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Synthesis, Properties, and Interaction with Paraquat of New Fluorenonocrownophanes Containing a Hydroquinone Fragment

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Abstract—New crownophane family was synthesized containing fragments of 2,7-dioxyfluorenone and hydroquinone connected with residues of tri- and tetraethylene glycols. The formation of inclusion complexes of these ligands with paraquat was established by means of mass spectrometry (fast-atom bombardment), ^{1}H NMR and electronic spectroscopy. The crownophane with a larger ring formed the more stable complex.

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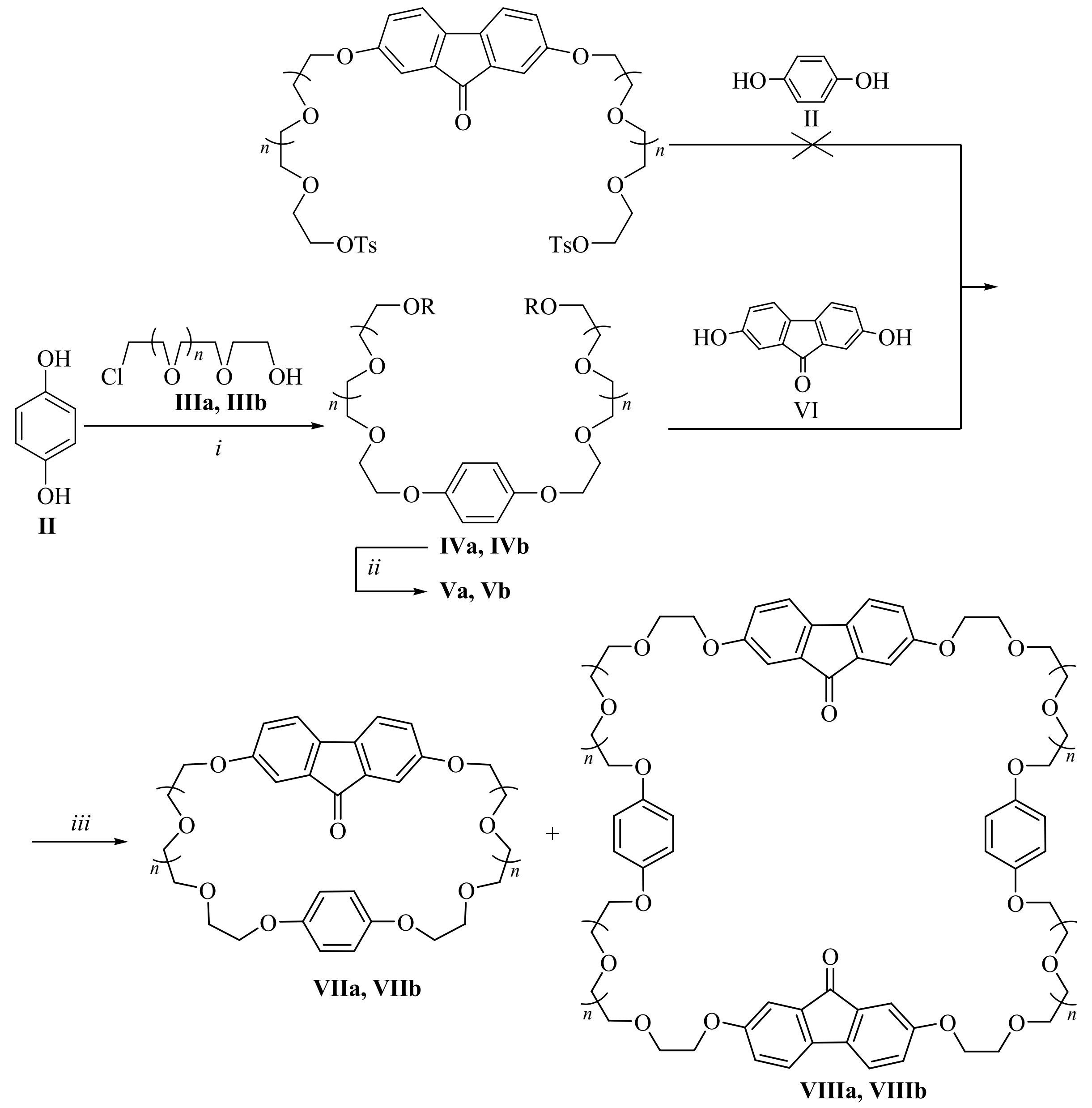
Crownophanes, cyclophanes [1] where aromatic fragments are linked by polyether chains, are among the main classes of macrocyclic receptors for ionic and neutral compounds [2]. They recently attracted a specific attention as initial objects for designing and synthesis of supramolecular systems: pseudorotaxanes, rotaxanes, and catenanes [3]. The efficiency of self-organization of these structures is governed by a series of noncovalent interactions of the electron-reach crownophane with the electron-deficient second component of the structure [4], including the hydrogen bond formation [5], solvatophobic effects [6], coordination with metals [7], and π–π interactions between the donor and acceptor aromatic fragments of the partners [8]. Inasmuch as the electrostatic component of the intermolecular interactions in the most cases dominates [9], the introduction of polar aromatic units into the framework of the crownophane should increase its electrostatic interaction with the electron-deficient substrates. In this respect as matrices for the synthesis of pseudorotaxanes, rotaxanes, and catenanes fluorenonocrownophanes seem promising for they contain a large polarized π electron system of the fluorenone alongside the other π-donor aromatic fragment [10].

