Synthesis and molecular structure of new phosphorous-crown compounds containing the thiophosphoryl group

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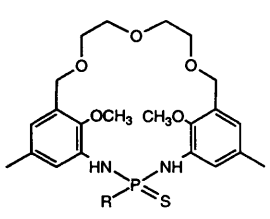
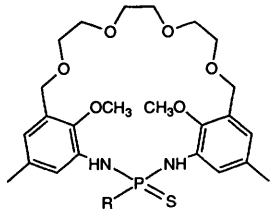
The synthesis and characterization of four phosphorus macrocycles (1–4) are reported. The X-ray crystal structures of compounds 1–4 and solvate 1·H_2O show the molecules in asymmetric conformations with at least one methyl group of the phenoxy substituents oriented toward the centre of the macrocyclic cavity. Variable-temperature ^1H NMR experiments show that in solution the molecules exist mainly as rapidly interconverting conformers. In the 18-membered ring 1, the dynamic process results in the enantiomerization of asymmetric conformers with a barrier of 8 kcal mol^{-1}.‡ The 21-membered ring 3 is more flexible and exists in several conformations.

Recent developments in the chemistry of macrocyclic phosphorus compounds have provided significant information about the molecular structure and the complexing properties of these new ligands.[1] As compared to crown ethers and other analogues containing oxygen or nitrogen binding sites, the stereochemistry of the phosphorus environment usually prevents molecular (re)organization that leads to the optimized structure of the complex. Previously, we have demonstrated that it was possible to synthesize phosphorus-containing crown ethers by a simple ring closure reaction of a diamine with a bis(dimethylamino)phosphane.[2–4] In solution these molecules exist mainly as rapidly interconverting conformers. This generally leads to a decrease of the stability of complexes with cationic species. Furthermore, the phosphorus group is seldom involved in complex formation because of its unfavourable orientation relative to the macrocyclic cavity.[4,5] One possible approach to improve the binding capabilities of these compounds is to freeze them in a conformation containing a preorganized macrocyclic cavity suitable for complexation of adapted guests. This can be achieved by rigidifying the whole structure by adding a bridging unit between the two NH phosphoramide groups, leading to a pseudo-hemispherand structure.[6,7]

In this paper we report the synthesis and molecular structures of four thiophosphonamide macrocyclic compounds with a partial crown ether structure (**1–4**). These compounds are precursors of a family of constrained phosphahemispherands which are potentially efficient binders towards alkali metal and ammonium cations.[7] Compounds **1–4** differ in the size of the macrocycle and the methyl or phenyl substituent of the thiophosphoryl group. The combination of a phosphonamide unit with anisyl units results in greater molecular rigidity and can lead to partially organized ligands that incorporate additional binding sites in a complementary manner to the phosphorus moieties. We undertook a study of their structures to gain reliable information on the molecular structure of these flexible partners, and particularly on the existence of a preformed cavity, and on the environment of the phosphorus atom which is involved in further rigidification steps. Finally, variable-temperature ^1H NMR studies have been performed, and the conformational behaviour of **1** and **3** is discussed. The thiophosphoryl P=S derivatives are described in this paper. Phosphoryl P=O compounds are also accessible and will be described elsewhere.



1 R = CH_3
2 R = C_6H_5



3 R = CH_3
4 R = C_6H_5

Experimental

General

All manipulations involving air-sensitive species were carried out under dry nitrogen or argon. Solvents were purified by standard procedures. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC200 or AM300 and Varian Unity +500 spectrometers. Chemical shifts are in δ values relative to $SiMe_4$ (^1H and ^{13}C) or H_3PO_4 85% (^{31}P). J values are given in Hz. ^{13}C and ^{31}P NMR spectra are proton decoupled unless otherwise noted. The reported multiplicities of ^{13}C NMR spectra represent ^{31}P–^{13}C couplings. Mass spectra were obtained by the electron impact (EI) or chemical ionization (CI) methods. Elemental analyses were performed by the Service Central d'Analyses, CNRS. Melting points were determined on a DSC apparatus or with a Reichert melting point apparatus. Reactions were monitored by ^{31}P NMR and thin layer chromatography (Merck Kieselgel $60F_{254}$). Silica gel used for column chromatography was Merck Kieselgel 60. Di- and tri-ethylene glycol ditosylate were prepared according to the literature procedure.[8]

Preparation of 6-bromomethyl-4-methyl-2-nitrophenol 6

A solution of 47% HBr (600 ml) was cooled with an ice bath and acetic acid (325 ml) was then added dropwise. 4-Methyl-2-nitrophenol **5** (96.51 g, 0.630 mol), paraformaldehyde (58 g)

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‡ 1 cal = 4.184 J.

and acetic anhydride (62 ml), were successively added. The mixture was heated to 80 °C for 24 h. A yellow precipitate formed. After cooling to room temp., the yellow solid was filtered off, washed with water and dried *in vacuo* (148.8 g, 96%). Mp 127 °C; $\delta_H(CDCl_3)$ 2.33 (3 H, s, CH_3), 4.55 (2 H, s, CH_2Br), 7.48 (1 H, s, ArH), 7.86 (1 H, s, ArH), 10.87 (1 H, s, OH); $\delta_C(CDCl_3)$ 20.21 (CH_3), 26.31 (CH_2Br), 124.95, 139.54 (ArC), 128.43, 129.67, 133.46, 151.15 (ArCq). Anal. Calc. for $C_8H_8NO_3Br$: C, 39.05; H, 3.28; N, 5.69; Br, 32.47%; Found: C, 39.28; H, 3.20; N, 5.74; Br, 32.57%.

Preparation of 6-hydroxymethyl-4-methyl-2-nitrophenol 7

A solution of 6-bromomethyl-4-methyl-2-nitrophenol **6** (10 g, 41 mmol) dissolved in 1-methyl-2-pyrrolidinone (170 ml) and water (30 ml) was heated at 120 °C for 11 h. After cooling to room temp., the reaction mixture was poured into 400 ml of water and extracted with Et_2O (3 × 200 ml). The organic layers were washed with water (2 × 200 ml), dried ($MgSO_4$), and concentrated *in vacuo* to give a yellow powder. The product was recrystallized from CH_2Cl_2–hexane to give 5.17 g of pure **7** (69%); mp 97 °C; $\delta_H(CDCl_3)$ 2.33 (3 H, s, CH_3), 4.76 (2 H, s, CH_2O), 7.48 (1 H, br s, ArH), 7.82 (1 H, br s, ArH), 10.78 (1 H, s, OH); $\delta_C(CDCl_3)$ 20.36 (CH_3), 60.47 (CH_2O), 123.47, 137.28 (ArCH), 129.7, 131.34, 133.06, 150.86 (ArCq). Anal. Calc. for $C_8H_9NO_4$: C, 52.46; H, 4.95; N, 7.65%; Found: C, 52.56; H, 4.94; N, 7.50%.

