

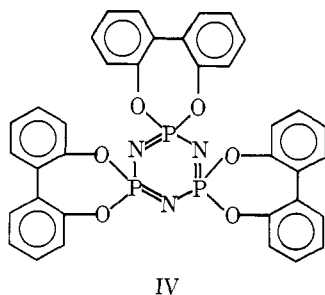
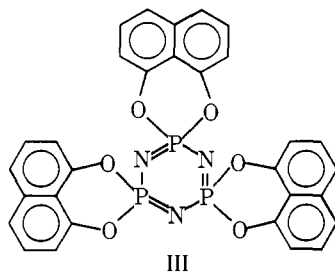
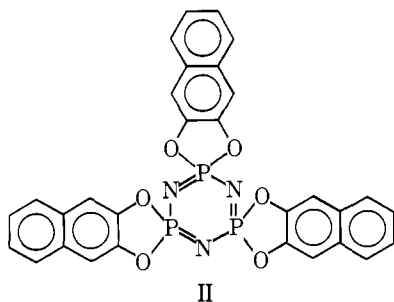
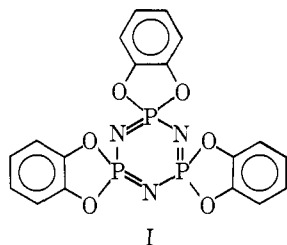
Molecular Motion and Molecular Separations in Cyclophosphazene Clathrates^{1,2}

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Abstract: The molecular inclusion clathrates formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I), tris(2,3-naphthalenedioxy)cyclotriphosphazene (II), and tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) have been examined from the viewpoint of the molecular motions of guest molecules trapped in the tunnel systems. The ease with which one guest molecule can replace another, and the results of competition for the tunnel space by two or more potential guest molecules have also been examined. Mass spectrometry, broadline ¹H NMR, and single-crystal x-ray diffraction techniques were employed. A reexamination of the x-ray structure of I is described.

The formation of clathrate inclusion adducts by spirocyclophosphazenes, such as tris(*o*-phenylenedioxy)cyclotriphosphazene (I), tris(2,3-naphthalenedioxy)cyclotriphosphazene (II), and tris(1,8-naphthalenedioxy)cyclotriphosphazene (III), has been described in earlier papers.³⁻⁶ The crystal structure of a related derivative that did not form clathrates, tris(2,2'-biphenylenedioxy)cyclotriphosphazene (IV), has also been reported.⁷



Compounds I-III form tunnel or channel clathrate adducts with organic molecules when recrystallized from organic solvents. Moreover, compound I forms adducts spontaneously when the pure host is allowed to come in contact with the liquid or even the vapor phase of the guest component.³ The earlier work also showed that subtle separations of guest compounds could be achieved during clathration from either the liquid or the vapor phase.

X-ray single-crystal structure studies of tunnel clathrates formed by I-III have been reported.⁴⁻⁶ However, although the main features of the clathrate structures formed by I were known,^{3,4} certain features of the structure (such as the molecular parameters of the phosphazene side groups and the disposition of the guest molecules) were not well resolved.⁴ For this reason, we have reinvestigated the structure of several adducts formed by I with the use of x-ray diffraction techniques.

The aim of the present work was, first, to examine the conditions under which guest molecules in the lattice of I, II, or III can undergo extensive thermal motions or occupy fixed positions. Second, it was of interest to explain why and how one guest molecule can be incorporated into a particular lattice with exclusion of another molecule, and why clathrates are formed at all.

Experimental Section

Synthesis of Host Compounds. Compounds I, II, and III were synthesized by the general methods described previously.⁸⁻¹⁰ Specifically, catechol, 2,3-naphthalenediol, or 1,8-naphthalenediol were allowed to react with hexachlorocyclotriphosphazene in the presence of sodium carbonate. Compound I was purified by triple sublimation at 175 °C (0.1 Torr) to give material with mp 245-246 °C. Compound II was also vacuum sublimed at 250 °C (0.1 Torr) to yield material with mp 335-338 °C. Compound III melted at 388-391 °C.

Guest Compounds. *o*-Xylene (Eastman), *p*-xylene (Eastman), mesitylene (Aldrich), and 1,3,5-triethylbenzene (Eastman) were washed with sulfuric acid, dried with phosphorus pentoxide, and distilled before use. Benzene (J. T. Baker) was refluxed over calcium hydride and distilled before use. *n*-Hexadecane, cyclohexane, *n*-heptane, isooctane, decalin, and chloroform were obtained from Eastman Organic Chemicals.

Formation of Adducts. The adducts formed by I, II, and III were prepared by recrystallization techniques or by direct guest imbibition. For example, I, II, or III were dissolved in the minimum amount of hot benzene, *o*-xylene, *p*-xylene, mesitylene, or 1,3,5-triethylbenzene. After the solutions were cooled, crystals of the adduct were collected by suction filtration and were dried at 25 °C under vacuum for 15 h.

