra of solutions of **1a**,**b**/EtNH₃⁺ and **1a**,**b**/⁺H₃N(CH₂)_{*n*}NH₃⁺ (n = 3-7) start to resemble the spectra of dibenzylidene cyclopentanone and cyclohexanone derivatives without donor groups, which absorb at a shorter wavelength (see, for example, the spectrum of **3b** in Fig. 5*a*).

A different picture is observed in the absorption spectra of solutions of **1a,b** during the titration of $1,\omega$ -alkanediammonium diperchlorates (⁺H₃N(CH₂)_nNH₃⁺) with polymethylene chain length n = 8-10, 12. The absorption spectra of **1a,b** show blue shifts and decreasing intensity of the LWABs of dienones **1a,b**; however, no maxima appear at 331 nm (**1a**) and 320 nm (**1b**) (Fig. 6). Apparently, in these cases, stable pseudocyclic 1:1 complexes are formed (see, for example, Fig. 3b), because the length of the polymethylene chain is now sufficient for diammonium ion binding to both azacrown ether residues of **1a,b**, although complete geometrical match is not yet attained, which may give rise to steric strain in dye molecules. In these complexes, nitrogen LPs may be conjugated to chromophores to a higher extent. This assumption is indirectly confirmed by changes in the ¹H NMR spectra of **1a** upon the addition of ⁺H₃N(CH₂)₁₂NH₃⁺ (Fig. 2c).

For the **1a**,**b**/EtNH₃⁺ and **1a**,**b**/⁺H₃N(CH₂)_{*n*}NH₃⁺ (n = 2-10, 12) systems, the concentration dependences of the absorption spectra are in good agreement with the model that includes two equilibria (1) and (2).

Relying on the results of spectrophotometric titration in MeCN, considering equilibria (1) and (2), we determined the stability constants of the resulting complexes. In the concentration ranges we studied, dienones **1a,b** form 1:1 and 1:2 complexes with EtNH₃⁺ and ⁺H₃N (CH₂)₂NH₃⁺ ions (Tables 3 and 4). The stability constants of complexes **1a,b**.⁺H₃N(CH₂)_{*n*}NH₃⁺ are much higher than those of **1a,b**.EtNH₃⁺. Apparently, this is due to higher positive charge densities on the ammonium groups of the ⁺H₃N(CH₂)_{*n*}NH₃⁺ dication.



Fig. 5. Absorption spectra of solutions of **1a** ($C_{1a} = 1 \times 10^{-5}$ M) depending on concentrations of EtNH₃⁺ ($C_A = 0 - 4 \times 10^{-3}$ M) (*a*) and ⁺H₃N(CH₂)₂NH₃⁺ ($C_A = 0 - 9 \times 10^{-4}$ M) (*b*); **1b** ($C_{1b} = 1 \times 10^{-5}$ M) depending on the concentrations of EtNH₃⁺ ($C_A = 0 - 4.3 \times 10^{-3}$ M) (*c*) and ⁺H₃N(CH₂)₂NH₃⁺ ($C_A = 0 - 9 \times 10^{-4}$ M) (*d*), in MeCN and at 0.01 M Bu₄NClO₄ ionic strength. The red curves are the spectra of free dyes **1a**,**b**, the dashed line is the spectrum of model dienone **3b** ($C_{3b} = 1 \times 10^{-5}$ M); the blue lines are the calculated spectra of complexes **1a**,**b**·EtNH₃⁺ and **1a**,**b**·⁺H₃N(CH₂)₂NH₃⁺; green curves are the calculated spectra of complexes **1a**,**b**·(EtNH₃⁺)₂ and **1a**,**b**·(⁺H₃N(CH₂)₂NH₃⁺)₂.

In the case of ${}^{+}H_3N(CH_2)_nNH_3^+$ ions with polymethylene chain length n = 2-7, the complexes with 1:1 and 1:2 stoichiometry are formed, while cations with n = 8-10, 12 tend to form only pseudocyclic 1:1 complexes.