Preparation of 2-methoxy-5-methyl-3-nitrobenzyl alcohol 8

A mixture of 6-hydroxymethyl-4-methyl-2-nitrophenol **7** (9.14 g, 50 mmol), potassium carbonate (6.9 g, 50 mmol) and dimethyl sulfate (6.3 g, 50 mmol) in 160 ml of acetone was refluxed for 4 h. The reaction mixture was concentrated and ice (25 g) and 15 ml of a concentrated ammonium hydroxide solution in water were added to the residue. The solution was then acidified with concentrated HCl and the mixture extracted with Et_2O. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give a brown oil which was used without further purification: crystallized on standing, yield 9.2 g (93%); mp < 30 °C; $\delta_H(CDCl_3)$ 2.27 (3 H, s, CH_3), 3.79 (3 H, s, OCH_3), 4.65 (2 H, s, CH_2O), 7.41 (1 H, br s, ArH), 7.46 (1 H, br s, ArH); $\delta_C(CDCl_3)$ 20.40 (CH_3), 59.52 (CH_2O), 62.68 (OCH_3), 124.45, 134.05 (ArCH), 134.32, 136.58, 142.91, 148.70 (ArCq).

Preparation of 2-methoxy-5-methyl-3-aminobenzyl alcohol 9

To 2-methoxy-5-methyl-3-nitrobenzyl alcohol **8** (10 g, 51 mmol) and 10% Pd/C (700 mg) dissolved in 95% ethanol (250 ml) was added dropwise 7.4 ml of hydrazine monohydrate (153 mmol). The mixture was stirred at reflux temperature for 2 h and then filtered through a pad of celite to remove the catalyst. Solvent and excess hydrazine were removed *in vacuo* to give the crude product as on oil which was used without further purification (8.4 g, 98%); $\delta_H(CDCl_3)$ 2.20 (3 H, s, CH_3), 3.74 (5 H, s, OCH_3 and NH_2), 4.61 (2 H, s, CH_2O), 6.50 (1 H, br s, ArH), 6.52 (1 H, br s, ArH); $\delta_C(CDCl_3)$ 20.88 (CH_3), 60.05 (OCH_3), 61.00 (CH_2O), 116.46, 119.17 (ArCH), 133.57, 134.46, 139.41, 142.96 (ArCq); Anal. Calc. for $C_9H_{13}NO_2$: C, 64.65; H, 7.83; N, 8.38%; Found: C, 63.98; H, 7.83; N, 8.23%.

Preparation of 1,9-Bis(2-methoxy-5-methyl-3-aminophenyl-2,5,8-trioxanonane 10

A solution of 2-methoxy-5-methyl-3-aminobenzyl alcohol **9** (4 g, 24 mmol) in tetrahydrofuran (80 ml) was added to a solution of diethyleneglycol ditosylate (4.96 g, 12 mmol) and NaH (1.06 g, 60% in oil, 26 mmol) in tetrahydrofuran (140 ml). The mixture was heated under reflux for 48 h and then left overnight at room temp. A minimum amount of water was added and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, washed with dilute NaOH solution and water, and dried ($MgSO_4$). Removal of the solvent gave a yellowish oil which was subjected to flash chromatography on silica. Elution with CH_2Cl_2–ethyl acetate (1:1) yielded **10** as an oil (3.15 g, 65%); $\delta_H(CDCl_3)$ 2.19 (6 H, s, CH_3), 3.49 (4 H, br s, NH_2), 3.66 (8 H, s, OCH_2CH_2O), 3.72 (6 H, s, OCH_3), 4.52 (4 H, s, $ArCH_2O$), 6.49 (2 H, br d, ArH, *J* 1.6, 6.57 (2 H, br, d, ArH, *J* 1.6); $\delta_C(CDCl_3)$ 20.92 (CH_3), 60.37 (OCH_3), 68.18, 69.49, 70.54 (OCH_2), 116.40, 120.18 (ArCH), 130.78, 134.05, 139.39, 143.46 (ArCq); Anal. Calc. for $C_{22}H_{32}N_2O_5 \cdot 0.5H_2O$: C, 63.90; H, 8.04; N, 6.77%; Found: C, 64.31; H, 7.93; N, 6.61%.

Preparation of 1,12-Bis(2-methoxy-5-methyl-3-aminophenyl-2,5,8,11-tetraoxadodecane 11

The diamine **11** was prepared as above from 2-methoxy-5-methyl-3-aminobenzyl alcohol **9** (4.35 g, 26 mmol) in THF (80 ml); triethyleneglycol ditosylate (6.56 g, 14 mmol) and NaH (1.14 g, 60% in oil, 29 mmol) in THF (180 ml). Reflux for 48 h. Chromatography on silica eluting with CH_2Cl_2, followed by CH_2Cl_2–ethyl acetate (1:1) afforded **11** (3.3 g, 56%) as a pale-yellow oil; $\delta_H(CDCl_3)$ 2.19 (6 H, s, CH_3), 3.64 (16 H, m, OCH_2 and NH_2), 3.72 (6 H, s, OCH_3), 4.51 (4 H, s, CH_2O), 6.50 (2 H, br d, ArH), 6.56 (2 H, br d, ArH); $\delta_C(CDCl_3)$ 20.91 (CH_3), 60.34 (OCH_3), 68.13, 69.45, 70.53, 70.53 (OCH_2), 116.37, 120.13 (ArCH), 130.76, 134.02, 139.36, 143.45 (ArCq); Anal. Calc. for $C_{24}H_{36}N_2O_6 \cdot 0.5H_2O$: C, 63.00; H, 8.15; N, 6.12%; Found: C, 63.06; H, 8.05; N, 6.22%.

Synthesis of macrocycles 1–4

A typical experimental procedure is as follows.

3,7,21-Trimethyl-23,24-dimethoxy-11,14,17-trioxa-2,4-diaza-3λ^5-phosphatricyclo[17.3.1.1^{5,9}]tetracosa-1(23),5,7,9(24),19,21-hexaene-3-thione 1. A solution of bis(dimethylamino)methylphosphine (0.75 g, 5.6 mmol) and the diamine **10** (2.06 g, 5.1 mmol) in toluene (500 ml) was stirred for 3 d at 80 °C. The dimethylamine formed during the reaction was evacuated by a stream of dry nitrogen or argon. After completion of the reaction, sulfur (0.2 g, excess) was added and the heating stopped. The mixture was further stirred until it reached room temp. The solvent was rotary evaporated and the residue was first purified by column chromatography on silica with 9:1 CH_2Cl_2–ethyl acetate as eluent, and recrystallized from CH_2Cl_2–hexane at −20 °C yielding pure **1** (1.15 g, 47%), mp 122 °C; $\delta_H(CDCl_3)$ 2.21 (6 H, s, CH_3), 2.33 (3 H, d, PCH_3, J_{PH} 14.6), 3.35 (6 H, s, OCH_3) 3.26–3.51 (8 H, m, OCH_2CH_2O), 4.32, 4.34 (4 H, AB, $ArCH_2$, J_{AB} 12), 5.58 (2 H, d, NH, J_{PH} 7.3), 6.65 (2 H, br s, ArH), 7.42 (2 H, br s, ArH); $\delta_C(CDCl_3)$ 21.04 (CH_3), 26.15 (PCH_3, *J* 97.1), 61.78 (OCH_3), 67.98, 68.60, 70.17 (OCH_2), 120.05 (ArC, *J* 4), 125.42, 130.65, 133.14 (ArC, *J* 4), 133.32, 146.87 (ArC, *J* 7); $\delta_P(CDCl_3)$ 56.1 ppm.; *m/z* (Cl) 481 (M + H), 498 (M + H + NH_3); Anal. Calc. for $C_{23}H_{33}N_2O_5PS$: C, 57.48; H, 6.92; N, 5.83; P, 6.44; S, 6.67%; Found: C, 57.30; H, 6.83; N, 6.03; P, 6.61; S, 6.75%.

