Synthesis of new macrocyclic aminomethylphosphines based on 4,4′-diaminodiphenylmethane and its derivatives

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The reaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane in DMF afforded 1,1′,5,5′-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (**1**) whose structure was established by X-ray diffraction analysis. Sulfurization and oxidation of macrocyclic tetraphosphine **1** gave rise to products **2** and **3**, respectively, compound **3** being obtained as a stable hexahydrate. The reaction of bis(hydroxymethyl)phenylphosphine with bis(4-*N*-methylaminophenyl)methane in DMF followed by sulfurization yielded monocyclic bis{methylenedi[*p*-phenylene(*N*-methyl)aminomethyl]}di(*P*-phenyl)phosphine sulfide (**4**).

Key words: macrocyclic aminomethylphosphines, X-ray diffraction analysis, 4,4′-bis(hydroxymethyl)phenylphosphine, diaminodiphenylmethane.

Previously,[1] it has been demonstrated that the reactions of primary aromatic diamines with bis(hydroxymethyl)phosphines in EtOH afforded oligomers containing several diazadiphosphacyclooctane fragments. In the preliminary communication,[2] we have reported the synthesis of the first representative of a new class of macrocyclic aminomethylphosphines, *viz.*, 1,1′,5,5′-bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (**1**), based on the reaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane in DMF. This result suggested that the main type of the resulting oligomers depends primarily on the structure of the diamine used as well as on the reaction conditions, in particular, on the nature of the solvent. The presently known nitrogen-containing macrocyclic phosphines[3,4] are few in number and belong to monocyclic compounds. Macrocycle **1** is most structurally close to 1,7,21,27-tetraaza-3,5,23,25-tetraphospha-4,24-dimolybda[7.1.7.1]paracyclophane, which is also a macrocyclic dimer containing the aminomethylphosphine and diphenylmethane fragments.[5] Macrocyclic tetraphosphine **1** is distinguished primarily by the cage structure. In this connection, it was of interest to study its three-dimensional structure in detail and to examine the possibility of the formation of macrocyclic dimers in the reactions of various hydroxymethylphosphines with diaminodiphenylmethane and its derivatives.

Results and Discussion

Macrocyclic tetraphosphine **1** was obtained as the major product in the reaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane in a dilute DMF solution at 80—100 °C. After cooling of the reaction mixture, compound **1** was isolated as a crystalline precipitate (Scheme 1). As mentioned above, the reaction performed in EtOH afforded a mixture of oligo(diazaphosphacyclooctanes).[1] Compound **1** was obtained as white crystals with the distinct melting point. Dilution of the reaction mixture and its additional stirring at ~20 °C for 2 days allowed us to increase the yield of macrocycle **1**.

The IR spectrum of compound **1** has no absorption bands of the terminal hydroxy and amino groups, which are present in the starting compounds. The FAB mass spectrum of compound **1** has a molecular ion peak at *m/z* 932. The ^{31}P NMR spectrum shows one signal at δ_P −52.59. This chemical shift is close to those observed for 1,5-diaryl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctanes,[6] which is evidence for the equivalence of all the four phosphorus atoms and, consequently, for the symmetrical structure of the macrocycle in solutions. This is also confirmed by the ^{1}H NMR spectroscopic data. The methylene groups of both eight-membered phosphorus-containing heterocycles are equivalent, and their signals form an $(AB)_2X$ system typical of diazadiphosphacyclooctanes, *viz.*, two doublet of doublets at δ 4.05 ($^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 13.8 Hz) and δ 4.49 ($^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 3.5 Hz). The constants $^2J_{PH}$ are indicative of the equatorial orientations of all substituents at the phosphorus atoms. The structure of macrocycle **1** was also established by X-ray diffraction analysis.

