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The equatorial isomer of perhydrotriphenylene (PHTP) gives rise to a wide variety of inclusion compounds with different kinds of molecules, ranging from those with a nearly spherical (e.g., CCl_4) or planar shape (benzene) to linear molecules and macromolecules. All the investigated adducts have a channel-like structure, with the PHTP molecules arranged in infinite stacks whose axes are parallel to the threefold axis of the molecules. The structures of three different adducts are described: (a) one with a n-hydrocarbon, n-heptane (which is isomorphous with those containing n-ethers, n-carboxylic acids, n-esters, and also iso-octane and CCl_4); (b) that with CHCl_3 ; (c) that with cyclohexane. In case (a) no coherence is observed between the rows of included molecules and the host structure, but in (b) and (c) the presence of simple molecular ratios between the host and guest compounds leads to formation of more complex structures. In the (b) adduct two kinds of non-equivalent included molecules are present; the (c) structure results from the packing of parallel PHTP molecules arranged along helices with a small radius (0.40 Å) and nine residues in two pitches, with rows of regularly spaced cyclohexane molecules. Other different crystal structures have been observed: with dioxan; with benzene, or toluene, or bromoform; and with some substituted polybuta-1,4-dienes. The structural results on two different modifications of pure PHTP showing different stability at room temperature, are also reported.

INTEREST in inclusion compounds has increased considerably both as regards their structure and their possible practical applications.^{1,2} Among the most important channel-like inclusion compounds are those of urea and thiourea,³ of tri-*o*-thymotide,⁴ and of cyclodextrins.⁵

The equatorial isomer of perhydrotriphenylene (PHTP),⁶ a new kind of host molecule, forms very stable channel-like inclusion compounds, particularly with linear molecules.⁷ The many different crystal modifications depend on the nature of the guest molecule. The most important properties of the adducts are: (1) their melting points are often higher than those of both host and guest compounds; (2) the existence of inclusion compounds with linear polymers, such as polyethylene, polybuta-1,4-diene, polyoxyethylene;⁸ (3) the fact that the host-host and host-guest interactions

involve only van der Waals forces, with complete absence of dipolar interactions and hydrogen-bonding.

Classes of inclusion compounds of PHTP with different structures are those (a) with linear hydrocarbons, including polyethylene; linear ethers, esters, and monocarboxylic acids;⁷ polyoxyethylene,⁸ CCl_4 , and iso-octane; (b) with CHCl_3 ; (c) with cyclohexane; (c') with dioxan; (d) with benzene, or toluene, or CHBr_3 ; (e) with poly-(2,3-dimethyl-*trans*-buta-1,4-diene); (f) with isotactic poly-(1-methyl-*trans*-buta-1,4-diene). We have also found two crystal modifications of pure PHTP.

The structures of pure PHTP and of a single representative of classes (a), (b), (c), and (c') are described here, together with some information on the (d) class. In Part II⁹ we shall deal with the conformations of some included molecules. Lists of atomic co-ordinates and of observed and calculated structure factors for (a), (b), (c), and PHTP will be published elsewhere.¹⁰

⁶ M. Farina, G. Natta, G. Allegra, and M. Löffelholz, Preprints of the International Symposium on Macromolecular Chemistry, Prague, 1965 (P493); *J. Polymer Sci.*, Part C, in the press.

⁹ G. Allegra, M. Farina, A. Colombo, G. Casagrande Tettamanti, U. Rossi, and G. Natta, following Paper.

¹⁰ G. Allegra, A. Immirzi, A. Colombo, G. Casagrande Tettamanti, and E. Torti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, in the press.

¹ S. M. Hagan, 'Clathrate Inclusion Compounds,' Reinhold, New York, 1962.

² L. Mandelcorn, 'Non Stoichiometric Compounds,' Academic Press, New York, 1964.

³ W. Schlenk, jun., *Fortschr. Chem. Forsch.*, 1951, 2, 92.

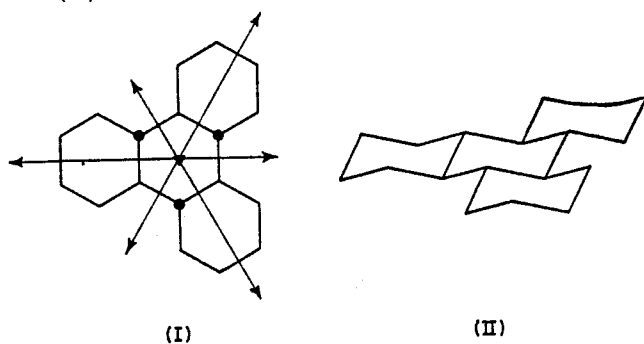
⁴ D. Lawton and H. M. Powell, *J. Chem. Soc.*, 1958, 2339.

⁵ F. Cramer, *Angew. Chem.*, 1952, 64, 437.

⁶ M. Farina, *Tetrahedron Letters*, 1963, 2097.

⁷ M. Farina, G. Allegra, and G. Natta, *J. Amer. Chem. Soc.*, 1964, 86, 516.

Preparation and Characterisation of Perhydrotriphenylene Inclusion Compounds.—*trans,anti,trans,anti,trans*-Perhydrotriphenylene (PHTP) is obtained by catalytic hydrogenation of dodecahydrotriphenylene under very drastic conditions (Pd-C, 300°, 100–200 atm., heptane solvent).⁶ It has a completely equatorial structure and molecular symmetry D_3 . Therefore, it exists in two enantiomorphous forms, one of which is shown in (I) and (II).



The crystalline adducts form readily on crystallisation of PHTP from the guest component, or in the presence of a non-interacting solvent (methyl ethyl ketone, α -pinene, hexachlorobutadiene, and, for very stable adducts, also toluene and methanol).

