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Inclusion Compounds of Octakis-Diphenoxy-phosphoryloxy-, Octakis-Tosyloxytetra methylcalix[4] Resorcinarenes and Bis-(Diisopropoxyphosphoryl) Dibenzo-18-Crown-6 with Benzene Derivatives

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Inclusion Compounds of Octakis-Diphenoxyphosphoryloxy-, Octakis-Tosyloxytetra methylcalix[4] Resorcinarenes and Bis-(Diisopropoxyphosphoryl) Dibenzo-18-Crown-6 with Benzene Derivatives

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Crystalline complexes of composition 1:1 of calixresorcinarenes **1** and **2**, and crown ether **3**, with a number of benzene derivatives have been synthesized. By means of X-ray crystallography and NMR-spectroscopy the structures of the host molecules and the complexes in the solid state and solutions have been investigated. It was shown that calixresorcinarenes **1** and **2** exist in the boat conformation both in the solid state and in solution. The guest molecules in complexes of calixresorcinarenes **1** are located within channels in the host crystal lattice. The selectivity of binding of benzene derivatives was investigated and the role of the hydrogen bonds and CH $\cdots \pi$ interaction was estimated.

INTRODUCTION

The design of supramolecular crystal complexes of the host-guest type is an object of intensive investigation. This is due mainly to both theoretical interest in the nature of the host-guest interactions and by the significant role of these complexes in techniques[1] and technology.[2]

It has been shown that such macrocyclic compounds as crown-ethers[3], cyclophanes[4], cyclodextrins[5], cyclotricatehilenes[6], calixarenes[7] and calixresorcinarenes[7] are able to form crystalline complexes with neutral organic guest molecules.

In recent times there has been particular interest in calixarenes and calixresorcinarenes, which have intramolecular cavities in which guest molecules, corresponding in size and architecture to

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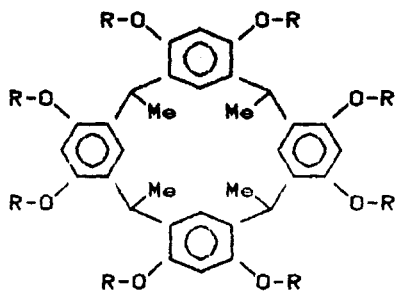
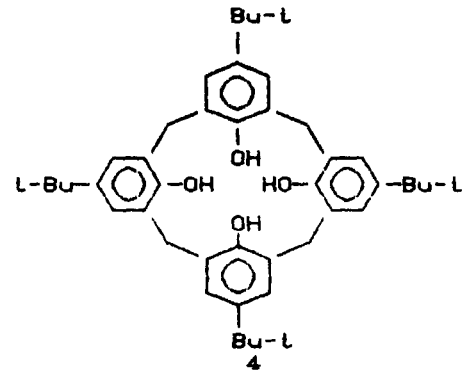


1, 2

R = $SO_2C_6H_4Me$-n 1

$P(O)(OC_6H_5)_2$ 2



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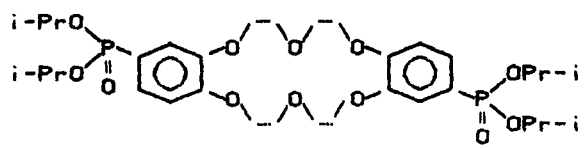

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the host, can be bound and retained. Such complementarity leads to high binding selectivity of calixarenes as demonstrated by Vicens in the case of the separation of xylenes[9] and by Atwood[10] and later by Shinkai[11] in the case of purification of fullerene C_{60}.

Recently, we have reported that calixresorcinarenes **1**[12] and **2**[13] and crown-ether **3**[14] form crystalline complexes with some benzene derivatives. The goal of the present paper is to investigate the nature of these complexes and selectivity of the complexation.

RESULTS AND DISCUSSION

Calixresorcinarenes **1** and **2** form stable crystalline complexes of composition 1:1 with benzene and its derivatives — toluene, bromo(iodo)-benzene, xylenes (ortho-, para- and meta-isomers) and bromotoluene (ortho- and para-isomers). However the complexation with the more bulky guest molecules mesitylene and 2,4,6-triisopropylbenzene does not take place. Crown ether **3** also forms crystalline complexes with benzene derivatives.[14] The composition of the above-mentioned complexes of compounds **1–3** was determined by integration of the ^1H NMR signals of guest and host in the spectra of the complexes and, in the case of crown ether **3**, they were additionally proved by elemental analysis (Table I).

The complexes of calixresorcinarenes **1** and **2** are colourless prisms which are transformed into white powders when stored in air several hours owing to loss of the guest molecules. The complexes of crown ether **3** (also prisms) are more stable and can be kept in air at room temperature for several days or even months, depending on the nature of the guest.

It should be noted that the stability of the complex **3**.C_6H_6 strongly depends on the configuration of the phosphoryl groups in the host molecule.