7,21-Dimethyl-23,24-dimethoxy-3-phenyl-11,14,17-trioxa-2,4-diaza-3λ^5-phosphatricyclo[17.3.1.1^{5,9}]tetracosa-1(23),5,7,9(24),19,21-hexaene-3-thione 2.[2] The title compound was similarly prepared from the diamine **10** (2.29 g, 5.6 mmol) and 1.1 equiv. of bis(dimethylamino)phenylphosphine in refluxing toluene (600 ml) for 10 d. The crude product was purified by column chromatography on silica with 9:1 CH_2Cl_2–ethyl acetate as eluent followed by increasing quantities of ethyl acetate (up to 1:1). Recrystallization from CH_2Cl_2–hexane yielded pure **2** (0.303 g, 10%), mp 150 °C; $\delta_H(CDCl_3)$ 2.09 (6 H, s, CH_3), 3.25–3.51 (8 H, m, OCH_2CH_2O), 3.38 (6 H, s, OCH_3), 4.31, 4.40 (4 H, AB, $ArCH_2$, J_{AB} 11.7), 5.97 (2 H, d, NH, J_{PH} 6.2), 6.63 (2 H, s, ArH), 7.23 (2 H, s, ArH), 7.45–7.63 (3 H, m, ArH), 7.87–8.05 (2 H, m, ArH); $\delta_C(CDCl_3)$ 21.01 (CH_3), 61.93 (OCH_3), 68.04, 68.43, 70.10 (OCH_2), 120.29 (*J* 3.6), 125.48, 129.24 (P-ArC, *J* 14.2), 129.98 (P-ArC, *J* 11.2), 130.42 (ArCq), 132.03 (P-ArC, *J* 3.2), 133.28 (ArCq), 133.31 (ArCq, *J* 3.6), 136.46 (P-ArCq, *J* 134.5), 146.96 (ArCq, *J* 7); $\delta_P(CDCl_3)$ 52.3; *m/z* (EI) 542 (M^+); Anal. Calc. for $C_{28}H_{35}N_2O_5PS$: C,

61.98; H, 6.50; N, 5.16; P, 5.71; S, 5.91%; Found: C, 61.87; H, 6.54; N, 5.34; P, 5.16; S, 6.22%.

3,7,24-Trimethyl-26,27-dimethoxy-11,14,17,20-tetraoxa-2,4-diaza-3λ⁵-phosphatricyclo[20.3.1.1⁵,⁹]heptacosa-1(26),5,7,9(27),22,24-hexaene-3-thione 3. The title compound was prepared as above from the appropriate diamine **11** (2.34 g, 5.2 mmol) and bis(dimethylamino)methylphosphine (0.75 g, 5.6 mmol) in toluene (525 ml) at 80 °C for 3 d. Chromatography on silica first with CH_2Cl_2, and then a 1:1 CH_2Cl_2–ethyl acetate mixture as eluent, yielded **3** as a colourless oil which was recrystallized from 95% ethanol to give pure **3** (1.09 g, 40%), mp 106 °C; $\delta_H(CDCl_3)$ 2.12 (3 H, d, PCH_3, J_{PH} 14.6), 2.17 (6 H, s, CH_3), 3.28–3.80 (12 H, m, OCH_2CH_2O), 3.58 (6 H, s, OCH_3), 4.33, 4.44 (4 H, AB d, $ArCH_2$, J_{AB} 11), 5.56 (2 H, d, NH, J_{PH} 7.3), 6.74 (2 H, br d, ArH), 7.16 (2 H, br d, ArH); $\delta_C(CDCl_3)$ 20.85 (CH_3), 23.79 (PCH_3, J 92.5), 61.94 (OCH_3), 67.71, 69.28, 70.45, 70.55 (OCH_2), 121.15 (ArCH, J 3.3), 125.42 (ArCH), 130.74, 132.44 (ArCq, J 2.5), 133.67, 147.28 (ArCq, J 6.6); $\delta_P(CDCl_3)$ 59.5; *m/z* (Cl) 525 (M + H), 542 (M + H + NH_3); Anal. Calc. 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, 57.16; H, 6.96; N, 5.50; P, 6.12; S, 6.17%.

Isolation of the non-cyclic intermediate 12. The above chromatographic work-up afforded traces of compound **12** which was identified from its NMR data; $\delta_H(CDCl_3)$ 1.95 (3 H, d, PCH_3, J_{PH} 13.8), 2.19 (3 H, s, CH_3), 2.25 (3 H, s, CH_3), 2.63 (6 H, d, NCH_3, J_{PH} 13.7), 3.45–3.65 (12 H, m, OCH_2), 3.72 (3 H, s, OCH_3), 3.73 (3 H, s, OCH_3), 4.50 (4 H, s, $ArCH_2$), 5.52 (1 H, d, NH, J_{PH} 7.3), 6.50 (1 H, m, ArH), 6.56 (1 H, m, ArH), 6.78 (1 H, m, ArH), 6.92 (1 H, m, ArH); $\delta_P(CDCl_3)$ 71.2.

7,24-Dimethyl-26,27-dimethoxy-3-phenyl-11,14,17,20-tetraoxa-2,4-diaza-3λ⁵-phosphatricyclo[20.3.1.1⁵,⁹]heptacosa-1(26),5,7,9(27),22,24-hexaene-3-thione 4.[2] The title compound was similarly prepared from the diamine **11** (2.02 g, 4.5 mmol) and 1.1 equiv. of bis(dimethylamino)phenylphosphine in refluxing toluene (500 ml) for 10 d. The crude product was purified by column chromatography on silica with 9:1 CH_2Cl_2–ethyl acetate as eluent followed by increasing quantities of ethyl acetate (up to 1:1). Recrystallization from CH_2Cl_2–hexane yielded pure **4** (0.527 g, 20%), mp 139 °C; $\delta_H(CDCl_3)$ 1.99 (6 H, s, CH_3), 3.47–3.56 (12 H, m, OCH_2), 3.68 (6 H, s, OCH_3), 4.28, 4.51 (4 H, AB, $ArCH_2$, J_{AB} 10.6), 5.77 (2 H, NH, J_{PH} 6.2), 6.69 (4 H, s, ArH), 7.32–7.47 (3 H, m, ArH), 7.74–7.82 (2 H, m, ArH); $\delta_C(CDCl_3)$ 20.87 (CH_3), 62.42 (OCH_3), 68.19, 69.69, 70.65, 70.82 (OCH_2), 122.53 (ArCH, J 3), 126.03 (ArCH), 128.54 (P-ArCH, J 14), 130.65 (ArCq), 131.14 (P-ArCH, J 11), 131.91 (P-ArCH), 132.60 (ArCq), 133.71 (ArCq), 134.74 (P-ArCq, J 126), 148.04 (ArCq, J 7); $\delta_P(CDCl_3)$ 57.2; *m/z* (Cl) 587 (M + H), 604 (M + H + NH_3); Anal. Calc. for $C_{30}H_{39}N_2O_6PS$: C, 61.42; H, 6.70; N, 4.77; P, 5.28; S, 5.46%; Found: C, 61.20; H, 6.66; N, 4.71; P, 4.92; S, 5.41%.

