

# Clathration by Tris(2,3-naphthalenedioxy)cyclotriphosphazene. An X-Ray Crystal and Molecular Structure Study<sup>1</sup>

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**Abstract:** Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II) forms channel inclusion adducts with a number of organic molecules. An X-ray single-crystal study of a benzene adduct has shown that at 23° the benzene molecules are disordered and are probably tumbling within the channels, with six benzene molecules being close packed in the channel space within each unit cell. The unit cell is hexagonal, with space group  $P6_3/m$ , and with  $a = 15.726$  (8) Å,  $c = 10.076$  (6) Å, and  $Z =$  two host and six benzene molecules. The structure was solved by Patterson, Fourier, and difference syntheses, and refinement to an  $R$  index of 0.10 was accomplished by difference-Fourier and least-squares techniques. The mean bond distances and angles within the spirophosphazene molecule are P-N = 1.56 (2) Å, P-O = 1.61 (1) Å, N-P-N = 116 (1)°, P-N-P = 124 (1)°, N-P-O = 111 (1)°, and O-P-O = 96 (1)°. The phosphazene ring is planar with the phenylenedioxyphosphole unit lying in a plane that bisects the N-P-N angle. However, the naphthalene unit is bent 2.5° at the bond which joins the two phenyl residues.

The unusual clathration behavior of tris(*o*-phenylenedioxy)cyclotriphosphazene (I) has been described in an earlier paper.<sup>2</sup> Compound I crystallizes from solution to yield hexagonal crystals which contain solvent molecules retained in channels. Clathration of organic molecules from the vapor phase also occurs with I, and the inclusion phenomenon can be used to effect a subtle separation of closely related guest molecules.<sup>2</sup> A single-crystal X-ray structure investigation of I has also been published.<sup>3</sup>

In the course of further synthetic studies, several other spirocyclophosphazenes were shown to yield inclusion adducts when crystallized from organic media.<sup>4,5</sup> Among these are tris(2,3-naphthalenedioxy)cyclotriphosphazene (II) and tris(1,8-naphthalenedioxy)cyclotriphosphazene (III).

In view of the potential importance of the clathration phenomenon in hydrocarbon separation processes, and the current fundamental interest in the behavior of molecules trapped in a crystal lattice, the X-ray crystal structures of II and III have been studied. The investigation of compound II is described here, and the structure of a clathrate formed by III will be described in a later paper.

## Experimental Section

**Preparation of Crystals.** Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II) was prepared from hexachlorocyclotriphosphazene and 2,3-dihydroxynaphthalene by the method described previously.<sup>4</sup>

Crystals of II were first grown from *o*-xylene (Aldrich) because xylene adducts had been found previously to be more stable than benzene adducts.<sup>4</sup> However, single-crystal X-ray analysis of crystals grown from xylene showed that they were twinned. Adducts were grown thereafter from benzene (Fisher Spectroanalyzed). Crystals grown rapidly (during ~8 hr), powdered and lost benzene during several days when subsequently exposed to the atmosphere at 25°. Loss of the guest was retarded in an atmosphere that contained benzene vapor. After the data collection was completed, it

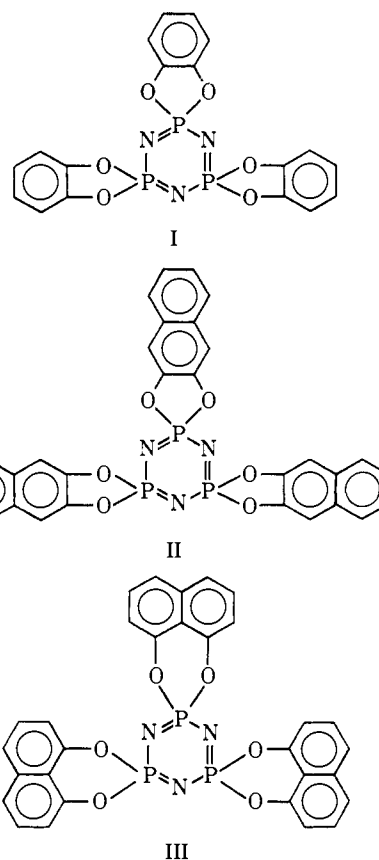
(1) This paper is Part XVII in a series on phosphorus-nitrogen compounds. Part XVI by H. R. Allcock, E. C. Bissell, and E. T. Shawl, *Inorg. Chem.*, **12**, 2963 (1973).

