Articles

Synthesis and Crystal Structure of Tris(9,10-phenanthrenedioxy)cyclotriphosphazene. A New Clathration System

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Tris(9,10-phenanthrenedioxy)cyclotriphosphazene forms inclusion adducts with a wide range of organic small molecules. This novel host molecule crystallized with *p*-xylene to form a triclinic 1:1 inclusion adduct, space group $P\bar{1}$ (No. 2), having unit cell of dimensions $a = 12.724(3)$ Å, $b = 19.347(5)$ Å, $c = 9.124(5)$ Å and $\alpha = 97.55(3)°$, $\beta = 106.13(3)°$, $\gamma = 72.46(2)°$, Z = 2. In this adduct, *p*-xylene is confined within both cage and tunnel-like voids of the host lattice. The same host crystallized with 1,2-dichlorobenzene to form an orthorhombic inclusion adduct, space group $P2_12_12_1$ (No. 19), having a unit cell of dimensions $a = 14.880(3)$ Å, $b = 23.277(4)$ Å, $c = 13.429(4)$ Å, and $Z = 4$. In general, the guest to host molar ratios for the 1,2-dichlorobenzene adduct varied from 1.1:1 to 1.3:1. 1,2-Dichlorobenzene, *o*-xylene, *p*-xylene, benzene, tetrahydrofuran, and cyclohexane were directly imbibed by tris(9,10-phenanthrenedioxy)cyclotriphosphazene to form air stable inclusion adducts. Powder X-ray diffraction of these adducts indicated that the crystal lattice formed is highly guest dependent. Inclusion adducts containing 1,2-dichlorobenzene, *o*-xylene, and *p*-xylene as guests were more stable than those containing tetrahydrofuran, benzene, or hexane. Selective inclusion of cyclohexane and *o*-xylene was achieved from hexane/cyclohexane and *p*-xylene/*o*-xylene mixtures.

Introduction

The incorporation of guest species within well-ordered cavities of intercalation compounds,[1] zeolites,[2] or crystals of organic compounds[3] has been utilized for various purposes. Zeolites are used extensively in oil refining as microchambers for acid catalyzed "cracking" of olefins.[4] Unlike zeolites, the inclusion adducts formed from organic host compounds are held together by weaker, noncovalent forces. Such inclusion adducts have been studied for use in separations,[5] regio- and stereoselective control of free-radical polymerizations,[6] and stabilization of sensitive or toxic substances.[7] The advantages in using organic host compounds for adduct formation include the possibilities for host structural tailorability, ease of adduct formation, and possible guest selectivity based on differential host–guest forces. Some well-studied organic host compounds include urea,[8] perhydrotriphenylene,[9] dianin,[10] and wheel-and-axle type compounds.[11]

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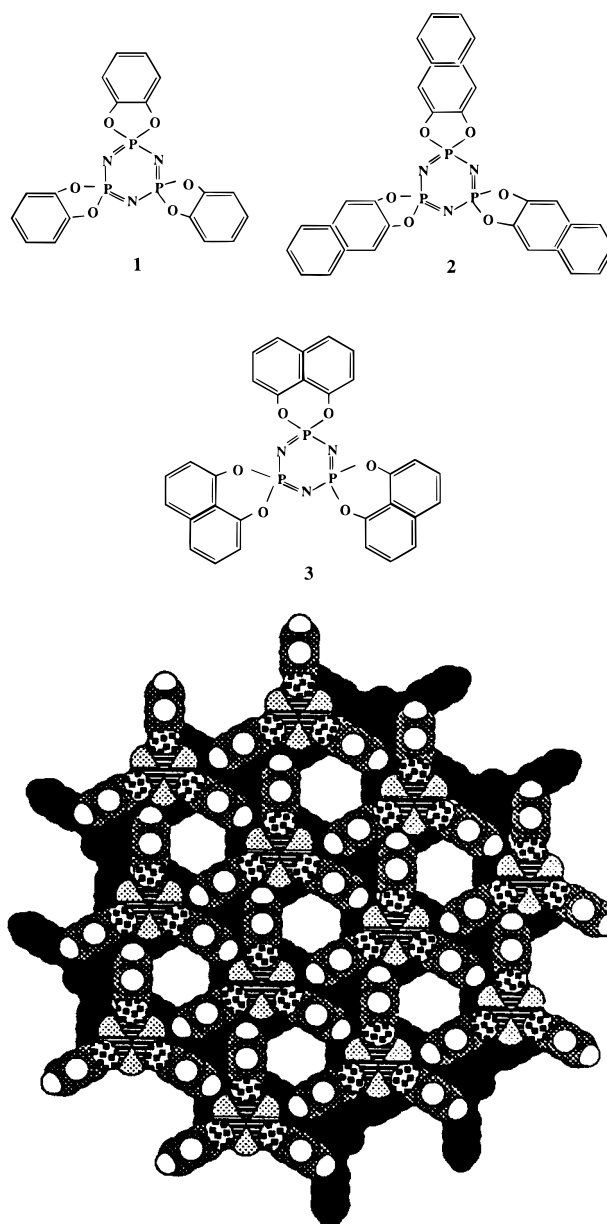(3) Vögtle, F. In *Supramolecular Chemistry*; Wiley: Chichester, 1991; p 171.