Many PHTP inclusion compounds are stable up to their melting points, which are higher than those of the components (Table 1). They melt very sharply, and

TABLE 1

Melting points * of some PHTP inclusion compounds
(m. p. of pure PHTP, 128°)

Guest molecule	M. p. of guest	M. p. of adduct
C_{12} n-Hydrocarbon	-9.6°	140.5°
C_{16} "	18.1	148
C_{20} "	36.8	152.5
C_{24} "	61.4	160
C_{28} "	76.2	164
C_{36} "		
Dihexyl ether	<room temp.	134.5
Diocetyl ether	<room temp.	145
Dihexadecyl ether	55	158
C_8 Monocarboxylic acid	-3.2	137.5
C_{12} "	16.5	143.5
C_{16} "	44	153
C_{18} "	64	158
C_{18} "	69	160
Adipic acid	151	166
Sorbic acid	135	138
Methyl laurate	4.8	138.5
Ethyl laurate	<room temp.	142
Octyl laurate	<room temp.	147.5
Methyl stearate	39	147.5
Octyl stearate	32	152.5
Polyethylene	135	181
Poly- <i>trans</i> -buta-1,4-diene	142	183
Poly- <i>cis</i> -buta-1,4-diene	<0	158
Isotactic poly- <i>trans</i> -penta-1,4-diene	91	183
Polyoxyethylene glycol (M.W. 4000)	53	142.5

* Measured with a hot-plate polarising microscope or by differential thermal analysis.

there is no additional peak except for the case of low-boiling guest molecules, where a peak due to the de-

composition of the adduct is observed before melting of pure PHTP.

The method of analysis depends on the guest component: titration with alkali in hot ethanol for carboxylic acids; thermogravimetric methods for highly volatile compounds; removal of PHTP by selective extraction for macromolecular compounds; infrared analysis in the 700–750 cm^{-1} region for n-hydrocarbons; g.l.c. and n.m.r. analysis.

TABLE 2

Composition of some PHTP inclusion compounds

Guest molecule	X-Ray analysis % in weight *	Independent analysis % in weight	Method ‡
n- C_8 Monocarboxylic acid	10.5	10.48	A
n- C_{12} "	10.4	10.47	A
n- C_{14} "	10.1	9.95	A
n- C_{16} "	10.3	10.18	A
n- C_{18} "	10.6	10.44	A
Cyclohexane	11.7	11.7	B
n-Heptane	8.3	8.5	B
n-Nonane	8.7	8.7	C
CCl_4	20.5 †	19.8	B
CHCl_3	19.5	19.4	B
Dioxan	13.0	12.9	B

* These values are drawn from the repeat distances along the c -axis determined by X-ray analysis (see text and ref. 8).
† Repeat: 5.77 Å. ‡ A, Acidimetric titration; B, thermogravimetric analysis; C, infrared analysis.

The good agreement between some of the data obtained and the X-ray results⁹ (Table 2) shows that the guest molecules take up the whole space available in the crystals. Only in the case of a very volatile guest (CHCl_3 , n-hexane, etc.) do crystals tend to fade, changing into mixtures progressively enriched in pure PHTP.

As a check on the purity of high-melting adducts, we verified the absence of endothermal transitions around 128°. A more general method consists of the examination of the X-ray powder spectra; the diffraction peak at $d = 7.60$ Å indicates the presence of an excess of PHTP.

The Two Crystalline Forms of Pure Perhydrotriphenylene.—The most common crystal modification of pure PHTP (modification I) (Table 3) occurs either by crystallisation from a solvent unable to give inclusion compounds (e.g., methyl ethyl ketone, α -pinene) or by sublimation. It has also been obtained by extraction of the volatile guest molecules (e.g., n-heptane, chloroform, cyclohexane) from the corresponding inclusion compounds, or by slow cooling of the melt. This modification is stable under normal conditions.

Since our main requirement was knowledge of the crystal packing, we confined our analysis to two two-dimensional projections, along c and b . At the end of our structural refinement, carried on by Fourier techniques, the disagreement factor R was 0.20 for 202 observed reflections [0.18 and 0.25 for the (h 00) and (h 01) structure factors, respectively], taking isotropic thermal factors for the 18 independent C atoms, and including the 30 related H atoms in the expected positions. The low accuracy of the refinement on the

($h0l$) reflections is essentially due to extended overlapping, both intra and inter-molecular, among C atoms. The resulting figures of the C-C bond lengths and of the CCC bond angles do not differ significantly from the normal values.

TABLE 3

Space groups, unit cell dimensions, number of molecules per unit cell, and densities for all the investigated PHTP modifications

PHTP (modification I)

$a = 19.59 \pm 0.07$, $b = 15.39 \pm 0.06$, $c = 5.36 \pm 0.03$ Å, $\beta = 109.7^\circ \pm 0.3^\circ$; $V = 1522 \pm 9$ Å³; $Z = 4$; Space group $P2_1/a$; $D_c = 1.07$, $D_m = 1.05$ g./cm.³

PHTP (modification II)

$a = 16.94 \pm 0.08$, $b = 10.41 \pm 0.05$, $c = 9.73 \pm 0.05$ Å, $\beta = 113.5^\circ \pm 0.5^\circ$; $V = 1574 \pm 12$ Å³; $Z = 4$; Space group $C2/c$; $D_c = 1.04$, $D_m = 1.03$ g./cm.³

(a) PHTP-*n*-heptane

$a = b = 14.40 \pm 0.05$, $c = 4.78 \pm 0.02$ Å; $\gamma = 120^\circ$; $V = 858 \pm 7$ Å³; $Z(\text{PHTP}) = 2$, $Z(\text{n-heptane}) = 0.45$; Space group $P6_3/m$; $D_c = 1.04$, $D_m = 1.03$ g./cm.³

(b) PHTP-CHCl₃

$a = b = 25.08 \pm 0.10$ Å, $c = 4.78 \pm 0.02$ Å; $\gamma = 120^\circ$; $V = 2600 \pm 21$ Å³; $Z(\text{PHTP}) = 6$, $Z(\text{CHCl}_3) = 3$; Space group $P6_3/m$; $D_c = 1.17$, $D_m = 1.14$ g./cm.³

(c) PHTP-Cyclohexane

$a = b = 25.55 \pm 0.10$ Å, $c = 43.02 \pm 0.20$ Å; $\gamma = 120^\circ$; $V = 24300 \pm 200$ Å³; $Z(\text{PHTP}) = 54$, $Z(\text{cyclohexane}) = 21$; Space group $R\bar{3}$; $D_c = 1.02$, $D_m = 1.01$ g./cm.³

(c') PHTP-Dioxan

$a = b = 25.11 \pm 0.10$ Å, $c = 28.68 \pm 0.15$ Å; $\gamma = 120^\circ$; $V = 15660 \pm 125$ Å³; $Z(\text{PHTP}) = 36$, $Z(\text{dioxan}) = 15$; Probable space group $R\bar{3}$; $D_c = 1.07$, $D_m = 1.05$ g./cm.³

(d) PHTP-benzene or -toluene or -CHBr₃

$a = 15.70$,* $b = 13.85$,* $c = 4.78 \pm 0.02$ Å, $\gamma = 121^\circ \pm 1^\circ$; $V = 890$ Å³; $Z(\text{PHTP}) = 2$; Space group, monoclinic (unique axis c)

* Average values

The molecular packing is represented in Figure 1. The average plane of the molecules is inclined at about 63° to the c -axis. All intermolecular (C...C) distances exceed 3.9 Å, which is very near to the van der Waals limiting value for hydrogen-screened tetrahedral carbon atoms.