In extension of our investigations on fluorenonocrownophanes [10–12] we report here on the synthesis, properties, and preliminary results of the study of the interaction with paraquat of the new fluorenonocrownophanes **VIIa**, **VIIb** and **VIIIa**, **VIIIb** containing fragments of 2,7-dihydroxyfluorenone and hydroquinone.

The condensation of ditosylate **Ia** with hydroquinone (**II**) similarly to the synthesis of bis(fluorenono)crownophanes we had described earlier [12] resulted in the formation of a large amount of tarry products where we failed to detect a tangible amount of the target cyclic compounds. Fluorenonocrownophanes **VIIa**, **VIIb** were obtained in a moderate yield by the reaction of tosylates **Va, Vb** with 2,7-dihydroxyfluorenone (**VI**) in DMF at large dilution in the presence of anhydrous potassium carbonate at 80–85°C. Alongside these compounds we succeeded in isolation from the reaction mixture of their cyclic dimers **VIIIa**, **VIIIb**, the products of [2+2]-condensation (Scheme 1).

The ^{1}H NMR spectra of fluorenonocrownophanes **VIIa**, **VIIb** and **VIIIa**, **VIIIb** contain a typical set of signals of oligoethylene glycol fragments in the region δ 3.65–4.26 ppm. Fluorenone protons give rise to characteristic signals (two doublets and a doublet of doublets), and hydroquinone protons appear as a singlet (Fig. 1a). Presumably due to the reciprocal shielding by the opposite aromatic fragments the signals of hydroquinone protons and of H^c proton of fluorenone in compounds **VIIa**, **VIIb** suffered a considerable upfield shift compared to the position of the corresponding protons in the spectra of model compounds, 2,7-dimethoxyfluorenone (**IX**) and 1,4-dimethoxybenzene (**X**) (Table 1, Scheme 2). These displacement values decrease with the growing ring size in the pairs of monomeric **VIIa**, **VIIb** and dimeric crownophanes **VIIIa**, **VIIIb**. The shifts of fluorenone protons H^a and H^b are of small value and of different sign.

Scheme 1.



$n = 1$ (**a**), 2 (**b**); R = H (**IV**), Ts (**V**); *i*: *t*-BuOK–*t*-BuOH or K_2CO_3–DMF; *ii*: TsCl, NEt_3–CH_2Cl_2 or Py–$CHCl_3$, 0–5°C; *iii*: K_2CO_3–DMF, 80°C.

Scheme 2.

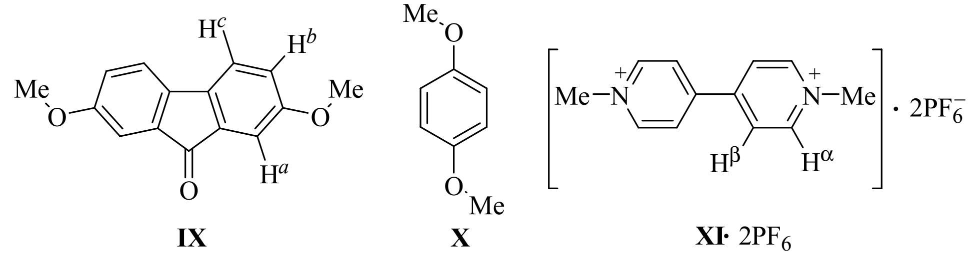


Table 1. Absolute (δ, ppm) and relative (Δδ, ppm) chemical shifts of aromatic protons of fluorenonocrownophanes **VIIa**, **VIIb**, **VIIIa**, **VIIIb**, and model compounds **IX** and **X** in $CDCl_3$