Molecule **1** is a centrosymmetrical "dimer" whose crystallographically independent portions each consist of one

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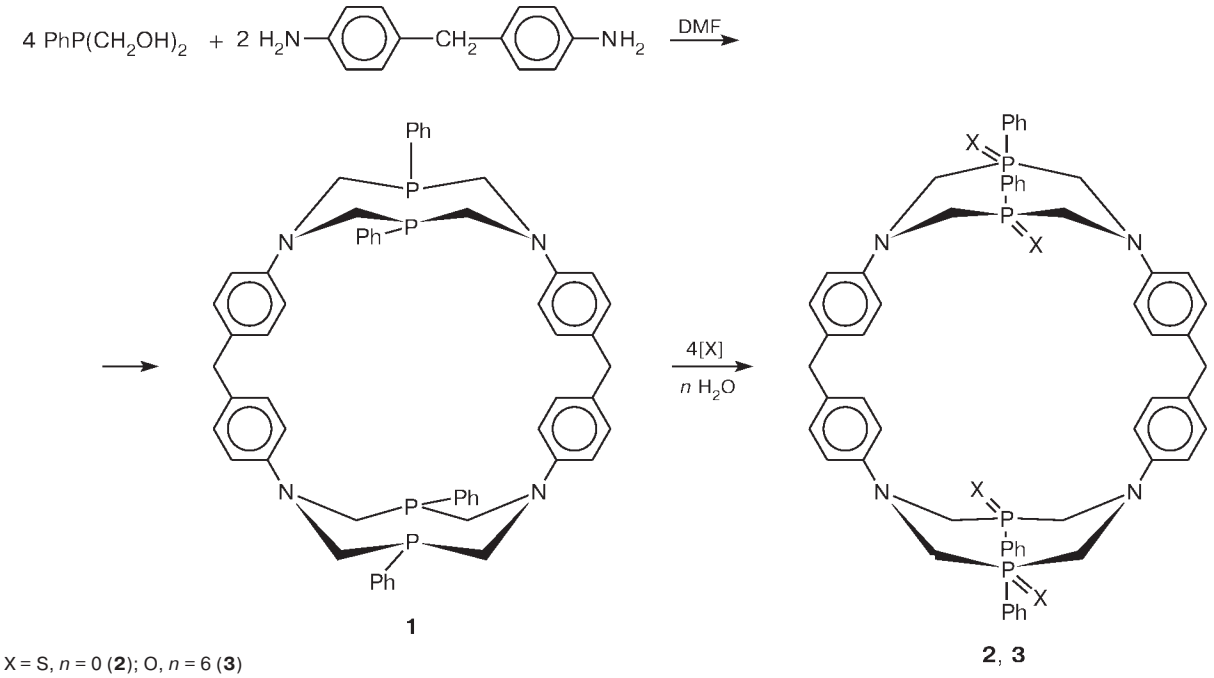
Scheme 1



eight-membered diazadiphosphacyclooctane ring, two benzene rings at the nitrogen atoms of the eight-membered ring, and one bridging CH_2 group (Fig. 1). The eight-membered heterocycles of molecule **1** adopt a chair—chair (crown) conformation, the phenyl substituents at the phosphorus atoms are in the equatorial positions, and the aromatic substituents at the nitrogen atoms are in the axial positions. An analogous conformation of the 1,5,3,7-diazadiphosphacyclooctane heterocycle was also observed in the structure of 1,5,3,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane.[7] The principal geometric parameters of molecule **1** (the bond lengths and bond angles; see Table 1) are identical (to within the experimental error) with those found in 1,5,3,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane. The nitrogen atoms in these compounds have a planar-trigonal configuration due to conjugation of the lone electron pairs with the π-systems of the benzene rings. This conjugation is responsible for the fixation of the conformations of the aromatic fragments at the nitrogen atoms and the rigid conformation of the macrocycle as a whole. The bond angle at the bridging C(17) atom (113.1(3)°) is somewhat increased due, apparently, to the closure of the macrocycle. The volume of the inner cavity of the macrocycle accessible for solvate molecules is only 16 Å^3, which is insufficient even for a water molecule. The lone electron pairs of the phosphorus atoms are located inside the macrocycle, which is favorable for incorporation of small metal ions (for example, alkali metal ions).

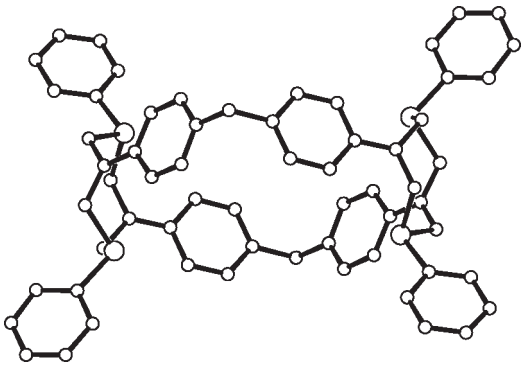


Fig. 1. Crystal structure of macrocycle **1**. The DMF molecules of solvation are omitted.