A metastable modification (modification II) was obtained by rapid cooling of the melt (Table 3); it changes completely in a few hours into modification I. For this reason no quantitative evaluation of the observed structure factors was possible; however, qualitative comparison of the X-ray intensities with the calculated structure factors enabled us to find out the essential features of the molecular packing. On the basis of the systematic absence of the reflections with ($h k 0$), $h + k$ odd, and with ($h 0 l$), l odd, both Cc and $C2/c$ were possible space groups. By trial and error, we proved that the latter is correct, the molecules being located around crystallographic twofold axes (Figure 2) with their mean planes approximately perpendicular to c . The most satisfactory molecular packing corresponds to the overlap along c

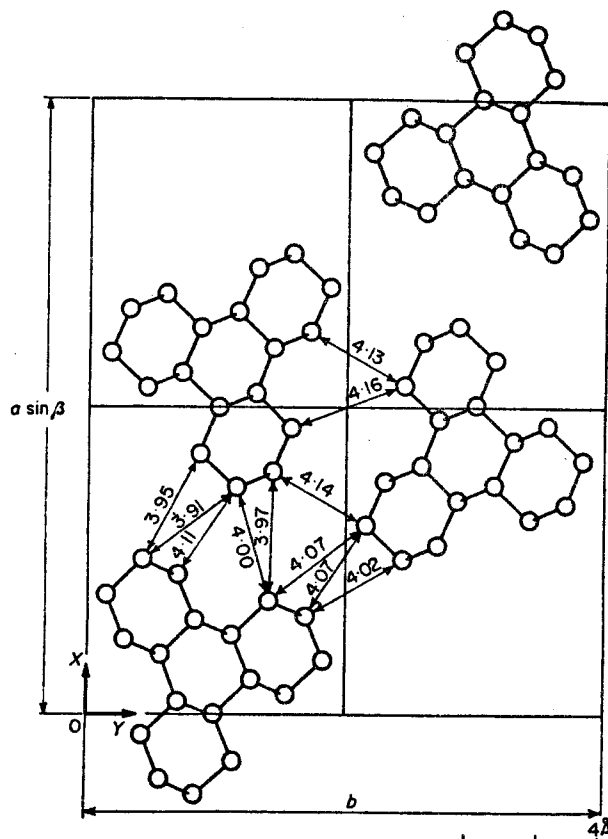


FIGURE 1 Molecular packing of crystalline PHTP, modification I, in projection along c ; the hydrogen atoms have been omitted. The shortest intermolecular (C...C) distances are indicated

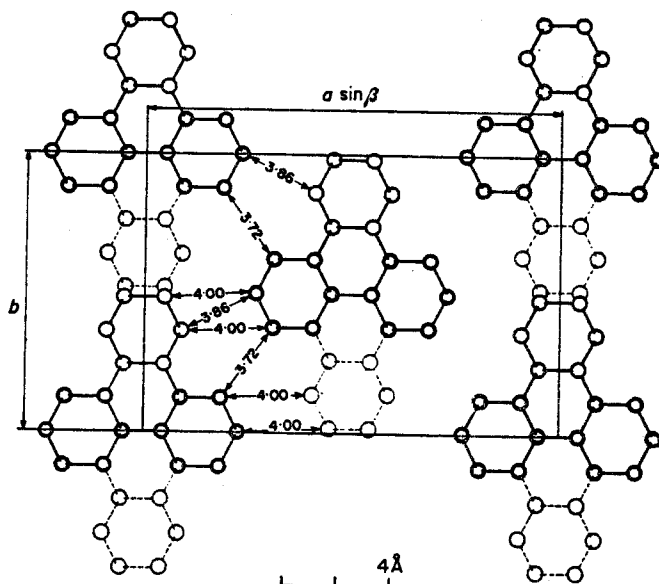


FIGURE 2 Molecular packing of crystalline PHTP modification II, in projection along c . The shortest (C...C) distances are indicated

of two outer rings between neighbouring molecules in opposite orientations; this explains why the c distance is nearly twice that in most PHTP inclusion compounds,

where the molecules exactly repeat along their threefold axes.

The Structure of Some Crystalline Perhydrotriphenylene Inclusion Compounds.—(a) *With linear hydrocarbons.* We report the results for the n-heptane adduct, an example from this isomorphous series. The parameters of the hexagonal unit cell are in Table 3; the equatorial dimensions are slightly greater for some isomorphous adducts containing more bulky molecules (+0.17 Å for CCl₄; +0.31 Å for iso-octane).

On the basis of the reciprocal lattice symmetry, and of the systematic absence of the (000*l*) reflections with *l* odd, possible space groups were $P6_3$ or $P6_3/m$. Good agreement between experimental and observed data on the reflections with *l* ≠ 0 was obtained only by assuming the presence of a crystallographic mirror plane

C—C bond lengths and CCC bond angles do not differ appreciably from the standard values.

No precise location of the n-heptane molecules can be given either in the *ab*-projection or along the *c*-axis; in the electron-density projection along *c* (Figure 3) the image of the n-heptane molecules appears as a diffuse ring around the origin. Their carbon atoms have been assumed to be statistically spread on the surface of a cylinder, whose axis is coincident with the *c*-axis of the unit cell, and whose radius is 0.65 Å. In this assumption the included molecules must contribute only to the (*hki*0) reflections, and the final figures of the disagreement factor on 252 observed independent reflections ($R = 0.12$ for *l* = 0; 0.11 for *l* = 1; 0.13 for *l* = 2) have proved its validity.

