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Synthesis and Structure Elucidation of Large Phosphorus Macrocycles

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Abstract

The simple reaction between 1,ω-diamino derivatives and R-bis-(dimethylamino)-phosphane (R = CH_3, C_6H_5), followed by an oxidation step led to the formation of the expected macrocyclic phosphorus compounds. By this way 17- to 27-membered macrocycles were easily obtained. During the synthesis, the formation of dimeric (40- and 52-membered rings) and trimeric (78-membered rings) macrocyclic species were obtained from **3** and **5** and fully characterized by NMR and mass spectrometry. The P(III) phosphorus species exchange in solution and the macrocycle/oligomers ratio is temperature and concentration dependent. The crystal structure analysis of macrocycles **1**, **5**, **7** and **8** show that voids are minimized in the solid so that the macrocyclic cavity is filled up with part of the molecule itself or with a guest molecule, when the size of the macrocycle does not allow molecular folding for self-filling the cavity.

Introduction

Very large macrocycles and cyclic oligomers are potentially interesting for investigating recognition phenomena. Their synthesis and characterization provide useful information for the development of original supramolecular assemblies. They can afford new hosts with molecular cavity of unusual size and functionality, to produce original multicomponent assemblies of high complexity. The monomer-oligomer rearrangement is well documented and is particularly important in macrocyclization processes [1]. These equilibria have been used to design macromolecules and supramolecular systems and are currently developed through combinatorial chemistry, where exchange processes lead to defined oligomeric species [2]. The rational design of large macrocycles proved to be attained in the synthesis of the crown-like phosphoramide macrorings following a very simple synthetic methodology that was already applied for small and medium size phosphorus cyclic compounds [3]. We have been particularly interested in the complexation behavior of phosphorus macrocyclic ligands because phosphorus groups are efficient binding sites particularly when they are introduced in preorganized systems [4–6]. While small and medium size cyclic compounds containing the N–P–N group have been available for a long time, analogous very large rings were not described although the ring closure reaction between a 1,ω-diamino compound and a diaminophosphane could be performed with fairly good yields. This approach is based on the remarkable propensity of cyclic compounds to be formed as the most stable structures compared to (linear) oligomeric materials in the P(III) state, which are then converted, after oxidation of the phosphorus atom, into the oxide P(O) or sulfide P(S) compounds.

We wish to present herein the synthesis of large mono-phosphorus macrocycles, up to 27-membered rings, which have been prepared by using the method previously described for related medium sized compounds. Moreover, cyclic oligomeric derivatives of the parent macrocyclic monomeric compounds can be obtained and isolated. We are reporting on the synthesis, X-ray structures, and NMR study of macrocycles **1**–**9**, together with dimeric and trimeric structures of some of them. For instance, the 78-membered cyclic trimer **5T**, which represents the largest cyclic phosphorus compounds ever obtained. was isolated and characterized.

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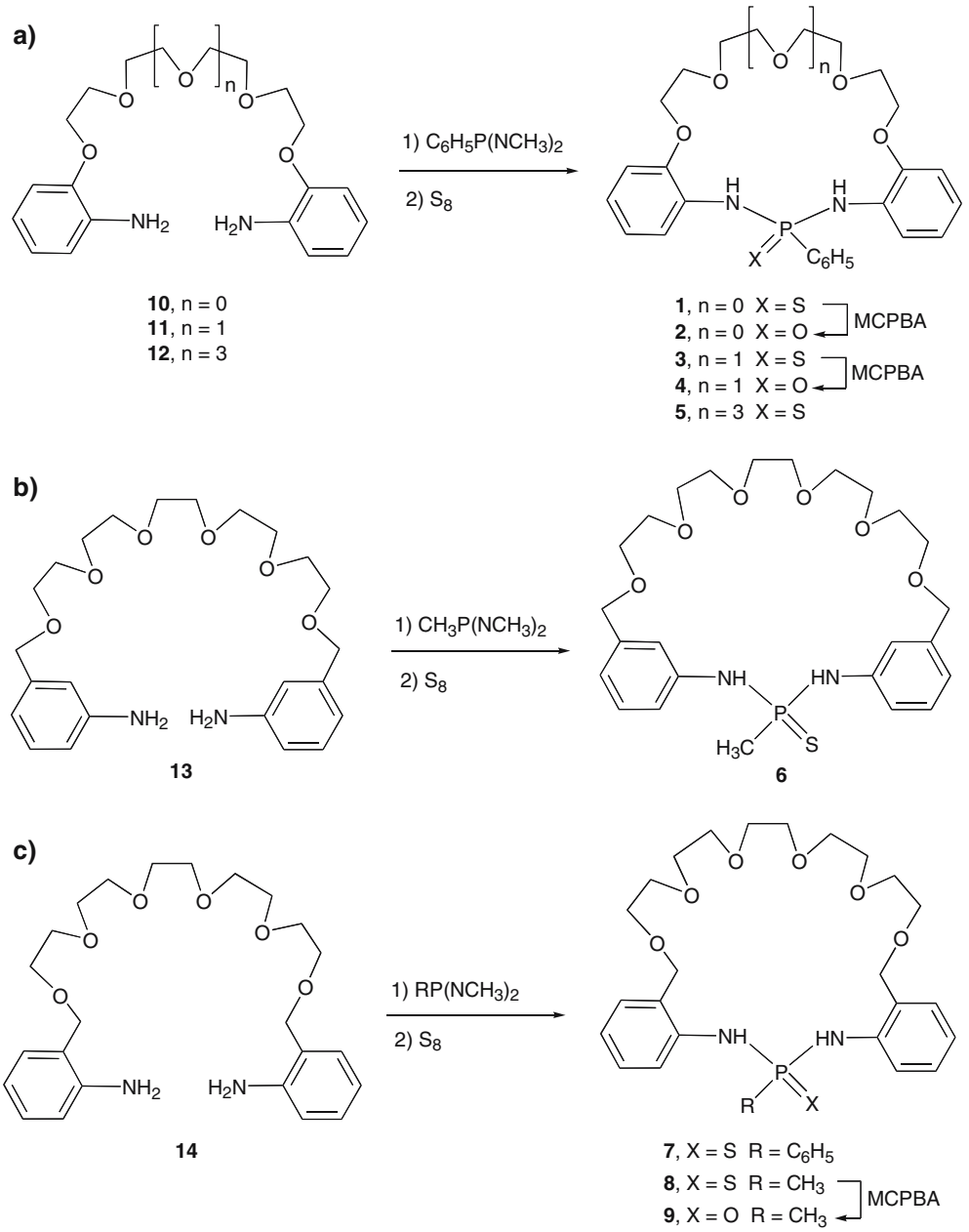
Results and discussion

Synthesis

The short route to phosphorus macrocycles **1**–**9** was devised by application of the straightforward phosphorylation procedure described in Scheme 1. In this method the cyclization reaction takes place in refluxing toluene under moderate dilution conditions and without any templating partner to give the P(III) derivatives, which are easily oxidized with sulfur into the P(S) compounds, which in turn can give the P(O) compounds by reaction with *m*-chloroperoxybenzoic acid (MCPBA). This reaction has already been used previously to prepare compounds **1** and **3** [7]. The starting diamines **10**–**14** were prepared from 1,ω-oligoethylene-glycol-ditosylates by reaction with *o*-nitro-phenol (**10**–**12**), 3-aminobenzyl alcohol (**13**) or 2-aminobenzyl alcohol (**14**). The reduction of the nitro groups was performed with hydrazine and Pd/C as catalyst. The ring closure reaction with $CH_3P[N(CH_3)_2]_2$ or $C_6H_5P[N(CH_3)_2]_2$ yielded the macrocyclic three-coordinated phosphorus derivatives, which were subsequently allowed to react with sulfur to give the P(V) macrocycles in fairly good yields (Table 1), with a better reactivity with the methyl phosphine relatively to the phenyl one in the case of **7** and **8**.

