Targeting large phosp(III)azane macrocyles $[\{P(\mu\text{-}NR)\}_2(LL)]_n$ ($n \geq 2$)

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Received 23rd May 2006, Accepted 10th July 2006
First published as an Advance Article on the web 21st July 2006
DOI: 10.1039/b607332h

The condensation reactions of the dimer $[ClP(\mu\text{-}NR)]_2$ (**7**) with organic diacids $[LL(H)_2]$, possessing linear orientations of their organic groups, result in the formation of phospha(III)zane macrocyles of the type $[\{P(\mu\text{-}NR)\}_2(LL)]_n$ of various sizes. The series of macrocycles $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$ (**1**), $[\{P(\mu\text{-}NCy)\}_2(1,5\text{-}O_2C_{10}H_6)]_n$ [$n = 3$ (**2a**); $n = 4$ (**2b**)], $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2C_6H_4\}]_4$ (**3**), $[\{P(\mu\text{-}N^tBu)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**4**), $[\{P(\mu\text{-}NCy)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**5**) and $[\{P(\mu\text{-}N^tBu)\}_2\{(NH)C_6H_4OC_6H_4(NH)\}]_2$ (**6**) can be related to classical organic frameworks, like calixarenes.

Introduction

Phosph(III)azane dimers of the type $[ClP(\mu\text{-}NR)]_2$ are excellent building blocks for the formation of a range of inorganic macrocycles. This is at least in part due to the fact that the thermodynamic preference for the *cis*-isomers results in pre-organisation of the reactions to cyclise rather than form polymers.[1] For some time it has been known that the condensation reactions of these dimers with bifunctional organic acids $LL'(H_2)$ give cyclic oligomers of the type $[\{P(\mu\text{-}NR)\}_2\{LL'\}]_n$. However, until recently there was only unequivocal evidence[2] for the existence of monomers of this type ($n = 1$).[3] Monomers appear to be particularly prevalent where more flexible aliphatic spacers are involved (Fig. 1). More recently, it was found that macrocyclic dimers ($n = 2$) can be obtained from these reactions,[4] depending on the reaction conditions employed and the orientation of the organic substituents present in the organic spacer. In particular, rigid aromatic spacers possessing *ortho*- or *para*-substituents normally give rise to dimeric macrocycles of this type (Fig. 2).[4b,c]

Our interest in these species stems not only from their ease of synthesis but also from the multifaceted behaviour of macrocyles of this type, which can function potentially as P-donors (at their peripheries),[5] or as metal or anion hosts (within their cavities).[6] In order to realise the full potential of these ligands, our attention has been focused most recently on exploring the synthesis of macrocyles larger than dimers—whose small, elliptical cavities appear to be unsuitable for the coordination of hosts. We report here the syntheses of $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_7\}]_3$ (**1**),[7] $[\{P(\mu\text{-}NCy)\}_2(1,5\text{-}O_2C_{10}H_7)]_n$ [$n = 3$ (**2a**); $n = 4$ (**2b**)], $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2C_6H_4\}]_4$ (**3**),[8] $[\{P(\mu\text{-}N^tBu)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**4**), $[\{P(\mu\text{-}NCy)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**5**) and $[\{P(\mu\text{-}N^tBu)\}_2\{(NH)C_6H_4OC_6H_4(NH)\}]_2$ (**6**), containing a variety of spacers, and on the observation of host–ndash behaviour which mirrors that found commonly in related calixarenes.

Results and discussion

The syntheses and structures of the trimer $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_7\}]_3$ (**1**)[7] and tetramer $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2\text{-}C_6H_4\}]_4$ (**3**) (Fig. 3),[8] containing N-functionalised bridging organic groups, have been communicated by us previously. Both complexes are generated by the condensation reactions of $[ClP(\mu\text{-}N^tBu)]_2$ with 1,5-diamino-naphthalene or phenylenediamine in the presence of Et_3N. Compounds **1** and **3** are of interest in that they are the only examples of macrocycles of this type bigger than dimers. The presence of *endo*-directed N–H groups in these macrocycles potentially allows these species to behave as H-bonding, anion receptors. In the current study we wanted, in particular, to explore the synthesis of larger macrocycles of this type containing donor O-functionality which (like crown ethers) might be capable of the coordination of cations. The new macrocycles $[\{P(\mu\text{-}N^tBu)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**4**) and $[\{P(\mu\text{-}N^tBu)\}_2\{(NH)C_6H_4OC_6H_4(NH)\}]_2$ (**6**)

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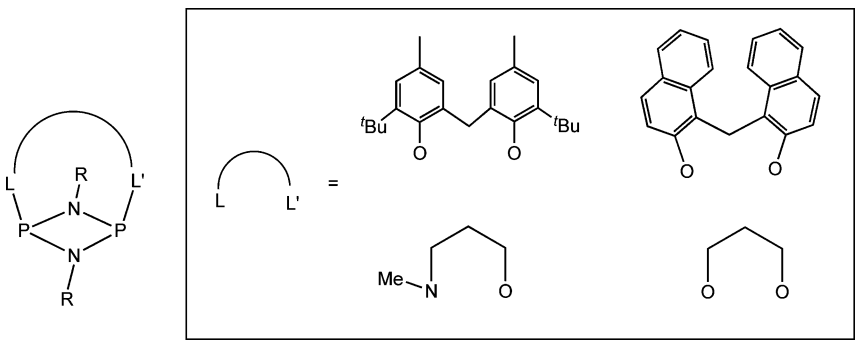


Fig. 1 Monomers ($n = 1$) formed by various organic spacers.

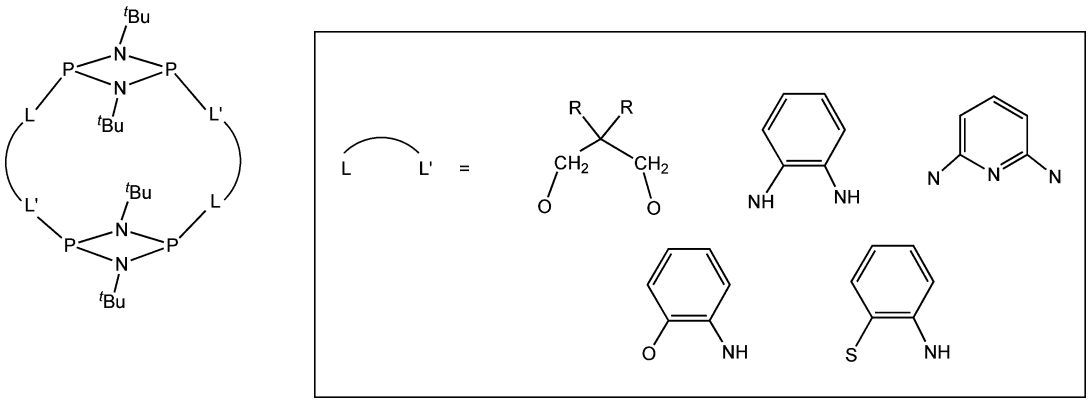


Fig. 2 Dimers ($n = 2$) formed by various organic spacers.

