

A New Host for Polymer and Small-Molecule Clathration

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The synthesis and inclusion properties of a new clathration host, tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene, is described. The guest-free structure has a triclinic unit cell, space group $P\bar{1}$, with unit cell dimensions $a = 9.418(1)$ Å, $b = 17.887(4)$ Å, $c = 8.036(2)$ Å, $\alpha = 95.50(2)^\circ$, $\beta = 100.57(1)^\circ$, and $\gamma = 95.58(1)^\circ$. Recrystallization of the host from dioxane or from a poly(tetramethylene oxide)/benzene mixture afforded two different guest-included structures. The tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene–dioxane inclusion adduct crystallizes in a monoclinic system, space group $P2_1/c$, with unit cell dimensions $a = 9.3481(1)$, $b = 19.6569(1)$, $c = 16.4099(3)$, and $\beta = 97.351(1)^\circ$. The guest occupies a cagelike void located between the phosphazene rings. The poly(tetramethylene oxide) adduct crystallizes in a hexagonal system, space group $P6_3/m$, with unit cell dimensions $a = 11.4902(2)$ Å and $c = 13.3138(3)$ Å. In this case, the polymeric guest is located in tunnels created along the c -axis. Adduct formation also occurs between tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene and other cyclic, linear, and polymeric species such as tetrahydrofuran, methylene chloride, polyethylene, and *cis*-polybutadiene. Thermogravimetric analysis and differential scanning calorimetry were used to characterize the thermal behavior of the inclusion adducts. Crystal engineering of these spirocyclotriphosphazene hosts is facilitated by the ease in which the void and tunnel diameter can be tailored by systematic adjustments to the size and nature of the side group.

Introduction

Considerable interest exists in new supramolecular guest/host structures which are held together by weak, reversible interactions such as hydrogen bonding, metal coordination, van der Waals forces, and π - π stacking forces.^{1–6} Such structures include intercalation compounds and inclusion adducts.^{4,7} Ward and co-workers^{8,9} have recently reported a new class of crystalline clathrates which are formed by the interaction of guanidinium cations and organosulfonate anions. Porous packing of these two ions is directed by hydrogen-bonding forces and is stabilized by the presence of neutral guest species. The host lattice may be tailored by slight changes in the ions to produce lattice voids of various sizes and shapes. In addition to charged host

species, a wide selection of neutral organic or organo-metallic host compounds form clathrates or inclusion adducts. These include Hoffman- and Werner-type compounds,^{10,11} urea,¹² thiourea,¹³ perhydrotriphenylene,¹⁴ deoxycholic acid,¹⁵ and cyclic phosphazenes.¹⁶ A number of these compounds have proved useful for chromatographic separations and as hosts for inclusion polymerization of unsaturated guests.

The discovery of new host compounds that form inclusion adducts has often been a matter of serendipity. In a few cases, small changes to one host structure create a family of host compounds each having slightly different clathration properties, but the fine structure of many hosts cannot be modified easily. However, one class of clathration hosts, the spirocyclophosphazenes (Scheme 1), can be generated through reaction of different aryloxy or arylamino compounds with a central, reactive cyclophosphazene hub. Variations on this simple one-step reaction allow the formation of a number of bulky, rigid host compounds. Bulkiness and

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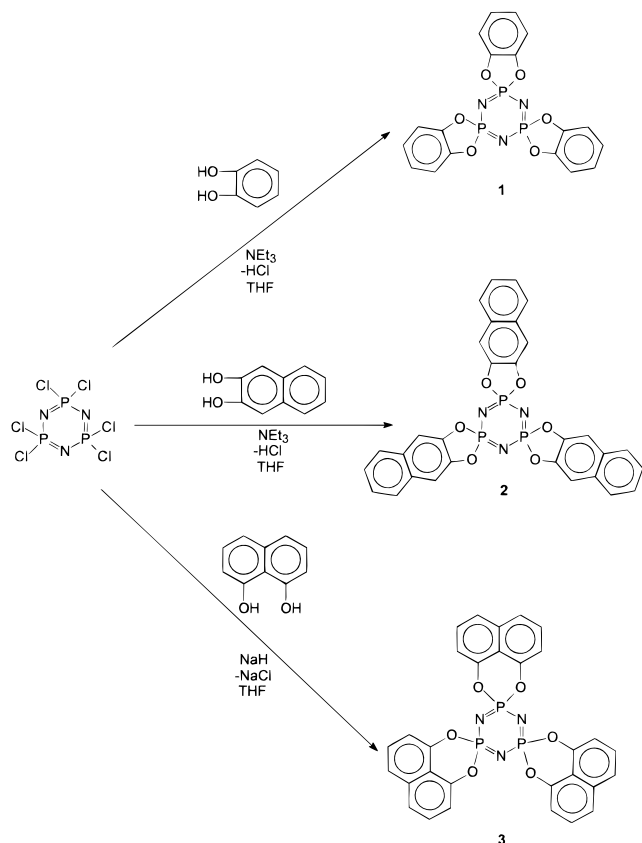
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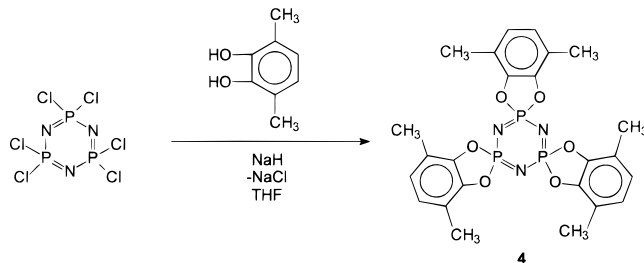
Scheme 1. Synthesis of Cyclotriphosphazene Hosts



molecular rigidity are two properties often required for the formation of inclusion adducts.¹⁶

