

action temperature were injected into stirred iodine solutions under 1 atm. of carbon monoxide at the reaction temperature. After allowing about a minute for equilibrium to be reached, the rate of gas evolution was measured. Rate constants were calculated on the basis of the experimental infinity values. About six to twelve separate readings were taken in each run during three to five half-lives. The *t*-butyl hypochlorite reactions were carried out by injecting pure *t*-butyl hypochlorite into a stirred solution of the cobalt complex at the reaction temperature under 1 atm. of carbon monoxide and measuring the rate of gas evolution.

**Iodocobalt Tricarbonyl Triphenylphosphine from Cobalt Hydrocarbonyl.**—In the same apparatus used for the rate measurements above, was placed 23.5 ml. of 0.25 *M* cobalt hydrocarbonyl in pentane solution<sup>15</sup> at 0° under 1 atm. of carbon monoxide. Then, 5.9 ml. of 1.0 *M* triphenylphosphine in ether solution was added. About 120 ml. of gas was evolved in 2 min. and the reaction stopped. Some of the product, cobalt hydrotricarboxyl triphenylphosphine, separated from the solution as tan crystals. To this solution and solid was added 25 ml. of 0.25 *M* iodoform in methylene chloride. The solution immediately turned a dark red and about 5 ml. of gas was evolved. After 15 minutes at 0°, the solvent was removed *in vacuo* and the solid was taken up in methylene chloride, all operations being carried out under nitrogen. The black extracts were centrifuged and the clear black solution was concentrated at room temperature under vacuum to about 3 ml., and 10 ml. of pentane was added. Black crystals of the product soon separated. After cooling in Dry Ice, the product was separated by centrifuging and then was recrystallized again from methylene chloride-pentane with cooling in Dry Ice. There was obtained 1.60 g. of brown-black needles, m.p. 141–144° dec. The infrared spectrum in methylene chloride solution had a sharp, strong carbonyl band at 1995 cm.<sup>-1</sup> and a much weaker band at 1920 cm.<sup>-1</sup>.

**Iodocobalt Tricarbonyl Triphenylphosphine from Acetylcobalt Tricarbonyl Triphenylphosphine.**—In a cappable heavy-walled

(15) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953).

Pyrex tube was placed 0.43 g. (1 mmole) of acetylcobalt tricarbonyl triphenylphosphine.<sup>12</sup> The tube was capped with a butyl rubber-lined metal cap with two holes in it for "hypodermic" injections and flushed with nitrogen through a 20-gauge needle. Methylene chloride (3 ml.) was injected and then this solution was added to 0.25 g. of iodine contained at a similar tube under nitrogen (evacuated at Dry Ice temperature to keep the iodine from evaporating) precooled in a Dry Ice-acetone bath. The mixture was shaken and allowed to warm up slightly until the solid iodine had all dissolved (about 10 min.) and then warmed to 0° and concentrated to about 1 ml. under vacuum. The addition of about 2 ml. of pentane caused a black oil to separate. This was quickly removed by centrifuging and the addition of about 5 ml. more of pentane to the solution caused black crystals of the product to crystallize out. After cooling to -80° these crystals were separated by centrifuging and then dried *in vacuo* at room temperature. There was obtained 0.332 g. of product (62%), m.p. 142 up to 189° depending upon the sample and the rate of heating. The infrared spectrum was identical with that obtained from the cobalt hydrocarbonyl reaction product above.

*Anal.* Calcd. for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>PiCo: C, 47.39; H, 2.84; I, 23.85. Found: C, 47.53; H, 3.29; I, 23.97.