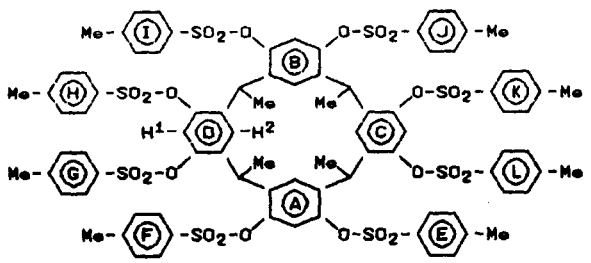
TABLE I Crystal Complexes of bis-(diisopropoxyphosphoryl)-dibenzo-18-crown-6 with benzene and its derivatives

Guest	Mp, °C	Found %	Formula	Calcd %
Benzene	120–123	**P** 8.07	$C_{38}H_{56}O_{12}P_2$	**P** 8.08
		C 58.25		**C** 59.52
		H 6.89		**H** 6.28
Fluorobenzene	111–113	**P** 7.12	$C_{38}H_{55}FO_{12}P_2$	**P** 7.89
Bromobenzene	95–112	**P** 6.86	$C_{38}H_{55}BrO_{12}P_2$	**P** 7.32
		Br 8.30		**Br** 9.45
Iodobenzene	97–102	**P** 7.46	$C_{38}H_{55}IO_{12}P_2$	**P** 6.94
		I 13.87		**I** 14.22
Toluene	97–99	**P** 8.38	$C_{39}H_{58}O_{12}P_2$	**P** 7.93
Phenol	108–111	**P** 8.07	$C_{38}H_{56}O_{13}P_2$	**P** 7.92

The cis-isomer of crown-ether **3** gives a less stable inclusion compound with benzene, total loss of the guest in air at room temperature is finished after a few days, whereas the complex $\mathbf{3}.C_6H_6$ is stable for several months.

The replacement of the iso-propyl groups of the phosphoryl fragments by n-propyl or ethyl groups leads to a similar result. In the case of disubstituted derivatives of dibenzo-18-crown-6 containing less bulky groups (NH_2, Br, I, C(O)Me, Me_3C), complexation with benzene was not observed.

It has been shown[14] by means of X-ray analysis that, due to the peculiarity of spatial orientation of the peripheral phosphoryl groups, molecules of crown ether **3** form molecular cavities able to include benzene[14a] as well as phenol[14b] in the crystalline state. The shortest distances between oxygen atoms of the macrocycle and carbon atoms of benzene ring of the guest are equal to 3.82, 3.86, 3.87 Å. This indicates the existence of a specific electrostatic interaction between the host and guest in the supramolecular benzene complex.[14a] In the case of the phenol complex hydrogen bonds between hydroxyl groups of the guest and macrocyclic oxygen atoms are formed.[14b]



Benzene rings nomenclature
octakis-tosyloxytetramethylcalix[4]resorcinarenes **1**.

In order to investigate the nature of the host-guest interaction for calixresorcinarene **1**, an X-ray analysis of complex $\mathbf{1}.C_6H_5CH_3$ has been performed (Tables II–IV, Figures 1–3).

As shown in Figure 1, calixresorcinarene **1** exists in the boat conformation in the solid state. In this conformation, diametrically opposed benzene rings **A** and **B** lie in the main molecular plane formed by C2, C8, C14, C20 carbon atoms of the CH links, but benzene rings **C** and **D** are perpendicular to this plane. The declination the main molecular plane of C25, C26, C27, C28 carbon atoms of the benzene rings forming the 16-membered rim of macrocycle is 0.74 Å.

The four methyl groups connected to the carbon atoms of the links lie in sterically less strained axial positions and all have a cis-configuration. The distances from the methyl groups carbon atoms C2M, C8M, C14M, C20M to the main molecular plane are in the range 1.38–1.53 Å. The torsion angles around the C2 linking fragment are –38 and 120°. The torsion angles around the other linking atoms are C8, –106 and 32; C14, 117 and –37; C20, 34 and –110°.

TABLE II Crystal and experimental data

Formula	$C_{95}H_{88}O_{24}S_8$
F.W.	1870
Crystal dimensions, mm	0.30 × 0.35 × 0.15
Radiation	CuK_α
(λ = 1.54178 Å, graphite monocromater)	
Temperature (degree)	293 ± 1K
Space group	$P2_1/n$
a (Å)	17.249(2)
b (Å)	23.380(4)
c (Å)	23.686(4)
β	104.2(4)
V ($Å^3$)	9260(3)
Z	4
D (calc.) (g × cm^{-3})	1.341
Diffractometer	Enraf-Nonius CAD-4
$\mu(CuK_\alpha)$ (cm^{-1})	23.54
$(\sin/\lambda)_{max}$	0.6315
N-Reflection I ≥ 2.5 | σ (I)	11236
N-Refainment parameters	1408
R(hkl)	0.058
$R(hkl)_w$	0.053
w	$2.3096/\lambda\sigma^2(F)$
Max peak in final diff. map	0.5e/$Å^3$
Min peak in final diff. map	−0.5e/$Å^3$

TABLE III Fractional atomic coordinates (*10**4) and B(eq)

