

pressure transducer. The apparatus and procedure have been described previously,<sup>18</sup> with the exception that all the valves exposed to the F<sub>2</sub>-PFCB mixtures being added to the reactor were changed. The valves initially used had Kd-F sealing seats which became charred and appeared to frequently initiate reaction explosions in many of the early experiments. The explosions were avoided by using only valves having metal-metal sealing surfaces, *i.e.*, eliminating all polymeric material from the manifold used to add the F<sub>2</sub>-PFCB mixtures.

Passivating the Monel bulb surface proved to be quite difficult. Even after being treated several times with fluorine, the most severe treatment being 800 mm of fluorine at 425° for 2 days, the surface appeared to cause a heterogeneous contribution to the observed reaction velocities at the lower temperatures used. The cause of the assumed heterogeneous contribution to the reaction was never isolated. However, the divergence at lower temperatures from the

(18) J. B. Levy and R. C. Kennedy, *J. Amer. Chem. Soc.*, **94**, 3302 (1972).

straight line Arrhenius plot in Figure 1 steadily decreased with repeated experiments, until the limiting values reported were reproducible. The lack of heterogeneous reaction in the reported results is supported by obtaining comparable results in a Monel tubular reactor ( $A/V = 8.7 \text{ cm}^{-1}$ ) to those in the bulb reactor ( $A/V = 0.6 \text{ cm}^{-1}$ ). Data taken in both reactors are indicated in Figure 1.

Perfluorocyclobutane "Freon C-318" (99.99%) and fluorine (98.0%) were purchased from Matheson Gas Products. Quantities of CF<sub>4</sub>, CF<sub>3</sub>OF, C<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, *n*-C<sub>4</sub>F<sub>10</sub>, and *c*-C<sub>4</sub>F<sub>12</sub> were purchased from Peninsular ChemResearch, Inc. All of the gases were used as received.

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## A *p*-Xylene Clathrate of Tris(1,8-naphthalenedioxy)cyclotriphosphazene. X-Ray Crystal and Molecular Structure<sup>1,2</sup>

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**Abstract:** Tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) forms a clathrate inclusion adduct with *p*-xylene. An X-ray single-crystal study has shown that the *p*-xylene molecules are physically trapped in a fixed position within channels that penetrate the lattice. The naphthalenedioxy side groups of the host molecules (III) are bent at the oxygen atoms in such a way that strong host-host interactions stabilize the channel structure. The unit cell is triclinic, with space group  $P\bar{1}$  and with  $a = 8.206 (17) \text{ \AA}$ ,  $b = 14.747 (25) \text{ \AA}$ ,  $c = 13.318 (23) \text{ \AA}$ ,  $\alpha = 101.97 (7)^\circ$ ,  $\beta = 90.77 (7)^\circ$ ,  $\gamma = 109.13 (5)^\circ$ , and  $Z =$  two host molecules and one *p*-xylene. The structure was solved by symbolic addition methods, and refinement to an  $R$  index of 0.058 was accomplished by Fourier and least-squares techniques. The important mean bond angles and distances within the host molecules are P-N = 1.57 Å, P-O = 1.59 Å, N-P-N = 117.9°, P-N-P = 122.1°, N-P-O = 106.7–110.9°, and O-P-O = 102.2°. The phosphazene ring is puckered in a boat conformation.

We have earlier drawn attention to the unusual crystalline inclusion adducts that are formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I)<sup>3,4</sup> or tris(2,3-naphthalenedioxy)cyclotriphosphazene (II)<sup>2,5</sup> with organic molecules. In particular it has been shown that the channel inclusion adducts formed by I or II with benzene contain benzene molecules that are free to translate or tumble in the channels. This paper describes a different clathrate arrangement formed between tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) and *p*-xylene.

### Experimental Section

**Preparation of Crystals.** Tris(1,8-naphthalenedioxy)cyclotriphosphazene (III) was prepared by the reaction of hexachlorocyclotriphosphazene with 1,8-naphthalenediol as described previously.<sup>6</sup>

(1) This paper is Part XVIII in a series on phosphorus-nitrogen compounds.

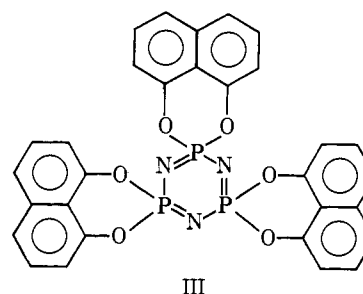
(2) Part XVII: H. R. Allcock and M. T. Stein, *J. Amer. Chem. Soc.*, **96**, 49 (1974).

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

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

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

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



III

Crystals of III can be grown from a variety of solvents (alcohols, alkanes, cycloalkanes, aromatic compounds), but the crystals for this X-ray study were obtained from *p*-xylene (Fisher, histological grade), which had been dried previously over calcium hydride. The adduct of III with *p*-xylene was stable at room temperature for at least 1 year, but it released *p*-xylene at about 210°. The crystals melted at 360°. *p*-Xylene could also be removed from the adduct at 100–130° (25 mm) to yield a form of III which gave a Debye-Scherrer pattern different from that of the adduct. Subsequent recrystallization from *p*-xylene regenerated the original adduct. Crystals grown from toluene and other solvents produced powder patterns similar to those of the *p*-xylene adduct, and the morphology and color (light orange) were also similar. Thus, it appears likely that the *p*-xylene adduct is typical of several other clathrates formed by III.