We have reported previously the synthesis and inclusion properties of several spirocyclophosphazene clathrates, including tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**),^{17–20} tris(2,3-naphthalenedioxy)cyclotriphosphazene (**2**),^{21–23} and tris(1,8-naphthalenedioxy)cyclotriphosphazene (**3**)²⁴ (Scheme 1). These rigid, paddle wheel shaped hosts are formed through the reaction of various aromatic diols with hexachlorocyclotriphosphazene. Compounds **1** and **2** form crystalline channel or tunnel-type adducts with tunnel diameters of 5 and 10 Å, respectively. The clathrates have crystal structures that are different from those of the guest-free systems. For example, hosts **1** and **2** in the absence of guest occupy monoclinic systems, but yield clathrates that have hexagonal structures with tunnels that penetrate the lattice down the *c*-axis. The difference in the tunnel diameter is directly related to the differences in “arm length” in the two host molecules. This illustrates the tailorability that may be achieved using this class of hosts. The ability to tune the tunnel

Scheme 2. Synthesis of Tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene (**4**)



diameter of the spirocyclophosphazene hosts through systematic, stepwise adjustments to the size of the side group demonstrates a versatile route for crystal engineering of these clathrates. Most recently, we have found that **1** forms inclusion adducts with macromolecules such as polyethylene or poly(ethylene oxide).²⁵ Moreover, dienes and other monomers can be polymerized within the channel voids of **1** and **2** through exposure of the adduct to γ -irradiation.^{26–30}

The objective of this present work was to synthesize and determine the properties of a new potential clathration host, tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene (**4**). In this compound (Scheme 2), as in **1** and **2**, slightly strained five-membered rings, formed by the ring phosphorus atoms and the oxygen and carbon atoms of the pendent side groups, connect the aryl side units to the phosphazene ring. This strained geometry probably increases the overall rigidity of the compound, thus increasing the likelihood of adduct formation. Previous studies of hosts **1** and **2** indicated that the side groups are aligned normal to the planar phosphazene ring. This ability to lock the organic side groups in a near perpendicular arrangement to the phosphazene ring distinguishes this host system from many others which rely on planar aromatic groups or axial allyl groups to impart rigidity to the overall host structure.

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was recrystallized from heptane and sublimed. Tetrahydrofuran (OmniSolve) was distilled from sodium–benzophenone. Sodium hydride (60% dispersion in mineral oil) was used as received and was stored in an argon-inert atmosphere glovebox. Catechol (Aldrich) was sublimed before use. Morpholine and acetic anhydride (37% solution in water) (Aldrich) were used as received.

The organic liquids examined as guests for inclusion adduct formation were used as received from Aldrich. Poly(tetramethylene oxide) ($M_n = 250$), 99% unsaturated polybutadiene ($M_n = 1500$), *cis*-1,4-polybutadiene (av MW = 2–3 million), and poly(ethylene glycol) ($M_n = 1500$) were used as received from Aldrich. Polyethylene (av MW = 1000) was used as received from Polysciences.

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Instruments. ^{31}P NMR spectra were recorded with the use of a Bruker WM-360 NMR spectrometer operating at 146 MHz. ^1H and ^{13}C NMR spectra were recorded with a Bruker WM-360 spectrometer operated at 360 and 90.5 MHz, respectively. Electron impact mass spectra were obtained with the use of a KRATOS MS9/50 spectrometer. X-ray single-crystal crystallographic data were collected on a Rigaku AFC6S diffractometer with graphite monochromated Mo K α radiation, and a Siemens P4/CCD diffractometer. X-ray powder diffraction was obtained using a Philips analytical X-ray X'PERT MPD ($2\theta = 5\text{--}40^\circ$, $1^\circ/\text{min}$). The thermal behavior of inclusion adducts containing small molecule guests was determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using a Perkin-Elmer 7 series thermal analysis system. A heating rate of $20^\circ\text{C}/\text{min}$ was employed, and an indium standard was used for calibration.

Synthesis of 3,6-Bis(morpholinomethyl)catechol (5). This compound was synthesized according to a literature procedure.³¹ Morpholine (42 g, 0.48 mol) was added to catechol (27.5 g, 0.25 mol), and 95% ethanol (100 mL) was added. The mixture was cooled with a water bath, and acetic anhydride (45 mL) was added dropwise. This mixture was stirred for 5 days, filtered, and washed five times with ethanol. Recrystallization from ethanol afforded the pure product. Yield: 29.35 g, 39%. ^1H NMR: 2.51 (s, br, 8H), 3.65–3.69 (m, 12H), 6.51 (s, 2H).