Atom	X/a	y/b	z/c	B(eq)
S(1) (**E**)	7843(1)	579(1)	−949(0)	4.31(2)
O(11)	7872(1)	555(1)	−266(1)	3.91(9)
O(12)	8489(2)	251(1)	−1061(1)	5.4(1)
O(13)	7773(2)	1173(1)	−1080(1)	6.9(1)
S(2) (**L**)	7689(1)	1436(0)	1028(0)	3.46(2)
O(21)	8363(1)	984(1)	1319(1)	3.06(7)
O(22)	7028(1)	1084(1)	759(1)	4.55(9)
O(23)	8016(2)	1836(1)	692(1)	4.37(9)
S(3) (**K**)	10346(1)	2496(1)	2813(1)	5.10(3)
O(31)	10500(2)	1817(1)	2773(1)	3.96(9)
O(32)	9524(2)	2603(1)	2563(1)	7.2(1)
O(33)	10939(2)	2797(1)	2608(1)	6.8(1)
S(4) (**J**)	13801(1)	1958(1)	3224(1)	6.81(5)
O(41)	12878(2)	1801(1)	3136(1)	5.9(1)
O(42)	13789(3)	2488(2)	2937(2)	10.5(1)
O(43)	14214(2)	1468(2)	3073(2)	9.0(1)
S(5) (**I**)	13637(1)	−124(1)	4447(0)	5.10(3)
O(51)	12761(2)	−63(1)	4018(1)	4.79(9)
O(52)	13542(2)	−590(1)	4810(1)	6.8(1)
O(53)	13899(2)	414(1)	4695(1)	6.0(1)
S(6) (**H**)	10072(1)	513(1)	3849(0)	4.43(3)
O(61)	10527(2)	59(1)	3549(1)	5.3(1)
O(62)	9542(2)	210(2)	4115(1)	7.0(1)
O(63)	9751(2)	949(1)	3440(1)	7.3(1)
S(7) (**G**)	7544(1)	−452(1)	2220(1)	4.37(3)
O(71)	8284(2)	−529(2)	1961(1)	6.8(1)
O(72)	7495(2)	120(2)	2366(2)	8.8(1)
O(73)	7570(2)	−873(2)	2653(1)	7.8(1)
S(8) (**F**)	7674(1)	−1764(1)	3(1)	4.75(3)
O(81)	7853(1)	−1336(1)	549(1)	3.91(7)
O(82)	8370(2)	−1756(1)	−240(1)	6.7(1)
O(83)	6905(2)	−1635(1)	−346(1)	7.1(1)
C(1)	8944(2)	252(1)	515(1)	2.55(9)
C(2)	9344(2)	835(2)	522(1)	2.6(1)
C(2M)	9972(3)	812(2)	157(2)	3.8(1)
C(3)	9678(2)	1058(1)	1133(1)	2.5(1)
C(4)	9165(2)	1167(2)	1500(2)	3.0(1)
C(5)	9431(3)	1414(2)	2045(2)	3.3(1)
C(6)	10224(2)	1557(2)	2219(2)	3.3(1)
C(7)	10776(2)	1425(2)	1905(2)	3.1(1)
C(8)	11656(2)	1527(2)	2160(2)	4.0(1)
C(8M)	12160(3)	1544(3)	1711(2)	5.8(1)
C(9)	11991(2)	1092(2)	2642(2)	3.5(1)
C(10)	12602(2)	1233(2)	3115(2)	3.9(1)
C(11)	12891(3)	869(2)	3574(2)	4.3(1)
C(12)	12556(2)	326(2)	3547(2)	3.8(1)
C(13)	11951(2)	142(2)	3077(2)	3.2(1)
C(14)	11607(3)	−461(2)	3046(2)	3.7(1)
C(14M)	12107(4)	−838(3)	2732(3)	5.8(2)
C(15)	10762(2)	−483(2)	2766(2)	3.1(1)
C(16)	10176(2)	−212(2)	3016(2)	3.9(1)
C(17)	9362(3)	−225(2)	2779(2)	5.0(1)
C(18)	9088(2)	−520(2)	2265(2)	3.9(1)
C(19)	9595(2)	−812(2)	1990(2)	3.0(1)

The perpendicular benzene rings **C** and **D** make dihedral angles 98.9(1) and 81.2(2)° with the main plane of the macrocycle. For the coplanar rings **A**, **B** the dihedral angles are 6.3(1) and 2.8(1)° accordingly. Each pair of neighboring benzene rings (**A**, **B** and **C**, **D**) forms dihedral angles of 9.0(1) for **A**–**B** and 17.9° for **C**–**D**. These results determine the symmetry of the macrocyclic skeleton in the molecule of compound **1** to be C_{2V}.

The orientation of the tosyl groups at the upper rim of macrocycle leads to asymmetry in the conformation of the molecule as a whole (Figure 2). The benzene rings of tosyl groups **E** and **F** make dihedral angles 86.2(2) and 54.5(2)° with coplanar fragment **A** respectively. The dihedral angles between benzene rings **I** and **J** on the opposite fragment **B** are 55.5(2) and 101.0(2)°, respectively. The equivalent dihedral angles for the perpendicular fragments **C** and **D** are essentially different, however, fragments **K** and **L** form angles of 34.7(2)