Usually, a chromatographic separation was performed to isolate the pure monomeric compounds, although in some cases they were directly obtained by crystallization from the crude reaction mixtures. Further elution during the chromatographic separation often



Scheme 1.

Table 1. Experimental data for compounds **1-9**, **3D**, **5D** and **5T**

Compd.	**1**	**2**	**3**	**3D** *trans*/*cis*		**4**	**5**	**5D**	**5T**	**6**	**7**	**8**	**9**
Ring size	17	17	20	40	40	20	26	52	78	27	25	25	25
δ ^{31}P (ppm)	54.8	11.45	55.60	53.21	53.15	11.5	55.15	52.56	52.33	53.8	53.93	58.11	19.74
mp (°C)	161	147	154 (dec)	191	147	179	104.5	Oil	Oil	102	90	99	Oil
Yield	80%	68%	74%	(a)		69%	39%	(a)	(a)	31%	30%	49%	75%

(a) Yields for dimers and trimers have been estimated from the recovered and purified compounds (see Experimental section).

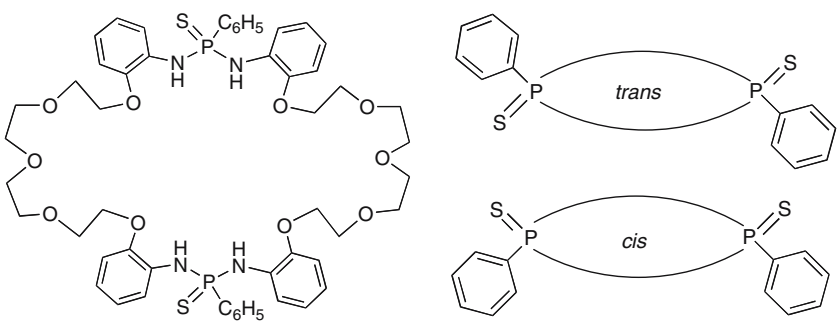
allowed the separation of the higher cyclic oligomers. This is probably a general feature, which has been illustrated with **3** and **5** in the present work. The cyclic dimers of **3**, *trans*-**3D** and *cis*-**3D**, and the dimeric (**5D**) and trimeric (**5T**) cyclic forms of **5** were unambiguously characterized. The compounds are stable under normal conditions and are crystalline or oily materials for the very large ones.

In the case of **3**, the two expected 40-membered cyclic dimers *trans*-**3D** and *cis*-**3D** (Figure 1) were isolated by column chromatography. Both compounds are crystalline materials with different melting points (Table 1). In the *trans*-**3D** isomer the sulfur atoms are located on opposite sides of the mean plane defined by the macrocyclic structure; they are on the same side in *cis*-**3D** .

The ^{1}H and ^{13}C NMR spectra of the *cis* and *trans* isomers are roughly superposable (see experimental section), whereas the ^{31}P chemical shifts differ by 0.06 ppm. ESI mass spectrometry revealed clearly the corresponding mass 1029.1 ($[MH]^+$) without difference between both isomers. Only an X-ray structure analysis would provide the complete assignment of the *cis* and *trans* compounds. However, crystals of **3D** were of poor quality and did not allow us to determine with high confidence the respective molecular structures of both isomers.

The reaction of diamine **12** with $C_6H_5P[N(CH_3)_2]_2$ followed by addition of sulfur, led to the 26-membered ring **5** as a solid crystalline compound in 39% yield (see structural details below). Chromatographic separation allowed isolation of higher molecular weight derivatives. Macrocyclic dimer **5D** and trimer **5T** were isolated and characterized (Figure 2). Two isomers for **5D** and **5T** (namely *cis* and *trans* isomers) were expected, however, we were not able to separate the different isomers, which have probably similar physical properties. **5D** and **5T** are viscous oils with identical ^{1}H NMR spectra superposable to that of the parent monomer **5**. Only ^{31}P NMR spectra can distinguish between **5**, **5D** and **5T**. Only one single resonance was observed for each compound, although we suspect to have mixtures of *trans* and *cis* isomers for **5D** (δ 52.56 ppm) and **5T** (δ 52.33 ppm). Thus, mass spectrometry was essential to characterize unambiguously these molecules. FAB(+) MS showed the main $[MH^+]$ peak (100%) at *m*/*z* 603.1, 1205.3 and 1807.5 for **5**, **5D** and **5T**, respectively.

In the course of our work on macrocyclic phosphorus ligands, we have been involved in the chemistry of rigidified and preorganized structures for complexation studies. The *meta*-aminobenzyl precursor (Scheme 1b) revealed to be a good candidate for the design of chiral cyclic phosphoramide molecular receptors [8] or hemispherand like structures containing one phosphoryl group and ether oxygen atoms as binding sites [4, 5]. For instance, 18- and 21-membered compounds have been previously described and were synthesized according to the present procedure (44% and 38% yields respectively) [9, 10]. In this work, the 27-membered compound **6** was obtained in 31% yield. The *ortho*-substituted bisbenzylamine (Scheme 1c) was also synthesized to introduce a new geometry around the phosphorus group. By this way, we prepared the 25-membered macrocycles **7** and **8** differing by the phenyl or methyl group on the phosphorus atom in 30% and 49% yield, respectively.



3D

Figure 1. Structure of the dimers **3D**.

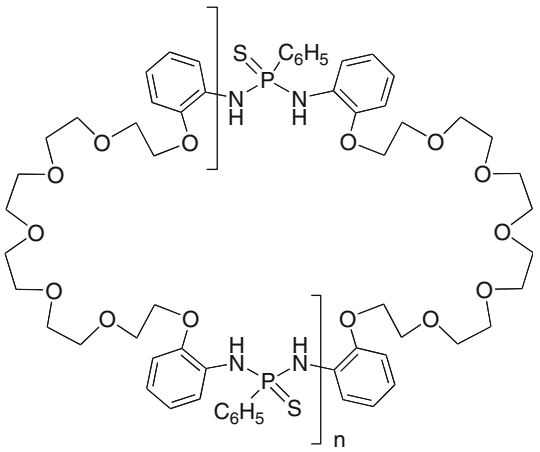


Figure 2. Cyclic oligomers of **5** ($n = 0$): dimer **5D** ($n = 1$) and trimer **5T** ($n = 2$).

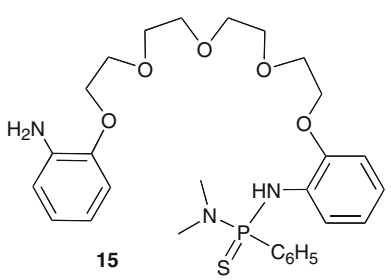
In view of the complexation potential of these macrocyclic compounds, it was interesting to obtain derivatives bearing a strong polar P(O) group to bind hard cationic species. The conversion of P(S) to P(O) compounds was easily achieved using *m*-chloroperoxybenzoic acid (MCPBA) as oxidizing agent. This procedure has been already used with macrocyclic compounds [5, 9], and was applied to **1**, **3** and **8** to give respectively compounds **2**, **4** and **9** with good yields (Table 1).