In the crystal of compound **1**, there are four DMF molecules of solvation per molecule **1**. The methyl groups of two DMF molecules reside in the macrocyclic cavity on both sides (Fig. 2). Two other DMF molecules are located outside the cavity and are involved in intermolecular C—H...O interactions with the protons of the phenyl substituents (d(C(36)—O(81)) = 3.649(6) Å, d(H(36)...O(81)) = 2.58(3) Å, ω(C(36)—H(36)...O(81)) = 171(2)°). In addition, the DMF molecules form intermolecular contacts with each other. It should be noted that in the crystal packing of compound **1**, the regions containing the solvate molecules are localized resulting in the formation of alternating layers containing the macrocycles and the DMF molecules, respectively (Fig. 3). The layers are parallel to the crystallographic plane 0yz and the phenyl substituents of the macrocycles are located in the

Table 1. Selected geometric parameters of the structure of **1**

Bond	d/Å
P(3)—C(2)	1.872(4)
P(3)—C(4)	1.848(5)
P(3)—C(31)	1.831(4)
P(7)—C(6)	1.863(4)
P(7)—C(8)	1.854(4)
P(7)—C(71)	1.811(4)
O(81)—C(81)	1.234(7)
O(91)—C(91)	1.21(1)
O(92)—C(92)	1.37(1)
N(1)—C(2)	1.459(5)
N(1)—C(8)	1.459(5)
N(1)—C(11)	1.389(5)
N(5)—C(4)	1.432(5)
N(5)—C(6)	1.443(5)
N(5)—C(51)	1.376(5)
N(80)—C(81)	1.298(7)
N(80)—C(82)	1.410(8)
N(80)—C(83)	1.421(8)
N(90)—C(91)	1.379(7)
N(90)—C(92)	1.397(9)
N(90)—C(93)	1.410(9)

Bond angle	ω/deg
C(2)—P(3)—C(4)	100.0(2)
C(2)—P(3)—C(31)	99.9(2)
C(4)—P(3)—C(31)	98.3(2)
C(6)—P(7)—C(8)	100.1(2)
C(6)—P(7)—C(71)	100.5(2)
C(8)—P(7)—C(71)	97.9(2)
C(2)—N(1)—C(8)	118.6(3)
C(2)—N(1)—C(11)	120.2(3)
C(8)—N(1)—C(11)	121.2(3)
C(4)—N(5)—C(6)	117.7(3)
C(4)—N(5)—C(51)	123.2(3)
C(6)—N(5)—C(51)	119.0(3)
P(3)—C(2)—N(1)	113.1(3)
P(3)—C(4)—N(5)	117.5(3)
P(7)—C(6)—N(5)	113.5(3)
P(7)—C(8)—N(1)	115.8(3)
C(81)—N(80)—C(82)	123.4(5)
C(81)—N(80)—C(83)	118.8(5)
C(82)—N(80)—C(83)	117.7(5)
C(91)—N(90)—C(92)	124.9(5)
C(91)—N(90)—C(93)	115.6(5)
C(92)—N(90)—C(93)	119.4(5)
C(14)—C(17)—C(54)	113.1(3)