Compound no.	H^a		H^b		H^c		C_6H_4	
	δ	Δδ[a]	δ	Δδ[a]	δ	Δδ[a]	δ	Δδ[a]
VIIa	7.17	0.01	7.03	0.09	7.18	–0.10	6.45	–0.39
VIIb	7.14	–0.02	6.94	0	7.22	–0.06	6.77	–0.07
VIIIa	7.13	–0.03	6.97	0.03	7.18	–0.10	6.59	–0.25
VIIIb	7.13	–0.03	6.93	–0.01	7.23	–0.05	6.78	–0.06
IX	7.16	–	6.94	–	7.28	–	–	–
X	–	–	–	–	–	–	6.84	–

[a] Δδ is equal to the difference between the chemical shifts of the corresponding protons in compounds **IX, X** and compounds **VIIa, VIIb, VIIIa, VIIIb**.

These spectral features apparently indicate that in the solutions exist mainly the conformations of crownophanes **VIIa**, **VIIb** and **VIIIa**, **VIIIb** where the fragments of fluorenone and hydroquinone interact by the type rib–plane [13]; as a result the proton H^c of fluorenone occurs in the field of the anisotropic influence of the aromatic fragment of hydroquinone.

Compound **XI**·$2PF_6$ and its derivatives (*N,N'*-dialkyl-4,4'-bipyridinium salts) are among the most often tested electron-acceptor “guests” forming stable inclusion complexes with cyclophanes and crownophanes. In particular, a large number of pseudorotaxanes are known, complexes of paraquat-ions with benzocrown ethers, cryptands, cyclophanes and other macrocyclic molecules [14]. Fluorenonocrownophanes **VIIa**, **VIIb** containing two π-electron-donor aromatic fragments apparently also should form inclusion complexes with dication $[\mathbf{XI}]^{2+}$. These complexes are commonly registered by mass spectrometry [15]. We investigated the possibility of the formation of inclusion complexes with paraquat