Synthesis of 3,6-Bis(acetoxymethyl)catechol (6). Compound 5 (29.35 g, 0.98 mol) was placed in a three-necked flask, and acetic anhydride (97.80 mL, 1.21 mol) was added. This was refluxed overnight. The solvent was removed, and 600 mL of water was added to the residue. This mixture was filtered, and the solid was dried under vacuum. The solid was then washed with hot ethanol (100 mL) and filtered through decolorizing activated carbon. Recrystallization from ethyl acetate afforded the pure product. Yield: 15.4 g, 47%. ^1H NMR: 2.05 (s, 6H), 2.30 (s, 6H), 5.06 (s, 4H), 7.35 (s, 2H).

Synthesis of Dimethylcatechol (7). Compound 6 (8 g, 0.024 mol) was dissolved in ethyl acetate (110 mL) by warming. This solution was transferred to a 500-mL Parr hydrogenation bottle and 70% HClO_4 (0.8 mL) and 10% Pd/C (0.16 g in 8 mL of ethyl acetate) were added. The initial hydrogen pressure was set to 54 psi, and the mixture was shaken overnight. After the mixture had settled for 1 h, the solution was filtered using Celite. Removal of the solvent yielded an oil which was dissolved in methanol (40 mL). Perchloric acid (70%, 0.4 mL) was added, and the solution was refluxed overnight. This was cooled and neutralized to pH 7–8 using sodium bicarbonate. The residue was washed with boiling hexane (5×50 mL), and was recrystallized in hexane. Yield: 0.76 g (23%). ^1H NMR: 2.21 (s, 6H), 4.93 (s, 2H), 6.59 (s, 2H).

Synthesis of Tris(3,6-dimethylphenylenedioxy)cyclo-triphosphazene (4). THF (20 mL) was added to 60% NaH (0.33 g, 8.6 mmol). Compound 7 (0.50 g, 3.6 mmol) in THF (15 mL) was added dropwise to the NaH solution via a syringe, and this mixture was stirred for 90 min. The resultant blue solution was transferred to an addition funnel and added dropwise to hexachlorocyclo-triphosphazene (0.42 g, 1.2 mmol). This was stirred overnight. Solvent was removed under vacuum, and the residue was washed with water for 1 h. It was then washed quickly with methanol. Yield: 0.48 g (74%). ^{31}P NMR: 34 ppm. ^1H NMR: 2.29 (s, 6H), 6.73 (s, 2H). Mp: decomposes near $320\text{--}330^\circ\text{C}$. MS (m/e): calcd 543; found 543.

Adduct Formation. X-ray-quality crystals of the dioxane–4 adduct were grown through slow evaporation of a dioxane solution saturated with 4. A suitable crystal was selected and sealed in a capillary tube. Crystals of the poly(tetramethylene oxide)–4 adduct were grown through slow evaporation of benzene from a solution containing poly(tetramethylene oxide) and saturated with 4. The polyethylene–4, linear 1,4-polybutadiene–4, and *cis*-polybutadiene–4 inclusion adducts were prepared by refluxing an equal weight

of host 4 and the desired polymer in hot benzene overnight. After the solution cooled, the benzene was removed under vacuum, and excess polymer was washed away with hexane. The powdered material was then evacuated for 1 h at 110°C to remove residual traces of small molecules. Crystalline adducts containing benzene, methylene chloride, and tetrahydrofuran were formed through evaporation of these solvents from a solution saturated with 4. Attempts were also made to form the hexane–4 and acetone–4 adducts by wetting 4 with these solvents.

X-ray Structure Determination. Crystallographic work on 4 was performed at the University of Calgary and that on dioxane–4 and poly(tetramethylene oxide)–4 (PTMO–4) at the University of Delaware. Crystallographic data are summarized in Table 1. For guest-free 4, no evidence for diffraction symmetry higher than triclinic was observed and the centrosymmetric alternative was chosen on the basis of the well-behaved results of refinement in this setting. Systematic absences in the diffraction data allowed a unique space group assignment of $P2_1/c$ for dioxane–4. Diffraction symmetry indicated that the crystals of poly(tetramethylene oxide)–4 (PTMO–4) belonged to the hexagonal system with $6/m$ Laue symmetry. Systematic absences indicated either $P6_3$ or $P6_3/m$. The centrosymmetric alternative was selected on the basis of E statistics and was confirmed by the presence of inversional symmetry. In all cases, the uniform crystal dimensions and low absorption coefficients obviated corrections for absorption. All structures were solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms except for the atoms of the guest molecules in PTMO–4. Hydrogen atoms were placed in idealized locations except for those associated with the poly(tetramethylene oxide) molecule; in this case they were ignored. In PTMO–4 the guest polymer was fully disordered along the 3-fold axis and was resolvable only as a linear chain. Although an attempt was made to identify the location of the oxygen atoms in the chain on the basis of thermal parameters, there is limited certainty that the assignment is uniquely correct.

Computations for 4 used the TeXsan software library (Molecular Structure Corporation, The Woodlands, TX). For the two guest structures the SHELXTL (Siemens XRD, Madison, WI) software library was used.

Results and Discussion

Small Molecule Inclusion. Tris(3,6-dimethylphenylenedioxy)cyclo-triphosphazene (4) forms inclusion adducts when crystallized from a number of small-molecule solvents (Table 2). The presence of guest (solvent) molecules within the crystal structure was demonstrated by a variety of techniques including X-ray crystallography and loss of weight following the escape of volatile small molecules from the lattice. As shown in Table 2, the stability of these adducts varied according to the guest included. After 48 h in air at 25°C , the host solid retained significant amounts of dioxane, tetrahydrofuran, benzene, and methylene chloride. However, hexane and acetone did not form stable adducts with 4.