**Iodocobalt Dicarboxyl Bis(trimethylolpropane phosphite).**—A solution of 0.48 g. of acetylcobalt dicarbonyl bis(trimethylolpropane phosphite)<sup>12</sup> in 10 ml. of methylene chloride at 0° under a nitrogen atmosphere was treated with 20 ml. of 0.05 *M* iodine in methylene chloride solution. In 30 min. almost 16 ml. of gas had been evolved and the reaction stopped. The solution was evaporated to about 3 ml. *in vacuo* at room temperature, and the product was precipitated by adding 10 ml. of ether. A green oil separated initially and on standing it crystallized. The complex was recrystallized twice more from tetrahydrofuran-ether. There was obtained 0.35 g. of pale yellow crystals, m.p. 261–263° dec. The infrared spectrum in chloroform solution had a strong band at 2020 cm.<sup>-1</sup> and a weaker one at 2045 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>8</sub>IP<sub>2</sub>Co: C, 29.70; H, 3.92. Found: C, 29.17; H, 4.57.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT]

## Phosponitric Compounds. III.<sup>1</sup> Molecular Inclusion Compounds of Tris(*o*-phenylenedioxy)phosponitric Trimer

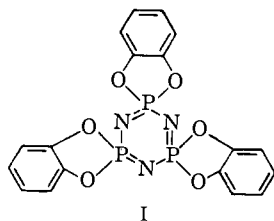
BY H. R. ALLCOCK AND L. A. SIEGEL

RECEIVED AUGUST 7, 1964

Tris(*o*-phenylenedioxy)phosponitric trimer forms crystalline inclusion compounds when recrystallized from organic solvents. Similar adducts are formed by an unusual spontaneous inclusion process, accompanied by a change in crystal structure, which occurs when the solid is brought into contact with the liquid or vapor of many organic compounds. For these adducts, the ratio of host to guest compound depends on the molecular dimensions of the included species. In specific cases, one included compound can be displaced from the adduct by another, and selective absorption from mixed liquids also takes place. X-Ray single crystal and powder diffraction data suggest that at 25° the pure phosponitric compound exists as a monoclinic or triclinic structure with an eight-molecule unit cell. In the adduct form, the material exists as a hexagonal structure which contains two molecules of phosponitric compound and generally not more than one included molecule. The mode of crystal packing is discussed, and the results are interpreted in terms of clathrate or channel-compound formation.

### Results and Discussion

**The Evidence for Adduct Formation.**—The preparation and identification of tris(*o*-phenylenedioxy)phosponitric trimer (I) was described in a recent paper.<sup>1</sup>



This compound, when purified by sublimation, was a white, crystalline solid, m.p. 244–245°. It was only sparingly soluble in most organic liquids. The ability

of I to form stable inclusion compounds was indicated by the following unusual behavior. When sublimed samples of I were brought into contact with organic liquids or vapors, a rapid swelling and disintegration of the crystallites occurred, and the solids, after careful drying, were found to have undergone a weight increase. X-Ray powder patterns of these treated samples were distinctly different from that of the starting material, which indicated that a structural transformation had taken place. Microanalysis, infrared spectroscopy, and mass spectrometry also demonstrated that molecules of the organic compound were present in the solid products. Similar results were obtained for samples of I which had been recrystallized from organic solvents. For these recrystallized products, the unit-cell molecular weight, calculated from single-crystal X-ray data and density

(1) Part II: H. R. Allcock, *J. Am. Chem. Soc.*, **86**, 2591 (1964).

measurements, gave values which did not correspond to simple multiples of the known molecular weight of I. This result was attributed to the presence of trapped molecules.

In general, the dried adducts were stable at room temperature. Those adducts which were less stable were formed by direct inclusion of low molecular weight, volatile guest compounds such as carbon disulfide or methanol, in which case a slow loss of the guest component occurred over several weeks. However, no significant loss of the included component occurred when *recrystallized* adducts were exposed to the atmosphere at room temperature for 1 year, or when the same materials were held under vacuum at 0.1 mm. at 25° for 3 days. The included material could be driven off, however, with more drastic treatment. Thus, prolonged heating at 100 to 150° at 0.1 mm. pressure removed included benzene. A more rapid removal of the included compounds could be effected at reduced pressure at temperatures close to the melting point. After removal of the guest component, the host compound had reverted to the original crystal structure. Similarly, thermogravimetric analysis of the adducts in an atmosphere of nitrogen showed a discrete weight loss below the melting point as the guest material was driven off. Visual observation of the adducts indicated that a disruption of the crystals took place between about 170° and the melting point and that small amounts of included liquid or vapor were released.