(2) H. R. Allcock and L. A. Siegel, *J. Amer. Chem. Soc.*, **86**, 5140 (1964).

(3) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967).

(4) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).

(5) H. R. Allcock and E. J. Walsh, *Inorg. Chem.*, **10**, 1643 (1971).



was found that crystals grown much more slowly were stable for weeks in the absence of solvent. Benzene could be removed from the adduct crystals at 65° and 25 mm, regardless of the initial crystal growth rate. At atmospheric pressure the visible loss of benzene occurred at temperatures between 101 and 108°.

Thermogravimetric analysis of several different batches of crystals indicated that the ratio of host to guest ranged from 1:2 to 1:3.5, with most samples having ratios close to 1:3. Density measurements also indicated a ratio of one host to three guest molecules.

**Crystal Data.** The unit cell is hexagonal with  $a = 15.726$  (8) Å,  $c = 10.076$  (6) Å (measured by least-squares refinement of 12 reflections centered on the automated diffractometer),  $V = 2158.0$  Å<sup>3</sup>,  $d_{\text{meas}} = 1.28\text{--}1.29$  g cm<sup>-3</sup> (by flotation in *n*-heptane-carbon tetrachloride mixtures),  $Z =$  two host molecules and six benzene molecules,  $d_{\text{calcd}} = 1.30$  g cm<sup>-3</sup>, mol wt = 2(609.3) + 6(78.1), and  $\mu(\text{Cu K}\alpha) = 17.8$  cm<sup>-1</sup>. The space group is  $P6_3/m$  ( $C^{2h}_{6h}$ , no. 176).

**X-Ray Data Collection and Reduction.** A crystal of II with dimensions  $0.12 \times 0.18 \times 0.12$  mm was mounted on a eucentric goniometer head and placed on a Syntex four-circle, computer-controlled diffractometer. Nickel-filtered Cu X-radiation (1.54178 Å) was used for data collection in the  $\theta$ - $2\theta$  scan mode.

The crystals presented special problems during data collection because of their instability in the air. The method finally chosen for data collection utilized a local atmosphere of benzene vapor maintained around the crystal within a glass cabinet that surrounded the diffractometer. A scan width of  $2.25^\circ$  ( $2\theta$ ) and a 10-sec background count were used. The intensity of the check reflection (500) fluctuated only  $\pm 2\%$ . The scan rate was  $2^\circ/\text{min}$ , and 499 of the 760 unique, mechanically available reflections had net intensities greater than  $3\sigma(I)$ . The integrated intensity ( $I$ ) and  $\sigma(I)$ , was calculated by the standard method described previously,<sup>6</sup> where Lorentz and polarization corrections, and the resultant  $F_o$  values were used in the refinement. Careful investigation at lower source power demonstrated that none of the reflections had saturated the counting system. Since the linear absorption coefficient,  $\mu$ , was relatively small, and rotation of the crystals around the  $\phi$  axis at  $\chi = 90^\circ$  showed little variation in reflection intensity, no absorption corrections were made to the data. An agreement factor, defined as  $R_{\text{min}} \equiv \sum_i |F_i - \langle F_i \rangle| / \sum F_i$ , had a value of  $R_{\text{min}} = 0.062$ , where the index runs over all multiply determined reflections and  $\langle F_i \rangle$  is the mean value for the corresponding data point.