Monomer-oligomers equilibrium with the P(III) phosphorus species

We did not explore all the possibilities concerning the obtaining of oligomeric species, and we only report in this work the cases of **3** and **5**, for which dimeric and trimeric compounds were characterized. An interesting point that should be highlighted is the reversibility of the formation of oligomeric species during the ring closure reaction with the three-coordinated phosphorus species. According to previous observation, monomeric and oligomeric species are in thermodynamical equilibrium when phosphorus is not oxidized (P(III) species). This has been particularly investigated with cyclic phosphonite derivatives [11–17], and this seems to be more general and was observed with the present diaminophosphorus compounds.

To illustrate this feature, we followed by ^{31}P NMR and analytical gel permeation chromatography (GPC) the evolution of the crude reaction mixture of the P(III) parent compounds of **3**. Samples were withdrawn from the crude reaction mixture and immediately reacted with sulfur to avoid further evolution of the reaction. Under these conditions, the sulfurization is very fast and the content of the sample is an image of the mixture of the P(III) parent compounds. When the reaction was considered to be over, the starting reagent $C_6H_5P(S)[N(CH_3)_2]_2$ ($t = 17.2$ min; $\delta\,^{31}P = 82.4$ ppm) and the assumed intermediate **15** ($t = 14.9$ min; $\delta\,^{31}P = 66.8$ ppm) [18] were no more detected in the sample, and the GPC analysis showed one major signal at $t = 15.4$ min corresponding to compound **3**, one signal at $t = 14.3$ min for the dimeric species **3D**, and several peaks at $t \leq 13.6$ min for higher molecular weight derivatives (see Figure 3a).

The crude reaction mixture was then diluted with toluene before sulfurization, and heated at reflux temperature for 5 days. A new equilibrium was reached where peaks at $t = 15.4$ min and $t = 14.3$ min prevailed with very little signal at $t \leq 13.6$ min (Figure 3b). The corresponding ^{31}P NMR spectrum exhibited a major singlet at $\delta\,^{31}P = 55.6$ ppm for **3**, the two 1:1 signals for the dimers **3D** and a minor signal at $\delta\,^{31}P \approx 52$ ppm attributed to higher molecular weight species. This means that the monomer/oligomers ratio is temperature and concentration dependent and can be optimized towards the formation of one or the other species. This should be interesting in controlling and optimizing the formation of very large macroring species.



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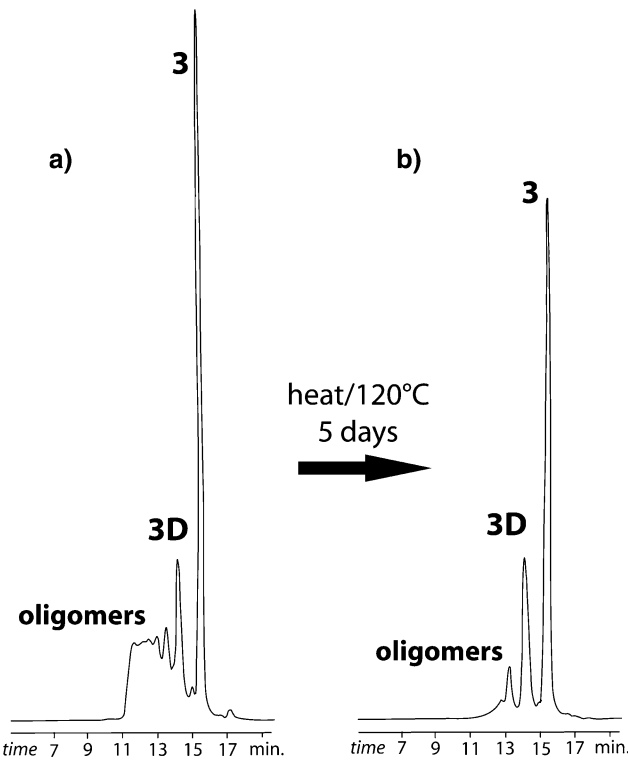

Figure 3. GPC chromatograms of the sulfurized reaction mixture (a) before and (b) after dilution in toluene and heating.

Structural studies by X-ray diffraction

The role of H-bonding in the structural organization of the host is crucial and water molecules often interfere to form hydrates. We have previously reported on the influence of water complexation on the structure of the host in organic media. Two possible conformations of macrocyclic phosphoramide ligands were found in the solid state by X-ray diffraction analysis, depending on the presence or not of a guest water molecule. Without bound guest, the macrocycle is folded to minimize voids through intramolecular H-bonds and dipolar interactions. Alternatively, complexation of water molecule induced strong conformational changes. The guest water is located in a well-defined opened cavity stabilized by H-bonding with the NH and ether oxygen atoms of the host [19, 20]. Herein we provide a new example of this conformational behavior with the crystal structure of the hydrate form of **1**.

The structure analysis shows that in the crystal, macrocyle **1** contains one molecule of water embedded in the crown cavity. The complex is stabilized through H-bonds with all the O and N atoms of the ligand, which are roughly coplanar (deviations from their least squares plane: 0.18, −0.25, −0.08, 0.18, −0.32, and 0.13 Å, for N2, O11, O14, O17, O20 and N4 atoms, respectively). The water encapsulated in the crown lies 1.23 Å above this plane and is coordinated to the heteroatoms of the macrocycle as shown in Table 2. The water complex implies an extended conformation of the ring with the substituents at phosphorus directed outwards (Figure 4), characterized by the *anti* conformation around the P−N bonds. The encapsulation of the water guest is also evidenced in chloroform solution as the NMR water signal is shifted to 3.2 ppm at 20 °C, indicative of H-bonds formation, compared to the usual 1.5−1.6 ppm resonance of water in chloroform solution.

It is interesting to compare the structure of **1** with the more flexible macrocycle **5**, which differs by the number of ethyleneoxy groups in the ring. As viewed in Figures 5 and 6, the macrocyclic cavity of **5** is not really defined and is self-occupied by part of the molecule. The sulfur and phenyl group at phosphorus are out of the cavity and the hexa-ethyleneoxy chain adopts an *S* shape, each curve of the *S* defining a pseudo-cyclic

Table 2. Bond distances (Å) and angles (°) of intramolecular H bonds in **1**·H_2O

	d(D−H)	d(H···A)	d(D···A)	(D−H···A)
Ow−Ha···O11	0.85	2.44	3.059	130
Ow−Ha···O14	0.85	2.08	2.807	143
Ow−Hb···O17	0.76	2.07	2.784	157
Ow−Hb···O20	0.76	2.59	3.132	129
N2−H···Ow	0.86	2.26	2.970	139
N2−H···O20	0.86	2.16	2.582	110
N4−H···Ow	0.86	2.25	2.968	141
N4−H···O11	0.86	2.17	2.598	110

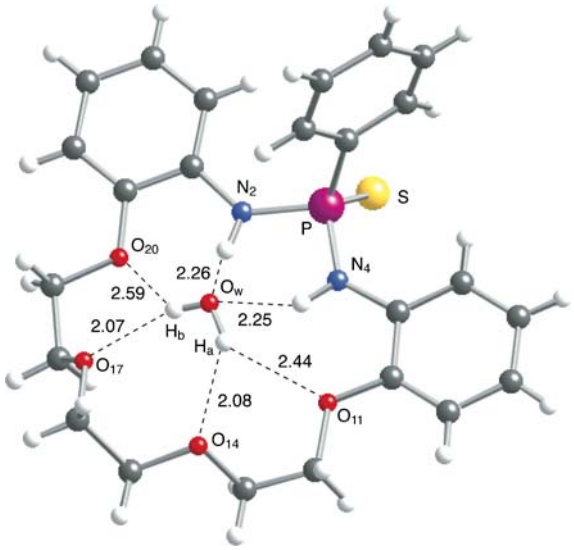

Figure 4. X-Ray molecular structure of **1**·H_2O with H-bond lengths (Å).

crown-ether part with the hydrogen of the corresponding NH group pointing inwards (see Figure 6). This conformation is obtained by the tight folding of the molecule and is further stabilized by the predominance of favorable *aga* conformations of the OCH_2CH_2O moieties. It is surprising to see how self-folding allows to optimize the space available thus eliminating voids from the structure. In this example, the elemental analysis does not show additional water molecule and the ^1H NMR in chloroform shows the H_2O signal at 1.9 ppm indicating that in solution the host molecule does not form strong H-bond with residual water.