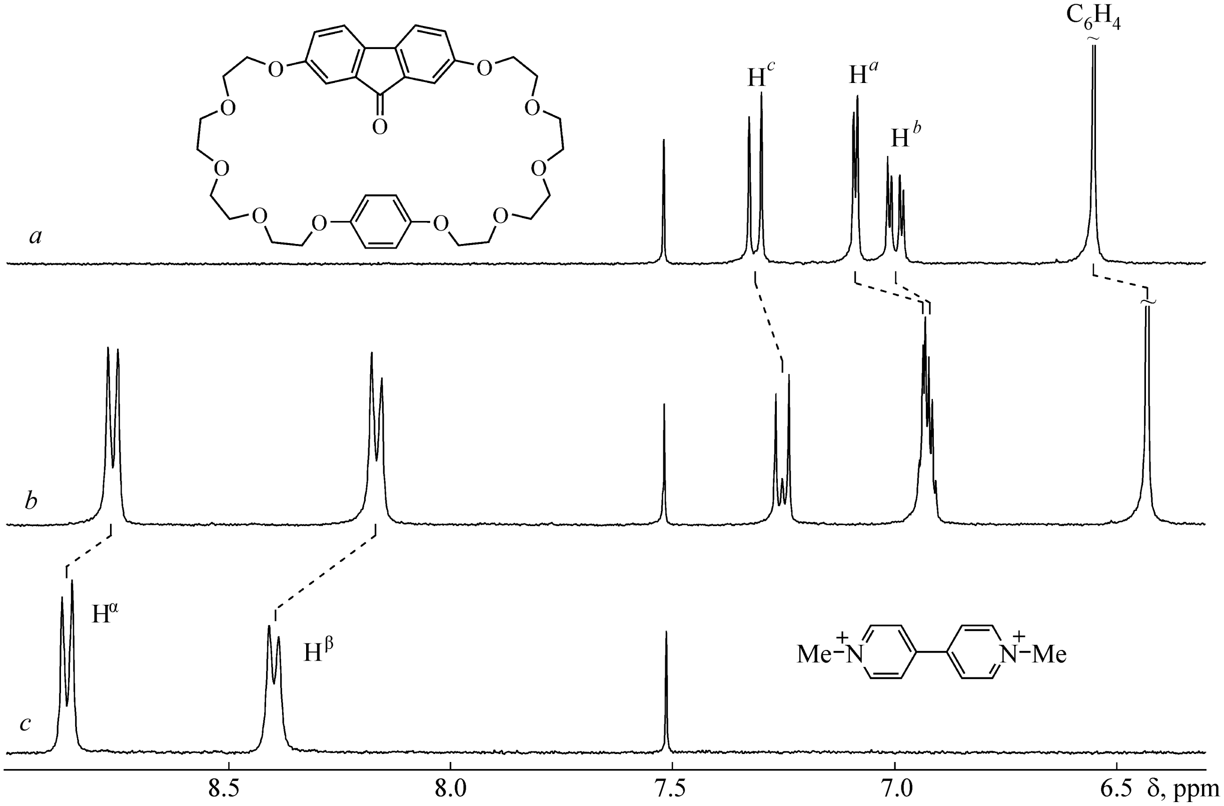


Fig. 1. Fragments of ^1H NMR spectra of crownophane **VIIb** (*a*), its equimolar mixture with paraquat (**XI**·$2PF_6$) (*b*), and paraquat (**XI**·$2PF_6$) in a mixture CD_3CN–$CDCl_3$, 4 : 3 (*c*).

(**XI**)·2PF$_6$ by fluorenonocrownophanes **VIIa**, **VIIb** and performed the qualitative estimation of their relative stability under the conditions of competitive complexing by means of fast-atom bombardment mass spectrometry (FAB). The mass spectrum of a solution of equivalent amounts of crownophanes **VIIa**, **VIIb** and 4 equiv of paraquat (**XI**)·2PF$_6$ in 3-nitrobenzyl alcohol contained molecular ion peaks of compounds **VIIa**, *m/z* 550, **VIIb**, *m/z* 638, paraquat (**XI**) $[M - PF_6]^+$, *m/z* 331, and peaks corresponding to the loss of a hexafluorophosphate anion by the complexes of these crownophanes with paraquat (**XI**)·2PF$_6$, (1:1) $[M - PF_6]^+$ (*m/z* 881 and 969 respectively). This spectral pattern is characteristic of the most rotaxanes and pseudorotaxanes [16] and confirmes the formation of sufficiently stable complexes [(**VIIa**) · (**XI**)]·2PF$_6$ and [(**VIIb**)·(**XI**)]·2PF$_6$ presumably with the pseudorotaxane structure. However the intensity of the peak of the complex ion [(**VIIb**)·(**XI**)]·PF$_6^+$ is approximately 7 times higher than that of the peak [(**VIIa**)·(**XI**)]·PF$_6^+$. Evidently this indicates the higher stability of the complex [(**VIIb**)·(**XI**)]·2PF$_6$ compared to complex [(**VIIa**)·(**XI**)]·2PF$_6$.

On addition of equimolar amount of paraquat (**XI**)·2PF$_6$ to solutions of crownophanes **VIIa**, **VIIb** in acetonitrile the color changed from orange to red. Therewith in the visible region of the electron absorption spectra (EAS) appeared a wide band, λ_{max} ~495 and 475 nm respectively that overlapped with the absorption band of fluorenonocrownophanes. The appearance of this band is due to the formation of complexes stabilized by the donor-acceptor interactions with a charge transfer between the π-donor aromatic subunits of crownophanes with π-acceptor bipyridinium fragments of paraquat (**XI**)·2PF$_6$ located in the cavity of the macrocycle [16, 17]. The intensity of this band grew with the growing molar ratio paraquat–crownophane. The relative change in its intensity is more significant in the spectrum of crownophane **VIIb** apparently because of the greater stability of its complex with paraquat (Fig. 2).

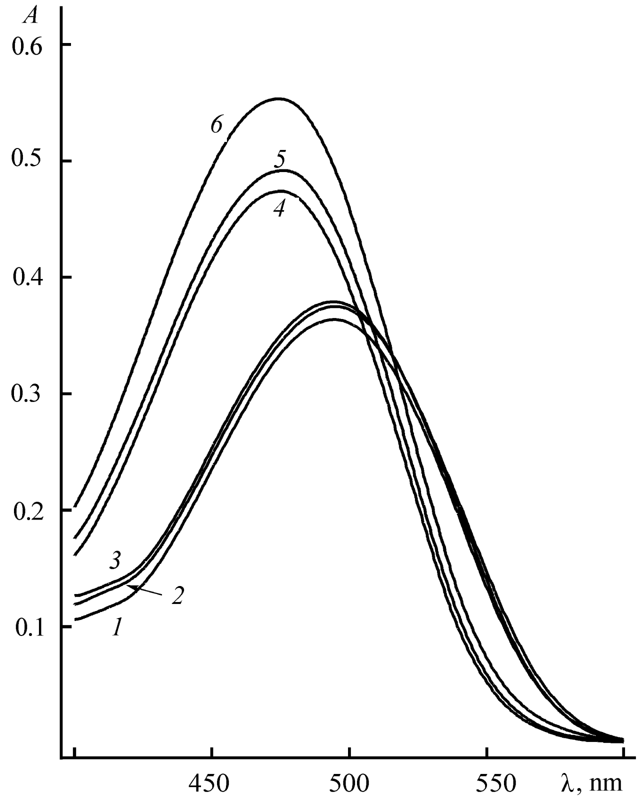


Fig. 2. Electron absorption spectra of crownophanes **VIIa** (*1*), **VIIb** (*4*), and their mixtures with paraquat (**XI**)·2PF$_6$ in ratios 1:1 (*2*), and (*5*), 1:5 (*3*) and (*6*) respectively in acetonitrile.

