# Self-organization of crown-containing hetarylphenylethenes, phthalic acid, and potassium cations into supramolecular assemblies

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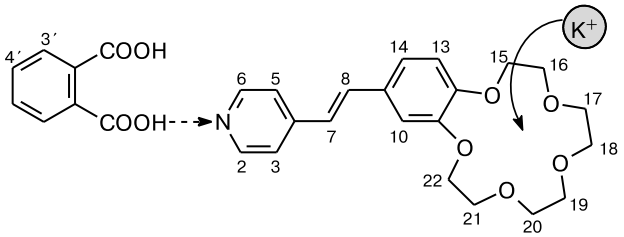
Multicomponent molecular assemblies of 15-crown-5-containing 4-styrylpyridine with phthalic acid in the presence of potassium perchlorate were studied. The structure of the obtained complicated assemblies was determined by $^{1}H$ and $^{13}C$ NMR spectroscopy, UV spectroscopy, and X-ray analysis. The composition of the supramolecular complexes was established by spectrophotometric titration, and the stability constants were calculated. The quantum yields of fluorescence for the ligand and its complexes of various nature were determined.

**Key words:** crown ethers, 4-styrylpyridine, potassium perchlorate, phthalic acid, complexation, spectrophotometry.

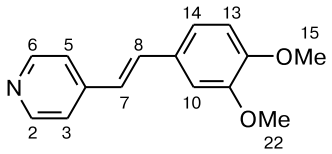
Development of supramolecular assemblies of organic molecules is a modern direction of investigation in physical organic chemistry having both fundamental and applied aspects. Understanding of laws determining the dependence of the manifested properties on the architecture of a supramolecular assembly makes it possible to produce new systems and materials using modern approaches.

As known, ligands synthesized from hetarylphenylethene derivatives are widely used for synthesis of supramolecular assemblies.[1—3] In the present study, we investigated the properties of 4-styrylpyridine containing the macrocyclic moiety of 15-crown-5. The construction of multicomponent molecular systems is based on the ability of the nitrogen atom of the heterocyclic compound to form strong coordination bonds with metal cations due to a lone electron pair and to form hydrogen bonds with carboxyl groups of other organic molecules. It is assumed that similar ligands and related supramolecular assemblies can be used to determine concentrations of heavy metals, in chemical analysis, in modeling of biological systems,[4] in medicine for the development of drugs against HIV,[5] as selective fluorescent labels that can be included into the DNA structure,[6] for the construction of molecular devices with good luminescence characteristics[7,8] and materials for photonics, optoelectronics,[9] and electrochemical analysis.[10,11]

In this work we present the results of studying the formation of supramolecular assemblies based on hetarylphenylethene **1** and **2**, potassium perchlorate, and phthalic acid. The nitrogen atom of the heterocyclic residue of hetarylphenylethenes can form bonds with the carboxyl group of carboxylic acids. It was assumed that dicarboxylic acids can bind two molecules of hetarylphenylethenes due to coordination with their heterocyclic pyridine residues. In the case of crown-containing hetarylphenylethenes, for example, ligand **1**, the presence in solution of large cations of alkaline or alkaline-earth metals can favor an additional coordination of metal to the crown ether fragment due to sandwich complexation.[12] Potassium cation was chosen as a metal cation. Hetarylphenylethene **2** containing two methoxy groups instead of the crown ether fragment was used for comparative analyses.




**1**




**2**

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The structure, stoichiometry, and stability of the complexes formed were studied using a combination of physicochemical methods including $^1$H and $^{13}$C NMR spectroscopy, UV spectroscopy, ESI (electrospray ionization at atmospheric pressure) mass spectrometry, and X-ray diffraction analysis.

## Experimental

Potassium perchlorate was dried *in vacuo* at 230 °C. The syntheses of 4-[2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecen-2-yl)vinyl]pyridine (**1**) and 4-[2-(3,4-dimethoxyphenyl)vinyl]pyridine (**2**) have been described earlier.[13] Preparation of solutions and all studies were carried out under red light.

Acetonitrile (special purity grade, sort 1, KRIOKhROM) was used for spectrophotometry. Electronic absorption spectra were recorded on a Specord-M40 spectrophotometer (Carl Zeiss Jena) connected with a computer. Control of the spectrophotometer, data collection, and simplest computer processing of spectra were performed by the SPECORD standard program (version 2.0, Etalon). Fluorescence emission spectra were obtained on a Shimadzu RF-5301 PC fluorimeter connected with a computer. Control of the spectrofluorimeter and data collection were performed using the Hyper RF 1.57 program.

$^1$H and $^{13}$C NMR spectra were recorded on an Avance 600 spectrometer (Bruker) in acetonitrile-$d_3$ at frequencies of 600.22 and 150.93 MHz, respectively. Chemical shifts were determined relative to residual signals of the solvent ($CD_3CN$) and recalculated to the internal standard ($Me_4Si$). The gs-HMQC, gs-HMBS, and gs-COSY 2D procedures with pulse field gradients were used for signal assignment in NMR spectra. The phase-sensitive gs-NOESY or gs-ROESY 2D procedures were used for structural assignments.

Mass spectra (ESI) were detected in the mode of full mass scanning of positive ions on a Finnigan LCQ Advantage tandem dynamic mass spectrometer (USA) equipped with a mass analyzer with an octapole ionic trap, an MS Surveyor pump, a Surveyor autosampler, a Schmidlin-Lab nitrogen generator (Germany), and a system of data collection and processing using the X Calibur program, version 1.3 (Finnigan). The temperature of the transfer capillary was 150 °C, and the field strength between the needle and the counter electrode was 4.5 kV. Samples with $10^{-4}$ mol L$^{-1}$ concentration in a MeCN solution were introduced into the ion source with direct inlet with a low rate of 50 μL min$^{-1}$ through a Reodyne injector with a loop of 20 μL.

**$^1$H and $^{13}$C NMR spectra of ligands 1 and 2 and their complexes with potassium perchlorate and phthalic acid ($H_2A$). Ligand 1.** Ligand **1** (2.2 mg, 0.006 mmol) was dissolved in $CD_3CN$ (0.6 mL) under red light. $^1$H NMR, δ: 3.60—3.62 (m, 4 H, H(18), H(19)); 3.63—3.65 (m, 4 H, H(17), H(20)); 3.78—3.82 (m, 4 H, H(16), H(21)); 4.07—4.09 (m, 2 H, H(15)), 4.11—4.14 (m, 2 H, H(22)); 6.91 (d, 1 H, H(13), $J$ = 8.3 Hz); 7.03 (d, 1 H, H(7), $J$ = 16.3 Hz); 7.11 (dd, 1 H, H(14), $J$ = 8.4 Hz, $J$ = 2.0 Hz); 7.20 (d, 1 H, H(10), $J$ = 2.1 Hz); 7.35 (d, 1 H, H(8), $J$ = 16.3 Hz); 7.41 (d, 2 H, H(3), H(5), $J$ = 6.4 Hz); 8.49 (d, 2 H, H(2), H(6), $J$ = 6.2 Hz). $^{13}$C NMR, δ: 68.54 (C(15)), 68.68 (C(22)), 68.95 (C(16)), 69.05 (C(21)), 69.87, 69.92 (C(18), C(19)), 70.56, 70.57 (C(17), C(20)), 111.44 (C(10)), 113.42 (C(13)), 120.54 (C(3), C(5)), 121.21 (C(14)), 123.94 (C(8)), 129.70 (C(9)), 132.80 (C(7)), 144.94 (C(4)), 149.14 (C(12)), 149.78 (C(11)), 150.14 (C(2), C(6)).

**Ligand 1 in the presence of 0.5 equiv. $KClO_4$.** Ligand **1** (2.2 mg, 0.006 mmol) and $KClO_4$ (0.4 mg, 0.003 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1$H NMR, δ: 3.67—3.68 (m, 4 H, H(18), H(19)); 3.76—3.78 (m, 8 H, H(16), H(17), H(20), H(21)); 3.95—3.97 (m, 2 H, H(22)); 4.02—4.04 (m, 2 H, H(15)); 6.82 (d, 1 H, H(13), $J$ = 8.4 Hz); 6.98 (s, 1 H, H(10)); 6.98 (d, 1 H, H(7), $J$ = 16.3 Hz); 7.12 (d, 1 H, H(14), $J$ = 9.7 Hz); 7.32 (d, 1 H, H(8), $J$ = 16.3 Hz); 7.36 (d, 2 H, H(3), H(5), $J$ = 5.7 Hz); 8.47 (d, 2 H, H(2), H(6), $J$ = 5.3 Hz). $^{13}$C NMR, δ: 67.16—67.33 (C(15), C(16), C(21), C(22)), 67.84, 67.87 (C(18), C(19)), 68.67, 68.72 (C(17), C(20)), 110.95 (C(10)), 112.97 (C(13)), 120.53 (C(3), C(5)), 121.46 (C(14)), 124.32 (C(8)), 130.10 (C(9)), 132.51 (C(7)), 144.74 (C(4)), 147.85 (C(12)), 148.38 (C(11)), 150.06 (C(2), C(6)).

**Ligand 1 in the presence of 5 equiv. $KClO_4$.** Ligand **1** (2.2 mg, 0.006 mmol) and $KClO_4$ (4.2 mg, 0.03 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1$H NMR, δ: 3.71—3.72 (m, 4 H, H(18), H(19)); 3.79—3.77 (m, 4 H, H(17), H(20)); 3.84—3.88 (m, 4 H, H(16), H(21)); 4.21—4.22 (m, 2 H, H(15)); 4.24—4.25 (m, 2 H, H(22)); 7.03 (d, 1 H, H(13), $J$ = 8.3 Hz); 7.12 (d, 1 H, H(7), $J$ = 16.4 Hz); 7.24 (d, 1 H, H(14), $J$ = 8.3 Hz); 7.29 (s, 1 H, H(10)); 7.44 (d, 1 H, H(8), $J$ = 16.4 Hz); 7.49 (d, 2 H, H(3), H(5), $J$ = 6.1 Hz); 8.57 (d, 2 H, H(2), H(6), $J$ = 6.1 Hz).

