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2,6,8,12-Tetraoxa-4,10(1,4)-dibenzena-1,7(2,7)-difluorenacyclododecaphane-1^9,7^9-dione—A New Macrocyclic Receptor for Polar Organic Molecules

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Abstract—The results of computer-assisted molecular modeling showed that 2,6,8,12-tetraoxa-4,10(1,4)-dibenzena-1,7(2,7)-difluorenacyclododecaphane-1^9,7^9-dione is promising as a receptor for polar organic molecules. This compound was synthesized by the reaction of 1,4-bis(bromomethyl)benzene with 2,7-dihydroxyfluoren-9-one in DMF in the presence of anhydrous potassium carbonate under strong dilution. Crystalline complexes of the title compound with DMF and nitrobenzene were isolated and studied by X-ray diffraction. In both complexes the substrate is located in the ligand cavity.

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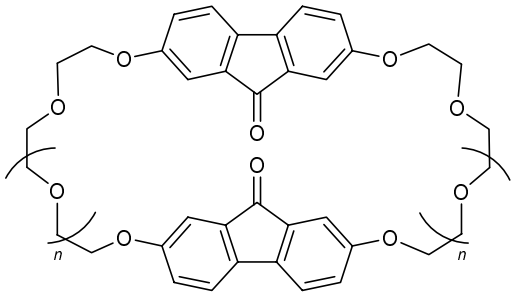
One of the main problems of supramolecular chemistry is design of simple and highly organized systems capable of selectively recognizing ions, molecules, and molecular fragments, i.e., systems acquiring chemical information at the molecular level [1]. Macrorings including aromatic fragments attract much attention due to their excellent ability to strongly and selectively bind cations and neutral substrates, which makes it possible to study fundamental intramolecular interaction processes in the nature and opens new prospects in the design of sensors, catalysts, molecular switches, and other molecular devices [2]. Typical examples of such synthetic receptors are cavitands and carcerands [3], calixarenes [4], and cyclophanes [5].

The structure, stability, and selectivity of formation of molecular complexes and supramolecular systems are determined by a large number of nonvalence interaction between the host and guest molecules. Among these, the most significant are hydrogen bonds, π–π stacking, ion–dipole, dipole–dipole, and hydrophobic interactions, and coordination with metal ion [6]. Variation of the strength and nature of such interactions via introduction of appropriate structural fragments and functional groups into macrocyclic receptor molecule ensures fairly effective control over its complexing properties. Another equally effective way of enhancing the stability of complexes involves synthetic preorganization of the open intramolecular receptor cavity in accordance with steric and electronic requirements of the substrate [3–5, 7].

In most cases, electrostatic constituent of intermolecular interactions plays the determining role. If the macrocyclic framework of a host molecule contains polar subsystems, the selectivity of complex formation and the energy of stabilization of the complex to be formed may be estimated in terms of the energy of electrostatic interactions [8]. This means that introduction of polar aromatic units into the macroring should enhance electrostatic interactions with polar substrates and hence increase the efficiency of complex formation. In this respect, fluorenone fragment possessing an extended and polarized π-electron system attracts interest as a structural unit of macrocyclic receptors for polar organic substrates.

We recently described the synthesis and properties of first representatives of bis(fluorenono)crownophanes **I** in which two fluorenone fragments are linked through flexible polyether chains [9, 10]. These com-

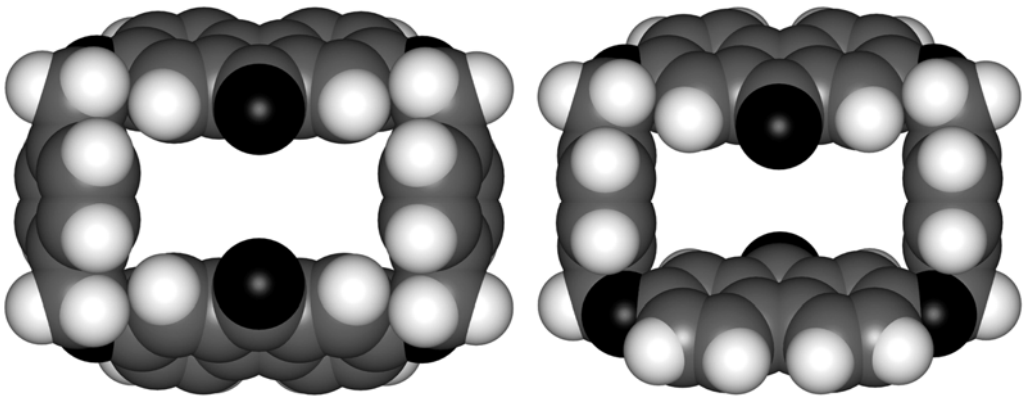
pounds in crystal have a closed intramolecular cavity due to π–π stacking of the aromatic fragments. On the other hand, compounds **I** in solution give rise to numerous conformations which allow 4,4'-dimethylbipyridyl (paraquat) to be incorporated into the cavity [10]. It is obvious that the formation of inclusion complexes requires some energy to be consumed for the conformational adjustment of the cavity to meet steric requirements of the substrate. Therefore, we believed it to be more promising to design fluorenonophanes including more rigid side fragments which would hold the intramolecular cavity open and structurally preorganized.