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The design of new inclusion host systems to generate specific adduct properties is of great interest. In theory, sensitive host−guest interactions, which often control adduct formation, may be exploited as a means to separate chemical species that are difficult to isolate by other methods. The design of inclusion host systems from first principles is still a matter of much research. However, certain traits are common to many of the available host compounds. Molecular rigidity, bulkiness, and an ability to undergo hydrogen bonding are characteristics commonly found in compounds that behave as hosts in adduct formation. Several difficulties are encountered in the synthesis of hosts that possess some or all of these traits. In general, the synthesis of very bulky host compounds often requires costly multistep procedures. In many host compounds, aromatic, alkyne, or cyclic groups provide rigidity to the overall structure. Host compounds containing these rigid groups are often planar or rod-like in nature.

We have reported previously the synthesis and properties of several bulky (aryloxy)cyclotriphosphazene host compounds including tris(*o*-phenylenedioxy)cyclotriphosphazene (**1**),[12−15] tris(2,3-naphthalenedioxy)cyclotriphosphazene (**2**),[16] and tris(1,8-naphthalenedioxy)cyclotriphosphazene (**3**).[17] (Chart 1) These compounds are formed by the reactions of aromatic diols with hexachlorocyclotriphosphazene. Cyclotriphosphazene host compounds are unique in that side groups are attached to a central molecular hub that, in turn, yields bulky, rigid, three-dimensional structures. Compound **1** has proved to be the most versatile host, since it directly imbibes a wide range of guest molecules as liquids or vapors. The ability of **1** to directly absorb guests led to its use as a host for the inclusion polymerization of various vinyl, diene, and acrylate monomers.[18−22] Previous work has also indicated that **1** can separate small molecules on the basis of guest size selectivity. For example, when an equimolar mixture of cyclohexane and heptane was exposed to **1**, heptane was preferen-

Chart 1

Figure 1. Adduct crystal arrangement of **1** in which the 5 Å diameter tunnel voids are visible.

tially absorbed, with almost 100% exclusion of cyclohexane.[12] This selectivity has stimulated applications in separations technology,[23] and in the design of vapor-phase sensors.[24]

As illustrated in Figure 1, the hexagonal host lattice of **1** in its clathrate form has tunnel-like cavities that are approximately 5 Å wide. Previous studies have indicated that this lattice structure is stabilized by the presence of guest molecules within the tunnels.[13] Host **2** forms a very similar type of adduct with benzene, in which the tunnel diameter is expanded to about 10 Å.[16] In these two adducts, hosts **1** and **2** are arranged in a

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**Scheme 1. Synthesis of
Tris(9,10-phenanthrenedioxy)cyclotriphosphazene**
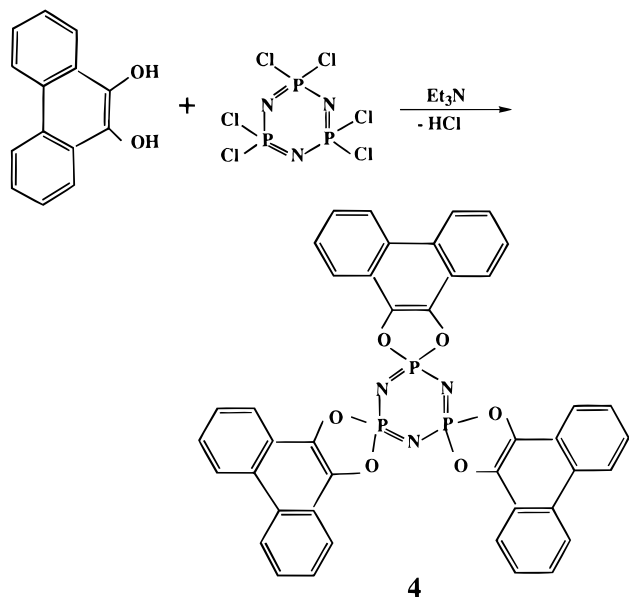
3-fold symmetrical manner. Near 3-fold symmetry has also been found for **2** in other adduct structures.[25,26] However, significant deviation from 3-fold molecular symmetry exists in guest-free **1**.[13] In all cases, the aryl side groups of hosts **1** and **2** lie near perpendicular to the plane of the phosphazene ring in a paddle-wheel-type arrangement. This particular alignment may be characteristic of cyclotriphosphazene host compounds with strained spirocyclic rings connecting the aryl side group to the phosphazene ring.

The aim of this work was to synthesize a new phosphazene host compound similar in structure to hosts **1**–**3**, yet able to form inclusion adducts having cavity sizes larger than those formed by existing examples. In this paper we describe the synthesis and inclusion adduct properties of tris(9,10-phenanthrenedioxy)cyclotriphosphazene (**4**) (Scheme 1).