Torsion angle	τ/deg
C(4)—P(3)—C(2)—N(1)	−80.3(3)
C(31)—P(3)—C(2)—N(1)	179.4(3)
C(2)—P(3)—C(4)—N(5)	81.1(3)
C(31)—P(3)—C(4)—N(5)	−177.3(3)
C(2)—P(3)—C(31)—C(32)	−128.3(4)
C(2)—P(3)—C(31)—C(36)	49.1(4)
C(4)—P(3)—C(31)—C(32)	130.0(3)
C(4)—P(3)—C(31)—C(36)	−52.7(4)
C(8)—P(7)—C(6)—N(5)	−82.3(3)
C(71)—P(7)—C(6)—N(5)	177.6(3)
C(6)—P(7)—C(8)—N(1)	80.3(3)
C(71)—P(7)—C(8)—N(1)	−177.5(3)
C(6)—P(7)—C(71)—C(72)	26.0(4)
C(6)—P(7)—C(71)—C(76)	−153.0(4)
C(8)—P(7)—C(71)—C(72)	−75.9(4)
C(8)—P(7)—C(71)—C(76)	105.1(4)
C(8)—N(1)—C(2)—P(3)	107.5(3)
C(11)—N(1)—C(2)—P(3)	−74.8(4)
C(2)—N(1)—C(8)—P(7)	−106.7(3)
C(11)—N(1)—C(8)—P(7)	75.6(4)
C(2)—N(1)—C(11)—C(12)	−179.6(4)
C(2)—N(1)—C(11)—C(16)	−2.7(5)
C(8)—N(1)—C(11)—C(12)	−1.9(5)
C(8)—N(1)—C(11)—C(16)	175.0(4)
C(6)—N(5)—C(4)—P(3)	−107.0(3)
C(51)—N(5)—C(4)—P(3)	76.6(4)
C(4)—N(5)—C(6)—P(7)	107.7(3)
C(51)—N(5)—C(6)—P(7)	−75.8(4)
C(4)—N(5)—C(51)—C(52)	−5.2(6)
C(4)—N(5)—C(51)—C(56)	173.2(4)
C(6)—N(5)—C(51)—C(52)	178.4(4)
C(6)—N(5)—C(51)—C(56)	−3.2(6)

layers formed by the solvate molecules. This mutual arrangement of the molecules leads to the rather close crystal packing (the free volume of the unit cell is 65 Å^3), while the presence of a substantial amount of the solvent in the crystal results in instability of molecules **1**.

It can be assumed that the preferential formation of the macrocycle of this type, which can be considered as a "cyclic dimer", is associated with the spatial structure of the starting diamine favorable for this process. A series of macrocyclic diphosphonites[8] and metallamacrocycles[9] were prepared based on 4,4′-dihydroxydiphenylmethanes and their thio analogs. The synthesis of dimeric tetraazatetraphosphadimolybdacyclophanes based on diaminodiphenylmethane was also described.[5] Apparently, the use of DMF as the solvent prevents "premature" precipitation of acyclic products and makes it possible to separate compound **1** from other reaction products. However, attempts to transform a mixture of oligo{5-[*p*-(*p*-phenylenemethyl)phenyl]-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctan-1-yls} into compound **1** by heating in DMF failed. Probably, macrocycle **1** was also formed in the reaction performed in an ethanolic solution,[1] its fraction in a mixture of the reaction products (a mixture of oligomers) being variable.

Compound **1** exhibits the properties typical of usual diazadiphosphacyclooctanes. Its treatment with elemental sulfur in boiling DMF afforded the corresponding tetraphosphine sulfide **2**. The ^{31}P NMR spectrum of compound **2** has one signal at δ_P 30.40, which is slightly shifted upfield compared to the signals of monocyclic disulfides of diazadiphosphacyclooctanes (*cf.* δ_P 36 [10]). In the ^{1}H NMR spectrum of compound **2**, the signals for the protons of the methylene groups of the P—$\underline{CH_2}$—N fragments are observed as two doublets at δ 4.49 and 4.74 ($^2J_{HH}$ = 15.5 Hz). In addition, the ^{1}H NMR spectrum has a singlet for the bridging methylene group at δ 3.56, two doublets for the protons of the *p*-phenylene fragments at δ 6.86 and 7.25 ($^3J_{HH}$ = 8.5 Hz), and a multiplet for the protons of the phenyl groups at δ 7.40—8.40. The integral intensity ratio is 2 : 4 : 4 : 4 : 4 : 10. The small constants $^2J_{PH}$ (<2 Hz) observed for the protons of the heterocyclic fragments are indicative of the equatorial orientation of