**Crystal Data.** The unit cell of the *p*-xylene adduct of III is triclinic:  $a = 8.206$  (17),  $b = 14.747$  (25),  $c = 13.318$  (23) Å;  $\alpha = 101.97$  (7),  $\beta = 90.77$  (7),  $\gamma = 109.13$  (5) $^\circ$  (measured by least-squares refinement of nine reflections centered on the automated diffractometer);  $V = 1484$  Å $^3$ ;  $d_{\text{measd}} = 1.49$  (by flotation in *n*-heptane-carbon tetrachloride mixtures),  $d_{\text{calcd}} = 1.48$  g cm $^{-3}$ ;  $Z =$  two host molecules and one xylene molecule; mol wt = 2·(609.3) + 106.2; and  $\mu(\text{Cu K}\alpha) = 23.6$  cm $^{-1}$ . The space group is  $P\bar{1}$ .

**X-Ray Data Collection and Reduction.** A crystal of III with dimensions  $0.31 \times 0.14 \times 0.04$  mm was mounted with  $c^*$  parallel to the  $\phi$  axis of a Syntex four-circle, computer-controlled diffractometer. Because the clathrate was stable at room temperature, no special treatment for the crystal was required. Data collection took place at 20–22 $^\circ$  with the use of Cu X-radiation (1.54178 Å), nickel-filtered on the incident beam side, with the diffractometer conditions as specified previously.<sup>2</sup> A  $\theta$ - $2\theta$  collection mode was employed with a scan rate of 2 $^\circ$ /min and with a scan width for each reflection of 2.25 $^\circ$ . Each background count was one-half of the scan time for the peak. Thus the intensity equation reduced to  $I = [S - (B_1 + B_2)]$ , where  $S$  is the scan count and  $B_1$  and  $B_2$  are the background counts. Two check reflections, 103 and 121, were remeasured after every 25 reflections. Their intensity fluctuated  $\pm 1\%$ . Of the 3464 reflections accessible within the mechanical limits of the instrument, 2031 reflections had intensities greater than  $3\sigma(I)$  and were considered to be observed. The standard deviation,  $\sigma(I)$ , defined according to counting statistics, reduced to  $\sigma(I) = (S + (B_1 + B_2))^{1/2}$  for this data collection, and subsequent Lorentz and polarization corrections produced values of  $F_o$  and  $\sigma(F_o)$ . The value of  $R_{\text{min}}$ , as defined previously,<sup>2</sup> was found to be 2.7% for the observed duplicate reflections.

Since  $\mu$ , the linear absorption coefficient, was relatively small, and rotation of the crystal around the  $\phi$  axis at  $\chi = 90^\circ$  showed little variation in the intensity of reflections along the  $\phi$  axis, no absorption corrections were made to the data set.

**Solution and Refinement of the Structure.** The triclinic space group for compound III may be either  $P1$  or  $P\bar{1}$ . Wilson statistics favor the choice of  $P\bar{1}$ . Attempts to solve the structure from an analysis of the three-dimensional Patterson map were unsuccessful. The structure was solved by MULTAN, a symbolic addition program package intended for use with noncentrosymmetric space groups. Of the 411 reflections with  $E > 1.5$ , no phases were determined by the  $\Sigma_1$  relationship<sup>7</sup> at the 0.90 probability level. The three origin specifying reflections and four additional reflections were automatically selected as the starting set by the program CONVERGE. With these reflections as input, the program FASTAN produced 16 phase sets in which all 411 reflections were phased by the Sayre relationship. The  $E$  map, calculated from the phase set with the highest figure of merit (0.991) revealed 21 atom positions. A figure of merit greater than 1.0 usually indicates a meaningful solution. This phase set contained 201 negative and 210 positive phases, an even distribution between 0 and  $\pi$ , as expected. With the atoms located from the  $E$  map in the model,  $R$  was initially 0.43.

One cycle of least-squares refinement followed by a Fourier synthesis revealed the other 21 atoms of the host molecule. In two cycles of refinement, assuming isotropic vibration of all atoms,  $R$  dropped to 0.18. At this point, a difference synthesis revealed the xylene carbon atoms. It became evident that two high order reflections had exceptionally large  $\Delta$ 's, twice the value of any other reflection. Rejection of these reflections, 3,9,10 and 2,4,13, was justified by the observation that instrument malfunction had occasionally caused abnormally long counting times either during a scan or while on the background. Convergence of least-squares refinement with isotropic thermal parameters for each of the 46 non-hydrogen atoms resulted in a crystallographic  $R$  factor of 0.114. Introduction of anisotropic vibration for all 46 atoms resulted in an  $R$  factor of 0.091. All but one of the host hydrogen atoms were located in a difference synthesis at this point in the refinement. The remaining hydrogen positions were calculated by the programs HFINDR and FIXUP.  $R$  became 0.078 and weighted  $R_w = 0.079$  ( $R_w = \sum_w(|F_o| - |F_c|)^2 / \sum_w |F_o|^2$ ). Initially a unit weighting scheme was used for this refinement and then  $\delta'(F_o)$  of 1.0, 1.1, and 1.2 depending on the value of  $\delta(F_o)/F_o$  for the reflection.<sup>2</sup> Post-refinement examination of the data revealed five additional reflections with unacceptable intensity values. This disagreement was traced

to instrument malfunction, and these data were removed. Refinement of the naphthyl hydrogen positions had only a marginal influence on  $R$ . Attempts to refine the hydrogen atom positions for the xylene molecules were unsatisfactory, a result that was ascribed to thermal motion, especially in the methyl units. The final  $R$  value was 0.058 and  $R_w$  was 0.064.

