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Crystal structure of the host-guest complex of *trans-meta, meta'* -bis-diisopropoxyphosphorylidibenzo-18-crown-6 with phenol

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The crystal structure of the inclusion complex of phenol in the matrix formed by the *trans* isomer of *meta, meta'*-bis-diisopropoxyphosphoryldibenzo-18-crown-6 was determined by X-ray diffraction methods. The molecular structure of the crown ether and the packing of the molecules in crystal is discussed. The statistical disorder of the phenol molecule in two positions with occupancy of 0.5 is due to the location of the molecule on the crystallographic two-fold axis. Additionally, the disorder of the phosphoryl substituent was revealed. Interaction between the hydroxyl group, as well as the hydrogen atom in the *ortho* position of the phenol with the system of oxygen atoms of the crown ether in the crystal influences the conformation of the macrocycle. In solution the host and guest molecules are associated by the hydrogen bonds formed between the hydroxyl group of phenol and the oxygen atom of the exocylic phosphoryl group of the crown ether.

INTRODUCTION

Crown ethers[1] form guest-host complexes with cationic species[2] (i.e. metal cations, amine salts), as well as with neutral organic molecules possessing functional groups having active donor protons (acidic OH, NH, CH groups) which are able to form hydrogen bonds with the oxygen atoms of the macrocycle.[3] More inert molecules which do not have defined proton donor character, e.g. benzene and its derivatives, mainly form stable complexes only with macrocyclic molecules like cyclodextrins,[4] cyclophanes,[5] calixarenes,[6] and cavitands[7] in which large molecular cavities occur and the guest molecule is held in the cavity by means of a large number of non-bonding interactions (London forces, Van der Waals forces, H-π, solvatophobic interactions and others). It is known that complexation of crown ethers with the neutral guest molecules in solution as well as in the solid state may be substantially improved by modification of the macrocyclic skeleton with appropriate functional group.[8] For example, the *trans*-isomer of the *meta,meta'*-bis-diisopropoxyphosphoryl derivative of dibenzo-18-crown-6, **1**, in contrast to nonsubstituted dibenzo-18-crown-6, as well as its halogen-, nitro-, amino-, acethyl-, formyl-, alkylderivatives, forms a very stable 1:1 crystal complex A (Fig. 1) with a benzene molecule.[9]

As it was established with X-ray analysis[9] of the complex A, two bulky diisopropoxyphosphoryl groups define pseudocavities in separated crown-ether molecules and play an essential role in forming cavities of fixed parameters, able to accommodate benzene molecules.

In the course of studying the nature of bonding of neutral molecules by crown ethers,[9,10] the crystal struc-

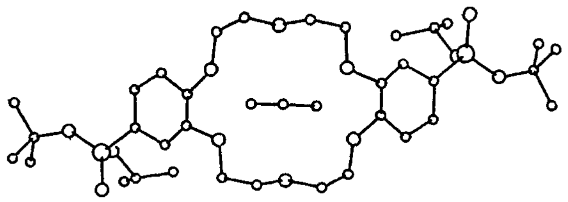

Figure 1 Top view of complex A (crown ether **1** and benzene).

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*To whom correspondence should be addressed ture of the complex of bis-diisopropoxyphosphoryl-dibenzo-18-crown-6,1, with phenol was solved and is presented here (structure B, Fig. 2,3).

EXPERIMENTAL

Trans meta, meta'-bis-diisopropoxyphosphoryldibenzo-18-crown-6, **1**, was synthesized according to the method already described[11] and the pure macrocyclic compound was released from the complex with benzene, which is formed as the final product of the synthesis by dissolving it in acetone and evaporating the solvent.