These results cannot be attributed to adsorption of the organic compound onto the crystal surfaces. The change in X-ray diffraction pattern indicates that the phenomenon relates to the bulk of the solid rather than to the surface, and the amounts of organic compound retained by I are generally greater than would be expected for a surface effect. Furthermore, a wide variety of nonbonding organic compounds formed adducts with I, and these induced essentially the same crystal transformation. Accordingly, it appears more appropriate to consider the phenomenon as a formation of molecular inclusion adducts rather than as a "solvent of crystallization" effect.

**Influence of the Included Molecules.**—Inclusion adducts were prepared with a wide variety of organic compounds. Table I lists representative compounds which were examined. Liquids studied which failed to induce the crystal transformation were methanol, water, triethylamine, pyridine, and acetic acid. The latter two compounds reacted with I. Those inert liquids which formed adducts with I included aliphatic and aromatic hydrocarbons, halocarbons, esters, ethers, ketones, nitriles, carbon disulfide, and ethanol. There was no correlation between inclusion behavior and polarity,  $\pi$ -character, or hydrogen-bonding capacity. The inclusion phenomenon took place with guest molecules which had widely differing molecular dimensions. Compounds as small as carbon disulfide, acrylonitrile, or ethanol and as bulky as decalin, norbornadiene, or isooctane were included. The dimensions of the organic species influenced the ratio of host to guest compound when the adducts were prepared by spontaneous inclusion. Table I demonstrates the effect of steric size on the adduct ratios. Large guest molecules were retained in the lattice to a

greater extent than were the smaller molecules. This is probably due to the greater ease with which the smaller guest species can leave the lattice. In this respect, adducts of I differed from the inclusion compounds formed by many other host materials,<sup>2</sup> in which smaller molecules are frequently retained in larger quantities.

There appeared to be no simple numerical relationship between the host and guest molecules when the adducts were prepared by the direct addition technique. The highest ratios found were in the range of one molecule of guest to two host molecules. Adducts with cumene, *o*-xylene, *trans*-decalin, isooctane, norbornadiene, and tetralin approximated to this ratio. Below a certain guest to host ratio, however, the adduct crystal form was no longer retained. For example, adducts formed with carbon disulfide and ethanol, which contained 20 and 11 mole % of these compounds, respectively, showed X-ray patterns which appeared to be composites of those of the sublimed and adduct forms. Methanol, which was present only to the extent of 3 mole %, was not retained in sufficient amounts to permit the stabilization of the adduct crystal form. The possibility that a spontaneous recrystallization occurs during the direct guest uptake, *i.e.*, that crystallites rapidly dissolve and precipitate as adducts, is considered unlikely in view of the instantaneous nature of the process and the fact that spontaneous inclusion will occur with vapors as well as with liquids.

The adducts which were prepared by recrystallization from benzene, xylene, cyclohexane, styrene, and chloroform, contained more of the guest species than did equivalent adducts prepared by direct addition: in each case the ratio approximated to one molecule of guest to two of host. The crystals prepared by recrystallization were invariably much larger than the crystallites produced by the spontaneous process. The discrepancies between the ratios of adducts formed by the two methods may thus reflect differences in the surface area available for loss of the guest component during the drying process.

**Selective Absorption and Replacement of Included Species.**—Addition of mixed liquids, such as heptane-cyclohexane, hexane-benzene, or carbon tetrachloride-benzene, to I resulted in a preferential incorporation of one component into the adduct. These results are shown in Table II. In each case, the noncyclic component was incorporated into the adduct with the almost total exclusion of the cyclic component. Apparently the bulkier molecules are excluded relative to those with smaller cross sections because the latter can more easily penetrate the host lattice.