The complexes formed by dienones **1a**,**b** and ⁺H₃N(CH₂)_nNH₃⁺ dications with the polymethylene chain length n = 8-10, 12 have markedly higher stability constants (Tables 3 and 4). Apparently, this is a consequence of diammonium ion binding to both azacrown ether residues of molecules **1a**,**b** without generation of a considerable conformation strain, which makes an additional contribution to the stability. The most pronounced changes in the absorption spectra take place in the titration of dienones **1a**,**b** with 1,12-dodecanediammonium diperchlorate ⁺H₃N(CH₂)₁₂NH₃⁺ (Fig. 6). The complex formation is accompanied by pronounced blue shifts of the LWAB ($\Delta \lambda_{max} = 23$ and 26 nm). This may be indicative of substantial distortion of the planar structure of the chromophores associated with the necessity of rotation of the phenylazacrown moieties relative to the dienone moieties. Possibly, 1,12-dodecanediammonium diperchlorate provides the

highest geometric match between the components, caused by similarity of distances between the ammonium groups of $^{+}H_3N(CH_2)_{12}NH_3^+$ and the binding sites of **1a**,**b**. In this case, the most stable 1:1 complexes are formed (see Fig. 3*b*).

In general, the observed stability constants of complexes formed by **1b** with the EtNH₃⁺ and ⁺H₃N(CH₂)_nNH₃⁺ (n = 2-10, 12) ions are higher than analogous constants of the complexes involving **1a**. This is attributable to the fact that the benzene rings, C=C bonds, and the carbonyl group of **1a** are located virtually in one plane, which attests to a high degree of conjugation in the molecule [14,32]. Meanwhile, the benzene rings of **1b** deviate from the plane of the molecule, and their contribution to the conjugation in the dienone moiety is moderate [14,32]. In other words, electron-withdrawing properties of the C=O group in **1b** are manifested to a lesser extent and, therefore, the complexation constants should be higher than those of **1a**; this is actually observed experimentally. The trends inherent in the complexation of **1a** with 1, ω -alkanediammonium salts hold also for **1b**. The stability constants of



Fig. 6. Absorption spectra of solutions of **1a** ($C_{1a} = 1 \times 10^{-5}$ M) depending on the concentration of the ⁺H₃N(CH₂)₁₂NH⁺₃ ions ($C_A = 0 - 1.5 \times 10^{-4}$ M) (*a*) and **1b** ($C_{1b} = 1 \times 10^{-5}$ M) depending on the concentration of ⁺H₃N(CH₂)₁₂NH⁺₃ ions ($C_A = 0 - 1.3 \times 10^{-4}$ M) (*b*) in MeCN at 0.01 M Bu₄NClO₄ ionic strength. The red curves are the spectra of free dyes **1a**,**b**, blue curves are the calculated spectra of complexes **1a**·⁺H₃N(CH₂)₁₂NH⁺₃ and **1b**·⁺H₃N(CH₂)₁₂NH⁺₃.

the supramolecular complexes of dienone 1b with ethylammonium perchlorate and $1,\!\omega\text{-alkanediammonium}$ salts are summarized in Table 4.

It is noteworthy that for both **1a** and (to some extent) **1b**, the $\Delta\lambda$ and log $K_{1:1}$ values alternate, depending on the length of the polymethylene chain of the ⁺H₃N(CH₂)_nNH₃⁺ ion with n = 3-7. This trend indirectly indicates that 2:2 complexes make a certain contribution to the formation of 1:1 complexes. The structure and stability of 2:2 complexes are possibly related to the spatial structure of the carbon skeletons of the 1, ω -alkanediammonium ions (Fig. 7).

When the number of carbon atoms is even, the blue shift of the LWAB maximum is smaller (the chromophores are pseudoparallel), while in the case of odd number of carbon atoms, the shift is greater (nonparallel).

Starting from n = 8, the alternation is no longer observed, which apparently attests to a greater contribution of the pseudocyclic 1:1 complexes.

We recorded the fluorescence spectra of free dyes **1a**,**b** and their complexes with the EtNH₃⁺ and ⁺H₃N(CH₂)_nNH₃⁺ (n = 2-10, 12) ions. Quenching of the dye fluorescence was observed for the **1a**,**b**/EtNH₃⁺ and **1a**,**b**/⁺H₃N(CH₂)_nNH₃⁺ (n = 2-8) systems (see Fig. 8a,b). The fluorescence quenching by short-chained diammonium ions results from the possibility for internal rotation in the exited state of the complex.