In the ^{1}H NMR spectra of equimolar mixtures of crownophanes **VIIa**, **VIIb** with paraquat (**XI**)·2PF$_6$ an upfield shift occurred of all the protons of aromatic fragments of crownophanes and paraquat compared with their position in the spectra of individual compounds (Table 1, Fig. 1). This is a characteristic spectral indication of the formation of inclusion complexes since only in this case might occur the mutual shielding of the two aromatic fragments of the crownophane and the pyridinium rings of paraquat [4]. Therewith it is possible to consider in the first approximation that the displacement value of the signals of paraquat protons H$^{\alpha}$ and H$^{\beta}$ for complexes of the like structure is proportional to their stability. Consequently, crownophane **VIIb** formed with paraquat a more stable complex than compound **VIIa** (Table 2). This conclusion is well consisten with the results of mass spectrometry (FAB) and EAS.

Evidently the difference in the spectral behavior and in the stability of the complexes of cyclophanes **VIIa,**

Table . Upfield shift (–Δδ) of the signals of aromatic protons of crownophanes **VIIa, VIIb** and paraquat (**XI**)·2PF$_6$ in the ^{1}H NMR spectra of their equimolar mixtures in (CD$_3$CN–CDCl$_3$, 4 : 3)

Compound no.	–Δδ, ppm					
	H^a	H^b	H^c	C$_6$H$_4$	H$^{\alpha}$	H$^{\beta}$
VIIa	0.05	0.02	0.02	0.02	0.02	0.10
VIIb	~0.15^a	~0.07^a	0.06	0.12	0.10	0.23

[a] Signals of protons H^a and H^b overlapped.

VIIb with paraquat (**XI**)·$2PF_6$ are governed by their structure, However we failed to obtain single crystals of these complexes suitable for XRD analysis. Therefore we performed the search for the optimum structures of this complexes by the method of statistical mechanics Monte-Carlo (force field MMFF94, program package Spartan'06 [18]) with the subsequent refining of the geometry of the revealed energetically most feasible conformations in the framework of the semiempirical procedure PM3.

The calculated structures of complexes of crownophanes **VIIa, VIIb** with paraquat dication $[\mathbf{XI}]^{2+}$ have significant differences. Complex $[(\mathbf{VIIa})\cdot(\mathbf{XI})]^{2+}$ exists in a *T*-like conformation where only one pyridinium ring of the paraquat dication is located in the macrocycle cavity. In contrast, in complex $[(\mathbf{VIIb})\cdot(\mathbf{XI})]^{2+}$ the paraquat-dication pierced the crownophanecavity forming a typical pseudorotaxane (Fig. 3). In both complexes the H^β protons of paraquat occur in the place of the maximum anisotropic influence of the aromatic fragments of crownophanes that is seen in the larger upfield shift of their signals in the ^1H NMR spectra of complexes compared with the signals of H^α protons (Table 2). In complex $[(\mathbf{VIIa})\cdot(\mathbf{XI})]^{2+}$ the fragments of hydroquinone and fluorenone in cyclophane **VIIa** and one pyridinium ring of the paraquat-dication are located nearly parallel at the distance between their centroids ~3.9 Å. This makes it possible for their involvement into a π–π stacking-interaction by the type plane–plane [13]. In complex $[(\mathbf{VIIb})\cdot(\mathbf{XI})]^{2+}$ the aromatic fragments of crownophane **VIIb** interact with two pyridinium rings of the paraquat-dication by the type rib–plane that is more favorable energetically [13, 19]. In both complexes $[(\mathbf{VIIa})\cdot(\mathbf{XI})]^{2+}$ and $[(\mathbf{VIIb})\cdot(\mathbf{XI})]^{2+}$ exist the structure-stabilizing interactions C–H···O [20] between the atoms H^α and H^β of paraquat and oxygen atoms of the polyether chains of the cyclophanes and the carbonyl group of fluorenone. In general the stabilization energy of pseudo-rotaxane $[(\mathbf{VIIb})\cdot(\mathbf{XI})]^{2+}$ is larger than that of the *T*-like complex $[(\mathbf{VIIa})\cdot(\mathbf{XI})]^{2+}$ ($-\Delta E$ 168 and 142 kJ mol^{-1} respectively) in good agreement with the experimental data.