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene was obtained from a trimer-tetramer mixture (Ethyl Corp./ Nippon Fine Chemical) after two recrystallizations from heptane followed by vacuum sublimation (40 °C, 0.05 Torr). Tetrahydrofuran (OmniSolve) was distilled from sodium–benzophenone. Triethylamine (Baker) was predried over CaH_2 and then distilled from sodium. Potassium borohydride (Aldrich) was stored in a glovebox and used as received. HPLC-grade 1,2-dichlorobenzene, *p*-xylene, and *o*-xylene were used as received from Aldrich.

Synthesis of 9,10-Dihydroxyphenanthrene. This compound was synthesized by a modification of a previously described method.[27] 9,10-Phenanthraquinone (10.0 g) was dissolved in 100% ethanol (500 mL) to give a dark-orange solution/suspension. KBH_4 (10.25 g, 3.95 equiv) was added slowly to this over 3 h via a Schlenk addition tube. The solution was stirred for 48 h. The reaction mixture was cooled with an ice-bath, and cold, dilute hydrochloric acid was added to

deactivate the excess borohydride. Most of the ethanol was then removed in vacuo and the product was precipitated in 500 mL of ice−water. The compound was collected by filtration and was dried in vacuo. The identity of this compound was confirmed by ^1H and ^{13}C NMR; mp 143−147 °C; EI MS *m/z* calcd 210, *m/z* found 210.

Synthesis of Tris(9,10-phenanthrenedioxy)cyclotriphosphazene, 4 (Scheme 1). Hexachlorocyclotriphosphazene (3.05 g, 8.80 mmol) was dissolved in dry tetrahydrofuran (THF) (75 mL). 9,10-Dihydroxyphenanthrene (5.53 g, 3.0 equiv.) and triethylamine (5.32 g, 6.0 equiv.) in THF were added slowly, and the mixture was stirred for 24 h. The precipitate was isolated by filtration, and the triethylamine hydrochloride salts were removed by washing with water. A final wash with a minimal amount of CH_2Cl_2 yielded 2.98 g (45% yield) of **4** as a yellowish solid. ^{31}P NMR (THF-d_8) δ 38.3 ppm (s); mp 345−350 °C with decomposition; EI MS *m/z* calcd. 759, *m/z* found 759. Anal. Calcd: C, 66.4; H, 3.16; N, 5.53. Found: C, 66.04; H, 3.55; N, 5.41.

Crystal Preparation. Crystals for single-crystal X-ray diffraction were grown from *o*-xylene, *p*-xylene, and 1,2-dichlorobenzene by slow evaporation of a saturated solution. Suitable crystals were selected and sealed in capillary tubes with the mother liquor. Inclusion adduct crystals examined by thermal analysis were recrystallized quickly from refluxing saturated solutions. Attempts were made to sublime guest-free single crystals of **4** at both high temperature (310 °C, 0.020 mmHg) and low temperature (250 °C, 0.020 mmHg) settings using a thermal gradient sublimer.[28] However, these attempts did not produce crystals of sufficient size or quality for single-crystal X-ray diffraction.

Powder Adduct Preparation. The removal of residual CH_2Cl_2 from **4** was required in order to dry the solid host. This was achieved through simple evacuation (0.05 Torr) of the solid at 80 °C for 1 h. Pure **4** was then exposed to various solvents and dried by evaporation at either atmospheric pressure or under vacuum. The variation of direct imbibition by **4** with host mesh size was not examined.

Instruments. ^{31}P NMR spectra were recorded with the use of a Bruker WM-360 NMR spectrometer operated at 146 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm, with positive shift values downfield from the reference. ^1H and ^{13}C NMR spectra were recorded with a Bruker WM-360 spectrometer operating at 360 and 90.5 MHz, respectively. Chemical shifts are relative to tetramethylsilane at δ = 0. Electron impact mass spectra were obtained with the use of a KRATOS MS9/50 spectrometer. The X-ray powder diffraction patterns were obtained using both a Rigaku Giegerflex with a Dmax-B controller (2θ = 3−60°, 1°/min) and a Philips analytical X-ray X'PERT MPD (2θ = 5−60°, 1°/min). Elemental analysis were obtained by Galbraith Laboratories, Knoxville, TN.

X-ray Structure Determination (*p*-Xylene Adduct of 4). A colorless needle-like crystal of $C_{42}H_{24}N_3O_6P_3 \cdot C_8H_{10}$ with approximate dimensions $0.70 \times 0.25 \times 0.10$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation. Details of data collection, data reduction, structure solution and refinement are provided in Table 1.