**Ligand 1 in the presence of 0.5 equiv. $H_2A$.** Ligand **1** (4.4 mg, 0.012 mmol) and phthalic acid (1 mg, 0.006 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1$H NMR, δ: 3.69—3.70 (m, 4 H, 2 H(18), H(19)); 3.71—3.73 (m, 4 H, 2 H(17), H(22)); 3.84—3.86 (m, 4 H, H(16), H(21)); 4.10—4.12 (m, 2 H, H(22)); 4.13—4.14 (m, 2 H, H(15)); 6.91 (d, 1 H, H(13), $J$ = 8.8 Hz); 7.16 (s, 1 H, H(10)); 7.06 (d, 1 H, H(7), $J$ = 16.3 Hz); 7.16 (d, 1 H, H(14), $J$ = 5.7 Hz); 7.60—7.59 (m, 2 H, H(4′), H(5′)); 7.47 (d, 1 H, H(8), $J$ = 16.3 Hz); 7.61 (d, 2 H, H(3), H(5), $J$ = 6.2 Hz); 8.23—8.22 (m, 2 H, H(3′), H(6′)); 8.57 (d, 2 H, H(2), H(6), $J$ = 6.2 Hz). $^{13}$C NMR, δ: 68.31, 68.40 (C(15), C(22)), 68.89, 69.02 (C(16), C(21)), 69.64, 69.78 (C(18), C(19)), 70.26, 70.41 (C(17), C(20)), 111.34 (C(10)), 113.05 (C(13)), 121.50 (C(3), C(5)), 122.06 (C(14)), 122.47 (C(8)), 128.99 (C(9)), 130.85 (C(4′), C(5′)), 132.01 (C(3′), C(6′)), 134.15 (C(1′), C(2′)), 136.63 (C(7)), 145.60 (C(2), C(6)), 148.89 (C(12)), 149.78 (C(4)), 150.32 (C(11)), 167.57 (COOH).

**Ligand 1 in the presence of 1 equiv. $H_2A$.** Ligand **1** (4.4 mg, 0.012 mmol) and phthalic acid (2 mg, 0.012 mmol) was dissolved in $CD_3CN$ (0.6 mL) under red light. $^1$H NMR, δ: 3.66—3.72 (m, 8 H, H(17), H(18), H(19), H(20)); 3.82—3.84 (m, 4 H, H(16), H(21)); 4.03—4.05 (m, 2 H, H(22)); 4.09—4.12 (m, 2 H, H(15)); 6.86 (d, 1 H, H(13), $J$ = 8.8 Hz); 7.08 (d, 1 H, H(10), $J$ = 1.6 Hz); 7.01 (d, 1 H, H(7), $J$ = 16.2 Hz); 7.13 (dd, 1 H, H(14), $J$ = 8.3 Hz, $J$ = 1.9 Hz); 7.54—7.59 (m, 2 H, H(4′), H(5′)); 7.47 (d, 1 H, H(8), $J$ = 16.5 Hz); 7.65 (d, 2 H, H(3), H(5), $J$ = 6.4 Hz); 8.06—8.09 (m, 2 H, H(3′), H(6′)); 8.55 (d, 2 H, H(2), H(6), $J$ = 6.4 Hz). $^{13}$C NMR, δ: 68.27, 68.34 (C(15), C(22)), 68.86, 68.99 (C(16), C(21)), 69.58, 69.74 (C(18), C(19)), 70.20, 70.37 (C(17), C(20)), 111.32 (C(10)), 113.00 (C(13)), 121.70 (C(3), C(5)), 122.18 (C(14)), 122.26 (C(8)), 128.85 (C(9)), 130.92 (C(4′), C(5′)), 131.45 (C(3′), C(6′)), 133.77 (C(1′), C(2′)), 137.44 (C(7)), 144.70 (C(2), C(6)), 148.85 (C(12)), 150.43 (C(4)), 150.79 (C(11)), 169.26 (COOH).

**Ligand 1 in the presence of 0.5 equiv. $H_2A$ and 0.5 equiv. $KClO_4$.** Ligand **1** (4.4 mg, 0.012 mmol), phthalic acid (1 mg,

0.006 mmol), and $KClO_4$ (0.8 mg, 0.006 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1H$ NMR, δ: 3.68—3.69 (m, 4 H, H(18), H(19)); 3.76—3.80 (m, 8 H, H(16), H(17), H(20), H(21)); 3.92—3.93 (m, 2 H, H(22)); 4.09—4.10 (m, 2 H, H(15)); 6.88 (d, 1 H, H(13), $J$ = 7.9 Hz); 6.95 (s, 1 H, H(10)); 6.99 (d, 1 H, H(7), $J$ = 16.7 Hz); 7.17 (dd, 1 H, H(14), $J$ = 8.4 Hz, $J$ = 1.3 Hz); 7.41 (d, 1 H, H(8), $J$ = 16.3 Hz); 7.49 (d, 2 H, H(3), H(5), $J$ = 6.2 Hz); 7.61—7.62 (m, 2 H, H(4′), H(5′)); 8.09—8.11 (m, 2 H, H(3′), H(6′)); 8.44 (d, 2 H, H(2), H(6), $J$ = 5.7 Hz). $^{13}C$ NMR, δ: 67.24—67.38 (C(15), C(22), C(16), C(21)), 67.88, 67.97 (C(18), C(19)), 68.72, 68.82 (C(17), C(20)), 111.13 (C(10)), 112.84 (C(13)), 121.27 (C(3), C(5)), 122.24 (C(14)), 123.17 (C(8)), 129.53 (C(9)), 130.98 (C(4′), C(5′)), 131.06 (C(3′), C(6′)), 133.65 (C(1′), C(2′)), 135.50 (C(7)), 146.80 (C(2), C(6)), 147.89 (C(12)), 148.43 (C(4)), 149.06 (C(11)), 169.52 (COOH).

**Ligand 2.** Ligand **2** (0.3 mg, 0.001 mmol) was dissolved in $CD_3CN$ (0.6 mL) under red light. $^1H$ NMR, δ: 3.84, 3.88 (both s, 3 H each, H(15), H(22)); 6.96 (d, 1 H, H(13), $J$ = 8.5 Hz); 7.06, 7.38 (both d, 1 H each, H(7), H(8), $J$ = 16.5 Hz); 7.14 (dd, 1 H, H(14), $J$ = 9.4 Hz, $J$ = 1.8 Hz); 7.24 (s, 1 H, H(10)); 7.41 (d, 2 H, H(3), H(5), $J$ = 5.5 Hz); 8.52 (d, 2 H, H(2), H(6), $J$ = 5.5 Hz).

**Ligand 2 in the presence of 0.5 equiv. $H_2A$.** Ligand **2** (0.3 mg, 0.001 mmol) and phthalic acid (0.10 mg, 0.0005 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1H$ NMR, δ: 3.86, 3.89 (both s, 3 H each, H(15), H(22)); 6.99 (d, 1 H, H(13), $J$ = 8.2 Hz); 7.15, 7.55 (both d, 1 H each, H(7), H(8), $J$ = 16.2 Hz); 7.20 (dd, 1 H, H(14), $J$ = 8.2 Hz, $J$ = 1.4 Hz); 7.28 (s, 1 H, H(10)); 7.59—7.61 (m, 2 H, H(4′), H(5′)); 7.69 (d, 2 H, H(3), H(5), $J$ = 5.9 Hz); 8.22—8.23 (m, 2 H, H(3′), H(6′)); 8.60 (d, 2 H, H(2), H(6), $J$ = 5.9 Hz).

**Ligand 2 in the presence of 0.5 equiv. $H_2A$ and 0.5 equiv. $KClO_4$.** Ligand **2** (0.3 mg, 0.001 mmol), phthalic acid (0.09 mg, 0.0005 mmol), and $KClO_4$ (0.08 mg, 0.0005 mmol) were dissolved in $CD_3CN$ (0.6 mL) under red light. $^1H$ NMR, δ: 3.86, 3.89 (both s, 3 H each, H(15), H(22)); 6.99 (d, 1 H, H(13), $J$ = 8.2 Hz); 7.16, 7.58 (both d, 1 H each, H(7), H(8), $J$ = 16.2 Hz); 7.20 (d, 1 H, H(14), $J$ = 8.2 Hz); 7.28 (s, 1 H, H(10)); 7.59—7.62 (m, 2 H, H(4′), H(5′)); 7.71 (d, 2 H, H(3), H(5), $J$ = 5.9 Hz); 8.21—8.23 (m, 2 H, H(3′), H(6′)); 8.59 (d, 2 H, H(2), H(6), $J$ = 5.0 Hz).

**Calculation of the optimal geometry** of complexes of ligand **1** with potassium cations and phthalic acid performed by the molecular mechanics method using the MM+ force field (HyperChem program package, version 7.5).

**Calculation of the stability constants of the complexes of ligand 1 with potassium perchlorate and phthalic acid.** The method of spectrophotometric titration at 20±1 °C was used for measuring stability constants of the complexes. For spectrophotometric titration, we prepared solutions in MeCN of ligand **1** ($C_1$ = $= 4.3 \cdot 10^{-5}$ mol $L^{-1}$), potassium perchlorate ($C_{K+} = 1 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ mol $L^{-1}$), and phthalic acid ($C_{H2A} = 1 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$ mol $L^{-1}$). A solution of ligand **1** was titrated with a solution of potassium perchlorate or phthalic acid as follows: the known volume of a solution of ligand **1** in MeCN was poured to a quartz cell and the absorption spectrum was recorded. Then a solution of potassium perchlorate or phthalic acid with a known total concentration was added in portions to the cell. After each addition, absorption spectra of solutions were recorded. Titration was stopped, when the absorption spectra of the solutions remained almost unchanged upon the further addition of potassium salt or acid. This indicated the complexation, or the changes were explained by dilution only, which was accompanied by a uniform decrease in the absorbance over the whole absorption spectrum. The results of spectrophotometric titration were processed and the stability constants of the complexes were calculated using the SPECFIT/32 program.

**Calculation of the fluorescence quantum yields.** The fluorescence emission spectra of ligand **1** and the complexes with $K^+$ cation and phthalic acid were measured upon photoexcitation with λ = 330 nm. An aqueous solution of quinine sulfate in 1 *N* $H_2SO_4$ ($\varphi_{fl}$ = 0.55±0.03)[14] was used as a standard for ligand **1**. All measurements were carried out at low absorbances of the solution at the excitation wavelength of the ligands.

To determine the fluorescence quantum yield $\varphi_{fl}$ of the ligand and its complexes with potassium cations, we recorded noncorrected fluorescence spectra of the studied solution and solution of the standard substance. The fluorescence quantum yields were calculated by the formula[15]:

$$\varphi_i = \varphi_0 \frac{(1-10^{-D_0})S_i n_0^2}{(1-10^{-D_i})S_0 n_i^2},$$

where $\varphi_i$ and $\varphi_0$ are the fluorescence quantum yields of the analyzed solution and standard, respectively; $D_i$ and $D_0$ are the absorbances of the analyzed solution and standard, respectively; $S_i$ and $S_0$ are the surface areas under the curves of the fluorescence spectrum of the analyzed solution and standard, respectively; $n_i$ and $n_0$ are refractive indices of acetonitrile and 1 *N* $H_2SO_4$ (see Ref. 16), respectively.

**X-ray diffraction analysis.** Single crystals of complex **2** · $H_2A$ for X-ray diffraction analysis were obtained as follows: phthalic acid (2.16 mg, 0.013 mmol) and ligand **2** (10 mg, 0.026 mmol) were dissolved in 6 mL of MeCN under red light. The obtained crystals were left in the dark at 12—14 °C until transparent crystals precipitated. The crystals were filtered off.