With the exception of the tetrahydrofuran–4 adduct, the X-ray powder diffraction patterns of these solids matched the simulated powder patterns calculated from single-crystal crystallographic data for the dioxane–4 adduct. This suggests that the guest–host arrangement in the benzene and methylene chloride adducts of 4 is very similar to that of the dioxane–4 adduct. The tetrahydrofuran–4 adduct will be discussed later.

When stabilized in an atmosphere that contained dioxane vapor, crystals of the dioxane–4 adduct were found to have a guest/host ratio of 1. However, once this

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Table 1. Crystallographic Data

	4 (guest free)	dioxane-4	PTMO-4
formula	C ₂₄ H ₂₄ N ₃ O ₆ P ₃	C ₂₈ H ₃₂ N ₃ O ₈ P ₃	C ₂₈ H ₃₂ N ₃ O ₇ P ₃
formula weight	543.39	631.48	615.48
crystal system	triclinic	monoclinic	hexagonal
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 6 ₃ / <i>m</i>
<i>a</i> , Å	9.418(1)	9.3481(1)	11.4902(2)
<i>b</i> , Å	17.887(4)	19.6569(1)	—
<i>c</i> , Å	8.036(2)	16.4099(3)	13.3138(3)
α , deg	95.50(2)	—	—
β , deg	100.57(1)	97.351(1)	—
γ , deg	95.58(1)	—	—
<i>V</i> , Å ³	1315.4(4)	2990.61(7)	1522.26(5)
Z	2	4	2
cryst dimens. mm	0.60 × 0.30 × 0.27	0.50 × 0.50 × 0.40	0.50 × 0.50 × 0.40
cryst color, habit	colorless block	colorless block	colorless block
<i>D</i> (calc), g cm ⁻³	1.37	1.40	1.34
μ (Mo K α), cm ⁻¹	2.70	2.53	2.44
temp, K	170	193	198
<i>T</i> (max)/ <i>T</i> (min)	1.00/0.66	1.00/0.69	1.00/0.72
diffractometer	Rigaku AFC6S	Siemens P4/CCD	Siemens P4/CCD
radiation		Mo K α (λ = 0.71073 Å)	
2 θ scan range, deg	4–50	3–56	3–56
rflns collected	4990	11 775	6242
indpt. rflns	4679	6459	1244
indpt obsvd rflns	2890 (<i>n</i> = 5)	4920 (<i>n</i> = 4)	1117 (<i>n</i> = 4)
<i>F</i> _o ≥ <i>n</i> σ (<i>F</i> _o)			
<i>R</i> (<i>F</i>), % ^a	6.9	5.75	3.98
<i>R</i> (<i>wF</i>), % ^a	4.0	—	—
<i>R</i> (<i>wF</i> ²), % ^a	—	17.29	14.68
Δ (ρ), eÅ ⁻³	0.36	0.64	0.48
GOF	4.49	1.08	1.32

^a Quantity minimized = $\Sigma\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R(w) = \Sigma\Delta w^2/\Sigma(F_o w^2)$, $\Delta = |F_o - F_c|$, $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]$.

Table 2. Stability of Small Molecule-4 Inclusion Adducts

guest	guest/host molar ratio in air after	
	24 h	48 h
methylene chloride	0.26	0.09
tetrahydrofuran	0.76	0.68
benzene	0.36	0.34
dioxane	0.76	0.56
acetone	0.04	0.04
hexane	0.00	0.00

adduct was exposed to air, an immediate loss of dioxane began. Exposure to air for approximately 10–15 min caused the crystals to become opaque. Moreover, weight analysis indicated that the guest/host ratio decreased with time (Table 2) and, after 4 days of exposure to air, the ratio fell to 0.25. The same phenomenon was also seen for the crystalline adducts with *benzene* or *methylene chloride*. However, for these last two adducts, loss of guest occurred at a much faster rate. As seen in Table 2, the guest/host ratios for these two adducts were lower than that for the dioxane-4 adduct. This lower ratio is probably related to the size of the guest, since methylene chloride, the smallest of these three guests, was retained least within crystals of 4. It is interesting to note that unlike the adducts with dioxane and methylene chloride, loss of benzene from 4 seems to reach a plateau after 24 h, after which very little additional guest loss occurs. This suggests that a minimum amount of benzene is retained by 4 in order to maintain an energetically favored lattice structure. Such guest/host behavior has been observed earlier for small molecule adducts of 1.

Powder X-ray diffraction results indicated that 4 crystallizes with tetrahydrofuran to form an adduct crystal structure which is different from that of the dioxane-4 adduct (crystallographic quality single crys-

tals could not be obtained to determine this structure). This difference in crystal structure could explain the observation that the amount of tetrahydrofuran retained by 4 after 48 h is higher than that of any other small molecule listed in Table 2. This higher retention is unexpected in view of the relatively small size of the guest. However, this adduct has a different crystal structure that may generate small cavities which can more easily retain the tetrahydrofuran molecules.