Crown ether—phenol complex B

Mixture of 0.3 mmol of 1 and 1.5 mmol of phenol was dissolved in 6 mL of hot mixed solvent hexane-acetone (1:3). Precipitated crystals were filtered, washed with hexane and dried in vacuum (12 mm Hg) at 20 °C for half hour. Yield 50%, m.p. 108–111 °C. ^{1}H NMR (δ ppm, acetone-d_6): 1.11 d, 1.23 d (24H, CH_3, $^3J_{HH}$ 6.2 Hz), 3.85–3.93 m (8H, CH_2OCH_2), 4.10–4.17 m (8H, $ArOCH_2$), 4.40–4.60 m (4H, CHOP), 6.96–7.33 m (11H, C_6H_3 + C_6H_5). ^{31}P NMR (acetone-d_6): δ_P 18.0 ppm. Microanalysis found: C, 58.62; H, 7.55; P, 8.07%. $C_{38}H_{56}O_{13}P_2$. Requires: C, 58.30; H, 7.21; P, 7.92.

X-Ray data collection and structure determination

Prismatic colorless single crystals are monoclinic with cell dimensions a = 26.918(10), b = 8.490(3), c = 20.022(7) Å, β = 117.06(5)°, Z = 4, molecular formula $C_{38}H_{56}O_{13}P_2$, D_x = 1.274 g.cm^{-3}, space group *C*2/*c*. Cell parameters are very close to those found for the inclusion compound with benzene, A: a = 27.04, b = 8.519, c = 20.050 Å, β = 117.3°. The unit cell volumes are also very similar: 4075 Å^3 for B and 4097 Å^3 for A.

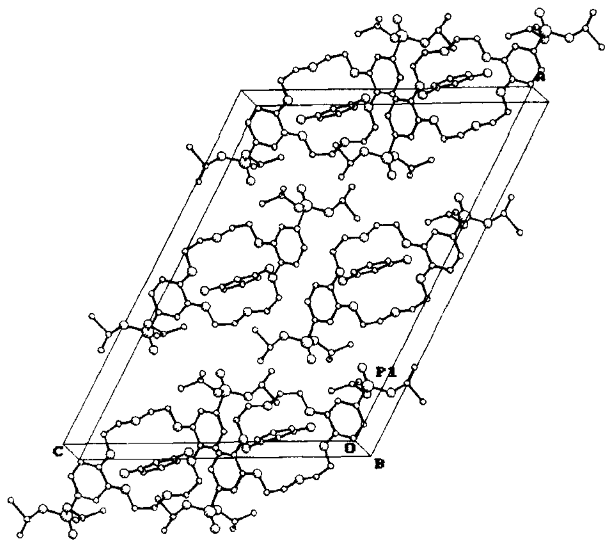


Figure 2 Top view of crystal structure of complex B (crown ether 1 and phenol).

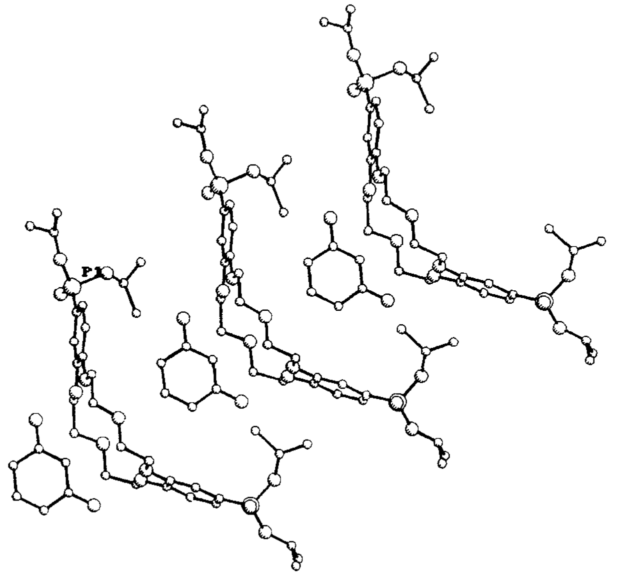


Figure 3 Side view of crystal structure of complex B (crown ether 1 and phenol).