X-ray Structure Determination (1,2-Dichlorobenzene Adduct of 4). A colorless prismatic crystal of $C_{42}H_{24}N_3O_6P_3 \cdot 2C_6H_4Cl_2$ having approximate dimensions of $0.55 \times 0.22 \times 0.17$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite mono-chromated Mo−Kα radiation following procedures very similar to these used for the *p*-xylene−**4** inclusion adduct. Details of data collection, data reduction, structure solution, and refinement are provided in Table 1.

The structure was solved by direct methods.[29] P, N, and Cl atoms were refined anisotropically, while the rest were refined isotropically: Cl(3) was disordered over two sites with site

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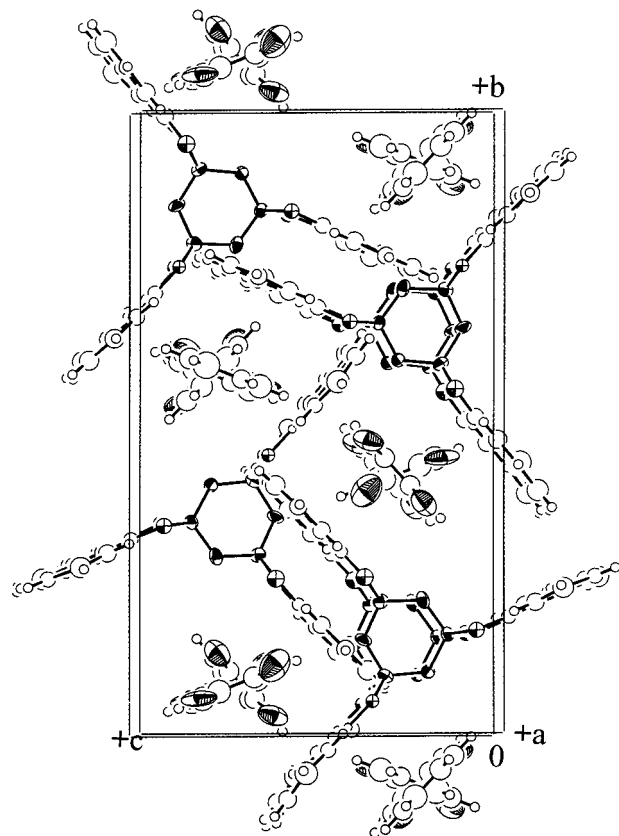
Table 1. Crystallographic Data

formula	$C_{42}H_{24}N_3O_6P_3\cdot$ $2C_6H_4Cl_2$	$C_{42}H_{24}N_3O_6P_3\cdot$ C_8H_{10}
formula weight	1053.54	865.76
crystal system	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	P$\bar{1}$ (No. 2)
a, Å	14.880(3)	12.724(3)
b, Å	23.277(4)	19.347(5)
c, Å	13.429(4)	9.124(5)
α, deg		97.55(3)
β, deg		106.13(3)
γ, deg		72.46(2)
volume, Å³	4651(2)	2054(1)
Z	4	2
crystal size, mm³	$0.55 \times 0.22 \times 0.17$	$0.70 \times 0.25 \times 0.10$
crystal color, habit	colorless, prismatic	colorless, needle
density (calcd), Mg/m³	1.504	1.399
absorption coefficient, mm⁻¹	0.416	0.202
temperature, K	200(2)	170(2)
diffractometer	Rigaku AFC6S	Rigaku AFC6S
wavelength, Å	0.71069	0.71069
max. and min. transmission	0.933 and 0.804	1.00 and 0.743
F(000)	2152	896
θ range for data collection, deg	2.0 to 25.0	2.0 to 25.0
reflections collected	4556	7627
observed data	1460[a]	2577[b]
programs used	SHELXL97	teXsan
refinement method	full-matrix least-squares	full-matrix least-squares
parameters refined	347	519
coefficients used	F^2	F
goodness-of-fit	0.988	3.18
final R and wR indices	0.073, 0.195	0.082, 0.070
max., min. diff. peaks, e Å⁻³	0.748 and −0.464	0.45 and −0.404

[a] $[I > 2.0\sigma(I)]$. [b] $[I > 3.0\sigma(I)]$.

occupancy factors Cl(3A) 0.78(1) and Cl(3B) 0.22(1). Hydrogen atoms were included at geometrically idealized positions. The final cycle of full-matrix least-squares refinement[30] was based on 1405 observed reflections ($I > 3.00\sigma(I)$) and 314 variable parameters and converged (largest parameter shift was 0.10 times its esd) with R and wR of 0.0614 and 0.0625, respectively. The maximum and minimum peaks in the final difference Fourier Map corresponded to 0.45 and −0.38 e⁻/Å³, respectively.