Table 3

Stability constants and spectral characteristics of the complexes of dienone **1a** with the EtNH₃⁺ and ⁺H₃N(CH₂)_nNH₃⁺ (n = 2-10, 12) ions in MeCN at 0.01 M Bu₄NClO₄ ionic strength^a.

| | 0 | | | | | | |
|--|-------------------------------|--------------------------|------------------------------------|-----------------------------|--------------------------|----------------------------------|--|
| Ammoniu ions | m log <i>K</i> _{1:1} | λ _{max} , nm | $\Delta \lambda$, nm ^b | log <i>K</i> _{1:2} | λ _{max} , nm | $\Delta\lambda,$ nm ^b | |
| EtNH ₃ ⁺ ⁺ H ₃ N (CH ₂) ₂ N | 2.74 | 452 | -14 | 2.03 | 420 | -46 | |
| n=2 | 4.06 | 457 | -9 | 2.75 | 419 | -47 | |
| n = 3 | 3.46 | 454 | -12 | 2.48 | 440 | -26 | |
| n = 4 | 3.44 | 463 | -3 | 2.41 | 432 | -34 | |
| n = 5 | 3.64 | 454 | -12 | 2.31 | 447 | -19 | |
| n = 6 | 3.56 | 460 | -6 | 2.34 | 443 | -23 | |
| n = 7 | 3.69 | 457 | _9 | 2.80 | 453 | -13 | |
| n = 8 | 3.96 | 449 | -17 | | | | |
| n = 9 | 4.91 | 447 | -21 | | | | |
| n = 10 | 5.17 | 444 | -22 | | | | |
| n = 12 | 5.57 | 443 | -23 | | | | |
| | | | | | | | |

^a Spectrophotometric titration, room temperature; experimental error of measurement of $K_{1:1}$ and $K_{1:2}$ is ±20%.

^b $\Delta \lambda = \lambda_{max}(complex) - \lambda_{max}(free 1a).$

On the contrary, the $1a,b/^+H_3N(CH_2)_nNH_3^+$ (n = 9, 10, 12) systems showed slightly enhanced fluorescence intensity of dienones 1a,b (see, for example, Fig. 8c). Apparently, the length of the polymethylene chain in the $^+H_3N(CH_2)_nNH_3^+$ (n = 9, 10, 12) ion is sufficient for ditopic binding of the NH_3^+ groups simultaneously to both azacrown ether residues of dienones. In this case, rigid structure of the complexes is attained, which is responsible for increasing fluorescence intensity of 1a, **b**. The most pronounced (~1.25-fold) increase in the fluorescence intensity was observed for complexes of 1a,b with the 1,12-dodecanediammonium diperchlorate. According to the obtained data, the selectivities of 1a and 1b towards $^+H_3N(CH_2)_nNH_3^+$ ions are comparable.

3.4. Quantum chemical calculations

The calculated structure of dye **1a** is shown in Fig. 9*a*. For its 1:1 complex with $EtNH_3^+$, two stable conformers were found (Fig. 9*b* and Fig. S17 of Supplementary data) both with two N–H...O and one N–H...N hydrogen bonds and the ammonium ion lying on the opposite side of the crown ether from the phenyl ring. For the 1:2 complex with $EtNH_3^+$, we found two low-lying conformers: one with both crown ether moieties adopting the same conformation as the complexed moiety of the 1:1

Table 4

Stability constants and spectral characteristics of complexes of dienone **1b** with the EtNH₃⁺ and ⁺H₃N(CH₂)_nNH₃⁺ (n = 2–10, 12) ions in MeCN at 0.01 M Bu₄N-ClO₄ ionic strength^a.

| Ammonium ions | log <i>K</i> _{1:1} | λ _{max} , nm | $\Delta\lambda$, nm ^b | log <i>K</i> _{1:2} | λ _{max} , nm | $\Delta\lambda,$ nm ^b |
|--|-----------------------------|--------------------------|-----------------------------------|-----------------------------|--------------------------|-------------------------------------|
| $EtNH_3^+$ ^+H_3N $(CH_2)_nNH_3^+$ | 3.08 | 428 | -11 | 2.26 | 398 | -41 |
| n=2 | 4.43 | 432 | -4 | 2.96 | 407 | -32 |
| n = 3 | 3.74 | 431 | -8 | 2.73 | 409 | -30 |
| <i>n</i> = 4 | 3.59 | 430 | -9 | 2.56 | 401 | -39 |
| n = 5 | 3.66 | 433 | -6 | 2.73 | 409 | -30 |
| n = 6 | 3.56 | 432 | -7 | 2.27 | 422 | -17 |
| n = 7 | 3.78 | 434 | -5 | 2.92 | 425 | -14 |
| n = 8 | 4.02 | 423 | -16 | | | |
| n = 9 | 4.45 | 420 | -20 | | | |
| n = 10 | 4.92 | 416 | -24 | | | |
| n = 12 | 5.62 | 414 | -26 | | | |

^a Spectrophotometric titration, room temperature; experimental error of measurement of $K_{1:1}$ and $K_{1:2}$ is ±20%.