Atomic and thermal parameters are shown in Tables I–III. Observed and calculated structure factors appear in Table IV.<sup>8</sup>

**Table I.** Atomic Parameters in Fractional Coordinates for Tris(1,8-naphthalenedioxy)cyclotriphosphazene, *p*-Xylene Adduct

Atom	X	Y	Z
P(1)	-0.3391 (3)	0.1523 (2)	-0.0823 (2)
N(2)	-0.3462 (9)	0.2560 (5)	-0.0955 (5)
P(3)	-0.2898 (3)	0.2974 (2)	-0.1919 (2)
N(4)	-0.204 (1)	0.2381 (5)	-0.2741 (5)
P(5)	-0.1941 (3)	0.1359 (2)	-0.2662 (2)
N(6)	-0.2693 (9)	0.0918 (5)	-0.1722 (5)
O(1)	-0.2304 (7)	0.1669 (4)	0.0226 (4)
O'(1)	-0.5254 (7)	0.0844 (4)	-0.0612 (4)
O(3)	-0.1590 (7)	0.4067 (4)	-0.1603 (4)
O'(3)	-0.4499 (7)	0.3098 (4)	-0.2499 (4)
O(5)	0.0049 (7)	0.1438 (4)	-0.2696 (4)
O'(5)	-0.2824 (8)	0.0595 (4)	-0.3698 (4)
C(1)	-0.297 (1)	0.1974 (6)	0.1131 (5)
C(2)	-0.190 (1)	0.2557 (8)	0.1979 (7)
C(3)	-0.255 (2)	0.2870 (8)	0.2892 (7)
C(4)	-0.429 (2)	0.2618 (9)	0.2933 (8)
C(5)	-0.725 (2)	0.1723 (8)	0.2106 (9)
C(6)	-0.831 (1)	0.1234 (8)	0.125 (1)
C(7)	-0.768 (1)	0.0917 (7)	0.0323 (8)
C(8)	-0.593 (1)	0.1160 (7)	0.0318 (7)
C(9)	-0.480 (1)	0.1712 (6)	0.1167 (6)
C(10)	-0.544 (2)	0.2058 (7)	0.2092 (7)
C(11)	-0.218 (1)	0.4851 (6)	-0.1202 (6)
C(12)	-0.107 (1)	0.5691 (7)	-0.0606 (7)
C(13)	-0.165 (1)	0.6482 (7)	-0.0236 (7)
C(14)	-0.332 (1)	0.6402 (6)	-0.0449 (7)
C(15)	-0.622 (1)	0.5449 (7)	-0.1340 (7)
C(16)	-0.730 (1)	0.4604 (8)	-0.1943 (7)
C(17)	-0.676 (1)	0.3787 (7)	-0.2327 (7)
C(18)	-0.509 (1)	0.3887 (6)	-0.2086 (6)
C(19)	-0.394 (1)	0.4741 (6)	-0.1461 (6)
C(20)	-0.450 (1)	0.5544 (6)	-0.1070 (6)
C(21)	0.046 (1)	0.0585 (7)	-0.3039 (6)
C(22)	0.206 (1)	0.0579 (7)	-0.2715 (7)
C(23)	0.253 (2)	-0.0246 (9)	-0.3100 (9)
C(24)	0.146 (2)	-0.1001 (8)	-0.3777 (9)
C(25)	-0.135 (2)	-0.1823 (7)	-0.4853 (7)
C(26)	-0.290 (2)	-0.1802 (8)	-0.5160 (7)
C(27)	-0.343 (1)	-0.0992 (7)	-0.4767 (7)
C(28)	-0.233 (1)	-0.0230 (6)	-0.4085 (6)
C(29)	-0.068 (1)	-0.0206 (6)	-0.3748 (6)
C(30)	-0.016 (1)	-0.1032 (7)	-0.4151 (7)
CX1	0.084 (2)	0.447 (1)	-0.465 (1)
CX2	-0.063 (2)	0.458 (1)	-0.421 (1)
CX3	0.151 (2)	0.486 (1)	-0.5471 (9)
CMX3	0.311 (3)	0.467 (2)	-0.598 (2)

**Computer Programs.** The programs UCLS, FORDAP, SFLS-5, MEAN PLANE (NRC-22), HFINDR, and DISTAN were as used previously.<sup>2</sup> A program, FIXUP, which enabled calculation of the atomic parameters for methyl hydrogen atoms, was written by E. T. Shawl at The Pennsylvania State University. MULTAN, a set of three FORTRAN programs, SIGMA2, CONVERGE, and FASTAN, was developed by G. Germain, P. Main, and M. M. Woolfson.

## Results and Discussion

**General Structural Features.** The structure of compound III is crystallographically more complex than that of I<sup>4</sup> or II<sup>2</sup> because an entire molecule of III is included in the asymmetric unit. However, the structure of III is of particular interest because III forms

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

(7) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," ACA Monograph No. 3, Polycrystal Book Series, Pittsburgh, Pa., 1953.