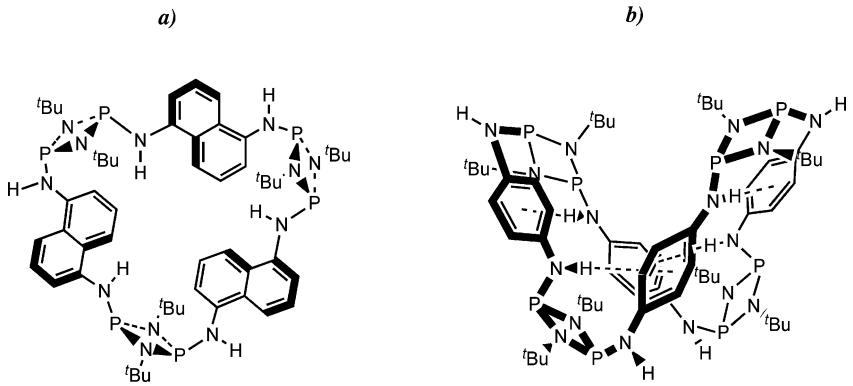
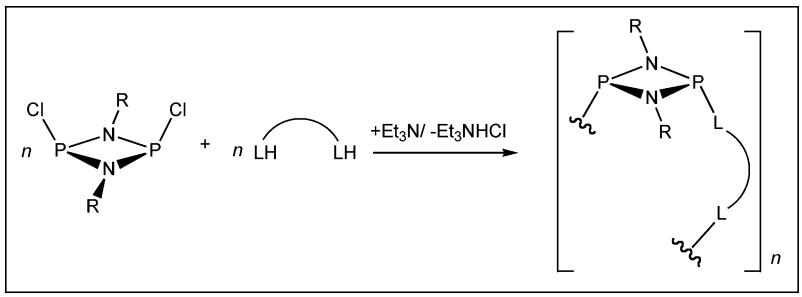


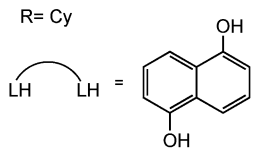
Fig. 3 Structures of (a) the bowl-shaped trimeric macrocycle **1** and (b) the folded macrocycle **3**.

were obtained in a similar manner to **1** and **3** from the reactions of the dimer $[ClP(\mu\text{-}N^tBu)]_2$ with the appropriate organic diacids in the presence of Et_3N as the Brønsted base. $[\{P(\mu\text{-}NCy)\}_2(1,5\text{-}O_2C_{10}H_7)]_3$ (**2**) and $[\{P(\mu\text{-}NCy)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**5**) were obtained from reactions involving the novel dimer $[ClP(\mu\text{-}NCy)]_2$ (**7**) (Scheme 1).

The macrocycles **2**, **4**, **5** and **6** were characterised using a combination of NMR and mass spectroscopic techniques. Although elemental analysis was also employed in the case of **4** and **6**, satisfactory analysis was difficult to obtain on these species despite repeated attempts. The reaction of 1,5-dihydroxy-naphthalene with $[ClP(\mu\text{-}NCy)]_2$ produces a *ca.* 1 : 1 mixture of two distinct macrocylic oligomers (Fig. 4). Their presence can be discerned from the room-temperature ^{31}P NMR spectrum in $CDCl_3$ which consists of two singlets at $\delta = 138.6$ and 134.9. These resonances both split into 1 : 1 singlets at 250 and 265 K, respectively, resulting from the resolution of the *exo*- and *endo*-P atoms of the macrocylic framework (Fig. 5). Mass spectroscopy shows that these species are a trimer (**2a**) ($m/e = 1244.0$, $[trimerH]^+$) and a tetramer (**2b**) ($m/e = 1656.6$, $[tetramerH]^+$) (Fig. 4). Fractional crystallisation of **2** led to the isolation of crystals of the trimer **2a**, which was characterised by X-ray crystallography (see later). Interestingly, the closely related reaction of $[ClP(\mu\text{-}^tBu)]_2$ with 1,5-diamino-naphthalene gives only the trimer $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$ (**1**) (as shown by *in situ* ^{31}P NMR studies). This difference is probably due to a combination of the different geometric demands of the N atoms and different steric demands of the ^{t}Bu groups in **1**. In particular, the lower steric demands of the Cy groups within the P_2N_2 units of **2** will allow the formation of larger oligomers, by reducing the overall steric congestion at the periphery of the macrocycles. A further difference between **1** and **2** is the far lower activation energy for the interconversion of the *exo*- and *endo*-P atoms in **2** (obtained from ^{31}P NMR spectroscopic studies).[9] Whereas the activation Gibb's free energy for this process is similar for the two oligomers of **2** at $\Delta G^{\ddagger} \approx$ 43–45 kJ mol^{-1}, two distinct resonances for these environments are found for the analogous N-functionalised trimer **1** at room temperature, with no interconversion between *exo*- and *endo*-P environments in toluene solvent up to a temperature of 333 K. The $\Delta G^{\ddagger}$ found for the oligomers of **2** compares to 31 kJ mol^{-1} found for the dimer $[\{P(\mu\text{-}N^tBu)\}_2(OCH_2C(Me)_2CH_2O)]_2$, containing a flexible $OCH_2C(Me)_2CH_2O$ linker.[4c]

The major P-containing products formed in the reactions of hydroquinone with $[ClP(\mu\text{-}N^tBu)]_2$ or $[ClP(\mu\text{-}NCy)]_2$ are the trimers $[\{P(\mu\text{-}N^tBu)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**4**) and $[\{P(\mu\text{-}NCy)\}_2(1,4\text{-}O_2C_6H_4)]_3$ (**5**), as shown by an *in situ* ^{31}P NMR spectrum of the reaction mixtures (Fig. 6). The room-temperature ^{31}P NMR spectra of both species consist of singlets ($\delta = 136.6$ for **4** and 141.2 for **5**). These resonances split into two singlets for both compounds at low temperature (*ca.* 240 K for **4**; *ca.* 250 K for **5**) with associated activation Gibb's free energies ($\Delta G^{\ddagger} \approx 43$ kJ mol^{-1} for **4**; 41 kJ mol^{-1} for **5**) which are very similar to those found for the O-functionalised trimer (**2a**) and tetramer (**2b**). Again, comparison can be made with the behaviour of the previously reported trimer (**3a**) and tetramer (**3b**) formed in the reaction of phenylenediamine with $[ClP(\mu\text{-}N^tBu)]_2$. The *exo*- and *endo*-P atoms in both of these





