Cyclo-bis{1-[*p*-(*p*-phenylenomethyl)phenyl]-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane} as the first representative of a new type of nitrogen-containing macroheterocyclic phosphines

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The title compound was synthesised by the interaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane in a dilute DMF solution.

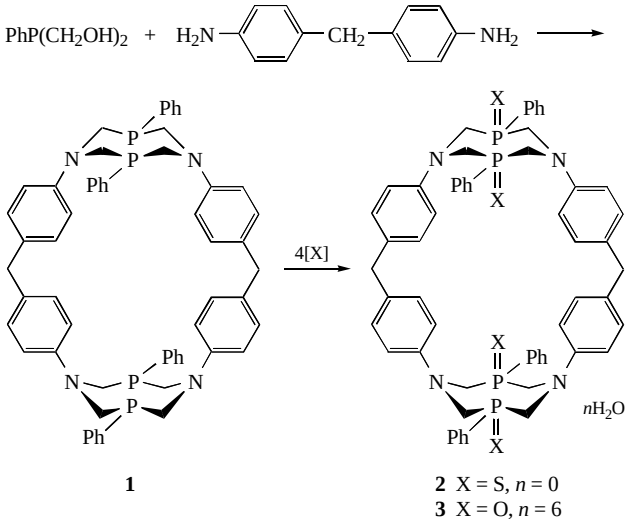
We have previously shown that oligomers with diazadiphosphacyclooctane units can be prepared by the polycondensation of either di(hydroxymethyl)phenylphosphine with diamines or *p*-bis(dihydroxymethylphosphino)xylilene with primary amines.[1] However, the same reactions can lead to the formation of macrocyclic structures with several heterocyclic fragments, which differ considerably from the known nitrogen-containing macrocyclic phosphines.[2,3]

Here we report a synthesis of the first representative of a new type of tricyclic macroheterocycles, *viz.*, cyclo-bis{1-[*p*-(*p*-phenylenomethyl)phenyl]-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane} **1**. Compound **1** was obtained by the interaction of bis(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane upon mixing dilute solutions of the reactants in degassed DMF followed by stirring the reaction mixture for several hours at 80–100 °C: **1** crystallised after cooling the reaction mixture to ambient temperature. The yield of **1** increased with increasing dilution and in the case of additional stirring for 2 days at room temperature. The mother liquor also contained **1** in a mixture with other oligo(diazadiphosphacyclooctanes). The predominant formation of the macrocycle is most likely determined by a favourable spatial structure of the initial diamine, because a series of macrocyclic diphosphonites obtained from 4,4′-dihydroxydiphenylmethane were described.[4] The absorption bands of hydroxyl and amino groups are absent in the IR spectrum of **1**; in general, the spectrum is almost identical to the spectrum of the corresponding oligomer.[1] The ^{31}P NMR spectrum shows one signal with a chemical shift of –52.59 ppm (the average chemical shift of diazadiphosphacyclooctanes is –51 ppm[5]) and points to the equivalence of all phosphorus atoms and hence to a symmetrical structure of the macrocycle in solutions.† The structure of macrocycle **1** was finally confirmed by single-crystal X-ray diffraction analysis.‡

The molecule of **1** is a centrosymmetric macrocyclic ring (Figure 1). The eight-membered heterocycles have chair–chair conformations, and *P*-phenyl substituents are equatorial. The conformations along the P–C(Ph) bonds are staggered. Thus, the lone electron pairs of phosphorus atoms are directed inward the macrocyclic cavity.

The aryl substituents at the nitrogen atoms are axial, and the conformations along the exocyclic N–C(Ph) bonds are eclipsed [the torsion angles C–N–C–C are –1.9(5) and –3.2(6)°]. The nitrogen atoms of the heterocycles are in planar trigonal configurations (the sums of the bond angles are 360 and 359.9°). Note that a similar conformation was previously observed for an isolated molecule of 1,5,3,7-tetraphenyl-1,5,3,7-diazadiphosphacyclooctane.[8]

The peculiarity of the crystal structure of **1** is the presence of two disordered DMF molecules in the macrocyclic cavity with the methyl groups directed inward the cavity. Two other solvate DMF molecules are outside of the macrocycle. Short contacts between the methyl groups of DMF and the centres of gravity of the benzene rings constituting the macrocycle and multiple contacts corresponding to the C–H···O-type hydrogen bonds between the hydrogen atoms of aryl fragments and the oxygen atoms of DMF molecules are observed.



1

2 X = S, *n* = 0
3 X = O, *n* = 6

Compound **1** exhibits properties typical of diazadiphosphacyclooctanes and their analogues, oligo(diazadiphosphaoctanes). Tetrasulfide **2** was obtained by the interaction of **1** with elemental sulfur in boiling DMF. Its ^{31}P NMR spectrum also shows one signal with a chemical shift of 30.40 ppm.§ The stable hexa-

† All new compounds synthesised had satisfactory elemental analysis data. **1**: yield 51%, mp 210 °C (DMF). ^{31}P NMR (DMF) δ: –52.59. IR (KBr, Nujol, ν/cm^{-1}): 696 (s, $\delta_{C-H_{ar}}$), 752 (s, $\delta_{C-H_{ar}}$), 794 (s, $\delta_{C-H_{ar}}$), 834 (m), 872 (m), 892 (m), 984 (m), 1154 (s), 1188 (s), 1204 (s), 1224 (s), 1254 (s), 1280 (m), 1330 (m), 1368 (s), 1376 (s), 1450 (s), 1460 (s), 1482 (m), 1512 (vs, $\nu_{C=C_{ar}}$), 1612 (s, $\nu_{C=C_{ar}}$), 3044 (w, $\nu_{C-H_{ar}}$), 3068 (w, $\nu_{C-H_{ar}}$).