**Table II.** Thermal Parameters, Mean Square Amplitude of Vibration ( $U$ ) and Equivalent Isotropic  $B$  (EQB), for Tris(1,8-naphthalenedioxy)cyclotriphosphazene,  $p$ -Xylene Adduct

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	EQB
P(1)	0.054 (1)	0.045 (1)	0.027 (1)	0.021 (1)	0.011 (1)	0.006 (1)	3.2 (1)
N(2)	0.059 (4)	0.045 (4)	0.027 (3)	0.028 (3)	0.001 (3)	-0.008 (3)	3.4 (2)
P(3)	0.055 (1)	0.047 (1)	0.032 (1)	0.027 (1)	0.009 (1)	0.006 (1)	3.4 (1)
N(4)	0.075 (5)	0.058 (5)	0.050 (4)	0.037 (4)	0.023 (4)	0.017 (4)	4.5 (2)
P(5)	0.060 (2)	0.049 (1)	0.030 (1)	0.028 (1)	0.012 (1)	0.001 (1)	3.6 (1)
N(6)	0.073 (5)	0.054 (4)	0.020 (3)	0.037 (4)	0.006 (3)	-0.004 (3)	3.7 (2)
O(1)	0.058 (3)	0.067 (4)	0.019 (3)	0.029 (3)	0.013 (3)	0.005 (3)	3.7 (1)
O'(1)	0.051 (3)	0.050 (3)	0.037 (3)	0.013 (3)	0.011 (3)	0.007 (3)	3.7 (1)
O(3)	0.045 (3)	0.043 (3)	0.052 (3)	0.019 (3)	0.009 (3)	0.011 (3)	3.6 (1)
O'(3)	0.059 (4)	0.047 (4)	0.042 (3)	0.024 (3)	-0.004 (3)	0.000 (3)	3.9 (2)
O(5)	0.052 (3)	0.051 (4)	0.052 (3)	0.024 (3)	0.012 (3)	-0.002 (3)	4.1 (2)
O'(5)	0.062 (4)	0.065 (4)	0.033 (3)	0.031 (3)	0.004 (3)	-0.001 (3)	4.1 (2)
C(1)	0.078 (6)	0.059 (6)	0.001 (3)	0.034 (4)	-0.007 (4)	0.004 (4)	3.5 (3)
C(2)	0.088 (7)	0.082 (7)	0.034 (5)	0.032 (5)	-0.001 (5)	0.014 (4)	5.3 (3)
C(3)	0.13 (1)	0.087 (7)	0.022 (5)	0.042 (7)	-0.018 (6)	0.002 (4)	6.3 (4)
C(4)	0.129 (9)	0.092 (7)	0.029 (5)	0.060 (7)	0.021 (6)	0.013 (4)	6.1 (4)
C(5)	0.115 (9)	0.068 (7)	0.060 (7)	0.039 (6)	0.057 (6)	0.024 (5)	6.1 (4)
C(6)	0.063 (7)	0.060 (7)	0.101 (8)	0.012 (5)	0.035 (6)	0.022 (5)	6.0 (4)
C(7)	0.070 (6)	0.059 (6)	0.057 (6)	0.021 (5)	0.013 (5)	0.009 (4)	5.0 (3)
C(8)	0.049 (5)	0.053 (5)	0.051 (5)	0.020 (4)	0.020 (5)	0.015 (4)	3.9 (3)
C(9)	0.065 (6)	0.045 (5)	0.031 (4)	0.026 (4)	0.001 (4)	0.007 (4)	3.6 (3)
C(10)	0.092 (8)	0.063 (6)	0.031 (5)	0.038 (5)	0.026 (5)	0.011 (4)	4.6 (3)
C(11)	0.053 (5)	0.042 (5)	0.040 (4)	0.019 (4)	0.001 (4)	0.013 (4)	3.5 (2)
C(12)	0.043 (5)	0.051 (6)	0.048 (5)	0.012 (4)	0.002 (4)	0.007 (4)	3.9 (3)
C(13)	0.056 (6)	0.047 (6)	0.066 (6)	0.007 (5)	-0.001 (5)	0.006 (4)	4.7 (3)
C(14)	0.085 (7)	0.044 (6)	0.041 (5)	0.026 (5)	0.010 (5)	0.012 (4)	4.3 (3)
C(15)	0.061 (6)	0.056 (6)	0.064 (6)	0.029 (5)	0.005 (5)	0.017 (5)	4.5 (3)
C(16)	0.043 (5)	0.095 (7)	0.060 (6)	0.037 (5)	0.013 (5)	0.032 (5)	4.8 (3)
C(17)	0.053 (6)	0.077 (7)	0.044 (5)	0.019 (5)	-0.007 (4)	0.011 (4)	4.7 (3)
C(18)	0.050 (5)	0.052 (5)	0.024 (4)	0.020 (4)	0.006 (4)	0.013 (4)	3.3 (2)
C(19)	0.047 (5)	0.043 (5)	0.017 (3)	0.016 (4)	0.000 (4)	0.005 (4)	2.8 (2)
C(20)	0.049 (5)	0.046 (6)	0.037 (5)	0.022 (5)	0.018 (4)	0.012 (4)	3.3 (3)
C(21)	0.064 (6)	0.058 (6)	0.031 (5)	0.030 (5)	0.016 (5)	0.017 (4)	3.8 (3)
C(22)	0.062 (6)	0.076 (7)	0.059 (7)	0.030 (5)	0.013 (5)	0.023 (5)	5.0 (4)
C(23)	0.082 (8)	0.097 (9)	0.097 (9)	0.047 (7)	0.020 (7)	0.039 (7)	6.7 (5)
C(24)	0.101 (9)	0.081 (9)	0.100 (9)	0.065 (7)	0.054 (7)	0.041 (7)	6.5 (5)
C(25)	0.15 (1)	0.053 (7)	0.041 (6)	0.040 (7)	0.018 (7)	0.010 (5)	6.2 (4)
C(26)	0.15 (1)	0.066 (7)	0.024 (5)	0.026 (7)	-0.002 (6)	-0.019 (4)	6.8 (4)
C(27)	0.095 (8)	0.068 (7)	0.032 (5)	0.019 (6)	-0.002 (5)	-0.008 (4)	5.5 (4)
C(28)	0.074 (7)	0.056 (6)	0.012 (3)	0.029 (5)	0.016 (4)	0.005 (4)	3.6 (3)
C(29)	0.073 (6)	0.054 (6)	0.026 (4)	0.029 (5)	0.016 (4)	0.016 (4)	3.8 (3)
C(30)	0.088 (8)	0.063 (6)	0.040 (5)	0.040 (6)	0.028 (5)	0.027 (4)	4.5 (3)
CX1	0.19 (2)	0.11 (1)	0.077 (9)	0.06 (1)	-0.03 (1)	0.011 (8)	9.9 (7)
CX2	0.21 (2)	0.09 (1)	0.071 (9)	0.01 (1)	0.00 (1)	0.055 (8)	10.2 (8)
CX3	0.23 (2)	0.12 (1)	0.034 (8)	0.03 (1)	-0.01 (1)	0.025 (7)	10.7 (7)
CMX3	0.23 (2)	0.37 (4)	0.15 (2)	0.16 (3)	0.09 (2)	0.09 (2)	18.0 (2)