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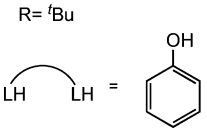

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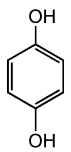

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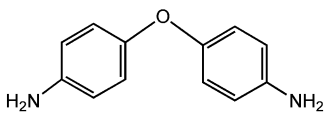

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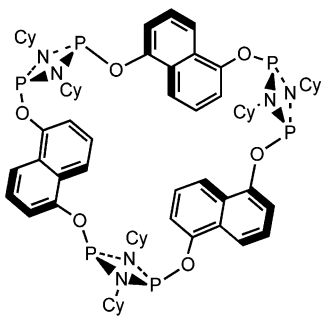
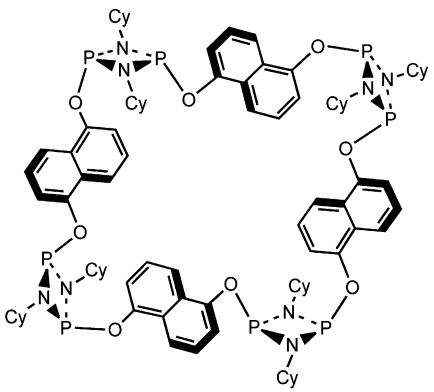
Scheme 1



2a



2b

Fig. 4 Structures of the trimer and tetramer of **2**.

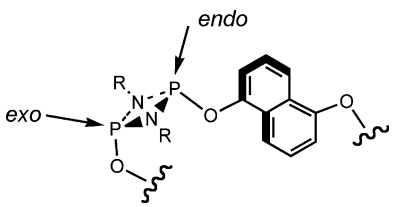
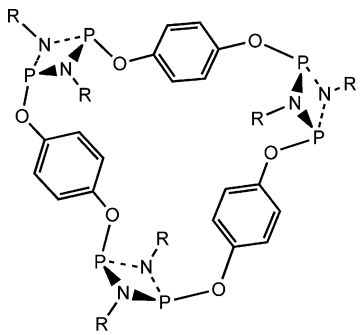


Fig. 5 *exo*- and *endo*-P atoms in the trimer and tetramer of **2**.

oligomers do not interconvert at room temperature. In the case of the tetramer **3b** the activation Gibb's free energy for this process ($\Delta G^{\ddagger} = 83$ kJ mol^{-1}) is considerably higher than that found for the various oligomers of **2**, **4** or **5**. Despite repeated attempts, we were unable to obtain crystals of **5** for X-ray analysis, although mass spectroscopy suggests the presence of a trimer (observed as a low-abundance [trimerH]$^{+}$ peak). However, suitable crystals of



R = ^{t}Bu (**4**)
R= Cy (**5**)

Fig. 6 Trimeric arrangement of **4** and **5**.

the closely related macrocycle **4** were grown from *n*-pentane and the compound confirmed to be trimeric in the solid state (see later).

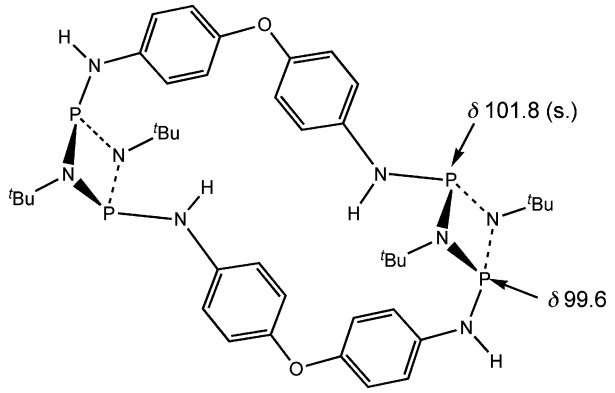


Fig. 7 Structure of the macrocyclic dimer **6**.

The reaction of the O/N-functionalised spacer 4,4′-oxydianiline with $[ClP(\mu\text{-}N^tBu)]_2$ was undertaken as a potential alternative strategy towards larger phosphazane macrocycles. It transpires, however, that the only product of this reaction is the dimer $[\{P(\mu\text{-}N^tBu)\}_2\{(NH)C_6H_4OC_6H_4(NH)\}]_2$ (**6**) (Fig. 7). Although similar in connectivity to previously reported dimers of this type, nonetheless the size of the organic spacer results in a large macrocyclic cavity. NMR spectroscopy of **6** provides extremely clear evidence of the macrocyclic nature of its structure. The room-temperature ^{31}P NMR spectrum of **6** consists of two singlets (δ = 101.8, 99.6) for the *exo*- and *endo*-P atoms of the macrocyle (the resonance at δ 99.6 splitting into a 1 : 1 doublet as a result of coupling to an N–H proton). The rigidity of the macrocyle at room temperature results in the inequivalence of the two aromatic rings of the NH–C_6H_4–O–C_6H_4–NH linker. Thus, the aromatic ring next to the *exo*-P centres H-atoms are inequivalent to the aromatic ring next to the *endo*-P atom, with the result that two sets of doublets are observed in the aromatic region of the room-temperature ^1H NMR spectrum. In addition, the *exo*- and *endo*-directed N–H groups also appear as two separate doublets (as a result of coupling to their respective P centres).

Low-temperature X-ray structures of the new macrocycles **2a**·thf·*n*-pentane, **4** and **6**·2toluene provide unequivocal evidence of the structures of the compounds, supporting the preliminary analytical and spectroscopic results described above. For completeness, the structure of the dimeric precursor **7** was also obtained. Details of the data collections and refinements of these compounds are provided in Table 1 (Experimental section). The three compounds **2a**, **4** and **7** all presented difficulties in refinement, due to problems either with the quality of the crystals or with inherent crystallographic features. As a result, bond lengths and angles are of little value for detailed comparative purposes. Where appropriate, selected bond lengths and angles are given in the figure captions to each of the structures.