A single crystal covered with perfluorinated oil was placed on a Bruker SMART-CCD diffractometer under a cooled nitrogen flow. A set of experimental reflections was obtained in the ω scan mode of reflections from single crystals on Mo-Kα radiation (λ = 0.71073 Å). The primary processing of experimental reflections was performed using the Bruker SAINT program package.[17] The structure was determined by direct methods and refined by least squares in the full-matrix anisotropic approximation on $F^2$. Hydrogen atoms were revealed from the difference Fourier synthesis. Their refinement was performed in the isotropic approximation. All calculations were carried out using the SHELXTL-Plus program package.[18] The main crystallographic parameters and characteristics of X-ray diffraction experiment are presented in Table 1.

## Results and Discussion

**Electronic absorption spectra.** The electronic absorption spectrum of ligand **1** in MeCN is characterized by an intense long-wavelength absorption band (LWAB) with a maximum at λ = 330 nm. As we have shown earlier,[12] ligand **1** is capable of complex forming with alkaline-earth metal cations at the crown ether moiety, which results in the hypsochromic shift in the absorption spectrum by

**Table 1.** Selected crystallographic characteristics for complex **2** · $H_2A$

| Parameter | Value |
|---|---|
| Molecular formula | $C_{23}H_{21}NO_6$ |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$/Å | 9.2780(3) |
| $b$/Å | 10.7899(4) |
| $c$/Å | 11.3279(4) |
| α/deg | 65.9840(10) |
| β/deg | 82.5030(10) |
| γ/deg | 67.8690(10) |
| $V$/Å$^{-3}$ | 959.19(6) |
| $Z$ | 2 |
| $d_{calc}$/g cm$^{-3}$ | 1.411 |
| $F$(000) | 428 |
| μ/mm$^{-1}$ | 0.103 |
| Crystal size/mm | 0.36×0.24×0.22 |
| Temperature/K | 120.0(2) |
| Scan range, θ/deg | 1.97—28.99 |
| Range of $h$, $k$, $l$ | $-12 \le h \le 12$ |
| | $-13 \le k \le 14$ |
| | $-12 \le l \le 15$ |
| Number of measured reflections | 5875 |
| Number of independent reflections ($R_{int}$) | 4724 (0.0123) |
| Number of reflections with $I > 2\sigma(I)$ | 4015 |
| Number of refined parameters | 356 |
| $R$ factors on reflections with $I > 2\sigma(I)$ | |
| $R_1$ | 0.0402 |
| $wR_2$ | 0.1159 |
| $R$ factor (on all reflections) | |
| $R_1$ | 0.0476 |
| $wR_2$ | 0.1217 |
| Goodness-of-fit on $F^2$ | 1.070 |
| Residual electron density, e · Å$^{-3}$, $\rho_{min}/\rho_{max}$ | −0.246/0.356 |

14—16 nm. The addition of potassium perchlorate to a solution of compound **1** ($2 \cdot 10^{-4}$ mol L$^{-1}$) in MeCN induces a hypsochromic shift of the LWAB by 9 nm (Fig. 1), indicating the occurrence of a complexation process involving the crown ether moiety. The electrostatic interaction of the positively charged metal ion with heteroatoms of crown ether decreases the electron-donating ability of the crown ether moiety, due to which the hypsochromic shift of the electronic absorption spectrum was observed.

The addition of phthalic acid to a solution of **1** in MeCN generates a new absorption band with a maximum at λ = 394 nm (Fig. 2).

The spectral changes presented above are similar to those observed previously for the interaction of **1** with perchloric acid,[12] resulting in the protonation of the nitrogen atom of the pyridine residue. As known, derivatives in nitrogen-containing styryl heterocycles in the presence of appropriate Brönsted acids can be protonated at the nitrogen atom, which is accompanied by the bathochromic

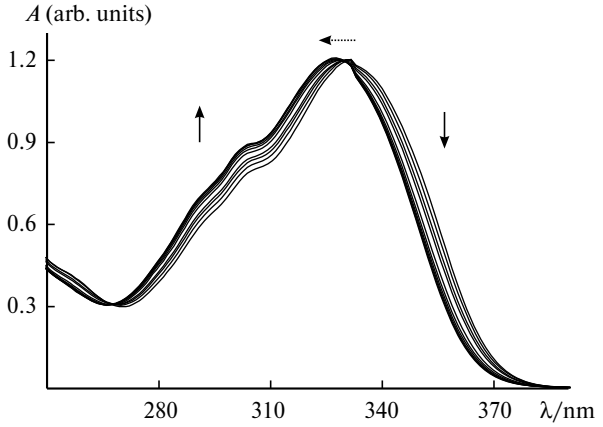



**Fig. 1.** Electronic absorption spectra of a solution of ligand **1** ($C_1 = 4 \cdot 10^{-5}$ mol L$^{-1}$) at various concentrations of cations $K^+$ in the solution ($C_{K^+} = 0$—$2.7 \cdot 10^{-3}$ mol L$^{-1}$). Solvent acetonitrile, temperature 20±1 °C.

shift of the LWAB in the electronic absorption spectra.[19—23] Phthalic acid in MeCN is a very weak acid for which the acidity constants of the first and second dissociation steps[24] are 14.3 and 29.8, respectively; therefore, a substantial excess of phthalic acid is necessary for the complete protonation of compound **1**.

**Complexation.** Complexation of **1** with potassium perchlorate and phthalic acid was studied using ESI mass spectrometry, spectrophotometric titration, and $^1$H and $^{13}$C NMR spectroscopy.

It is known that large cations and derivatives of benzo-15-crown-5 are characterized by the formation of 2 : 1 sandwich complexes.[25] The formation of stable 2 : 1 complexes with barium cations was observed for 15-crown-5-containing 4-styrylpyridine **1** in acetonitrile.[12] Complexes with potassium cations of compositions 1 : 1 and 2 : 1 were observed for benzo-15-crown-5 in MeCN.[12a] Crown-containing benzobistiazole with two fragments of benzo-15-

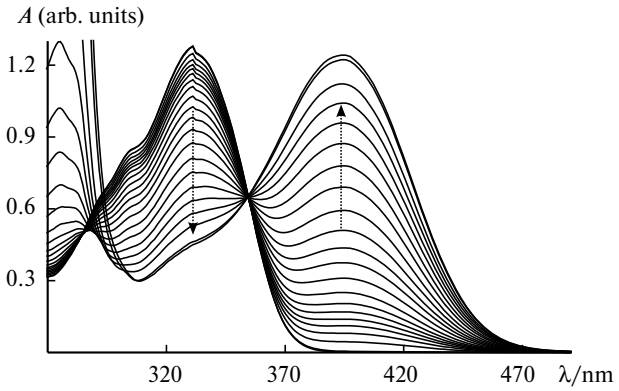



**Fig. 2.** Electronic absorption spectra of a solution of ligand **1** ($C_1 = 4.3 \cdot 10^{-5}$ mol L$^{-1}$) at various concentrations of phthalic acid in the solution ($C_{H_2A} = 0$—$1.8 \cdot 10^{-3}$ mol L$^{-1}$). Solvent acetonitrile, temperature 20±1 °C.

**Table 2.** Mass spectra (ESI) of complexes **1** with various anions in MeCN

| Ligand | Anion | *m/z* |
|---|---|---|
| **1** | $K^+$ | 410.1 $[\mathbf{1}\cdot K]^+$, 780.9 $[(\mathbf{1})_2\cdot K]^+$ |
| **1** | $Na^+$ | 394.3 $[\mathbf{1}\cdot Na]^+$ |
| **1** | $H^+$ | 372.3 $[\mathbf{1}\cdot H]^+$, 742.9 $[(\mathbf{1})_2\cdot H]^+$ |

crown-5 in one molecule with potassium cations in MeCN forms a 2 : 2 sandwich complex.[26] In the latter case, the formation of the sandwich complex is favored by stacking interaction of two neutral molecules of the ligand. It should be mentioned that the formation of only 1 : 1 complex of the butadienyl cationic dye containing the fragment of benzo-15-crown-5 and potassium perchlorate in MeCN was observed.[27] This is related, most likely, to the fact that the ligand molecule is positively charged, in this case, and hence, is not prone to stacking interaction.

To establish what types of complexes are formed between compound **1** and potassium cations, we studied the products of their reaction in MeCN using electrospray ionization mass spectrometry. It was found that even at a tenfold excess of potassium perchlorate both $\mathbf{1}\cdot K^+$ and $(\mathbf{1})_2\cdot K^+$ complexes are present in a MeCN solution of ligand **1**, and the peak intensity of complex $(\mathbf{1})_2\cdot K^+$ in the mass spectra is higher than that of complex $\mathbf{1}\cdot K^+$. The data obtained indicate that ligand **1** is capable of forming with potassium cations rather stable sandwich complexes $(\mathbf{1})_2\cdot K^+$. It should be mentioned that only 1 : 1 complexes were found in a solution of ligand **1** in the presence of sodium perchlorate under similar conditions of analysis (Table 2).

Both the protonated form of compound **1** and the reaction product of **1** with its protonated form $(\mathbf{1})_2\cdot H^+$ were found by ESI mass spectrometry in a solution of ligand **1** in MeCN acidified with perchloric acid (see Table 2).

To determine the values of stability constants of complexes of **1** with potassium perchlorate in MeCN, we used the method of spectrophotometric titration. The spectrophotometric titration data were processed by the SPECFIT/32 program assuming that complexes $\mathbf{1}\cdot K^+$ and $(\mathbf{1})_2\cdot K^+$ were formed upon complexation. The values determined for the stability constants are listed in Table 3. Calculations using the obtained values of complexation showed that in a solution of ligand **1** with the total concentration $C_1 = 5\cdot10^{-5}$ mol $L^{-1}$ the maximum concentration of complex $(\mathbf{1})_2\cdot K^+$ is observed at the total concentration of $KClO_4$ equal to $2\cdot10^{-4}$ mol $L^{-1}$. In this case, 45% of complex **1** exist as complex $(\mathbf{1})_2\cdot K^+$. For the $^1H$ NMR study of the complexation of ligand **1** with $KClO_4$, the initial concentration of the ligand was 0.01 mol $L^{-1}$. The content of compound **1** in the form of complex $(\mathbf{1})_2\cdot K^+$ reached 94% of its total amount.

The reaction of phthalic acid with ligand **1** was also studied by spectrophotometric titration (see Fig. 2). The appearance of the LWAB with a maximum at $\lambda = 394$ nm upon the addition of phthalic acid to a solution of **1** can be due to the transfer of a proton from phthalic acid to the nitrogen atom of the pyridine moiety of molecule **1**. It has been shown earlier[12] that compound **1** is readily protonated in the presence of perchloric acid, resulting in the appearance of the LWAB with a maximum at $\lambda = 398$ nm in the absorption spectrum. The LWAB maxima of compound **1** in the presence of perchloric and phthalic acid differ by 4 nm, indicating that the products formed are different.