‡ *Crystal data for* **1**. $C_{58}H_{56}N_4P_4 \cdot 4C_3H_7NO$, M = 1225.38, orthorhombic, space group *Pbca*, a = 21.526(2), b = 14.658(4), c = 21.793(3) Å, V = = 6876.4 Å^3, Z = 4 (the molecule in a special position at the centre of symmetry), d_{calc} = 1.62 g cm^{-3}, T = 20 °C, F(000) = 2576. The cell parameters and the intensities of 8271 independent reflections (3719 with $I \geq 3\sigma$) were measured on an Enraf-Nonius CAD-4 diffractometer (λMoKα, graphite monochromator, $\omega/2\theta$ scan, $\theta \leq 26.3°$). The linear decay correction of the intensities of reflections was carried out (the intensities of the 3 control reflections decreased by 34%), the absorption correction was not applied (μMo = 1.56 cm^{-1}). The structure was solved by the direct methods using the SIR program[6] and refined in isotropic and finally in anisotropic approximations. The oxygen atom of one of the solvate DMF molecules is disordered between two positions with the equal occupancies 0.5. Hydrogen atoms were solved from the difference electron density synthesis (except hydrogen atoms of the disordered fragments) and were refined isotropically. The final values of the discrepancy factors are R_1 = 0.048 and wR_2 = 0.055 for 3363 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried out on a DEC Alpha Station computer using the MolEN program.[7] Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2000. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/63.

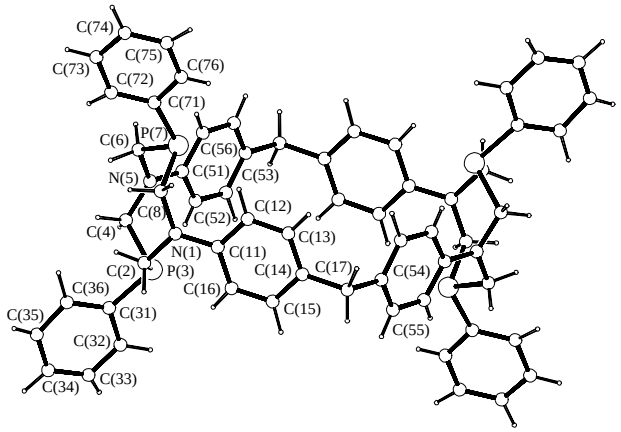


Figure 1 Molecular structure of compound **1**.

hydrate of tetraoxide **3** was obtained by oxidation of **1** with aqueous hydrogen peroxide in acetone. The IR spectrum of **3** exhibits an absorption band of the phosphoryl group at 1186 cm^{-1}, an intense broad absorption band of water hydroxyl groups at 3400 cm^{-1} and a broad absorption band of water molecules at 1660 cm^{-1}. The ^{31}P NMR spectrum shows a signal with the chemical shift 24.74 ppm, which is characteristic of cyclic aminomethylphosphine oxides and points to the retention of the molecular skeleton.¶

Thus, the interaction of di(hydroxymethyl)phenylphosphine with 4,4′-diaminodiphenylmethane afforded a new macrocyclic tetraphosphine.

§ **2**: yield 70%, mp 218–220 °C (DMF). ^{31}P NMR (DMSO) δ: 30.40. IR (KBr, Nujol, ν/cm^{-1}): 694 (s, $\delta_{C-H_{ar}}$), 728 (s, $\delta_{C-H_{ar}}$), 798 (s, $\delta_{C-H_{ar}}$), 864 (s), 908 (s), 1000 (w), 1024 (w), 1100 (s), 1168 (s), 1188 (m), 1208 (m), 1224 (m), 1252 (m), 1276 (m), 1290 (m), 1328 (m), 1352 (s), 1376 (s), 1404 (w), 1436 (s), 1460 (s), 1488 (w), 1514 (vs, $\nu_{C=C_{ar}}$), 1610 (s, $\nu_{C=C_{ar}}$), 3052 (w, $\nu_{C-H_{ar}}$).

¶ **3**: yield 98%, mp 250–253 °C (acetone). ^{31}P NMR (DMSO) δ: 24.74. IR (KBr, Nujol, ν/cm^{-1}): 696 (s, $\delta_{C-H_{ar}}$), 716 (s), 732 (s), 752 (s, $\delta_{C-H_{ar}}$), 804 (s, $\delta_{C-H_{ar}}$), 886 (w), 998 (w), 1016 (w), 1028 (w), 1072 (w), 1108 (s), 1146 (s), 1186 (br. vs, $\nu_{P=O}$), 1256 (m), 1280 (m), 1308 (m), 1354 (s), 1366 (s), 1436 (s), 1460 (s), 1518 (vs, $\nu_{C=C_{ar}}$), 1610 (s, $\nu_{C=C_{ar}}$), 1660 (br. m, δ_{H_2O}), 3060 (w, $\nu_{C-H_{ar}}$), 3416 (br. s, ν_{H_2O}).

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