Cyclophosphazene Clathrates—Exploring the Adjustable Tunnel

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Clathrates, or molecular inclusion adducts, are crystalline solids in which "guest" molecules occupy cavities, channels, or tunnels in the host lattice.[1,2] The clathrates formed when either urea or thiourea is allowed to crystallize from organic solvents are well-known. Similarly, the clathration of rare gas atoms or halogen molecules in ice crystals has been studied for many years.[1-3] Other clathration systems include those in which the host is hydroquinone,[1,2,4] tri-o-thymotide,[5] perhydrotriphenylene,[6] or one of the zeolites.[1] The intercalation compounds formed by graphite[7-10] and the starch–iodine adduct[1,2] are related systems.
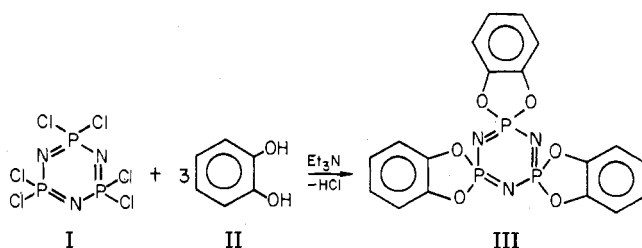
Interest in clathrate structures stems from the fundamental information that such systems provide about lattice forces and van der Waals potentials and, on a more practical level, from the use of the clathration phenomenon to store guest molecules or separate one type of guest molecule from another.

Cyclophosphazenes are six-, eight-, or higher-membered ring systems built on a framework of alternating phosphorus and nitrogen atoms. Two side groups are attached to each phosphorus. The earliest known members of this class of compounds are hexachlorocyclotriphosphazene (I) and the related tetramer $(NPCl_2)_4$. These compounds are synthesized from ammonium chloride and phosphorus pentachloride. Replacement of the halogen atoms in chlorophosphazenes by organic nucleophiles allows the synthesis of a large number of *organo*phosphazenes. Certain organophosphazenes are now known to form the host lattices of a new class of molecular inclusion adducts, and these clathrate systems display a number of surprising and unusual features. They were discovered by accident.

In 1963, I was engaged in the search for a synthetic route for the preparation of inorganic high polymers. As part of that project, a reaction was carried out

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between hexachlorocyclotriphosphazene (I) and cate-

chol (II) in the presence of triethylamine to yield the hitherto unknown spirocyclophosphazene, shown in III.[11,12] I had hoped to polymerize this product by opening of the phosphazene ring, but the purification of III proved to be a problem. Recrystallization of III from benzene yielded white needle-shaped crystals which showed the correct molecular weight (by mass spectrometry) and the expected infrared, ultraviolet, and NMR spectra, but which consistently gave incorrect microanalysis data. Curiously, in spite of its apparent spectroscopic purity, the compound showed a broad melting range (222–245 °C), but the melting point sharpened to 245 °C after several vacuum sublimations.

X-ray powder photographs of the sublimed and unsublimed materials showed that the latter had a hexagonal crystal structure, whereas the former was monoclinic or triclinic. By x-ray and mass spectroscopic examination of powder samples and single crystals of III isolated from a wide range of solvents, it was finally concluded that III is capable of forming a highly unusual series of clathrate inclusion adducts.[13] Since that