**Solution and Refinement of the Structure.** The Laue group  $6/m$  and the systematic absences for the X-ray data of the benzene adduct of II, which are  $000l:l = 2n + 1$ , suggest that the hexagonal space group is  $P6_3$  or  $P6_3/m$ . In  $P6_3$ , the centers of the two molecules would fall in one of the special positions  $a$  or  $b$  of threefold symmetry:  $x = 0, y = 0, z$  and  $x = 0, y = 0, z + 1/2$  or  $x = 1/3, y = 2/3, z$  and  $x = 2/3, y = 1/3, z = 1/2$ . In  $P6_3/m$ , the two molecules in the unit cell must occupy special positions  $a, c$ , or  $d$  of symmetry  $\bar{6}$ . The molecule would contain mirror symmetry as well as threefold symmetry in  $P6_3/m$ .

Examination of the Patterson synthesis, particularly the peaks in the Harker section at  $w = 1/2$ , enabled assignment of the positions of the phosphazene ring centers. The observed pattern consisted of large peaks at  $u = 1/3, v = 2/3$  and  $u = 2/3, v = 1/3$  which were surrounded by a triangle of smaller peaks. This pattern was produced by intermolecular vectors between phosphorus atoms of the cyclotriphosphazene rings at  $x = 1/3, y = 2/3, z$  and  $x = 2/3, y = 1/3, z + 1/2$ . In parallel refinements in the space groups  $P6_3$  and  $P6_3/m$ ,  $z$  was arbitrarily chosen as 0 and  $1/4$ , respectively. One-third of a molecule (14 atoms excluding hydrogen atoms) constituted the asymmetric unit in  $P6_3$  and one-sixth of a molecule (eight atoms excluding hydrogen atoms) in  $P6_3/m$ .

The  $R$  factor was 57% after the initial cycle of least-squares refinement in  $P6_3$  phased on phosphorus and nitrogen atoms, the positions of which were deduced from the Harker section at  $w = 1/2$ . A difference synthesis revealed the locations of the oxygen atoms. After additional cycles of least-squares followed by difference syntheses, all the naphthyl carbon atoms were found. In space group  $P6_3$ ,  $R$  decreased to 19% for this model, which had completely isotropic thermal parameters. The inclusion of anisotropic vibration for the phosphorus, nitrogen, and oxygen atoms reduced  $R$  to 13.9% in  $P6_3$  and 15.2% in  $P6_3/m$ . Least-squares refinement with anisotropic temperature factors for carbon atoms lowered  $R$  only to 13.5 and 14.7%, respectively. Hamilton's criterion<sup>7</sup> for the significance of a change in  $R$  indicated that this lowering was insignificant. In subsequent refinement the carbon atoms were assumed to be vibrating isotropically. At this point, Hamilton's significance test was applied to the  $R$  factors for the two space groups  $P6_3$  and  $P6_3/m$ . It showed that the  $R$  factors were the same at the 10–25% confidence level. The space group  $P6_3/m$  is preferred because it requires fewer parameters.

With the host molecule refined to convergence in  $P6_3/m$  ( $R = 14.7\%$ ), a difference synthesis revealed an approximately spherical residual of electron density, 3 Å in radius, within the channels of the crystal. The elongated peaks surrounding the center of this sphere, which was located at (0.26, 0.07, 0.25) on the mirror plane, had a density of about  $3 e/\text{Å}^3$ . However, these peaks could not be accounted for by a rigid-body benzene molecule in discrete orientations or by a statistically disordered benzene model. Each of these calculations led to  $R$  factors greater than 15%.

Introduction of a spherically symmetrical benzene model, *i.e.*, with free rotation of the benzene molecule about its center, improved the model significantly.  $R$  dropped to 10.7% after several cycles of refinement. The scattering factor  $f'$  for a spherically symmetrical distribution of carbon and hydrogen atoms was calculated from the equation

$$f' = 6f_c \frac{\sin \phi_c}{\phi_c} + 6f_H \frac{\sin \phi_H}{\phi_H}$$

where  $f_c$  and  $f_H$  are the normal scattering curves at various values of  $\sin \theta/\lambda$  and  $\phi_c$  and  $\phi_H$  are  $4\pi r \sin \theta/\lambda$ .<sup>8</sup> The constant  $r$  is 1.4 Å for carbon and 2.4 Å for hydrogen. For a temperature factor of  $B = 0$ , the value of  $f'$  decreases rapidly to zero at  $\sin \theta/\lambda = 0.18$  and oscillates around zero several times. A similar profile was found when a value of  $B$  of 18.6 was employed. The value of  $f'$  is affected very little by such a large temperature factor presumably because the electron density distribution is already diffuse.