X-Ray analysis

Suitable crystals were obtained as follows: for **1**, by several recrystallizations from methanol; for **1**·H_2O, the crystals appeared during unsuccessful attempts to complex the ligand with lithium; they were obtained by slow evaporation from methanol–water solution (1:9) containing $LiNO_3$; for **2** by evaporation from an isopropyl alcohol solution; for **3** by diffusion of hexane through an acetone solution; for **4** by evaporation from an ethanol solution.

Crystal data, data collection and refinement parameters are summarized in Table 1. The lattice parameters were refined using a minimum of 15 reflections in the 2θ range 5–30 °C. The measurements were performed with a Huber four-circle diffractometer equipped with graphite monochromatized Cu-Kα for **1** or Mo-Kα radiation for **2**–**4** and **1**·H_2O. For all data collections, one standard reflection was monitored every 50 measurements, no significant deviation was observed. The five structures were solved by direct methods with SHELXS86[9] and refined anisotropically for non-H atoms using F^2 values with SHELXL93.[10] In each case the positions of the H atoms were calculated with AFIX and included in the refinement with a common isotropic temperature factor. In the structures of **2** and **4** some disorder was observed. For **2**, two positions (A and B) of the atoms C(15) and C(16) of the second independent molecule were refined; the occupation factors converge to 0.42 (position A) and 0.58 (position B) at the end of the refinement. For **4**, the atom O(11) also occupied two positions with occupation factors of 0.59 and 0.41. In both cases, restraints on bond lengths and non-bonded 1–3 distances involving the disordered atoms were applied. Scattering factors were taken from ref. 11.

Atomic coordinates, bond lengths and angles, and thermal parameters for **1**, **1**·H_2O, **2**, **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/21.

Results and discussion

Synthesis

Phosphorus corands **1**–**4** were prepared by reacting 1,9-bis(2-methoxy-5-methyl-3-phenylamino)-2,5,8-trioxanonane (**10**) or 1,12-bis(2-methoxy-5-methyl-3-phenylamino)-2,5,8,11-tetraoxadodecane (**11**) with 1.1 equiv. of bis(dimethylamino)methyl phosphine or bis(dimethylamino)phenyl phosphine in refluxing toluene, followed by *in situ* oxidation with sulfur.[2] Diamines **10** and **11** were synthesized according to Scheme 1. Reaction of 2-nitro-*p*-cresol **5** with HBr and paraformaldehyde in acetic acid–acetic anhydride produced **6** in 96% yield. Hydrolysis of **6** in a 1-methylpyrrolidin-2-one–water mixture, afforded a 69% yield of recrystallized **7**. Methylation of the phenol group in **7** with dimethyl sulfate, in the presence of K_2CO_3 in actone, gave a 94% yield of the nitrobenzyl alcohol **8**, which was reduced with hydrazine–Pd/C to aminobenzyl alcohol **9** in 98% yield. Treatment of **9** with NaH and the appropriate ditosylate produced diamines **10** and **11** in yields of 65 and 56% respectively. Cyclization of **10** and **11** with bis(dimethylamino)methylphosphine or bis(dimethylamino)phenylphosphine followed by the addition of a slight excess of sulfur, gave phosphorous corands **1**–**4** in yields of 47, 10, 40 and 20%, respectively.

The ring closure reaction does not need high dilution conditions, and a 10^{-2} M concentration is usual. The sulfurization step is quantitative and does not affect the ratios of the different species present in the mixture. The chromatographic work-up performed with compound **3**, afforded a trace of the initially formed non-macrocyclic intermediate **12**, whose structure was easily confirmed from its ^1H and ^{31}P NMR spectra. The first step of the macrocyclization reaction probably involved such an uncyclized intermediate containing a diaminophosphane and a primary amine as functional groups which react intramolecularly to give the P^{III} macrocycle.

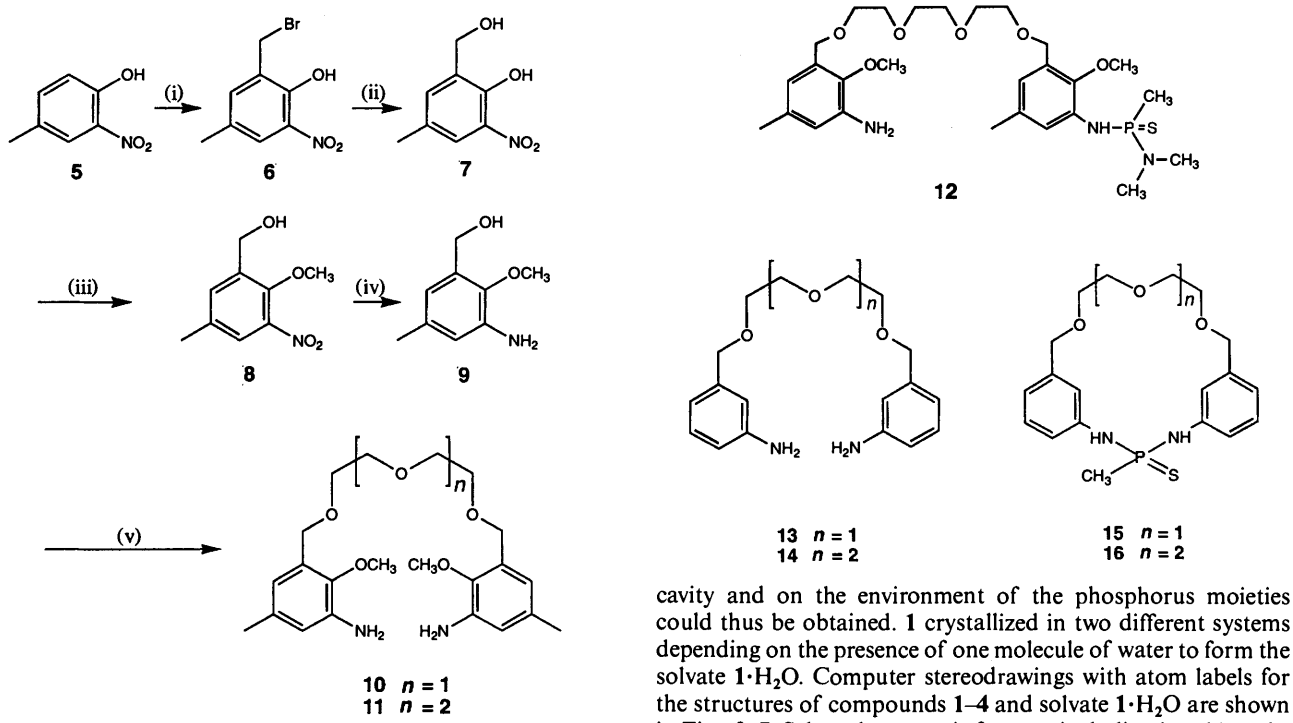
From previous studies on related macrocycles there is evidence that the type of aromatic ring incorporated in the diamines is an important factor controlling the formation of new corands. Under similar experimental conditions, lower reactivities were observed with the related diamines **13** and **14**, which were used to prepare analogues **15** and **16** respectively, suggesting favourable electronic effects for the substituted *o*-anisidine compounds **10** and **11**. Indeed, attempted ring closure reactions of diamines **13** and **14** with bis(dimethylamino)phenylphosphine failed. Only the methyl phosphorous derivative led to the expected macrocyclic structures **14** and **16**.[4]