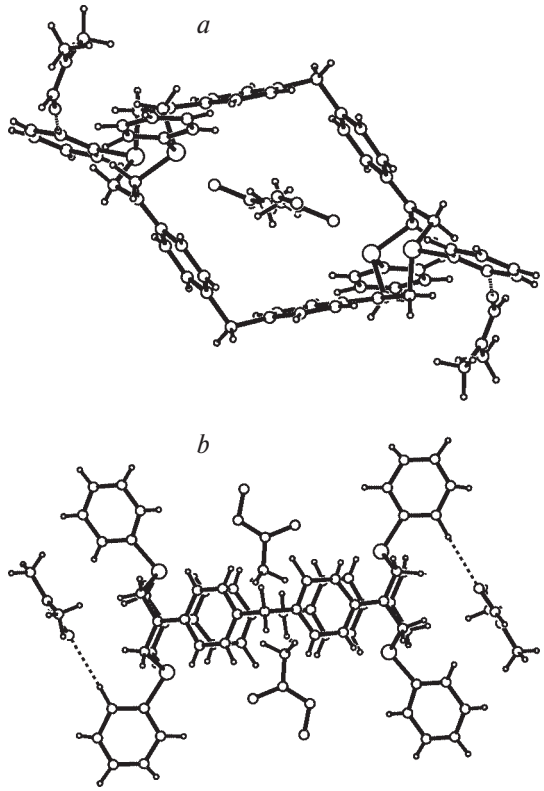


Fig. 2. Mutual arrangement of the molecules of DMF and **1** in the crystal structure: *a*, a view along the direction close to the crystallographic axis 0*x*; *b*, a view along the crystallographic axis 0*y*. The hydrogen bond is indicated by a dashed line.

the P=S bonds. Apparently, the eight-membered ring in compound **2**, like that in 1,5-di-*p*-tolyl-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclooctane,[10] adopts a distorted boat—boat conformation. Oxidation of macrocyclic phosphine **1** with aqueous H_2O_2 in acetone gave rise to a white crystalline compound whose IR spectrum has a stretching vibration band of the phosphoryl group at

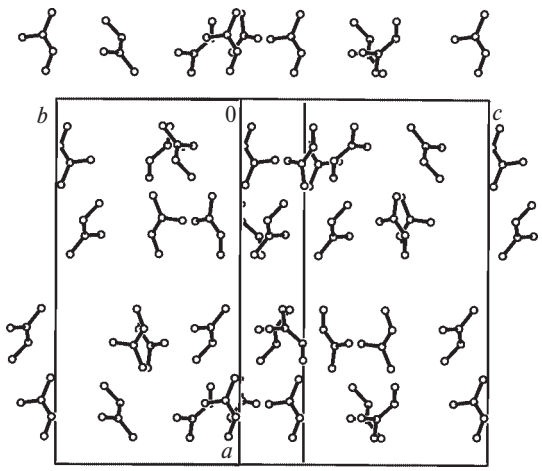


Fig. 3. Layered structure in the crystal of compound **1**. Only solvate DMF molecules are shown.

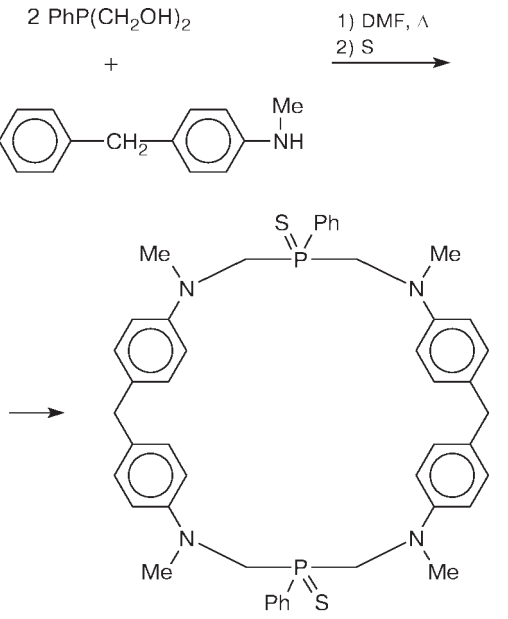
1186 cm^{-1}, an intense broad stretching vibration band of the hydroxy groups with the maximum (ν_{max}) at 3400 cm^{-1}, and a broad band with the maximum at 1660 cm^{-1} belonging, most likely, to bending vibrations of the hydroxy groups of the water molecules. The ^{31}P NMR spectrum of this compound has a signal at δ_P 24.74 typical of diazadiphosphacyclooctane oxides, which suggests that the skeleton of the molecule did not undergo hydrolytic cleavage. The ^1H NMR spectrum of a solution of compound **1** in DMSO-d_6 shows four groups of signals, *viz.*, a singlet of the bridging methylene group at δ 3.71, a broad singlet of the methylene protons of the diazadiphosphacyclooctane fragments at δ 4.42, an AB system of the protons of the *p*-phenylene fragments at δ 6.89 and 7.02 ($^3J_{HH}$ = 8.15 Hz), and a multiplet of the phenyl protons at δ 7.52—8.26; the intensity ratio is 2 : 8 : 4 : 4 : 10. Unfortunately, the signal for the methylene protons of the heterocyclic fragments is generated, which does not allow us to judge the predominant conformation of the molecule in solution. Taking into account also the data from elemental analysis, the structure of 1,1′,5,5′-bis[methylenedi(*p*-phenylene)]di(3,7-dioxo-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) hexahydrate (**3**) was assigned to the product of oxidation of compound **1**. Hexahydrate **3** is a very stable compound. Water is retained in the compound both upon recrystallization from DMSO and upon prolonged drying *in vacuo*. In spite of the presence of the hydrophilic fragments, compound **3** is insoluble in water and its mixtures with organic solvents.