Because the occupancy factor and the temperature parameter were strongly correlated (0.8), each of these was refined successively. The value converged to approximately 0.5 and 18.6, respectively. A difference synthesis revealed three naphthyl hydrogen atoms and refinement with these parameters included converged to  $R = 10.0\%$  and  $R_w = 11.2\%$ . The largest shift in the last cycle was  $0.5\sigma$ .  $R_w$  is  $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ . Observed and calculated structure factors appear in Table I.<sup>9</sup> Atomic and thermal parameters are reported in Table II.

**Table II.** Atomic Parameters in Fractional Coordinates and Thermal Parameters<sup>a</sup> for Tris(2,3-naphthalenedioxy)cyclotriphosphazene, Benzene Adduct

Atom	X	Y	Z	EQB		
P(1)	0.5828 (4)	0.3615 (4)	0.2500 (0)	3.6 (2)		
N(2)	0.6940 (11)	0.4415 (11)	0.2500 (0)	3.9 (6)		
O(1)	0.5257 (6)	0.3811 (6)	0.3684 (8)	4.3 (4)		
C(3)	0.4586 (9)	0.4031 (8)	0.3204 (11)	3.6 (3)		
C(4)	0.3964 (9)	0.4229 (8)	0.3924 (13)	3.8 (3)		
C(5)	0.2700 (9)	0.4709 (9)	0.3894 (14)	4.7 (3)		
C(6)	0.2096 (10)	0.4956 (10)	0.3213 (14)	6.1 (3)		
C(10)	0.3330 (8)	0.4451 (8)	0.3208 (12)	3.9 (3)		
BENZ	0.2278 (20)	0.0667 (22)	0.2500 (0)	18.6 (16)		
H(4)	0.3971	0.4265	0.5012	5.6		
H(5)	0.2680	0.4775	0.4977	6.4		
H(6)	0.1533	0.5138	0.3547	8.2		
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P(1)	47 (4)	55 (4)	37 (3)	27 (4)		
N(2)	52 (11)	59 (11)	48 (10)	35 (10)		
O(1)	69 (8)	87 (7)	30 (5)	56 (6)	0 (5)	-1 (5)

<sup>a</sup> Mean square amplitudes of vibration ( $U$ )  $\times 10^3$  and equivalent isotropic B (EQB).

The weighting scheme used in the refinement of this crystal structure was as follows. Unit weights were initially applied to the data. When all atoms had been located, a step function based on  $\sigma(F_o)/F_o$  was employed to weight the reflections. For a weak reflection, which had  $\sigma(F_o)/F_o$  greater than 0.2,  $\sigma$  was 1.2 ( $w = 1/\sigma^2$ ). Strong reflections, which had  $\sigma(F_o)/F_o$  less than 0.05, were assigned a  $\sigma$  of 1.1. Those reflections for which  $\sigma(F_o)/F_o$  fell between 0.20 and 0.05 were given unit weights.

One reflection, 100, was not included in the refinement, because it was very close to the low  $\sin \theta/\lambda$  limit of the diffractometer and the lower background count had been cut off.

**Computer Programs.** Unit cell parameters were obtained from the least-squares program UCLS, supplied by A. Christensen of Syntex Analytical Instruments. FORFAP, which was used to calculate Patterson, Fourier, and difference Fourier syntheses, was adapted from Zalkin's Fourier program, as modified by Hamilton and Ibers at Brookhaven National Laboratory. The structure factor calculations and least-squares structural refinement were performed with the program SFLS-5. It was written originally by

(6) H. R. Allcock, M. T. Stein, and J. A. Stanko, *J. Amer. Chem. Soc.*, **93**, 3173 (1971).

(7) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(8) R. W. James, "The Crystalline State," Vol. II, G. Bell and Sons, London, 1950, p 231.

(9) See paragraph at end of paper regarding supplementary material.