The structure of **2a** is that of a trimer, in which the P_2N_2 ring units are linked into a cyclic structure by 1,5-$O_2C_{10}H_6$ groups (Fig. 8). This is very similar to that of the nitrogen analogue $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$ (**1**) reported previously (Fig. 3a).[7] Like **1**, macrocyclic molecules of **2a** have approximate C_3 symmetry in which the naphthyl groups are arranged in a bowl (or cone) shape which is reminiscent of the conformation of a calixarene.[10] The cavity of **2a** is considerably smaller than that of **1** [with a mean radius of *ca*. 3.5 Å measured from the three *endo*-O atoms O(2), O(4) and O(6) to their centroid; *cf*. *ca*. 4.4 Å in **1** measured with respect to the three *endo*-N(H) atoms[7]]. The more compact nature of the structure of **2a** is also evident in the far greater inclination

Table 1 Crystal data and structure refinements for **2a**·thf·*n*-pentane, **4**, **6**·2toluene and **7**[a]

	2a·thf.·*n*-pentane	**4**	**6**·2toluene	**7**
Empirical formula	$C_{79}H_{112}N_6O_8P_6$	$C_{42}H_{66}N_6O_6P_6$	$C_{54}H_{72}N_8O_2P_4$	$C_{12}H_{22}Cl_2N_2P_2$
Fw	1459.57	936.83	989.08	327.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C2/m$
a/Å	13.205(3)	17.410(4)	17.832(4)	13.707(3)
b/Å	33.184(7)	15.925(3)	13.419(3)	5.4813(11)
c/Å	18.385(4)	37.093(7)	23.472(5)	21.039(4)
β/°	102.98(3)	100.04(3)	92.05(3)	91.74(3)
Z	4	8	4	2
V/Å^3	7850(3)	10126(4)	5615(2)	1580(5)
ρ(calc)/Mg m^{-3}	1.235	1.229	1.170	1.375
μ(Mo-Kα)/mm^{-1}	0.194	0.260	0.180	0.599
F(000)	3128	3984	2114	6888
Refl. collected	49553	25649	22915	5658
Crystal size/mm	0.16 × 0.16 × 0.14	0.25 × 0.05 × 0.05	0.42 × 0.16 × 0.16	0.18 × 0.08 × 0.05
θ range/°	3.51–21.05	3.53–19.00	3.57–24.00	3.60–25.00
Indep. refns. (R_{int})	8441 (0.048)	7246 (0.157)	8650 (0.089)	1545 (0.054)
Absorp. corr.	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.971, 0.906	0.991, 0.722	0.997, 0.867	0.971, 0.898
Data/restraints/parameters	8441/61/879	7235/1032/901	8650/0/580	1545/15/116
Goodness-of-fit on F^2	1.071	1.132	1.036	1.088
R indices [$I > 2\sigma(I)$]	$R1 = 0.079$, $wR2 = 0.197$	$R1 = 0.169$, $wR2 = 0.373$	$R1 = 0.063$, $wR2 = 0.146$	$R1 = 0.051$, $wR2 = 0.123$
R indices (all data)	$R1 = 0.096$, $wR2 = 0.207$	$R1 = 0.198$, $wR2 = 0.373$	$R1 = 0.117$, $wR2 = 0.165$	$R1 = 0.079$, $wR2 = 0.134$
Absolute structure parameter	0.699, −0.558	0.981, −0.573	0.698, −0.426	0.142, −0.146
largest peak and hole/e Å^{-3}				

[a] Data in common; T = 180(2) K, λ = 0.71073 Å.

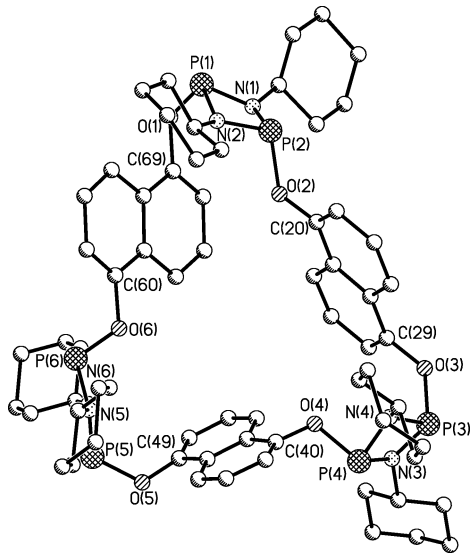


Fig. 8 Structure of trimeric molecules of **2a** (thf and *n*-hexane molecules in the lattice and H-atoms have been removed for clarity).

of the planes of the naphthyl rings with respect to the mean plane of the molecule (*i.e.*, through the six *exo*- and *endo*-O atoms which are within 0.67 Å of a plane in **2a**). In **2a**, these naphthyl rings are inclined at 49.4–74.2° to the major plane, whereas in **1** a shallower and more regular angle of *ca.* 35.5° is observed.[6] Thus, the bowl-shaped cavity of **2a** is deeper and narrower than that of **1**.

An interesting feature of the structure of **2a** is the inclusion of a thf molecule within the macrocyclic cavity (Fig. 9a). The thf O-atom, which was assigned tentatively on the basis of initial peak height and atomic displacements parameters, is directed outwards from the core so that the predominant guest–host interaction appears to be hydrophobic, a situation similar to that found in **1**,[7] in which the Me group of one toluene molecule is orientated towards the centroid of the macrocycle, forming long-range C–H···arene contacts with the naphthylene rings (Fig. 9b).[6,11] The inclusion of toluene and thf molecules in **1** and **2a** respectively is similar to that found previously in the structures of clathrates of calix[4]arenes, *e.g.*, in the [*p*-^{t}Bu-MeO-calix[4]arene·Na·toluene]$^+$ cation[12] and [*p*-^{t}Bu-OH-calix[4]arene·toluene].[13] The remaining thf and *n*-pentane molecules in **2a** are located between the molecules in the lattice.