^b $\Delta \lambda = \lambda_{\max}(\text{complex}) - \lambda_{\max}(\text{free 1b}).$

complex (Fig. 9c) and the other one with three N-H...O hydrogen bonds

Journal of Photochemistry & Photobiology, A: Chemistry 402 (2020) 112801



Fig. 8. Fluorescence spectra of **1a** ($C_{1a} = 1 \times 10^{-5}$ M) (red curves). Blue curves: **1a**/EtNH₃⁺ ($C_A = 4 \times 10^{-3}$ M) (*a*); **1a**/⁺H₃N(CH₂)₂NH₃⁺ ($C_A = 9 \times 10^{-4}$ M) (*b*), **1a**/⁺H₃N(CH₂)₁₂NH₃⁺ ($C_A = 1.5 \times 10^{-4}$ M) (*c*) in MeCN. Fluorescence was excited at 403 nm (*a*), 381 nm (*b*), and 437 nm (*c*).



a







c, 62%

Fig. 9. The most stable structure of 1a (a), the dominant structures of $1a \cdot \text{EtNH}_3^+$ (b) and $1a \cdot (\text{EtNH}_3^+)_2$ (c) with their molar fractions calculated from the relative energies. Most of hydrogen atoms are not shown.

and the ammonium ion lying on the same side of the crown ether with the phenyl ring (Fig. S18 of Supplementary data). The N–H...N hydrogen bond causes strong (almost tetrahedral) pyramidalization of the crown ether nitrogen. On the other hand, coordination with only N–H...O hydrogen bonds can result in either planar or slightly pyramidal crown ether nitrogen. This can affect the absorption spectra [33–37]. Fig. 10. We have found two low-energy conformers with almost equal molar fractions, one with the hydrocarbon chain lying approximately parallel to the chromophore plane and the other one with the chain perpendicular to the chromophore plane. The NH_3^+ groups are coordinated *via* three N—H…O hydrogen bonds; nevertheless, the crown ether nitrogen is slightly pyramidal.

The calculated structures of $1a\cdot^+\text{H}_3\text{N}(\text{CH}_2)_{12}\text{NH}_3^+$ are shown in

The calculated absorption bands of 1a and its complexes are

Table 5

Calculated absorption spectra of 1a and its complexes.

| | | _ | | |
|---|----------------|-------|-----------------------------------|-------|
| Compound | λ , nm | f | $\Delta\lambda$, nm ^a | ψ, ° |
| 1a | 463 | 1.921 | | 0 |
| 1a·(EtNH ₃ ⁺) Conf 1 | 454 | 1.399 | _9 | 27; 0 |
| 1a·(EtNH ₃ ⁺) Conf 2 | 457 | 1.338 | -6 | 27; 0 |
| 1a · (EtNH ₃ ⁺) ₂ N-coordinated | 386 | 0.000 | _b | 27 |
| | 373 | 1.617 | -90 | |
| 1a (EtNH ₃ ⁺) ₂ O-coordinated | 432 | 1.702 | -31 | 12 |
| | 379 | 0.014 | _b | |
| 1a. ⁺ H ₃ N(CH ₂) ₁₂ NH ⁺ ₃ parallel | 424 | 1.595 | -38 | 8; 9 |
| $1a^{+}H_3N(CH_2)_{12}NH_3^{+}$ perpendicular | 429 | 1.569 | -34 | 9; 15 |

^a $\Delta \lambda = \lambda_{max}(complex) - \lambda_{max}(free 1a).$

^b The shifts cannot be calculated since the oscillator strength is negligible.

summarized in Table 5; the orbitals responsible for the transitions are shown in Fig. S19 of Supplementary data. The complexation-induced absorption shifts $\Delta \lambda$ are in good agreement with the experiment.

We relate the complexation-induced absorption shifts $\Delta\lambda$ to the pyramidality of the crown ether nitrogen N_{cr} [33–37]. The pyramidality ψ is calculated as 360° minus the sum of the C—N—C angles. Participation of N_{cr} in the coordination with the cation, especially through the N—H…N hydrogen bond, causes strong blue shift of the absorption band. On the other hand, the very presence of the cation near N_{cr}

Journal of Photochemistry & Photobiology, A: Chemistry 402 (2020) 112801

without bonding may make it pyramidal to some extent and cause a blue shift of the absorption band.