I

In the present communication we describe a reasonable approach to the design of macrocyclic receptors on the basis of the results of computer-assisted molecular modeling and the synthesis and properties of cyclophane **IV** and crystalline structure of its complexes with nitrobenzene and dimethylformamide. Preliminary molecular modeling showed that a cyclophane molecule consisting of two 2,7-dihydroxyfluorenone fragments linked through *p*-xylylene units should possess an open intramolecular cavity. Monte Carlo conformational search (MMFF force field, Spartan'02 software package [11]) revealed that the most favorable are *syn* and *anti* conformations of molecule **IV**, which differ by mutual orientations of the carbonyl groups (Fig. 1).

Both conformers have an open intramolecular cavity which is well fitted for interactions with a potential guest molecule. The fluorenone and side arene fragments in the *anti* conformer are coplanar to each other. The molecule adopts a chair-like conformation in which the fluorenone fragments are displaced relative to each other. The rectangular cavity has an average size of 7.5 Å between the fluorenone units and 10.8 Å between the lateral arene fragments. In the *syn* conformer, the fluorenone and benzene subunits are turned apart with respect to each other, and the dihedral angles between their planes are 42.4 and 30.9°, respectively. The intramolecular cavity has a cone shape with average dimensions of ~10.7×7.1 Å. The energy difference between the *syn* and *anti* conformers of cyclophane **IV** is not large, ΔE = 0.37 kcal/mol; this difference implies their relative population 35:65, at least in a vacuum. If interconversion of the conformers is possible, their ratio in solution may change considerably due to intermolecular interactions. The possibility for such interconversion is a very important problem. It may be presumed *a priori* that the *anti* conformer is more suitable for formation of inclusion complexes with guest molecules having two electron-deficient centers (e.g., with organic dications, derivatives of dicarboxylic acids, and structurally related species) and that the *syn* conformer should preferentially bind polar substrates with a single electron-deficient center (such as organic cations, nitro compounds, acids, and amides). However, taking into account structural rigidity of molecule **IV**, the possibility for *sin–anti* interconversion is not obvious. Therefore, we calculated the energy profile for the interconversion via rotation of



syn *anti*

Fig. 1. Calculated most favorable conformations of cyclophane **IV**.

one fluorenone fragment about its longitudinal axis by 360° as a possible way of conformational isomerization of cyclophane **IV** (Fig. 2).

It is seen that the *anti–syn* interconversion of molecule **IV** can take two paths; the corresponding potential energy barriers are 7.4 and 14.9 kcal/mol. These values approach the heat energy of the molecule at room temperature; therefore, under standard conditions the *anti* and *syn* conformers of **IV** should occur in thermodynamic equilibrium. Complex formation should displace the equilibrium toward that conformer which forms a stronger complex. In other words, cyclophane **IV** can act as an acceptor of polar molecules having both one and two electron-deficient centers.