The reaction of phthalic acid ($H_2A$) with **1** can be described by the equation

$$H_2A + \mathbf{1} \rightleftharpoons HA^-\cdot\mathbf{1}\cdot H^+ \rightleftharpoons HA^- + \mathbf{1}\cdot H^+. \qquad (1)$$

The difference in the reaction products of **1** with perchloric and phthalic acids may indicate that the second equilibrium in Eq. (1) is shifted toward the formation of nondissociated compound $HA^-\cdot\mathbf{1}\cdot H^+$. The formation of similar ion pairs in MeCN has been observed earlier for the system pyridinium cation—benzoate anion.[28]

**Table 3.** Spectral characteristics and stability constants of the complexes of ligand **1** with the potassium cation ($K^+$) and phthalic acid ($H_2A$)

| Compound | $\lambda^{abs}$ ($\Delta\lambda^{abs}$)/nm | $\varepsilon\cdot10^{-4}$/L mol$^{-1}$ cm$^{-1}$ | log*K* | $\lambda^{fl}$ ($\Delta\lambda^{fl}$)/nm | $\varphi_{fl}\cdot10^{-2}$ |
|---|---|---|---|---|---|
| **1** | 332 | 2.96 | — | 427 | 1.2 |
| $\mathbf{1}\cdot H^+$ | 398 (66) | 3.23 | $\log K_{11} = 10.6 \pm 0.7$ | — | — |
| $\mathbf{1}\cdot K^+$ | 326 (–6) | 3.05 | $\log K_{11} = 3.7 \pm 0.2$ | 418 (–9) | 0.9 |
| $(\mathbf{1})_2\cdot K^+$ | 331 (–1) | 6.07 | $\log K_{21} = 8.5 \pm 0.3$ | | |
| $\mathbf{1}\cdot H^+\cdot HA^-$ | 394 (62) | 2.81 | $\log K_{11} = 7.7 \pm 0.1$ | 545 (118) | 3.4 |
| $\mathbf{1}\cdot H_2A$ | 394 (62) | 2.81 | $\log K_{11} = 4.0 \pm 0.1$ | 545 (118) | 3.4 |
| $\mathbf{1}\cdot K^+\cdot H_2A$ | 329 (–3); 388 (56) | 2.41; 3.19 | $\log K_{111} = 7.9 \pm 0.1$ | 418 (–9), 530 (103) | 1.2 |
| $(\mathbf{1})_2\cdot K^+\cdot H_2A$ | 388 (56) | 6.38 | $\log K_{121} = 14.0 \pm 0.17$ | 530 (103) | 4.3 |

*Note.* Spectral data are given for solutions in MeCN at 293 K. The values of $\Delta\lambda^{abs}$ and $\Delta\lambda^{fl}$ are presented relative to $\lambda^{abs}$ and $\lambda^{fl}$ of ligand **1**, respectively.

The data of spectrophotometric titration of compound **1** with phthalic acid were processed by the SPECFIT/32 program; the fixed values of acidity constants for the first and second dissociation steps of phthalic acid[24] for the following equations were used in the calculations:

$$\mathbf{1} + H^+ \rightleftharpoons \mathbf{1}\cdot H^+, \quad (2)$$

$$\mathbf{1} + 2\,H^+ + A^{2-} \rightleftharpoons \mathbf{1}\cdot H_2A. \quad (3)$$

As a result, we found the values of stability constants for the protonated form of compound **1** (Eq. (2)) and complex $\mathbf{1}\cdot H_2A$ formed according to Eq. (3) and of this complex, whose formation follows the reaction equations

$$\mathbf{1} + H_2A \rightleftharpoons \mathbf{1}\cdot H_2A \quad \text{and} \quad HA^- + \mathbf{1}\cdot H^+ \rightleftharpoons \mathbf{1}\cdot H_2A$$

(see Table 3). The calculation of the solution composition during titration using the determined values of stability constants for the complexes showed that nondissociated complex $\mathbf{1}\cdot H_2A$ was predominantly formed, while the concentration of free protonated form $\mathbf{1}\cdot H^+$ was low.

An analysis of the data of spectrophotometric titration of a solution of the complexes of ligand **1** with potassium perchlorate and phthalic acid was carried out taking into account absorption spectra of $(\mathbf{1})_2\cdot K^+$ and $\mathbf{1}\cdot K^+$. It turned out that at least two mixed complexes with different stoichiometry are formed during titration. At low concentrations of phthalic acid, complex $(\mathbf{1})_2\cdot K^+\cdot H_2A$ predominates in which two ligand molecules are bonded, on the one hand, to the potassium cation and, on the other hand, to one acid molecule. The absorption spectrum of this complex contains two long-wavelength bands with absorption maxima corresponding to the absorption of the protonated and nonprotonated forms of ligand **1**. It is most likely that in this complex one molecule of ligand **1** is protonated by one carboxyl group of phthalic acid, and the second molecule of **1** forms a hydrogen bond with the second carboxyl group of phthalic acid. This assumption is confirmed by the fact that the addition of phthalic acid to complex $(\mathbf{1})_2\cdot K^+$ is more efficient ($\log K_{121} - \log K_{21} = 5.5$) than the addition of phthalic acid to molecule **1** ($\log K_{11} = 4.0$). An increase in the concentration of phthalic acid in the solution affords one more mixed complex. This complex can be either $\mathbf{1}\cdot K^+\cdot H_2A$ or $(\mathbf{1})_2\cdot K^+\cdot (H_2A)_2$; however, we could not make an unambiguous choice because of the complicated character of the system considered. Therefore, the stability constant for a simpler complex $\mathbf{1}\cdot K^+\cdot H_2A$ is given in Table 3 (Scheme 1).

Based on the data of spectrophotometric titration and obtained values of stability constants for the complexes, we calculated the absorption spectra of the complex of ligand **1** with potassium cations and phthalic acid using the SPECFIT/32 program (Fig. 3).

The optimized spatial structures of the complexes of ligand **1** with potassium cations and phthalic acid calculated by the MM+ molecular mechanics method are presented in Fig. 4.

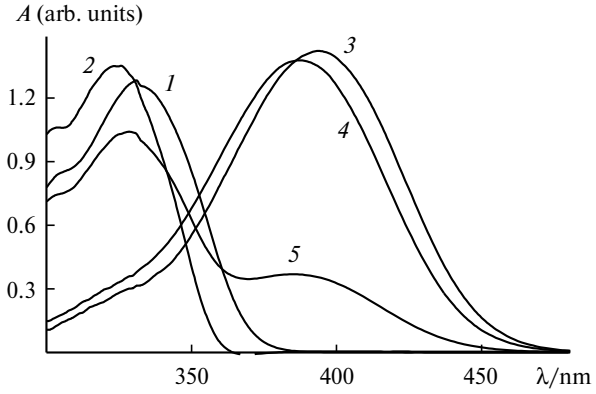



**Fig. 3.** Theoretical absorption spectra of a solution of ligand **1** (*1*) and its complexes with the potassium cation and phthalic acid: $(\mathbf{1})_2\cdot K^+$(*2*), $\mathbf{1}\cdot H_2A$ (*3*), $\mathbf{1}\cdot K^+\cdot H_2A$ (*4*), and $(\mathbf{1})_2\cdot K^+\cdot H_2A$ (*5*) calculated by the data of spectrophotometric titration.

Using the complexation constants obtained, we calculated the amount of $K^+$ cations bonded by ligand **1** in the presence and in the absence of phthalic acid. Figure 5 shows that the concentration of free cations $K^+$ decreases with an increase in the phthalic acid concentration in the system containing the constant total amount of ligand **1** (curve *1*). Coordination of a phthalic acid molecule by dimeric complex $(\mathbf{1})_2\cdot K^+$ additionally stabilizes the latter.

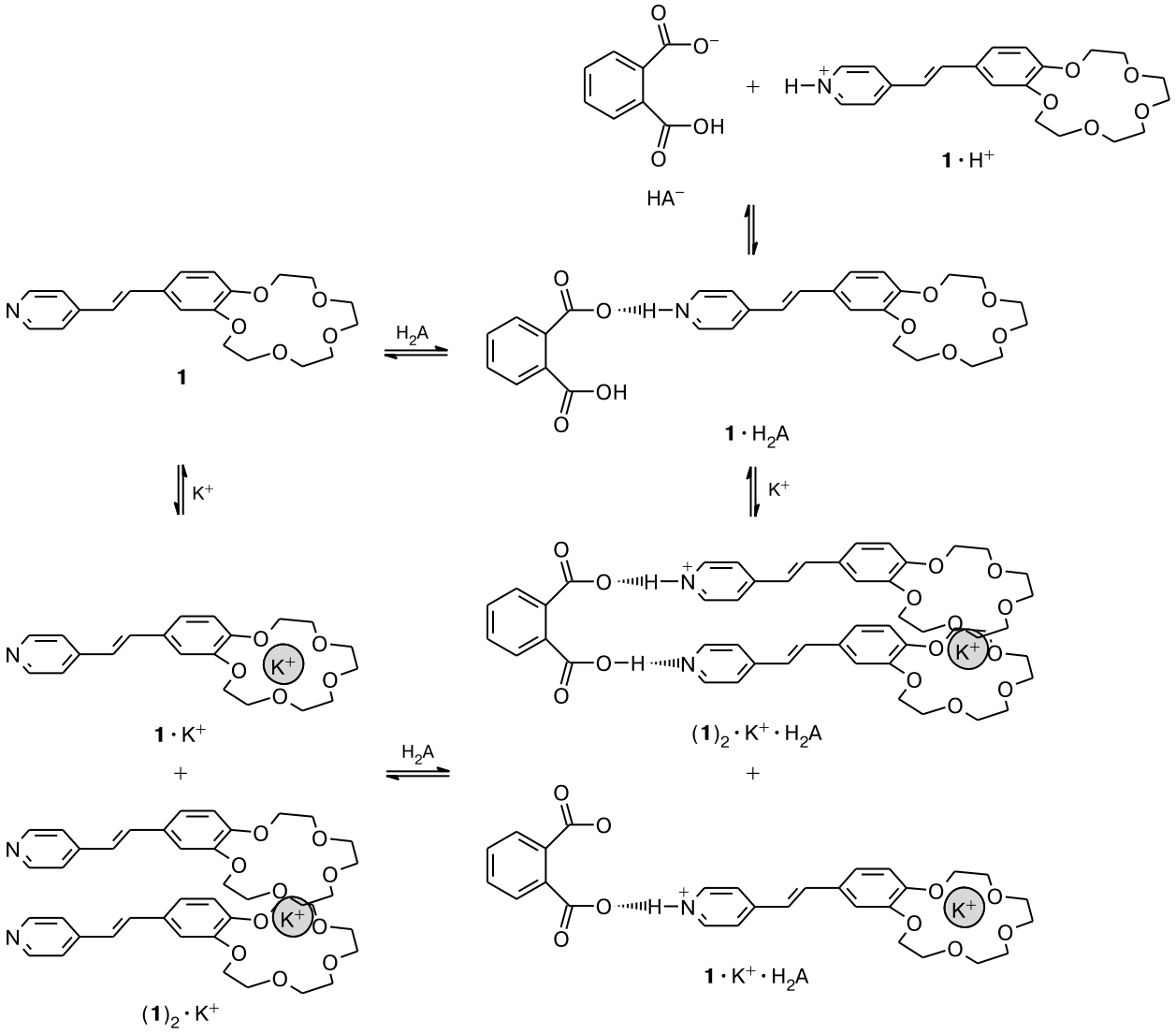
**Spectral luminescence properties.** To study the influence of the structural organization of molecules on their fluorescence characteristics, we measured the fluorescence emission spectra and calculated the fluorescence quantum yields of ligand **1** and its complexes with potassium cations and phthalic acid.