The intense long-wavelength absorption band (HOMO \rightarrow LUMO $\pi \rightarrow \pi$ transition) of the 1:1 complex with EtNH₃⁺ is only slightly blue-shifted with respect to the free dye, because the HOMO is localized in the part of the π system adjacent to the uncomplexed crown ether moiety with planar N_{cr}. On the contrary, the blue shift in the *N*-coordinated conformer of the 1:2 complex is large, so that the intense $\pi \rightarrow \pi$ transition becomes higher in energy than the dark $n \rightarrow \pi$ transition, which correlates with the pronounced pyramidalization (27°) of N_{cr}. In the *O*-coordinated conformer of the same complex, the blue shift is smaller, which is explained by the less pronounced (12°) pyramidalization of N_{cr}. The coexistence of the two conformers explains the presence of two intense absorption bands in the evaluated experimental spectrum of the 1:2 complex (Fig. 5a, green curve).

The complexes with $^+\mathrm{H}_3N(\mathrm{CH}_2)_{12}N\mathrm{H}_3^+$ have slightly pyramidal (8–15°) crown ether nitrogen and exhibit a moderate blue shift of 34–38 nm. The absence of the dark transitions in the pseudocyclic $1a\cdot^+\mathrm{H}_3N(\mathrm{CH}_2)_{12}N\mathrm{H}_3^+$ complex, together with its rather rigid structure preventing the internal rotation of the chromophore in the excited state, explains the fluorescence enhancement in this complex (Fig. 8c).

The calculated ¹H NMR chemical shifts of selected protons are given in Table S1 in the Supporting Information. The calculated complexationinduced changes in the chemical shifts ($\Delta \delta_{\rm H}$) of **1a** are in qualitative



Parallel, 42%

Fig. 10. The dominant structures of 1a·⁺H₃N(CH₂)₁₂NH₃⁺ with their molar fractions calculated from the relative energies. Most of hydrogen atoms are not shown.

agreement with experimental data. All the target proton signals shift downfield, although the calculated $\Delta \delta_{\rm H}$ are much larger than the observed ones. This may result from the fact that solvent effects were not included in the calculation of the NMR spectra, and the local electrostatic fields in the molecules are unscreened, thus causing too strong changes in the chemical shifts. This may be also due to the fact that observed $\Delta \delta_{\rm H}$ values are derived from NMR spectra, *i.e.*, the difference may be due to incomplete complexation in the real spectra.

Analysis of the calculated chemical shifts of individual protons without averaging shows that the chemical shifts of 3'-H and 5'-H correlate with the pyramidality of the adjacent crown ether nitrogen (Table S2 of Supplementary data). The correlation for 2'-H and 6'-H is less pronounced.

4. Conclusions

The synthesis of bis-aza-18-crown-6-containing dienones derived from cyclopentanone and cyclohexanone was developed and their complexation with the EtNH₃⁺ and alkanediammonium $^{+}H_3N(CH_2)_nNH_3^+$ (n = 2-10, 12) ions was studied by spectral methods and by quantum chemical calculations. The stoichiometry, stability, and structure of their supramolecular complexes were established. It was found that these dienones form 1:1, 2:2, and 1:2 complexes with mono- and diammonium ions; the 1:1 complexes formed by these dyes with long-chain diammonium ions (n = 8-10, 12) are pseudocyclic. Binding of two ammonium groups of the alkanediammonium ion simultaneously to both azacrown ether residues of dyes 1a,b contributes to the stability of the complexes. The most stable 1:1 complexes are formed between 1a,b and $^{+}H_{3}N(CH_{2})_{12}NH_{3}^{+}$. The formation of supramolecular complexes of **1a**,**b** with EtNH₃⁺ ions and alkanediammonium $^{+}H_3N(CH_2)_nNH_3^+$ (n = 2-8) ions is accompanied by a decrease in the dye fluorescence intensity, while the formation of supramolecular complexes of 1a,b with long-chain diammonium $^{+}H_3N(CH_2)_nNH_3^+$ (n = 9, 10, 12) ions is, conversely, accompanied by fluorescence enhancement. Quantum chemical calculations of the structure and absorption spectra support the conclusions drawn from experimental results and explain the observed spectral features. The investigation of a novel assembly of azacrown-containing ketocyanine dyes with diammonium ions may be used for targeted design of new types of highly stable photoactive supramolecular systems stabilized via the formation of numerous hydrogen bonds, in particular, for the development of ditopic optical molecular sensors for diammonium ions.

CRediT authorship contribution statement

Marina V. Fomina: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. Nikolai A. Kurchavov: Investigation. Alexandra Ya. Freidzon: Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing. Vyacheslav N. Nuriev: Methodology, Investigation. Artem I. Vedernikov: Investigation, Validation, Writing - review & editing. Yuri A. Strelenko: Investigation, Resources. Sergey P. Gromov: Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 112801.