Similar techniques were used to prepare adducts of I or II from solvent pair systems. For instance, compound I or II was recrystallized from solutions in equivolume mixtures of *n*-hexadecane-chloroform, *n*-hexadecane-cyclohexane, *n*-hexadecane-*n*-heptane, *n*-hexadecane-isooctane, *n*-hexadecane-benzene, *n*-hexadecane-decalin, and

benzene–heptane. These adducts were dried at 25 °C in the atmosphere (in order to avoid selective removal of one guest under vacuum).

Direct guest uptake was induced by stirring the crystals of pure, sublimed I or II at 25 °C for 24 h in equivolume solvent pair systems of *n*-hexadecane with chloroform, cyclohexane, *n*-heptane, isooctane, benzene, and decalin. In all cases the presence or relative concentrations of the guest molecules in the adducts was determined by infrared spectroscopy of the solids and by mass spectrometry. In the latter technique, samples were injected as solids at temperatures in the range of 50 to 250 °C.

NMR Technique. Broadline NMR spectra were obtained for solid samples with the use of a Varian HA 100 instrument. The sample temperature was varied over the range of –70 to +150 °C. The solid crystalline samples were examined in 4-mm i.d. NMR tubes.

X-Ray Crystallography of I. Single crystals of I which contained benzene, *o*-xylene, *p*-xylene, or mesitylene as included guests were prepared by the slow evaporation of solutions of I in the appropriate pure solvent at 25 °C. The crystals obtained were hexagonal prisms elongated along the unique axis. They showed no visible indication of loss of the guest component over a period of several weeks at 25 °C.

For the benzene, *o*-xylene, *p*-xylene, and mesitylene adducts, precession and Weissenberg photographs indicated the presence of a hexagonal unit cell with Laue symmetry 6/*m*. Reflections of the type 000/*l* were observed only for *l* = 2*n*, which indicated a twofold screw axis along the unique axis. This limited the possible space groups to *P*6₃ or *P*6₃/*m*. The unit cell dimensions for four different adducts were: benzene adduct,¹¹ *a* = 11.804 Å, *c* = 10.054 Å; *o*-xylene adduct,¹¹ *a* = 11.915 Å, *c* = 10.046 Å; *p*-xylene adduct,¹² *a* = 11.68 Å, *c* = 10.12 Å; mesitylene adduct,¹² *a* = 11.65 Å, *c* = 10.20 Å.

Crystals of the benzene and *o*-xylene adducts of I (0.32 × 0.26 × 0.22 mm and 0.20 × 0.20 × 0.16 mm, respectively) were mounted on eucentric goniometer heads and were placed on a Syntex four-circle, computer-controlled diffractometer for data collection at 25 °C. The benzene adduct crystal was mounted with the *c* axis parallel to the ϕ diffractometer axis, whereas the *o*-xylene adduct crystal was oriented with the *a* axis coincident with the ϕ axis of the diffractometer. The x-ray source was powered at 40 kV and 20 mA, with the use of Cu X radiation, nickel filtered in the incident beam. Data were collected in the θ – 2θ scan mode, with a 2θ scan rate of 2°/min for the benzene adduct, and 1°/min for the *o*-xylene adduct. The scan width employed for both crystals varied linearly from 2.00° at a 2θ value of 5° to 2.50° at a 2θ value of 120°. The background radiation was measured on each side of the peak for one-half of the total scan time. The 2θ scan range was set within the mechanical limits of the instrument by $0.05 \leq \sin \theta \leq 0.80$ for the benzene adduct and $0.03 \leq \sin \theta \leq 0.79$ for the xylene adduct. The 403 and 052 reflections served as standard reflections, with their intensities being measured every 25 reflections.

Net intensities were derived from the expression $I = [C_{15} - (B_1 + B_2)]$, where C_{15} represents the total counts in a scan, and B_1 and B_2 are the two background counts. "Observed" reflections were separated from the data by the criterion $I \geq 2.5\sigma(I)$ for the benzene adduct, and $I \geq 3.0\sigma(I)$ for the *o*-xylene adduct, where $\sigma(I)$ is the standard deviation of the net intensity derived from counting statistics by the formula $\sigma(I) = (C_{15} + B_1 + B_2)^{1/2}$. By these criteria, 439 of the 600 unique reflections measured for the benzene adduct and 317 of the 588 unique reflections for the *o*-xylene adduct were considered to be observed. The observed data were then corrected for Lorentz and polarization effects. At this point, a standard deviation for the least-squares refinement was assigned to each structure factor. The standard deviations were 1.1, 1.0, or 1.2 depending on the value of $\sigma(F_o)/F_o$. No absorption corrections were applied.