It is known that fluorescence and photoisomerization are two competing processes, where hindrance of rotation about the central double bond should increase the fluorescence quantum yield.[29–32] As shown previously,[33] rather efficient process of *E*-*Z*-photoisomerization ($\varphi_{E\to Z} = 0.45$) occurs in a solution of ligand **1** in MeCN. Therefore, it is not surprising that the value of fluorescence quantum yield for this compound is rather low $\varphi_{fl} = 1.2\cdot 10^{-2}$ (see Table 3).

An addition of potassium perchlorate to a solution of ligand **1** causes the hypsochromic shift of the emission spectrum by 9 nm (Fig. 6). It was shown that complexation at the crown ether moiety with cation $K^+$ insignificantly decreases the fluorescence quantum yield of ligand **1**, and this can be due to an enhancement of routes of vibrational relaxation of the excited state in "sandwich" complex $(\mathbf{1})_2\cdot K^+$.

The formation of complex $\mathbf{1}\cdot H_2A$ with phthalic acid induces a substantial red shift of $\lambda_{max}^{fl}$ of ligand **1** by 118 nm (see Fig. 6). The fluorescence quantum yield increases approximately threefold, being $\varphi_{fl} = 3.4\cdot 10^{-2}$. As shown

**Scheme 1**



earlier,[33] the protonation of ligand **1** favors decreasing the photoisomerization quantum yield and, as a consequence, increasing the probability of radiative deactivation of the excited state *via* fluorescence.

As can be seen from Fig. 6, the emission spectrum of complex $(\mathbf{1})_2 \cdot H_2A \cdot K^+$ has two broad bands with $\lambda_{max}^{fl}$ at 418 and 530 nm; this may indicate that in the complex only one molecule of ligand **1** is protonated and the second molecule is bonded with phthalic acid only by a hydrogen bond (see Scheme 1). When protonating the both molecules of ligand **1**, one should expect the appearance of only one emission band with a maximum about 530 nm. The formation of this complex does not result in fluorescence rising, and the value of fluorescence quantum yield of this complex approximately corresponds to the fluorescence quantum yield of free ligand **1**.

For the formation of complex $\mathbf{1} \cdot H_2A \cdot K^+$, fluorescence rises more than 3.5 times (see Fig. 6 and Table 3). In this case, ligand **1** in the complex is protonated, which, as shown above, increases the probability of deactivation of the excited state *via* fluorescence. It is most likely that coordination of cation $K^+$ to the crown ether moiety favors an increase in the fluorescence efficiency due to a decrease in crown ether mobility and, as a consequence, favors a decrease in the efficiency of thermal relaxation of the excited state.

Based on the presented results, we may assume that the interaction of dicarboxylic acids with heterocyclic bases can proceed *via* two routes (Scheme 2).

In the first case (route *A*), the proton is completely detached from the carboxyl group and adds to the heterocyclic residue. The protonation of pyridine heterocycle is

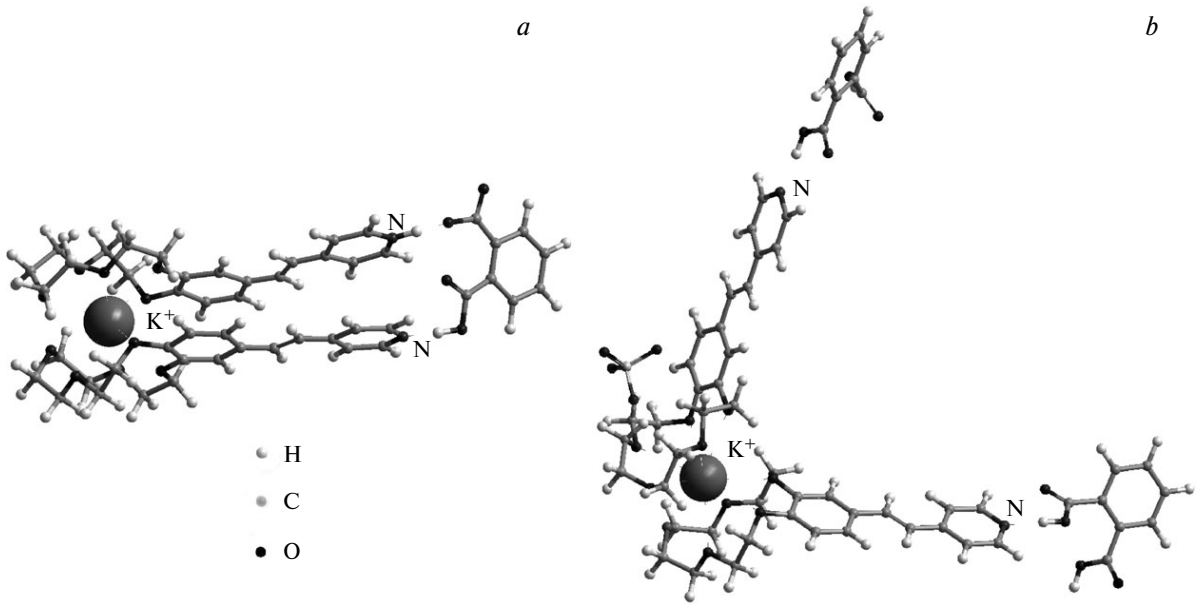
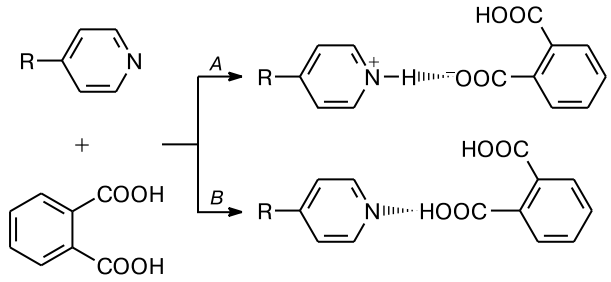



**Fig. 4.** Optimized structures of the complex of ligand **1** with the potassium cation $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$ (*a*) and phthalic acid $(\mathbf{1})_2 \cdot K^+ \cdot (H_2A)_2$ (*b*) according to the data of MM+ quantum chemical calculations.

**Scheme 2**




accompanied by a strong bathochromic shift of the long-wavelength absorption band. This situation is characteristic of complexes $\mathbf{1} \cdot H_2A$ and $\mathbf{1} \cdot H_2A \cdot K^+$ in which all ligands are protonated. In the second case (route *B*), association occurs due to hydrogen bonding between the heterocycle and hydrogen atom of the carboxyl group. This coordination does not necessarily lead to substantial changes in the absorption spectra. The second case partially occurs in complex $(\mathbf{1})_2 \cdot H_2A \cdot K^+$, where only one ligand molecule is protonated and the second molecule is linked with the carboxyl group of phthalic acid by hydrogen bond.

A possibility of protonation of the pyridine heterocycle of hydrogen bonding during the reaction of ligand **1** with acids should be determined by the strength of the acids and, hence, by easiness of their acidic dissociation. Since the dissociation of dibasic acids proceeds stepwise and the dissociation constant of the first step is higher than that of the second step,[16] it is reasonable to assume that at a certain combination of dissociation constants the ligands will be protonated only due to dissociation by the first step, while only hydrogen bonding will be possible with the second proton. Evidently, both these interactions occur in the mixed complexes of ligand **1** with potassium perchlorate and phthalic acid.

**X-ray diffraction analysis.** The X-ray diffraction data are an additional proof for coordination of 4-styrylpyridine to phthalic acid. We succeeded to obtain crystals of complex $\mathbf{2} \cdot H_2A$ and to study its structure by X-ray dif-

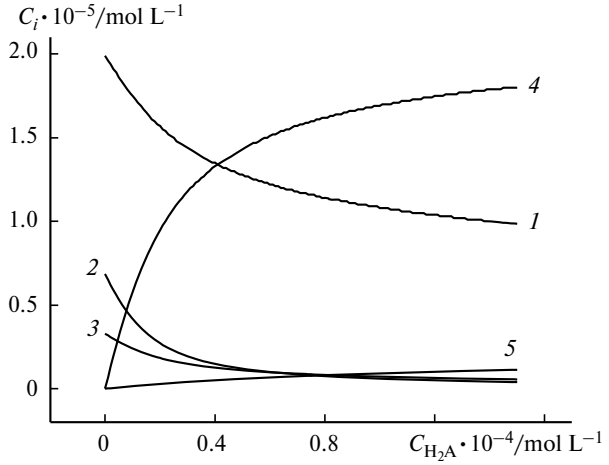



**Fig. 5.** Concentrations of the components ($C_i$) in a solution of ligand **1** and potassium perchlorate at their constant total concentration, depending on the phthalic acid concentration: $K^+$ (*1*), $(\mathbf{1})_2 \cdot K^+$ (*2*), $\mathbf{1} \cdot K^+$ (*3*), $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$ (*4*), and $\mathbf{1} \cdot K^+ \cdot H_2A$ (*5*). (Initial concentrations: $C_{\mathbf{1}} = 5 \cdot 10^{-5}$ mol L$^{-1}$, $C_{K^+} = 3.0 \cdot 10^{-5}$ mol L$^{-1}$, solvent MeCN).