(1) See, for example, the reviews by L. C. Fetterly (p 491), R. M. Barrer (p 309), H. M. Powell (p 438), and F. R. Senti and D. R. Erlander (p 568) in "Non Stoichiometric Compounds", L. Mandelcorn, Ed., Academic Press, New York, N.Y., 1964.
(2) M. Hagan, "Clathrate Inclusion Compounds", Reinhold, New York, N.Y., 1962.
(3) G. A. Jeffrey and R. K. McMullen, Prog. Inorg. Chem., 8, 43 (1967).
(4) D. E. Palin and H. M. Powell, J. Chem. Soc., 220 (1947).
(5) D. Lawton and H. M. Powell, J. Chem. Soc., 2339 (1958).
(6) M. Farina, G. Allegra, and G. Natta, J. Am. Chem. Soc., 86, 516 (1964).
(7) W. Rudorf, Adv. Inorg. Chem. Radiochem., 1, 223 (1959).
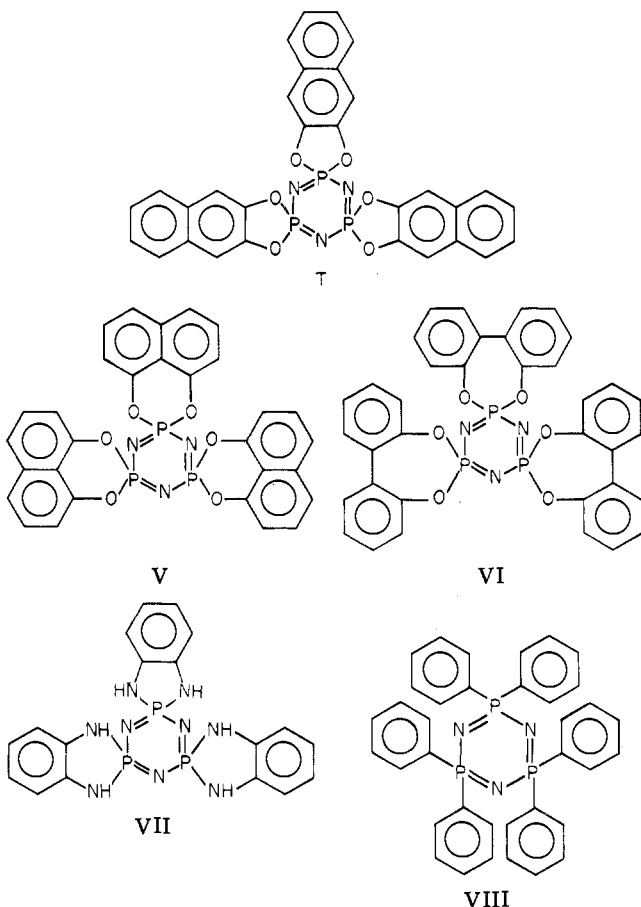(8) G. R. Henning, Prog. Inorg. Chem., 1, 125 (1959).
(9) R. C. Crofts, Q. Rev., Chem. Soc., 14, 1 (1960).
(10) Y. N. Novitov and M. E. Vol'pin, Usp. Khim., 40, 1568 (1971).
(11) H. R. Allcock, J. Am. Chem. Soc., 85, 4050 (1963).
(12) H. R. Allcock, J. Am. Chem. Soc., 86, 2591 (1964).

time at least four other cyclophosphazene systems (IV, V, VII, and VIII) have been shown to form inclusion

T

V

VI

VII

VIII

adducts, and complete x-ray structures have been completed on three. It now seems clear that this phenomenon results from the unique *shape* of cyclotriphosphazenes and from the nature of the intermolecular van der Waals forces in the crystal lattices.[14]

Inclusion Adducts from Tris(*o*-phenylenedioxy)cyclotriphosphazene (III)

Formation of the Adducts.[13] Tris(*o*-phenylenedioxy)cyclotriphosphazene (III) is sparingly soluble in most organic liquids. As mentioned already, III can be recrystallized from organic media, such as benzene or toluene, to yield elongated crystals that contain molecules of the solvent. More surprising is the fact that pure samples of III *directly* absorb organic liquids, such as *n*-heptane, ethyl acetate, or chloroform, to yield molecular inclusion adducts. The same phenomenon occurs when III is simply brought into contact with the *vapor* of organic materials. Under both sets of circumstances, the crystallites of III swell and disintegrate as the guest molecules are absorbed. The resultant solids, after careful drying, are found to have undergone a weight increase, and microanalysis, infrared spectroscopy, or mass spectrometry can be used to confirm the presence of the guest compounds. Furthermore, the clathrate single crystals obtained by recrystallization

(13) H. R. Allcock and L. A. Siegel, *J. Am. Chem. Soc.*, **86**, 5140 (1964).
(14) For recent general reviews of phosphazene chemistry, see H. R. Allcock, "Phosphorus-Nitrogen Chemistry", Academic Press, New York, N.Y., 1972; *Chem. Rev.*, **72**, 315 (1972). A review of the polymeric aspects of this field will be found in *Science*, **193**, 1214 (1976).

techniques yield x-ray unit cell molecular weight data that clearly demonstrate the presence of trapped guest molecules.

The range of inclusion adducts formed by III is very broad.[13] The guest species range from aliphatic and aromatic hydrocarbons to olefins, ethers, chlorocarbons, ketones, nitriles, and alcohols, with the molar proportion of host to guest varying from about 1:0.6 to 1:0.03. Clearly, the direct *chemical* binding of guest to host cannot explain the phenomenon nor can the invocation of π-complex forces. In fact, the *size* of the guest molecule appears to exert a strong influence on the retention of the guest, as expected for a clathration system. Bulky guest molecules, such as cumene, *o*-xylene, *trans*-decalin, isooctane, or norbornadiene, are retained by the lattice in the largest amounts.

In general, the adducts are stable at room temperature, although volatile low molecular weight guest compounds, such as carbon disulfide or methanol, can diffuse from the crystals during several weeks exposure to the atmosphere. In this respect, adducts formed by recrystallization are more stable than those formed by direct liquid or vapor uptake, probably because the crystallite size is much smaller in the latter case. It is, in fact, quite common for the recrystallized adducts to retain the guest molecules for several years while exposed to the atmosphere at 25 °C. Most of the clathrates are also stable in vacuum at 25 °C. However, the guest molecules can be removed by heating at 100–150 °C at 0.1 torr. Rapid removal of the guest also occurs above 170 °C at atmospheric pressure. Under these conditions, in a melting point capillary tube, a striking crystal disruption can be observed, accompanied by condensation of the released guest in the cooler regions of the tube. X-ray powder analysis can be used to demonstrate that this process accompanies a reversion of the hexagonal to the monoclinic or triclinic guest-free form.