**Table III.** Atomic and Thermal Parameters for Hydrogen Atoms in Tris(1,8-naphthalenedioxy)cyclotriphosphazene,  $p$ -Xylene Adduct<sup>a</sup>

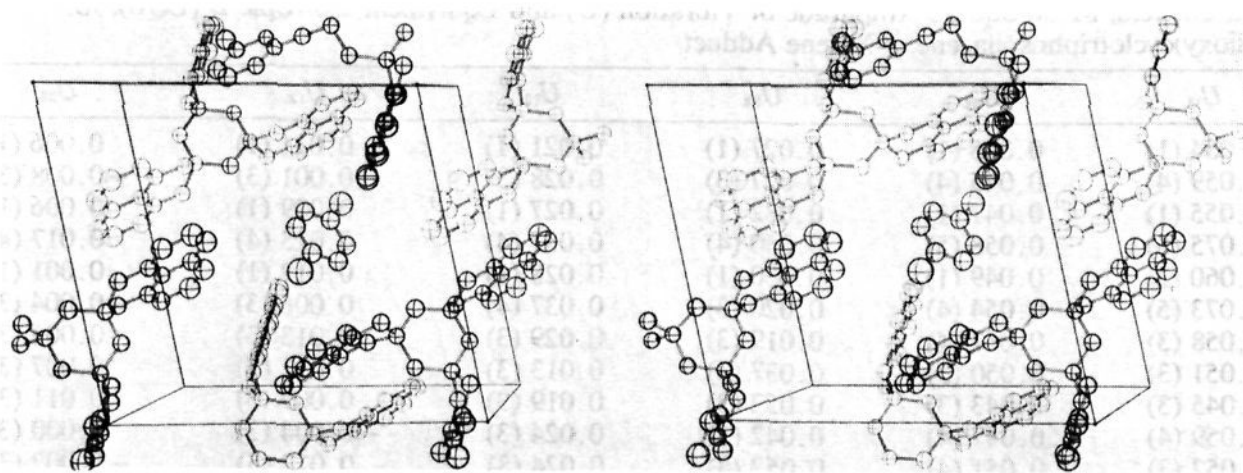
Atom	$X$	$Y$	$Z$	$B$
H(2)	-0.08 (1)	0.275 (5)	0.192 (5)	0 (2)
H(3)	-0.17 (1)	0.329 (6)	0.347 (7)	3 (2)
H(4)	-0.47 (1)	0.285 (5)	0.360 (6)	2 (2)
H(5)	-0.78 (1)	0.192 (6)	0.271 (6)	3 (2)
H(6)	-0.94 (1)	0.103 (5)	0.116 (5)	0 (2)
H(7)	-0.84 (1)	0.053 (6)	-0.035 (6)	2 (2)
H(12)	0.01 (1)	0.580 (5)	-0.049 (5)	1 (2)
H(13)	-0.08 (1)	0.704 (6)	0.015 (6)	2 (2)
H(14)	-0.37 (1)	0.690 (6)	-0.025 (6)	2 (2)
H(15)	-0.66 (1)	0.601 (7)	-0.116 (7)	5 (3)
H(16)	-0.83 (1)	0.454 (6)	-0.213 (6)	2 (2)
H(17)	-0.75 (1)	0.321 (6)	-0.275 (6)	2 (2)
H(22)	0.27 (1)	0.115 (5)	-0.216 (5)	1 (2)
H(23)	0.35 (1)	-0.026 (8)	-0.288 (8)	6 (3)
H(24)	0.17 (1)	-0.157 (6)	-0.414 (7)	3 (2)
H(25)	-0.12 (1)	-0.252 (9)	-0.510 (8)	7 (3)
H(26)	-0.36 (1)	-0.228 (7)	-0.565 (7)	4 (2)
H(27)	-0.46 (1)	-0.103 (5)	-0.485 (5)	1 (2)

<sup>a</sup> The xylyl hydrogen atoms are not included for the reason discussed in the text.