The structures of the two closely related macrocycles **7** and **8** are interesting. The conformation of these compounds is dramatically dependent on the phenyl or methyl substituent at phosphorus. In compound **7**, the phenyl and sulfur are out of the macrocyclic part, and are located on the same side of a plane passing through the phosphorus atom as defined in Figure 7a, the other side of this plane being occupied by the cyclic part of the molecule. The macrocycle adopts a bended structure defining a loop with some free space at the cavity level defined by the ethyleneoxy units and the phosphorus group (Figure 8).

This is absolutely not the case with **8**, where the methyl group is embedded in the macrocyclic cavity (Figure 7b). Therefore, there is no free space and the macrocycle adopts a saddle like conformation (Figure 9). It is interesting to compare the dihedral angles sequences observed in each structure with respect to the molecular shape and conformation that result in the solid compounds. The main structuring factors are due to (i) H-bonding with the NH groups and H-bond acceptors (ether oxygens), (ii) the geometry around the phosphorus atom, and (iii) interaction with co-crystallized solvent molecules. In the examples described herein, the conformations are mainly dependent on intramolecular interactions as no close intermolecular

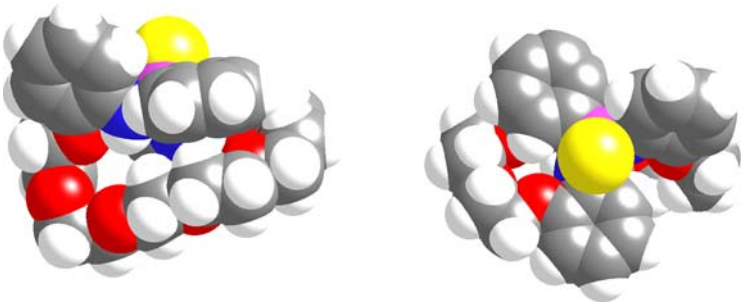

Figure 5. Side and top CPK views of the X-ray molecular structure of **5**.

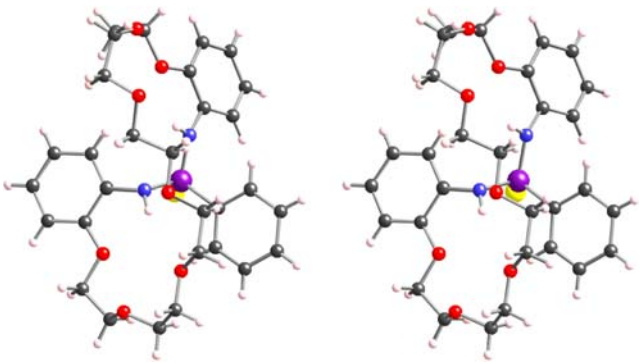

Figure 6. Stereoview of the X-ray molecular structure of **5**.

contacts were observed in the solid-state structures. With macrorings **5** and **7** a bended conformation is observed with the polar oxygen ether atoms mainly oriented inwards with respect to the macrocyclic cavity. In **1** and **8**, the cavity is occupied either by a guest molecule, water in **1**, or by a part of the molecule itself, the P−Me group in **8**. These two situations give rise to dramatically different structures, which are the results of the optimized occupancy of the macrocyclic cavity. In **1** the extended conformation of the macrocycle allowed to fit exactly one water molecule in the cavity, characterized by the *aga* and *agg* conformations of the OCH_2CH_2O sequences and the *anti* conformations around the P−N bonds. Such conformations are characteristic of the encapsulation of a water molecule in the 17-membered ring [10]. The arrangement in **8** displays only the *aga* conformation along the poly-ethyleneoxy chain, favorable for wrapping a guest, and adopts a *gg* conformation at phosphorus, which directs the P−Me group inwards.

Experimental section

General

All manipulations involving air-sensitive species were carried out under dry argon. Toluene was distilled from Na prior to use. Reactions were monitored by ^{31}P NMR and thin layer chromatography (Merck Kieselgel 60F254). Silica gel (Merck Kieselgel 60, 0.040−0.063 mm) and aluminiumoxide (Merck 0.063−0.200 mm) were used for column chromatography. Analytical GPC was performed on Merck Li-Chrogel (PS4 + 2×PS1 columns; 5 μm), with CH_2Cl_2 as eluent (5 mm/min; UV detection at 254 nm). Elemental analyses and mass spectra were performed by the Service Central d'Analyses, CNRS and the Centre de Spectrométrie de Masse, University Claude Bernard Lyon. Melting points were measured with a DSC7 Perkin Elmer calorimeter.

^1H, ^{13}C and ^{31}P NMR spectra were recorded on Varian Unity 500 and Bruker DPX 200 spectrometers. J Coupling constants are in Hz; chemical shifts are in δ values relative to Me_4Si (^1H and ^{13}C) or H_3PO_4 85% (^{31}P). ^{13}C and ^{31}P NMR spectra are proton decoupled. The reported multiplicities of ^{13}C NMR spectra represent J_{PC} couplings.

20-Phenyl-6,7,9,10,12,13,20,21-octahydro-19H-dibenzo[b,g][1,9,12,15,4,6,5]-tetraoxa-diazaphosphacycloheptadecin 20-sulfide (1) [7]

A solution of diamine **10** (9.795 g, 29.5 mmol) [21] and $C_6H_5P[N(CH_3)_2]_2$ (5.782 g, 29.5 mmol) in toluene (1000 ml) was refluxed for 7 days. Sulfur (1.04 g) was then added to the hot solution and the mixture was allowed to reach room temperature. The solvent was

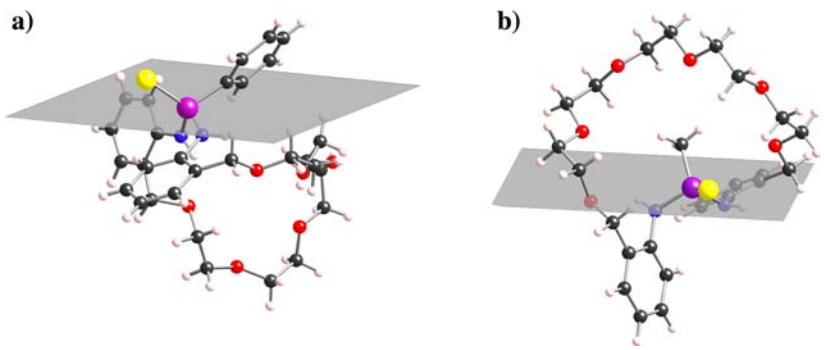

Figure 7. Structures of **7** (a) and **8** (b), showing the cavity occupancy.

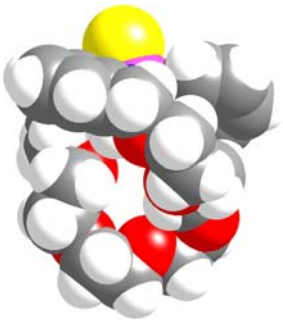

Figure 8. CPK view of the X-ray structure of **7**.