Insofar as nonvalence intermolecular interactions between polar molecules originate mainly from electrostatic forces, useful information concerning complexing ability can be obtained by calculating the electrostatic potential (EP) surfaces of the receptor and probable substrates. The magnitude of electrostatic potential corresponds to the energy of interaction of a unit positive charge with wave functions of all nuclei and electrons in a molecule to be tested [12, 13]. In other words, EP reflects the balance between the Coulomb repulsion of a test charge and all nuclei of a molecule and Coulomb attraction of a test charge and all electrons of the same molecule. Molecular EP map demonstrates real charge distribution over the isoelectronic density surface and provides important chemical information on the electronic parameters of a molecule, which may be used to estimate its reactivity, regioselectivity of reactions, and reaction mechanism. In the recent years, molecular EP was extensively used to elucidate the nature of intermolecular interactions in the formation of supramolecular complexes, to predict the efficiency of interactions between substrates and receptors, to search for potential substrates for receptor molecules (most frequently macrocyclic), and finally to design receptors for definite substrates [14–17]. Klärner et al. [18, 19] recently found that EP on the inner surface of molecules having a concave–convex topology (molecular *tweezers* and *clips*) is unusually high for hydrocarbons and is considerably greater than on the outer surface. Analogous results were also obtained for some model nonconjugated cyclophanes having a *cone* or *bowl* conformation.

We revealed a similar nonequivalence of the EPs on the inner and outer sides of the aromatic fragments in molecule **IV** [20]. The EP values measured at the geometric centers of the fluorenone and benzene fragments in *anti*-**IV** were –17.6 and –16.6 kcal/mol, respectively, on the outer surfaces and –21.8 and –18.2 kcal/mol on the inner surfaces. The corresponding values for *syn*-**IV** were –17.5, –16.4 and –20.6, –22.1 kcal/mol; i.e., the molecular EP in the intramolecular cavity is considerably greater in both limiting conformations of cyclophane **IV**. This means that cyclophane **IV** with electron-deficient substrates should form preferentially host–guest complexes rather than outer complexes. The largest negative EP values were found at the carbonyl oxygen atoms in the fluorenone fragments, while the largest positive EP values were observed on the hydrogen atoms on the opposite side of the fluorenone plane. Such distribution of EP indicates that the *syn* conformer of **IV** is well suited for interactions with polar organic molecules having one electron-deficient center (they are characterized by analogous molecular EP distribution but with the opposite sign). By contrast, the formation of inclusion complexes by the *anti* conformer and electron-deficient molecules seems to be hardly probable, for the opposite fluorenone fragments in *anti*-**IV** are characterized

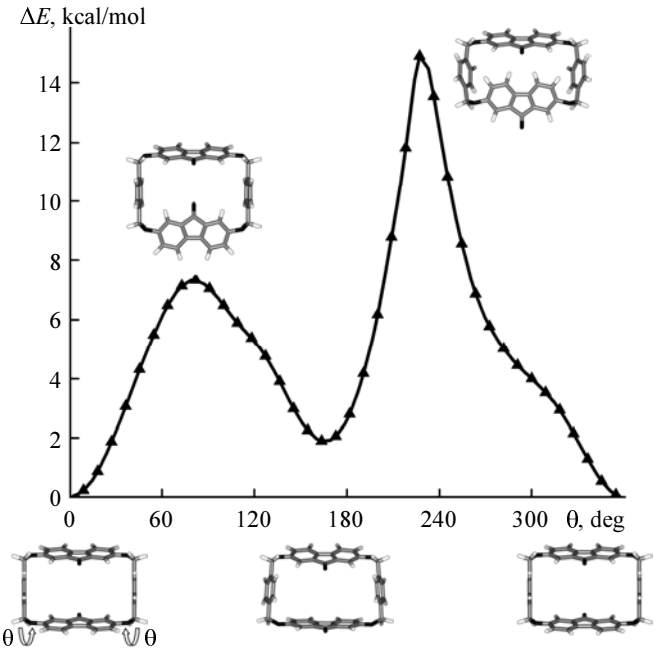
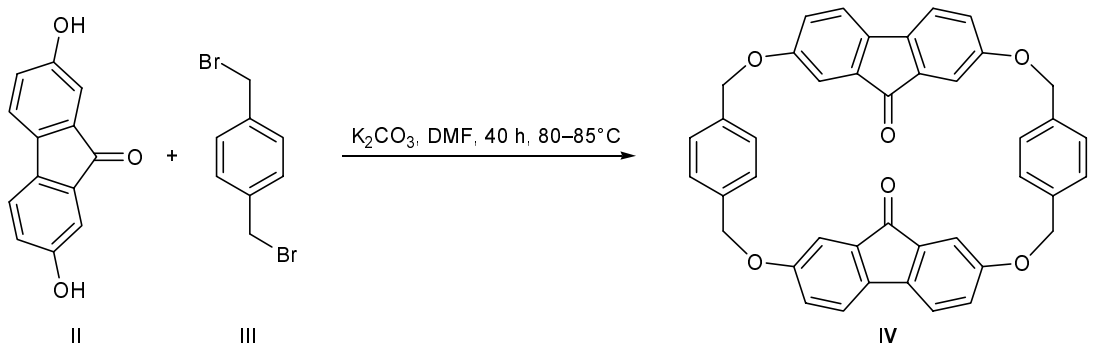