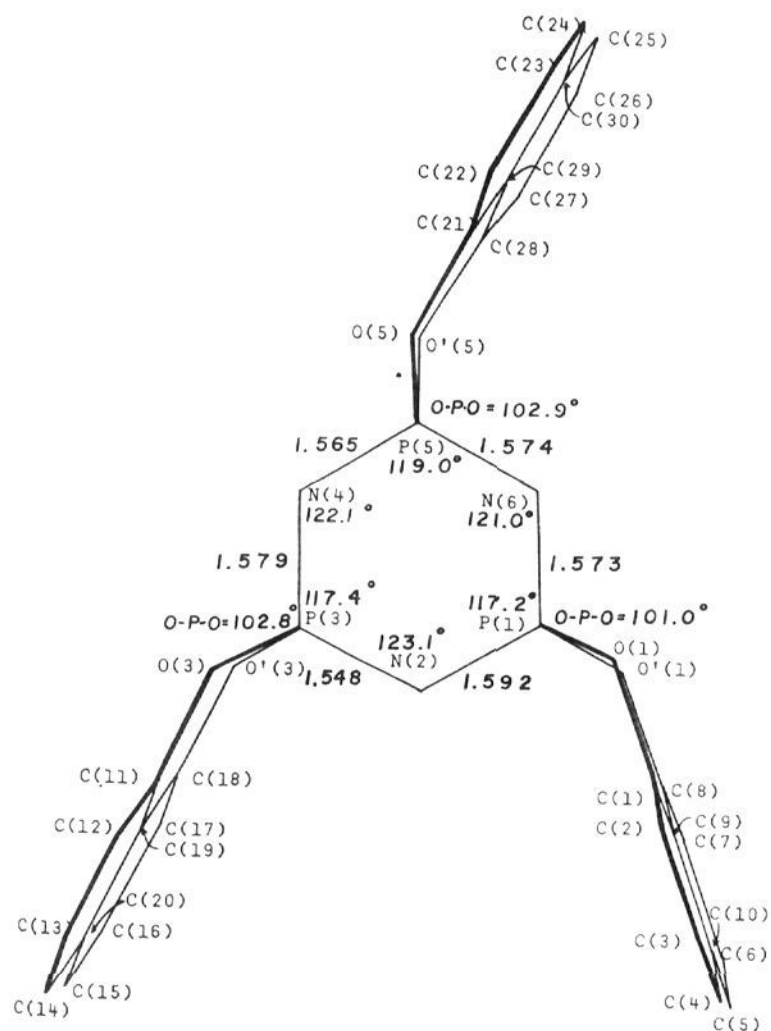
inclusion adducts comparable to I and II and yet does not have the  $6_3$  symmetry hitherto considered necessary for clathration in spirocyclic phosphazenes.<sup>2,3</sup> In the following analysis of the clathration by III, four aspects will be considered. First, a brief comparison will be made between the general structural features of III and those of I and II. Second, the bent orientation of the side groups in III will be considered. Third, the packing of host molecules of III in the crystal will be analyzed from the viewpoint of the clathration phenomenon. Finally, an examination of the arrangement of the guest molecules in the channels will be used to clarify the host-guest interactions.

The disposition of the host and guest molecules in the unit cell is illustrated in Figure 1. It is apparent that the  $p$ -xylene molecules are retained in channels which penetrate the lattice between the side groups of the host molecules.

Considering first the molecular structure of III, it was found that the phosphazene ring is puckered in a boat conformation and that the bond angles and intermolecular distances are within the ranges expected for a



**Figure 1.** Stereoscopic view of the unit cell arrangement for the *p*-xylene clathrate of III. The unit cell is viewed down the channel axis with the *p*-xylene molecule occupying the point  $(0, \frac{1}{2}, \frac{1}{2})$ .



**Figure 2.** Molecular conformation and atomic labeling scheme for tris(1,8-naphthalenedioxy)cyclotriphosphazene (III).

cyclotriphosphazene.<sup>9</sup> The complete sets of interatomic distance and bond angles values for III are tabulated in Tables V,<sup>8</sup> VI,<sup>8</sup> and VII.<sup>8</sup> A summary of the most important data is given in Table VIII. The labeling of the atomic positions is illustrated in Figure 2. The O–P–O angle in III comprises part of a six-membered unstrained ring. Its value of  $102.2^\circ$  is comparable to exocyclic angles found in tris(2,2'-biphenylenedioxy)cyclotriphosphazene (IV),<sup>10</sup> in hexachlorocyclotriphosphazene,<sup>11,12</sup> and in a number of other cyclotriphosphazenes.<sup>9</sup> However, it is significantly wider than the values of  $97$  and  $95.5^\circ$  found in I and II,<sup>2,4</sup> respectively, where

(9) A tabulation of structural parameters for a number of phosphazenes is available: H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N. Y., 1973, Appendix I; H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972).

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**Table VIII.** Summary of Interatomic Distances (Å) and Bond Angles (deg)<sup>a</sup>

	Mean values	Range
P–N	1.57	1.548 (6)–1.592 (6)
P–O	1.59	1.578 (6)–1.597 (6)
C–O	1.40	1.388 (8)–1.414 (9)
C–C (naphthyl)	1.36, 1.40	1.32 (2)–1.43 (1)
C–C (phenyl)	1.38	1.38 (2)–1.39 (3)
C–C (phenyl–methyl)	1.56	1.56 (3)
C–H (naphthyl)	0.94	0.85 (7)–1.07 (9)
N–P–N	117.9	117.2 (4)–119.0 (4)
P–N–P	122.1	121.0 (4)–123.1 (4)
O–P–O	102.2	101.0 (3)–102.9 (3)
P–O–C	119.4	117.1 (5)–122.1 (5)
C–C–C (naphthyl)	120.5	117 (1)–126 (1)
C–C–C (xylyl ring)	119.7	113 (1)–124 (1)

<sup>a</sup> A complete listing of interatomic distances and bond angles will be found in Tables V–VII in the microfilm edition (see ref 8).

the angles reflect the restrictions of a five-membered ring.

**Orientation of the Side Groups.** Figure 2 demonstrates the most striking feature of the host molecule in III. Each side group is bent significantly at the oxygen atoms. The values for this bend are  $44.1^\circ$  for the group at P(1),  $-34.7^\circ$  for the group at P(3), and  $31.6^\circ$  for the group at P(5). Because of the negative bending angle at the side group on P(3), the naphthalene groups attached to P(3) and P(5) lie at an angle of  $186.3$  or  $173.7^\circ$  to each other.