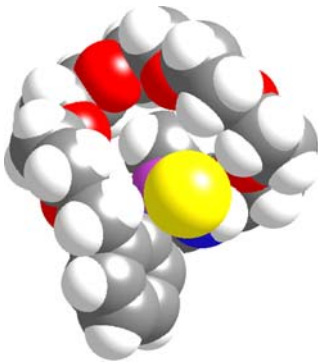

Figure 9. CPK view of the X-ray structure of **8**.

evaporated under reduced pressure to give a solid that was recovered by filtration and dried under vacuum. Recrystallization from dichloromethane afforded crystals of **1**·H_2O (mp 161°C dec., 80% yield). FAB(+) MS 471 $[MH]^+$. Anal. Calcd for $C_{24}H_{27}N_2O_4PS \cdot H_2O$: C 59.01; H 5.98; N 5.73; P 6.34; S 6.56. Found: C 58.87; H 5.89; N 5.70; P 5.93; S 6.61.

20-Phenyl-6,7,9,10,12,13,20,21-octahydro-19H-dibenzo[b,g][1,9,12,15,4,6,5]-tetraoxa-diazaphosphacycloheptadecin 20-oxide (2)

A solution of *m*-chloroperoxybenzoic acid (MCPBA, 0.992 g, 5.75 mmol) in CH_2Cl_2 (25 ml) was added dropwise to a solution of the parent sulfide derivative **1** (2.17 g, 4.61 mmol) in CH_2Cl_2 (350 ml) at 0 °C. After 2 h, a 1 M solution of Na_2CO_3 in H_2O (300 ml) was added. The aqueous phase was extracted with CH_2Cl_2 and the organic phase was washed with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a solid material, which was recrystallized from a mixture of toluene/*n*-hexane or $CHCl_3$/*n*-hexane to give **2** as a crystalline material (mp 147 °C; 68% yield). ESI MS 455.4 $[MH]^+$. ^{1}H NMR ($CDCl_3$): 3.60–3.82 (8H, m, OCH_2), 4.10 (4H, m, OCH_2), 6.35 (2H, d, J_{PH} = 9.7, NH), 6.77 (6H, m, ArH), 7.37 (3H, m, ArH), 7.51 (2H, m, ArH), 7.96 (2H, m, ArH). ^{13}C NMR ($CDCl_3$): 69.07, 69.36, 70.44 (OCH_2), 113.63, 118.32 (J = 1.4), 121.43, 122.28, 128.41 (J = 14.3, PAr), 131.44 (J = 1.9), 131.78 (J = 2.4, PAr), 131.99 (J = 157.0, PAr), 132.22 (J = 10.5, PAr), 147.17 (J = 8.4). ^{31}P NMR ($CDCl_3$): 11.45. Anal. Calcd for $C_{24}H_{27}N_2O_5P \cdot H_2O$: C, 61.01: H, 6.19; N, 5.93; P, 6.56. Found: C, 61.76; H, 5.99; N, 5.69; P, 6.56.

20-Phenyl-6,7,9,10,12,13,15,16,23,24-decahydro-22H-dibenzo[b,g][1,9,12,15,18,4,6,5]-penta-oxadiazaphosphacycloeicosin 23-sulfide (3)

A solution of diamine **11** (3.76 g, 10^{-2} mmol) and $C_6H_5P[N(CH_3)_2]_2$ (2.16 g, 1.1 10^{-2} mmol) in toluene (500 ml) was refluxed for several days until disappearance of the phosphorus reagent. The reaction was monitored by ^{31}P NMR and size exclusion chromatography (SEC). In the present case 17 days were necessary to optimize the formation of the macrocyclic compound. The eventual evaporation of the solvent was compensated by further adduct of equivalent quantities of toluene to the reaction mixture. The formation of polymeric materials was evidenced by ^{31}P NMR and GPC, and addition of more toluene (500 ml) and refluxing for 5 days more, allowed to optimize the formation of the macrocyclic P(III) compound. Sulfur (0.35 g, excess) was then added to the hot solution and the mixture was allowed to reach room temperature. The solvent was evaporated under reduced pressure and the residue was triturated with dichloromethane and pentane to give a first crop of solid compound (63% yield), which was recrystallized from dichloromethane-hexane (mp 154°C dec.). The residue was then carefully purified by column chromatography on silica gel (CH_2Cl_2-acetone 85:15) to give more **3** (total yield: 74%; mp 154 °C (dec)), and the two cyclic dimers *trans*-**3D** and *cis*-**3D**, which were recrystallized from CH_2Cl_2-ethanol (0.12% yield). Higher yields are expected from optimized experimental procedures.

Monomer 3: ESI MS 515.0 $[MH]^+$. ^{1}H NMR (497.85 MHz, $CDCl_3$): 3.50–3.65 (8H, m, OCH_2), 3.66–3.71 (2H, m, OCH_2), 3.75–3.80 (2H, m, OCH_2), 4.08–4.19 (4H, m, OCH_2), 6.34 (2H, d, J_{PH} = 6.5, NH), 6.81 (6H, m, ArH), 7.38–7.47 (3H, d, ArH), 7.50 (2H, d, ArH), 8.11 (2H, m, ArH). ^{13}C NMR (50.32 MHz, $CDCl_3$): 68.43, 69.56, 70.43, 71.12 (OCH_2), 112.15 (ArCH), 118.91 (J = 3.9, ArCH), 121.24, 121.47 (ArCH), 128.27 (J = 14.2, PArCH), 130.54 (J = 2.1, ArCN), 131.61 (J = 3.1, PArCH), 131.82 (J = 12.3, PArCH), 135.49 (J = 120.8, PArC), 148.11 (J = 8.1, ArCO). ^{31}P NMR ($CDCl_3$): 55.60 ppm. Anal. Calcd for $C_{26}H_{31}N_2O_5PS$: C, 60.69; H, 6.07; N, 5.44; P, 6.02; S, 6.23. Found: C, 60.12; H, 6.20; N, 5.37; P, 6.02; S, 6.04.

Dimer 1 *trans* or *cis*-**3D**: mp 191 °C. ESI MS 1029.1 $[MH]^+$. ^{1}H NMR (497.85 MHz, $CDCl_3$): 3.45 (8H, m, OCH_2), 3.52 (8H, m, OCH_2), 3.70 (8H, m, OCH_2), 4.05 (8H, m, OCH_2), 6.03 (4H, d, J_{PH} = 8.6, NH), 6.75–6.85 (12H, m, ArH), 7.28 (4H, d, ArH), 7.36–7.45 (6H, m, ArH), 7.97 (4H, m, ArH). ^{13}C NMR (125.19 MHz, $CDCl_3$): 68.94, 69.47, 70.52, 70.72 (OCH_2), 112.79 (ArCH), 118.58 (J = 3.6, PArCH), 121.50, 122.00 (ArCH), 128.68 (J = 14.3, PArCH), 130.36 (ArCH), 130.87 (J = 12.0, PArCH), 131.99 (J = 3.1, ArCN), 134.83 (J = 126.2, PArC), 147.97 (J = 7.8, ArCO). ^{31}P NMR ($CDCl_3$): 53.21 ppm.

Dimer 2 *cis* or *trans*-**3D**: mp 147 °C. ESI MS: 1029.1 $[MH]^+$. ^{1}H NMR (497.85 MHz, $CDCl_3$): 3.44 (8H, m, OCH_2), 3.51 (8H, m, OCH_2), 3.69 (8H, m, OCH_2), 4.06 (8H, m, OCH_2), 6.01 (4H, d, J_{PH} = 8.7, NH), 6.75−6.85 (12H, m, ArH), 7.28 (4H, d, ArH), 7.33−7.50 (6H, m, ArH), 7.96 (4H, m, ArH). ^{13}C NMR (125.19 MHz, $CDCl_3$): 68.97, 69.47, 70.51, 70.74 (OCH_2), 112.81 (ArCH), 118.55 (J = 3.7, PArCH), 121.51, 122.01 (ArCH), 128.70 (J = 14.3, PArCH), 130.36 (ArCH), 130.81 (J = 12.1, PArCH), 131.99 (J = 3.0, ArCN), 134.85 (J = 125.4, PArC), 147.96 (J = 7.9, ArCO). ^{31}P NMR ($CDCl_3$): 53.15 ppm.