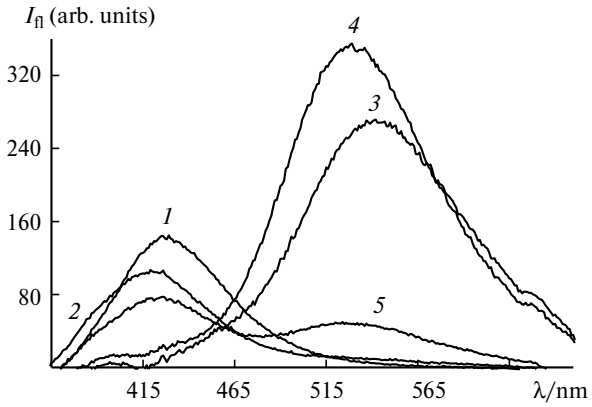



**Fig. 6.** Fluorescence emission spectra of ligand **1** (*1*) and its complexes with the potassium cation and phthalic acid: $(\mathbf{1})_2 \cdot K^+$ (*2*), $\mathbf{1} \cdot H_2A$ (*3*), $\mathbf{1} \cdot K^+ \cdot H_2A$ (*4*), and $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$ (*5*). ($C_{\mathbf{1}} = 9.5 \cdot 10^{-5}$ mol $L^{-1}$, $\lambda_{exc}$ = 330 nm, solvent acetonitrile, temperature 20±1 °C).

fraction analysis. In the presence of the acid, the complex consisting of one molecule **2** and one molecule of phthalic acid is formed, and one of the protons of phthalic acid is covalently bonded to the nitrogen atom of the pyridine fragment and H-bonded to the carbonylic oxygen atom. The composition and structure of the independent part of the crystal lattice are shown in Fig. 7.

The crystal of complex $\mathbf{2} \cdot H_2A$ is formed by two structural units: protonated styrylpyridine and anion of the monobasic residue of phthalic acid. In the anion the H(2) proton of the carboxyl group predominantly bonded with the O(4) atom is involved in an intramolecular hydrogen bond with the O(6) atom of deprotonated carboxylate. The parameters of this hydrogen bond are the following: distance O(6)...H(2) 1.32(3) Å, angle O(4)—H(2)...O(6) 177(1)°; the O(3)—C(22) and O(4)—C(22) bond lengths in the carboxyl group are 1.221(1) and 1.304(1) Å, respectively; and the O(5)—C(23) and O(6)—C(23) bond lengths in the deprotonated carboxyl group are 1.248(1) and 1.304(1) Å, respectively. This completely agrees with the localization of the H(2) hydrogen atom at the O(4) oxygen atom.

The cation has characteristic features typical of both styryl dyes and preceding bases. It is almost planar. The dihedral angle between the plane of the pyridine cycle and the plane of the ethylene fragment C(3)—C(6)=C(7)—C(8) is 4.0°, the angle between the latter plane and the benzene ring plane is 10.4°, and that between the planes of the pyridine and benzene rings is 14.0°. This geometry corresponds to good conditions for π-electron density delocalization over the whole cation. Nevertheless, as usually, the ethylene bond is substantially localized and is equal to 1.342(1) Å, whereas the both ordinary C(3)—C(6) and C(7)—C(8) bonds are 1.461(1) Å. The bond length distribution in the pyridine cycle indicates a substantial contribution of the *para*-quinoid structure. The sequence of bonds in the chain N(1)—C(1)—C(2)—C(3) (bond lengths are 1.342(1), 1.377(2), and 1.403(1) Å, respectively) is almost the same as in chain N(1)—C(5)—C(4)—C(3) (bond lengths are 1.348(1), 1.372(2), 1.408(1) Å, respectively). The bonds alternate along one half of the benzene ring: C(8)—C(9)—C(10)—C(11) (1.409(1), 1.381(1), and 1.412(1) Å). They are almost completely delocalized over another half: C(8)—C(13)—C(12)—C(11) (1.395(2), 1.391(2), 1.387(2) Å). As usually, deformation of the external bond angles at the C(10) and C(11) atoms is observed and contradicts the existence of steric repulsion between the *ortho*-substituents (oxygen atoms O(1) and O(2)). Indeed, the angles O(1)—C(11)—C(10) and O(2)—C(10)—C(11), which should be increased due to the indicated steric repulsion, are considerably decreased in fact, being 115.48(9) and 115.62(9)°, respectively, while the angles O(1)—C(11)—C(12) and O(2)—C(10)—C(9), on the contrary, are considerably increased, being 125.2(1) and 124.8(1)°, respectively. This deformation of the styryl fragment geometry is due to conjugation and involvement of lone electron pairs of the oxygen atoms on the *p*-orbitals in this conjugation. The total electronic effect of two methoxy groups, one of which is in the *para*-position and another is in the *meta*-position to the ethylene substituent of the benzene ring, induces the above discussed nonsymmetric distribution of bonds in this ring and the deformation of the bond angles.

In crystal, complex $\mathbf{2} \cdot H_2A$ forms layers consisting of infinite ribbons linked by hydrogen bonds of cations and anions (see Fig. 7). The cation (type A) and the anion (type C) are linked by a pair of hydrogen bonds N(1A)—H(1A)...O(5C) and O(6C)...H(5AA)—C(5A) with the geometry N—H and N—H...O (1.70(2) Å and 174.9(8)°). In addition, the neighboring anion (type E) with the same cation (type A) forms weak hydrogen bonds O(3E)...H(4AA)—C(4E) and O(3E)...H(7AA)—C(7E) with the parameters O...H and C—H...O 2.48(3) Å and 155.6(9)° for the first one and 2.35(3) Å and 160.9(9)° for the second of them. Two adjacent cations (type A and type C) also form a centrosymmetric pair due to weak interactions of the type O(2A)...H(15I)—C(15I) with the geometric parameters 2.42(3) Å and 142(1)°. All these interactions are repeated in symmetrically bound structural crystal units. The adjacent layers in crystals are mainly joined, most likely, by van der Waals interactions, since any significant projection of conjugated fragments of the structural units onto each other is absent.

**NMR spectroscopy.** The data of NMR spectroscopy ($^1$H, COSY, NOESY, ROESY) were used to establish specific features of the structures of ligand **1** and its complexes with potassium perchlorate and phthalic acid. Based on the value of spin-spin coupling constant for the protons at the double bond, we concluded that in solution ligand **1** exists as an *E*-isomer. The full assignments of signals of protons in the $^1$H NMR spectra of both the ligand and its

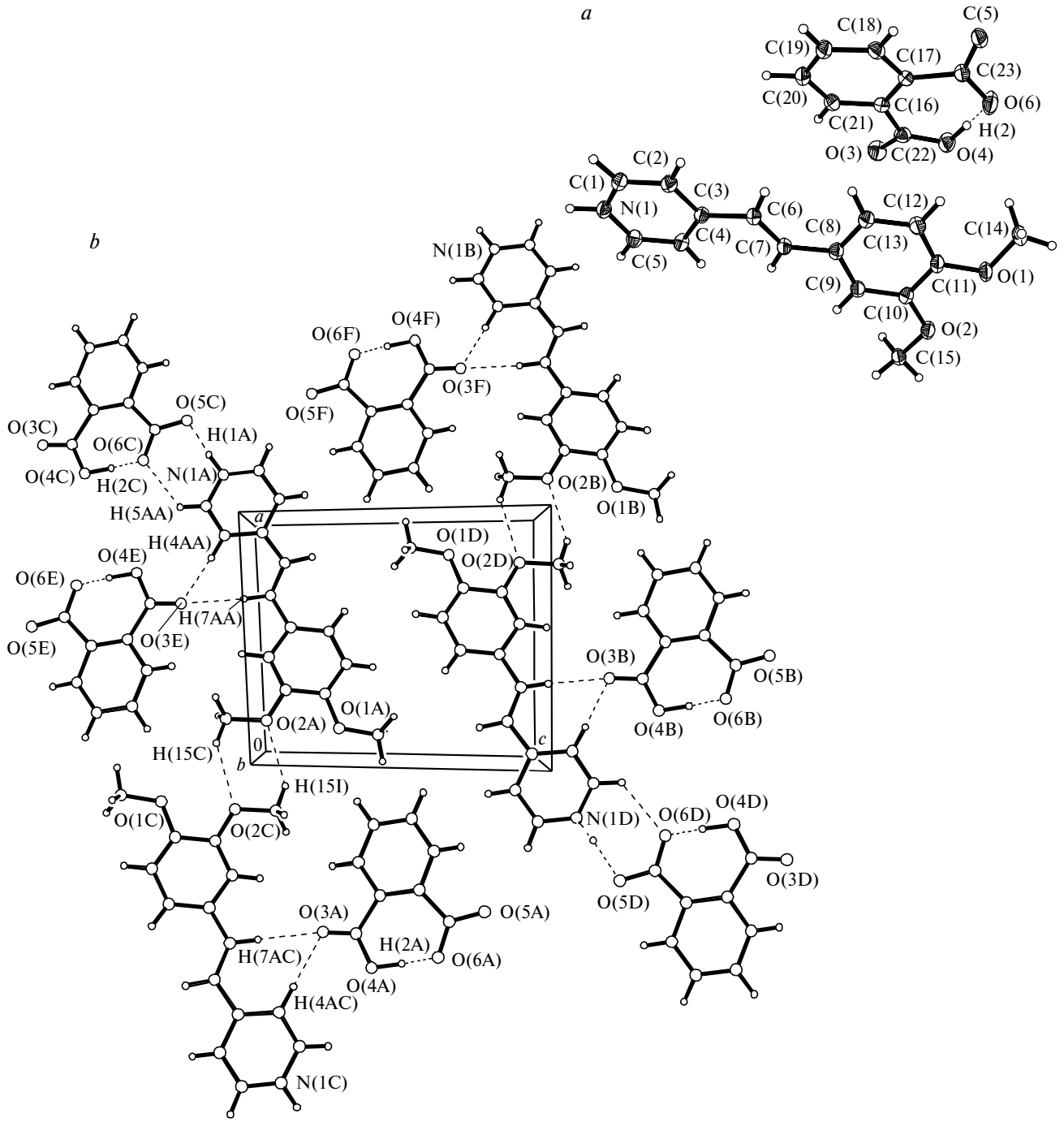



**Fig. 7.** Structure of complex $2 \cdot H_2A$ (*a*) according to the X-ray diffraction data. Non-hydrogen atoms are shown by thermal vibration ellipsoids with 50% probability. Crystal packing of $2 \cdot H_2A$ (*b*) (view of perpendicular crystalline axis *b*). Hydrogen bonds are shown by dashed lines.

complexes was made on the basis of 2D spectroscopy (COSY, NOESY (for **1**, $(\mathbf{1})_2 \cdot K^+$, and $\mathbf{1} \cdot H_2A$), ROESY (for $\mathbf{1} \cdot H_2A \cdot K^+$)). An analysis of the COSY spectrum of free ligand **1**, reflecting spin-spin coupling of the protons, showed cross-peaks of the protons of the aromatic part of the ligand H(2), H(6) and H(3), H(5); H(7) and H(8), H(13) and H(14), as well as the protons H(15) and H(16), H(22) and H(21) of the crown ether fragment. It was shown on the basis of correlations in the COSY spectra and the cross-peaks of H(10) and H(22), H(13) and H(15) in the NOESY spectra of ligand **1** (Fig. 8), reflecting the spatial interaction of the protons of the crown ether frag-