A three-dimensional Patterson synthesis was performed initially for both adducts. In both cases, interatomic vectors located in the Harker plane at $w = 1/2$ revealed the positions of the phosphorus and nitrogen atoms. For the benzene adduct, two cycles of least-squares refinement in space group *P*6₃, followed by a Fourier synthesis phased by the phosphorus and nitrogen atoms, revealed the locations of the oxygen atom and three carbon atoms. However, eight successive least-squares cycles with both isotropic and anisotropic thermal factors failed to refine the structure. Thus, space group *P*6₃ was abandoned in favor of *P*6₃/*m*. Later, a Hamilton *R* factor test confirmed that the space group was *P*6₃/*m*.

Both the benzene and *o*-xylene adduct structures were then refined in *P*6₃/*m*. For the benzene adduct, two least-squares cycles with

Table V. Atomic Parameters for the Benzene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P	0.4542 (6)	–0.3580 (6)	0.250
N	0.307 (2)	–0.476 (2)	0.250
O	0.534 (1)	–0.377 (1)	0.371 (1)
C(1)	0.634 (1)	–0.394 (1)	0.321 (1)
C(2)	0.722 (2)	–0.412 (2)	0.393 (2)
C(3)	0.814 (2)	–0.428 (2)	0.322 (2)
H(2)	0.71 (1)	–0.41 (1)	0.49 (2)
H(3)	0.90 (2)	–0.42 (2)	0.40 (2)

Table VI. Atomic Parameters for the *o*-Xylene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene

Atom	<i>x</i>	<i>y</i>	<i>z</i>
P	0.454 (1)	–0.359 (1)	0.250
N	0.307 (3)	–0.476 (3)	0.250
O	0.534 (2)	–0.376 (2)	0.370 (1)
C(1)	0.630 (3)	–0.396 (2)	0.320 (2)
C(2)	0.716 (3)	–0.414 (3)	0.389 (3)
C(3)	0.806 (4)	–0.431 (3)	0.320 (2)
H(2)	0.70 (2)	–0.40 (2)	0.47 (2)
H(3)	0.91 (3)	–0.41 (3)	0.38 (3)

isotropic thermal factors and two cycles with anisotropic thermal factors gave a smooth refinement. Hydrogen atoms were added at the calculated positions and three additional least-squares cycles with anisotropic thermal factors for all atoms except hydrogen lowered the unweighted *R* value to 0.097. For the *o*-xylene adduct, two least-squares cycles followed by a Fourier synthesis revealed the oxygen atom and three carbon atoms. Three isotropic and two anisotropic least-squares cycles reduced the unweighted *R* value to 0.107. This value was reduced to 0.102 by two cycles of anisotropic least squares with anomalous dispersion. At this point, a difference Fourier permitted the location of one hydrogen atom. Three additional least-squares cycles lowered *R* to 0.092. Two further cycles followed by a difference Fourier synthesis generated the position of the last hydrogen atom, and three additional least-squares cycles (anisotropic for all atoms except hydrogen) lowered the unweighted *R* factor to 0.091.

Difference Fourier maps were then generated for both the benzene and *o*-xylene adduct structures. Residual spheroidal-shaped electron density (max = 3.1 e/Å³) was found in the tunnel space, and this was attributed to the presence of benzene or *o*-xylene molecules. All attempts to further resolve this electron density failed. Introduction of a spherical electron density model⁵ to simulate a tumbling benzene or xylene molecule lowered the *R* factor slightly, but this effect was not considered to be significant because the residual density was not decreased evenly by this procedure.

Observed and calculated structure factors are shown in Tables I and II.¹³ Thermal parameters are given in Tables III and IV, and fractional crystal coordinates appear in Tables V and VI.

Results and Discussion

Selective Inclusion of Organic Molecules. In earlier work it was shown that compound I formed crystalline inclusion adducts with a wide variety of organic molecules.³ These ranged in size from tetralin and norbornadiene to carbon disulfide, acrylonitrile, or ethanol. The amount of guest component retained depended on the dimensions of the guest molecules, larger quantities being retained for the bulkier guest molecules. For example, the molar ratio of I varied from 0.59 for tetralin to 0.11 for ethanol. Furthermore, it was found that when I was allowed to interact with heptane–benzene, the noncyclic component was preferentially absorbed into the clathrate.³ It had also been shown that II formed clathrates with benzene or *o*-xylene during recrystallization from those solvents,⁵ and that III formed clathrates when recrystallized from *p*-xylene, toluene, cycloalkanes, alkanes, or alcohols.^{6,10}

In the present study an attempt was made to compare these three host systems with respect to their ability to selectively clathrate one component from a mixed solvent system. *n*-Hexadecane was chosen as the component common to all the mixed solvent systems. This choice was made to determine the ease with which a medium length hydrocarbon could penetrate the lattice during crystallization, especially in competition with smaller molecules. Unfortunately, the amounts of guest clathrated by III were too small to permit an accurate analysis of the clathration effectiveness of the different guests.