23-Phenyl-6,7,9,10,12,13,15,16,23,24-decahydro-22H-dibenzo[b,g][1,9,12,15,18,4,6,5]-pentaoxadiazaphosphacycloeicosine 23-oxyde (4)

A solution of *m*-chloroperoxybenzoic acid (MCPBA, 0.676 g, 3.9 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a solution of the parent sulfide derivative **3** (1 g, 1.95 mmol) in CH_2Cl_2 (200 ml) at 0 °C. After 1 h, a 1 M solution of K_2CO_3 in H_2O (100 ml) was added. The aqueous phase was extracted with CH_2Cl_2 (50 ml) and the combined organic phases were successively washed with K_2CO_3 1 M solution in water (100 ml), water (100 ml), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was then purified by column chromatography on silica gel (CH_2Cl_2/acetone 9:1) to give a white solid which was recrystallized from a mixture of acetone/CH_2Cl_2/*n*-hexane to give **4** as a crystalline material (mp 179 °C; 69% yield). ESI MS: 499.1 $[M + H]^+$, 521.1 $[M + Na]^+$, 537.1 $[M + K]^+$. ^{1}H NMR (200.13 MHz; $CDCl_3$): 3.66 (8H, m, OCH_2), 3.81 (4H, m, OCH_2), 4.12 (4H, m, OCH_2), 6.59 (2H, d, NH, J_{PH} = 10.5), 6.79 (6H, m, ArH), 7.36 (3H, m, ArH), 7.54 (2H, m, ArH), 7.98 (2H, m, ArH). ^{13}C NMR (50.32 MHz; $CDCl_3$): 68.65, 69.54, 70.47, 71.21 (OCH_2), 112.26, 118.21 (J = 2.8), 121.24, 121.84, 128.39 (J = 10.3, PAr), 130.99 (J = 2.2), 131.78 (J = 2.9, PAr), 132.11 (J = 10.3, PAr), 132.36 (J = 155.4, PAr), 147.23 (J = 8.7). ^{31}P NMR (81.02 MHz, $CDCl_3$): 11.5. Anal. Calcd for $C_{26}H_{31}N_2O_5PS$: C, 62.64; H, 6.27; N, 5.62; P, 6.21. Found: C, 62.72; H, 6.46; N, 5.72; P, 6.07.

29-Phenyl-6,7,9,10,12,13,15,16,18,19,21,22,29,30-tetradecahydro-28H-dibenzo[b,g][1,9,12,15,18,21,24,4,6,5]-heptaoxadiazaphosphacyclohexacosin 29-sulfide (5)

A solution of diamine **12** (13.21 g, 28.4 mmol) and $C_6H_5P[N(CH_3)_2]_2$ (5.98 g, 30.5 mmol) in toluene (1000 ml) was heated at reflux temperature for several days until complete disappearing of the starting compounds. Sulfur (1.0 g, 1.1 eq.) was then added and the mixture was allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the crude compound was purified by column chromatography on silica gel (CH_2Cl_2/acetone 85:15). To give **5** (39% yield). Recrystallization from ethanol afforded crystals of the pure compound (mp 104.5 °C). Further elution with CH_2Cl_2/acetone 7:3 then 1:1, led to the separation of the dimeric **5D** (≈500 mg) and trimeric **5T** (≈290 mg) macrocyclic compounds as oils. The recovery of the dimer and trimer derivatives was not optimized. More derivatives are still mixed in several fractions of the chromatography.

Monomer 5. FAB(+) MS 603.1 $[MH]^+$. ^{1}H NMR (497.85 MHz, $CDCl_3$): 3.42−3.60 (m, 16H, OCH_2), 3.76 (m, 4H, OCH_2), 4.12 (m, 4H, OCH_2), 6.09 (d, J_{PH} = 6.9 Hz, 2H, NH), 6.79−6.86 (m, 6H, ArH), 7.37 (d, 2H, ArH), 7.40−7.50 (m, 3H, ArH), 8.06 (m, 2H, ArH). ^{13}C NMR (125.19 MHz, $CDCl_3$): 69.28, 69.54, 70.55, 70.68 (2C), 70.84 (OCH_2), 112.92 (ArCH), 119.12 (J = 3.9, PArCH), 121.48, 121.96 (ArCH), 128.54 (J = 14.3, PArCH), 130.58 (ArCH), 131.48 (J = 12.0, PArCH), 131.92 (J = 3.3, ArCN), 135.04 (J = 125.3, PArC), 148.24 (J = 7.8, ArCO). ^{31}P NMR ($CDCl_3$) 55.15 ppm. Anal. Calcd for $C_{30}H_{39}N_2O_7PS$: C, 59.79; H, 6.52; N, 4.65; P, 5.14; S, 5.32. Found C, 59.91; H, 6.65; N, 4.68; P, 5.13; S, 5.18.

Dimer 5D. FAB(+) MS 1205.3 $[MH]^+$. ^{1}H NMR spectrum identical to that of **5**. ^{31}P NMR ($CDCl_3$) 52.56 ppm.

Trimer 5T. FAB(+) MS 1807.5 $[MH]^+$. ^{1}H NMR spectrum identical to that of **5**. ^{31}P NMR ($CDCl_3$) 52.33 ppm.

3-Methyl-11,14,17,20,23,26-hexaoxa-2,4,3-diazaphosphatricyclo[26,3,1,1^{5,9}]-tritiaconta-1(32),5,7,9(33),28,30-hexaene-3-sulfide (6)

A solution of diamine **13** (2 g, 4.46 mmol) and $CH_3P[N(CH_3)_2]_2$ (0.65 ml) in toluene (200 ml) was heated at 70−80 °C for 20 h. Sulfur (0.2 g, 1.4 eq.) was then added and the mixture was allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the crude compound was purified by column chromatography on silica gel (CH_2Cl_2/acetone 9:1). Recrystallization from ethanol 95% gave pure **6** (mp 102 °C, 31% yield). CI MS: 525 $[MH]^+$. ^{1}H NMR ($CDCl_3$; 200.13 MHz) 2.12 (3H, d, PCH_3, J_{PH} 14.5 Hz), 3.5−3.8 (20H, m, OCH_2CH_2O), 4.48, 4.53 (4H, AB d, $ArCH_2$, J_{AB} = 13.0 Hz), 5.85 (2H, d, NH, J_{PH} = 11.6 Hz), 6.75 (2H, d, Ar), 6.99 (2H, br d, Ar), 7.12 (2H, t, Ar), 7.29 (2H, br s, Ar). ^{13}C NMR ($CDCl_3$; 50.32 MHz) 21.79 (PCH_3, J = 91.1 Hz), 68.95, 70.48, 70.69, 70.78, 70.78, 72.29 (OCH_2), 116.78 (Ar, J = 6.3 Hz), 117.55 (Ar, J = 6.9 Hz), 120.51, 129.01, 139.68 (Ar), 140.59 (Ar, J = 4.0 Hz). ^{31}P NMR ($CDCl_3$; 81 MHz) 53.8 ppm. Anal. Calcd for: $C_{25}H_{37}N_2O_6PS \cdot 1.5H_2O$: C, 54.43; H, 7.31; P, 5.61; S, 5.81. Found : C, 54.71; H, 7.34; P, 5.73; S, 5.64.