Although acetone was not retained by 4 to any significant extent, X-ray powder diffraction of this solid indicated that a change in the crystal packing of 4 occurs following wetting of the host by acetone. Thus, it appears that transient adduct formation does occur, but removal of the host solid from acetone results in rapid guest loss. No evidence was found that adduct formation occurred between 4 and hexane, despite the slight solubility of 4 in hexane.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to examine the thermal behavior of both the benzene and dioxane adducts of 4. DSC and TGA scans of the *benzene*-4 adduct are shown in Figure 1. The TGA curve indicated that rapid loss of benzene occurred over a temperature range of 70–90 °C. A corresponding exothermic transition appeared in the DSC scan. DSC and TGA scans of the *dioxane*-4 adduct gave results very similar to that seen in Figure 1. However, guest loss, as indicated by TGA, occurred between 80 and 100 °C. These temperatures lie very close to the boiling points of these two guests (80 °C for benzene and 101 °C for dioxane). This suggests that these guests are not strongly bound within the cavities of 4.

The release of energy during disruption of this guest/host structure is somewhat unprecedented, since it has

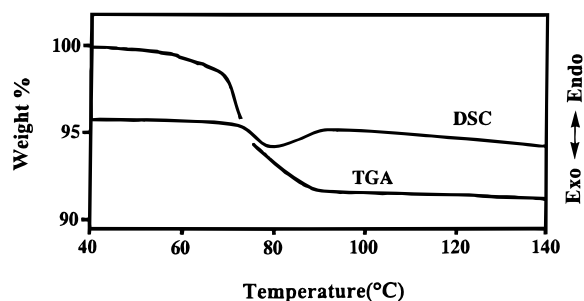


Figure 1. DSC and TGA plots for the benzene-4 adduct.

been reported that loss of small molecule guests from perhydrotriphenylene (PHTP)- and urea-based inclusion adducts is accompanied by an *absorption* of heat (endothermic transition). However, the exothermic transition in the *benzene-4* adduct occurred well after benzene loss from **4** had begun and suggests that the release of heat may not be a direct consequence of guest loss, but of a crystal transformation that occurs during or following guest loss. It is possible that the loss of benzene causes **4** to revert immediately to a more favored guest-free packing structure in an exothermic process. This structural transformation was confirmed by comparing the magnitude of the enthalpy values obtained from the exotherm in the benzene-4, dioxane-4, methylene chloride-4, and the tetrahydrofuran-4 adducts. The enthalpy values for the first three adducts are near -27 kJ/mol, and that for the tetrahydrofuran-4 adduct is -9.7 kJ/mol. These values suggest that the exotherm in the first three compounds is indeed due to a reversion from a monoclinic guest-included to a triclinic guest-free structure, and not to the departure of the guest from the cages of the host, which would produce an endotherm. It is interesting to note that the heats of vaporization for the amount of benzene, dioxane, and methylene chloride retained in the cages of the host are different from one another, yet the magnitude of the exotherm is not affected by this difference. This implies that the exotherm is driven by a structural transformation, and that the guests may in fact be behaving as a gas inside the cavities of the host. The higher value in the tetrahydrofuran-4 adduct suggests that the guest-included structure is indeed different from the other three adducts, as shown by the different powder X-ray diffraction pattern.

Polymer Inclusion. Various oligomers and polymers were investigated for possible inclusion in host **4**, through exposure of the host to a solution of the polymer in benzene. Poly(tetramethylene oxide) (MW = 250), polyethylene (MW = 1000), *cis*-polybutadiene (MW = 2–3 million), poly(ethylene glycol) (MW = 1500) and linear polybutadiene (MW = 1500) were studied. Only the first three were clathrated. Since both the polymers and the host are soluble in benzene, adduct formation probably occurs through a crystallization process. This suggests that formation of the polymer adduct is thermodynamically favored over formation of the benzene adduct, even though a small amount of benzene is co-included in the host.

Only poly(tetramethylene oxide)-**4** gave crystals suitable for single-crystal X-ray analysis. Thus, the change in host crystal structure following inclusion of these polymers was followed mainly by powder X-ray diffrac-

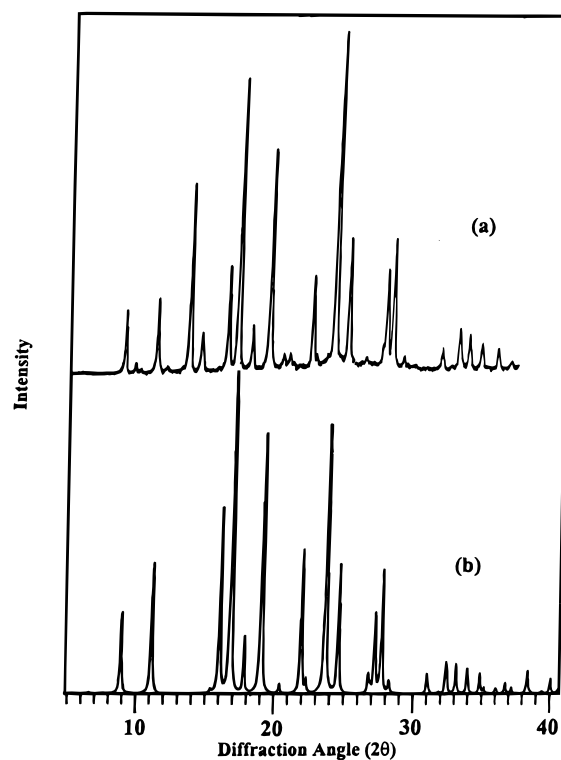


Figure 2. X-ray diffractograms of (a) poly(tetramethylene oxide)-4, (b) simulated poly(tetramethylene oxide)-4.

tion. The powder X-ray diffraction results matched well the simulated powder pattern calculated from the single-crystal crystallographic data of poly(tetramethylene oxide)-**4** (Figure 2). This resemblance suggests that the packing arrangement of the other two host/polymer systems is similar to that in poly(tetramethylene oxide)-**4**.