A consideration of the  $\chi^2$  values for important planes in III indicates that the phosphazene ring is not planar. P(3) and N(6) are  $0.051$  and  $0.044$  Å below the least-squares plane, and P(1), N(2), N(4), and P(5) are  $0.021$ ,  $0.026$ ,  $0.028$ , and  $0.019$  Å above this plane. Thus the side group at P(3) is tilted down, and the other two side groups are pointed up. The naphthalene unit as a whole is not planar, but the two six-membered phenyl rings, joined along C(9)–C(10), are planar. The angle of bend between the phenyl residues in the naphthalene groups is about  $1.2^\circ$  in each case (compared with  $2.5^\circ$  for II).

The variation in bond lengths and angles of the host molecule reflects distortions in the molecular framework. Deviations from the mean values are definitely significant for the P–N bonds, the C–C bonds, and all the angles immediately adjacent to the cyclotriphosphazene ring. Most of these differences (P–N bond, N–P–N angle, P–N–P angle, and O–P–O angle) probably arise because of the nonplanarity of the phosphazene

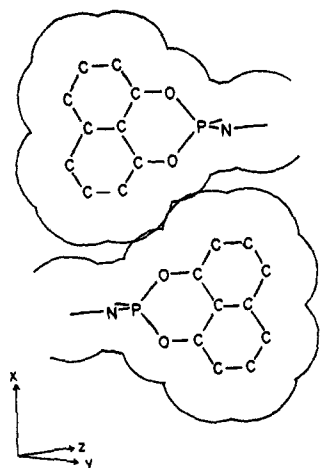


Figure 3. Complementary fitting of the P(3) side group van der Waals boundaries in clathrate crystals of III.

ring. Two sets of C–C bond lengths, C(3)–C(4) and C(1)–C(2), are considerably shorter (1.36 Å) than the other values (1.40 Å). This shortening is predicted theoretically, and is observed crystallographically (1.365 Å) for the naphthalene molecule itself.<sup>13</sup>

**Packing of the Host Molecules.** The crystal structure of III is stabilized by a series of unusual host–host interactions. These interactions are a consequence of the configuration of the molecule and are interrelated with the fact that the naphthalenedioxy side groups are bent in the manner described in the last section.

One strong host–host interaction is shown in Figure 3 for the side group at P(3) and its centrosymmetrically related side group. The complementary fitting is excellent. Closer approach of the side groups is limited by the interaction of side group 3 with side group 1, toward which group 3 is displaced. In order to improve the shape fitting, the phosphazene ring of one molecule is bent toward the side group at P(3) of the other. Consequently the P–N ring is nonplanar, and P(3) is one of the farthest atoms from the least-squares phosphazene plane.

Other important host–host interactions include a coplanar orientation of the naphthalene residues at P(5) from adjacent molecules and a close approach between the side groups at P(1) and P(5) around the origin.

**The Channels and Host–Guest Interactions.** The existence of the main channel is a direct consequence of the fact that the side group at P(3) is bent toward rather than away from the side group at P(1). In the alternative orientation, the side group at P(3) would fill the channel space itself. In its present orientation it provides one of the sides of the channel. Figure 4 represents a view down the channel (down the *a* axis). The guest molecule is at  $(0, \frac{1}{2}, \frac{1}{2})$ . In the projection, the phosphazene ring is tilted 24° from the *yz* plane along the bond N(4)–P(5) or P(1)–N(2), both of which are parallel to the *y* axis. The free diameter of the channel varies from 5.2 to 7.0 Å.

Figure 4 also illustrates how the *p*-xylene molecule fits neatly into the space between the side groups attached to P(1) and P(3). For simplicity, Figure 4 shows

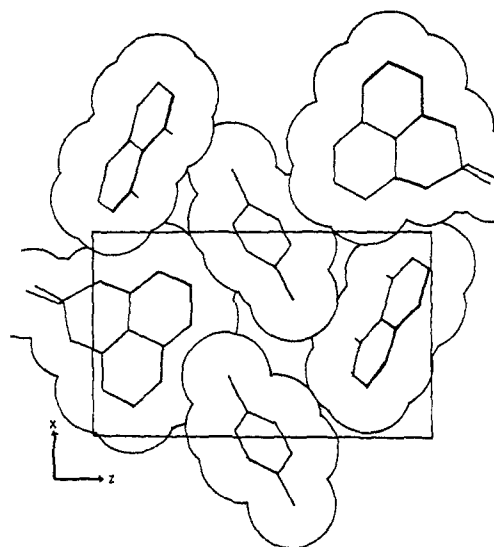


Figure 4. van der Waals boundaries of the *p*-xylene and naphthalenedioxy side group units at P(1) and P(3). An *xz* projection of the channel region is shown.

only the two groups that lie behind the *p*-xylene molecule. In reality, columns of identical P(1)- or P(3)-attached side groups are stacked along *a* on each side of the xylene molecule.

Because of the efficient packing of the host side of groups in this crystal, the host–host interactions are probably stronger than host–guest interactions. However, the fact that the *p*-xylene molecule is restricted to one position indicates that the host–guest interactions are more significant than, for example, in II.<sup>2</sup>

A second but unoccupied channel system exists at the origin between side groups at P(1) and P(5). The channel can be viewed along its axis if the unit cell is rotated around *z* approximately 40° counterclockwise from the larger channel axis. The channel is about 4 Å in diameter, and small guests such as argon or perhaps tetrachloroethylene could perhaps be retained in it. (Tetrachloroethane adducts were prepared, but these were not stable in air at 25°.)