28-Phenyl-7,8,10,11,13,14,16,17,19,20,28,29-dodecahydro-5H,22H-dibenzo[c,h][1,11,14,17,20,23,5,7,6]-hexaoxadiazaphosphacyclopentacosine 28-sulfide (7)

A solution of diamine **14** (1.208 g, 2.70 mmol) and $C_6H_5P[N(CH_3)_2]_2$ (0.600 g, 3.06 mmol) in toluene (100 ml) was heated at 80 °C for 2 days. Sulfur (0.11 g, 1.1 eq.) was then added and the mixture was allowed to cool to room temperature. The solvent was evaporated

under reduced pressure and the crude compound was purified by column chromatography on silica gel (CH_2Cl_2/acetone 9:1) to give **7** as an oil, which solidified on standing (mp 90 °C, 30% yield). ^{1}H NMR (200 MHz, $CDCl_3$) : 3.40−3.65 (m, 20H, OCH_2), 4.57 & 4.54 (4H, dAB, J_{AB} = 11.9, $ArCH_2$), 6.77 (2H, d, J_{PH} = 8.2, NH), 6.90 (t, 2H, ArH), 7.08−7.20 (m, 4H, ArH), 7.39−7.47 (m, 5H, ArH), 8.02−8.15 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): 69.42, 70.30, 70.58, 70.68, 70.76, 72.73 (OCH_2), 121.10 (CH, J = 4.0), 122.07 (CH), 127.53 (Cq, J = 7.8), 128.54 (PAr, J = 14.2), 128.76, 129.61, 131.20 (PAr, J = 12.1), 131.87 (PAr, J = 3.1), 135.61 (PAr, J = 123.2), 140.19. ^{31}P NMR ($CDCl_3$): 53.93 ppm. Anal. Calcd for $C_{30}H_{39}N_2O_6PS$: C, 61.42; H, 6.70; P, 5.28; S, 5.47. Found: C, 61.41; H, 6.63; P, 5.28; S, 5.36.

28-Methyl-7,8,10,11,13,14,16,17,19,20,28,29-dodecahydro-5H,22H-dibenzo[c,h][1,11,14,17,20,23,5,7,6]-hexaoxadiazaphosphacyclopentacosine 28-sulfide (8)

A solution of diamine **14** (1.29 g, 2.87 mmol) and $CH_3P[N(CH_3)_2]_2$ (0.500 g) in toluene (150 ml) was heated at 110°C for 4 days. Sulfur (0.14 g) was then added and the mixture was allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the crude compound was purified by column chromatography on silica gel (CH_2Cl_2/acetone 9:1). Recrystallization from ethanol 95% gave pure **8** (mp 99 °C, 49% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 2.17 (3H, d, J_{PH} = 14.0, PCH_3), 3.50−3.75 (m, 20H, OCH_2), 4.67 and 4.55 (4H, dAB, J_{AB} = 11.5, $ArCH_2$), 6.46 (2H, d, J_{PH} = 9.0, NH), 6.92 (t, 2H, ArH), 7.10−7.24 (m, 4H, ArH), 7.55 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): 22.62 (PCH_3, J = 89.0), 69.59, 70.48, 70.48, 70.65, 70.73, 72.69 (OCH_2), 120.51 (J = 4.0), 122.05, 127.49 (Cq, J = 7.5), 129.02 (CH), 129.67 (CH), 140.44 (Cq, J = 3.5). ^{31}P NMR ($CDCl_3$): 58.11 ppm. Anal. Calcd for $C_{25}H_{37}N_2O_6PS$: C, 57.24; H, 7.11; N, 5.34; P, 5.90; S, 6.11. Found: C, 57.34; H, 7.32; N, 5.45; P, 5.60; S, 6.11.

28-Methyl-7,8,10,11,13,14,16,17,19,20,28,29-dodecahydro-5H,22H-dibenzo[c,h][1,11,14,17,20,23,5,7,6]-hexaoxadiazaphosphacyclopentacosine 28-oxyde (9)

A solution of *m*-chloroperoxybenzoic acid (MCPBA, 0.271 g, 1.57 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a solution of the parent sulfide macrocycle **8** (0.685 g, 1.31 mmol) in CH_2Cl_2 (100 ml) at 0 °C. The mixture is stirred overnight at room temperature and 0.175 g of MCPBA were then added and the mixture was heated to reflux temperature until the disappearing of the starting compound (TLC, elution with CH_2Cl_2/acetone 9:1). A concentrated solution of K_2CO_3 in H_2O (100 ml) was added, and the organic phase was washed with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was then purified by column chromatography on silica gel (CH_2Cl_2/acetone 9:1, 1:1) to give **9** as an oil, which solidified on standing (75% yield). ^{1}H NMR (200 MHz, $CDCl_3$): 1.83 (3H, d, J_{PH} = 15.7, PCH_3), 3.40−3.65 (m, 20H, OCH_2), 4.57 & 4.54 (4H, dAB, J_{AB} = 11.8, $ArCH_2$), 6.51 (2H, d, J_{PH} = 11.0, NH), 6.88 (t, 2H, ArH), 7.09 (d, 2H, ArH), 7.19 (m, 2H, ArH), 7.55 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$): 15.84 (PCH_3, J = 116.9), 69.10, 70.37, 70.48, 70.68, 70.71, 72.48 (OCH_2), 119.64 (J = 2.9, CH), 121.43 (CH), 126.04 (Cq, J = 7.5), 129.30 (CH), 129.70 (CH), 140.68 (Cq). ^{31}P NMR ($CDCl_3$): 19.74 ppm. Anal. Calcd for $C_{25}H_{37}N_2O_7P \cdot 0.5\ H_2O$: C, 58.02; H, 7.40; N, 5.41; P, 5.98. Found: C, 58.32; H, 7.50; N, 5.29; P, 5.34.

Hexaethylene glycol bis(o-aminophenyl ether) (12)

Hexaethylene glycol bis(*o*-nitrophenyl ether): A mixture of hexaethyleneglycol ditosylate (60 g, 101.5 mmol) [22], 2-nitrophenol (28.26 g, 203 mmol) and K_2CO_3 (28.08 g, 203 mmol) in DMF (250 ml) was refluxed overnight. The reaction mixture was then poured on crushed ice and the aqueous solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting brown oil was dissolved in CH_2Cl_2 and filtered through a column of alumina and eluted with CH_2Cl_2. Evaporation of the solvent gave the expected compound as a yellow oil (84% yield). ^{1}H NMR (200.13 MHz, $CDCl_3$): 3.43−3.67 (m, 16H, OCH_2), 3.77 (m, 4H, OCH_2), 4.12 (m, 4H, OCH_2), 6.92 (m, 2H, ArH), 7.0 (m, 2H, ArH), 7.39 (m, 2H, ArH),7.66 (m, 2H, ArH). ^{13}C NMR (50.32 MHz, $CDCl_3$): 68.88, 69.22, 69.91, 70.14, 70.20, 70.85 (OCH_2), 114.90, 120.20, 125.05, 133.79, 139.89, 151.84 (ArC).