In Figure 4, which shows the molecular packing, only

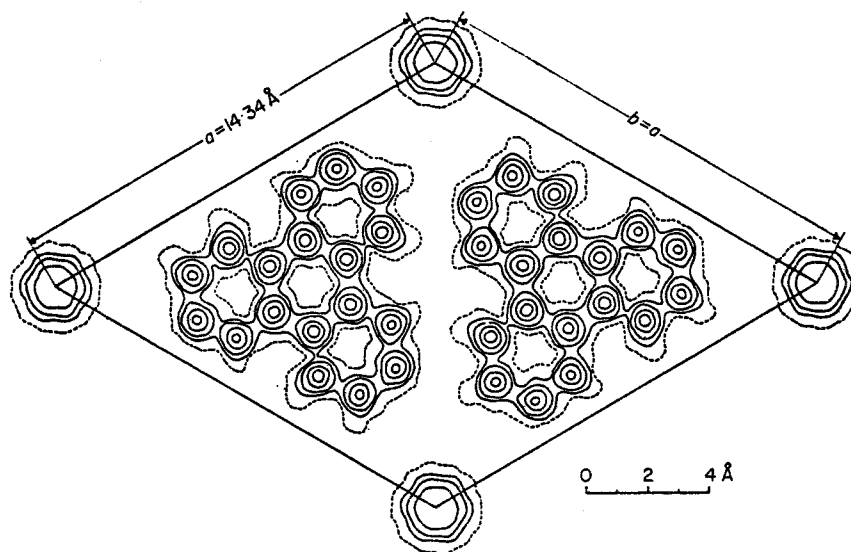


FIGURE 3 Electron density projection along *c* of the PHTP-n-heptane adduct. Contours are drawn at 2 (broken line), 3, 4 . . . e/Å³

(space group $P6_3/m$), coinciding with the average molecular plane. Since PHTP does not possess mirror symmetry, two enantiomorphous molecules must be statistically present in the same crystal site. However, a totally random substitution of any molecule with its mirror image cannot be supported on steric grounds; in such a case unusually short (H . . . H) intermolecular distances (<2.2 Å) would arise between molecules superimposed along *c*. Accordingly, we concluded that long stacks of isomorphous molecules, extending along the *c*-axis, are statistically replaced by stacks of molecules with an opposite optical sign. On the other hand, all the interatomic distances between molecules belonging to neighbouring stacks have practically the same values, whether they have the same optical sign or not.

The parameters of the six independent carbon atoms were determined by trial methods, and the structural refinement was performed through Fourier syntheses and application of least-squares methods, on the basis of the (*hki*0), (*hki*1), and (*hki*2) reflections. The average

an approximate indication of the included molecules is given. The lack of precise location of the heptane molecules along the *c*-axis suggests, in particular, that no simple ratio exists in the crystals between the included molecules and the host structure. The same conclusion was suggested by the presence of two completely diffuse streaks, which appear on the rotating crystal film perpendicular to the *c*-axis (Plate 1); they correspond to a periodicity of 10.69 Å,* due to the infinite rows of included molecules which repeat along the same axis without any coherence with the host structure.¹¹ Analogous streaks are observed with other linear included molecules, whether of the hydrocarbon type or not.

(b) *With chloroform.* The *c*-axis of this modification (Table 3) has exactly the same length as that in case (a),

* We previously reported this periodicity as 11.5 Å;⁷ the present figure results from more accurate measurements.

¹¹ A. E. Smith, *Acta Cryst.*, 1952, 5, 224.

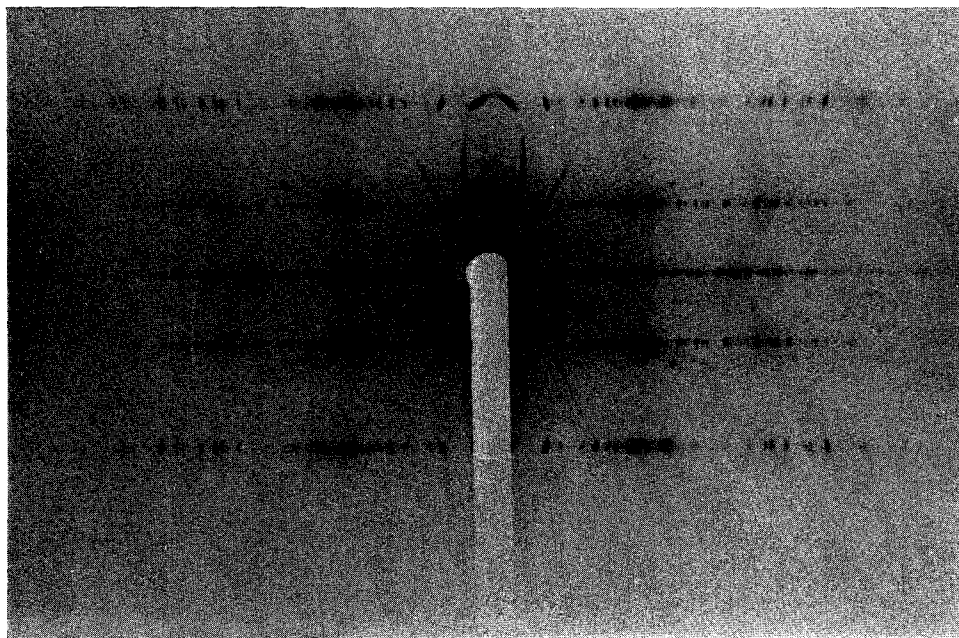


PLATE 1 Rotating-crystal photograph of the PHTP-n-heptane adduct, taken along the c -axis (cylindrical camera, $\text{Cu } K_\alpha$ radiation).
The continuous streaks between the $l = 0$ and $l = \pm 1$ layers are due to the n-heptane molecular rows