However, competition experiments were performed with the use of compounds I and II. Sublimed, unclathrated crystals of I were first allowed to stand in contact with the following solvent pairs: *n*-hexadecane-chloroform, *n*-hexadecane-*n*-heptane, and *n*-hexadecane-benzene. Mass spectrometric examination of the clathrates formed showed that chloroform, benzene, and smaller amounts of *n*-heptane were preferentially absorbed. Larger molecules, such as cyclohexane, isooctane, or decalin, were excluded from the lattice as was *n*-hexadecane, when *n*-hexadecane-cyclohexane, *n*-hexadecane-isooctane, or *n*-hexadecane-decalin mixtures were employed in a similar experiment. Thus, the clathration process discriminates against the larger guest molecules when *direct* guest absorption is possible.

The same solvent pairs were then examined in *recrystallization* experiments with compound I. Under these conditions, inclusion of guest molecules occurred with a broader range of guests. Benzene, chloroform, and *n*-heptane were included in substantial amounts (40–100 mol %). Cyclohexane, isooctane, and decalin were retained in smaller amounts (12–16 mol %), but in sufficient concentrations to stabilize the hexagonal crystal lattice. Small molecules, such as chloroform or benzene, promoted more ordered crystal growth, since these adducts yielded larger and more perfectly formed crystals. Moreover, the more efficient crystal growth that accompanied the inclusion of chloroform or benzene promoted the inclusion of *n*-hexadecane as well. Both of these adducts contained small amounts of *n*-hexadecane, whereas the other adducts did not.

Direct guest uptake from the same solvent pairs by compound II yielded clathrates with chloroform, benzene, cyclohexane, and *n*-heptane at 25 °C. Larger amounts of benzene or chloroform (100–200 mol %) were accommodated than with I, presumably because of the wider channel diameter.⁵ However, once again *n*-hexadecane was excluded from the lattice. Use of the recrystallization technique yielded adducts with benzene, chloroform, and *n*-heptane (50 to >200 mol %), and with inclusion of smaller amounts of cyclohexane, isooctane, or decalin. Again, *n*-hexadecane was clathrated only as a complementary guest when chloroform or benzene was also present. Vapor phase chromatography experiments indicated that the ratio of benzene to *n*-hexadecane was approximately 30:1.

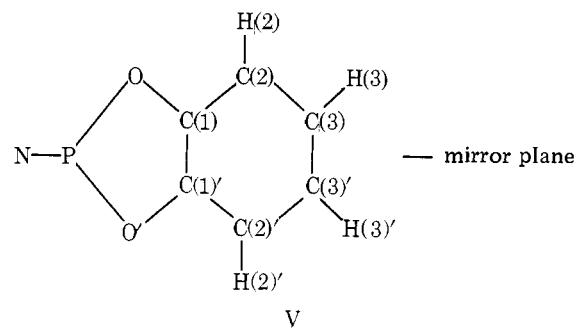
This suggests that long-chain molecules, such as *n*-hexadecane, can penetrate into or be trapped in a tunnel system that is already stabilized by smaller guest molecules, but that it cannot by itself initiate the growth of a hexagonal channel clathrate crystal system. The exclusion of *n*-hexadecane is certainly not due to an excessive extended molecular "diameter", since a clear cylindrical passage of about 4.5 and 10 Å diameter exists in crystals of I and II, respectively. However, coiling of the hexadecane chains would generate a pseudo-spherical unit with an effective diameter of at least 10–12 Å. Hence, it is inferred that the channels formed by I and II are too small to fully accommodate long-chain molecules except when an extended conformation is assumed by the guest.

Thermal Motion. X-Ray Diffraction Studies. The previously reported x-ray diffraction analysis of a *p*-xylene clathrate of III⁶ showed that the *p*-xylene molecules occupied fixed posi-

tions in the lattice at 25 °C. Only the methyl group hydrogen atoms showed evidence of extensive thermal motion. By contrast, an x-ray analysis of the benzene clathrate of II showed evidence of appreciable guest thermal motion at 25 °C.⁵ In fact, the structure was solved by the use of a model in which six tumbling benzene molecules occupied the channel space in one unit cell.

The crystal structures of benzene and bromobenzene adducts of I had been investigated earlier.⁴ However, the resolution was insufficient to define accurately the side group parameters or to identify the location of guest molecules in the lattice. In the present study, the crystal structures of the benzene and *o*-xylene adducts of I have been studied. The objective was to refine the structure to the point that the location and behavior of the guest molecules could be ascertained.

The present refinement of the benzene and *o*-xylene adducts of I in the space group $P6_3/m$ (rather than $P6_3$)⁴ resulted in significant improvements to the structure. The introduction of crystallographic mirror planes at $z = 1/4$ and $3/4$ requires the phosphazene ring to be situated on the mirror plane with the side units oriented perpendicular to the ring. The location of this plane and the atomic labeling scheme used are illustrated in V.