Attempts were also made to replace one included compound by treatment of an adduct with an excess of a second liquid. Included benzene, for example, could be totally displaced by xylene or carbon disulfide.

**Crystal Structure Changes.**—X-Ray diffraction studies were carried out with powder samples and, when available, with single crystals of the pure material and the adducts.

It was not found possible to prepare large, untwinned crystals of the pure material by sublimation, but preliminary work on a twinned specimen indicated a

(2) M. M. Hagan, "Clathrate Inclusion Compounds," Reinhold Publishing Corp., New York, N. Y., 1962.

TABLE I  
 INCLUSION COMPOUNDS OF TRIS(*o*-PHENYLENEDIOXY)PHOSPHONITRILE TRIMER (I)<sup>a</sup>

Included compound (II)	Moles II		Included compound (II)	Moles II	
	Moles I	Melting range, °C.		Moles I	Melting range, °C.
Tetralin	0.59	220-230	Tetrahydrofuran	0.35	233-244
Norbornadiene	0.51	236-275	Chloroform	0.34-0.42 <sup>e</sup>	224-245
Isooctane	0.48-0.50 <sup>e</sup>	231-245		(0.48 <sup>d</sup> -0.66 <sup>b</sup> )	240-244
<i>trans</i> -Decalin	0.47-0.66 <sup>e</sup>	237-245	Methyl methacrylate	0.33	230-267
<i>o</i> -Xylene	0.46	235-259	Diethyl ether	0.31	226-243
<i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes	(0.50 <sup>b,c</sup> )	241-256	Benzene	0.20 <sup>e</sup> -0.25	222-245
Cumene	0.45	228-248		(0.44 <sup>d</sup> -0.50 <sup>b,c</sup> )	244-255
Cyclohexane	0.41-0.42 <sup>e</sup>	233-245	Acetone	0.20	231-250
	(0.50 <sup>b</sup> )		Carbon disulfide	0.20 <sup>e</sup>	226-239
<i>n</i> -Heptane	0.38-0.5 <sup>e</sup>	247-253	Acrylonitrile	0.19	230-257
Styrene	0.38	239-256	Ethanol	0.11 <sup>e</sup>	231-243
	(0.50 <sup>b</sup> )	244-257	(Methanol) <sup>h</sup>	0.03 <sup>f</sup>	236-243
Ethyl acetate	0.37	233-243	(Triethylamine)	<i>f</i>	
Carbon tetrachloride	0.37	233-244			

<sup>a</sup> Unless specified otherwise, the adducts were prepared by spontaneous inclusion and the ratios were determined by weight increase after vacuum drying. <sup>b</sup> By mass spectrometry of recrystallized material. <sup>c</sup> By microanalysis of recrystallized material. <sup>d</sup> By weight loss on heating of recrystallized material. <sup>e</sup> Mixture of triclinic and hexagonal forms. <sup>f</sup> Triclinic form. <sup>g</sup> By mass spectrometry of direct addition adducts. <sup>h</sup> With methanol there was some evidence that the adduct was labile.

 TABLE II  
 INCLUSION FROM MIXED LIQUIDS

Organic liquid (guest)	Molar ratio of guest compounds in mixture	Molar ratio of guest compounds in adduct <sup>a</sup>
Heptane-cyclohexane	0.74	100
Hexane-benzene	0.73	20
Hexane-cyclohexane	0.91	33
Carbon tetrachloride-benzene	0.91	20

<sup>a</sup> By mass spectrometry.

large, eight-molecule, triclinic or monoclinic unit cell. The density of the material was in the range of 1.56 to 1.63 g./cm.<sup>3</sup>. One of the unit-cell axes was quite short, 5.94 Å., which may correspond to the 6.19-Å. axis of phosphonitrilic chloride trimer.<sup>3</sup>