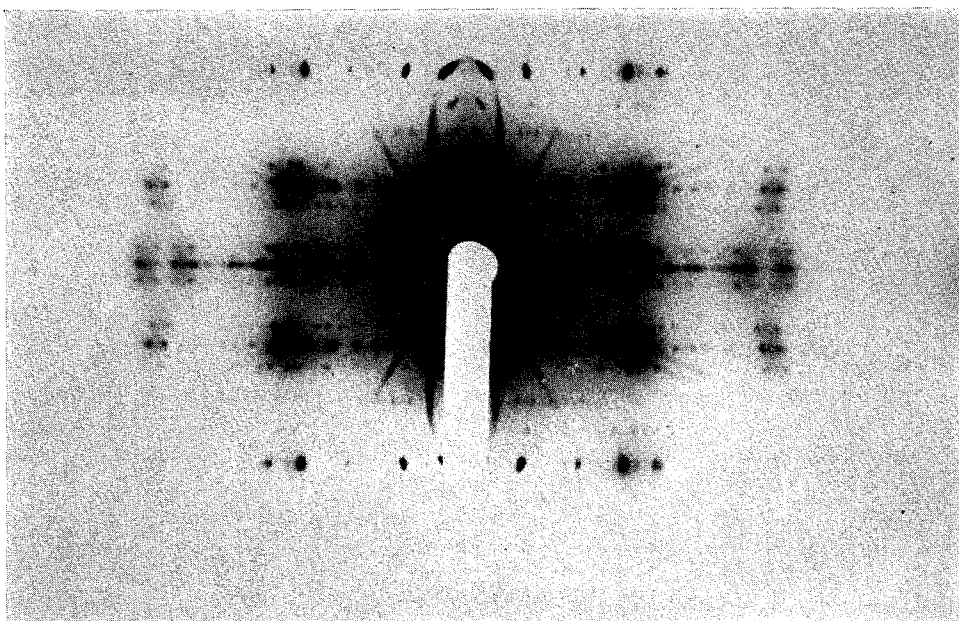


PLATE 2 Rotating-crystal photograph of the PHTP-cyclo-hexane adduct, taken along the c -axis (cylindrical camera, $\text{Cu } K_\alpha$ radiation)

and we concluded that the molecules are analogously packed in the c -direction. Moreover, a is now, to a good approximation, $\sqrt{3}$ times the value in case (a), allowing for 6 PHTP molecules instead of 2 in the unit cell.

On the basis of the X-ray intensity distribution on the $(hki0)$ reflections we arrived at the conclusion that the new axes should approximately correspond to the long diagonals of the previous case [Figure 5 (a)]. The reasons why the unit cell is now three times the size strictly required for crystallographic hexagonal symmetry were investigated. The non-equivalence between the symmetry axes 1 and 2 (Figure 5) might be due either to the presence of included CHCl_3 on some of these axes, with absence on others, or to non-equivalent arrangements of the included molecules on the two axes, or to non-equivalent molecular packing of the PHTP molecules

difference Fourier syntheses and least-squares techniques on the $(hki0)$, $(hki1)$, and $(hki2)$ reflections; R is 0.16 for the three reciprocal layers (315 observed reflections).

In the electron-density map on the ab -projection (Figure 6), an unusual structural feature is the presence of two non-equivalent guest molecules in the unit cell, while the centres of the PHTP molecules are slightly displaced from the positions indicated in Figure 5(a) so as to reduce the hexagonal symmetry of the axes labelled as 2 to threefold symmetry [Figure 5(b)]. The CHCl_3 molecule placed on the hexagonal axis is split into two images according to the symmetry requirements, the axis is in fact of type 6_3 , and it generates two identical units rotated by 60° at a distance $c/2$ ($= 2.39 \text{ \AA}$) through a screw operation. This can happen only by the presence of one molecule in either orientation in every unit

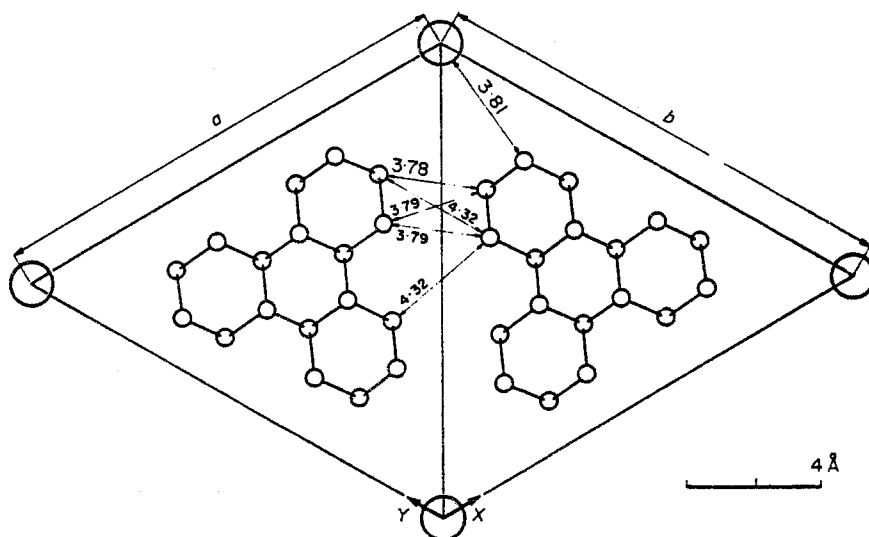


FIGURE 4 Molecular packing of the PHTP-n-heptane adduct, in projection along c . The n-heptane molecules are indicated by circles with a radius of 0.65 \AA (average radial distance of the C atoms from the channel axis). The shortest intermolecular (C...C) distances are indicated

around them, or, eventually, to some of these causes taken together.

The absence of continuous streaks in the rotating-crystal photographs suggests that the chloroform molecules are disposed along the channels at the same repeat distance as occurs for the PHTP molecules; this assumption is in agreement with van der Waals requirements. Moreover, the molar ratio of CHCl_3 to PHTP inside the crystals (Table 2) is close to 1:2, thus suggesting that one chloroform molecule per unit cell is placed in every channel.

The structural resolution started from the ab -projection, mainly using Patterson informations; then the structure factor calculations on the reflections with $l = 0$ proved that the correct space group is $P6_3/m$, with the same kind of statistical substitution among enantiomorphous molecules as resulted for the PHTP-n-hydrocarbon adducts.

The structural refinement was performed through

cell, since their simultaneous presence is forbidden on steric grounds. At the end of the structural refinement, a surprisingly high value of the average thermal factor of the chlorine atoms has resulted ($\bar{B} > 15 \text{ \AA}^2$); this is certainly related to some positional freedom of the CHCl_3 molecules inside the channels.

Analysis of the crystal packing shows reasonable interatomic distances between different molecules (Figure 7); the mutual orientation of two PHTP molecules at van der Waals contact is still very close to that observed in the PHTP-n-hydrocarbon adducts.