TABLE III *(continued)*

Atom	X/a	y/b	z/c	B(eq)
C(20)	9248(2)	-1124(2)	1419(2)	3.1(1)
C(20M)	9839(3)	-1525(2)	1230(2)	4.3(1)
C(21)	8907(2)	-694(2)	938(2)	2.7(1)
C(22)	8235(2)	-808(2)	509(2)	3.1(1)
C(23)	7896(2)	-414(2)	87(2)	3.4(1)
C(24)	8256(2)	109(2)	102(1)	3.0(1)
C(25)	9261(2)	-160(2)	926(2)	2.7(1)
C(26)	10405(2)	-777(2)	2250(2)	3.1(1)
C(27)	11679(2)	540(2)	2630(2)	3.3(1)
C(28)	10475(2)	1182(2)	1357(2)	3.1(1)
C(11F)	6938(2)	238(2)	-1263(2)	3.6(1)
C(12F)	6906(3)	-137(2)	-1709(2)	6.3(2)
C(13F)	6205(4)	-410(3)	-1953(3)	8.4(2)
C(14F)	5527(3)	-322(2)	-1761(3)	6.7(2)
C(15F)	5572(4)	60(3)	-1333(3)	7.2(2)
C(16F)	6265(3)	348(3)	-1079(2)	5.9(1)
C(14P)	4763(5)	-657(5)	-2006(6)	11.7(4)
C(21F)	7466(2)	1805(2)	1617(2)	3.5(1)
C(22F)	7705(3)	2354(2)	1722(2)	5.2(1)
C(23F)	7465(3)	2657(2)	2149(2)	6.1(2)
C(24F)	6998(3)	2410(2)	2469(2)	6.1(2)
C(25F)	6784(4)	1849(3)	2372(3)	8.2(2)
C(26F)	7009(4)	1541(2)	1934(3)	6.5(2)
C(24P)	6737(8)	2757(5)	2939(5)	10.1(4)
C(31F)	10555(3)	2536(2)	3576(2)	4.4(1)
C(32F)	10024(3)	2266(2)	3844(2)	5.0(1)
C(33F)	10197(3)	2281(2)	4442(2)	5.3(2)
C(34F)	10856(3)	2552(2)	4769(2)	5.4(1)
C(35F)	11356(3)	2831(2)	4485(2)	6.0(1)
C(36F)	11210(3)	2818(2)	3880(2)	5.3(1)
C(34P)	11018(6)	2536(4)	5429(3)	8.3(3)
C(41F)	14106(3)	2074(2)	3977(2)	4.4(1)
C(42F)	14616(3)	1694(2)	4320(3)	5.6(1)
C(43F)	14862(3)	1789(2)	4916(2)	5.7(1)
C(44F)	14596(3)	2260(2)	5160(2)	4.9(1)
C(45F)	14077(3)	2624(2)	4810(3)	5.3(1)
C(46F)	13825(3)	2540(2)	4212(2)	4.8(1)
C(44P)	14879(8)	2373(4)	5812(3)	8.9(3)
C(51F)	14229(3)	-342(2)	3977(2)	4.7(1)
C(52F)	14837(4)	0(3)	3894(3)	7.6(2)
C(53F)	15282(5)	-174(3)	3522(4)	9.3(3)
C(54F)	15131(4)	-684(3)	3221(3)	7.6(2)
C(55F)	14529(4)	-1026(3)	3316(3)	6.6(2)
C(56F)	14089(4)	-859(3)	3704(3)	5.9(1)
C(54P)	15602(8)	-878(5)	2791(6)	11.1(4)
C(61F)	10904(3)	749(2)	4368(2)	4.2(1)
C(62F)	11403(3)	1158(2)	4226(2)	5.0(1)
C(63F)	12062(3)	1339(3)	4638(3)	6.0(2)
C(64F)	12243(3)	1123(3)	5199(3)	6.5(2)
C(65F)	11737(4)	720(3)	5333(3)	8.0(2)
C(66F)	11066(4)	535(3)	4925(2)	6.9(2)
C(64P)	12989(7)	1314(6)	5640(5)	11.1(4)
C(71F)	6827(2)	-615(2)	1585(2)	4.0(1)
C(72F)	6715(3)	-248(2)	1114(3)	5.2(1)

TABLE III *(continued)*

Atom	X/a	y/b	z/c	B(eq)
C(72F)	6715(3)	-248(2)	1114(3)	5.2(1)
C(73F)	6176(3)	-390(3)	603(3)	5.5(1)
C(74F)	5737(3)	-886(3)	551(2)	5.4(1)
C(75F)	5841(3)	-1231(3)	1018(3)	5.7(1)
C(76F)	6388(3)	-1115(2)	1534(3)	5.0(1)
C(74P)	5151(6)	-1037(6)	-15(5)	8.9(3)
C(81F)	7649(3)	-2412(2)	377(2)	4.3(1)
C(82F)	6977(4)	-2569(2)	531(3)	6.5(2)
C(83F)	6970(4)	-3093(3)	803(3)	7.5(2)
C(84F)	7605(4)	-3456(2)	905(3)	6.9(2)
C(85F)	8255(4)	-3285(3)	733(3)	7.8(2)
C(86F)	8295(4)	-2763(2)	480(3)	6.4(2)
C(84P)	7570(9)	-4061(5)	1168(10)	11.5(5)

Fractional atomic coordinates (*10**4) for quest non-hydrogen atoms (refined as rigid group)