Selective Guest Absorption and Guest Displacement.[13] In a competition process in which two or more guest molecules can enter the lattice of III simultaneously from either the liquid or vapor state, one guest is usually admitted with the almost total exclusion of the other. For example, if pure III is brought into contact with a mixture of liquid heptane and cyclohexane, the heptane is absorbed with 100% exclusion of the cyclohexane. The noncyclic component is similarly preferred when hexane–benzene, hexane–cyclohexane, or carbon tetrachloride–benzene mixtures are employed.[13] Apparently, the larger molecules are excluded relative to those with smaller cross sections because the latter can more easily penetrate the host lattice. Clearly, this phenomenon has widespread implications for the separation of complex organic mixtures, a prospect that is mentioned at the end of this Account.

Before turning to the structural features of this clathrate system, it is worthwhile to note that some guest molecules, such as benzene, can be displaced from the lattice and replaced by xylene or carbon tetrachloride if an excess of the second liquid is employed. This implies that the guest components are retained in tunnels that are continuous through the crystals.

X-Ray Diffraction Analysis of III. First, it should be noted that the inclusion adducts formed by re-
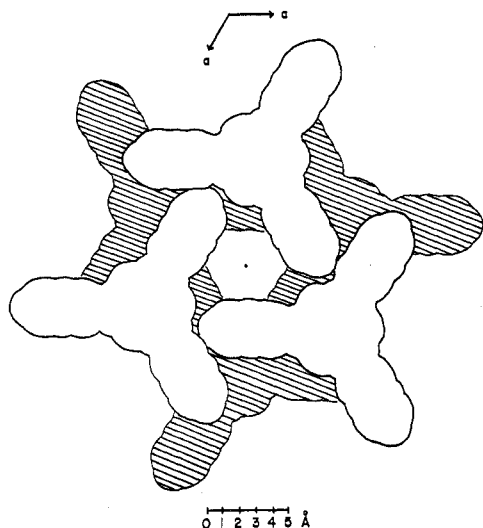
Figure 1. van der Waals boundaries of molecules of III in clathrates formed by III. The 4.5–5-Å diameter tunnel is clearly visible. By courtesy of L. A. Siegel.

crystallization, liquid contact, or vapor uptake give hexagonal-type powder patterns that are very similar to each other. Replacement of one guest by another brings about only minor changes in the unit cell parameters. For example, a 2% expansion in the a-axis parameter is observed when benzene is replaced by isooctane.

Second, it is significant that the triclinic-type, unclathrated form of III undergoes a visually observable pseudomorphism above 160–170 °C, the same temperature above which guest molecules are released by the host.[13] Coincidentally, above 170 °C, the unclathrated host gives x-ray powder patterns which indicate a coexistence of the triclinic and hexagonal modifications. Thus, it appears that the hexagonal form can exist in the absence of a guest if the thermal motions of the host are sufficiently large to reduce the free space in the lattice.

Single-crystal x-ray analyses of a benzene clathrate of III indicated a hexagonal-type unit cell with $c = 10.05$ Å and $a = 11.80$ Å.[15,16] The space group is $P6_3/m$.[16] Two host molecules and one benzene molecule occupy the unit cell.[13] The space group symmetry alone, and the three-dimensional diffractometer data, indicate that the host framework consists of alternating layers of molecules, with each layer separated by approximately 5 Å. This distance is too small to allow the guest molecules to be "sandwiched" *between* the layers (as, for example, in graphite intercalation systems). Hence, the guests must occupy the spaces between the side groups of III.[13]

Each phosphazene molecule possesses a regular "paddle wheel" shape, with the side groups oriented at right angles to the plane of the inorganic ring.[15,16] The disposition of the molecules is shown in Figure 1, in which the location of the tunnel is clearly visible. This tunnel is approximately 4.5–5 Å in diameter at its narrowest point. The stereoview shown in Figure 2 provides a good illustration of the way in which, at high temperatures, the vibrating side groups could themselves partly fill the tunnel space.

Guest molecules, such as benzene or bromobenzene, do not occupy fixed positions in the tunnels. Difference Fourier maps show the presence of diffuse electron density within the tunnels,[15] and some coalescence of electron density into pseudospherical regions can be observed for benzene clathrates,[16] but it is clear that at 25 °C benzene or bromobenzene can translate and rotate quite freely in the tunnel space. This is, of course, quite consistent with the ease with which one guest component can be replaced by another. This question of guest mobility is considered in a later section.