References

- [1] J.-M. Lehn, Supramolecular Chemistry. Concepts and Perspectives, VCH, Weinheim, 1995.
- [2] J.H. Hartley, T.D. James, C.J. Ward, Synthetic receptors, J. Chem. Soc. Perkin Trans. 1 (2000) 3155–3184, https://doi.org/10.1039/A909641H.
- [3] A.I. Vedernikov, E.N. Ushakov, N.A. Lobova, A.A. Kiselev, M.V. Alfimov, S. P. Gromov, Photosensitive molecular tweezers. 3. Synthesis and homoditopic complex formation of a bisstyryl dye containing two crown-ether fragments with diammonium salts, Russ. Chem. Bull. 54 (2005) 666–672, https://doi.org/ 10.1007/s11172-005-0303-7.
- [4] S.P. Gromov, A.I. Vedernikov, L.G. Kuz'mina, N.A. Lobova, S.S. Basok, Y. A. Strelenko, M.V. Alfimov, Stereoselective [2+2] photocycloaddition in bispseudosandwich complexes of bis(18-crown-6)stilbene with alkanediammonium ions, Russ. Chem. Bull. 58 (2009) 108–114, https://doi.org/ 10.1007/s11172-009-0016-4.
- [5] S.P. Gromov, A.I. Vedernikov, N.A. Lobova, L.G. Kuz'mina, S.S. Basok, Y. A. Strelenko, M.V. Alfimov, J.A.K. Howard, Controlled self-assembly of bis(crown) stilbenes into unusual bis-sandwich complexes: structure and stereoselective [2+2] photocycloaddition, New J. Chem. 35 (2011) 724–737, https://doi.org/10.1039/ C0NJ00780C.
- [6] M.V. Fomina, A.S. Nikiforov, A.I. Vedernikov, N.A. Kurchavov, S.P. Gromov, Selfassembly of supramolecular complexes of cyanine dyes containing terminal ammonium groups with bis(18-crown-6)stilbene, Mendeleev Commun. 24 (2014) 295–297, https://doi.org/10.1016/j.mencom.2014.09.016.
- [7] E.N. Ushakov, T.P. Martyanov, A.I. Vedernikov, O.V. Pikalov, A.A. Efremova, L. G. Kuz'mina, J.A.K. Howard, M.V. Alfimov, S.P. Gromov, Self-assembly through hydrogen bonding and photochemical properties of supramolecular complexes of bis(18-crown-6)stilbene with alkanediammonium ions, J. Photochem. Photobiol. A 340 (2017) 80–87, https://doi.org/10.1016/j.jphotochem.2017.03.003.
- [8] S.P. Gromov, A.I. Vedernikov, E.N. Ushakov, N.A. Lobova, A.A. Botsmanova, L. G. Kuz'mina, A.V. Churakov, Y.A. Strelenko, M.V. Alfimov, J.A.K. Howard, D. Johnels, U.G. Edlund, Novel supramolecular charge-transfer systems based on bis(18-crown-6)stilbene and viologen analogues bearing two ammonioalkyl groups, New J. Chem. 29 (2005) 881–894, https://doi.org/10.1039/B500667H.
- [9] K.P. Butin, A.A. Moiseeva, S.P. Gromov, A.I. Vedernikov, A.A. Botsmanova, E. N. Ushakov, M.V. Alfimov, Prospects of electroanalytical investigations of supramolecular complexes of a bis-crown stilbene with viologen-like compounds bearing two ammonioalkyl groups, J. Electroanal. Chem. 547 (2003) 93–102, https://doi.org/10.1016/S0022-0728(03)00142-6.
- [10] N. Marcotte, S. Fery-Forgues, D. Lavabre, S. Marguet, V.G. Pivovarenko, Spectroscopic study of a symmetrical bis-crown fluoroionophore of the diphenylpentadienone series, J. Phys. Chem. A 103 (1999) 3163–3170, https:// doi.org/10.1021/jp9846328.
- [11] A.O. Doroshenko, L.B. Sychevskaya, A.V. Grygorovych, V.G. Pivovarenko, Fluorescence probing of cell membranes with azacrown substituted ketocyanine dyes, J. Fluoresc. 12 (2002) 455–464, https://doi.org/10.1023/A: 1021374212498.
- [12] A.O. Doroshenko, A.V. Grigorovich, E.A. Posokhov, V.G. Pivovarenko, A. P. Demchenko, A.D. Sheiko, Complex formation between azacrown derivatives of dibenzylidenecyclopentanone and alkali-earth metal ions, Russ. Chem. Bull. 50 (2001) 404–412, https://doi.org/10.1023/A:1011392619954.
- [13] N. Marcotte, F. Rodrigues, D. Lavabre, S. Fery-Forgues, Biscrown fluoroionophores: has the dye conformation an influence upon the formation of sandwich complexes in the ketocyanine series? New J. Chem. 28 (2004) 295–301, https://doi.org/ 10.1039/B311690E.
- [14] S.Z. Vatsadze, G.V. Gavrilova, F.S. Zyuz'kevich, V.N. Nuriev, D.P. Krut'ko, A. A. Moiseeva, A.V. Shumyantsev, A.I. Vedernikov, A.V. Churakov, L.G. Kuz'mina, J. A.K. Howard, S.P. Gromov, Synthesis, structure, electrochemistry, and photophysics of 2,5-dibenzylidenecyclopentanones containing in benzene rings substituents different in polarity, Russ. Chem. Bull. 65 (2016) 1761–1772, https://doi.org/10.1007/s11172-016-1508-7.
- [15] P. Deveci, B. Taner, Z. Üstündağ, E. Özcan, A.O. Solak, Z. Kılıç, Synthesis, enhanced spectroscopic characterization and electrochemical grafting of N-(4aminophenyl)aza-18-crown-6: application of DEPT, HETCOR, HMBC-NMR and X-