**Stability of the Inclusion Adduct.** The *p*-xylene adduct of III is stable in the atmosphere for long periods of time. Differential thermal analysis curves suggest that loss of *p*-xylene probably occurs when the adduct is heated to 223–242°, a temperature well below the melting point of III (~360°). In any case, the stability of this clathrate is much higher than that of II with benzene.<sup>2</sup> The high stability of the clathrate formed between III and *p*-xylene can be attributed to two causes. First, as discussed earlier, the host–host interactions appear to be very strong, and the need for the guest to “cushion” and stabilize the structure may be minimal. Second, the channels in III are constricted at certain points along their length, and the small diameter at the constrictions may retard loss of the guest molecules.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of the part of this work and Robert W. Allen for help with the computations.

**Supplementary Material Available.** A listing of structure factor amplitudes (Table IV) and Tables V–VII will appear following

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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

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## $\sigma$ - $\pi$ Rearrangements of Organotransition Metals.

### XI. Platinum(II) $\pi$ -Vinyl Alcohol Complexes

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**Abstract:** The stable vinyl alcohol complex, chloro(acetylacetonato)( $\pi$ -ethenol)platinum(II), has been prepared by two separate approaches: preparation and hydrolysis of the analogous  $\pi$ -vinyl trimethylsilyl ether complex and the reaction of chloro(acetylacetonato)(ethylene)platinum(II) and acetaldehyde in the presence of aqueous base. This complex, the first well-characterized  $\pi$ -enol metal complex, was found to be a moderately strong acid ( $pK_a = 3.5$ ) and nmr indicates that in solution it is in rapid equilibrium with its conjugate base, a  $\sigma$ -bonded  $\beta$ -oxoethyl complex. Evidence for a similar equilibrium in the case of the  $\pi$ -acetylacetonate complex  $\text{HPt}(\text{acac})_2\text{Cl}$  suggests that this complex might be best described by a localized enol structure rather than the delocalized structure previously proposed. A chloro(acetylacetonato)( $\pi$ -2-propenol)platinum(II) complex and attempts to prepare other platinum-(II) enol complexes are also described.

While it is well established that a variety of unstable compounds such as cyclobutadiene,<sup>1</sup> benzyne,<sup>2</sup> carbene,<sup>3</sup> and ketenimine<sup>4</sup> can be isolated through coordination with transition metals, only recently has an interest in such complexes of vinyl alcohols (enols) appeared in the literature. In the earliest report, Ariyaratne and Green<sup>5</sup> found that cyclopentadienyldicarbonyl( $\beta$ -oxoethyl)iron could be protonated to give a complex which they tentatively described as the  $\pi$ -enol complex. This is principally based on the infrared spectrum which revealed the absence of the aldehydic C=O absorption of the  $\beta$ -oxoethyl complex and new intense absorptions in the 2400–2800  $\text{cm}^{-1}$  region, assignable to O–H stretching vibrations. However, the unexplained  $A_2X$  pattern assigned to the three vinyl protons of the  $\pi$ -bonded ethenol has led some to reject this structure for the protonated derivative.<sup>6</sup> In a later study, Wakatsuki, Nozakura, and Murahashi,<sup>7</sup> employing a different synthetic approach, obtained 1,3-bis( $\pi$ -ethenol)-2,4-dichloro- $\mu$ -dichloro-platinum(II) by hydrolysis of the vinyl trimethylsilyl ether complex. The nmr spectrum of the compound could not be obtained due to its poor solubility and again the structural assignment was based on infrared data. This work, however, has been questioned by Thyret<sup>6</sup> who reported it to be unreproducible. Employing a vinyl trimethylsilyl ether intermediate, he was able to isolate tetracarbonyl( $\pi$ -ethenol)iron by low

temperature hydrolysis. The complex decomposed above  $-70^\circ$ , but the nmr spectrum obtained at  $-75^\circ$  revealed the expected ABX pattern for the three vinyl protons in contrast to Ariyaratne and Green's results.

The synthetic approach employed by Wakatsuki suggested the possibility of preparing the  $\pi$ -ethenol analog of chloro(acetylacetonato)( $\pi$ -ethylene)platinum(II),<sup>8</sup> hopefully providing a complex of greater solubility than that of Wakatsuki's. This complex has been prepared, and its stability and high solubility have allowed its thorough characterization by nmr,<sup>9</sup> X-ray diffraction,<sup>10</sup> and exchange studies.<sup>11</sup> The rapid equilibrium observed between this  $\pi$ -enol and a  $\sigma$ -bonded  $\beta$ -oxoethyl complex not only explains the  $A_2X$  pattern observed for the vinyl protons here and in Ariyaratne and Green's iron complex but also suggests a localized  $\pi$ -enol structure for the  $\pi$ -acetylacetonate complex  $\text{HPt}(\text{acac})_2\text{Cl}$  for which a delocalized structure has been postulated.<sup>12</sup>

#### Results and Discussion

The stable vinyl alcohol complex, chloro(acetylacetonato)( $\pi$ -ethenol)platinum(II), can be prepared by either of two methods. The procedure first employed<sup>9</sup> involved the preparation and hydrolysis of the intermediate vinyl trimethylsilyl ether complex. Thus a benzene solution of vinyl trimethylsilyl ether and chloro(acetylacetonato)(ethylene)platinum(II) allowed to stand at room temperature for 60 hr yielded the chloro(acetylacetonato)( $\pi$ -vinyl trimethylsilyl ether)platinum(II) complex, **1**, as a viscous yellow oil upon

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