Clathrates from Tris(2,3-naphthalenedioxy)cyclotriphosphazene (IV)[17,18]

Following the discovery of the clathration behavior of III, the next step was the synthesis of tris(2,3-naphthalenedioxy)cyclotriphosphazene (IV) from I and 2,3-dihydroxynaphthalene.[17] This compound is a colorless crystalline material which, when pure, melts at 335–336 °C. Material crystallized from benzene undergoes a visually detectable crystal transformation at 250 °C, with the concurrent release of benzene.[18] The clathrated benzene can also be completely removed by sublimation at 350 °C (0.5 torr). However, permanent *spontaneous* benzene absorption appears not to occur with IV. X-ray powder evidence was obtained to show that treatment of pure IV with benzene induced a crystal structure change from a lower symmetry state to hexagonal. However, as soon as the adduct was dried in the atmosphere, the included benzene was lost, and the crystal structure reverted to its original form.

Even clathrates formed by *recrystallization* of IV from benzene are less stable than those of III.[17] Immediately following recrystallization, the molar ratio of IV to benzene is frequently as high as 1:3.5, but exposure to the atmosphere results in a loss of benzene until the ratio is 1:2, or even lower. Interestingly, a marked decrease in the amount of benzene contained in the clathrate frequently does not result in reversion of the crystal structure. Some crystals retain a 1:3 ratio of IV to benzene after long periods of exposure to the atmosphere. Apparently, the larger the crystals the less rapid is the rate of benzene loss. All this strongly suggests that the tunnels in IV are much wider than those in III and that benzene molecules can escape from the lattice of IV more readily.

This implication was confirmed by the single-crystal x-ray analysis.[18] First, it was found that the unit cell was hexagonal with $a = 15.73$ Å and $c = 10.08$ Å with space group $P6_3/m$. Thus, the c-axis parameter is virtually identical with that found for III, but the a axis is larger. This in itself suggests that the crystal structure is very similar to that of III, with an almost identical separation between the molecular layers, but with a markedly expanded structure at right angles to the tunnel axis.

The three-dimensional structure solution[18] showed that this is indeed the case. The phosphazene molecules again have the "paddle wheel" type of structure seen for III. Figure 3 illustrates the disposition of the host molecules and their van der Waals boundaries. The

(15) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. A*, 817 (1967).
(16) H. R. Allcock, R. W. Allen, E. C. Bissell, L. A. Smeltz, and M. Teeter, *J. Am. Chem. Soc.*, **98**, 5120 (1976).

(17) H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, **5**, 1016 (1966).
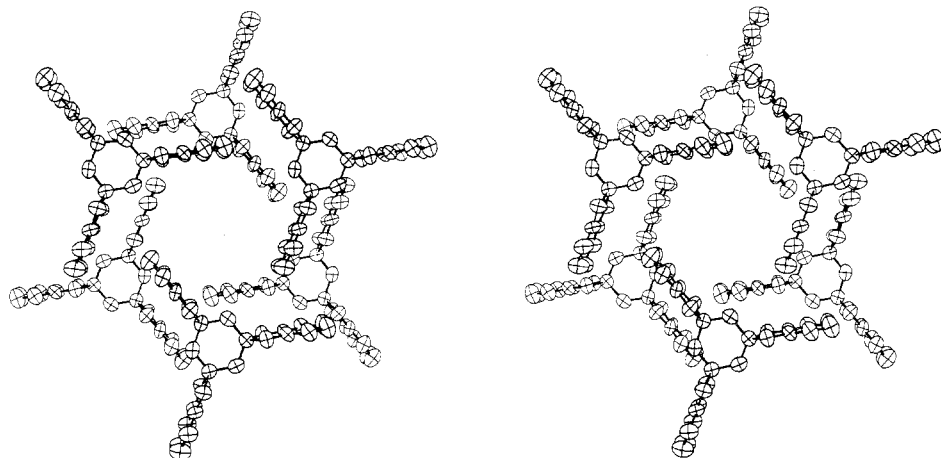(18) H. R. Allcock and M. Teeter-Stein, *J. Am. Chem. Soc.*, **96**, 49 (1974).

Figure 2. Stereoscopic view down the tunnel of a clathrate formed by III (from ref 16).
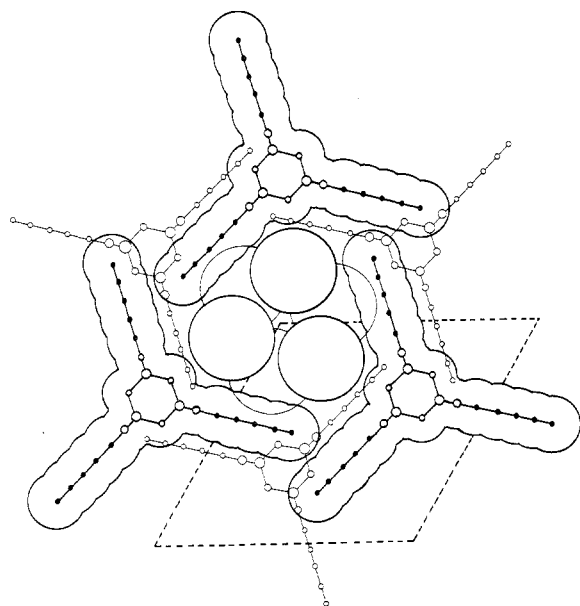