M.V. Fomina et al.

ray photoelectron spectroscopy, J. Mol. Struct. 982 (2010) 162–168, https://doi.org/10.1016/j.molstruc.2010.08.024.

- [16] F. Stauffert, J. Serra-Vinardell, M. Gómez-Grau, H. Michelakakis, I. Mavridou, D. Grinberg, L. Vilageliu, J. Casas, A. Bodlenner, A. Delgado, P. Compain, Stereodivergent synthesis of right- and lefthanded iminoxylitol heterodimers and monomers. Study of their impact on β-glucocerebrosidase activity, Org. Biomol. Chem. 15 (2017) 3681–3705, https://doi.org/10.1039/C7OB00443E.
- [17] E. Oliveira, R.M.F. Baptista, S.P.G. Costa, M.M.M. Raposo, C. Lodeiro, Exploring the emissive properties of new azacrown compounds bearing aryl, furyl, or thienyl moieties: a special case of chelation enhancement of fluorescence upon interaction with Ca2+, Cu2+, or Ni2+, Inorg. Chem. 49 (2010) 10847–10857, https://doi. org/10.1021/ic101095.
- [18] A.M. Tsedilin, A.N. Fakhrutdinov, D.B. Eremin, S.S. Zalesskiy, A.O. Chizhov, N. G. Kolotyrkina, V.P. Ananikov, How sensitive and accurate are routine NMR and MS measurements, Mendeleev Commun. 25 (2015) 454–456, https://doi.org/ 10.1016/j.mencom.2015.11.019.
- [19] C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M.S. Moruzzi, A. Vacca, Nuclear magnetic resonance as a tool for determining protonation constants of natural polyprotic bases in solution, Anal. Biochem. 231 (1995) 374–382, https://doi.org. 10.1006/abio.1995.9984.
- [20] P. Gans, A. Sabatini, A. Vacca, Investigation of equilibria in solution. Determination of equilibrium constants with the HYPERQUAD suite of programs, Talanta 43 (1996) 1739–1753, https://doi.org/10.1016/0039-9140(96)01958-3.
- [21] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865, https://doi.org/10.1103/ PhysRevLett.77.3865.
- [22] D.N. Laikov, Fast evaluation of density functional exchange-correlation terms using the expansion of the electron density in auxiliary basis sets, Chem. Phys. Lett. 281 (1997) 151–156, https://doi.org/10.1016/S0009-2614(97)01206-2.
- [23] D.N. Laikov, Y.A. Ustynyuk, PRIRODA-04: a quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing, Russ. Chem. Bull. 54 (2005) 820–826, https://doi.org/10.1007/ s11172-005-0329-x.
- [24] Granovsky AA. Firefly version 8.2.0. http://classic.chem.msu.su/gran/firefly/in dex.html. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA. General atomic and molecular electronic structure system. J Comput Chem 1993; 14:1347–1363. https://doi.org/10.1002/jcc.540141112.
- [25] J. Tomasi, B. Mennucci, R. Cammi, Quantum mechanical continuum solvation models, Chem. Rev. 105 (2005) 2999–3094, https://doi.org/10.1021/cr9904009.
- [26] A.I. Vedernikov, S.N. Dmitrieva, L.G. Kuz'mina, N.A. Kurchavov, Y.A. Strelenko, J. A.K. Howard, S.P. Gromov, Benzoaza-15-crown-5 ethers: synthesis, structure, and complex formation with metal and ethylammonium ions, Russ Chem Bull 58 (2009) 978–1001, https://doi.org/10.1007/s11172-009-0127-v.
- [27] S.P. Gromov, S.N. Dmitrieva, A.I. Vedernikov, N.A. Kurchavov, L.G. Kuz'mina, Y. A. Strelenko, M.V. Alfimov, J.A.K. Howard, N-Methylbenzoazacrown ethers with

