

Tetraphenylene Molecular Inclusion Complexes. Crystal Structures of 2(Tetraphenylene) · X, with X = Benzene, Cyclohexane

F. H. HERBSTEIN*

Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel 32000

T. C. W. MAK

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

G. M. REISNER

Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel 32000

and

H. N. C. WONG**

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract. The crystal structures of two compounds belonging to the isomorphous series of clathrate inclusion complexes of tetraphenylene, $2C_{24}H_{16} \cdot X$ (with X = benzene (I) and X = cyclohexane (II)), were solved. For (I), $a = 10.0691(1)$, $c = 18.431(5)$ Å, space group PA_2/n , $Z = 2$; (II) has a very similar cell.

Crystal structure analyses (Nicolet R3m four-circle diffractometer, graphite-monochromated MoK α ; (I) 926 reflections, $R_F = 12.8\%$; (II) 1180 reflections, $R_F = 10\%$) showed that the tetraphenylene molecules use crystallographic C_2 symmetry in the construction of a nearly spherical cavity of point symmetry $\bar{4}$ located about $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. The geometry of the tetraphenylene molecule agrees well with that reported earlier for the crystals of neat tetraphenylene. The enclosed benzene and cyclohexane guests are necessarily disordered. The disorder found for the cyclohexane guest is consistent with its expected *chair* conformation. Analysis of the cell dimensions of a number of complexes shows that the tetraphenylene framework adjusts itself according to the steric requirements of the guests.

Key words: Inclusion, clathrate, clathrand, host/guest, X-ray analysis, tetraphenylene complexes.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82003. To obtain copies, see page ii of this issue.

1. Introduction

Clathrate inclusion compounds of tetraphenylene were first studied by Rapson and Shuttleworth [1]. Recently the preparation, overall crystal structure, and preliminary studies of these complexes, all conforming to the general formula $2C_{24}H_{16} \cdot X$ (X = guest), have been reported [2].

* Author for correspondence.

** Also known as N. Z. Huang.

It was found that the tetraphenylene molecules employ crystallographic C_2 symmetry in the construction of a nearly spherical cavity (free diameter 7.0–7.2 Å) centered around Wyckoff position $2a$ of symmetry $\bar{4}$. The cavity can accommodate a wide variety of guests which must, of course, conform to the requirements of $\bar{4}$ site symmetry, if necessary *via* disorder.

We now report the complete structures of $2C_{24}H_{16} \cdot X$ ($X =$ benzene (**I**) and $X =$ cyclohexane (**II**)). This was undertaken in order to obtain a better understanding of the geometrical properties of the cavity, the way the guests attain the required $\bar{4}$ site symmetry and also in order to compare the geometry of the host with that previously reported for the neat crystal of tetraphenylene.

2. Experimental

Both compounds were handled in the same manner. A selected crystal was taken from the mother liquor and immediately covered with petroleum jelly. It was cleaved with a blade to give an approximately equi-dimensional portion ($0.4 \times 0.4 \times 0.2$ mm for **I**; $0.5 \times 0.4 \times 0.4$ for **II**), which was then lodged in a 0.5-mm-diameter Lindemann glass capillary and sealed with epoxy resin. Determinations of the crystal class, orientation matrix, and accurate unit-cell dimensions (Table I) was performed on a Nicolet R3m four-circle diffractometer [graphite-monochromatized $MoK\alpha$ radiation, $\lambda = 0.71069$ Å] according to established procedures [3].

Table I. Crystal data

Formula	$2C_{24}H_{16} \cdot C_6H_6$	$2C_{24}H_{16} \cdot C_6H_{12}$
a	10.069(1) Å	10.073(1)
c	18.431(5)	18.712(2)
V	1868.6 Å ³	1898.6
Z	2	2
D_c	1.221	1.212
D_m g cm ⁻³	1.221	1.229
Space Group ^a	$P4_2/n$ (No. 86)	$P4_2/n$ (No. 86)
μ (MoK α)	0.64 cm ⁻¹	0.64 cm ⁻¹

^a Origin at $\bar{1}$.