Figure 3. van der Waals boundaries of molecules of tris(2,3-naphthalenedioxy)cyclotriphosphazene (IV) in a benzene clathrate system. The circles represent spheres of electron density within the tunnel. They correspond to tumbling benzene molecules (from ref 18).

channels are 9–10 Å across at the narrowest point. Figure 3 also illustrates one of the most surprising features of this structure—that considerable electron density was detected in the channels and could be resolved into six "spheres" of electron density per cell. These spheres clearly represent tumbling benzene molecules closely packed in the channel space. The mobility of these guest molecules is discussed later.

Tris(1,8-naphthalenedioxy)cyclotriphosphazene (V)

This compound was synthesized from I and 1,8-naphthalenediol.[19] Crystals of V can be grown from a wide variety of organic compounds, such as alcohols, alkanes, cycloalkanes, and aromatic compounds.[20] The products crystallized from xylenes have been studied the most intensively; x-ray powder data suggest that these materials are typical of the crystals obtained from other solvent systems.
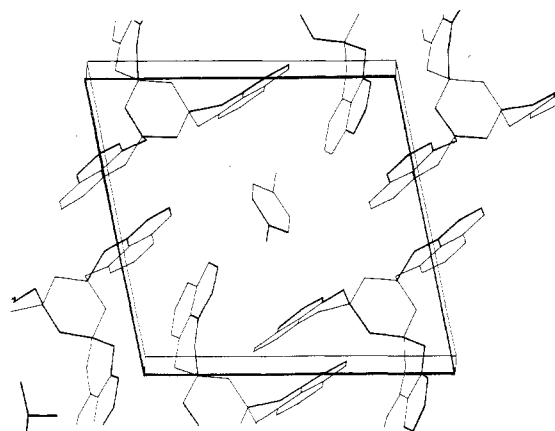
(19) H. R. Allcock and E. J. Walsh, *Inorg. Chem.*, **10**, 1643 (1971).
(20) H. R. Allcock, M. Teeter-Stein, and E. C. Bissell, *J. Am. Chem. Soc.*, **96**, 4795 (1974).

Figure 4. View of the unit cell contents of a xylene clathrate of tris(1,8-naphthalenedioxy)cyclotriphosphazene (V) (from ref 20).

Phosphazene V crystallizes from *p*-xylene to yield very pale orange crystals. When heated, the crystals release *p*-xylene at about 210 °C and then melt at 360 °C. The x-ray powder patterns of crystals obtained from xylene and those that have been heated are different, but the original pattern can be regenerated by recrystallization from xylene. Thus, the evidence for clathrate formation is again convincing. Samples of this clathrate have retained their integrity for more than a year while exposed to the atmosphere.

The *p*-xylene adduct of V forms triclinic crystals (space group $P\bar{1}$). A single-crystal analysis showed that two host molecules and one xylene molecule occupy a *fixed* position in the structure.[20] The arrangement of the molecules in the cell is shown in Figure 4. Again, the xylene molecules are packed between the side groups of the phosphazene molecules in a tunnel that extends down the *a* axis of the cell. However, in contrast to the structures found for III and IV, the tunnels in V are constricted at certain points along their length, and the small diameter at the constrictions may retard loss of the guest molecules. The restriction of the small tunnel diameter partially explains why the *p*-xylene molecules undergo only minimal thermal motion at 25 °C.

It is clear from Figure 4 that the molecular conformation of V differs strikingly from those of III or IV. The side groups are bent at the oxygen atoms, and the direction of bend is not radially symmetric. In fact, it

appears that clathration would be impossible if the third side group did not bend in the opposite direction to the other two since it bends *away from* the tunnel and forms one wall of the tunnel. In the completely symmetric structure, this side group would itself fill the tunnel.

Tris(2,2′-biphenyldioxy)cyclotriphosphazene (VI)[21]

The pattern that emerges from the foregoing discussion is that the clathration phenomenon is a consequence of the threefold symmetry of cyclophosphazenes, coupled with the rigidity of the phosphazene ring and the presence of bulky substituent groups. We have seen that the extension of the *length* of each side group, as in IV, retains the capacity for adduct formation, and that an increase in the *"depth"* of the side group, as in V, similarly permits clathration to persist. The question that we now pose concerns the effect of further increases in the "depth" of the side units by the introduction of biphenyldioxy substituent groups in compound VI.