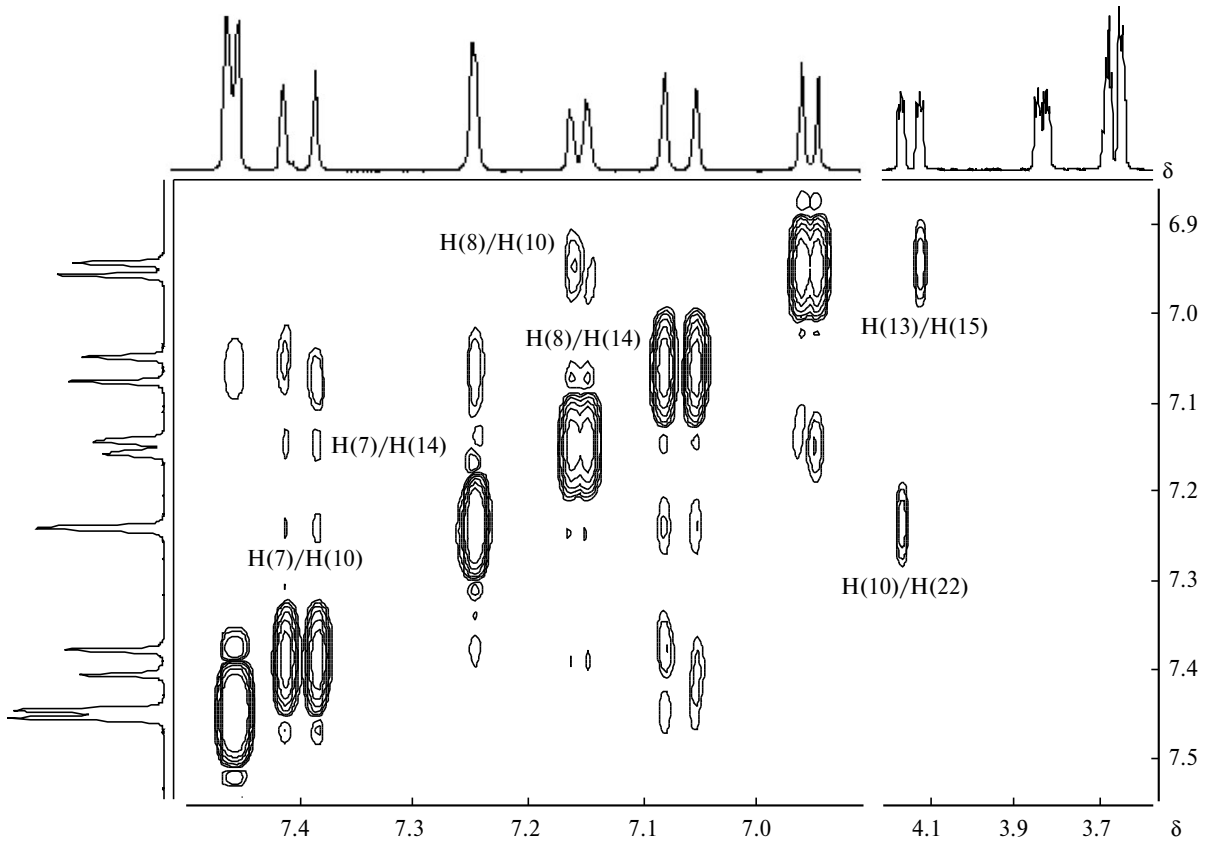



**Fig. 8.** $^1$H—$^1$H NOESY NMR spectrum ($CD_3CN$) of ligand **1**; $C_{\mathbf{1}} = 1 \cdot 10^{-2}$ mol L$^{-1}$.

ment of the molecule with the aromatic moiety that the signal from the proton H(22) of crown ether exists in a weaker field than the signal from the proton H(15). However, the interaction of the ligand with potassium perchlorate and phthalic acid with the formation of complexes $(\mathbf{1})_2 \cdot K^+$, $\mathbf{1} \cdot H_2A$, and $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$ results in the upfield shift of the proton H(22) (Fig. 10). The presence of cross-peaks of the protons H(8) and H(10), H(8) and H(14), H(7) and H(10), and H(7) and H(14) in the NOESY spectrum of ligand **1** suggests that a mixture of two conformers of the ligand exists in solution. This can be due to hindered rotation of fragments of the molecule about the C—C ordinary bond located between the double bond and benzo-15-crown-5. In the case of the complexes, analogous cross-peaks were observed in the NOESY (ROESY) spectra, suggesting that the both conformers are involved in complexation (Figs 9 and 10).

The addition of potassium perchlorate to a solution of ligand **1** changes the $^1$H NMR spectrum (Table 4). At the ratio $\mathbf{1} : K^+ = 2 : 1$ the most significant downfield shifts of protons ($\Delta\delta_H$) were observed for the groups of proton of crown ether H(17)—H(20). At the same time, signals of the protons H(10) and H(13), of the ethylene and heterocyclic fragments, and the proton H(22) of crown ether undergo upfield shifts. The characteristic changes in positions of proton signals made it possible to assign "sandwich" structure $(\mathbf{1})_2 \cdot K^+$ with the arrangement of chromophoric systems **1** in a stack above each other due to intermolecular π—π-interactions to the complex formed (see Scheme 1).

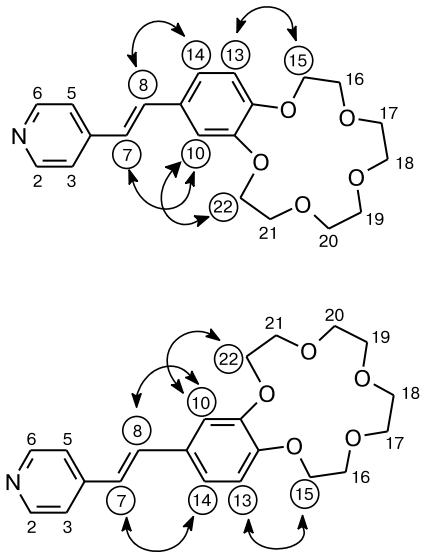



**Fig. 9.** Scheme of key correlations for protons of the conformers of ligand **1** in the $^1$H—$^1$H NOESY NMR spectra.

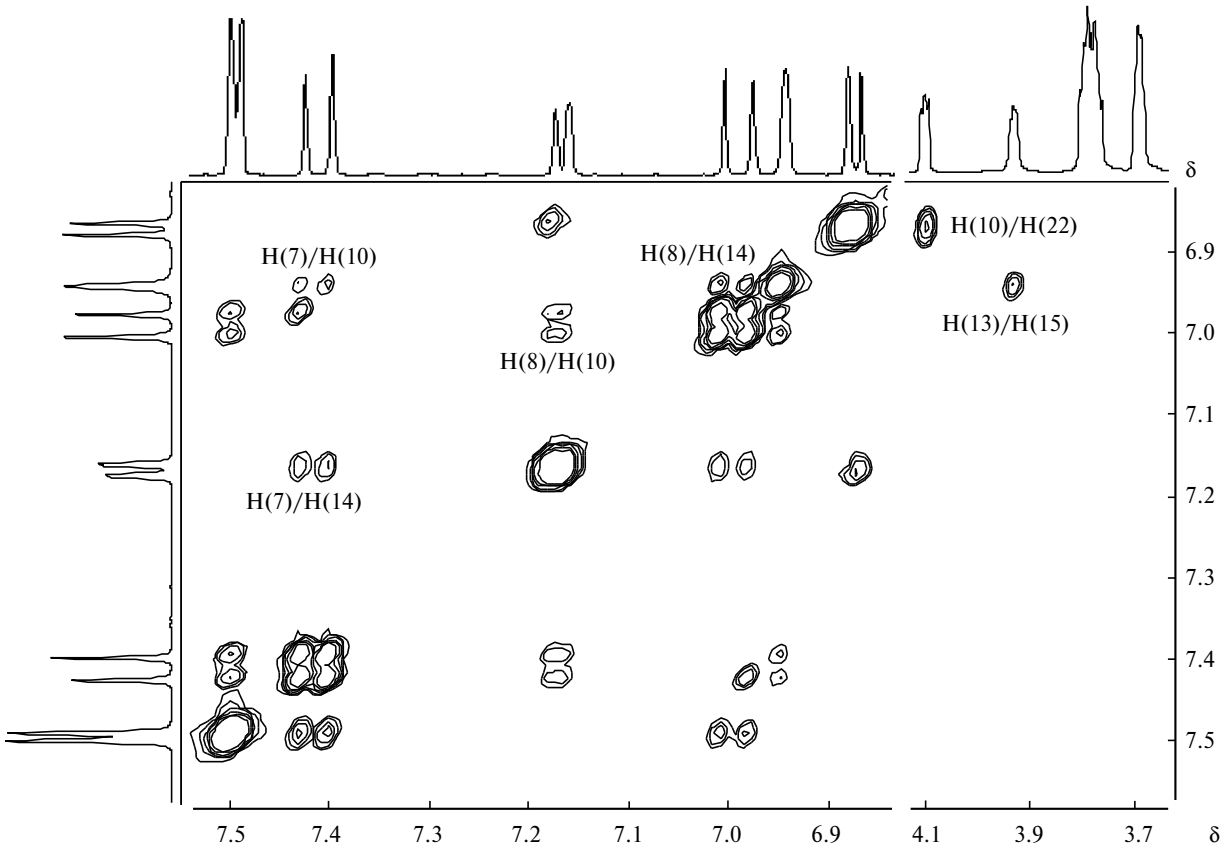



**Fig. 10.** $^1$H—$^1$H NOESY NMR spectrum ($CD_3CN$) of complex $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$, $C_{\mathbf{1}} = 1 \cdot 10^{-2}$ mol L$^{-1}$.