Data collection was performed on an Enraf-Nonius CAD-4 automatic diffractometer using MoKα radiation and the ω − 2θ scan technique. 2498 unique reflections with I > 3σ(I) were used to solve and refine the structure (CRYSRULER[12]). The structure was solved by direct methods and full-matrix least-squares refinement was performed. From the systematic absences two space groups are possible: the noncentrosymmetric *C*2 and the centrosymmetric *C*2/*c*. In the latter case the complex should have two-fold symmetry which was found in the complex with benzene, A. Two-fold symmetry results in the disorder of the phenol molecule into two equivalent positions with site occupancy factor 0.5. By analogy to the structure A, two-fold symmetry of the complex was assumed. In both cases the disorder of the phosphoryl substituents is observed and seems to play an important role in forming a loose crystal structure of the host molecules with void space able to accommodate the guest molecules.

The final *R* factor was 0.086. Atomic coordinates are in Table 1 and bond lengths and bond angles are in Table 2. Numeration of the atoms is shown on Fig. 4.

IR spectroscopy

IR spectra were recorded on a Specord M-80 apparatus. Hydrogen bonds of the crown ethers with phenol were investigated in CCl_4 solution. The concentration of phenol and crown ethers was in range from 1×10^{-3} to 5×10^{-3} mol.L^{-1}, and thickness of the absorption cell was 1 cm. The complexation equilibrium constants were calculated according to the method described elsewhere[13] from the intensity of the band (OH) of the nonassociated phenol molecules. The energy of the hydrogen bonding was evaluated graphically from the

Table 1 Fractional atomic coordinates [1×10^4] and B_{eq} for non-hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
O (1)	1062 (1)	645 (3)	3684 (1)	4.34 (.09)
C (2)	1361 (2)	−247 (5)	3389 (2)	4.16 (.14)
C (3)	1411 (2)	688 (5)	2786 (2)	4.14 (.12)
O (4)	881 (1)	657 (3)	2134 (1)	4.14 (.09)
C (5)	829 (2)	1538 (5)	1536 (2)	3.56 (.13)
C (6)	285 (1)	1612 (5)	939 (2)	3.60 (.14)
O (7)	−109 (1)	797 (3)	1046 (1)	4.36 (.10)
C (8)	−675 (2)	855 (5)	469 (2)	4.31 (.13)
C (9)	−1020 (2)	−135 (5)	718 (2)	4.32 (.14)
C (11)	185 (2)	2500 (5)	309 (2)	4.39 (.15)
C (12)	614 (2)	3283 (5)	255 (2)	4.55 (.15)
C (13)	1156 (2)	3195 (5)	837 (2)	4.03 (.15)
C (14)	1254 (2)	2295 (5)	1477 (2)	3.80 (.14)
P	1758 (3)	4099 (11)	861 (2)	6.04 (.26)
O (01)	2266 (2)	3691 (7)	1348 (3)	4.83 (.22)
O (22)	1621 (2)	6082 (4)	917 (2)	3.85 (.14)
O (03)	1561 (5)	4192 (11)	−54 (6)	4.68 (.26)
C (21)	1729 (5)	6432 (12)	2224 (5)	6.73 (.41)
C (22)	2066 (9)	8346 (25)	1589(11)	8.69 (.79)
C (23)	1939 (4)	6832 (11)	1656 (5)	5.17 (.31)
C (24)	1859 (5)	4884 (12)	−379 (5)	5.79 (.38)
C (25)	2280 (6)	4214 (29)	−412 (9)	17.41 (1.12)
C (26)	1337 (7)	5206 (17)	−1230 (6)	10.44 (.68)
P'	−1701 (4)	4327 (20)	4239 (8)	2.98 (.18)
O (01')	−2293 (6)	2836 (19)	3923 (9)	7.72 (.63)
O (02')	−2048 (5)	5242 (18)	3508 (7)	8.34 (.62)
O (03')	−1564 (12)	4742 (28)	4912 (16)	6.90 (.88)
C (21')	−1479 (10)	6784 (32)	3030 (13)	10.70 (.90)
C (22')	−1895 (17)	8389 (61)	3619 (26)	12.49 (1.52)
C (23')	−1723 (9)	6585 (30)	3472 (14)	8.75 (.90)
C (24')	−1653 (9)	5473 (27)	5509 (13)	9.24 (.85)
C (25')	−2239 (8)	6312 (23)	5098 (13)	9.59 (.62)
C (26')	−1554 (10)	4661 (32)	6190 (14)	10.71 (.93)
O (A)	292 (3)	−2443 (8)	3431 (3)	6.20 (.24)
C (A2)	147 (2)	−3210 (7)	2022 (3)	6.60 (.24)
C (A3)	152 (3)	−4878 (8)	2002 (4)	9.38 (.31)
C (A4)	0 (0)	−5687(17)	2500 (0)	19.02 (.52)
C (A1)	0 (0)	−2404 (8)	2500 (0)	9.00 (.23)