Intensity data were collected at 22 ± 1 °C using the $\omega/2\theta$ technique in the bisecting mode for $2\theta_{\max} = 54$ °, with variable scan speeds from 2.02 to 8.37° min⁻¹ and a scan width from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Background counts were taken for half the scan time at each end of the scan. The crystal remained stable throughout the diffraction experiment, since three standard reflections monitored every 50 data measurements showed only random deviations within 1% of their mean values. The intensities were processed with the learned profile procedure [4], redundant and equivalent reflections were averaged and converted to unscaled $|F_0|$ values following corrections for Lorentz and polarization factors.

3. Solution and Refinement

Both structures were solved by SHELX direct methods which revealed the positions of all the 12 carbons of the asymmetric unit of tetraphenylene. All further refinement (which will be described separately for (**I**) and (**II**)) was performed using the SHELX-77 system of programmes [5].

3.1 COMPOUND (I)

The tetraphenylene part of the structure refined to $R = 23\%$ (anisotropic temperature factors for C and isotropic for H). A difference Fourier map calculated at this stage showed residual electron densities of about $3 \text{ e } \text{\AA}^{-3}$ around $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ in a plane parallel to (001). Four stronger peaks were found and also four weaker ones (of course, only one of the stronger peaks and one of the weaker peaks are crystallographically independent, the others being obtained by the $\bar{4}$ symmetry operation). The stronger peak was resolved into two peaks which are both independent. The $\bar{4}$ symmetry operation thus gives here eight peaks which, together with the four mentioned above, give 12 peaks in all. These could be fitted by two idealised benzene rings (C–C = 1.395 \AA) mutually rotated by 30° . These were then treated as rigid bodies with isotropic temperature factors $U = 0.08 \text{ \AA}^2$ and occupancies of 0.5: benzene hydrogens were not included. Experiment showed that the benzenes could not be refined because of high correlation factors. The benzenes were held fixed and the rest of the structure further refined to convergence at $R_F = 12.8\%$. In all, 141 parameters were refined using 926 reflections for which $F(\text{obs}) > 3.0\sigma[F(\text{obs})]$ (out of a total of 2053). A final difference synthesis showed an electron density residue of about $0.5 \text{ e } \text{\AA}^{-3}$ in the region occupied by benzene.

3.2 COMPOUND (II)

Based on tetraphenylene alone the R factor converged at 19% . A difference Fourier map again showed residual electron density about $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ but this time extending also above and below the plane parallel to (001) and passing through $z = \frac{1}{4}$. Four strong peaks (only one of which is crystallographically independent) were located at $z = \frac{1}{4}$ and eight much weaker ones (two crystallographically independent having identical x and y coordinates) were situated above and below $z = \frac{1}{4}$. As in the case of the benzene guest, the strong peak was resolved into two (both crystallographically independent). The four independent peaks (with occupancies of 0.5 for the two situated at $z = \frac{1}{4}$ and 0.25 for those above and below $z = \frac{1}{4}$) could be fitted into four *chair* conformation cyclohexanes (two pairs, each pair having the four in-plane carbons in common). The cyclohexane could be only partially refined because of high correlation. The C–C distance (1.540 \AA) and the isotropic temperature factor ($U_{\text{iso}} = 0.08 \text{ \AA}^2$) were held constant during refinement, while the cyclohexane hydrogens were not included. The refinement converged at $R_F = 10.0\%$. In all, 147 parameters were refined using 1180 reflections (out of a total of 1662) with $F(\text{obs}) > 3.0\sigma[F(\text{obs})]$. A final difference synthesis showed an electron density residue of about $0.7 \text{ e } \text{\AA}^{-3}$ in the region occupied by cyclohexane. Final atomic coordinates and equivalent isotropic temperature factors are in Table II. Structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division under SUP. 82003.

4. Results and Discussion

4.1. OVERALL MOLECULAR ARRANGEMENT

A packing stereodiagram of the crystal structure of (I) is given in Figure 2. Eight tetraphenylene molecules are arranged so as to form an approximately spherical cavity around $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. The positions of both disordered benzene molecules (which together satisfy the $\bar{4}$ site symmetry) are shown. The host-host and host-guest interactions are of the van der Waals' type.