Columnar single crystals of an adduct were obtained by recrystallization from hot benzene. Rotation and Weissenberg patterns of these crystals indicated a hexagonal unit cell with  $c = 10.08$  Å. and  $a = 11.73$  Å. A density value of 1.39 g./cm.<sup>3</sup> corresponded to two host molecules and approximately one benzene molecule per unit cell. The symmetry of the Weissenberg patterns corresponded to Laue group 6/ $m$ , and reflections of the class 000 $l$  were observed only for  $l$  even. These latter two factors limit the space-group possibilities to  $P6_3$  and  $P6_3/m$ . It appears likely that the symmetry elements of the two host molecules in each unit cell are associated with the symmetry elements of the space group and that the molecules have threefold symmetry axes which lie along the triad or hexad axes of the space group. In this case, space group  $P6_3$  would impose no further molecular symmetry requirements. In space group  $P6_3/m$ , however, each of the two molecules would be required to have a mirror plane perpendicular to the threefold axis. On this basis,  $P6_3$  may be the more suitable choice. In both space groups, there would be at least two "holes" in each unit cell available for trapped molecules, and these locations are presumably occupied statistically. Single crystal data for material recrystallized from xylene and chloroform yielded similar results, with slightly different lattice constants.

The results obtained from powder diffraction patterns were in general agreement with those of the single-

crystal investigation. The powder pattern of a benzene adduct, for example, was consistent with the hexagonal unit cell described previously. Adducts prepared by spontaneous liquid or vapor absorption gave powder patterns which were very similar to those of equivalent recrystallized adducts, although the host to guest ratios were different. The back-reflection region of the powder patterns was so weak, however, that small lattice parameter changes could have been overlooked. There was no evidence from the diffraction patterns that the different host to guest ratios reflected the presence of different mixtures of guest-saturated and guest-free host.

The inclusion compounds, as a group, gave powder patterns which were strikingly similar for different guest molecules. Some shifts of line position and intensity occurred according to the variations of size, shape, and scattering power of the guest molecules, but the unit-cell dimensions were comparable. For example, the powder pattern for an isooctane adduct indicated that the  $a$ -axis was about 2% larger, and the  $c$ -axis about 1% smaller than those of the benzene adduct. For adducts which involved guest molecules of similar scattering power but different molecular dimensions, such as benzene and  $n$ -hexane, the line intensities and positions were remarkably similar. This suggests that there is no appreciable variation in the spatial arrangement of the host and guest molecules. It is possible, however, that significant intensity differences were obscured owing to the considerable overlap and superposition of the powder pattern lines.

At room temperature, the hexagonal unit cell was found for samples of I which contained included molecules. It was considered likely, however, that the hexagonal form of I might be stable at high temperatures in the absence of included molecules. Accordingly, the powder pattern of I was observed as the temperature was raised to the melting point. Below about 170° the pattern remained similar to that of the triclinic structure. Above this temperature, the diffraction peaks changed markedly and assumed a pattern in which the triclinic form appeared to coexist with the hexagonal form. Visual observation of pure crystals of I during heating showed a gradual onset of pseudomorphism above 160 to 170°, which was con-

(3) A. Wilson and D. F. Carroll, *J. Chem. Soc.*, 2548 (1960).

sistent with the crystal transition detected by X-ray diffraction.