The structure of the phosph(III)azane precursor to **2a**, the dimer [ClP(μ-NCy)]$_2$ (**7**), was also problematic due to its disorder across a crystallographic mirror plane so that, at first sight, the presence of either the *cis* or the *trans* isomer appears equally possible. However only three atoms of the P_2N_2 unit lie in the mirror plane and the fourth, P(1), lies slightly out of the plane (see Experimental section), and due to the proximity of the mirror plane to P(1) the two P–Cl bond lengths were constrained to be equal in the refinement. This evidence of a puckered P_2N_2 ring unit strongly suggests a *cis* geometry of the Cl atoms with respect to the P_2N_2 ring unit (as depicted in Fig. 10).[1,14] The Cy ring is a less sterically demanding R-group than ^{t}Bu (and has low electronegativity[1]) so

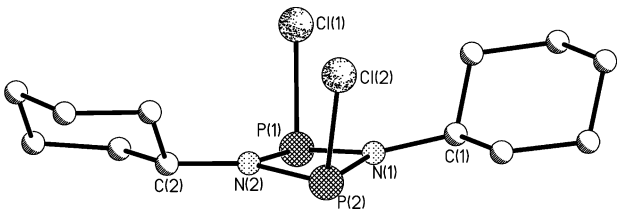


Fig. 10 Structure of the dimer **7**, the precursor to **2a**, showing one component of the 50 : 50% disorder present in the crystal. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); mean P–Cl 2.167(1), P(1)–N(1) 1.711(2), P(1)–N(2) 1.686(2), P(2)–N(2) 1.702(2), P(2)–N(1) 1.680(2); N(1)–P(1)–N(2) 81.1(1), N(2)–P(2)–N(1) 81.5(1), P(1)–N(1)–P(2) 97.9(1), P(2)–N(2)–P(1) 98.0(1), puckering of P_2N_2 ring 167.6.

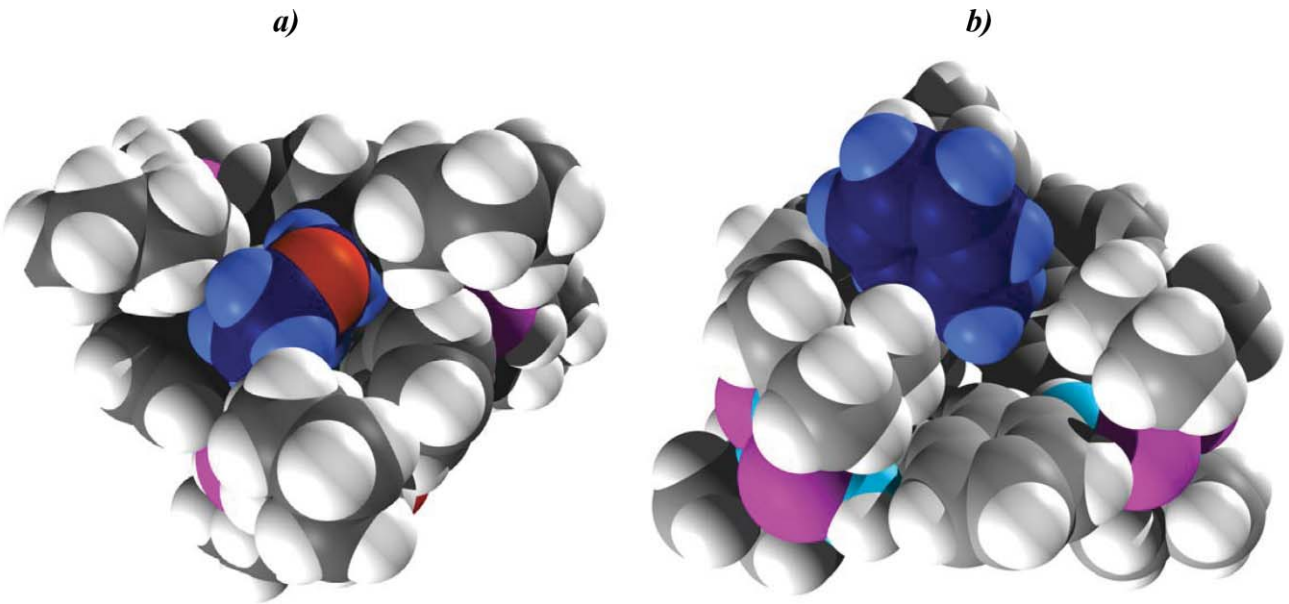


Fig. 9 Space-filling diagrams of *a*) the thf inclusion in **2a**, and *b*) the toluene inclusion in **1** (the included thf and toluene molecules are highlighted in darker shades).

that the *cis* geometry (which is also found for $[ClP(\mu\text{-}N^tBu)]_2$, the precursor to **1**, **3**, **4** and **6**) is not unexpected, but nevertheless it suggests that pre-organisation of the phosph(III)azane precursor is one of the factors directing cyclisation in the condensation reaction producing **2a**.

Despite repeated attempts we were unable to obtain good quality crystals of **4**, but nonetheless the X-ray study established that like **2a**, **4** is a trimeric macrocycle, confirming the results obtained from mass spectroscopy, and the connectivity is established unequivocally. Two independent, chemically equivalent molecules (*A* and *B*) are found in the asymmetric unit and Fig. 11a shows one of these molecules. All the trimeric macrocycles have approximate C_3 symmetry but in contrast to **1**[7] and **2a** which have bowl-shaped arrangements, the planes of the aromatic spacers in **4** adopt a more propeller-like conformation in both independent molecules. Although again the individual bond lengths in **4** are not suitable for detailed comparisons it is apparent that several structural features are very similar to those found for **2a**. In particular, the six O-atoms of both molecules of **4** are almost coplanar [maximum deviation 0.65 Å (mean); *cf*. 0.67 Å in **2a**] and the size of the cavities [radius 3.4 Å (mean) measured to from the three *endo*-O atoms to their centroid] is significantly smaller than that found in the closest N-analogue **1** of 4.4 Å and close to the radius of 3.5 Å in **2a**).

One interesting difference between the two molecules **1**[7] and **2a**, and **4** is the absence of solvent inclusion within the cavity of the macrocycle in the latter. We assume that this is due to a combination of the conformational differences between the cavities of these macrocycles and to the more sterically crowded nature of the periphery of **4** (containing ^{t}Bu rather than Cy groups). Instead of coordinating a molecule of solvent, the two independent molecules of **4** interlock using one of the ^{t}Bu groups from molecule **B** (effectively 'self-inclusion', shown in Fig. 11b); a similar interlocking occurs between molecule **B** and a ^{t}Bu group of molecule **A** in the asymmetric unit of the next unit cell at x, 1 + y, z and so generates infinite chains of interlocked macrocycles running parallel to the *b*-axis of the unit cell. This association involves a combination of relatively short C–H $\cdots$ π-arene (3.12–3.19 Å; *cf*. 2.85–3.15 Å estimated for a van der Waals interaction[10]) and C–H $\cdots$ O (2.87–2.89 Å; *cf*. 2.70–2.95 Å estimated for a van der Waals interaction[10]) contacts.