(c) *With cyclohexane.* The unit cell of this modification is rhombohedral (Table 3). The c -axis is exactly nine times as large as in the two previously discussed structures; moreover, the reciprocal layers with $l = 9n$ are outstandingly intense. Also, the a ($= b$) axis is nearly the same as in the PHTP- CHCl_3 adduct; therefore we conclude that nine molecules, more or less superimposed along c , are in the cell c -edge, while there

are six stacks of molecules in the *ab*-projection (thus giving a total of 54 PHTP molecules per non-primitive unit cell, and three molecules in the asymmetric unit).

The number of cyclohexane molecules per unit cell was simultaneously derived from inspection of the rotating-crystal photographs along *c* and by thermogravimetric

the analysis. The repeat distance per cyclohexane molecule is therefore 6.14 Å (cf. 6.30 Å for benzene and 5.69 Å for dioxan).

The rotating-crystal photographs along *c* show that only the layers with $l = 9n$ (strong) and $9n \pm 2$ (faint) are detectable (Plate 2). This is in agreement with the

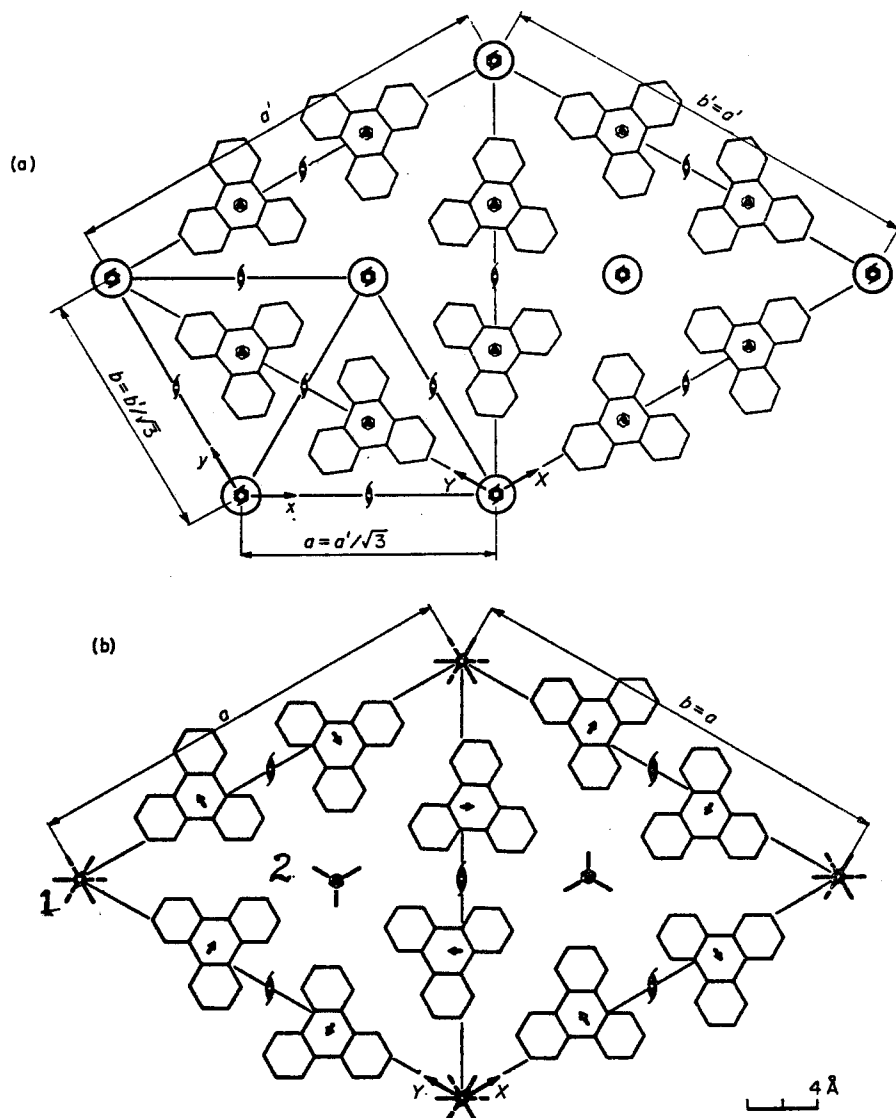


FIGURE 5 Schematic comparison of the molecular packing between (a) the PHTP-n-heptane and (b) the PHTP-CHCl₃ adducts. In case (b) the molecular centres are shifted from the positions corresponding to case (a) along the arrows; this leads to an increase by a factor of 3 of the unit cell size; in (a) the geometrical relationship between the two unit cells is evident. The n-heptane molecules are represented by circles, and the CHCl₃ molecules by three short segments at 120°

analysis (Table 2). In particular, the presence of reflections with low ξ values on the 7th and on the 14th layers, not attributable to diffraction effects due to the PHTP molecules, lead us to conclude that 7 cyclohexane molecules are contained in a *c* length along one channel (21 cyclohexane molecules per unit cell), in accord with

¹³ W. Cochran, F. H. C. Crick, and V. Vand, *Acta Cryst.*, 1952, 5, 581.

hypothesis of a small helical displacement of the PHTP molecules around the crystallographic threefold axes, two pitches of the helix being comprised per every repeat distance.¹² The structural resolution was carried out by trial and error; R $\bar{3}$ has proved to be the correct space group (R3 could also be possible *a priori*, on the basis of the reciprocal lattice symmetry), so every helix, containing the centres of nearly superimposed PHTP

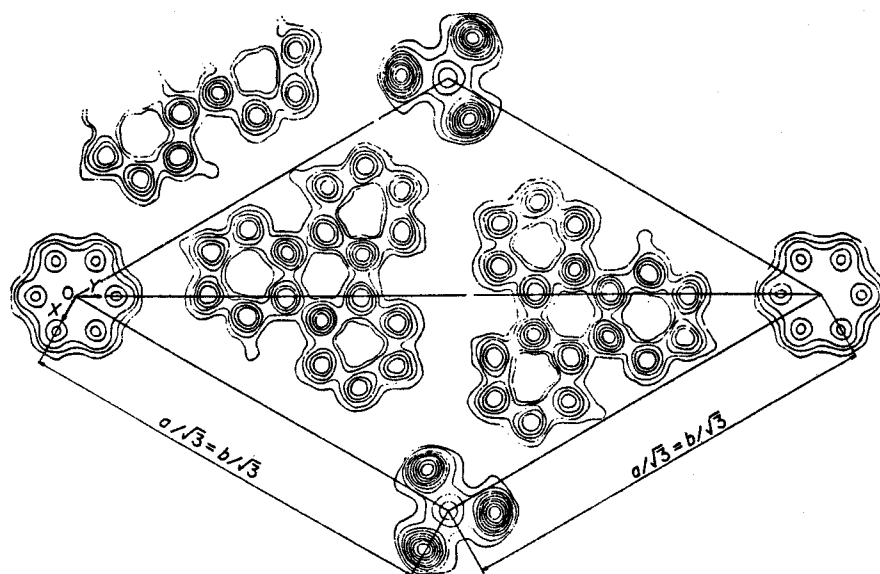


FIGURE 6 Electron density projection along c of the PHTP- CHCl_3 adduct; approximately $1/3$ of the unit cell area is shown. Contours are drawn at 2, 3, 4... $\text{el}/\text{\AA}^2$