Fig. 2. Calculated energy profile for the *anti–syn* interconversion of cyclophane **IV** on successive and simultaneous variation of the dihedral angles θ from 0 to 360° through a step of 9°. The molecular structure was optimized at each step by the molecular-mechanics procedure (MMFF force field), followed by refinement of the energy of the optimal conformation in terms of the HF/3-21G$^{(*)}$ model. The relative energies (ΔE) were calculated as the difference between the energies of the current conformation and the lowest-energy conformation along the interconversion path.

Scheme 1.



II III IV

by antisymmetric EP gradient; as a result, electrostatic interactions of these fragments with a guest molecule should be opposite in sign.

Thus analysis of the results of molecular modeling almost unambiguously indicates that compound **IV** is promising as potential receptor for polar organic molecules. This prompted us to synthesize cyclophane **IV**. The synthesis was performed in one step, by reaction of 2,7-dihydroxyfluoren-9-one (**II**) with 1,4-bis(bromomethyl)benzene (**III**) (Scheme 1) under conditions of strong dilution. A dilute solution of the reactants in DMF was slowly added (over a period of 10 h) to a suspension of anhydrous potassium carbonate in DMF under stirring at 80–85°C, and the mixture was then stirred for 30 h at that temperature. Compound **IV** was isolated in about 8% yield by standard treatment of the reaction mixture, followed by chromatographic purification on silica gel. Raising the temperature to 95–105°C led to an appreciably reduced yield of **IV**. It is known that cesium cation favors formation of many macrocyclic systems ("cesium effect") [21]; however, the preparative yield of compound **IV** did not increase when potassium carbonate was replaced by cesium carbonate. Presumably, in this case the effect of the cation as matrix is weak or absent. The structure of cyclophane **IV** was confirmed by the ^{1}H and ^{13}C NMR and mass spectra. In the NMR spectra recorded at room temperature we observed only one set of proton and carbon signals from each molecular fragment. This spectral pattern suggests fast (on the NMR time scale) conformational equilibrium, in keeping with the results of calculations.

Cyclophane **IV** is poorly soluble in most organic solvents, which complicates study of complex formation in solution. By slow crystallization from dilute solutions of **IV** in DMF and nitrobenzene we succeeded in obtaining single crystals of its complexes **V** and **VI** with the corresponding solvents and examined them by the X-ray diffraction method.

The ratio cyclophane **IV**–DMF in complex **V** is 1:1. The complex has a C_s symmetry with a mirror plane passing through the carbonyl groups $C^1{=}O^1$ and $C^{22}{=}O^4$ (Fig. 3). The macroring in **IV** fully corresponds to the C_s point symmetry group, while the DMF molecule is located near the symmetry plane, so that it is disordered by two positions with equal probabilities (50%). The cyclophane–nitrobenzene ratio in complex **VI** is 1:2. Here, one nitrobenzene molecule resides inside the macroring cavity, and the other is located in the outer sphere. Crystals of the complex belong to space group $P2_1/a$.

Unlike previously studied bis(fluorenono)crownophanes **I** [10] in which the fluorenone fragments are oriented *anti* with respect to each other regardless of the length of the oxapolymethylene chain, the corresponding fragments of cyclophane **IV** in both complexes **V** and **VI** are arranged *syn*. The macroring in complex **V** has a trapezoid shape where the opposite faces (*p*-xylylene and fluorenone fragments) are separated by four bridging oxygen atoms. The torsion angles $C^6O^2C^8C^9$ and $C^{16}O^3C^{15}C^{12}$ are very similar, 67.8(4) and –67.1(4)°, respectively. Although an analogous orientation of the fluorenone fragments is typical of cyclophane **IV**, their structures somewhat differ in the degree of flattening of the carbon skeleton. In the C^1–C^7 fluorenone fragment, the dihedral angle between the planes of the six-membered (C^2–C^7) and five-membered rings (C^1–C^{3A}) is 0.8(3)°. The mean-square deviation of the carbon atoms from the plane of the fluorenone fragment does not exceed 0.009 Å, and the oxygen atoms linked to the fluorenone moiety almost do not deviate from that plane. The second fluorenone fragment (C^{16}–C^{22}) is more convex: the dihedral angle between the planes of the six-membered (C^{16}–C^{21}) and five-membered rings (C^{19}–C^{20A}) is 1.8(2)°, and the carbon atoms deviate from the mean-square fluorenone plane by no more than 0.020 Å. The fluorenone fragments are turned apart through an angle