relationship $\ln K_{eq.} - 1/T$. To establish hydrogen bonding between crown ether and $CDCl_3$ the solution of the ether in $CDCl_3$ of concentration 3×10^{-1} mol.L^{-1} was investigated. The thickness of the absorption cell was 6.5 $\times 10^{-3}$ cm. In the reference cell $CDCl_3$ was used. In these conditions the C-D bands associated $CDCl_3$ molecules only are observed in the range 2200–2300 cm^{-1}. [$\Delta\nu(CD) = 2255 - \nu_{as}$].

DISCUSSION

Figs. 2 and 3 show the projection of crystal structure B in two different directions of the unit cell. The structure consists of two types of neutral molecules: crown ether and phenol both on a special position in *C2/c*. The C(1A) and C(4A) atoms of the phenol molecule lie on the crystallographic two-fold axis which is, at the same time, perpendicular to 18-crown-6 plane and passes through its center. Peripheral phosphoryl groups do not interact with the guest molecule. The disorder of the phosphoryl groups seems to be a necessary condition to form the loose host crystal structure with void space to accommodate the guest molecules. The scheme of disorder found in benzene complex A[9] is different from that found in the phenol complex B. In the first structure only one isopropyl group is disordered; in the second one, the displacement of all atoms and, at the same time, the rotation of the isopropyl groups around the P-O bond is observed. The conformation of the macrocyclic ring is characterized by twelve *trans* C-O bonds, four *gauche* and two *cis* C-C bonds, and is described by torsion angles shown in Table 2. As it was described previously for complex A, the conformation of macrocycle B is similar to the one existing in the complexes of dibenzo-18-crown-6 with the alkali metal cations.[14] Bond lengths in the P(O)(OPr-i)$_2$ substituents are given in Table 2 and are common for organophosphorus compounds of this type.[15] The crown ether molecule is V-shaped in such a way that the dihedral angle between the two benzene rings is close to 70°. For the host-guest interaction in complex B the formation of a forked hydrogen bond between the hydroxyl group of guest and two oxygen atoms from the catechol units of the host is present [O(A) ... O(4) and O(A) ... O(7) distances are 3.02 and 2.97 Å, respectively]. These interactions, as well as possible ones between oxygen atoms of the crown ether and the proton bound to C(A1) of the another phenol molecule (Fig. 2, 3), seem to be responsible for the conformational reorganization of the macrocyclic skeleton of the host molecule.

In spite of the similarities in the solid state, complexes A and B show differences in solution. In CCl_4 solution ^{1}H NMR as well as IR spectra of the host and guest molecules of the benzene complex A do not display any visible differences with these spectra of the individual crown ether 1 and benzene, due to full dissociation of the complex. Just the contrary is observed for complex B in CCl_4 solution where the crown ether and phenol molecules are associated. The IR spectra of mixtures of phenol and crown ether 1 as well as other phosphoryl derivatives of dibenzo-18-crown-6 2–5 and monobenzo-15-crown-5 6-10[11] (Table 3) recorded in conditions of excess of the crown ether in the mixture manifest a single ν(OH) band for hydrogen bonded associates (Fig. 5). The maximum of this band, depending on the type of substituents at the phosphorus atom, is shifted from 360 to 565 cm^{-1} in relation to ν(OH) of the free hydroxyl group of nonassociated phenol. Together with the increasing value of ν(OH), the value of the enthalpy of complexation, phenol—crown ether, also increases, and the highest values of $-\Delta H^{16}$ are observed in case of crown ethers 5 and 10, having the most electron donor diethylamine substituents (Table 3).