C. T. Prewitt but was modified to include a simple rigid body routine by M. J. Bennett and B. Foxman, at Massachusetts Institute of Technology. Least-squares plane and  $\chi^2$  plane calculations were performed by the program MEAN PLANE (NRC-22), written by M. E. Pippy and F. R. Ahmed of the Canadian National Research Council in Ottawa. This program was modified to enable calculation of the angles between the least-squares planes.

The program, HFINDR, which enabled calculation of the atomic parameters for the phenyl hydrogen atoms, was written and modified by D. Johnston at The Pennsylvania State University. The program DISTAN was also modified by Dr. Johnston for our system. This program was used for distance and angle calculations. All calculations were performed with an IBM 360/67 computer.

## Results and Discussion

**General Structural Features.** The crystal structure of II resembles the structure of tris(*o*-phenylenedioxy)cyclotriphosphazene (I). However, there are noteworthy differences between the two, and these are discussed below.

The unit cell arrangement of the host and guest molecules in the benzene adduct of II is illustrated in Figure 1 and a summary of bond angles and lengths for this compound is given in Table III. The labeling of the

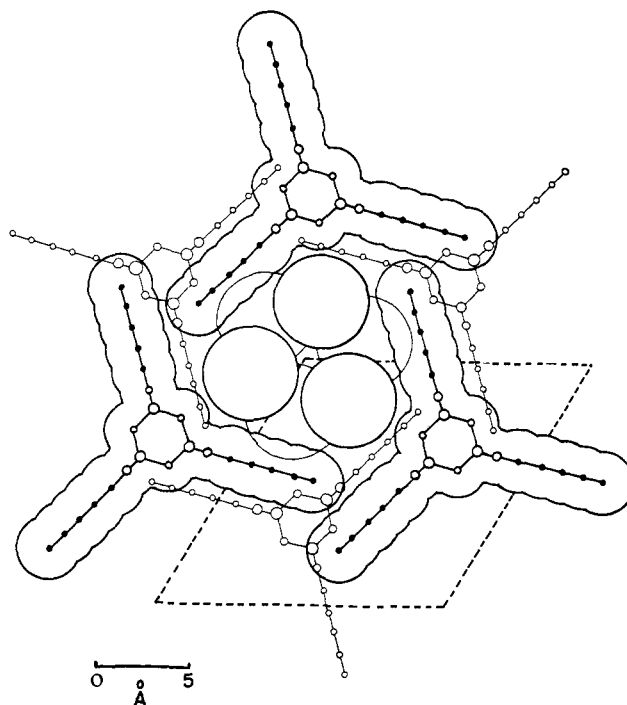


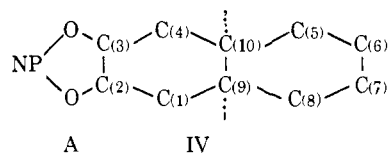
Figure 1. Unit cell arrangement and van der Waals boundaries for the benzene adduct of tris(2,3-naphthalenedioxy)cyclotriphosphazene (II). Also shown are the locations of the benzene electron density "spheres."

Table III. Bond Lengths (Å) and Bond Angles (deg) for Tris(2,3-naphthalenedioxy)cyclotriphosphazene (II)<sup>a</sup>

P-N	1.562 (16)	C(5)-C(10)	1.42 (2)
P'-N	1.558 (16)	C(5)-C(6)	1.38 (2)
P-O	1.613 (9)	C(6)-C(7)	1.44 (3)
O-C(3)	1.354 (15)	C(9)-C(10)	1.43 (2)
C(2)-C(3)	1.42 (2)	C(4)-H(4)	1.10 (2)
C(3)-C(4)	1.37 (2)	C(5)-H(5)	1.10 (2)
C(4)-C(10)	1.41 (2)	C(6)-H(6)	1.11 (2)
P-N-P	123.7 (11)	C(2)-C(3)-C(4)	121.9 (8)
N-P-N	116.3 (11)	C(3)-C(4)-C(10)	117.1 (13)
N-P-O	110.6 (5)	C(10)-C(5)-C(6)	120.8 (14)
	110.9 (5)		
O-P-O	95.5 (7)	C(5)-C(6)-C(7)	120.0 (9)
P-O-C(3)	111.4 (7)	C(4)-C(10)-C(9)	121.0 (8)
O-C(3)-C(2)	110.8 (6)	C(5)-C(10)-C(9)	119.1 (8)
O-C(3)-C(4)	127.3 (11)	C(4)-C(10)-C(5)	119.8 (12)

<sup>a</sup> Standard deviations in parentheses refer to the least significant figures.

atoms in each substituent group unit is illustrated in structure IV.