Compound VI can be prepared from I and 2,2′-dihydroxybiphenyl, but so far no conditions have been found in which VI forms inclusion adducts.[17] Recrystallization from xylene or from other aromatic hydrocarbons yields colorless crystals without the retention of solvent molecules. An x-ray single-crystal analysis of VI[21] revealed one of the reasons for this difference. In order to relieve the potential ring strain, the seven-membered rings in VI twist in a propeller-like conformation. However, the direction of the twist of one side group is opposite to that of the other two. There is, in fact, no free space in the unit cell that could accommodate a guest molecule. The counter-twist of the unique side group serves to fill the only free volume that might exist in this structure. It appears that this symmetry-reducing twist is a result of an avoidance of intermolecular close contacts. Hence, if the side-group structure is sufficiently flexible, the potential voids in the lattice will not exist.

Other Cyclophosphazenes

What *are* the structural and conformational limits to clathrate formation in cyclophosphazenes? The answer to this question is currently under investigation in our laboratory. However, clues indicate that we have by no means exhausted the possibilities for different host structures.

For example, tris(*o*-phenylenediamino)cyclotriphosphazene (VII) (synthesized from I and *o*-phenylenediamine) forms a crystalline inclusion adduct with methyl ethyl ketone[17] in which the ratio of host to guest is 1:1.8. The guest can be removed at 80 °C (1 torr), and a crystal transformation accompanies this change. Hydrogen bonding between guest and host may stabilize this structure, and this possibility is currently being investigated. 1,1-Dichloro-3,3,5,5-tetraphenylcyclotriphosphazene retains acetonitrile after recrystallization from that solvent,[22,23] and *cis*-1,3,5-tri-chloro-1,3,5-triphenylcyclotriphosphazene retains benezene[24] in a manner that is strongly suggestive of a clathrate formation. Hexaphenylcyclotriphosphazene (VIII) retains appreciable quantities of *sym*-tetrachloroethane when recrystallized from that solvent.[25-27] However, during exposure of the crystals to the atmosphere, the guest component is lost, crystal disintegration occurs, and a change in crystallographic morphology is detected from x-ray powder patterns. The adduct with tetrachloroethane is so labile that mere grinding of the crystals is sufficient to release the guest.

The crystal and molecular structure of VIII in an unclathrated form has been reported.[28] The unit cell is triclinic, space group *P*1̄, with two molecules per unit cell. However, attempts to obtain single-crystal data on the clathrated form have so far proved unsuccessful. Crystallization from acetonitrile, benzene, or *o*-xylene does not yield inclusion adducts.[27]

Up to the present time no cyclo*tetra*phosphazenes,[14] including spirocyclic derivatives,[19] have been shown to form clathrates.

Mobility of the Guest Molecules

Both x-ray diffraction and broadline ^{1}H NMR spectroscopy have been employed to examine the mobility of guest molecules trapped in the lattices. It has already been pointed out that attempts to detect individual benzene or bromobenzene in a host lattice of tris(*o*-phenylenedioxy)cyclotriphosphazene (III) by x-ray techniques were unsuccessful. Only a diffuse pseudospherical electron-density residual was found to occupy the center of each channel when benzene or *o*-xylene were present.[16] It seems clear that at 25 °C considerable guest molecular mobility exists in this system. Moreover, variable-temperature broadline ^{1}H NMR experiments[16] with benzene, *o*-xylene, and *p*-xylene clathrates of III suggested that the guest molecular motions are significant, even at −60 °C.

Benzene clathrates of IV contain larger amounts of guest molecules at 25 °C, and, as described earlier, the guest molecules can be rationalized in x-ray difference maps as "spheres" of tumbling benzene units.[18] It is, of course, impossible by x-ray diffraction techniques to distinguish between freely tumbling molecules and guest molecules that have different fixed orientations in different unit cells. NMR proton spectra were, therefore, obtained for the pure solid host material, for the powdered benzene clathrate, and for pure benzene over the temperature range of −60 to +80 °C.[16] As might be expected, the pure host crystals yielded a very broad spectrum that was virtually indistinguishable from the background. The benzene clathrate showed a weak singlet at temperatures below −45 °C, which is consistent with restricted molecular motions of the guest molecules. However, above −40 °C the spectrum expanded to a strong singlet, ~2000 Hz wide, that is indicative of considerable molecular motion. In fact,

(21) H. R. Allcock, M. Teeter-Stein, and J. A. Stanko, *J. Am. Chem. Soc.*, **93**, 3173 (1971).

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

(23) R. D. Whitaker and W. C. Guida, *J. Inorg. Nucl. Chem.*, **31**, 875 (1969).

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

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

(26) R. D. Whitaker, A. J. Barreiro, P. A. Furman, W. C. Guida, and E. S. Stallings, *J. Inorg. Nucl. Chem.*, **30**, 2921 (1968).

(27) H. R. Allcock and E. G. Stroh, unpublished work, 1969.