Attempts to prepare analogous macrocyclic tetraphosphines based on 4,4′-diaminodiphenylmethane and other bis(hydroxymethyl)phosphines, *viz.*, bis(hydroxymethyl)mesitylphosphine and bis(hydroxymethyl)(5-allyl-2-ethoxybenzyl)phosphine, failed. In both cases, the reactions afforded mixtures of cyclic and linear oligomers and neither fractional crystallization nor reprecipitation allowed us to isolate the target macrocyclic phosphines. The compounds cannot also be separated by chromatographic methods due to their low solubility. Hence, the difference in the solubility of macrocyclic aminomethylphosphines and acyclic oligomeric compounds formed as by-products is of great (probably, decisive) importance in obtaining the desired compounds in the pure form.

The importance of this factor was confirmed by the results of the synthesis of a monocyclic macrocycle based on the diaminodiphenylmethane derivative, *viz.*, bis[4-(*N*-methylamino)phenyl]methane. Refluxing of bis(hydroxymethyl)phenylphosphine in MeCN afforded a complex mixture of low-molecular-weight oligomeric aminomethylphosphines. To increase the yield of the macrocyclic compounds, we carried out the reaction in DMF, which was ~2.5 times more dilute than that used in the synthesis of compound **1**. It should be noted that even this rather small decrease in the concentration of the re-

agents led to substantial deceleration of the process and the reaction was completed only upon prolonged heating of the mixture at 100 °C (25 h instead of 3-4 h in the synthesis of macrocycle **1**). In the ^{31}P NMR spectrum of the reaction mixture, the predominant signal is observed at δ_P −39.15 and corresponds, apparently, to a macrocyclic product. We succeeded in separating the latter from impurities of other oligomers only by converting it into the corresponding diphosphine disulfide. After the removal of the solvent, extraction of the residue followed by fractional crystallization afforded bis{methylenedi[*p*-phenylene(*N*-methyl)aminomethyl]}di[(*P*-phenyl)phosphine sulfide] (**4**) in very low yield (3.4%). This low yield is, evidently, explained by large losses in the course of purification due to the insignificant difference in solubility of macrocycle **4** and other oligomers. Chromatographic separation did not meet with success as well.

Scheme 2



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Like analogous sulfide **2**, macrocycle **4** is a poorly soluble high-melting crystalline compound. Its IR spectrum has no vibration bands of the terminal hydroxy and amino groups, and its ^{31}P NMR spectrum shows one signal at δ_P 40.03. The ^1H NMR spectrum of compound **4** provides indirect evidence for its cyclic structure because the protons of the methylene groups of the P—CH_2—N fragments are nonequivalent and give an AB system, *viz.*, two doublets at δ 4.20 and 4.32 with $^2J_{HH}$ = 15.75 Hz; $^2J_{PH} \approx 0$. The cyclic structure of dimer **4** was confirmed by its FAB mass spectrum containing the corresponding molecular ion peak at *m/z* 784 (100%).

To summarize, the reactions of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane and its *N*,*N*′-dimethyl derivative afforded previously unknown macrocyclic compounds with the structures of cyclic "dimers" as the major products.

Experimental

The ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer (161 MHz, 85% H_3PO_4 as the external standard). The ^1H NMR spectra were measured on a Bruker WM-250 spectrometer (250 MHz). The IR spectra were recorded on a Specord M-80 spectrometer (Nujol mulls). All operations with phosphines were carried out under an inert atmosphere. The FAB mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer.

