

## The first representative of novel 36-membered P,N,O-containing cyclophanes

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1<sup>3</sup>,1<sup>7</sup>,7<sup>3</sup>,7<sup>7</sup>-Tetraphenyl-3,5,9,11-tetraoxa-1,7(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,6,8,12(1,4),4,10(1,3)-hexabenzencyclo-dodecaphane was obtained by the condensation of bis(hydroxymethyl)phenylphosphine with 1,3-bis(4-aminophenoxy)benzene and structurally characterised by X-ray single-crystal diffraction.

Macrocycles containing three-coordinated phosphorus atoms as soft donor centres and internal cavities as non-valent binding sites for organic substrates have potential applications in supramolecular and synthetic organic chemistry,<sup>1</sup> in particular, as ligands for transition-metal-catalysed reactions<sup>2</sup> or receptors and sensors.<sup>3</sup> Relatively few cyclophanes with trivalent phosphorus atoms in the cycle and large and deep intramolecular cavities have been reported up to now.<sup>1,4,5</sup> A recently found approach to the synthesis of 28-membered cage P,N-containing cyclophanes, namely, 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzencyclooctaphanes, is based on the covalent self-assembly<sup>6</sup> of the macrocycles in the course of condensation between bis(hydroxymethyl)organylphosphines and primary diamines formed by two *p*-aniline fragments linked by various one-atom bridges.<sup>7</sup> These diamines are pre-disposed for the macrocyclization due to the appropriate turning angles<sup>8</sup> (about 100–120°) and the possibility of the open-book<sup>9</sup> conformations of their spacers, which are favourable for the conjugation of nitrogen electron lone pairs with the  $\pi$  systems of benzene rings in the resulting cyclophanes. 1,3-Bis(4-aminophenoxy)benzene **1** contains a longer and more flexible spacer, but one of its possible conformations (Scheme 1) has a similar geometry. Diamine **1** may also react with bis(hydroxymethyl)-organylphosphines as a bridging building unit to form similar macrocyclic tetraphosphines of a larger size. Only few examples of macrocycles with 1,5(1,4),3(1,3)-tribenzenapentaphane<sup>5(a),10</sup>

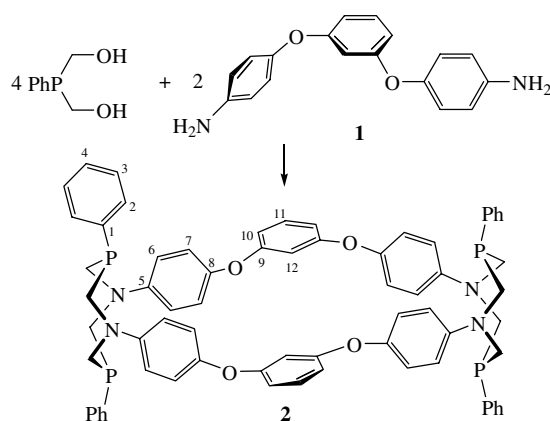
and 2,4-dioxa-1,5(1,4),3(1,3)-tribenzenapentaphane<sup>9</sup> fragments are reported, and to the best of our knowledge diamine **1** has never been used before for cyclophane design.

The condensation of diamine **1** with bis(hydroxymethyl)-phenylphosphine was performed in DMF at 110 °C at a phosphine concentration of 0.45 mol dm<sup>-3</sup>. In the <sup>31</sup>P NMR spectrum of the resulting reaction mixture, the peak at  $\delta_P$  –51.7 ppm prevailed over the others and the relative concentration of the major product in the reaction mixture was about 80%. The main compound was isolated by spontaneous crystallization in a yield of 35% as an air-stable crystalline solid. Its mass spectrum (ESI<sub>pos</sub>) showed a peak with *m/z* 1121 for the protonated molecular ion of 1<sup>3</sup>,1<sup>7</sup>,7<sup>3</sup>,7<sup>7</sup>-tetraphenyl-3,5,9,11-tetraoxa-1,7(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,6,8,12(1,4),4,10(1,3)-hexabenzencyclo-dodecaphane **2** (Scheme 1).<sup>†</sup> The NMR spectra of **2** indicate the symmetrical structure of the macrocycle in solution (the atomic numbering scheme for the independent part of the molecule of **2** is shown in Scheme 1). The proton signals of the P–CH<sub>2</sub>–N fragments appear as the (AB)<sub>2</sub>X spin system. The coupling constants <sup>2</sup>*J*<sub>HH</sub> and <sup>2</sup>*J*<sub>PH</sub> indicate a prevailing chair–chair conformation of 1,5-diaza-3,7-diphosphacyclooctane fragments with an equatorial orientation of substituents on the phosphorus atoms.