Crystal structures

Single crystal X-ray diffraction was utilized to determine the molecular conformations of phosphorous macrocycles **1**–**4** in the solid state. Information on the existence of a preformed

Table 1 Data collection and refinement parameters

	1	1·H_2O	2	3	4
Formula	$C_{23}H_{33}N_2O_5PS$	$C_{23}H_{35}N_2O_6PS$	$C_{28}H_{35}N_2O_5PS$	$C_{25}H_{37}N_2O_6PS$	$C_{30}H_{39}N_2O_6PS$
M_r	480.54	498.56	542.61	524.60	586.66
System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$C2/c$	$Pna2_1$	$P2_1/n$	$P2_12_12_1$
a/Å	11.784(5)	16.117(2)	18.305(5)	9.764(1)	11.000(7)
b/Å	19.313(6)	15.354(2)	32.939(5)	12.920(2)	11.641(6)
c/Å	14.927(5)	21.941(3)	9.354(2)	22.286(3)	23.84(2)
α/°	90	90	90	90	90
β/°	132.88(5)	100.63(1)	90	90.52(1)	90
γ/°	90	90	90	90	90
V/Å^3	2489(2)	5336(1)	5640(2)	2811.3(7)	3054(3)
D_x/g cm^{-3}	1.282	1.241	1.278	1.239	1.276
Z	4	8	8	4	4
λ/Å	1.541 78	0.710 69	0.710 69	0.710 69	0.710 69
Cell parameters from (reflections)	17	30	24	30	15
2θ range	9–30	6–29	8–30	7–29	3–25
$F(000)$	1024	2128	2304	1120	1248
μ/cm^{-1}	20.58	2.19	2.11	2.12	2.02
Crystal size/mm	0.008 × 0.12 × 0.16	0.06 × 0.28 × 0.32	0.50 × 0.45 × 0.25	0.8 × 0.4 × 0.4	0.18 × 0.48 × 0.16
θ_{max} (°) for data collection	60	24	25	28	26
Range of hkl	$0 < h < 12$, $0 < k < 21$, $-16 < l < 11$	$0 < h < 18$, $0 < k < 17$, $-24 < l < 24$	$-3 < h < 21$, $-39 < k < 6$, $0 < l < 11$	$0 < h < 12$, $0 < k < 16$, $-28 < l < 28$	$0 < h < 13$, $0 < k < 14$, $-29 < l < 29$
Standard reflections	3 −1 −1	−2 2 4	−6 3 4	3 4 6	1 3 6
No. of measured reflections	3411	3950	5287	6456	6023
No. of observed reflections [$I > 2\sigma(I)$]	1189	2243	2943	4186	4943
U common for H atoms/(Å^2)	0.0770	0.128	0.125	0.085	0.082
Number of parameters	290	304	680	322	373
Number of restraints	0	0	15	0	6
R	0.0869	0.0659	0.0557	0.0508	0.0476
ωR	0.1482	0.1493	0.1155	0.1243	0.1169
$w = 1/(\sigma^2(F_o^2) + xP^2)$ where $P = (F_o^2 + 2F_c^2)/3$;					
x =	0.0651	0.0797	0.0665	0.0694	0.0803
S	0.828	1.011	0.952	1.014	1.01
(Δ/σ)	0.000(1)	0.021	0.000(1)	0.000(1)	0.000(1)
$\Delta\rho$(max,min) (e Å^{-3})	0.243, −0.242	0.589, −0.292	0.305, −0.398	0.385, −0.312	0.221, −0.178



Scheme 1 *Reagents and conditions*: i, HBr–HCHO in acetic acid–acetic anhydride; ii, H_2O–*N*-methylpyrrolidinone; iii, dimethyl sulfate, K_2CO_3 in acetone; iv, NH_2NH_2–Pd–C in ethanol; v, $TsOCH_2(CH_2OCH_2)_nCH_2OTs$, NaH in THF

cavity and on the environment of the phosphorus moieties could thus be obtained. **1** crystallized in two different systems depending on the presence of one molecule of water to form the solvate **1**·H_2O. Computer stereodrawings with atom labels for the structures of compounds **1**–**4** and solvate **1**·H_2O are shown in Figs. 3–7. Selected geometric features including bond lengths and bond angles around the phosphorus atom are given in Table 2. In the structure of **2**, there are two independent molecules, **2a** and **2b**, in the asymmetric unit. These two molecules

Table 2 Selected bond lengths and bond angles around the phosphorus atom in **1**–**4** and **1**·H_2O

Distances (Å) Angles (°)	1	1·H_2O	2	3	4
P=S	1.947(3)	1.942(2)	1.927(3) 1.926(3)	1.954(1)	1.939(1)
P–C	1.785(6)	1.801(4)	1.787(9) 1.786(7)	1.785(2)	1.807(3)
P–N(2)	1.677(7)	1.664(4)	1.649(5) 1.656(5)	1.661(2)	1.662(2)
P–N(4)	1.652(6)	1.665(3)	1.651(4) 1.650(5)	1.659(2)	1.672(3)
C–P=S	109.6(3)	113.2(2)	113.6(2) 114.1(2)	111.4(1)	113.1(1)
N(2)–P–N(4)	108.2(3)	109.1(2)	107.3(3) 106.9(3)	107.6(1)	100.0(1)
S=P–N(2)	115.5(2)	117.4(2)	117.8(2) 117.6(2)	117.6(1)	115.5(1)
S=P–N(4)	108.6(2)	107.6(2)	108.3(2) 108.9(2)	109.2(1)	118.0(1)
C–P–N(2)	102.0(3)	99.6(2)	100.7(3) 100.9(3)	100.7(1)	107.2(1)
C–P–N(4)	112.8(3)	109.8(2)	108.4(3) 107.7(3)	109.9(1)	101.1(1)
P–N(2)–C	129.7(6)	129.5(3)	126.1(5) 125.6(5)	127.7(1)	127.6(2)
P–N(4)–C	126.6(5)	125.9(3)	127.9(4) 129.7(5)	122.5(2)	123.2(2)

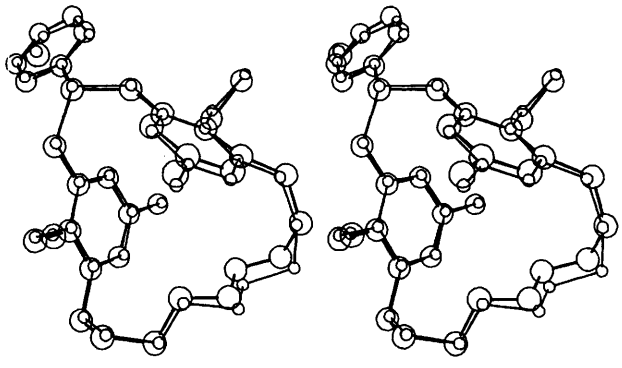


Fig. 1 Superposition of the two independent molecules of **2**.[14] [○, molecule **2a**; o, molecule **2b** first orientation of disordered C(15)–C(16)].