X-ray diffraction study of compound 1. Crystals of a solvate of **1** with four DMF molecules, **1**•$4C_3H_7NO$, M = 1225.38, are orthorhombic. At 20 °C, a = 21.526(2), b = 14.658(4), c = 21.793(3) Å, V = 6876.4 Å^3, d_{calc} = 1.18 g cm^{-3}, Z = 4, space group *Pbca* (molecule **1** occupies a special position, *viz.*, a center of symmetry). The unit cell parameters and the intensities of 8271 reflections (of which 3719 reflections were with $I = 3\sigma$) were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer (λMo-Kα, graphite monochromator, ω/2θ scanning technique, $\theta \le 26.3°$). The linear correction was applied to the intensities of the measured reflections based on the decrease in the intensities of three check reflections (34% decrease in the course of X-ray data collection). Absorption was ignored (μ_{Mo} = 1.56 cm^{-1}). The structure was solved by direct methods using the SIR program[11] and refined first isotropically and then anisotropically. The oxygen atom of one of the solvate dimethylformamide molecules is disordered over two positions with equal occupancies (0.5). At the final stage, the positions of the hydrogen atoms were revealed from difference electron density syntheses (except for the H atoms of the disordered fragments) and refined isotropically. The final reliability factors were as follows: R = 0.048, R_w = 0.055 using 3363 independent reflections with $F^2 \ge 3\sigma$. All calculations were carried out on a DEC Alpha Station 200 using the MolEN program package.[12] The atomic coordinates, bond lengths, bond angles, and thermal parameters were deposited with the Cambridge Structural Database (Cambridge Crystallographic Data Centre, CCDC 1135/63).

1,1′,5,5′-Bis[methylenedi(*p*-phenylene)]di(3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (1). Solid paraformaldehyde (0.38 g, 12.66 mmol) was added to $PhPH_2$ [13] (0.69 g, 6.27 mmol) and the reaction mixture was heated on a water bath until the mixture became homogeneous. Bis(hydroxymethyl)phenylphosphine that formed was dissolved in degassed DMF (15 mL), which was preliminarily dried and distilled over fused K_2CO_3, and then a solution of 4,4′-diaminodiphenylmethane (0.62 g, 3.13 mmol) in DMF (15 mL) was added. The reaction mixture was stirred at 100 °C for 3.5 h and then at ~20 °C for 2 days. The precipitate that formed was filtered off, washed successively with DMF and MeCN, and dried at 0.1 Torr for 2 h. Compound **1** was obtained in a yield of 0.75 g (51%), m.p. 210 °C. Found (%): C, 74.05; H, 5.99; N, 6.22; P, 12.87. $C_{58}H_{56}N_4P_4$. Calculated (%): C, 74.68; H, 6.01; N, 6.01;

P, 13.30. ^{1}H NMR (DMSO-d_6), δ: 3.48 (s, 4 H, C$\underline{H}_2$); 4.05 (dd, 8 H, P—C$\underline{H}_e$—N, $^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 13.8 Hz); 4.49 (dd, 8 H, P—C$\underline{H}_a$—N, $^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 3.5 Hz); 6.50 (d, 8 H, *ortho*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.6 Hz); 7.07 (d, 8 H, *meta*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.6 Hz); 7.40—7.70 (m, 20 H, C$_6\underline{H}_5$). ^{31}P NMR (DMF), δ: –52.59. MS (FAB$^+$, Xe, 7 kV), *m/z* (I_{rel} (%)): 932 [M$^+$]$^+$ (100).

1,1′,5,5′-Bis[methylenedi(*p*-phenylene)]di(3,7-bis(thioxo)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (2). A mixture of compound **1** (0.25 g, 0.27 mmol), S_8 (0.034 g, 1.06 mmol), and DMF (10 mL) was heated until the solid compounds were dissolved. After 16 h, the precipitate was filtered off, washed with MeCN, and dried at 0.1 Torr for 2 h. Compound **2** was obtained in a yield of 0.2 g (70%), m.p. 218—220 °C. Found (%): C, 65.31; H, 5.37; N, 5.52; P, 12.01; S, 12.41. $C_{58}H_{56}N_4P_4S_4$. Calculated (%): C, 65.66; H, 5.28; N, 5.28; P, 11.70; S, 12.08. ^{1}H NMR (DMSO-d_6), δ: 3.56 (s, 4 H, C$\underline{H}_2$); 4.49 (d, 8 H, P—C$\underline{H}_A$—N, $^2J_{HH}$ = 15.5 Hz); 4.74 (d, 8 H, P—C$\underline{H}_B$—N, $^2J_{HH}$ = 15.5 Hz); 6.86 (d, 8 H, *ortho*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.5 Hz); 7.25 (d, 8 H, *meta*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.5 Hz); 7.40—8.40 (m, 20 H, C$_6\underline{H}_5$). ^{31}P NMR (DMSO), δ: 30.40.