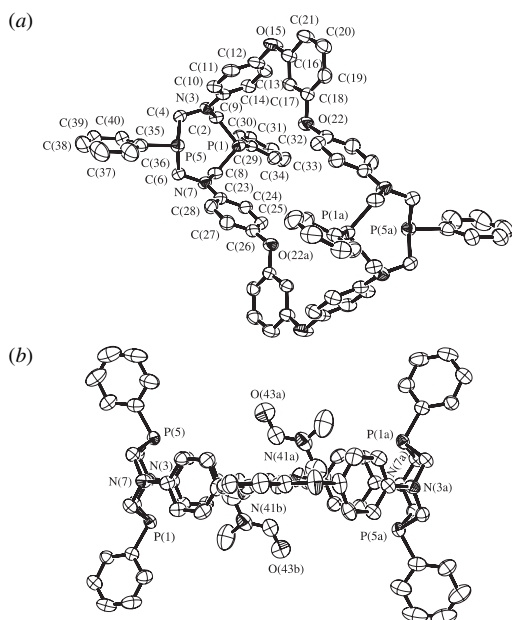
The structure of cyclophane **2** (Figure 1) was investigated by X-ray analysis.<sup>‡</sup> The single crystals of **2** were obtained as

<sup>†</sup> All manipulations were carried out by standard high-vacuum and dry-nitrogen techniques. NMR spectra: Avance DRX 400 (Bruker); standards: <sup>1</sup>H NMR (400 MHz): TMS; <sup>31</sup>P NMR (162 MHz), external 85% H<sub>3</sub>PO<sub>4</sub>. The ESI (positive) mass spectra were obtained on a Esquire 3000 Plus mass spectrometer.

**Cyclophane 2.** Bis(hydroxymethyl)phenylphosphine<sup>7</sup> (1.56 g, 9.2 mmol) was dissolved in dry degassed DMF (10 ml), and then a solution of diamine **1** (1.36 g, 4.6 mmol) in DMF (10 ml) was added. The reaction mixture was stirred at 110 °C for two days. The precipitate formed was filtered off, washed carefully with DMF and MeCN and dried at 0.1 Torr for 4 h. Yield of **2**, 0.91 g (35%); mp 212–214 °C. <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]DMSO)  $\delta$ : 4.16 (dd, 8H, P–CH<sub>2</sub>–N, <sup>2</sup>*J*<sub>HH</sub> 14.2 Hz, <sup>2</sup>*J*<sub>PH</sub> 13.2 Hz), 4.63 (dd, 8H, P–CH<sub>2</sub>–N, <sup>2</sup>*J*<sub>HH</sub> 14.2 Hz, <sup>2</sup>*J*<sub>PH</sub> 3.2 Hz), 5.99 (br. s, 2H, C<sup>12</sup>H), 6.35 (br. d, 4H, C<sup>10</sup>H, <sup>3</sup>*J*<sub>HH</sub> 7.8 Hz), 6.74 (d, 8H, C<sup>6</sup>H, <sup>3</sup>*J*<sub>HH</sub> 8.6 Hz), 6.97 (d, 8H, C<sup>7</sup>H, <sup>3</sup>*J*<sub>HH</sub> 8.6 Hz), 7.11 (t, 2H, C<sup>11</sup>H, <sup>3</sup>*J*<sub>HH</sub> 7.8 Hz), 7.50–7.52 (m, 12H, C<sup>2</sup>H, C<sup>4</sup>H), 7.72 (br. s, 8H, C<sup>3</sup>H). <sup>31</sup>P NMR ([<sup>2</sup>H<sub>6</sub>]DMSO)  $\delta$ : –53.8. MS (ESI<sub>pos</sub>), *m/z* (%): 1121 (100) [M + H]<sup>+</sup>. Found (%): C, 72.54; H, 5.67; N, 4.88; P, 11.39. Calc. for C<sub>68</sub>H<sub>60</sub>N<sub>4</sub>O<sub>4</sub>P<sub>4</sub> (1121.13) (%): C, 72.86; H, 5.36; N, 5.00; P, 11.07.