#### Formation and Nature of the Inclusion Adducts.—

The molecular structure of I can be inferred from the physical data described previously<sup>1</sup> and by analogy with related compounds. In other trimeric phosphonitrilic compounds, the  $sp^3$  hybridization imposes a near-tetrahedral configuration on the  $\sigma$ -bond angles at phosphorus.<sup>4,5</sup> For example, the phosphonitrilic ring in phosphonitrilic chloride trimer is arranged in the form of a near-planar hexagon at right angles to the plane of the Cl-P-Cl bonds.<sup>3</sup> For compound I, the X-ray results require a threefold symmetry axis, which is consistent with either a planar phosphonitrilic ring or a chair configuration. Preliminary polarized infrared data<sup>6</sup> also suggest that the planes of the benzodioxaphosphole groups are nearly parallel to the  $c$ -axis of I in the adduct form and are thus nearly perpendicular to the plane or mean plane of the phosphonitrilic ring. For crystallographic purposes, therefore, the molecule of I can be considered as a three-bladed "paddle-wheel" structure.

The molecular structure and dimensions of I are almost certainly responsible for the inclusion behavior. Crystals of the pure material probably involve an inefficient form of crystal packing and space utilization owing to the unusual shape of the molecule. Furthermore, the packing efficiency cannot be improved by a twisting of the benzodioxaphosphole groups from their perpendicular orientation because of the resistance to distortion of the tetrahedrally oriented phosphorus bonds. The resultant crystal structure would thus contain voids of appreciable size, which are bounded by a deformable arrangement of molecules. Organic molecules penetrate the crystal lattice to fill these voids and induce the crystal structure change. Presumably the hexagonal crystal structure is stabilized by the presence of the guest molecules because the combined space utilization of host and guest is improved. Thus, the inclusion phenomenon in this system is connected with the deformability of the crystal lattice of I rather than with the rigid framework of chemical bonds found in many other clathrate compounds.<sup>2</sup>

The coexistence of the triclinic and hexagonal forms of I at elevated temperatures, in the absence of included species, is probably due to thermal agitation which increases the effective molecular volume. In this way, the hexagonal structure will offer an improved utilization of the available space at high temperatures. Since this structure is stabilized under these conditions in the absence of included molecules, the loss of trapped species from adducts of I at high temperatures is understandable.

The exact location of the cavities occupied by the trapped molecules was not established unambiguously. However, the arrangement of the host molecules can be inferred from the space group information and from the molecular dimensions. The crystal structure of I in the adduct form can be considered as an alternating sequence of two different layers. Both types of layer

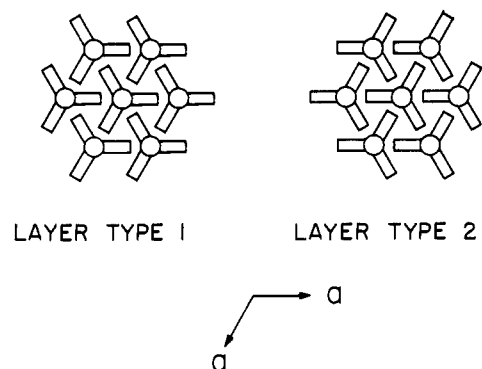


Fig. 1.—Diagrammatic representation of molecules of I in the hexagonal crystal form in the plane of the  $a$ -axis: the circles represent the phosphonitrilic rings and the radial arms depict the  $o$ -(phenylenedioxy) side groups.

consist of structurally equivalent host molecules centered on the hexagonal net formed by the  $a$ -axis translations. The mean plane of each phosphonitrilic ring lies in the layer plane which, in turn, is perpendicular to the  $c$ -axis. The large benzodioxaphosphole side groups are then nearly perpendicular to the layer plane, and the molecular dimensions suggest that these groups lie close to the  $a$ - $c$  plane of the unit cell. The two layer types differ by a  $180^\circ$  rotation of the molecules. This is illustrated in Fig. 1. The vertical separation of adjacent layers is  $c/2$ , or nearly  $5 \text{ \AA}$ ., too small a distance to allow guest molecules to be "sandwiched" between adjacent phosphonitrilic rings.