Atom	x/a	y/b	z/c
C(1G)	9276	2048	6467
C(2G)	9911	1738	6355
C(3G)	9768	1306	5938
C(4G)	8985	1184	5631
C(5G)	8349	1494	5742
C(6G)	8493	1926	6161
C(MG1)′	9430	2515	6917
C(MG2)′	10752	1870	6686
C(MG3)′	10451	973	5817
C(MG4)′	8830	719	5181
C(MG5)′	7508	1362	5414
C(MG6)′	7809	2260	6281

(′) carbon atoms from the methyl group disordered over six equivalent positions

and 53.9(2)° with fragment **C** and fragment **G** and **H** form angles of 93.7(2) and 108.9(2)° with fragment **D**. In this conformation, seven tosyl groups are oriented on one side of the macrocyclic plane. The eighth tosyl group are located at the opposite side and is oriented approximately parallel to the **CH-CH$_3$** bonds there.

The geometry of the tosyloxy groups of compound **1** is similar to that of ordinary tosyloxy compounds.[15] Bond distances C-S, S=O, S-O are in the ranges of 1.73–1.76, 1.39–1.45 and 1.55–1.62 Å, accordingly. Bond angles at sulphur atoms are close to tetrahedral angles.

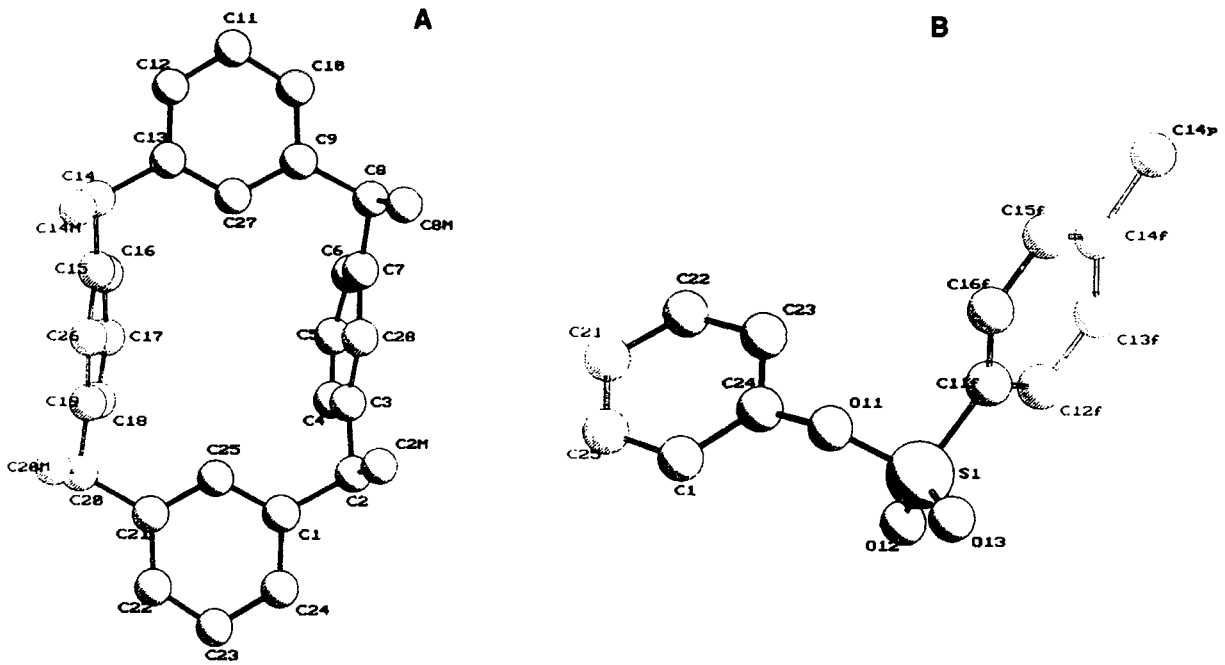


FIGURE 1 Numbering of atoms and view of macrocyclic skeleton for (a) octatosylate **1** and (b) its tosyl group.

The orientation of the exocyclic tosyl fragments determines the original packing of host molecules **1** in the crystal (Figure 3). In this case the benzene rings of one host molecule enter rather deep into cavity formed by benzene rings of a neighboring host molecule. Such molecular self assembly leads to formation of channels, which pierce the crystal structure in the direction of the b axis (Figure 3). The channel dimension is large enough for inclusion of benzene derivatives.

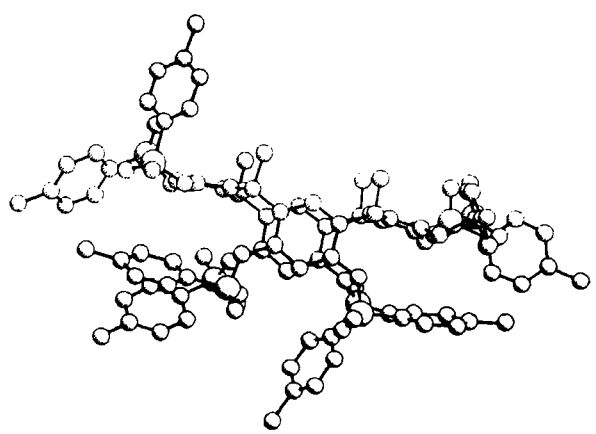


FIGURE 2 The structure of **1** (projection perpendicular to the benzene fragment).