1,1′,5,5′-Bis[methylenedi(*p*-phenylene)]di(3,7-dioxo-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane) (3). A 30% H_2O_2 aqueous solution (0.07 mL, 0.62 mmol) was added to a suspension of compound **1** (0.12 g, 0.13 mmol) in acetone (5 mL) and the reaction mixture was stirred at ~20 °C for 16 h. Then the precipitate that formed was filtered off, washed with Et_2O, and dried at 0.1 Torr for 2 h. Compound **3** was obtained in a yield of 0.14 g (98%), m.p. 250—253 °C. Found (%): C, 63.10; H, 5.81; N, 5.29; P, 10.96. $C_{58}H_{56}N_4P_4O_4 \cdot 6H_2O$. Calculated (%): C, 63.04; H, 6.16; N, 5.07; P, 11.23. IR, ν/cm^{-1}: 3410 (OH); 1650 (H_2O); 1186 (P=O). ^{1}H NMR (DMSO-d_6), δ: 3.71 (s, 4 H, C$\underline{H}_2$); 4.42 (br.s, 16 H, P—C$\underline{H}_2$—N); 6.89 (d, 8 H, *ortho*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.2 Hz); 7.02 (d, 8 H, *meta*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.2 Hz); 7.52—8.26 (m, 20 H, C$_6\underline{H}_5$). ^{31}P NMR (DMSO), δ: 24.74.

Bis{methylenedi[*p*-phenylene(*N*-methyl)aminomethyl]}di[*P*-(phenyl)phosphine sulfide] (4). A solution of bis[4-(*N*-methylamino)phenyl]methane (0.72 g, 3.18 mmol) in DMF (15 mL) was added to a solution of $PhP(CH_2OH)_2$ (0.54 g, 3.18 mmol) (see the synthesis of **1**) in dry degassed DMF (15 mL). The reaction mixture was stirred at 100 °C for 25 h and cooled to ~20 °C. Then sulfur (0.11 g, 3.43 mmol) was added and the reaction mixture was heated until the sulfur was dissolved. After 16 h, the solvent was removed *in vacuo*, the residue was extracted with a 1 : 2 mixture (15 mL) of MeCN and acetone on refluxing for 0.5 h. The adhesive precipitate, which was obtained after cooling of the extract, was recrystallized from DMF. The initially formed fine precipitate, which consisted of compound **4** and impurities of acyclic oligomers, was separated after which pale-yellow crystals of compound **4** precipitated from the mother liquor upon storage. The crystals were filtered off, washed with MeCN, and dried at 0.1 Torr for 3 h. Compound **4** was obtained in a yield of 0.042 g (3.4%), m.p. 242—246 °C. Found (%): C, 69.82; H, 6.18; N, 6.97; P, 7.93; S, 8.34. $C_{46}H_{50}N_4P_2S_2$. Calculated (%): C, 70.41; H, 6.37; N, 7.14; P, 7.90; S, 8.16. ^{1}H NMR (DMSO-d_6), δ: 2.75 (s, 12 H, NMe); 3.64 (s, 4 H, C$\underline{H}_2$); 4.20 (d, 4 H, P—C$\underline{H}_A$—N, $^2J_{HH}$ = 15.8 Hz); 4.32 (d, 4 H, P—C$\underline{H}_B$—N, $^2J_{HH}$ = 15.8 Hz); 6.64 (d, 8 H, *ortho*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.9 Hz); 6.89 (d, 8 H, *meta*-C$_6\underline{H}_4$, $^3J_{HH}$ = 8.9 Hz); 7.37—8.10 (m, 10 H, C$_6\underline{H}_5$). ^{31}P NMR (DMSO), δ: 40.03. MS (FAB$^+$, Xe, 7 kV), *m/z* (I_{rel} (%)): 784 [M$^+$]$^+$ (100).

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