Scheme 1



**Figure 1** (a) ORTEP view of **2** and (b) the side view of **2** with the two closest DMF molecules. Hydrogen atoms and other solvate molecules are omitted for clarity; ellipsoids are shown with 50% probability. Selected bond lengths (Å), bond and torsion angles (°): P(1)–C(29) 1.828(8), P(1)–C(2) 1.868(8), C(2)–N(3) 1.451(8), N(3)–C(9) 1.387(8), C(12)–O(15) 1.403(8); C(2)–P(1)–C(29) 100.7(4), C(8)–P(1)–C(29) 98.6(4), C(2)–P(1)–C(8) 100.3(4), C(2)–N(3)–C(4) 117.5(6), C(2)–N(3)–C(9) 120.9(7), C(4)–N(3)–C(9) 121.3(6), C(12)–O(15)–C(16) 118.2(6); C(11)–C(12)–O(15)–C(16) 80.9(6), C(12)–O(15)–C(16)–C(17) 2.5(6).

a solvate with nine molecules of DMF. The molecule of the cyclophane is in a special position at the inversion centre coinciding with the centre of cavity. The molecular structure of **2** can be described as two halves of a truncated rhombohedral prism, which are moved apart with the central resorcinol fragments. The phenyl substituents on the phosphorus atoms are in equatorial positions, so that the electron lone pairs of these atoms are directed into the macrocyclic cavity. The *p*-phenylene rings are practically orthogonal to the reference plane formed by four trigonal-planar nitrogen atoms (the dihedral angles are about 85–86°), whereas the central *m*-phenylene fragments are almost coplanar to it (the dihedral angles are about 5°). As a result, the cavity of **2** is elongated in comparison with the cavities of 1,5(1,5)-di(1,5-diaza-3,7-diphosapacyclooctana)-2,4,

‡ *Crystallographic data for 2*. Single crystal of  $2 \cdot 9\text{C}_3\text{H}_7\text{NO}$  was grown from DMF and placed on a Nonius KappaCCD sealed tube diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were collected with  $\omega$  and  $\varphi$  scans. Programs used: data collection, COLLECT;<sup>11</sup> cell refinement, Dirax/lsq;<sup>12</sup> data reduction, EvalCCD;<sup>13</sup> absorption correction, SADABS;<sup>14</sup> structure solution, SIR97<sup>15</sup> implemented in the WINGX package;<sup>16</sup> structure refinement by full-matrix least-squares against  $F^2$  using SHELXL-97.<sup>17</sup> All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in idealised positions and refined using a riding model. All disordered solvent molecules were refined with geometry and thermal displacement restraints.

Crystals of  $\text{C}_{68}\text{H}_{60}\text{N}_4\text{O}_4\text{P}_4 \cdot 9\text{C}_3\text{H}_7\text{NO}$  ( $0.60 \times 0.33 \times 0.22$  mm) are colourless, triclinic, space group  $P1$  (no. 2),  $M = 1778.94$ ,  $a = 13.252(1)$ ,  $b = 14.161(1)$  and  $c = 14.405(1)$  Å,  $\alpha = 112.30(1)$ ,  $\beta = 95.61(1)$  and  $\gamma = 101.85(1)^\circ$ ,  $V = 2401.3(3)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.230$  g cm<sup>−3</sup>,  $\mu = 0.145$  mm<sup>−1</sup>, empirical absorption correction ( $0.815 \leq T \leq 0.969$ ),  $Z = 1$ ,  $T = 198$  K, 53567 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ),  $[(\sin \theta)/\lambda] = 0.60$  Å<sup>−1</sup>, 8786 independent ( $R_{\text{int}} = 0.037$ ) and 6865 observed reflections [ $I \geq 2\sigma(I)$ ], 644 refined parameters,  $R = 0.058$ ,  $wR_2 = 0.155$ , maximum residual electron density  $0.45$  (−0.39) eÅ<sup>−3</sup>.

CCDC 638432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2007.

6,8(1,4)-tetrabenzenacyclooctaphanes: the P(1)–P(5a) distance is 12.3 Å (vs. 8.6–9.8 Å<sup>7</sup>). The O(22)–O(22a) distance in the narrowest part of the macrocycle is 6.48 Å. The free volume of the intramolecular cavity is about 165 Å<sup>3</sup> (vs. 100–120 Å<sup>3</sup> for 28-membered cyclophanes<sup>7</sup>).

All DMF molecules are strongly disordered. The methyl groups of two molecules penetrate into the macrocyclic cavity between two *p*-phenylene groups. Their positions indicate H– $\pi$  interactions between protons and both *p*-phenylene fragments of the cyclophane (the distances between their centroids and the closest protons are about 3.1–3.2 Å). The solvate complex is not very stable and prolonged washing with acetonitrile gives solvent-free microcrystalline cyclophane **2**.

The spontaneous selective formation of the first representative of novel 36-membered cage cyclophanes **2** at relatively high concentrations is a new example of covalent self-assembly processes in the course of Mannich-type condensations. Bis(4-aminophenyl)methanes and analogous diamines are not the only possible starting reagents for the synthesis of macrocyclic cage aminomethylphosphines, and this condensation may be used for the design of P,N-containing cyclophanes with various cavities.

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