As is shown in Figure 3 the all toluene molecules in the channels are strictly parallel and have distances of ~0.5b between aromatic ring due to disordering of the guest in the channels.

IR spectrum of octatosylate **1** and that of its toluene complex (in KBr tablet) are identical. This fact suggests the absence of any conformational change of the host molecules due to complexation.

The nature of the complexation for compound **1** is similar to that of channel complexes formed by urea[16], thiourea[17], deoxycholic acids[18], hexakis[4(tert-butyl)-phenyldimethyl]benzene[19] and some calixarene derivatives.[20] An interesting peculiarity of such type of complexes is the potential to perform various stereospecific transformations of the guest molecules in the channels.[21]

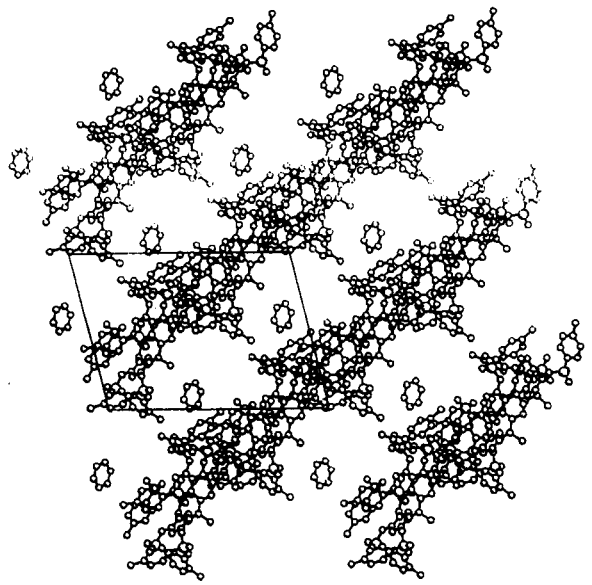


FIGURE 3 Crystal packing of 1 (projection along the b axis).

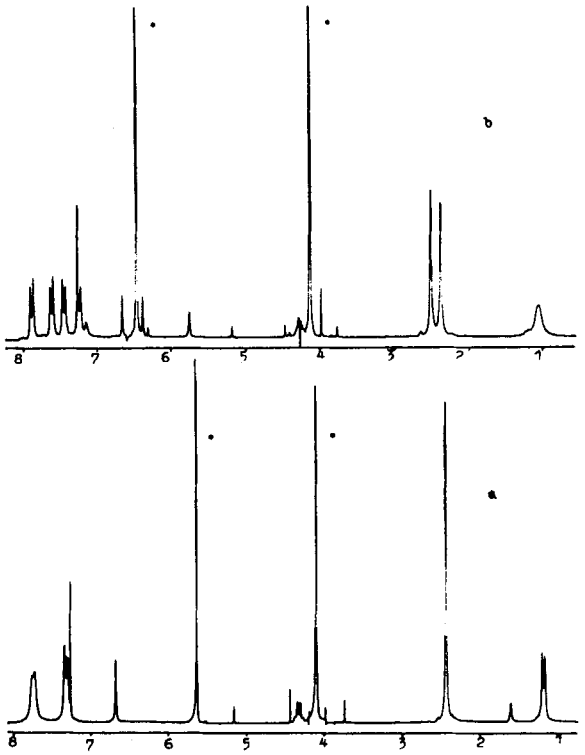


FIGURE 4 ^{1}H-NMR spectrum of **1** in $CDCl_3$: (a) at 30°C and (b) at –40°C. *CH_3OH signals.

The nature of the complexes of octaphosphorylated calixresorcinarene **2** with neutral molecules is probably the same. This presumption is confirmed by identity of conformations of the macrocyclic skeleton in compounds **1, 2** determined by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of octatosylate **1** in $CDCl_3$ solution (Figure 4a) contains a singlet due to the CH_3 groups of the tosyl fragments and a set of signals corresponding to aromatic protons: two singlets due to protons on the upper and lower macrocyclic rims (H^1 and H^2) and two doublets of AB spin system for the tosyl fragments. This spectral picture is in agreement with C_{4V} symmetry of the crown conformation of the macrocyclic skeleton (Figure 5b). This observed contradiction with the X-ray analysis data of compound **1** (C_{2V} symmetry) can be explained by the conformational flexibility of molecule **1** such that an exchange of coplanar and perpendicular macrocyclic skeleton benzene rings faster than the NMR timescale takes place in solution at room temperature (Figure 5). The spectral picture corresponding to the boat conformation with C_{2V} symmetry is fixed at –40°C only. Under these conditions, four singlets due to the aromatic protons of the macrocyclic skeleton as well as two singlets for the CH_3 groups of the tosyl fragments connected with coplanar and perpendicular benzene rings are observed (Figure 4b). The values of $\Delta G^{\#}$, $\Delta H^{\#}$, $\delta S^{\#}$ [23] for the boat-boat pseudorotation of compound 1 are 56.0 kJ mol^{-1}, 32.6 kJ mol^{-1} and 78.3 J mol^{-1}K^{-1} respectively. The same molecular dynamics in solution takes place for octaphosphate 2.[13] The process is additionally complicated by restricted internal rotation of phosphoryl groups around the P-OAr bonds.[13]