The equilibrium constant of the model system *meta*-diisopropoxyphosphorylbenzo-15-crown-5, **6**,—phenol is equal to 335 L.mol^{-1} and is close to the value 350 L.mol^{-1} found for the triethylphosphate—phenol sys-

Table 2 Selected bond lengths (Å), bond angles (°), and torsion angles (°) in complex B

bond lengths							
O(1)	-C(2)		1.416(6)	P	-C(13)P		1.77(1)
C(2)	-C(3)		1.502(6)	P	-O(01)		1.314(8)
C(3)	-O(4)		1.430(4)	P	-O(02)		1.74(1)
O(4)	-C(5)		1.364(4)	P	-O(03)		1.66(2)
C(5)	-C(6)		1.408(4)	O(02)	-C(23)		1.473(9)
C(5)	-C(14)		1.365(7)	O(03)	-C(24)		1.37(2)
C(6)	-O(7)		1.365(4)	C(21)	-C(23)		1.52(2)
C(6)	-C(11)		1.387(5)	C(22)	-C(23)		1.35(2)
O(7)	-C(8)		1.435(4)	C(24)	-C(25)		1.30(2)
C(8)	-C(9)		1.496(7)	C(24)	-C(26)		1.66(1)
C(9)	-O(1*)		1.416(5)	P'	-O(01')		1.90(2)
C(11)	-C(12)		1.379(7)	P'	-O(02')		1.54(2)
C(12)	-C(13)		1.396(5)	P'	-O(03')		1.28(3)
C(13)	-C(14)		1.412(6)	O(02')	-C(23')		1.46(3)
				O(03')	-C(24')		1.46(3)
O(A)	-C(A2)		1.312(8)	C(21')	-C(23')		1.33(4)
C(A1)	-C(A2)		1.37(1)	C(22')	-C(23')		1.66(6)
C(A2)	-C(A3)		1.418(9)	C(24')	-C(25')		1.58(3)
C(A3)	-C(A4)		1.41(1)	C(24')	-C(26')		1.44(4)
bond angles							
O(1)	-C(2)	-C(3)	109.1(4)	O(02)	-P-O(03)		93.1(6)
C(2)	-C(3)	-O(4)	108.0(4)	O(01)	-P-O(03)		122.2(8)
C(3)	-O(4)	-C(5)	116.9(3)	O(01)	-P-O(02)		112.9(7)
O(4)	-C(5)	-C(14)	125.3(4)	P	-O(02)	-C(23)	116.0(5)
C(5)	-C(6)	-C(7)	115.4(3)	P	-O(03)	-C(24)	125.4(9)
C(6)	-O(7)	-C(8)	118.2(3)	C(21)	-C(23)	-C(22)	119(1)
O(7)	-C(8)	-C(9)	107.7(3)	O(02)	-C(23)	-C(22)	111(1)
C(8)	-C(9)	-O(1*)	108.6(4)	O(02)	-C(23)	-C(21)	114.2(8)
C(12)	-C(13)	-P	126.7(4)	O(03)	-C(24)	-C(26)	99(1)
C(14)	-C(13)	-P	114.7(4)	O(03)	-C(24)	-C(25)	123(1)
C(13)	-P	-O(03)	99.2(6)	C(25)	-C(24)	-C(26)	112(1)
C(13)	-P	-O(02)	101.6(5)	O(02')	-P'	-O(03')	129(2)
C(13)	-P	-O(01)	112.4(7)	O(01')	-P'	-O(03')	109(2)
				O(01')	-P'	-O(02')	88(1)
				P'	-O(02')	-C(23')	109(1)
				P'	-O(03')	-C(24')	155(3)
C(A2)	-C(A1)	-C(A2*)	120.2(5)	C(21')	-C(23')	-C(22')	105(3)
C(A1)	-C(A2)	-C(A3)	121.8(3)	O(02')	-C(23')	-C(22')	119(3)
C(A2)	-C(A3)	-C(A4)	117.1(4)	O(02')	-C(23')	-C(21')	128(2)
C(A3)	-C(A4)	-C(A3*)	122.0(2)	O(03')	-C(24')	-C(26')	123(2)
O(A)	-C(A2)	-C(A1)	120.3(2)	O(03')	-C(24')	-C(25')	105(5)
O(A)	-C(A2)	-C(A3)	117.8(2)	C(25')	-C(24')	-C(26')	115(2)
torsion angles							
C(9*)	-O(1)	-C(2)	-C(3)	−177.3(4)			
O(1)	-C(2)	-C(3)	-O(4)	−75.1(4)			
C(2)	-C(3)	-O(4)	-C(5)	175.5(4)			
C(3)	-O(4)	-C(5)	-C(6)	−173.3(4)			
O(4)	-C(5)	-C(6)	-O(7)	0.2(5)			
C(5)	-C(6)	-O(7)	-C(8)	178.5(4)			
C(6)	-O(7)	-C(8)	-C(9)	179.5(3)			
O(7)	-C(8)	-C(9)	-O(1*)	70.7(4)			
C(8)	-C(9)	-O(1*)	-C(2*)	−177.2(4)			