The solid-state structure of **6** is that of a dimer which is closely related to those which we and others have reported previously (Fig. 12a).[4] The more congested nature of the cavities of **6** means that no inclusion of solvent into the molecule is observed. Instead, molecules associate into layers *via* weak N–H $\cdots$ O H-bonding [N $\cdots$ O 3.16 Å (H $\cdots$ O 2.53–2.66 Å), N–H $\cdots$ O 115.9–128.0°] (Fig. 12b),[10] between which ^{t}Bu groups interlock to form voids in which two toluene molecules per macrocyle are accommodated. The association of phosph(III)azane macrocycles *via* H-bonding has been seen before in $[\{P(\mu\text{-}N^tBu)\}_2\{2,6\text{-}(NH)_2C_5H_3N\}]_2$, in which N–H $\cdots$ P interactions also result in the formation of layers.[4b]

Conclusions

The current study has shown that larger phosp(III)azane macrocycles of the type $[\{P(\mu\text{-}NR)\}_2(LL')]_n$ with $n > 2$ can be readily prepared. Unlike the dimeric counterparts, trimeric macrocycles of this type have the ability to act as hosts to neutral guests, as witnessed in the structures of **2a** and **4**. The macrocycle **2a** is the first in which a substituent other than ^{t}Bu has been incorporated into these species. Further coordination studies in this area are planned.

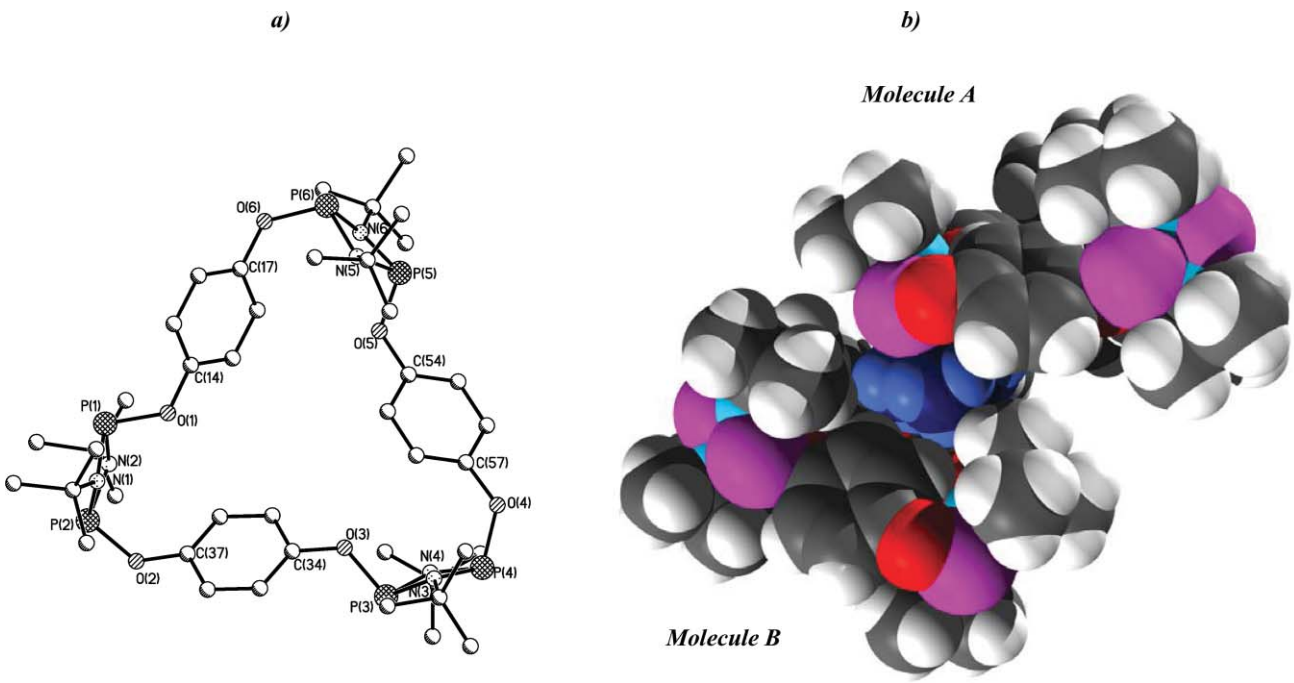


Fig. 11 ***a***) Structure of one of the molecules of **4** (*molecule A*) (H-atoms omitted for clarity), and ***b***) interlocking of *molecule A* and *B* in the crystal lattice (the included ^{t}Bu group of *molecule B* is highlighted in blue).

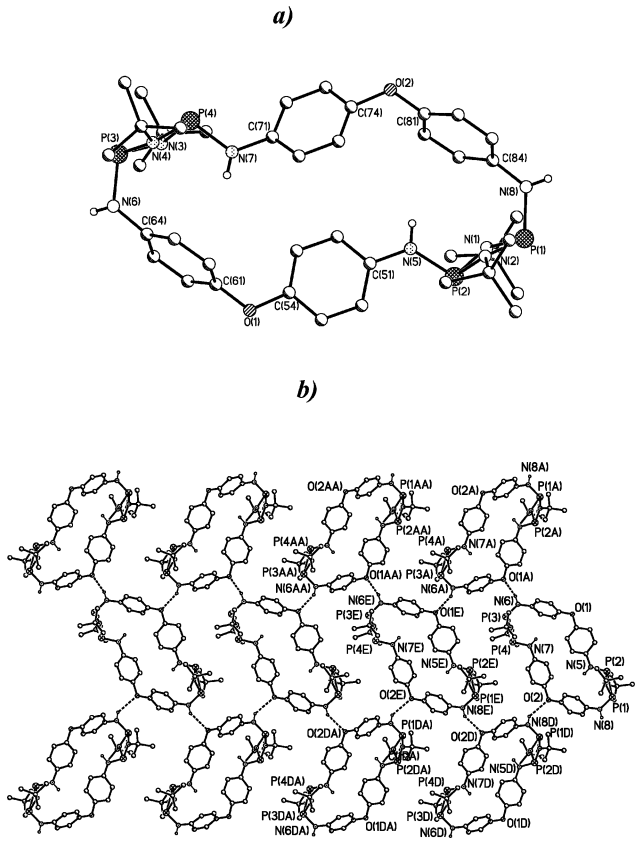


Fig. 12 *a*) Structure of one of the independent molecules of **6** (toluene molecules and H-atoms are omitted for clarity), and *b*) association of molecules into a layer structure *via* N-H···O H-bonding. Selected bond lengths (Å) and angles (°); P–μ-N(ᵗBu) range 1.713(3)–1.726(3), P–N(H) range 1.686(3)–1.702(3), P···P range 2.587(1)–2.593(1); P–N(H)–C range 123.5(3)–127.2(3), C–O(1,2)–C range 115.8(2)–118.0(2); N···O 3.16 (H···O 2.53–2.66), N–H···O 115.9–128.0, puckering of P_2N_2 rings 17.9–18.9.