(28) F. R. Ahmed, P. Singh, and W. H. Barnes, *Acta Crystallogr., Sect. B*, **25**, 316 (1969).

the motions were found to be far more extensive than those found in solid benzene itself. Interestingly enough, the space restrictions within the channels suggest that the tumbling motions of adjacent benzene molecules may occur in phase.

Compared to the adducts of III and IV, the *p*-xylene adduct of V exhibits little overall thermal motion of the guest molecules at 25 °C.[20] Proton NMR spectra provided no indication of extensive guest mobility, even when the temperature was raised to 100 °C.[16]

The Driving Force for Clathration

Perhaps the most intriguing feature of the clathration by cyclophosphazenes revolves around the question of *why* these compounds form inclusion adducts. More specifically, which molecular features of cyclophosphazenes favor clathrate formation? What forces hold the host molecules together in the clathrate? What function, if any, is served by the presence of the guest molecules? Why does the tunnel system usually collapse when the guest molecules are removed?

First, it appears that the clathration by host molecules, such as III, IV, V, and VIII, is connected with the unusual *shape* of the molecules. These "paddlewheel"-like molecules are difficult to pack together in a space-saving arrangement. The need for one sidegroup structure in VI to twist in a direction opposite to the other two to avoid intermolecular overlap illustrates this point. When molecules, such as III or IV, are packed together in a high symmetry (hexagonal) arrangement, substantial voids appear in the lattice. Under these circumstances, the presence of the guest molecules serves to fill the voids, to "cushion" the side groups, and to lower the enthalpy of the total system. In many respects, this behavior can be likened to that of a crystalline molecular sponge.

It is worthwhile to consider briefly the energetics of this process. By the use of differential thermal analysis, it can be shown that the loss of guest which occurs from III in the 170–220 °C region is an endothermic process,[18] whereas the spontaneous uptake of benzene by III is strongly exothermic at 25 °C.[13] The loss of benzene from IV at 120–121 °C is also endothermic.[18] From the vapor pressure of benzene over IV in the 37–51 °C range, the thermodynamic constants for loss of benzene have been estimated to be $\Delta H° = 28$ kcal, $\Delta G° = 8.5$ kcal, and $\Delta S° = 67$ cal/deg.[29] The stability differences between the benzene clathrates of III and IV undoubtedly reflect the different tunnel diameters in the two structures. As discussed earlier, the clathrate formed between V and *p*-xylene is much more stable than the clathrates formed by III or IV. Xylene is not released from the lattice of V until the adduct is heated to 223–240 °C,[20] a temperature well below the melting point of V (~360 °C). Presumably, this reflects the greater intrinsic stability of the triclinic lattice formed by V, a lattice that is stabilized by strong host–host interactions.

Thus, the relative stability of each clathrate depends mainly on the strength of the host–host interactions, and it is instructive to consider the nature of these forces. First, it should be emphasized that no evidence has been found for $\pi–\pi$ interactions involving the
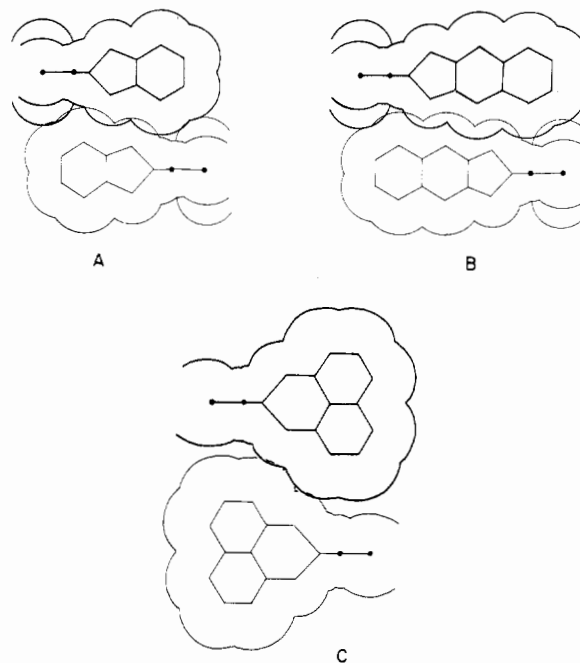

Figure 5. Efficient intermolecular packing arrangements of side groups in (A) III, (B) IV, and (C) V (from ref 20 and 30).

phosphorus–nitrogen rings. The interactions in III, IV, and V appear to fall into two classes—shape-fitting interactions and, just possibly, weak $\pi–\pi$ interactions between neighboring aromatic side groups.[18,20,30]

The shape-fitting feature of the structures is illustrated in Figure 5. There is a clear inducement in all three structures for the van der Waals contacts to maintain the tunnel structure. However, additional strong interactions are found in the structure formed by V. These include both the close contact between the guests and the host side groupings and a curious parallel packing of the aromatic groups on adjacent molecules. These could represent efficient van der Waals contacts, or, alternatively, they could indicate a $\pi–\pi$ interaction between neighboring aromatic rings.