*symmetry code: (-x,y,1/2−z)

tem.[17] Also, the values of ν(OH) for the investigated crown-ethers, 1–10, are only slightly different (15–20 cm^{-1}) from those observed for the associates of phenol with acyclic phosphates and phosphinoxides. The above

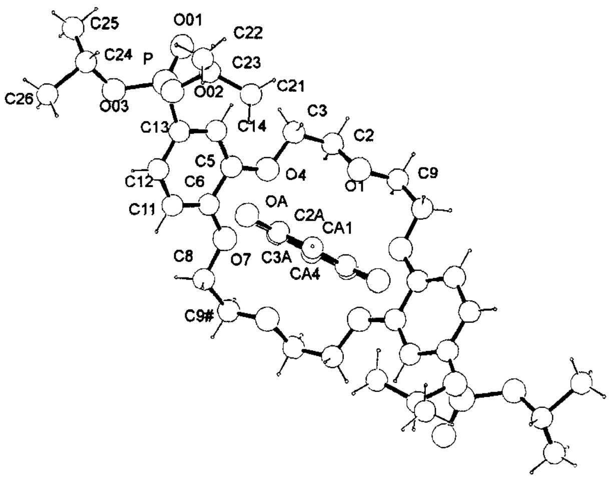


Figure 4 Numbering of atoms of host and guest in complex B.

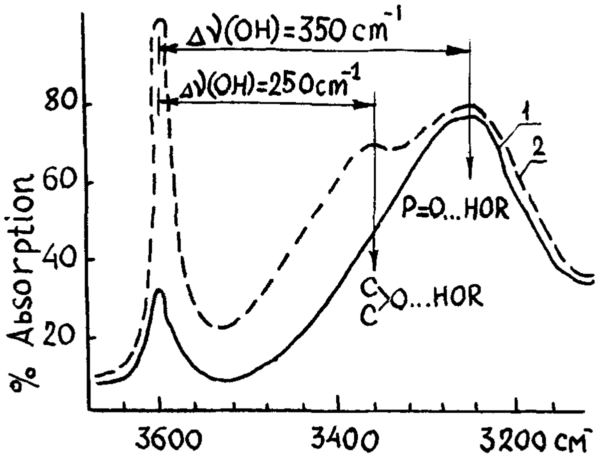


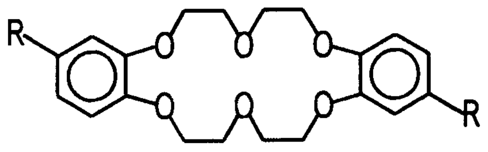
Figure 5 IR spectra of the crown ether 1 - phenol systems in CCl_4 solutions. 1 - concentration: phenol 0.005 $mol.L^{-1}$, crown ether 0.05 $mol.L^{-1}$ 2 - concentration: phenol 0.05 $mol.L^{-1}$, crown ether 0.005 $mol.L^{-1}$.