Experimental

General experimental

Compounds **2–7** were prepared under dry, O_2-free N_2 on a vacuum line. $[ClP(\mu\text{-}N^tBu)]_2$ was obtained from the 3 : 1 reaction of $^tBuNH_2$ with PCl_3, respectively, in thf in the manner described in the literature.[6a] Thf, toluene and *n*-pentane were dried by distillation over sodium or sodium/benzophenone prior to the reactions. Et_3N was dried over CaH_2. **2–7** were isolated and characterised with the aid of an N_2-filled glove box fitted with a Belle Technology O_2 and H_2O internal recirculation system. Elemental analyses were performed by first sealing the samples under argon in air-tight aluminium boats (1–2 mg) and C, H and N content was analysed using an Exeter Analytical CE-440. P analysis was obtained using spectrophotometric means. Elemental analysis of all of the compounds proved to be difficult and frequently the P and N contents were significantly lower than the theoretical values. This may be due to the formation of PN ceramics during combustion.[15] Where possible, mass spectroscopy was also used to augment elemental analysis. ^1H, ^{31}P NMR spectra were recorded on a Bruker ATM DRX500 spectrometer, in dry deuterated $CDCl_3$ (using the solvent resonances as the internal reference standard for ^1H NMR and 85% H_3PO_4/D_2O as the external standard for ^{31}P NMR). *In situ* ^{31}P NMR spectroscopic studies on reaction mixtures in non-deuterated solvents were recorded using an internal D_6-acetone capillary to obtain a lock.

Synthesis of 2

To a solution of 1,5-dihydroxynaphthalene (0.158 g, 1.0 mmol) in thf (30 ml) and Et_3N (1.0 ml) at −78 °C was added dropwise $[ClP(\mu\text{-}NCy)]_2$ (0.158 g, 1.0 mmol) in thf (30 ml) and the mixture stirred (1.5 h). The resulting suspension was allowed to warm to room temperature and then brought to reflux (48 h). The thf was removed under vacuum and the white residue extracted with *n*-pentane and filtered through Celite. The filtrate was reduced in volume under vacuum until precipitation of a white solid occurred. This was dissolved by the addition of a few drops of thf and heating. Storage of the solution at room temperature gave colourless needles of **2**. Yield 0.07 g (16%). ^1H NMR (+25 °C, $CDCl_3$, 500.2 MHz), $\delta = 8.3$–7.1 (mult., 6H, C–H naphthyl group), 3.14 (br.s., 2H, α-C–H of Cy), 2.3–0.8 (mult., 22H, Cy group). ^{31}P NMR (+25 °C, $CDCl_3$, 202.48 MHz), $\delta = 138.6$ (s.) (trimer) [splits into two resonances at *ca.* 250 K at $\delta = 139.4$ (d., $^3J31_{P-H} = 21.0$ hz) and 124.8 (d., $^3J31_{P-H} = 21.0$ hz) ($\Delta G^{\ddagger} \approx 42.8$ kJ mol^{-1})], 134.9 (tetramer) [splits into two resonances at *ca.* 265 K at $\delta = 145.0$ (s.) and 125.2 (s.) ($\Delta G^{\ddagger} \approx 44.7$ kJ mol^{-1})]. Mass spectroscopy (+ve ion) $m/e = 1656.6$ (tetramerH$^+$), 1244.0 (trimerH$^+$).

Synthesis of 4

To a solution of hydroquinone (1.0 mmol, 0.11 g) in thf (20 ml) and Et_3N (4.0 mmol, 0.6 ml) at −78 °C was added $[ClP(\mu\text{-}N^tBu)]_2$ (1.0 mmol, 0.28 g) in thf (20 ml) dropwise. The mixture was allowed to warm to room temperature and stirred (1 h) before being heated to reflux (16 h), resulting in a colourless suspension. The solvent was removed under vacuum, *n*-pentane added (40 ml) and the suspension filtered through Celite. The filtrate was reduced in volume until precipitation of a colourless solid occurred. This was warmed back into solution and storage at room temperature gave colourless crystals of **4**. Yield 0.14 g (45%). ^1H NMR (+25 °C, $CDCl_3$, 500.2 MHz), $\delta = 7.30$ [d. ($^2J_{HH} = 7.8$ hz), 2H, C–H aryl], 7.20 [d. ($^2J_{HH} = 7.8$ hz), 2H, C–H aryl], 1.28 [s., 36H, ^tBu] ^{31}P NMR (+25 °C, $CDCl_3$, 202.48 MHz), $\delta = 136.6$ (s.) (trimer) (other unidentified minor species at $\delta = 139.9$–142.4) [resonance for the trimer splits into two resonances at $\delta = 145.2$ (d.) and 123.7 (d.) at *ca.* 240 K ($\Delta G^{\ddagger} \approx 43$ kJ mol^{-1})]. Elemental analysis, found C 54.2, H 7.4, N 7.8, P 16.2; cald. for **4** C 53.8, H 7.1, N 9.0, P 19.9%.

Synthesis of 5

To a solution of hydroquinone (0.11 g, 1.0 mmol) in thf (40 ml) and Et_3N (0.5 ml) at −78 °C was added $[ClP(\mu\text{-}NCy)]_2$ in thf (40 ml). The mixture was stirred (1.5 h) then allowed to warm to room temperature and brought to reflux (24 h). The solvent was removed under vacuum and the white residue extracted with *n*-pentane (40 ml) and filtered through Celite. The solvent was removed under vacuum to yield a white powder of **5**. Yield 0.098 g (27%). ^1H NMR (+25 °C, $CDCl_3$, 500.2 MHz), $\delta = 5.94$ (s., aromatic C–H), 1.7–0.9 (mult., Cy group). ^{31}P NMR (+25 °C, $CDCl_3$, 202.48 MHz), $\delta =$ 141.2 (s.) [splits into two singlets at *ca.* 260 K at $\delta = 149.6$ and

127.3 ($\Delta G^{\ddagger} \approx 45$ kJ mol^{-1})]. Mass spectroscopy (+ve ion) m/e = 1093.7 (trimerH$^+$) (low abundance with higher m/e peaks being observed up to 1712.3).