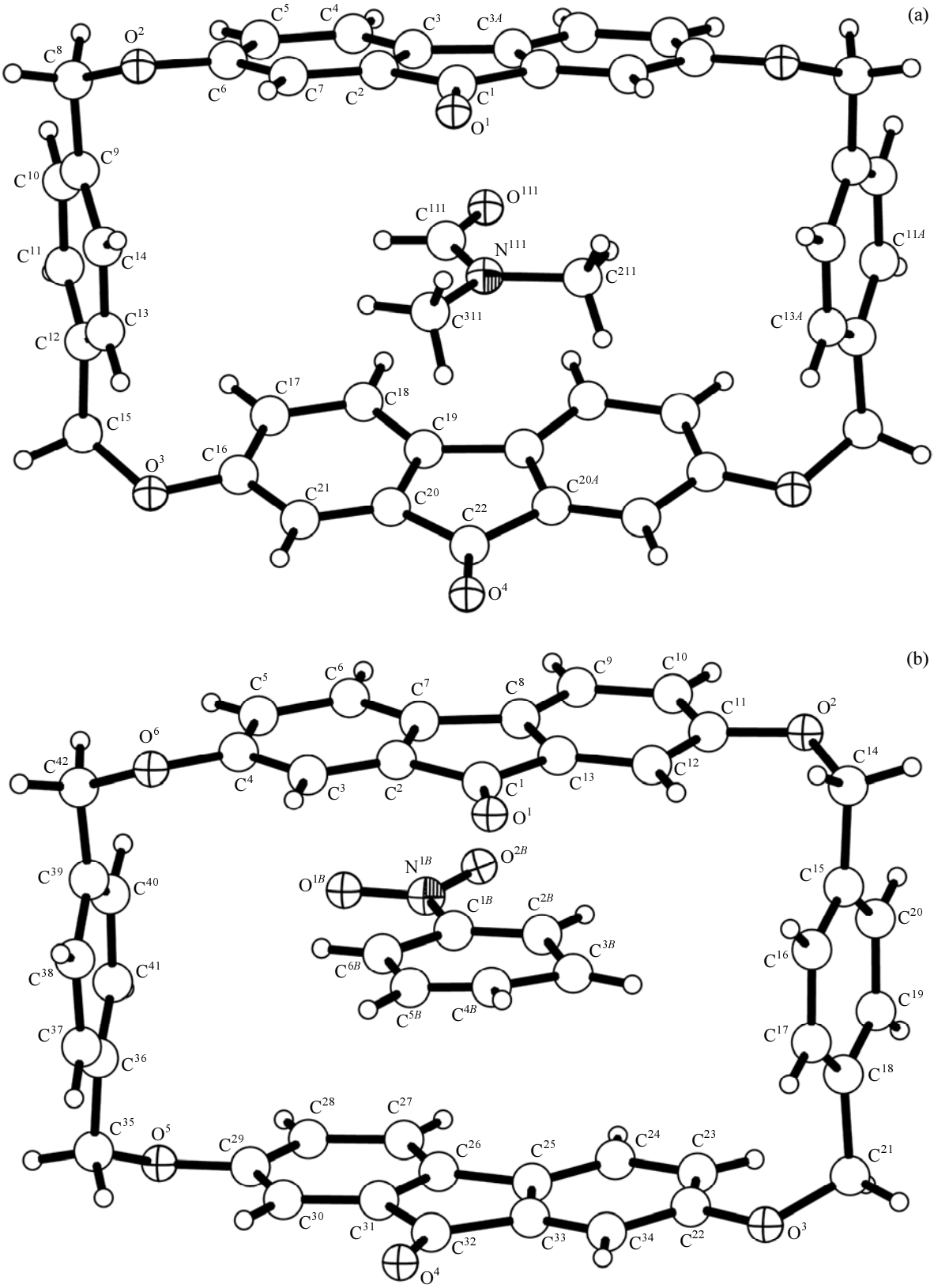


Fig. 3. Molecular structures of complexes (a) **V** and (b) **VI** formed by cyclophane **IV** with DMF and nitrobenzene, respectively, in crystal (the outer-sphere nitrobenzene molecule in complex **VI** is not shown).