The arrangement of the host molecules in the two clathrates of I, and the location of the tunnels, are shown in Figure 1. Lists of the important bond angles and interatomic distances are given in Tables VIII and IX. The phosphazene ring parameters fall within the range expected for cyclotriphosphazenes.^{14,15} The narrow O–P–O angle of 97° reflects the restricting influence of the five-membered ring. The bond angles within the aryl rings are more reasonable than those reported previously.⁴

One of the main reasons for the reexamination of the crystal structure of I was the need to obtain more information about the disposition and molecular freedom of the guest molecules retained in the channels. After solution of the structure for the host framework, a series of difference Fourier maps was generated for both the benzene and *o*-xylene adducts. In both systems, electron density was located along the *c* axis within the tunnels. In both adducts the strongest residual density (3.1 e/Å³) was found in the center of the tunnel at position 0, 0, 1/2, with subsidiary density occupying a three-lobed area at $z = 1/4$ and $3/4$ (Figure 2). Attempts to rationalize this residual density in terms of the shapes of benzene and *o*-xylene molecules were unsatisfactory. Thus, the data indicate considerable molecular motion of the guest molecules at 25 °C, although the coalescence of electron density at specific sites in the cell suggests that some restriction exists to free translation *through* the tunnel system. As described in the following section, both benzene and *o*-xylene at 25 °C are well above the temperature at which restricted motion occurs, and this explains the close similarity of the residual electron density shapes in the two cases.

Thermal Motion. NMR Studies. X-ray diffraction cannot provide unambiguous evidence for thermal motions in clathrate structures. Such results can be explained also by static disorder of the guest molecules. For this reason variable temperature,

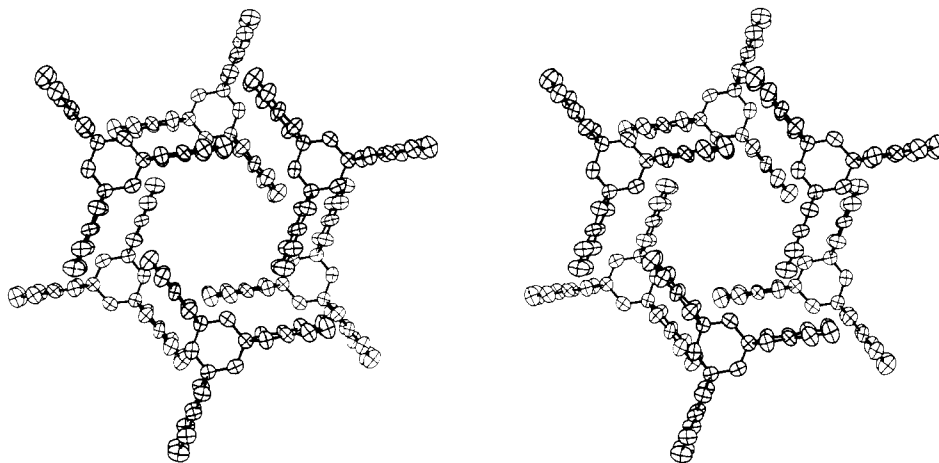


Figure 1. Stereoview showing the tunnels present in clathrate structures formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I) with benzene or *o*-xylene.

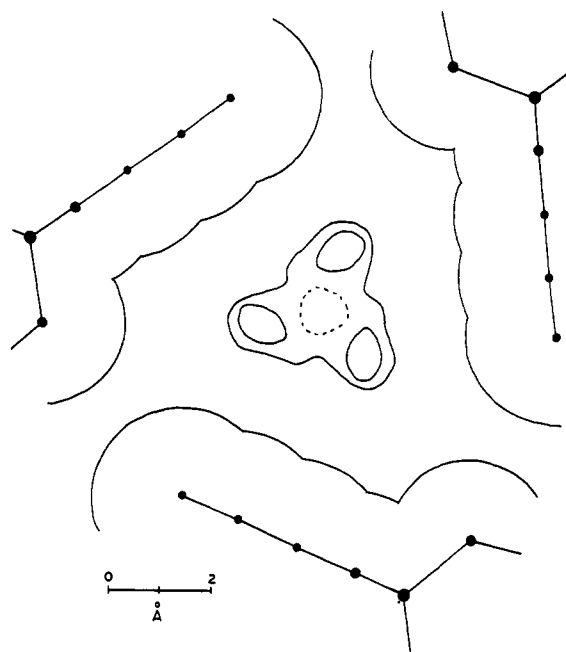


Figure 2. Residual electron density within the tunnel system of I, which represents the presence of tumbling benzene or *o*-xylene molecules.

broadline ^1H NMR experiments were performed on benzene, *p*-xylene, mesitylene, and 1,3,5-triethylbenzene recrystallization adducts of I, on the benzene and *p*-xylene adducts of II, and on the benzene and *p*-xylene adducts of III. Typical spectra are shown in Figures 3–5.

As might be expected, the NMR spectrum of solid, guest free I shows a broad, unresolved absorption that is typical of the efficient spin–spin relaxation processes found in solid species. However, even at $-55\text{ }^\circ\text{C}$, the spectrum of the benzene adduct of I showed a strong signal, 2000 Hz wide, from the clathrated benzene molecules. Comparisons with the spectrum of crystalline benzene revealed that the adduct spectrum was indicative of extensive benzene molecular motions not found in solid benzene itself. The signal persisted, virtually unchanged, as the temperature was raised to about $25\text{ }^\circ\text{C}$. At higher temperatures (Figure 3) the signal declined in intensity as benzene escaped from the crystal lattice.