Synthesis of 6

To a solution of 4,4′-oxydianiline (2.0 mmol, 0.40 g) in thf (40 ml) and Et_3N (8.0 mmol, 2.0 ml) at −78 °C was added a solution of [ClP(μ-N^{t}Bu)]$_2$ (2.0 mol, 0.55 g) in thf (30 ml) dropwise. The mixture was stirred at −78 °C (2 h) before being allowed to warm to room temperature and stirred (16 h). The solvent was removed under vacuum, the dry solid produced dissolved in toluene (40 ml) and filtered through Celite. Removal of the solvent under vacuum gave a colourless powder of **5**. Yield 0.45 g (56%). ^{1}H NMR (+25 °C, CD_2Cl_2, 500.20 MHz), δ = 7.25 (d. 1H, J = 8.6 Hz, C–H), 7.03 (d. 1H, J = 8.7 hz), 6.72 (d. 1H, J = 8.7 hz), 6.62 (d. 1H, J = 8.6 hz), 4.87 (d., 1H, N–H, $^2J_{P-H}$ = 36.6 hz), 4.67 (d., 1H, N–H, $^2J_{P-H}$ = 5.7 hz), 1.32 (s., 18H, ^{t}Bu). ^{31}P NMR (+25 °C, CD_2Cl_2, 202.48 MHz), δ = 101.8 (s.), 99.6 (s.) [splits into a 1 : 1 doublet ($^2J_{P-H}$ = 36.6 hz) at low temperature] [an *in situ* ^{31}P NMR study of the reaction solution (using d_6-acetone capillary to obtain a lock) showed that **5** is the only soluble P-containing compound formed]. Elemental analysis, found C 56.5, H 7.1, N 12.5, 14.1; cald. for **6** C 59.7, H 7.0, N 13.9, P 15.4%.

Synthesis of 7

To cyclohexylamine (11.5 ml, 100 mmol) in thf (200 ml) at −78 °C was added ^{n}BuLi (62.5 ml, 1.6 mol dm^{-3} in hexanes, 100 mmol). The solution was allowed to warm to room temperature and stirred (1 h). This was then added dropwise to a solution of PCl_3 (8.75 ml, 100 mmol) in thf (200 ml) at −78 °C. The mixture was stirred (2 h) before being allowed to warm to room temperature and stirred (48 h). The mixture was filtered through Celite, the solvent removed under vacuum and toluene was added (150 ml). The mixture was filtered and the toluene removed under vacuum to give an orange oil. Diethyl ether was added (40 ml) and then removed under vacuum. This was repeated. A viscous semi-solid was finally produced which was sublimed onto a water-cooled cold finger in a Schlenk tube (150 °C, 0.1 mmHg). Yield 1.64 g (20%). ^{31}P NMR (+25 °C, $CDCl_3$, 202.48 MHz), δ = 221.0 (s.). Mass spectroscopy (+ve ion) m/e = 327.2 [MH$^+$].

Crystal structures of 2a·thf·*n*-C_5H_{12}, 4, 6·2toluene and 7

Crystals of **2a**·thf·*n*-C_5H_{12}, **4**, **6**·2toluene and **7** were mounted directly from solution under argon using an inert oil which protects them from atmospheric oxygen and moisture. X-Ray intensity data were collected using a Nonius Kappa CCD diffractometer. Details of the data collections[16] and structural refinements are given in Table 1. For all four crystals the positions of the non-hydrogen atoms were located by direct methods. The overall features of the four new molecules are clearly established but only the data for compound **6** refined well. The three compounds, **2a**, **4** and **7** presented problems in refinement. The crystal of **2a** shows a trimeric macrocyclic molecule with an *n*-pentane and two thf solvate molecules in the lattice. Refinement of **2a** was rather unsatisfactory due to unfortunate alignment of two of the naphthyl units. Ring C(20)···C(29) is almost exactly parallel to the *ab* plane and ring C(40)···C(49) to the *ac* plane; additionally, the latter ring is very close to lying half way between the *c*-glide planes (*i.e.*, *y* for all ten C-atoms is 0.53). As a consequence of these factors some of the interatomic distances in the chemically equivalent bonds show a rather large discrepancy. Rather high ADP indicated some conformational disorder of the two thf and the *n*-pentane solvate molecules. The carbon atoms of one thf molecule and four in the *n*-pentane were resolved into two components. The crystal of **4** has two trimeric macrocycle molecules per equivalent position, and the very fine needle crystals diffracted poorly at high angle and refinement was very difficult. This was apparently mainly due to special relationships between equivalent atoms in the two molecules, *i.e.*, each atom in one molecule has nearly the same *z*-coordinates as the corresponding atom in the second molecule and each pair is separated by almost exactly 1/2 in *y*. To help in the refinement equivalent atoms in the two molecules were constrained to have the same bonding parameters, and constraints were also applied to the anisotropic ADP to prevent non-positive definite results. Despite the unsatisfactory refinement the main features of the macrocyclic molecule are clearly established. The problem in **7** is that that the molecule is disordered across the crystallographic mirror plane, with the P_2N_2 unit lying in the symmetry plane. This arrangement gave an unreasonably short P(1)–Cl(1) bond with a P(1) displacement ellipsoid very elongated in a direction perpendicular to the plane. It was concluded that the P_2N_2 unit was in fact slightly folded with two disordered components of P(1) sited too close to the mirror to be resolved in the initial Fourier maps. To obtain a better model in refinement the half-occupancy P(1) was moved slightly off the plane away from the Cl(1) atom and the two P–Cl lengths were constrained to be equal within an e.s.d. of 0.005 Å. From the disordered model with mirror symmetry the molecule might be in a *cis*- or *trans*-configuration, but the evidence that the P_2N_2 unit is folded, is consistent with the presence of the *cis*-isomer. The crystals of **6** consist of hydrogen bonded sheets of molecules parallel to the *ab* plane with two toluene solvates per molecule lying between the sheets. One of the toluene molecules is disordered with two overlapping components of *ca*. 70 : 30% occupancy. The hydrogen atoms for **2a**, **4** and **7** were placed in calculated positions with displacement parameters set equal 1.2 U_{eq} (or1.5 U_{eq} for methyl groups) of the parent carbon atoms. The nitrogen-bonded hydrogen atoms in **6** were directly located and included in the refinement without restraint, all other H-atoms being included in idealised sites. For all four structures anisotropic displacement parameters were assigned to all full occupancy atoms in the final cycles of full-matrix refinement based of F^2.[16]

CCDC reference numbers 608772–608775.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607332h

Acknowledgements

We gratefully acknowledge the EPSRC (F.D., F.G., R.A.K., M.McP., D.S.W.) and Wolfson College (Fellowship for F.G.) for financial support.

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