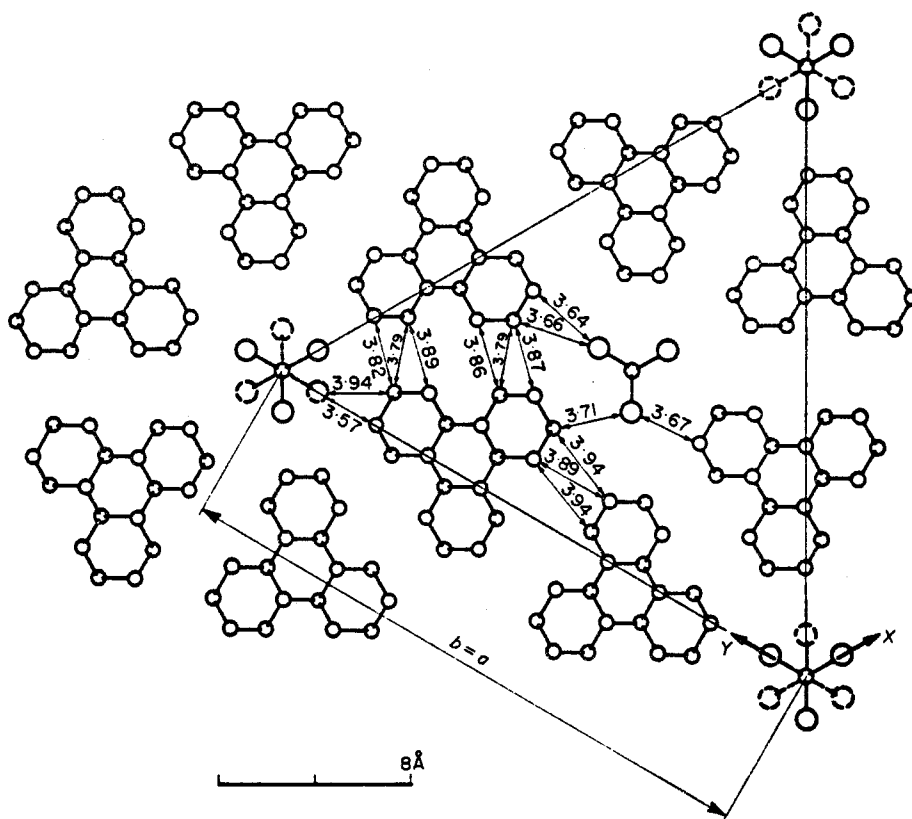


FIGURE 7 Molecular packing of the PHTP- CHCl_3 adduct, in projection along c . The chlorine atoms are represented by larger spheres; the shortest intermolecular ($\text{C}\cdots\text{C}$) and ($\text{C}\cdots\text{Cl}$) distances are shown

molecules, is surrounded by helices of the opposite sense (Figure 8). The best agreement ($R = 0.17$ on 198 observed independent reflections) was obtained assuming

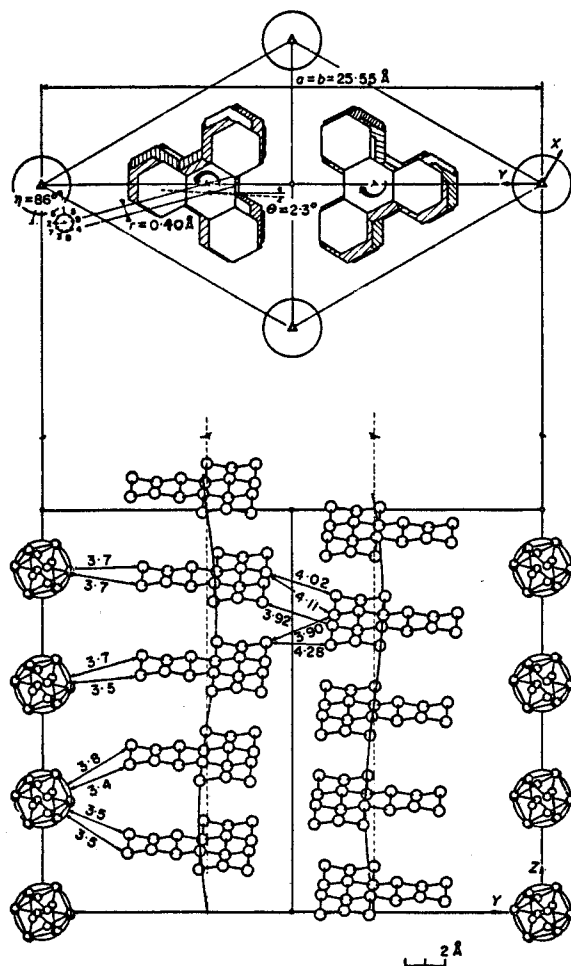


FIGURE 8 Molecular packing of the PHTP-cyclohexane adduct. In the upper part, the view of the structure along the trigonal axis is shown; for sake of clarity the PHTP molecules are represented as opaque objects, and only the C-C bonds are drawn, while the cyclohexane included molecules are indicated with circles. The η , θ , and γ parameters, which characterise the orientation of the PHTP molecules inside the unit cell, are also represented. The numbered points in the small circle correspond to centres of molecules at different z -levels:

$$1 \equiv (-\frac{1}{2}), 2 \equiv (-\frac{1}{2} + \frac{1}{2}), 3 \equiv (-\frac{1}{2} + \frac{3}{2}) \dots$$

In the part shown below, an axonometric view of the structure is represented; all hydrogen atoms are omitted. Only one PHTP molecule is shown in every site, neglecting the mirror-related one, which keeps the same average molecular plane. The $9/2$ helices connecting the molecular centres are also evident. The cyclohexane molecules are represented in three possible symmetrical arrangements. The shortest intermolecular distances are shown; those involving the cyclohexane rings are terminated at the surface of the spheres on which their carbon atoms are assumed to be homogeneously distributed

that the helix radius is 0.40 \AA , and that the mutual displacement between molecules which follow one to another along a helix is represented by a simple translation; moreover, also in the present case a statistical substitution between enantiomorphous molecules has

been assumed. The helical arrangement of the host molecules, which constitutes a very unusual structural feature, is related to the steric requirements of the 7 included cyclohexane molecules, which are properly interlocked with 9 PHTP molecules of every surrounding helix, and statistically disposed in many orientations.