There are two alternatives for the lateral relationship of neighboring layers. In the first case, no shift of adjacent planes occurs, both molecules of the unit cell lie on the same symmetry axis, and the phosphonitrilic rings of both layers are superimposed. This arrangement could produce channels between the benzodioxaphosphole groups within the crystal structure. In the second case, adjacent planes are displaced. The relative displacement of the phosphonitrilic rings in neighboring layers would be  $\sqrt{3}a/3$  along the  $[\bar{1}10]$  direction, since the two host molecules of the unit cell would lie on different symmetry axes. This structural arrangement could result in the formation of closed cavities bounded by benzodioxaphosphole groups. The present results do not distinguish between these alternatives. It is, in fact, possible that examples of both structures may exist. Both molecular arrangements would lead to at least two cavities or channels per unit cell. Since the adducts usually contain an average of not more than one guest molecule per unit cell, it is clear that the trapped molecules are randomly distributed through the solid in a manner which statistically satisfies the space-group requirements.

This interpretation of the phenomenon implies that related phosphonitrilic compounds with bulky side groups at phosphorus should behave in the same way. It is of interest, therefore, that tris(2,3-*o*-naphthyldioxy)phosphonitrile trimer (II) forms inclusion adducts in a similar manner.<sup>7</sup> Furthermore, it has been reported that other phosphonitrilic compounds retain solvents after recrystallization. For example, hexaphenylphosphonitrile trimer retains appreciable quantities of *sym*-tetrachloroethane,<sup>8</sup> 1,1-dichloro-3,3,5,5-

(4) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

(5) D. F. Craig and N. L. Paddock, *ibid.*, 4118 (1962).

(6) A polarized infrared examination of compound I has been undertaken by Mr. N. B. Colthup in these laboratories.

(7) Compound II was synthesized by a route similar to that described for I; the details will be published elsewhere.

(8) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

tetraphenylphosphonitrile trimer retains acetonitrile,<sup>9</sup> and *cis*-1,3,5-trichloro-1,3,5-triphenylphosphonitrile trimer retains benzene.<sup>10</sup> Explanations for this behavior have ranged from solvent of crystallization effects to Lewis acid phenomena. In view of the present results it would appear more likely that inclusion compounds are involved in these adducts also owing to the steric influence of the bulky phenyl side groups. The inclusion behavior of I can be compared to that of other compounds, such as tris-*o*-thymotide,<sup>11</sup> in which van der Waals forces act as the cohesive element for adduct formation. The unusual feature of the adduct formation by I is the fact that inclusion compounds are formed not only by the usual recrystallization procedure but also by direct and spontaneous absorption by the solid.<sup>12</sup> In this respect, the behavior of I in contact with organic liquids or vapors may be described as that of a crystalline molecular sponge.

### Experimental

**Preparation of Tris(*o*-phenylenedioxy)phosphonitrile Trimer.**—This compound was prepared as described previously.<sup>1</sup> Purification was effected by several recrystallizations from benzene or xylene followed by at least two sublimations at 230° (0.1 mm.) to remove included solvent. Analytical, infrared, and mass spectrometric data were used to demonstrate the purity of the product. Material purified in this way melted at 244–245° (cor.).

**Preparation of Adducts.**—The organic liquids used as second components were the purest materials available commercially and in most cases were spectrally pure grades. Where doubt existed as to the presence of trace impurities, the adducts were analyzed by mass spectrometry to confirm the presence of the expected compound. Three methods were used for the preparation of adducts.

**A. By Recrystallization.**—The low solubility of I in nearly all solvents except boiling xylene required that recrystallizations were performed from very dilute solutions in benzene, chlorobenzene, styrene, chloroform, cyclohexane, and tetrachloroethane. The recrystallized material was filtered off, air dried, and then dried for at least 24 hr. at 0.1 mm.