The powder X-ray diffraction results indicated that **4** crystallizes with poly(tetramethylene oxide), polyethylene, and *cis*-polybutadiene to form adducts, but that poly(ethylene glycol) and linear polybutadiene do not. Long-chain length does not appear to be a significant factor in this difference, because *cis*-polybutadiene with a molecular weight of 2–3 million was included within the crystal lattice. Instead, the microstructure of the oligomer or polymer is probably the defining factor, and this presumably affects the ability of the polymer to stabilize the hexagonal adduct structure. Moreover, it appears that the structure of the host plays a role in polymer inclusion, since tris(*o*-phenylenedioxy)cyclo-tri-phosphazene (**1**), unlike host **4**, forms inclusion adducts with a wider variety of polymers. Studies with **1** have shown that the stability of the adduct is related to the chain length of the included polymer. As the chain length increases, so does the stability of the system, as illustrated by an increase in the melting point of the clathrate. Similar studies could not be performed with **4**, due to its decomposition when heated at 320–330 °C. However, the included polymeric guests certainly stabilize the adducts as demonstrated by the retention of the polymer and the persistence of the host clathrate structure after long-term exposure to air. These results are similar to those from polymer adducts formed with **1**.

Single-Crystal X-ray Structures. *Guest-Free Adduct.* Guest-free tris(3,6-dimethylphenylenedioxy)cyclo-

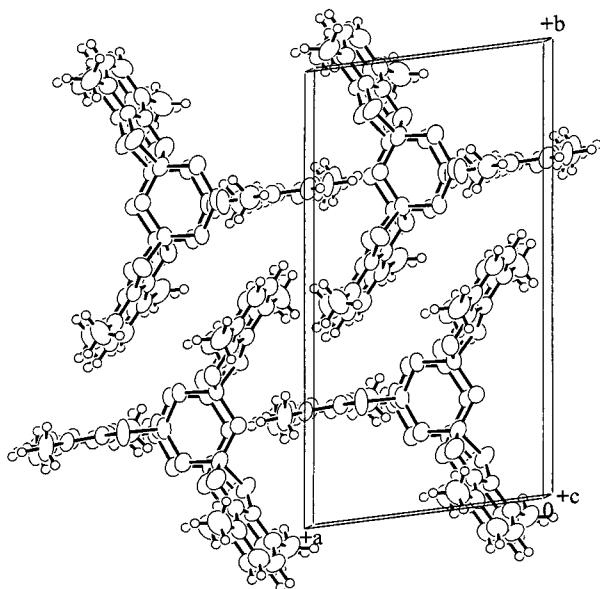


Figure 3. Triclinic unit cell for guest-free **4**.

triphosphazene, **4**, crystallizes in a triclinic unit cell, with space group $P\bar{1}$. As shown in Figure 3, the host molecules stack in a column-like manner along the c -axis. An ABAB layer packing arrangement along the c -axis was found with a distance of 8.036 Å between host layers. The distance between each molecule in a column is largely defined by the presence of the methyl groups on the phenyl rings. Moreover, the presence of these methyl groups creates a void space of 330.9 Å³ along the c -axis, *between* the planar phosphazene rings. This space seems larger than those of any other voids along the a - or b -axis.

The structure of guest-free **4** has two distinct features: (1) the presence of a planar cyclotriphosphazene ring, and (2) pendent side groups aligned perpendicular to the cyclotriphosphazene ring. These two features are also found in hosts **1** and **2**, but not in host **3**, which has a puckered phosphazene ring (Scheme 1). The reason for this departure from planarity in **3** may be explained by consideration of the O–P–O bond angles of the various hosts. The O–P–O bond angles in **1**, **2**, and **4** are narrowed to $\sim 97^\circ$, which is suggestive of ring strain. Host **3** has O–P–O angles of 102° and a six-membered spiro structure. This allows puckering of the ring. Strained five-membered rings appear to favor a paddle wheel structure based on a planar cyclotriphosphazene core.