The forces that stabilize the inclusion adducts formed by $(NPPh_2)_3$ (VIII) or tris(*o*-phenylenediamino)-cyclotriphosphazene (VII) are less clearly understood. For example, it is not clear why *sym*-tetrachloroethane forms a clathrate with VIII but xylene, benzene, or acetonitrile apparently do not.[27] The binding energy per mole of tetrachloroethane is only about 8.7 kcal,[26] a value which suggests that coordination or strong dipolar forces are not responsible for its unique behavior. Presumably, the low stability of this adduct can be ascribed to the weak host intermolecular forces in the crystal, which themselves may result from "spinning"-type vibrations of the side groups that are not possible in III, IV, or V. As mentioned earlier, the clathrate structure formed between VII and ketones, such as methyl ethyl ketone, may be stabilized by hydrogen bonding.[17]

Possible Uses

The initial publication describing the clathration behavior of III[13] stimulated the exploration of hydrocarbon separation processes based on this phenomenon.[31-33] These separations are based on the selective

(29) R. D. Whitaker, J. Simon, and D. Victor, *J. Inorg. Nucl. Chem.*, **33**, 2677 (1971).

(30) M. Teeter-Stein, Ph.D. Thesis, The Pennsylvania State University, June, 1973.

absorption of hydrocarbons from a mixture by III, followed by regeneration of the substrate and recovery of the separated organic component. The spirocyclophosphazene is deposited from xylene solution on to ground firebrick or diatomaceous earth, and this substrate is used for the absorption and purging cycles of the separation process. Specifically, processes have been described for the separation of saturated from unsaturated hydrocarbons, monoolefins from diolefins, and hydrocarbons with different chain lengths and different degrees of branching. The xylene isomers, ethylbenzene, styrene, and the C_8 and C_9 alkenyl aromatic hydrocarbons can be separated. The process

is exceedingly efficient. For example, *m*-xylene of 96% purity can be isolated in one step from a mixture of 25% of *p*-xylene, 25% ethylbenzene, and 50% *m*-xylene. It would seem feasible that the clathration phenomenon could also be used in analytical solid–vapor or solid–liquid chromatography separations.

The subject of cyclophosphazene inclusion adducts has grown from a chance observation to an intriguing new field with ramifications in synthesis, x-ray crystallography, solid-state phenomena, and analytical or commercial organic separation processes. We are currently working to further broaden the scope of this field and to delve deeper into the mechanism and uses of the phenomenon.

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Silver Iodide Based Solid Electrolytes

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In many papers in the literature, the term "solid electrolyte" has been used to describe the nature of a salt such as AgBr which has electrolytic conductivity because of its equilibrium concentration of point defects. That is, the conductivity results from annihilation and creation of defects that would not be present if the crystal were ideally perfect. One may say that, in a sense, such crystals have electrolytic conductivity "by accident", because, if they were ideally perfect and no defects were induced in them by an applied electric field, they would have no electrolytic conductivity. At room temperature such salts have specific conductivities in the range $\sim 10^{-6}$–10^{-12} $(\Omega\ cm)^{-1}$.

Electrolytic conductivity in a *true* solid electrolyte is an inherent property of the crystal and is directly associated with the crystal structure. The main structural characteristics of a true solid electrolyte are: (1) a large ratio (in the case of the AgI-based solid electrolytes, between 3 and 6) of sites available to the mobile cations (in some cases, such as the fluorites, the anions are the charge carriers) to the available number of mobile cations; (2) networks of passageways resulting from the face-sharing of anion polyhedra (in some cases, such as the fluorites, both anion and cation polyhedra are involved). These are the most important re-

quirements, but there are others that will emerge in subsequent parts of this Account.

The specific conductivities of these (true) solid electrolytes are several orders of magnitude higher than those that have their origin in point defects. The solid electrolyte with the highest room temperature conductivity is $RbAg_4I_5$, with $\sigma = 0.27$ $(\Omega\ cm)^{-1}$. This may be compared with the conductivity, 0.8 $(\Omega\ cm)^{-1}$, of 35% aqueous H_2SO_4.

This Account will deal mainly with the research carried out by the author and co-workers in the solid electrolyte field. Until very recently all this work has involved the structure and conductivity determination of AgI-based solid electrolytes and the relation between the two. A structure determination of the Cu^+ ion conductor, $(C_5H_5NH)_2Cu_5Br_7$, first reported by Sammells et al.[1] has recently been completed; the structure is related to those of the AgI-based solid electrolytes.

It will be noticed that the term "solid electrolyte" is used to describe the materials discussed in this paper. The use of the terms "super ionic conductor" or "superionic conductor" has become rather widespread. To say the least, such terms are unnecessary. The first is not even *structurally* correct from a linguistic point of view. Neither conveys a correct meaning to the uninitiated and perhaps even to those who are—as some of the literature attests. In fact, there are at least two cases in the literature[2,3] in which the term is reversed;

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