(c') *With dioxan.* In this modification, analogous to the previous one, the c -edge is 6 times as long as in cases (a) and (b) (see Table 3). The observed layers correspond to $l = 6n$ and $l = 6n \pm 1$, those with $l = 6n$ being outstandingly intense. The helical arrangement of the PHTP molecules corresponds in this case to six units per pitch, while there are 5 dioxan molecules in it. The rotating-crystal photographs taken along c show fairly strong reflections on the layer with $l = 5$ at low ξ values; they are mainly due to X-ray interference among the included molecules, their repeat distance being therefore 5.69 \AA .

(d) *With benzene or toluene or bromoform.* The crystals of these adducts were always either twinned or did not belong to a single crystal modification. The prevailing modification is the same for the three adducts, apart from minor changes in the a and b unit cell constants (see Table 3).

The crystal system is monoclinic. No systematic extinction over the observed reflections has been unambiguously assessed, so that the space group cannot be determined at present. The PHTP molecules must certainly lie very closely at right angles to the c -axis, owing to its characteristic length. Consequently the X-ray intensity distribution on the (hkl) reflections shows pseudohexagonal symmetry, which is particularly evident for $d < 1.5 \text{ \AA}$.

The guest molecules are included in channels parallel to c , as indicated by the streaks in the rotating-crystal photographs taken along the c -axis. The molecular repeat distances are 6.30 , 7.90 , and 7.50 \AA for benzene, toluene, and bromoform, respectively. From the diffraction spectra of PHTP-benzene, a series of very faint layers perpendicular to c are observed; their position coincides with that to be expected for (hkl) reciprocal layers with $l = n \pm \frac{1}{2}$. This seems to indicate the presence of a helical arrangement of the PHTP molecules along b , by analogy with the case of PHTP-cyclohexane. In the present case, the helix should contain 4 PHTP units per turn.

(e) *With poly-(2,3-dimethyl-trans-but-1,4-diene) and (f) with isotactic poly-(1-methyl-trans-but-1,4-diene).* The strongest reflections of the X-ray powder spectra are in Table 4, with the d and intensity values. Also included are data for the PHTP- n -heptane adduct. Although no single crystals of (e) and (f) have been obtained hitherto, it is apparent that they must belong to crystalline modifications different from all those previously listed.

Conclusions.—The inclusion compounds where the cage walls are not held together by strong bonds, such as covalent or hydrogen bonds, can vary to a considerable extent in the unit cell size as well as in the crystalline

TABLE 4

Comparison between the observed peaks in the powder spectra of the adducts: (a) PHTP-*n*-heptane; (b) PHTP-poly-(2,3-dimethyl-*trans*-buta-1,4-diene); (c) PHTP-isotactic poly-(1-methyl-*trans*-buta-1,4-diene)

(a)		(b)		(c)	
<i>d</i> (Å)	Rel. int.	<i>d</i> (Å)	Rel. int.	<i>d</i> (Å)	Rel. int.
12.3	100	12.7	57	12.2	30
7.40	21	11.5	48	7.28	15
6.15	14	7.58	30	6.15	7
4.68	40	6.95	20	4.49	100
3.44	3.5	4.96	33	3.82	8
		4.44	100		

structure depending on the nature of the included substances. This allows more or less radical variations of the structure, as already observed in the tri-*o*-thymotide inclusion compounds and largely demonstrated in the present paper for the PHTP adducts. In contrast with such systems, the classical inclusion compounds of hydroquinone, water, urea, and thiourea appear far more strictly bound to prefixed values of the intermolecular distances and, in particular, to a fairly fixed size of the guest molecules; as an example, urea can include linear hydrocarbons only, and thiourea only branched hydrocarbons, while PHTP can include both *n*-octane and iso-octane, both polyethylene and poly-2,3-dimethyl-*trans*-buta-1,4-diene.

The knowledge of different crystal structures involving a given substance, both in the pure state and as a host component, in a series of inclusion compounds, seems of great interest for a general understanding of the molecular aspects of crystallisation.

All the PHTP inclusion compounds are composed of

infinite stacks of host molecules, repeating at about 4.78 Å, parallel to the molecular threefold axes. The regular packing of the stacks gives rise to parallel channels (see Figures 5 and 8). Since the shortest interatomic distances between neighbouring stacks do not vary significantly with the optical sign of the corresponding molecules, a statistical substitution occurs between stacks containing enantiomorphous molecules.

In many cases (*e.g.*, with linear hydrocarbons, ethers, and acids, and also CCl₄ and iso-octane as included molecules) no coherence between the host and the guest structure has been observed. Sometimes, however, complete coherence exists; the corresponding crystal structures (PHTP-CHCl₃, PHTP-cyclohexane, and PHTP-dioxan) are characterised by larger unit cells, due to the particular mode of insertion of the guest molecules. Our *X*-ray analysis was favoured by the rigid conformation of the PHTP molecules; Fourier transform methods as well as Patterson projections were efficient tools for phase determination.

Most of the PHTP inclusion compounds possess hexagonal or trigonal symmetry, in common with other inclusion compounds such as those of urea, thiourea, and tri-*o*-thymotide. Trigonal or hexagonal molecular symmetry seems to be largely favourable for the formation of an inclusion compound; in this connection we note, in addition to PHTP, tri-*o*-thymotide,¹³ cycloveratril,¹³ and tris-(*o*-phenylenedioxy)phosphonitrile trimer.¹⁴

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