Note in conclusion that we obtained for the first time fluorenonocrownophanes including a fragment of 2,7-dihydroxyfluorenone and hydroquinone. It was shown by spectral methods and computer molecular simulation that they form inclusion complexes by reaction with paraquat hexafluorophosphate. This result indicates that they are promising for the synthesis on their basis of rotaxanes and catenanes.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequencies 300 and 75.5 MHz respectively from solutions in $CDCl_3$, ^1H NMR spectra of complexes, from solutions in a mixture $CDCl_3$–CD_3CN, 3:4 v/v. Mass spectra of electron impact ionization (70 eV) were taken on an instrument

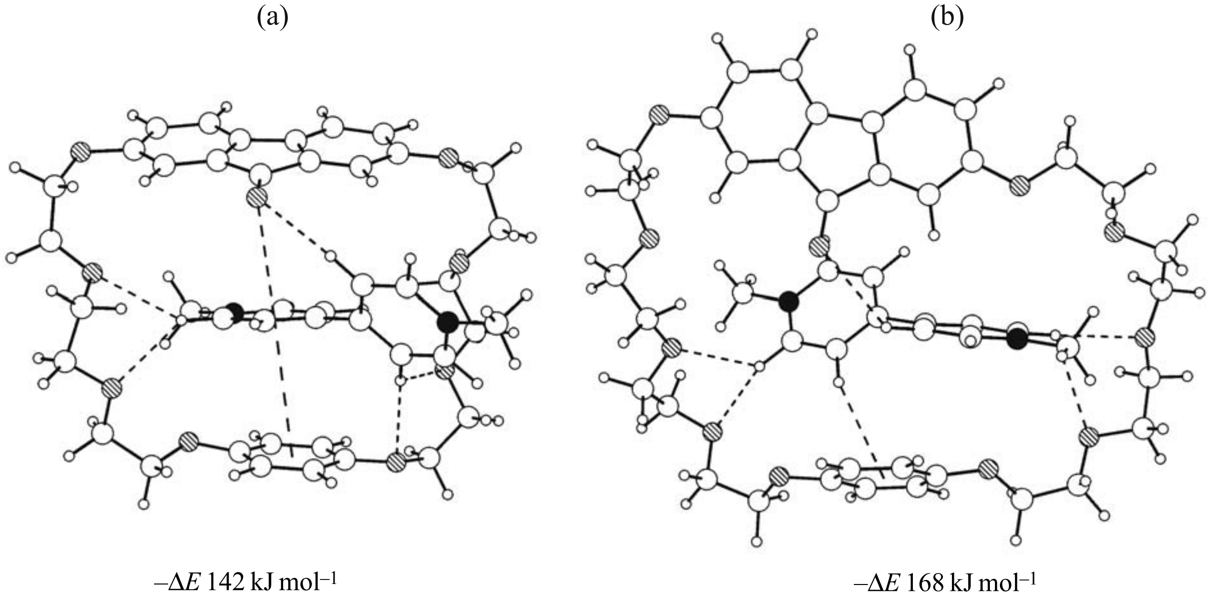


Fig. 3. Calculated structures and stabilization energy (ΔE) of complexes of crownophanes **VIIa** (a) and **VIIb** (b) with paraquat-dication $[\mathbf{XI}]^{2+}$. ΔE value was calculated as the difference between the energy of the complex and the sum of free energies of the host and the guest ($\Delta E = E_{\text{complex}} - E_{\text{host}} - E_{\text{guest}}$).

MKh-1321 with direct admission of the sample into the ion source, mass spectra FAB were obtained on a mass spectrometer VGEQ (Xe, 8 kV) in a 3-nitrobenzyl alcohol matrix. IR spectra were recorded on a spectrophotometer Shimadzu-8400S from KBr pellets, UV spectra, on a Specord instrument. The preparative column chromatography was performed on silica gel Kieselgel 60 (0.063–0.100 mm, Merck). The purity of all compounds synthesized was checked by TLC (Sorbfil UV-254) or GLC (3% OV-225, carrier Inerton-super, carrier gas helium). The melting points were measured in open capillaries and were reported without correction. Hydroquinone (**II**), chlorohydrin **IIIa**, and 1,4-dimethoxybenzene (**X**) were commercial products, tosylates **Ia** and **Ib** [12], chlorohydrin **IIIb** [21], compounds **IVa** [16], **Va** [22], **IVb**, and **Vb** [21], 2,7-dihydroxyfluoren-9-one (**VI**) [23], 2,7-dimethoxyfluoren-9-one (**IX**) [24], and paraquat hexafluorophosphate (**XI**)·$2PF_6$ [25] were prepared by described procedures.