Results and Discussion

Crystal Structures. (a) 1,2-Dichlorobenzene−4 Inclusion Adduct. Figure 2 shows the unit cell and packing arrangement in this adduct. The unit cell volume is 4651 Å³, with eight molecules of dichlorobenzene occupying voids that constitute 1642 Å³ of the total space. Thus, on average, each guest occupies approximately 210 Å³. The guest molecules are accommodated in tunnels that penetrate the lattice (Figure 3), with guests separated by roughly 3.4−3.7 Å down each tunnel. The closest Cl···H contact distances are 3.12 Å. Layers comprised of **4** and 1,2-dichlorobenzene lie perpendicular to the tunnel axis. Each of these layers has a similar guest−host packing arrangement. However, the stacking of these layers is offset from each other in an alternating ABAB manner. There are two symmetry independent guests within each layer. The walls of the cavities in each layer are comprised of two opposing phenanthrene side groups (Figure 3). The
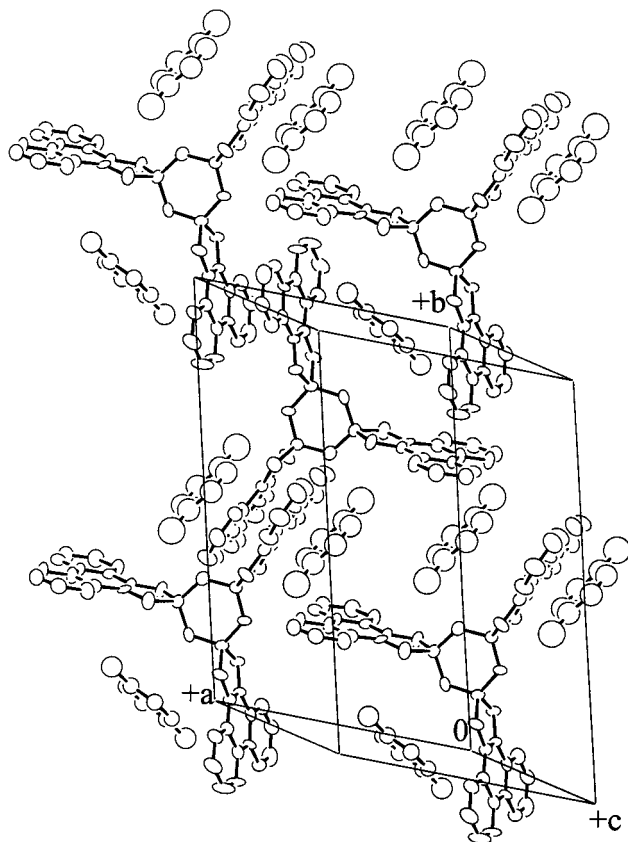
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Figure 2. View down the *a*-axis of the 1,2-dichlorobenzene−**4** inclusion adduct unit cell. Atom Cl(3B), representing the smaller fraction of the disordered Cl(3) atom, was ignored.
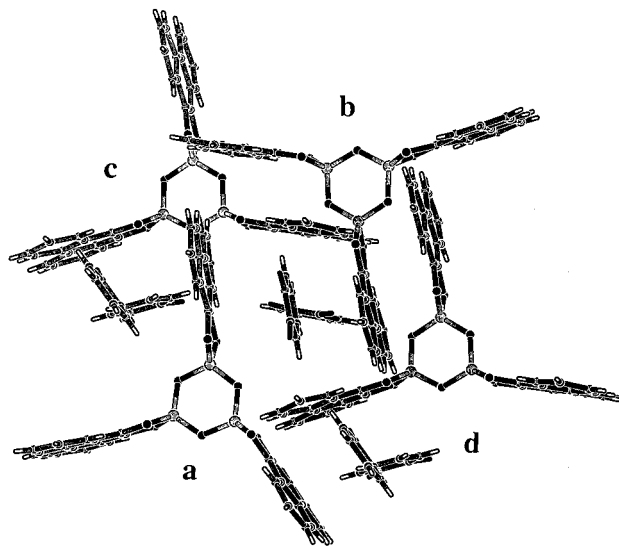
Figure 3. Close-up view of the 1,2-dichlorobenzene−**4** inclusion unit cell. (Some guest and host species have been omitted for clarity.)

phosphazene rings of host compounds **a** and **b** in Figure 3 lie within the same plane. In this layer, 1,2-dichlorobenzene is sandwiched between the two opposing phenanthrene side groups. The gap between these side groups marks the narrowest point along the tunnel and was found to be approximately 5.8 Å in diameter. Along the bottom layer, between hosts **c** and **d** in Figure 3, the walls of the tunnel are at their widest point. The tunnel at this point has an average width near 6.4 Å.

Figure 4. Unit cell of the *p*-xylene−**4** inclusion adduct.

Within this gap a 1,2-dichlorobenzene molecule lies parallel to the one phenanthrene side group that is directed away from the tunnel. This 1,2-dichlorobenzene molecule was determined by X-ray crystallography to be disordered about two positions that lie around an inversion axis. As seen in Figure 3, this disorder results in the appearance of three chlorine atoms on the phenyl ring. It is likely that the increased tunnel diameter at this point allows for this disorder.

Attempts to resolve the *o*-xylene−**4** inclusion adduct were unsuccessful. *o*-Xylene remained disordered within the host lattice even at temperatures near 173 K. However, single-crystal X-ray diffraction indicated that the host packing in this adduct was very similar to that seen in the 1,2-dichlorobenzene−**4** adduct.