In clathrates formed by both I and II the host molecules are both located at the threefold equipoint in the cell at  $1/3, 2/3, z$  and  $2/3, 1/3, z + 1/2$ . The analogous bond lengths and angles in the two structures are equal within two standard deviations.

The bond lengths and bond angles for II (Table III) are similar to the values for other cyclotriphosphazenes with the exception of the O-P-O angle, the N-P-N angle, and the P-N-P angle. An X-P-X angle is normally close to  $102^\circ$  in cyclotriphosphazenes but it is  $96^\circ$  in II. This small O-P-O angle is characteristic of cyclic phosphates with strained five-membered rings such as methylethylene phosphate ( $99^\circ$ )<sup>10</sup> and (*o*-phenyl-

enedioxy)chlorophosphine ( $99^\circ$ ).<sup>11</sup> It should be noted that, before the benzene "molecule" was added to the structure, the P-N-P angle was  $121(2)^\circ$  and the N-P-N angle was  $119(2)^\circ$ . Afterwards, the angles were  $124(1)$  and  $116(1)^\circ$ , respectively.

The bond angles inside and adjacent to the five-membered ring in compound II suggest that this ring is quite strained. Within the ring, the P-O-C(3) angle [ $111.4(7)^\circ$ ] is close to the  $109.5^\circ$  angle expected at the oxygen atom, but the O-C(3)-C(2) angle [ $110.8(6)^\circ$ ] is appreciably distorted from the trigonal angle of  $120^\circ$  for carbon. In response to the angular distortion, the other angles at this site assume values of  $127.3(11)^\circ$  [O-C(3)-C(4)] and  $121.9(8)^\circ$  [C(2)-C(3)-C(4)]. A similar pattern is found in I and in the tris(*o*-phenylenedioxy)phosphate anion.<sup>12</sup> The values for these two structures are respectively: P-O-C(3)  $110^\circ, 111.3^\circ$ ; O-C(3)-C(2)  $112^\circ, 113.0^\circ$ ; O-C(3)-C(4)  $123^\circ, 125.4^\circ$ ; C(2)-C(3)-C(4)  $125^\circ, 121.5^\circ$ .

**Planarity of the Phosphazene Ring and Exocyclic Rings.** The phosphazene ring in II is perfectly planar, since both phosphorus and nitrogen lie on the mirror plane. Also the plane of the phenylenedioxyphosphole unit (A in structure IV) is oriented exactly at  $90^\circ$  to the phosphazene ring plane. However, the naphthalene residue in II is not planar. This peculiar nonplanarity appears to result from a  $2.5^\circ$  bend in the naphthalene group at C(10) and C(9) (at the vertical dotted line in structure IV).  $\chi^2$  for the whole ring is 24.6 but, for the two phenyl rings, it is 0.5 and 0.01. The phenyl ring farthest from the central phosphazene ring bends away from the channel and toward the adjacent host molecule

(11) B. A. Arbuzov, V. A. Naumov, S. A. Shaidulin, and E. T. Mukmenev, *Dokl. Akad. Nauk SSSR*, **204** (4), 859 (1972).

(12) H. R. Allcock and E. C. Bissell, *J. Amer. Chem. Soc.*, **95**, 3154 (1973).

(10) T. A. Steitz and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **87**, 2488 (1965).

which lies above or below it. Thus, both the nitrogen atom adjacent to the channel and the terminal phenyl ring appear to be displaced away from the channel. This bend persists in the host structure even when no benzene is included in the model. Thus, the bend probably reflects a real avoidance of close contacts between the side group units and the molecules in the channel rather than inaccuracies in the guest model.