the nitrogen atom conjugated with the benzene ring: the improved synthesis and the reasons for the high stability of complexes with metal and ammonium cations, J. Phys. Org. Chem. 22 (2009) 823–833, https://doi.org/10.1002/poc.1527.

- [28] A.A. Khalaf, S.H. Etaiw, R.M. Issa, A.K. El-Shafei, Spectrophotometric study of some 1,5-diphenyl-1,5-pentadiene-3-ones, Rev. Roum. Chim. 22 (1977) 1251–1259.
- [29] G.V. Zakharova, F.S. Zyuz'kevich, V.N. Nuriev, S.Z. Vatsadze, V.G. Plotnikov, S. P. Gromov, A.K. Chibisov, Photonics of bis(diethylaminobenzylidene) cyclopentanone and its analogue with the bisazacrown moiety in acetonitrile, High Energy Chem. 50 (2016) 27–31, https://doi.org/10.1134/S0018143916010124.
- [30] G.V. Zakharova, F.S. Zyuz'kevich, V.N. Gutrov, V.N. Nuriev, S.Z. Vatsadze, V. G. Plotnikov, V.G. Avakyan, S.P. Gromov, A.K. Chibisov, Photoinduced processes in bis(diethylaminobenzylidene)cyclohexanone and its bis(aza-18-crown-6)-containing analogue in acetonitrile, High Energy Chem. 50 (2016) 442–446, https://doi.org/10.1134/S0018143916060205.
- [31] G.V. Zakharova, F.S. Zyuz'kevich, V.N. Gutrov, G.V. Gavrilova, V.N. Nuriev, S. Z. Vatsadze, V.G. Plotnikov, S.P. Gromov, A.K. Chibisov, Effect of substituents on spectral, luminescent and time-resolved characteristics of 2,5-diarylidene derivatives of cyclopentanone, High Energy Chem. 51 (2017) 113–117, https://doi.org/10.1134/S0018143917020126.
- [32] F.H. Herbstein, S. Hu, M. Kapon, Some errors from the crystallographic literature, some amplifications and a questionable result, Acta Crystallogr. Sect. B 58 (2002) 884–892, https://doi.org/10.1107/S0108768102010261.
- [33] A.Y. Freidzon, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, Recoordination of a metal ion in the cavity of a crown compound: a theoretical study. 1. Conformers of arylazacrown ethers and their complexes with Ca2+ cation, Russ. Chem. Bull. 52 (2003) 2646–2655, https://doi.org/10.1023/B:RUCB.0000019881.11535.8b.
- [34] A.Y. Freidzon, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, Recoordination of a metal ion in the cavity of a crown compound: a theoretical study. 2. Effect of the metal ion-solvent interaction on the conformations of calcium complexes of arylazacrown ethers, Russ. Chem. Bull. 54 (2005) 2042–2054, https://doi.org/ 10.1007/s11172-006-0076-7.
- [35] A.Y. Freidzon, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, Recoordination of a metal ion in the cavity of a crown compound: a theoretical study. 3. Absorption spectra and excited states of azacrown-containing styryl dyes and their complexes, Russ. Chem. Bull. 57 (2008) 2045–2055, https://doi.org/10.1007/s11172-008-0278-2.
- [36] A.Y. Freidzon, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, Recoordination of a metal ion in the cavity of an arylazacrown ether: model study of the conformations and microsolvation of calcium complexes of arylazacrown ethers, Int. J. Quantum Chem. 100 (2004) 617–625, https://doi.org/10.1002/qua.20184.
- [37] A.Y. Freidzon, K.G. Vladimirova, A.A. Bagatur'yants, S.P. Gromov, M.V. Alfimov, Theoretical study of complexation of alkali metal ions in the cavity of arylazacrown ethers, J. Mol. Struct. (THEOCHEM) 809 (2007) 61–71, https://doi.org/10.1016/j. theochem.2007.01.033.