The complexation selectivity of compounds **1–3** was explored by means of extractive crystallization[9,24] from solutions that contained two guests in a volume ratio of 50:50. The ratios between bound guests, characterizing the binding

TABLE IV Extractive crystallization of compounds **1–4** from solutions containing benzene derivatives

Guests	The ratioes between bound guests in the complex %			
	CRA–S8 1	CRA–P_8 2	DB18c6–P_2 3	t–Bu$C[_4]$A 4
benzene: perfluorobenzene	79:21	90:10	93:7	98:2
toluene: perfluorotoluene	88:12	90:10	95:5	99.6:0.4
toluene: mesitylene	100:0	100:0	96:4	100:0
toluene: o–xylene	45:55	60:40	—	81:19
toluene: π–xylene	90:10	51:49	—	15:85
toluene: o–bpomo–toluene	58:42	60:40	57:43	—
toluene: anisole	—	—	68:32	—

selectivity, were determined by using HPLC (Table IV). The data obtained were compared to the receptor properties of *p*-tert-butylcalix[4]arene, which were determined under the same conditions.

It is known that tert-butylcalix[4]arene forms stable crystalline endo complexes with benzene derivatives. In these complexes the guest molecule lies within the intramolecular cavity of the calixarene due to $CH_3 \cdots \pi$ interactions between methyl groups of tert-butyl fragments of the host and the π-system of the guest (Figure 6).

As one can see from the results of separation of mixtures containing toluene and its derivatives-xylenes (ortho-, para-isomers), bromotoluene, mesitylene, and anisole (Table IV), the binding selectivity depends on the dimensions of the guest molecules. The introduction in the toluene molecule of methyl groups or bromo atoms makes packing of the guest molecules within channels of the compounds **1–3** or within the intramolecular cavity of calixarene **4** difficult. As a result, preferable binding of toluene molecules is observed. An exception is the high selectivity of complexation by tert-butylcalix[4]arene of para-xylene as demonstrated by Vicens.[9] The binding selectivity depends not only on the dimension but also on the electronic characteristic of groups connected with the benzene rings of the guest molecules. Replacement of all H-atoms of benzene or toluene

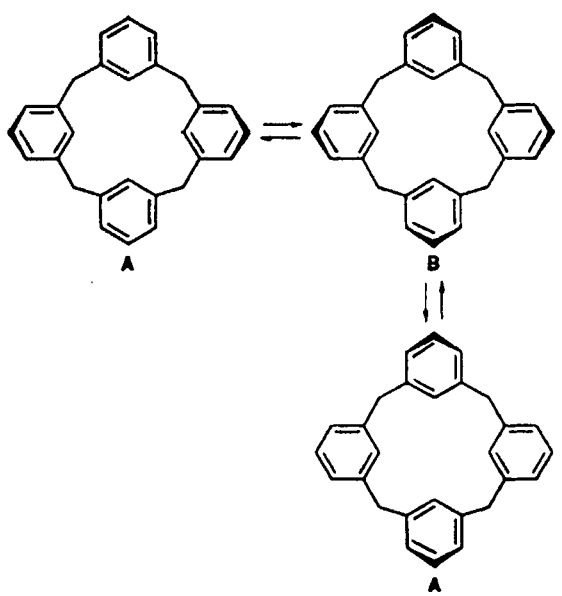


FIGURE 5 Boat-boat pseudorotation process of octasubstituted calixresorcinarenes, **A** boat conformation, **B** crown conformation.

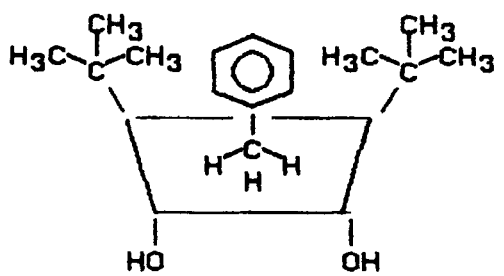


FIGURE 6 Structure of the complex of tert-butylcalix[4]arene with toluene.

molecules by F-atoms (covalent radius –0.03 and 0.064 nm accordingly) strongly decreases the binding (Table IV). In the case of calix[4]arene **4** the ratio between toluene and octafluorotoluene in the complex was determined as 99.6:0.4 (Table IV).

The large effect of binding of benzene or toluene molecules in comparison to their non-hydrogen analogues may indicate an important role of the hydrogen bonds for crown ether **3** and CH-π interaction for compounds **1, 2, 4.**

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded on a Bruker WP 200 spectrometer (at 200 MHz) as ca. 10% solutions in $CDCl_3$. The chemical shifts are reported in ppm (δ) down field from internal Me_4Si standard.

Infrared spectra were recorded on a Specord M80 instrument.

HPLC analysis was performed on HPC instrument (Czechoslovakia) in the following conditions: column C18, UV-detector with λ_{max} 254 nm, eluent methanol-water 70:30.