of 27.7(1)° with respect to each other, while the benzene ring planes form a dihedral angle of 33.7(1)° in such a way that the size of the cavity along the fluorenone fragments increases from 10.719(5) ($C^{13}\cdots C^{13A}$) to 12.081(8) Å ($C^{11}\cdots C^{11A}$) and the size in the orthogonal direction increases from 6.041(5) ($C^{4}\cdots C^{18}$) to 7.937(5) Å $O^{1}\cdots O^{4}$). These dimensions are sufficient to accommodate a molecule of DMF inside the cavity; all non-hydrogen atoms in the DMF molecule lie in one plane within 0.002 Å. The DMF molecule is located almost in the middle of the cyclophane cavity, forming dihedral angles of 12.7(3)° and 15.0(2)° with the fluorenone fragments. The amide carbonyl group in the guest molecule is oriented *anti* with respect to the fluorenone carbonyl groups and it falls into the region characterized by the maximal positive EP. The CH and methyl hydrogen atoms having the maximal positive EP values are almost orthogonal to the lateral benzene fragment. This arrangement of DMF molecule in the cavity of cyclophane **IV** is optimal from the viewpoint of intermolecular electrostatic interactions which are likely to contribute most to the energy of stabilization of the complex.

The macroring of cyclophane **IV** in nitrobenzene complex **VI** has a more regular shape than in complex **V**, which approaches an octahedral prism (Fig. 3). As in structure **V**, all torsion angles at the bridging C–O bonds in the macroring of complex **VI** correspond to *gauche* conformations: they range from 68.5(9) to 74.5(8)°. Unlike complex **V** where the fluorenone fragments are almost planar, the fluorenone fragments in **VI** adopt a shape of slightly convex arches with the dihedral angles between the six- and five-membered rings equal to 3.0(2)/1.6(2)° (C^{1}–C^{13}) and 3.1(2)/0.7(2)° (C^{22}–C^{34}). The opposite benzene and fluorenone fragments are almost coplanar in pairs. The dihedral angle between the fluorenone fragments is 3.3(1)°, and between the benzene rings, 11.2(2)°; as a result, the distances between the corresponding carbon atoms in the opposite benzene rings are different: 10.79(1)/10.85(1) Å for $C^{16}\cdots C^{38}/C^{17}\cdots C^{37}$ and 11.25(1)/11.27(1) Å for $C^{20}\cdots C^{40}/C^{19}\cdots C^{41}$; the latter distances characterize the maximal length of the macroring. The average distance between the planes of the two fluorenone fragments in complex **VI** is 6.85(1) Å. The nitrobenzene molecule is located in the middle of the cyclophane cavity and is coplanar to the fluorenone fragments; the distances from the latter to the nitrobenzene plane are almost similar [3.35(2)–3.75(1) Å from C^{1}–C^{13} and 3.25(1)–3.51(1) Å from C^{22}–C^{34}]. These distances imply overlap of the aromatic systems of cyclophane and nitrobenzene, i.e., intermolecular π–π stacking which stabilizes the complex. The nitro group falls out from the cyclophane cavity and is oriented *anti* with respect to the *syn*-oriented fluorenone carbonyl groups.

It should be noted that the observed formation of molecular complexes via inclusion of DMF or nitrobenzene molecule into the cavity of cyclophane **IV** is unusual for cyclophanes and related macrorings. Analysis of the data available from the Cambridge Crystallographic Data Center [22] revealed only one example of distinct inclusion of DMF molecule into the macroring cavity [23] and two examples of formation of inclusion complexes with nitrobenzene [24, 25]. We can conclude that using 2,6,8,12-tetraoxa-4,10(1,4)-dibenzena-1,7(2,7)-difluorenacyclododecaphane-1^{9},7^{9}-dione as an example we have demonstrated a new reasonable approach to the design of macrocyclic receptors for definite substrates on the basis of preliminary computer-assisted extended molecular modeling.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument at 300 and 75.5 MHz, respectively. The mass spectrum (electron impact, 70 eV) was obtained on an MKh-1321 mass spectrometer with direct sample admission into the ion source (ion source temperature 200°C). The UV spectrum was measured on a Specord M-40 spectrophotometer. Silica gel L (100–250 μm, Chemapol) was used for preparative column chromatography. The purity of the products was checked by TLC on Silufol UV-254 plates.