**B. By Spontaneous Absorption of Liquid.**—When I was treated with an excess of organic liquid at room temperature, an exothermic crystal disruption and absorption of the organic compound occurred. Excess liquid was removed by air drying followed by vacuum drying at 0.1 mm. for 24 hr. at 25°. The majority of the adducts studied in this work were prepared by this method. In experiments where mixed organic liquids were employed, the procedure was the same. For replacement experiments, an adduct was prepared initially with the first organic compound, and was dried and analyzed before addition of the second liquid.

**C. By Vapor Absorption.**—Sublimed samples of I in open glass vial were suspended within a closed vessel above the surface of organic liquids such as chloroform or benzene. At atmospheric pressure and 25°, spontaneous absorption of chloroform or benzene to form adducts took place. After 12 hr. the vial was removed and the solid was vacuum dried and analyzed.

**Determination of Adduct Ratios.**—Several methods were used to characterize the adducts. Mass spectrometry was employed to determine the ratio of guest compound to host: the adducts were volatilized at 300° into the ionization chamber of a Consolidated Electrodynamics Model 21-103 spectrometer. Included mixtures were analyzed in the same way. Microanalysis was used to determine the stoichiometry of some adducts, but this method was generally less accurate than the other techniques. Thermogravimetric analysis from 25 to 300° indicated the weight loss which accompanied volatilization of the included compound below the melting point of I at atmospheric pressure. Prolonged heating of recrystallized adducts in a vacuum oven at 100–150° (0.5 mm.) was also used to determine the weight loss which accompanied removal of the guest component, but the results were not always reproducible owing to volatilization of the host. Although occluded molecules could frequently be detected from the infrared spectra of Nujol or halocarbon mulls of the adducts, this method was not suitable for quantitative measurements. For adducts prepared by direct absorption, the ratios of the components were determined by weight increase after drying to constant weight under vacuum (0.5 mm.) at 25°.

**Thermal Analysis.**—Attempts were made to detect crystal transitions by the use of differential thermal analysis equipment<sup>13</sup> at a 10°/min. temperature increase. For I and its adducts, a broad exothermic peak was detected in the 130 to 170° region. The exothermic nature of the spontaneous inclusion process was demonstrated by a simple experiment within a thermally insulated assembly, in which thermocouples were embedded in I and in a dropping pipet which contained benzene. When approximately 0.13 g. of benzene was added to 0.5 g. of I, a 3° temperature increase occurred.

**Density Determinations.**—The densities of I and several adducts were determined by a flotation method in aqueous potassium iodide solution. Density measurements in organic liquids were unsatisfactory owing to incorporation of these materials into the crystals.

**X-Ray Apparatus and Technique.**—The single crystal photographs were obtained with a standard equi-inclination Weissenberg camera. The powder patterns were made using a 114.6-mm. diameter Debye-Scherrer camera. In both cases, Cu K $\alpha$  radiation (nickel filtered) was employed. Powder patterns were also obtained using an X-ray diffractometer with a heating attachment. The sample was contained in a nitrogen atmosphere, and measurements were made over an angle of 5 to 25°, and over the temperature range, 25 to 230°.

**Acknowledgments.**—We thank Mr. A. H. Struck and Mrs. R. H. Barritt for the mass spectrometry measurements, Miss E. C. Eberlin for the thermal analyses, Mr. W. R. Doughman for assistance with the X-ray measurements, and Mr. N. B. Colthup for discussions. We are indebted to Dr. R. L. Myers for his interest in this work.

(9) C. D. Schmulbach and C. Derderian, *J. Inorg. Nucl. Chem.*, **25**, 1395 (1963).

(10) B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, **3**, 623 (1964).

(11) D. Lawton and H. M. Powell, *J. Chem. Soc.*, 2339 (1958).

(12) A similar spontaneous inclusion behavior was reported for potassium benzenesulfonate: R. M. Barrer, J. Drake, and T. V. Whittam, *Proc. Roy. Soc. (London)*, **A219**, 32 (1953).

(13) J. J. Keavney and E. C. Eberlin, *J. Appl. Polymer Sci.*, **3**, 47 (1960).