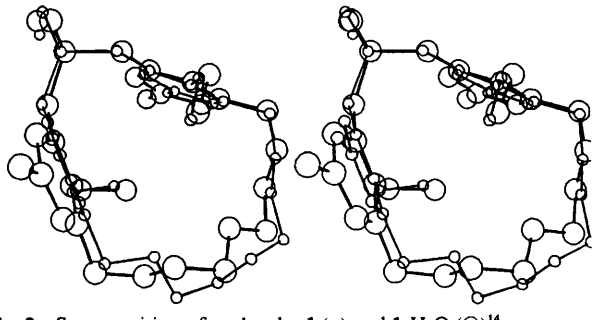


Fig. 2 Superposition of molecules **1** (o) and **1**·H_2O (○)[14]

have a very similar geometry, the root-mean-square deviation being 0.052 Å. Fig. 1 shows the superposition of the two molecules.

The 18-membered macrocycles **1** and **2** adopt unsymmetrical conformations where the two anisyl groups are arranged in an antiparallel orientation. Each methoxy group occupies one face of the macrocycle defined by the polyether crown part and the phosphorus moiety. In structures **1** and **1**·H_2O the methyl of both methoxy groups are directed inwards so that they overcrowd both sides of the macrocyclic cavity. This converging of the methoxy groups has been observed in other macrocycles containing anisyl units.[12] In **2** the methyl of one methoxy group is turned inwards to the macrocyclic cavity whereas the other is turned outwards. Due to the ($g^{\pm}g^{\pm}$) conformation around the P–N bonds, the two NH bonds are orientated in opposite directions, a conformation probably favoured by the formation of weak hydrogen bonds with the oxygen of the adjacent methoxy groups (see next paragraph).

Structures of **1** (Fig. 3) and **1**·H_2O (Fig. 4) have very close conformations. Fig. 2 shows a superposition view of the two molecules for which the root-mean-square deviation is 0.42 Å. Small differences arise from the conformation of the crown part which have ($ag^{\pm}a$)($ag^{\pm}a$) and ($ag^{\pm}g^{\pm}$)($ag^{\pm}a$) conformations respectively, and a dihedral angle around the C(10)–O(11) bond which is ($g^{\pm}$) and (a) respectively. For both **1** and **1**·H_2O one observes an intermolecular bond between the amino N(4)H and the ether oxygen O(31). The geometry is as follows: **1**: N(4)···O(31) = 3.147(9) Å; H(4)···O(31) = 2.31(4) Å; N–H···–O = 163(1)°; O(31) = $-x, 2-y, -z$; **1**·H_2O: N(4)···O(31) = 3.038(6) Å; H(4)···O(31) = 2.23(4) Å; N–H···O = 156(1)°; O(31): $2-x, y, 1.5-z$. In **1**·H_2O the water molecule is highly agitated and is localized above the macrocyclic cavity. It is more than likely that it is hydrogen bonded to the ether oxygen O(14), the distance O_w···O(14) being 3.09 Å.

In the crystal of **2**, the macrocyclic structure defines a closed compact cavity mainly occupied by one methoxy group and the methylene groups of the crown ether chain (Fig. 5). This is the result of the ($g^{\pm}ag^{\pm}$)($ag^{\pm}g^{\pm}$) torsional angles sequence of the polyether fragment. The plane of the phenyl group bound to the phosphorus atom is almost perpendicular to the plane defined by the atoms S, P and $C_{aromatic}$ as shown by the torsion angles S(26)–P(3)–C(25)–C(33) and S(26)–P(3)–C(25)–C(37) [−89.2(8) and 86.2(6)° in molecule **2a**, 82.5(7) and −96.7(7)° in molecule **2b**].

Crystal structural analysis of the 21-membered macrocycles **3** and **4** reveals the effects of ring size on conformation (Figs. 6 and 7). In these larger macrocycles, there is a significant cavity defined by the crown ether part and the phosphorus moiety. The two methoxy groups of the anisyl groups are roughly located on the same side of the macrocyclic cavity, and are orientated along the P–R direction [R = CH_3 (**3**) or C_6H_5 (**4**)]. In both structures one methyl of the methoxy groups is orientated inwards and occupies the centre of the macrocyclic cavity, whereas the other one is orientated outwards. The macrocycle **4** is disordered at O(11). The disorder is satisfactorily described with two different atomic positions for atom O(11), which define two conformations **4a** and **4b**. The phenyl group bound to

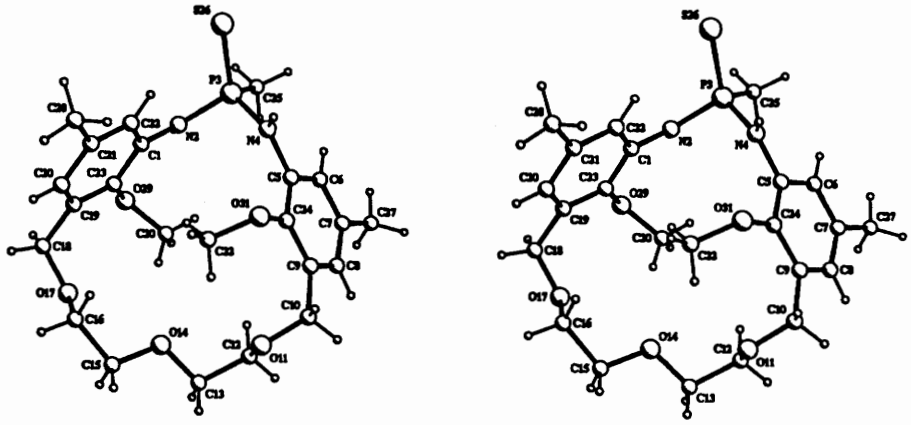


Fig. 3 Stereoscopic view of molecule **1**[13]

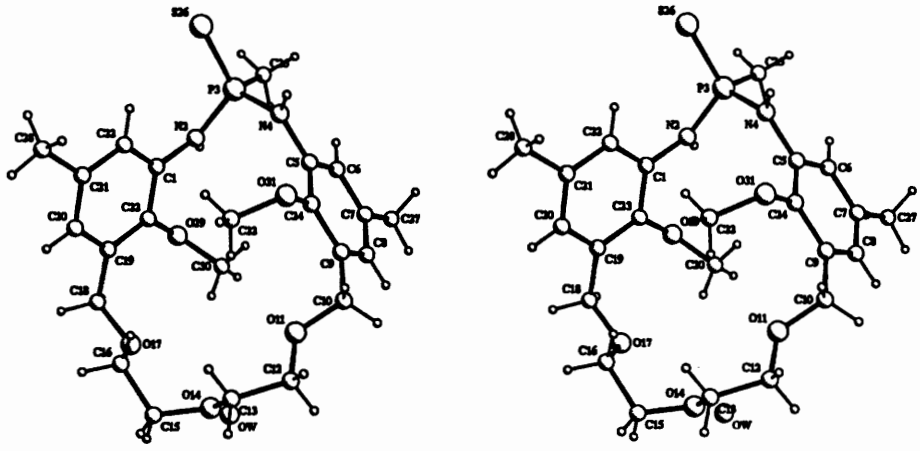


Fig. 4 Stereoscopic view of molecule **1**·H_2O[13]