(b) *p*-Xylene−4 Inclusion Adduct. The unit cell for the adduct between *p*-xylene and **4** is shown in Figure 4. There are only two xylene molecules in the unit cell. The unit cell volume is 2054 Å^3 of which 490 Å^3 constitutes the void volume occupied by the guest molecules. The two xylene molecules occupy two different environments. One xylene is coplanar with and 5.91 Å from one of the phenanthrene units. The second xylene occupies a tunnel-like cavity, approximately 7.3 Å wide, formed between the side group angles of two adjacent host molecules. In this location, the center of each xylene molecule is 4.32 Å from the nearest nitrogen atom of a phosphazene ring, but the closest distance between a hydrogen atom of the guest and carbon-1 of a phenanthrene side group is only 2.87 Å

Molecular Structures of 4. As is the case for hosts **1** through **3**, the spirocyclic side groups of **4** lie perpendicular to the plane of the phosphazene ring. One phenanthrene side group of **4** in the 1,2-dichlorobenzene

adduct is bent 44° at the oxygen atoms away from 3-fold symmetry. This bending probably occurs in order to better fit the 1,2-dichlorobenzene molecules within the channel space. The other side groups of **4** are slightly bent toward each other by less than 6°. The shape of **4** in this adduct is very similar to that of **3** in the *p*-xylene−**3** inclusion adduct.[17] However, the overall extent of side group bending in **4** is much less than that seen for **3**.

The side groups of **4** in the *p*-xylene inclusion adduct extend out from the phosphazene ring in a near perfect 3-fold manner. One phenanthrene side group of **4** deviates by 4° from a perpendicular alignment to the phosphazene ring. The conformation of **4** in this adduct differs greatly from the conformation of this host in the 1,2-dichlorobenzene adduct. This suggests that host−guest interactions within adducts of **4** markedly influence the conformation of the host. This sensitivity of the host conformation to changes in the guest structure is not found in the known adducts of hosts **1** and **2**.

The O−P−O bond angles of **4**, in both the *p*-xylene and 1,2-dichlorobenzene adducts, are between 97° and 99°. These reduced bond angles, indicative of ring strain, are also found in hosts **1** and **2**.[14,16] As was seen for hosts **1** and **2**, the side groups of **4** in both the *p*-xylene and 1,2-dichlorobenzene adduct lie near perpendicular to a planar phosphazene ring. This arrangement is different from that of host **3**, in its adduct form. The phosphazene ring of **3** is puckered in a boat conformation.[17] The side groups of a similar host compound, tris(2,2′-dioxybiphen-yl)cyclotriphosphazene (**5**), are severely tilted with respect to the phosphazene ring.[31] In both **3** and **5**, the heterocyclic rings attaching the side group to the phosphazene ring are larger than the strained five-membered rings in hosts **1**, **2**, and **4**. This suggests that increased symmetry of hosts **1**, **2**, and **4** over that of **3** and **5** may be related to the five-membered ring strain present within these structures.

Direct Imbibition of Guests. Pure host **4** directly imbibes 1,2-dichlorobenzene, *p*-xylene, *o*-xylene, benzene, tetrahydrofuran, and cyclohexane. Powder X-ray diffractograms for these adducts were different from that obtained for pure **4** dried from methylene chloride. Methylene chloride was used as a drying agent because of its inability to form a stable adduct with **4**. As shown in Figure 5, four different diffractograms were obtained for the adducts containing the four different guests, 1,2-dichlorobenzene, *p*-xylene, benzene, and cyclohexane. Differences in these diffractograms indicate that the adduct structure is highly guest dependent. Powder X-ray diffraction plots of the *p*-xylene and 1,2-dichlorobenzene adducts matched the respective plots simulated from the crystal data for each adduct. Very little difference was seen between the diffractogram of **4** that had absorbed 1,2-dichlorobenzene and that of **4** with *o*-xylene. This agrees with the X-ray single-crystal diffraction data which indicated that these two inclusion adducts are very similar. A cycling of adduct formation with *o*-xylene was achieved by drying the *o*-xylene adduct of **4**, (0.020 mmHg, 250 °C) and then subsequently reexposing the pure host to *o*-xylene. This was repeated three times without significant physical deg-