Crownophanes VIIa, **VIIb** and **VIIIa**, **VIIIb.** General procedure. To a dispersion of 8.28 g (0.06 mol) of dry potassium carbonate in 600 ml of anhydrous DMF was added dropwise at stirring within 10 h a solution of 2.12 g (0.01 mol) of compound **VI** and 0.01 mol of ditosylate **Va** or **Vb** in 400 ml of anhydrous DMF maintaining the temperature of the reaction mixture at 80°C. On completing the addition the mixture was stirred at the same temperature for 40 h. On cooling the reaction mixture was filtered, and the solvent was distilled off in a vacuum. The residue was boiled with 500 ml of toluene. The toluene solution was cooled to room temperature and filtered. All solid residues were treated with toluene repeatedly till the reaction product was completely isolated. Further treatment is described below.

2,5,8,11,23,26,29,32-Octaoxapentacyclo-[31.2.2.1^{12,16}.1^{18,22}.0^{15,19}]nonatriaconta-1(35), 12(39), 13,15,18(38),19,21,33,36-nonaen-17-one (VIIa) and **2,5,8,11,23,26,29,32,37,40,43,46,58,61,64,67-hexadecaoxanonacyclo-[66.2.2.2^{33,36}.1^{12,16}.1^{18,22}.1^{47,51}.1^{53,57}.0^{15,19}.0^{50,54}]octaheptaconta-1(70),12(78), 13,15, 18(77),19,21,33,35,47(74),48,50,53(73),54, 56,68,71, 75octadecaene-17,52-dione (VIIIa).** The combined toluene extracts were evaporated in a vacuum, the residue was dried and subjected to column chromatography on silica gel eluting with mixture chloroform–methanol, 100:1. Compound **VIIa** was recrystallized from acetonitrile. Yield 2.19 g (40%). Orange-red crystals, mp 156.5–157°C. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 272 (4.82), 472.5 (2.43). IR spectrum, ν, cm^{-1}: 1720 (C=O). ^1H NMR spectrum, δ, ppm: 3.72 s (16H, CH_2O), 3.88 m (4H, CH_2O), 4.23 m (4H, CH_2O), 6.45 s (4H, C_6H_4), 7.03 d.d (2H, H^b, ^3J 8.09, ^4J 2.49 Hz), 7.17 m (4H, H^a, H^c). ^{13}C NMR spectrum, δ, ppm: 67.6, 68.1, 69.8, 69.9, 70.9, 71.2, 110.8, 115.0, 120.5, 121.3, 135.8, 137.5, 152.7, 159.4, 193.3. Mass spectrum (Electron impact), *m/z* (I_{rel}, %): 550 [*M*]$^+$ (100), 275 (4), 239 (12), 212 (14), 109 (8), 45 (59). Found, %: C 67.63; H 5.98. $C_{31}H_{34}O_9$. Calculated, %: C 67.62; H 6.22.

Compound VIIIa. Yield 0.126 g (2%). Orange-red crystals, mp 180°C. IR spectrum, ν, cm^{-1}: 1720 (C=O). ^1H NMR spectrum, δ, ppm: 3.73 s (16H, CH_2O), 4.02 m (8H, CH_2O), 4.14 m (8H, CH_2O), 6.77 s (8H, C_6H_4), 6.94 d.d (4H, H^b, ^3J 8.09, ^4J 2.49 Hz), 7.14 d (4H, H^a, *J* 2.49 Hz), 7.22 d (4H, H^c, *J* 8.09 Hz). ^{13}C NMR spectrum, δ, ppm: 68.0, 68.1, 69.7, 69.9, 70.9, 71.0, 110.5, 115.6, 120.5, 121.1, 135.9, 137.6, 153.1, 159.3, 193.5. Mass spectrum (FAB), *m/z* (I_{rel}, %): 1101 [*M* + H]$^+$ (100). Found, %: C 67.82; H 6.39. $C_{62}H_{68}O_{18}$. Calculated, %: C 67.62; H 6.22.