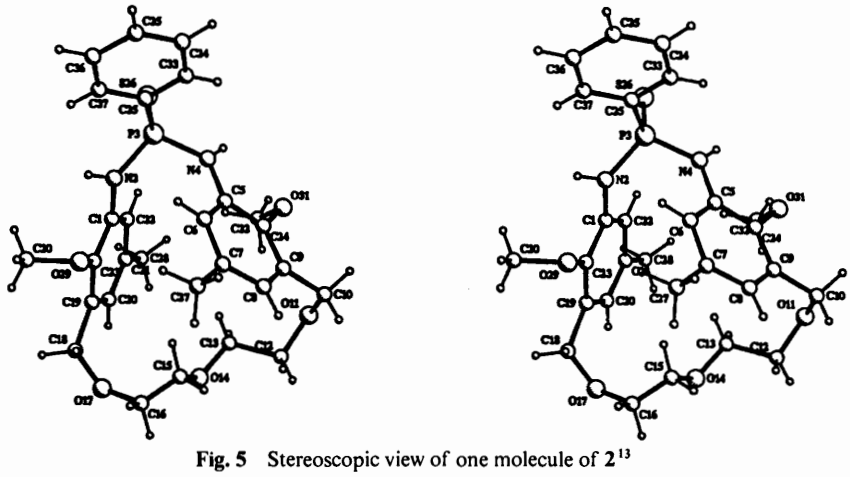


Fig. 5 Stereoscopic view of one molecule of **2**[13]

the phosphorus atom is almost coplanar to the plane defined by the S–P–$C_{aromatic}$ group [S(29)–P(3)–C(28)–C(36) = −20.4(3)°], a situation different from that observed with compound **2**. The crown ether parts adopt the $(ag^{\mp}a)(ag^{\pm}a)(ag^{\pm}a)$ (**3**) and the $(ag^{+}a)(ag^{-}a)(ag^{+}a)$ (**4a**) conformations respectively, which orientate the oxygen atoms towards the centre of the cavity, reflecting the predisposition of these corands to form complexes by means of the oxygen ether binding sites. However, the $(g^{-}aa)(ag^{-}a)(ag^{+}a)$ conformation in **4b** forces oxygen O(11) to be turned outward. The different conformations around the phosphorus moieties in **3** and **4** result in different relative orientations of the planes of the two anisyl aromatic rings in the molecules. The $(g^{+}a)$ conformation around the phosphorus–nitrogen bonds in **4** leads to different orientations of the NH bonds lying almost on the same side of the macrocyclic cavity. Consequently, one of the anisyl rings is more bent so that the methyl of the corresponding methoxy group is totally surrounded by the crown ether part. In this molecule the N(2)H is hydrogen bonded to the two methoxy oxygen atoms [N(2)···O(32) = 2.685(4) Å; H(2)···O(32) = 2.21(3) Å; N(2)···O(34) = 3.054(4) Å, H(2)···O(34) = 2.22(2) Å], whereas the N(4)H is not involved in any intramolecular H-bond, but is hydrogen bonded to O(14) of a symmetry related ligand [N(4)···O(14) = 3.122(5) Å, H(4)···O(14) = 2.30(3) Å, N–H···O = 171(1)° O(14): $1-x$, $y-0.5$, $0.5-z$]. The NH bonds in **3** are antiparallel; N(2)H is H-bonded to the adjacent methoxy oxygen O(32) [N(2)···O(32) = 2,712(2) Å; H(2)···O(32) = 2,39(2) Å], whereas N(4)H is not involved in any H-bond.

In the five structures, the phosphorus substituents are repelled outward from the macrocyclic cavity. As a result of this conformation, the thiophosphoryl group would not be available for cooperative interaction with a guest complexed within the cavity of the crown ether part of the ligand. However, rigidifi-

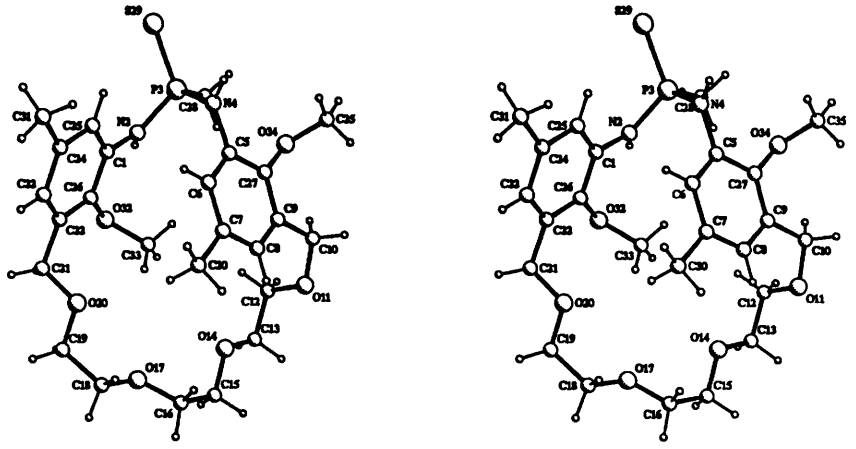


Fig. 6 Stereoscopic view ofmolecule 3[13]

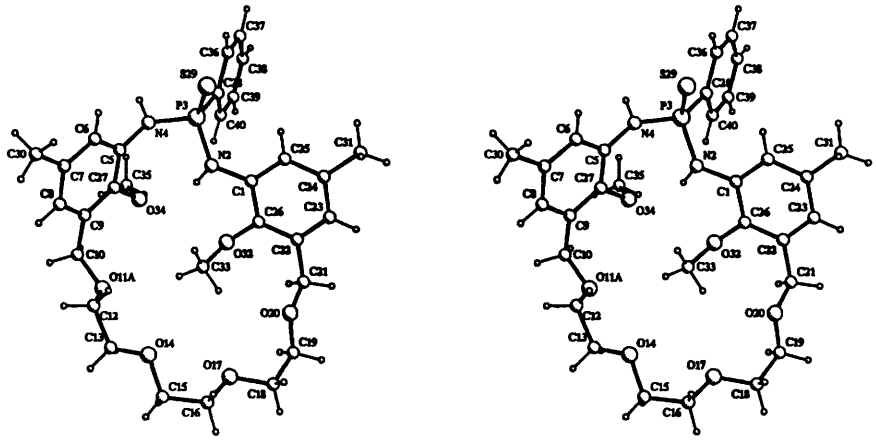


Fig. 7 Stereoscopic view of one molecule of 4[13]

cation of the structures by means of cyclosubstitution on the nitrogen atoms can lead to more preorganized corands with possible participation of the phosphorus binding sites in guest complexation.[7] It is interesting to note that in both 18- and 21-membered macrocycles **1–4**, the cavity mainly defined by the crown ether part of the molecules is occupied by one or both methyls of the methoxy groups.

It is impossible to evaluate correctly the planarity around the nitrogen atoms, but the large values of the P–N–C angles which are higher than 122° (averaged value 126.8°, Table 2) are indicative of sp^2 hybridization. Bond distances and angles around phosphorus are comparable with those observed in parent molecules (Table 2).[4] The differences observed between the two N–P=S and N–P–C angles belonging to the same molecule are mainly due to the different conformations around the P–N(2) and P–N(4) bonds, involving S=P–N–C and C–P–N–C dihedral angles. A *gauche* ($g^{\pm}$) conformation imposes a larger bond angle value as a consequence of steric hindrance around the phosphorus atom as compared to an *anti* (*a*) conformation.