data show that the phenol molecule interacts with crown ethers 1–10 exclusively via P = O oxygen atoms which have higher basicity compared to the ether oxygens. If the ratio of crown ether—phenol in the solution is increased to more than 1:1, an additional band appears in the IR spectrum (Fig. 5). This additional band represents hydrogen bonds between phenol and crown ether oxygen atoms. The more basic oxygen atoms of the phosphoryl groups in the investigated crown ethers are also the bond centers for other proton donor molecules, i.e. in the solution of crown ethers 1–10 in $CDCl_3$ two bands in the region of 2200–2255 cm^{-1} are presented in IR spectra. They represent two types of hydrogen bond associates between the crown ether and $CDCl_3$: one with $\Delta\nu$(CD) 7–8 cm^{-1} which represents the interaction with oxygen atoms of the macrocycle, and second with $\Delta\nu$(CD) 11–31 cm^{-1} which represents the interaction with the phosphoryl oxygen atoms. The increase of the electron donor properties of the substituents on the phosphorus atom increases the ν(C-D...O = P) value while the value of ν(C-D...O-C_{ether}) remains unchanged.

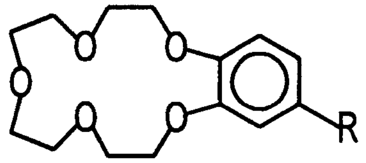
CONCLUSION

Bis-diisopropoxyphosphoryldibenzo-18-crown-6, **1**, due to a peculiarity of the spatial orientation of peripheral

Table 3 Complexation data of the crown ethers with phenol



1-5



6–10

Compound	*R*	*$\Delta\nu$(OH) [cm^{-1}]*	*$-\Delta H$* [$kcal.mol^{-1}$]*
	dibenzo-18-crown-6		
	H	257	5.10
1	$(i\text{-}PrO)_2P(O)$	375	6.25
2	$(n\text{-}PrO)_2P(O)$	360	6.10
3	$(EtO)_2P(O)$	365	6.20
4	$Ph_2P(O)$	440	6.80
5	$(Et_2N)_2P(O)$	565	7.70
	benzo-15-crown-5		
	H	257	5.10
6	$(i\text{-}PrO)_2P(O)$	375	6.25
7	$(n\text{-}PrO)_2P(O)$	360	6.10
8	$(EtO)_2P(O)$	370	6.20
9	$Ph_2P(O)$	440	6.80
10	$(Et_2N)_2P(O)$	565	7.70

*determined by the method in ref 16: $(\Delta H)^2 = 0.11\ (\Delta\upsilon - 20)$

phosphoryl groups, forms V-shaped molecular cavities able to include phenol molecules in the crystal state. These supramolecular crystal complexes can be classified as host-guest ones due to hydrogen bond formation between the hydroxyl group as well as *ortho* protons of the phenol with macrocyclic oxygen atoms. These cooperative interactions influence the conformation of the macrocycle in the complex, similar to that of metal cations. In contrast to the crystal state, the complex in solution is preferably formed due to association of the phenol hydroxyl group with peripheral P = O oxygen atoms having higher basicity compared to endocyclic oxygen atoms.

The crystal structure may serve as a suitable illustration to emphasize the importance of non-bonding (van der Waals type) interactions in determination the structure of inclusion compounds. When looking at the packing of guest and host molecules in the crystal lattice (Fig. 3), one immediately realizes the presence of guest-host hydrogen bonds that may easily be taken as the structure-determining factor. This, however, is not true, since substitution of phenol by benzene leads to exactly the same type of intermolecular packing, and even the lattice constants of the two compounds are nearly the same (ref 9). Thus, the structure-determining factor is bonding of the benzene aromatic ring inside the cavity formed by the crown host.

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