2,5,8,11,14,26,29,32,35,38-Decaoxapentacyclo-[37.2.2.1^{15,19}.1^{21,25}.0^{18,22}]pentatetraconta-1(41), 15(45),16,18,21(44),22,24,39,42-nonaen-20-one (VIIb) and **2,5,8,11,14,26,29,32,35,38,43,46,49, 52,55,67,70,73,76,79-icosaoxanonacyclo-[78.2.2.2^{39,42}.1^{15,19}.1^{21,25}.1^{56,60}.1^{62,66}.0^{18,22}.0^{59,63}]nonaconta-1(82),15(90),16,18,21(89),22,24,39,41,56(86), 57,59,62(85),63,65,80,83,87-octadecaene-20,61-dione (VIIIb).** The toluene extracts were washed in succession with 5% water solution of NaOH, water, 5% water solution of HCl, water, saturated NaCl solution, and dried with anhydrous $MgSO_4$. The products were purified and separated by column chromatography on silica gel eluting with mixture chloroform–methanol, 100:1.

Compound **VIIb** was recrystallized from 2-propanol. Yield 2.87 g (45%). Orange crystals, mp 88°C. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 272 (4.91), 472 (2.49). IR spectrum, ν, cm^{-1}: 1712 (C=O). ^1H NMR spectrum, δ, ppm: 3.72 m (20H, CH_2O), 3.85 m (8H, CH_2O), 4.15 m (4H, CH_2O), 6.59 s (4H, C_6H_4), 6.97 d.d (2H, H^b, ^3J 8.09, ^4J 2.49 Hz), 7.13 d (2H, H^a, *J* 2.18 Hz), 7.18 d (2H, H^c, *J* 8.10 Hz). ^{13}C NMR spectrum, δ, ppm: 67.7, 68.2, 69.5, 69.8, 70.5, 70.7, 70.9, 110.5, 115.1, 120.5, 121.1, 135.8, 137.5, 152.8, 159.3, 193.3. Mass spectrum (Electron impact), *m/z* (I_{rel}, %): 638 [*M*]$^+$ (100), 319 (4), 239 (12), 212 (8), 109 (4), 45 (55). Found, %: C 65.68; H 6.44. $C_{35}H_{42}O_{11}$. Calculated, %: C 65.82; H 6.63.

Compound **VIIIb** was recrystallized from 2-propanol. Yield 0.162 g (2.5%). Orange-red crystals, mp 112°C.

UV spectrum (CH_3CN), λ_{max}, nm (log ε): 272 (5.16), 474 (2.77). IR spectrum, ν, cm^{-1}: 1710 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.70 m (32H, CH_2O), 3.82 m (16H, CH_2O), 4.03 m (8H, CH_2O), 4.12 m (8H, CH_2O), 6.78 s (8H, C_6H_4), 6.93 d.d (4H, H^b, ^3J 8.40, ^4J 2.49 Hz), 7.13 d (4H, H^a, J 2.49 Hz), 7.23 d (4H, H^c, J 8.40 Hz). ^{13}C NMR spectrum, δ, ppm: 68.0, 68.1, 69.6, 69.8, 70.7, 70.8, 70.9, 110.4, 115.5, 120.5, 121.0, 135.9, 137.5, 153.0, 159.2, 193.4. Mass spectrum (FAB), m/z (I_{rel}, %): 1277 $[M + H]^+$ (100). Found, %: C 66.05; H 6.53. $C_{70}H_{84}O_{22}$. Calculated, %: C 65.82; H 6.63.

Molecular simulation. The search for the optimum structures of crownophanes **VIIa**, **VIIb** and of their complexes with paraquat-dication [**XI**]$^{2+}$ was performed in two stages. First we found energetically favorable conformations of crownophanes **VIIa**, **VIIb**, paraquat-dication [**XI**]$^{2+}$, and their complexes [(**VIIa**)·(**XI**)]$^{2+}$ and [(**VIIb**)·(**XI**)]$^{2+}$ by the method of statistical mechanics Monte-Carlo (force field MMFF94, program package Spartan’06 [18]). From the 100 structures of each compound obtained in the energy window 10 kcal mol^{-1} we selected 2–4 most feasible structures possessing overall population more than 90%. Each of these conformations was subjected to additional optimization in the framework of semiempirical method PM3, and the structuires of minimal energy were selected. The stabilization energy of pseudorotaxanes [(**VIIa**)·(**XI**)]$^{2+}$ and [(**VIIb**)·(**XI**)]$^{2+}$ (ΔE) [9] was calculated as the difference between the energy of their most favorable structures ($E_{complex}$) and the energies of the optimized conformations of the corresponding free crownophanes **VIIa**, **VIIb** (E_{host}) and paraquat-dication [**XI**]$^{2+}$ (E_{guest}) by the formula $\Delta E = E_{complex} - E_{host} - E_{guest}$

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