NMR spectroscopy

At room temperature the C_s time averaged symmetry of the molecules **1–4** in solution is demonstrated by analysis of their NMR data. The proton NMR spectra of compounds **1–4** in $CDCl_3$ show the expected AB pattern for the diastereotopic methylene protons of the benzyl groups, their chemical shifts difference ranging from 0.02 (**1**) to 0.23 ppm (**4**). Except for compound **4**, the aromatic protons of the benzyl groups appear as separate signals. The methyl or phenyl group bound to phosphorus presents characteristic resonances implying coupling with the phosphorus nucleus. The NH protons give a doublet (J_{PH} 6–7). Carbon spectra contain the expected signals for the molecules and the assignment of the P-aromatic carbons in **2** and **4** is unambiguous. The ^{13}C NMR chemical shifts are reported in the experimental section. The ^{31}P NMR chemical shifts are typical and lower field values are observed for the larger macrocycles [$\delta_{^{31}P}$ (**1**) 56.1; (**2**) 52.3; (**3**) 59.5; (**4**) 57.2]. Similarly, $^1J_{PC}$/Hz coupling constants are dependent on the size of the macrocycle with smaller values observed for the larger macrocycles (97.1 and 92.5 for **1** and **3** respectively; 134.5 and 126 for **2** and **4** respectively).

The temperature dependence of the 500 MHz ^1H NMR spectrum of compound **1** in CD_2Cl_2–CCl_2F_2 was investigated (Fig. 8). The asymmetric conformation of the ligand at low temperature is evidenced by the splittings observed in the spectrum. The AB pattern of the methylene protons of the benzyl groups coalesces at 183 K to give at a temperature below 173 K, two well separated broad signals at 4.67 and 3.75 ppm. Below 183 K the low field aromatic protons H_a and H_b split into two singlets (δ_{H_a} 8.42; δ_{H_b} 6.89). At 163 K, the spectrum was further split, with the two remaining aromatic protons H_c and H_d appearing as two singlets (δ_{H_c} 6.61 and δ_{H_d} 6.52). Concurrently, the NH protons gave two broad signals at 5.91 and 5.83 ppm. A temperature dependence was also shown for the OCH_2CH_2O multiplet and the OCH_3 resonance. Due to the overlapping of these signals, it is difficult to assign the methoxy resonances which split at temperature below 173 K. At this temperature, the methyl groups of the benzyl moieties were still not differentiated.

The conformational behaviour of **1** at low temperature shows that the molecule adopts preferentially an asymmetric conformation in solution. Such a chiral conformation should indeed lead to the NMR patterns observed at low temperature. The shift differences observed for the aromatic protons $H_{a,b}$ and $H_{c,d}$ are thought to reflect their exposure to highly differentiated environments. Assuming that the preferred conformation is similar to that observed in the solid state, H_a and H_b are thus assigned to the protons in the *ortho* position of the amide group as they interact with the phosphorus substituents (P=S or P–CH_3), and H_c and H_d to the protons in *para* position of the NH, which both interact with the crown part of the molecule.

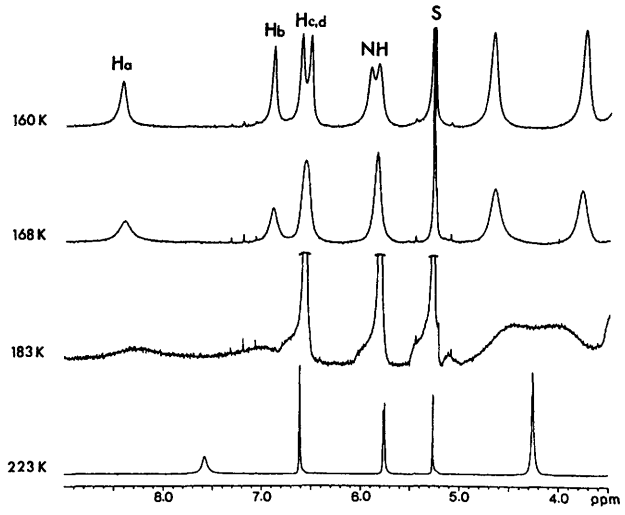
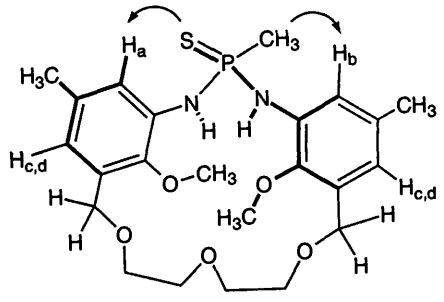


Fig. 8 Variable-temperature 500 MHz ^1H NMR spectra of **1** in CD_2Cl_2/CCl_2F_2 solution (S = solvent)

The large downfield shift observed for H_a is attributed to the anistropy of the thiophosphoryl group as compared to proton H_b which interacts with the P-CH_3 moiety.



The two resulting enantiomers interconvert rapidly at room temperature. The interconversion between the two enantiomers requires the passage of the anisyl group through the ring cavity. From the variable temperature ^1H NMR studies, the barrier to ring flipping of **1** was calculated as 8 kcal mol^{-1} (T_c 188 K for coalescence of H_a and H_b).

Macrocycle **3** was less temperature dependent as a consequence of the greater flexibilty of the compound. Upon lowering the temperature of a CD_2Cl_2–CCl_2F_2 solution of **3**, the 200 MHz ^1H NMR spectrum mainly showed an increase of the chemical shift difference $\Delta\delta_{AB}$ of the two methylene protons of the benzyl group ($\Delta\delta_{AB}$ 0,11 and 0.49 ppm at 300 and 183 K respectively), and a marked broadening of the highfield aromatic signal. We were not able to raise any coalescence state in the temperature range 300–183 K, and therefore no representative ring flipping barriers were measured. The process observed must involve the rapid exchange of several conformers in solution. Fast exchange between C_1 and C_s conformers could be a possible dynamic process which is in agreement with the observed data.

The C_s time averaged symmetry of compounds **2** and **4** indicates that they are comformationally mobile in solution. Their solid state structures show similar conformations, and they probably exhibit similar behaviour in solution, as for **1** and **3** respectively.

Conclusions

A convenient procedure for the synthesis of macrocyclic precursors of phosphahemispherands has been developed. This generalizes the simple methodology already used for the synthesis of macrocyclic phosphorus compounds incorporating a phosphoramide or thiophosphoramide unit and a benzocrown segment in a macrocyclic structure. The solid state structural analysis of the macrocycles **1**–**4** and the solvate **1**·H_2O present common features. The phosphorus corands exhibit unsymmetrical conformations with the phosphorus group repelled outward and the macrocyclic cavity filled with at least one methyl group of the methoxy groups belonging to the anisyl moieties. The low temperature ^1H NMR experiments provided significant information on the conformational mobility of molecules **1** and **3** in solution. At room temperature, these compounds mainly exist in solution as rapidly exchanging unsymmetrical conformers and extensive conformational changes should be necessary to provide a cavity that places the methoxy groups on the same face of the macrocycle and the thiophosphoryl group in a favourable orientation required for cooperative binding effects. Work is underway in our laboratory to investigate the complexing properties of these new ligands and the preorganized structures that can be obtained from these molecules.

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