Dioxane Inclusion Adduct. Recrystallization of **4** from dioxane gave crystals with a monoclinic unit cell with space group $P2_1/c$. As shown in Figure 4, the clathrate crystallizes to form a bent paddle wheel structure with an overall 1:1 host-to-guest ratio, with the guest molecules located in cage-like voids. The guest also forces other modifications in the host not seen in guest-free **4**: the host molecules are distorted to better accommodate the guest, as seen by the bent aryldioxy side groups (Figure 4). This distortion, which is not found in host **1** when it includes small molecules, is presumably due to the expansion of the alternating ABAB host layers along the a -axis following guest inclusion, and to a reduction in the interhost distance along the b - and c -axes. For example, the distance between host layers is increased

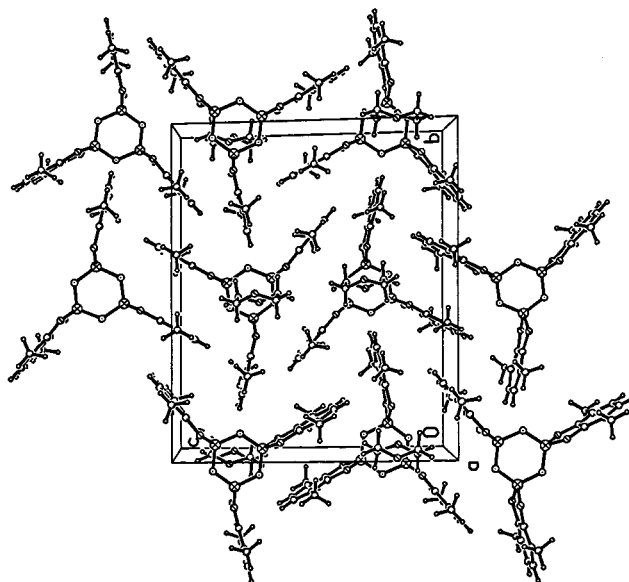


Figure 4. Monoclinic unit cell for dioxane–**4** adduct.

to 9.348 Å compared to the guest-free host lattice of 8.036 Å, presumably to accommodate the guest molecules. The host molecules are closer to each other along the c -axis (7 Å, Figure 4), compared to the interhost distance in guest free **4** (9 Å, Figure 3), measuring from the center of the cyclotriphosphazene rings.

It is important to note that the guest molecules lie *between* the planar phosphazene rings along the a -axis (Figure 5), rather than in a tunnel between the side groups. It appears that the voids above and below the phosphazene rings created by the pendent methyl groups are large enough to accommodate the guests. Indeed, incorporation of the guest enlarges the void volume between the planar rings to 622.3 Å³, which is nearly double that of the guest-free host (330.9 Å³). Furthermore, the distance between the host and the guest is too large for any strong intermolecular interaction to occur, since the guest is centered in the void. However, the guest appears to have a preferred position, with the oxygen atoms pointing toward the phosphazene rings. This is probably due to favorable van der Waals interactions between the guest and the host.

Poly(tetramethylene Oxide) Inclusion Adduct. Recrystallization of host **4** in the presence of poly(tetramethylene oxide) in benzene gave crystals with a hexagonal unit cell with space group $P6_3/m$ (Figure 6). The host crystallizes to form a paddle wheel structure similar to that of guest-free **4** and dioxane–**4**, but the polymeric guest forces modifications in the host packing arrangement that are different from the other two structures. The molecules of **4** are stacked in an alternating ABAB column-like manner, but tunnels between the side groups, rather than voids between the phosphazene rings, are created along the c -axis with a diameter of approximately 5 Å. This is analogous to the hexagonal, column-like packing of **1**, which forms tunnels with a diameter of 5 Å. However, the c -axis repeat in **4** is expanded compared to host **1**. Specifically, the c -axis repeat for poly(tetramethylene oxide)–**4** is 13.3138(3) Å, which is longer than the 10.0799(5) Å in PEO–**1** (Figure 6). This expansion is presumably due to the presence of the methyl groups on the phenyl rings, which are aligned along the c -axis. The poly(tetrameth-

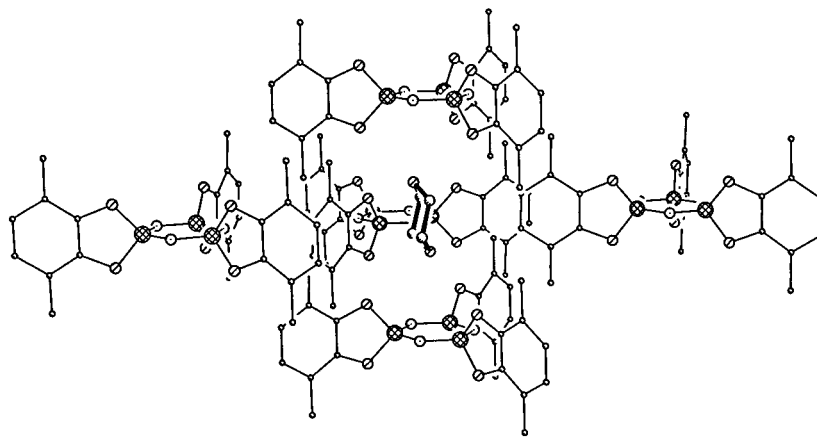


Figure 5. Void space of dioxane-4, as seen in a projection along the *c*-axis. The front host molecule has been removed for clarity.