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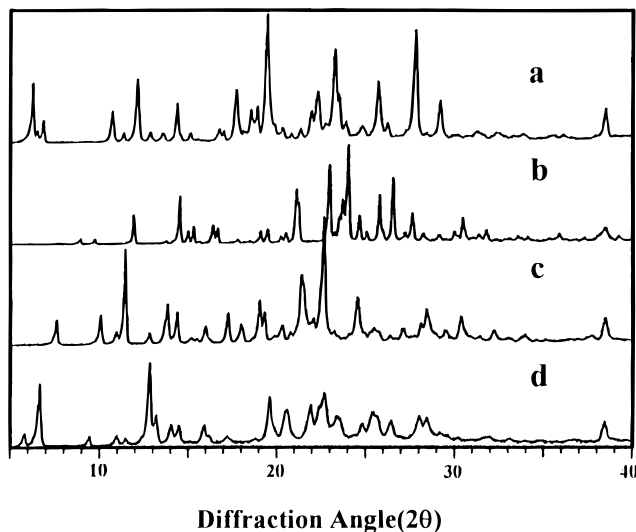
Figure 5. Powder X-ray diffractograms of the (a) cyclohexane−**4** adduct, (b) 1,2-dichlorobenzene−**4** adduct, (c) *p*-xylene−**4** adduct, and (d) benzene−**4** adduct.

Table 2. Stability of Small Molecule−4 Inclusion Adducts

guest included (Adduct)	guest/host ratio in air after		temperature range (°C) at which rapid guest loss occurs[a]
	5 h	24 h	
1,2-dichlorobenzene (**a**)	1.39	1.38	145−170
o-xylene (**b**)	1.44	1.36	130−155
p-xylene (**c**)	0.90	0.83	1st, 110−135), 2nd 145−185
benzene (**d**)	0.99	0.34	75−130
tetrahydrofuran (**e**)	1.00	0.68	75−130
cyclohexane (**f**)	0.28	0.23	

[a] Determined by TGA.

radation of the host solid. The guest-free diffraction pattern obtained during this process was different from that of **4** dried from CH_2Cl_2. This indicates that in some cases the guest-free packing of **4** may differ depending on which guest was employed as a template.

Moistening of **4** with ethanol or hexane did not result in the formation of air-stable inclusion adducts. X-ray powder diffraction indicated that the lattice of **4** does not change following exposure to ethanol. Moreover, TGA analysis indicated that minimal ethanol was retained by **4** after drying. However, moistening of **4** with hexane did result in a lattice rearrangement even though, after drying, the final crystal lattice matched that of **4** dried completely from *o*-xylene. Heating of **4** dried from hexane resulted in only a 2% reduction in weight. This suggests that hexane is lost rapidly from **4** following exposure to air.

Inclusion Adduct Stability. As determined by gravimetric studies, host **4** formed air-stable inclusion adducts with the guest molecules listed in Table 2. Adducts **4a**−**c** were obtained by recrystallization, while **4d**−**f** were formed by direct imbibition. The X-ray crystallographic results were consistent with guest-to-host ratios of 2:1 for both the 1,2-dichlorobenzene and *o*-xylene adducts and 1:1 for the *p*-xylene adduct. These values probably represent the maximum guest occupancy values because the crystals were maintained in contact with the guest liquid and vapor from the time of crystallization to the end of the single-crystal X-ray analysis. Other estimates of the guest-to-host ratios
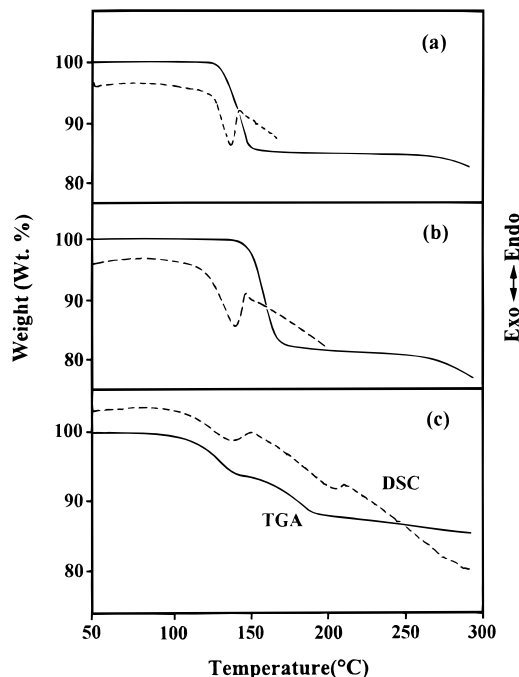
Figure 6. DSC and TGA thermograms (20 °C/min) of the (a) *o*-xylene−**4** adduct, (b) 1,2-dichlorobenzene−**4** adduct, and (c) *p*-xylene−**4** adduct.