An excess of potassium perchlorate in a solution of ligand **1** changes the complexation process, which is reflected in the $^1$H NMR spectra. At the ratio **1** : $K^+$ = 1 : 5 the upfield shifts from signals of the protons H(2), H(3), H(10), H(13), and H(14) of the aromatic moiety and the protons H(7) and H(8) of the ethylene bond in a molecule of ligand **1** disappear. Signals from the protons H(15) and H(17)—H(20) of the crown ether fragment remain shifted

**Table 4.** Change in chemical shifts of protons ($\Delta\delta_H$) in the $^1$H NMR spectra of ligands **1** and **2** in the presence of phthalic acid ($H_2A$) and $KClO_4$ [a]

| Ratio of reactants | $\Delta\delta_H$ | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | H(2) | H(3) | H(7) | H(8) | H(10) | H(13) | H(14) | H(22) | H(15) | H(16), H(21) | H(17), H(20) | H(18), H(19) | H(3′) | H(4′) |
| **1** : $K^+$ = 2 : 1 | –0.03 | –0.05 | –0.04 | –0.05 | –0.14 | –0.07 | –0.02 | –0.10 | –0.07 | –0.03 | 0.05 | 0.02 | — | — |
| **1** : $K^+$ = 1 : 1 | –0.04 | –0.06 | –0.04 | –0.06 | –0.17 | –0.07 | –0.01 | –0.09 | –0.09 | –0.04 | 0.07 | 0.03 | — | — |
| **1** : $K^+$ = 1 : 2 | –0.03 | –0.05 | –0.03 | –0.04 | –0.12 | –0.04 | 0.01 | –0.06 | –0.04 | –0.04 | 0.07 | 0.03 | — | — |
| **1** : $K^+$ = 1 : 5 | –0.01 | –0.02 | –0.01 | 0.00 | –0.03 | 0.02 | 0.04 | 0.00 | 0.04 | –0.02 | 0.07 | 0.04 | — | — |
| **1** : $H_2A$ = 2 : 1 | 0.08 | 0.20 | 0.11 | 0.03 | –0.04 | 0.00 | 0.05 | –0.02 | 0.05 | 0.05 | 0.08 | 0.08 | 0.50 | 0.00 |
| **1** : $H_2A$ = 1 : 1 | 0.06 | 0.24 | 0.11 | –0.02 | –0.12 | –0.05 | 0.02 | –0.09 | 0.02 | 0.03 | 0.07 | 0.07 | 0.35 | –0.03 |
| **1** : $H_2A$ : $K^+$ = = 2 : 1 : 1 [b] | –0.11 | –0.16 | –0.06 | –0.02 | –0.13 | 0.02 | 0.04 | –0.11 | 0.00 | –0.04 | 0.08 | 0.01 | 0.03 | 0.05 |
| **2** : $H_2A$ = 2 : 1 | 0.08 | 0.25 | 0.17 | 0.09 | 0.04 | 0.03 | 0.06 | 0.01 | 0.02 | — | — | — | 0.45 | –0.03 |
| **2** : $H_2A$ : $K^+$ = = 2 : 1 : 1 | 0.01 | 0.02 | 0.03 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | — | — | — | 0.00 | 0.01 |

[a] Solvent $CD_3CN$, temperature 293 K, $C_{\mathbf{1}} = 1.0 \cdot 10^{-2}$ mol L$^{-1}$, $C_{\mathbf{2}} = 2.0 \cdot 10^{-3}$ mol L$^{-1}$; $\Delta\delta_H = \delta_{complex} - \delta_L$.
[b] $\Delta\delta_H = \delta_{\mathbf{1}:H_2A:K^+} - \delta_{\mathbf{1}:H_2A\ (2:1)}$.

**Table 5.** Changes in chemical shifts of carbon atoms ($\Delta\delta_C$) in the $^{13}C$ NMR spectrum of ligand **1** in the presence of phthalic acid ($H_2A$) and $KClO_4$ [a]

| Ratio of reactants | $\Delta\delta_C$ | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C(2) | C(3) | C(4) | C(7) | C(8) | C(9) | C(10) | C(11) | C(12) | C(13) | C(14) | C(15), C(22) | C(16), C(21) | C(17), C(20) | C(18), C(19) |
| **1** : $K^+$ = 2 : 1 | −0.08 | −0.01 | −0.20 | −0.29 | 0.38 | 0.40 | −0.49 | −1.4 | −1.29 | −0.45 | 0.25 | −1.48, −1.34 | −1.72 | −1.87 | −2.03 |
| **1** : $H_2A$ = 2 : 1 | −4.54 | 0.96 | 4.84 | 3.83 | −1.47 | −0.71 | −0.10 | 0.54 | −0.25 | −0.37 | 0.85 | −0.33, −0.19 | −0.10, 0.00 | −0.23 | −0.18 |
| **1** : $H_2A$ = 1 : 1 | −5.44 | 1.16 | 5.49 | 4.64 | −1.68 | −0.85 | −0.12 | 1.01 | −0.29 | −0.42 | 0.97 | −0.38, −0.24 | −0.13, −0.03 | −0.29 | −0.23 |
| **1** : $H_2A$ : $K^+$ = = 2 : 1 : 1 [b] | 2.10 | −0.43 | −2.00 | −1.94 | 0.91 | 0.68 | −0.19 | −1.73 | −0.96 | −0.16 | 0.06 | −1.00, −1.06 | −1.54 | −1.51 | −1.73 |

[a] Solvent $CD_3CN$, temperature 293 K, $C_{\mathbf{1}} = 1.0 \cdot 10^{-2}$ mol $L^{-1}$; $\Delta\delta_C = \delta_{complex} - \delta_L$.
[b] $\Delta\delta_C = \delta_{\mathbf{1}:H_2A:K^+} - \delta_{\mathbf{1}:H_2A\ (2:1)}$.

to weak fields, indicating coordination of the potassium cations to this fragment (see Table 4). The character of chemical shifts suggested that 1 : 1 complex $\mathbf{1} \cdot K^+$ exists in the solution.

The addition of phthalic acid to a solution of **1** in the ratio **1** : $H_2A$ = 2 : 1 most considerably changes the positions of signals from the protons of the heterocyclic part and the proton H(7) of the double bond in the $^1H$ NMR spectrum (see Table 4). This corresponds to the scheme of interaction of the acid with the ligand. The scheme was proposed on the basis of optical studies (see Scheme 1). Indeed, the formation of associate "ligand—phthalic acid" by a hydrogen bond exerts an effect, first of all, on the position of signals of the heterocyclic protons. For the protons of phthalic acid, the strong shift of the signal from the proton H(3′) also confirms that the acid interacts with the pyridine moiety of **1**.

Almost all signals of protons of ligand exhibit upfield shifts upon the addition of potassium perchlorate to a solution of the complex of ligand **1** with phthalic acid in MeCN (see Table 4). Only the signals of the protons H(13) and H(14), H(17)—H(20) of the crown ether fragment exhibit downfield shifts, which confirms the complexation of cation $K^+$ with the crown ether fragment. The upfield shifts of signals from the protons of ligand **1** are explained by the formation a "sandwich" complex, whose structure is presented in Scheme 1. In complex $(\mathbf{1})_2 \cdot K^+ \cdot H_2A$, two chromophoric molecules exert an anisotropic effect on each other, resulting in the upfield shift of signals of the protons. Thus, the NMR spectroscopic data agree completely with the results of optical studies of ligand **1**.

We also analyzed the changes that occur in the $^1H$ NMR spectra of hetarylphenylethene **2** containing two methoxy groups instead of the crown ether moiety (see Table 4) upon the addition of potassium salt and phthalic acid to the solution of this ligand. The addition of phthalic acid to a solution of hetarylphenylethene **2** in the ratio **2** : $H_2A$ = 2 : 1 results in changes analogous to those observed in the $^1H$ NMR spectrum for ligand **1** (see Table 4). The addition of potassium perchlorate exerts no effect on the position of signals of the protons of the ligand and phthalic acid. Since the ligand containing no crown ether fragment cannot coordinate to metal cations, no associates containing ligand **2**, $K^+$, and phthalic acid are formed.

The $^{13}C$ NMR spectrum of potassium complex $(\mathbf{1})_2 \cdot K^+$ shows the upfield shift of signals from the $^{13}C$ nuclei of all methylene groups of crown ether. The value $\Delta\delta_C$ = = 1.48—2.03 (Tables 5 and 6) is typical of complexation of crown ethers.[34] The signals of the $^{13}C$ nuclei of the benzene ring C(11) and C(12) exhibit the most significant upfield shifts (−1.4 and −1.29 ppm), while the signals of the $^{13}C$ nuclei of the pyridine residue and double bond are shifted to a less extent. Coordination of phthalic acid to the nitrogen atom of the pyridine cycle results in the inverse pattern compared to complexation involving crown ether: the signals of the $^{13}C$ nuclei of the pyridine fragment and the double bond are shifted, whereas the signals of the macrocycle are insignificantly shifted. The forma-

**Table 6.** Changes in chemical shifts of carbon atoms ($\Delta\delta_C$) in the $^{13}C$ NMR spectrum of phthalic acid ($H_2A$) in the supramolecular complexes[a]

| Ratio of reactants | $\Delta\delta_C$ | | | |
|---|---|---|---|---|
| | COOH | C(2′) | C(3′) | C(4′) |
| **1** : $H_2A$ = 2 : 1 | 1.66 | 2.22 | 0.68 | 1.90 |
| **1** : $H_2A$ = 1 : 1 | 1.35 | 2.44 | 0.12 | 1.97 |
| **1** : $H_2A$ : $K^+$ = 2 : 1 : 1 [b] | 0.26 | −0.12 | −0.39 | 0.06 |

[a] Solvent $CD_3CN$, temperature 293 K, $C_{\mathbf{1}} = 1.0 \cdot 10^{-2}$ mol $L^{-1}$; $\Delta\delta_C = \delta_{complex} - \delta_{H_2A}$.
[b] $\Delta\delta_C = \delta_{\mathbf{1}:H_2A:K^+} - \delta_{\mathbf{1}:H_2A\ (2:1)}$.

tion of a complicated complex involving both the crown ether moiety and the pyridine fragment is accompanied by the shift of the positions of all signals from carbon of the initial ligand in the $^{13}C$ NMR spectrum. It is most likely that the values of $\Delta\delta_C$ for the $sp^2$-hybridized carbon atoms are mainly determined by two factors. The former is related to a decrease in multiplicity of the $O—C_{Ar}$ bonds due to switching-over of lone electron pairs of two oxygen atoms from conjugation with the π-system of the benzene ring to coordination of the potassium cation. The second factor is the electron density redistribution on the whole chromophore with alternating of its decrease and increase on even and odd atoms, respectively, caused by complexation. Sensitivity of the $^{13}C$ nuclei to anisotropic effects is low compared to the $^1H$ nuclei and no screening of the $^{13}C$ nuclei is observed.

Thus, the studies by UV and NMR spectroscopy, ESI mass spectroscopy, and X-ray diffraction analysis demonstrated that hetarylphenylethene, phthalic acid, and potassium cations can be self-organized into a single supramolecular system involving two binding centers of the ligand: crown ether and the heterocyclic residue, and the presence of potassium cations exert a substantial effect on the stability and composition of the complexes formed. Two types of noncovalent interactions participate in the formation of an assembly: hydrogen bonds between the heterocyclic residue and carboxylic acid and coordination interactions between the potassium cation and oxygen atoms of the crown ether fragment. The proposed principle of organization can be extended to other types of metals if nitrogen or sulfur atoms are introduced into the macrocyclic ligand composition. The change in the heterocyclic fragment also changes the position of absorption bands and emission of the supramolecular complexes and the strength of coordination with carboxylic acids.

The considerable optical changes upon binding of dicarboxylic acids with hetarylphenylethenes indicate that these compounds can be used as optical sensors to carboxylic acids.

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