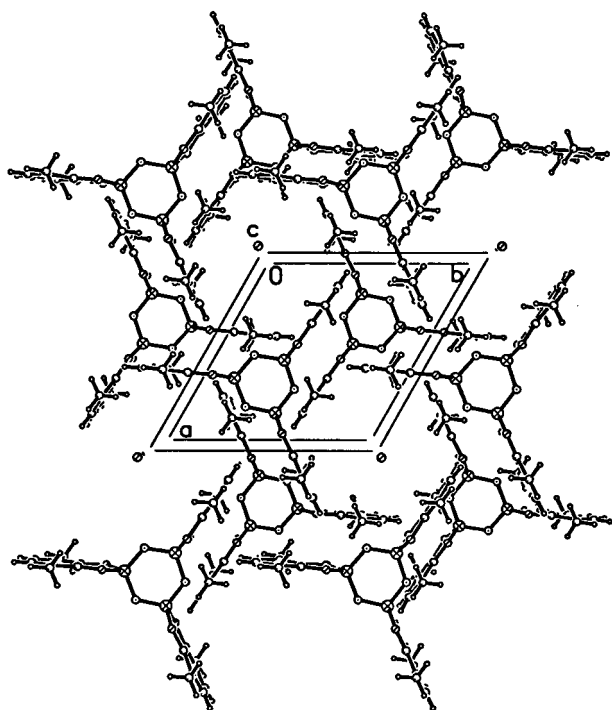


Figure 6. Hexagonal host lattice and poly(tetramethylene oxide) guests as seen along the *c*-axis.

ylene oxide) inclusion adduct of **4** is similar in general structure to the polyethylene and poly(ethylene oxide) inclusion adducts of **1**.²⁵ All have hexagonal packing patterns in which individual polymer chains are extended along tunnels.

It is proposed that the polymer chains seed the crystal growth of host **4** along the *c*-axis and serve as a template for the hexagonal packing structure. This is similar to the situation found earlier for the PEO-**1** adduct. There are 84 electrons in the void space of the unit cell of host **4**, which suggests that two tetramethylene oxide (40 electrons/monomer unit) repeating units are present in a unit cell. However, the polymer is fully disordered around the 3-fold axis, and is resolved only as a linear chain. Thus, no polymer chain conformation information could be extracted from the data. Previous single-crystal X-ray data for PE and PEO included in **1** indicated that the polymer chains are mobile within the host, as deduced from the limited certainty of their location within the tunnel void, which is presumably due to the

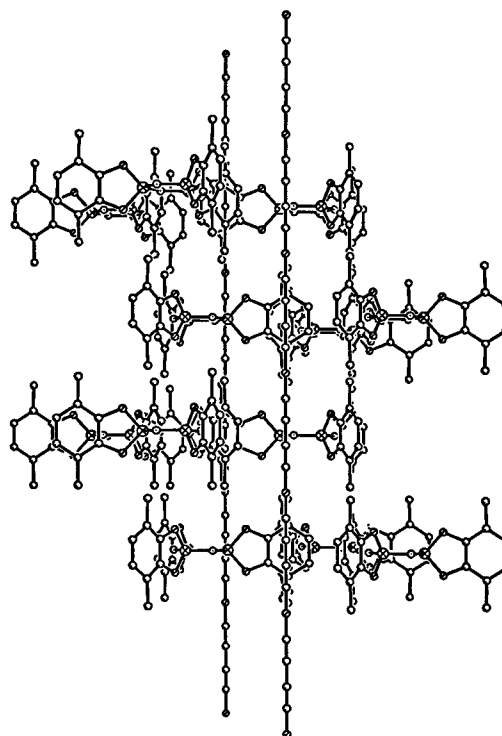


Figure 7. Projection of the hexagonal host lattice along the *a*-axis, showing the poly(tetramethylene oxide) chains extending through the tunnels.

very weak van der Waals interactions between the polymer and the host. The same situation probably exists for host **4**.

Conclusions

Tris(3,6-dimethylphenylenedioxy)cyclotriphosphazene, **4**, has a paddle wheel molecular structure with pendent dimethylphenyl groups linked perpendicularly to the planar cyclotriphosphazene ring through etheric oxygen linkages. In all cases, whether guest is included or not, the O-P-O bond angles are narrowed in a way that suggests ring strain. This has also been seen with other hosts, such as **1** and **2**, and is a characteristic feature in these paddle wheel structures.

Crystal engineering of these host systems is simplified by the ability to tailor the nature of the side group. Although the hosts are very similar in molecular

structure, the small molecule adducts of **1** and **4** are very different. The axial methyl groups in **4** cause this host to form cagelike adducts with guests such as benzene, methylene chloride, and dioxane. The stability of these inclusion adducts is relatively poor, as illustrated by the susceptibility of **4** to lose the guest in air. Thermal analysis indicated that guest loss occurs near the boiling points of these guests, and this is a difference from similar adducts formed by **1**. For **1**, benzene and dioxane are trapped within tunnel-like voids which are 5 Å wide. Those adducts are more stable in air, and loss of guests from **1** does not occur until the adduct is heated to temperatures above 130 °C. It is likely that these differences in adduct stability reflect the differences in both the size and shape of the voids formed by these compounds.

Host **4** also forms inclusion adducts with polymers and crystallizes in a hexagonal packing arrangement with 5 Å diameter tunnels which contain the polymeric molecules. These results indicate that host **4** may be useful for the separation of small molecules, and for the selective inclusion and separation of a variety of polymers based on chain length, different stereoregularities, and end-group functionality.

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Supporting Information Available: Tables of crystal data for guest-free **4**, dioxane-**4**, and poly(tetramethylene oxide)-**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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