were made by thermogravimetric analysis and by following the weight change of the adduct while it was exposed to the atmosphere at 25 °C or after storage in a vacuum. The values in Table 2 reflect the ease of guest loss when the adducts were exposed to air. These different methods of analysis suggested different guest-to-host ratios. For example, the ratios for the 1,2-dichlorobenzene aducts varied from approximately 1:1 to 1.4:1 Values for the *o*-xylene system ranged from 1.2:1 to 1.44:1. The *p*-xylene adduct retained its roughly 1:1 initial ratio irrespective of the method of analysis. These variations probably reflect difference in adduct stability during their manipulation during the various procedures. Adducts **4a**−**c** showed a similar stability in a vacuum (0.02 mm for 24 h) as they did when exposed to the atmosphere. However, evacuation of the cyclohexane adduct for 5 h resulted in complete removal of the guest. In general, those adducts formed by direct guest imbibition were less stable under vacuum than adducts formed by recrystallization, which may result from the small crystallite size of the imbibition species and the correspondingly greater surface area. Methylene chloride did not form a clathrate with **4**, a fact that probably reflects its small molecular size.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the adducts **4a**−**c** are shown in Figure 6. TGA and DSC analysis of the *o*-xylene−**4** and 1,2-dichlorobenzene−**4** adducts showed rapid loss of the guest at a temperature near the boiling point of the pure guest, accompanied by a corresponding exothermic transition. In both cases, the change in the weight following guest loss indicated a molar host:guest ratio in the range of 1.1:1 to 1.3:1, although this varied with sample history. As discussed earlier, the *p*-xylene−**4** adduct differs from the 1,2-dichlorobenzene and *o*-xylene counterparts, because it has two different types of host lattice voids in which the *p*-xylene molecules can

Table 3. Selective Inclusion from Small Molecule Mixtures

	molar ratio	
small molecule mixture	in solution	in adduct
p-xylene/*o*-xylene	50:50	25:75
1,2-dichlorobenzene/*o*-xylene	50:50	56:44
cyclohexane/hexane	50:50	94:6

be trapped. A TGA of the *p*-xylene adduct revealed two distinct temperatures at which guest loss occurred. An initial weight loss occurs near 120 °C, while subsequent guest loss occurs near 160 °C. Thus, some *p*-xylene is retained within **4** to a temperature that is 20 °C above the boiling point of the guest. Powder X-ray diffraction studies of the *p*-xylene−**4** adduct showed that an intermediate crystal phase was formed between the first and second temperatures of rapid guest loss. As seen in Figure 6c, the DSC plot for the *p*-xylene adduct showed two exothermic transitions near 130 and 200 °C. These are related to the two transitions seen in the TGA plot for this adduct. The DSC and TGA transitions shown in Figure 6 were only reproducible within a 15°−20° range, probably due to the difficulty of controlling crystal size and quality and percent guest occupancy. These factors undoubtedly affect adduct stability.

The exotherms that accompany the loss of *o*-xylene and 1,2-dichlorobenzene from crystals of **4** are probably due to a rearrangement of the host lattice. Exothermic transitions at the point of guest loss have been reported for layered phosphates that contain quaternary ammonium ions as guest.[32] Systems more similar to **4**, such as urea and perhydrotriphenylene, do not show this type of thermal behavior, probably because, unlike **4**, guest release from these other hosts is not accompanied by a rearrangement of the host crystal lattice.

Selective Absorption. As seen in Table 3, the moistening of **4** with a 50:50 molar mixture of *p*-xylene and *o*-xylene resulted in the preferred absorption of *o*-xylene. The powder X-ray diffractogram for the solid recovered from this 50:50 mixture matched that simulated from the single-crystal data for the *o*-xylene−**4** adduct. A slight preference exists for absorption of 1,2-

dichlorobenzene from the 1,2-dichlorobenzene/*o*-xylene mixture. Competition between the two types of host lattice structures was not likely in the case of the 1,2-dichlorobenzene/*o*-xylene mixture. This is because both of these guests form a similar type of adduct with **4**. Cyclohexane was preferentially absorbed by **4** from a 50:50 molar mixture of hexane and cyclohexane. The 93.5:6.5 selectivity ratio indicates that in this case the cyclic species is preferred over the linear aliphatic molecules. This selectivity is very different from that seen for host **1**, in which hexane was strongly preferred over cyclohexane.[12] This difference is probably due to the larger size of the lattice voids formed by **4** as compared to those formed by host **1**.

Conclusions

Tris(9,10-phenanthrenedioxy)cyclotriphosphazene (**4**) forms inclusion adducts with a range of cyclic guest molecules. The differences in the crystal structures of the *p*-xylene−**4** adduct and the *o*-xylene−**4** adduct indicate that sensitive guest−host forces influence the crystal structure of the inclusion adduct. Powder X-ray diffraction of other inclusion adducts of **4** also indicated that the guest plays a role in controlling the resultant host lattice structure. The most stable inclusion adducts formed by **4** are with guests with relatively large dimensions. By contrast, benzene and other guests of smaller size are more stable within the tunnels formed by **1**. This suggests that **4** may be used to absorb and immobilize guest molecules larger than those typically imbibed by **1**.

Supporting Information Available: Crystal data and structure refinement, atomic coordinates, anisotropic displacement coefficients, and observed and calculated structure factors for both the *p*-xylene and 1,2-dichlorobenzene adducts of **4**; structure factors and thermal parameters for the *o*-xylene adduct of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

(32) Danjo, M.; Baba, Y.; Tsuhako, M.; Yamaguchi, S.; Hayama, M.; Nariai, H.; Motooka, I. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1607.

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