The spectra obtained for the benzene adduct of II (Figure 4) illustrate dramatically that the guest molecular motions become restricted at temperatures below about $-40\text{ }^\circ\text{C}$. A *p*-xylene adduct of the same host showed restriction of guest mobility at temperatures below $+80\text{ }^\circ\text{C}$ with a more dramatic

Table VII. Temperatures at which Included Guests Undergo Extensive Molecular Motions in Adducts of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I), Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II), and Tris(1,8-naphthalenedioxy)cyclotriphosphazene (III)

Host	Included guest	Onset of guest molecular motion, $^\circ\text{C}$
I	Benzene	<-60
I	<i>p</i> -Xylene	-60
I	<i>o</i> -Xylene	-20
I	Mesitylene	0
I	1,3,5-Triethylbenzene	$+120$
II	Benzene	-40
II	<i>p</i> -Xylene	$+80$
III	Benzene	<i>a</i>
III	<i>p</i> -Xylene	<i>a</i>

^a Weak, diffuse proton NMR signals were seen over the entire temperature range. The spectra were virtually identical with that of the guest-free species.

Table VIII. Bond Lengths (\AA) and Bond Angles (deg) for the Benzene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I)

P–N	1.59 (2)	P–N–P	122 (1)
P–O	1.62 (1)	N–P–N	117 (1)
O–C(1)	1.39 (2)	N–P–O	110.5 (6)
C(1)–C(1')	1.43 (3)	O–P–O'	97.4 (8)
C(1)–C(2)	1.36 (2)	P–O–C(1)	110.2 (8)
C(2)–C(3)	1.39 (3)	O–C(1)–C(1')	111.1 (7)
C(3)–C(3')	1.45 (4)	O–C(1)–C(2)	127 (1)
C(2)–H(2)	1.0 (2)	C(1')–C(1)–C(2)	122 (1)
C(3)–H(3)	1.2 (2)	C(1)–C(2)–C(3)	117 (2)
		C(2)–C(3)–C(3')	121 (1)
		C(1)–C(2)–H(2)	110 (8)
		C(3)–C(2)–H(2)	133 (8)
		C(2)–C(3)–H(3)	111 (8)
		C(3')–C(3)–H(3)	127 (8)

change in the spectrum during the onset of molecular motion. The onset of guest thermal motion in the three different host systems is illustrated by the data in Table VII.

The following conclusions can be derived from these data. First, for the same guest molecule (e.g., benzene or *p*-xylene) in the three different host lattices, the onset of guest thermal motions occurs at progressively higher temperatures along the series of $\text{I} < \text{II} < \text{III}$. The diameters of the channels decrease in the order $\text{II} > \text{I} > \text{III}$, but more guest molecules can occupy

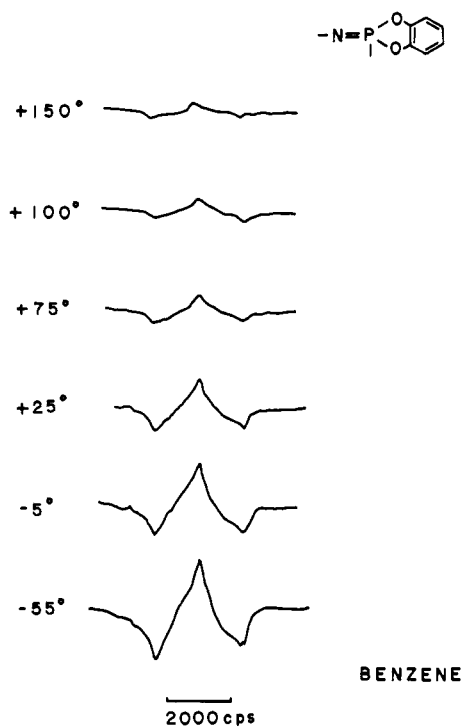


Figure 3. ^1H NMR spectra of a benzene adduct of tris(*o*-phenylenedioxy)cyclotriphosphazene (I).

Table IX. Bond Lengths (Å) and Bond Angles (deg) for the *o*-Xylene Adduct of Tris(*o*-phenylenedioxy)cyclotriphosphazene (I)

P-N	1.60 (3)	P-N-P	122 (2)
P-O	1.61 (2)	N-P-N	118 (2)
O-C(1)	1.37 (3)	N-P-O	110 (1)
C(1)-C(1')	1.40 (4)	O-P-O'	97 (1)
C(1)-C(2)	1.35 (4)	P-O-C(1)	110 (1)
C(2)-C(3)	1.38 (5)	O-C(1)-C(1')	112 (1)
C(3)-C(3')	1.41 (5)	O-C(1)-C(2)	127 (2)
C(2)-H(2)	0.9 (2)	C(1')-C(1)-C(2)	121 (1)
C(3)-H(3)	1.2 (3)	C(1)-C(2)-C(3)	118 (2)
		C(2)-C(3)-C(3')	121 (2)
		C(1)-C(2)-H(2)	106 (14)
		C(3)-C(2)-H(2)	135 (14)
		C(2)-C(3)-H(3)	118 (14)
		C(3')-C(3)-H(3)	119 (14)

the tunnel space in II, and guest-guest interactions probably lower the mobility in that system.