Hydrazine monohydrate (25 ml) was added dropwise under argon to a solution of the dinitro compound (44.7 g, 85 mmol) and Pd/C catalyst 10% (2 g) in ethanol (400 ml). The mixture was heated at reflux temperature for 2 h and then filtered at room temperature over celite®. The solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 and passed through a short column of alumina to give **12** as a yellow oil (85% yield). ^{1}H NMR (200.13 MHz, $CDCl_3$): 3.56−3.67 (m, 16H, OCH_2), 3.75 (m, 4H, OCH_2), 3.94 (br s, 4H, NH_2), 4.05 (m, 4H, OCH_2), 6.54−6.80 (m, 8H, ArH). ^{13}C NMR (50.3 MHz, $CDCl_3$): 67.92, 69.24, 70.08, 70.12 (2C), 70.20 (OCH_2), 112.59, 114.66, 117.43, 121.34, 138.96, 145.75 (ArC).

2,5,8,11,14,17-Hexaoxaoctadecane-1,18-diyl-bis(m-phenylamine) (13)

A solution of 3-aminobenzyl alcohol (4.43 g, 36 mmol) in THF (100 ml) was added dropwise to a solution of pentaethyleneglycol ditosylate (9.98 g, 18.3 mmol) and NaH (1.73 g, 60% in oil, 43.2 mmol) in THF (200 ml). The mixture was then refluxed for 32 h. Water was added and THF was evaporated under vacuum. The aqueous solution was extracted with CH_2Cl_2 and the organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave a brown oily residue, which was purified by column chromatography

on silica gel (CH_2Cl_2/ethyl acetate 1:1; then ethyl acetate) to give **13** (3.3 g, 41%) as a pale brown oil. ^{1}H NMR (200.13 MHz; $CDCl_3$) 3.5−3.6 (20H, br m, OCH_2CH_2O), 3.73 (4H, br s, NH_2), 4.40 (4H, s, $ArCH_2O$), 6.4−6.7 (6H, m, ArH), 7.03 (2H, t, J 7.8 Hz, ArH). ^{13}C NMR (50.32 MHz ; $CDCl_3$) 69.22, 70.51 (2C), 70.55 (2C), 73.07 (OCH_2), 114.16, 114.19, 117.62, 129.12, 139.42, 146.62 (ArC). Anal. Calcd for $C_{24}H_{36}N_2O_6$: C, 64.26; H, 8.09; N, 6.24. Found : C, 63.48; H, 7.89; N, 6.25.

2,5,8,11,14,17-Hexaoxaoctadecane-1,18-diyl-bis(o-phenylamine) (14)

A solution of 2-aminobenzyl alcohol (4.5 g, 37 mmol) in THF (100 ml) was added dropwise to a solution of pentaethyleneglycol ditosylate (9.99 g, 18.0 mmol) and NaH (1.76 g, 60% in oil, 44 mmol) in THF (200 ml). The mixture was then refluxed for 24 h. Water was added and THF was evaporated under vacuum. The aqueous solution was extracted with CH_2Cl_2 and the organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate 1:1, 2:3, 0:1) to give **14** as a pale yellow oil (4.74 g, 56%). ^{1}H NMR (200.13 MHz; $CDCl_3$) 3.50−3.75 (20H, br m, OCH_2CH_2O), 4.31 (4H, br s, NH_2), 4.53 (4H, s, $ArCH_2O$), 6.61−6.68 (4H, m, ArH), 7.0−7.13 (4H, m, ArH). ^{13}C NMR (50.32 MHz; $CDCl_3$) 68.47, 70.19, 70.29, 70.38 (2C), 72.13 (OCH_2), 115.54, 117.26, 121.79, 129.09, 129.76, 146.61 (ArC). Anal. Calcd for: $C_{24}H_{36}N_2O_6 \cdot 0.5\ H_2O$: C, 63.0; H, 8.15; N, 6.12. Found: C, 62.84; H, 8.20; N, 6.03.

X-ray diffraction analysis

Crystals suitable for X-ray diffraction were grown by slow evaporation of solutions of the compounds in dichloromethane (**1**) or ethanol (**5**, **7** and **8**). The X-ray intensity data were measured at room temperature for **1**, **7** and **8** using a Syntex P21 diffractometer. For compound **5**, the data were collected at 100 K with a MAR345 image plate; the crystal was mounted in inert oil and transferred to the cold gas stream for flash cooling. For each data collection, a graphite monochromatized MoKα radiation was used (λ = 0.71069 Å). The crystal data and the data collection parameters are summarized in Table 3. For the data collected with the Syntex diffractometer the unit cell parameters were refined using 15 reflections in the range $5° < 2\Theta < 30°$; for the data set at 100 K, the unit cell parameters were refined using all the collected spots after the integration process.

The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 using SHELXL97 [23] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by Fourier-difference when possible (it was

Table 3. Crystal data and refinement parameters for **1**·H_2O, **5**, **7** and **8**

	1 · H_2O	**5**	**7**	**8**
Formula	$C_{24}H_{27}N_2O_4PS \cdot H_2O$	$C_{30}H_{39}N_2O_7PS$	$C_{30}H_{39}N_2O_6PS$	$C_{25}H_{37}N_2O_6PS$
Formula wt	488.52	602.66	586.66	524.60
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	*P2$_1$/c*	*P2$_1$/n*	*P-1*	*Pbca*
a (Å)	10.839 (4)	13.943 (2)	9.3180 (12)	9.8690 (10)
b (Å)	8.679 (2)	13.629 (3)	9.503 (2)	19.064 (2)
c (Å)	25.601 (10)	16.683 (5)	17.411 (4)	28.630 (3)
α (deg)	90.00	90.00	92.74 (2)	90.00
β (deg)	91.76 (2)	96.24 (2)	96.34 (1)	90.00
γ (deg)	90.00	90.00	90.07 (1)	90.00
V (Å^3)	2407 (1)	3151 (1)	1530 (1)	5441 (1)
D_x (g cm^{-3})	1.35	1.27	1.27	1.28
Z	4	4	2	8
F(000)	1032	1280	624	2240
μ (mm^{-1})	0.239	0.200	0.202	0.393
Crystal size (mm)	0.25 × 0.15 × 0.12	0.40 × 0.32 × 0.30	0.32 × 0.30 × 0.20	0.40 × 0.22 × 0.20
$2\theta_{max}$ (deg)	47	52	44	49
Range of *hkl*	$0 \le H \le 12$	$0 \le h \le 17$	$-6 \le h \le 11$	$0 \le h \le 11$
	$0 \le k \le 19$	$0 \le k \le 16$	$-10 \le k \le 7$	$0 \le k \le 22$
	$-28 \le l \le 28$	$-20 \le l \le 19$	$-18 \le l \le 18$	$0 \le l \le 33$
No. of unique refl.	3453	6001	3717	4634
No. of observed refl. [$I \ge 2\sigma(I)$]	2137	5630	2109	3026
No. of parameters	324	378	382	428
R (*R* all data)	0.051 (0.091)	0.036 (0.038)	0.074 (0.129)	0.046 (0.077)
ωR	0.098	0.096	0.171	0.095
S	0.968	1.000	1.02	0.996
$\Delta\rho$ (max, min) (e Å^{-3})	0.20, −0.19	0.32, −0.32	0.36, −0.24	0.34, −0.19

the case for the H of the water molecule in **1**); otherwise they were calculated with AFIX. The H atoms were included in the refinement with a common isotropic temperature factor. In the structure of **1**, two positions were refined for atoms C15 and C16, restraints on bond lengths and angles of the disordered part were applied. For structure of **7**, C14 and O24 were disordered and refined on two sites. The details of the refinement and the final R indices are presented in Table 3.

Crystallographic data for **1**·H_2O, **5**, **7** and **8** have been deposited with the Cambridge Crystallographic Data Center as CIF files CCDC No 298646 (**5**), 298647 (**1**), 298648 (**8**) and 298649 (**7**) [24] Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.ac.uk).

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