X-ray structure determination. A colourless plate crystal of complex $1.C_6H_6CH_3$ having dimensions 0.30 × 0.35 × 0.15 mm was mounted in a glass capillary with some excess of the mother solution (toluene). Preliminary examination and data collection were performed with CuK_α radiation on an Enraf-Nonius CAD-4 diffractometer. Cell parameters and an orientation matrix were obtained from least square methods using the setting angles of 25 reflection in the angle range $15 \leq \Theta \leq 30°$. The data were collected at 293 K, using the $\Theta/2\Theta$ scan technique. A total of 20518 reflections (19527-crystallographically independent) were collected, of which 11236 were unique and "observed" [$I \geq 2.5\sigma(I)$]. As a check of crystal and diffractometer stability three reflections were measured every 1 h. Lorentz and polarisation factors were applied to the experimental intensities, but no absorption.

The initial structure model was obtained by direct methods. The structure was refined by using blocked full-matrix least-squares methods and anisotropic thermal parameters for S, O, C atoms. Hydrogen atoms were positioned and added to the structure factors calculation and refined isotropically. Although the six ring C atoms of the guest toluene molecule could easily be located in difference maps no unique position for the toluene methyl carbon was found during refinement of the structure. Statistical disordering of the guest was assumed as the reason for this – the CH_3 group may be disordered over six possible positions around the ring. The guest was treated as rigid body in the structure refinement.

The final R-factor for 11236 reflections is 0.058, Rw = 0.059, $w = 2.3096/\sigma^2(F)$. All calculations were performed using an IBM PC-computer (486/487-processor) using programs CRYSRULER[26], SHELX-76,[27] SHELX 86[28], PARST[29] and ORTEP.[30]

Synthesis of 3,5,10,12,17,19,24,26 — octakis tosyloxy — 1,8,15,22-tetramethyl-calix[4]resorcinolarene 1.3.7 mmol of calix[4]resorcinarene and 59 mmol of triethylamine were dissolved in 70 mL of dry acetonitrile. To the resulting solution 59 mmol of para-toluenesulphonyl chloride in 30 mL of dry acetonitrile was added and the mixture was stirred at room temperature. After 9 h the solid product was separated and washed with acetonitrile. The liquids was combined and evaporated to 20 mL. Ethyl ether was added, the precipitate was collected by filtration and recrystallized from toluene. The crystalline solid was collected, and dried under 0.05 torr vacuum at 20°C for 10 h. White powder with m.p. 253–255°C, yield 70%.

^{1}H NMR (DMSO-d_6): 1.11 (d, 12H, CH_3, $^3J_{HH}$ 7.2 Hz), 2.36 (s, 24H,$ArCH_3$), 4.04 (q, 4H, CH, $^3J_{HH}$ 7.2 Hz), 6.65 (s, 4H, H^1 arom), 7.40 (d, 16H, $^3J_{HH}$ 8.6 Hz, C_6H_4), 7.42 (s, 4H, H^2 arom), 7.59 (d, 16H, $^3J_{HH}$ 8.6 Hz, C_6H_4).

Anal. Calcd. for $C_{88}H_{80}S_8O_{24}$: C, 59.44; H, 4.53; S, 14.43 %. Found: C, 58.85; H, 4.65; S, 14.45 %. The samples of complex 1 $C_6H_5CH_3$ for X-ray analysis were obtained by crystallization 1 from toluene.

Synthesis and analysis of the complexes of compounds 1–4.

(a) t-Buthylcalix[4]arene **4** (30–40 mg) was crystallized from solutions containing two guests in volume ratio of 50:50. The crystalline solid was separated, and dried at 20°C for 40 days to constant weight.

(b) Octakis-diphenoxyphosphoryloxytetramethylcalix[4]resorcinarene **2** (70–80 mg) was crystallized from solutions containing methanol-(90%) and two guests in volume ratio of 50:50 –(10%). The colorless crystals were separated, washed rapidly with methanol (3 × 2 mL) and dried for 10 min in air.

(c) Octakis-tosyloxytetramethylcalix[4]resorcinarene **1** (70–80 mg) was crystallized from solutions containing two guests in volume ratio of 50:50. The colorless crystals were separated, washed rapidly with methanol (3 × 2 mL) and dried for 10 min on air.

(d) Bis-(diisopropoxyphosphoryl)dibenzo-18-crown-6 **3** (60–70 mg) was crystallized from solutions containing two guest in volume ratio of 50:50. The colorless crystals were separated and dried for 24 h on air.

Methanol (~1.0 mL) was added to the complexes. After 10 h the methanol extract was analysed by HPLC. Each experiment was run twice and three injections were made for each of them (error 10 %).

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$$K = K \frac{K_b T}{h} \exp(-\Delta G^{\#}/RT) \quad (a)$$

$$K = K \frac{K_b T}{h} \exp((-\Delta G^{\#} - T\Delta S)/RT) \quad (b)$$

The rate constants k were evaluated from the NMR spectra using the program developed in the Institute of Organic Chemistry for the computer ASPECT-2000 of the spectrometer Bruker WP-200 by complete bandshape analysis method (see: Sandstrom J. *Dynamic NMR Spectroscopy*, London, Academic Press, 1982).

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