Second, for a given host lattice the onset of significant thermal motions takes place at progressively higher temperatures as the dimensions of the guest molecules are increased. For example, the increase in "transition" temperature seen in the series *p*-xylene < *o*-xylene < mesitylene < 1,3,5-triethylbenzene in I undoubtedly reflects the increasing restrictions to tumbling motions as additional alkyl groups are introduced into the guest. This is also obvious when the benzene clathrate of II is compared with the *p*-xylene clathrate (Table VII).

Comparison of the Three Crystal Systems. The differences between the clathration behavior of I, II, and III can be attributed to the different tunnel shapes and diameters. Certainly, the most restrictive tunnel system is generated by III,⁶ although these tunnels do not have the smallest cross-sectional area. The tunnels in III have a cross-sectional diameter (Figure 6) which varies from about 5.2 to 7.0 Å. It is perhaps surprising that this free space permits neither random tumbling motions of *p*-xylene molecules nor loss of the guest at ambient temperatures and pressures. Loss of *p*-xylene does not occur at atmospheric pressure until the temperature is raised to 223–242 °C.⁶ This high stability is attributed to the small di-

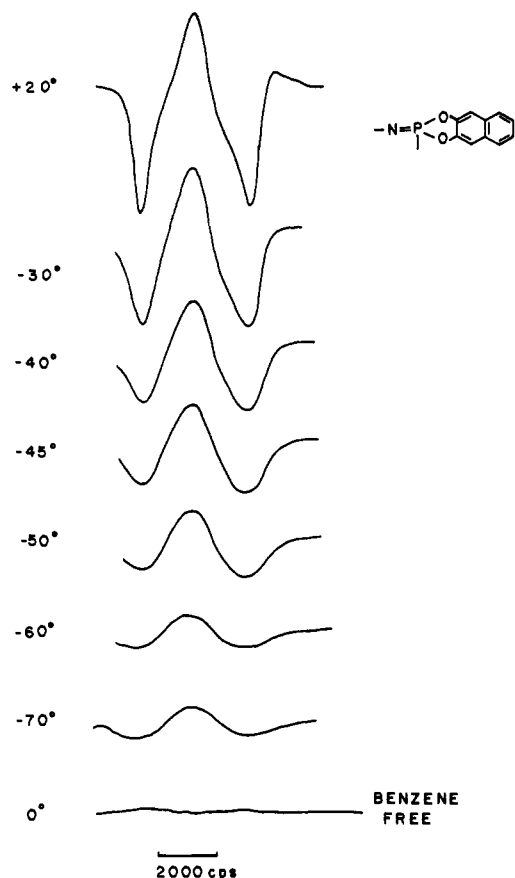


Figure 4. ^1H NMR spectra of a benzene adduct of tris(2,3-naphthalenedioxy)cyclotriphosphazene (II).

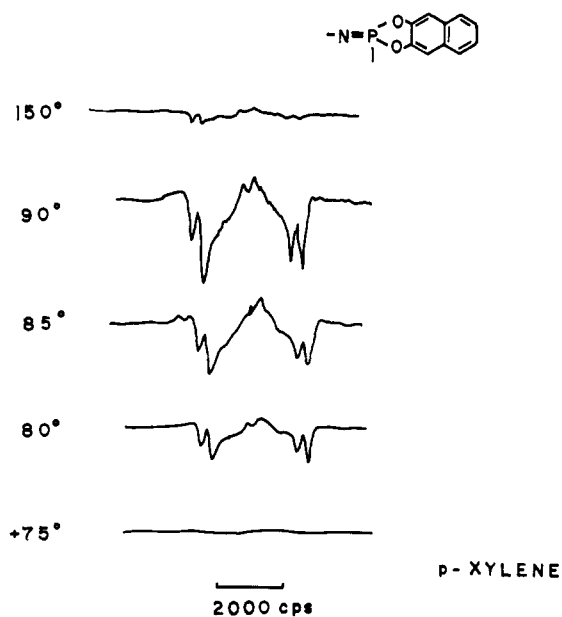


Figure 5. ^1H NMR spectra of a *p*-xylene adduct of tris(2,3-naphthalenedioxy)cyclotriphosphazene (II).

ameter of the *constrictions* in the tunnel and to strong host-host side group interactions that stabilize the structure even in the absence of guest. In fact, as shown in Figure 6, the lattice cavities in III are formed by an entirely different side group packing arrangement⁶ than these found in I and II.