2,6,8,12-Tetraoxa-4,10(1,4)-dibenzena-1,7(2,7)-difluorenacyclododecaphane-1^{9},7^{9}-dione (IV). A solution of 3.18 g (0.015 mol) of 2,7-dihydroxyfluoren-9-one (**II**) and 3.96 g (0.015 mol) of 1,4-bis(dibromomethyl)benzene (**III**) in 150 ml of anhydrous DMF was added over a period of 10 h to a suspension of 6.36 g (0.046 mol) of anhydrous potassium carbonate in 200 ml of anhydrous DMF under stirring at 80–85°C. The mixture was then stirred for 30 h at that temperature, cooled, and filtered, and the solvent was distilled off from the filtrate under reduced pressure. The residue was dissolved in 200 ml of chloroform, the solution was washed in succession with a 5% aqueous solution of sodium hydroxide and two portions of water and dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by column chromatography using chloro-

form–methanol (100:1) as eluent. Yield 0.76 g (8%), orange crystals, mp >300°C (decomp.). UV spectrum (1,4-dioxane), λ_{max}, nm (logε): 262 (5.11), 270 (5.07), 300 (3.81), 313 (3.81), 325 (3.44), 456 (2.73). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.21 s (8H, CH_2), 6.84 d (4H, 1-H, 8-H, J = 2.18 Hz), 6.96 d.d (4H, 3-H, 6-H, J = 8.09, 2.18 Hz), 7.18 d (4H, 4-H, 5-H, J = 8.09 Hz), 7.21 s (8H, C_6H_4). ^{13}C NMR spectrum (CF_3COOD), δ_C, ppm: 69.3, 121.5, 123.3, 124.5, 129.6, 135.2, 137.5, 138.9, 157.5, 197.3. Mass spectrum, m/z (I_{rel}, %): 628 $[M]^+$ (36), 314 (17), 212 (19), 201 (13), 104 (100), 91 (10). Found, %: C 80.44; H 4.76. $C_{42}H_{28}O_6$. Calculated, %: C 80.24; H 4.49.

X-Ray analysis of single crystals of complexes V and VI. Sets of experimental reflections were acquired on a Nonius Kappa CCD automatic diffractometer (MoK_α irradiation, graphite monochromator). Complex **V**: $\varphi/2\theta$ scanning, $2\Theta_{max}$ = 51.7°. Rhombic crystals, $C_{45}H_{35}NO_7$: a = 12.582(3), b = 15.974(4), c = 17.820(4) Å; V = 3581.6(2) Å^3; space group $Pnma$; Z = 4, d_{calc} = 1.301 g/cm^3; μ = 0.088 mm^{-1}, F(000) = 1472. The structure was solved by the direct method using 1169 reflections with $I > 2\sigma(I)$ in the full-matrix anisotropic (for O, N, and C atoms) and isotropic approximations (hydrogen atoms) to R = 0.0515, R_W = 0.0881 (no correction for absorption was introduced). GOF 0.789, $\Delta\rho_{max}$ = 0.149, $\Delta\rho_{min}$ = –0.188 eÅ^{-3}.

Complex **VI**: $\varphi/2\theta$ scanning to $2\Theta_{max}$ = 49.2°. Monoclinic crystals, $C_{54}H_{38}N_2O_{10}$: a = 12.905(3), b = 14.941(3), c = 23.162(5) Å; β = 105.27(3)°; V = 4308(2) Å^3; space group $P2_1/n$; Z = 4; d_{calc} = 1.349 g×cm^{-3}; μ = 0.094 mm^{-1}; F(000) = 1824. The structure was solved by the direct method using 1374 reflections with $I > 2\sigma(I)$ in the full-matrix anisotropic (for O, N, and C atoms) and isotropic approximations (hydrogen atoms) to R = 0.0686, R_W = 0.1159 (no correction for absorption was introduced). GOF 0.726, $\Delta\rho_{max}$ = 0.210, $\Delta\rho_{min}$ = –0.278 eÅ^{-3}.

The complete sets of crystallographic data (*.cif files) for complexes **V** and **VI** was deposited to the Cambridge Crystallographic Data Center (entry nos. CCDC 263273 and CCDC 263272).

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