**The Channels.** The channels found in the clathrate formed by II have a minimum diameter in the range of 9–10 Å. Six benzene “spheres” per unit cell are close packed in the wider segments of each channel (Figure 1). Thus, the channels in this structure are considerably wider than those found in the corresponding clathrate formed by I. In the latter structure the minimum channel diameter is less than 5 Å with only one benzene molecule statistically occupying the channel volume within each unit cell.

Examination of the van der Waals boundaries of II indicates that the *intermolecular* side group–side group contacts between adjacent molecules along *c* constitute a surprisingly efficient packing arrangement. This may perhaps provide an explanation for the fact that II can persist in the hexagonal crystalline arrangement even after most of the benzene has escaped from the channels.

**Stability of the Inclusion Adducts.** The benzene clathrate of I is stable at 25° whereas the benzene clathrate of II (prepared by rapid crystallization) breaks down during several days at this temperature. However, xylene clathrates of II show considerably greater stability than the benzene adduct. Thus, the ease with which the guest molecule can escape from the lattice has a marked influence on the stability of the inclusion adduct.

The difference between the stabilities of the benzene adducts of I and II was verified by a differential thermal analysis study.<sup>13</sup> With I, loss of benzene occurred at 218° (peak range = 200–221°) with a positive  $\Delta H$  value. Melting of the host in I subsequently occurred at 244–245°. With II, benzene was released sharply at 120–121°, with a positive  $\Delta H$  change, and melting of the host took place at 334–335°.

The stability differences between the benzene clathrates of I and II almost certainly reflect the different channel diameters in the two structures. Since benzene molecules apparently can tumble within the channels formed by II, they can presumably escape from these channels more readily than from the narrower channels formed by I.

In both compounds, it seems clear that the guest molecules “cushion” the packing of the “paddle-wheel” shaped host molecules and reduce the free volume within

(13) The DTA experiments were conducted with a du Pont Model 900 thermal analyzer fitted with a standard DTA cell and with the use of glass beads as a reference material. The heating rates were 20°/min. Several runs were made with each clathrate.

the crystal. Total loss of the guest causes a breakdown of the hexagonal crystal structure in both structures.

**Motions of the Guest Molecules.** As discussed earlier, models based on fixed orientations of the guest molecules within the channel failed to refine satisfactorily. These models included those with identical orientation of the benzene molecules in all unit cells and those with different orientations in different unit cells but with retention of the threefold symmetry requirement of the space group. The latter situation could possibly mimic a model in which active tumbling of the benzene molecules occurred. As described earlier, the structure could be refined to an acceptable *R* value only by the introduction of a spherical electron density cloud in the place of each benzene.

The question remaining is whether the benzene molecules do, in fact, undergo tumbling motions at room temperature or if this interpretation is an artifact of the X-ray refinement. Nmr proton spectra were, therefore, obtained for the pure host material, for the powdered benzene clathrate, and for benzene over the temperature range of –60 to +80°. The pure host crystals gave a very broad spectrum which was virtually indistinguishable from the background. The benzene clathrate showed a weak singlet at temperatures below –45° which was indicative of restricted molecular motions of the benzene molecules. However, above –40° the spectrum expanded to a strong singlet, ~2000 Hz wide, which was compatible with considerable molecular motion. A comparison with the spectrum of solid benzene indicated that the motions in the clathrate were far more extensive than the coordinated molecular reorientation about the sixfold axes found in crystalline benzene.<sup>15</sup> The space restrictions within the channels favor the view that the tumbling motions of the benzene molecules are probably highly correlated.

**Acknowledgment.** We thank Dr. E. C. Bissell for assistance with the structure solution. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-49.

(14) The nmr experiments were conducted with the use of a Varian HA 100 spectrometer. A detailed account of the molecular motions of guest molecules trapped in this and related host lattices will be published subsequently.

(15) E. R. Andrew and R. G. Eades, *Proc. Roy. Soc., Ser. A*, **218**, 553 (1953).