By contrast, the tunnels formed by II are wider⁵ (~9–10 Å) (Figure 6) and the guest molecules can leave the lattice more easily. Benzene can be lost slowly at 25 °C (760 Torr). Differential thermal analyses showed that benzene escapes rapidly

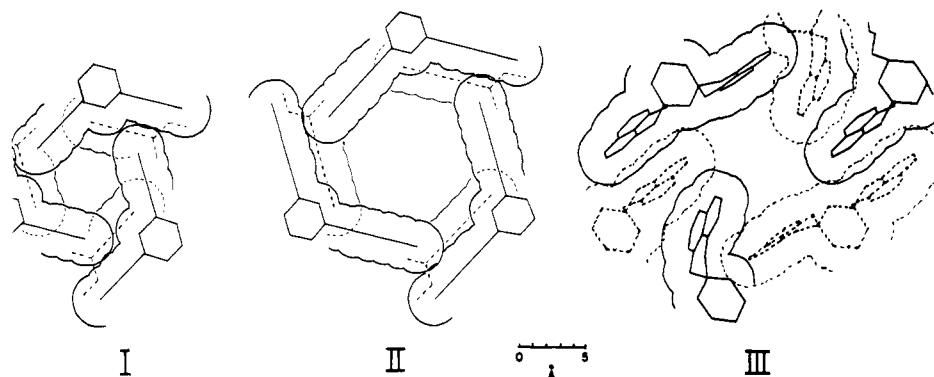


Figure 6. Comparison of the tunnel cross sections of tris(*o*-phenylenedioxy)cyclotriphosphazene (I), tris(2,3-naphthalenedioxy)cyclotriphosphazene (II), and tris(1,8-naphthalenedioxy)cyclotriphosphazene (III).

from the lattice at a temperature of 120–121 °C,⁵ and the variable temperature NMR work reported here indicates that *p*-xylene is lost between 100 and 120 °C.

The tunnel diameter in clathrates formed by I is approximately 5 Å. Thus, the tunnel diameter is actually smaller than in III, but the clathrates are, if anything, less stable than those formed by III. Guests, such as benzene and xylene, do not leave the tunnel system of I at 25 °C (760 Torr), but they can be removed slowly at temperatures above 75 °C. Guest molecules in the tunnels formed by I must be capable of broad translational movements since one guest can be replaced by another. Furthermore, the facile interconversion of the triclinic (unclathrated) and hexagonal (clathrated) forms of I undoubtedly facilitates both the release of guest molecules and their reabsorption.

The over-all evidence indicates that clathration in these three systems is a purely mechanical phenomenon, stabilized mainly by van der Waals forces. The binding between host and guest is usually sufficiently weak that the guest molecules can undergo extensive thermal motions within the tunnels. Only when the tunnels are constricted almost into a set of cavities (as in II), or when the guest dimensions are large (as in the adduct of I with triethylbenzene, or II with *p*-xylene), do the guest motions become restricted at ambient temperatures.

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Supplementary Material Available: Structure factors for benzene and *o*-xylene adducts of I, Tables I and II, respectively, and thermal parameters for benzene and *o*-xylene adducts of I, Tables III and IV, respectively (9 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) This paper is Part 26 in a series on phosphorus–nitrogen compounds.
- (2) Part XXV: H. R. Allcock and L. A. Smeitz, *J. Am. Chem. Soc.*, **98**, 4143 (1976).
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- (10) H. R. Allcock and E. J. Walsh, *Inorg. Chem.*, **10**, 1643 (1971).
- (11) Values measured at 25 °C using diffractometer settings for eight reflections centered on the K α peak of Cu radiation by a least-squares refinement.
- (12) Film measurements obtained with the use of Cu K α radiation.
- (13) Tables I to IV will appear in the microfilm edition. See the statement regarding Supplementary Material.
- (14) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972, Appendix I.
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A Preliminary Report of the Coordination of Lanthanum(III) in Lanthanum Chloride–Methanol Solutions¹

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Abstract: Methanolic solutions of LaCl₃ were studied by x-ray diffraction and by ¹³⁹La and ³⁵Cl NMR. An average inner coordination sphere species LaCl₃(CH₃OH)₅ is found with La–O and La–Cl distances of 2.48 and 2.95 Å, respectively. Long range interactions in the ARDF were used to propose a dichloro-bridge model, [LaCl₂(CH₃OH)₅]₂, for the average solute species.

In an earlier paper,² we identified octaquo-lanthanum(III) as the average coordination species in concentrated aqueous LaCl₃ solutions, both with and without added hydrochloric acid. La(H₂O)₈³⁺ has approximately cubic symmetry with an

inner-sphere La–O distance of ca. 2.48 Å. In the atomic radial distribution functions (ARDF) of these solutions, the ion-paired La...Cl interactions are easily identified at 4.7 Å. Brady³ reports the ion-paired Er...Cl distance to be 4.6 Å in aqueous