Table II. Atomic coordinates ($\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogens), equivalent isotropic temperature factors for non-hydrogen atoms ($\times 10^3$) and isotropic temperature factors for hydrogen atoms ($\times 10^2$). ($U_{eq} = 1/3 \text{ tr } (U)$ and $U_{iso} (\text{\AA}^2) = (1/8 \pi^2 B_{iso})$). The first entry is for tetraphenylene of compound (I), the second for (II).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}
C(1)	7135(8)	1849(8)	1409(4)	35(5)
	7151(5)	1852(5)	1373(3)	41(3)
C(2)	7352(10)	983(10)	1980(6)	47(5)
	7389(6)	984(6)	1946(4)	48(3)
C(3)	6703(11)	-211(10)	2030(6)	48(6)
	6732(6)	-215(6)	2014(3)	54(4)
C(4)	5791(11)	-555(11)	1523(6)	53(6)
	5796(7)	-551(6)	1509(3)	56(4)
C(5)	5527(10)	310(10)	959(5)	50(6)
	5514(7)	296(7)	951(4)	52(4)
C(6)	6217(8)	1517(8)	872(5)	37(4)
	6206(6)	1503(5)	864(3)	41(4)
C(7)	5866(10)	2399(8)	267(5)	33(5)
	5869(6)	2396(5)	250(3)	42(3)
C(8)	4574(11)	2839(11)	172(7)	59(7)
	4548(7)	2827(7)	154(4)	57(4)
C(9)	4171(14)	3648(11)	-391(8)	70(8)
	4177(8)	3620(7)	-408(4)	68(5)
C(10)	5111(16)	3956(12)	-896(7)	74(9)
	5096(8)	3993(7)	-906(4)	65(4)
C(11)	6386(15)	3549(11)	-834(6)	59(7)
	6398(8)	3552(6)	-846(4)	56(4)
C(12)	6806(10)	2758(9)	-266(5)	49(6)
	6804(6)	2751(5)	-271(3)	44(3)
H(2)	792(6)	101(6)	219(3)	1(2)
	801(5)	116(5)	226(3)	5(1)
H(3)	689(7)	-74(7)	230(4)	2(2)
	694(6)	-100(6)	243(3)	8(2)
H(4)	531(10)	-128(10)	161(5)	7(4)
	529(5)	-132(6)	152(3)	4(2)
H(5)	486(7)	19(7)	62(4)	2(2)
	497(7)	10(7)	67(3)	7(2)
H(8)	340(6)	263(6)	51(3)	1(2)
	398(5)	264(5)	49(3)	5(2)
H(9)	323(9)	382(9)	-32(5)	6(3)
	323(6)	389(5)	-36(3)	5(2)
H(10)	485(8)	446(8)	-116(5)	3(3)
	477(7)	447(7)	-141(4)	11(3)
H(11)	695(8)	381(9)	-110(5)	4(3)
	705(5)	378(5)	-119(3)	4(2)
Benzene				Occupancies
C(13)	1712	3639	2500	0.50
C(14)	3092	3752	2500	0.50
C(15)	1119	2387	2500	0.50
Cyclohexane				
C(13)	345(2)	337(2)	210	0.25
C(14)	222(2)	390(2)	250	0.50
C(15)	105(2)	291(2)	250	0.50
C(16)	345(2)	337(2)	290	0.25

4.2. HOST; TETRAPHENYLENE

The numbering system was identical for both compounds and is given in Figure 1. The crystallographic C_2 axis passes through the center of a pair of single bonds (C(1) – C(1') and C(12) – (12')) of the eight-membered ring. Chemically equivalent bond lengths, angles and torsion angles are averaged in Table III. All agree well with those reported earlier for the crystal of tetraphenylene [6].

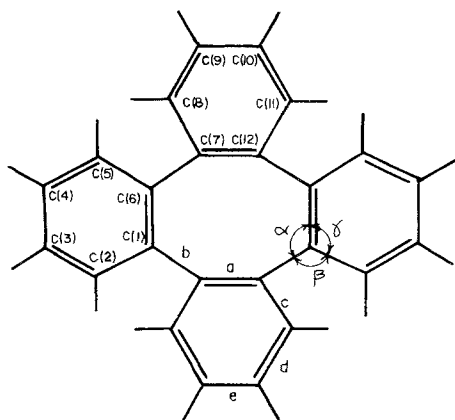


Fig. 1. Schematic representation of the tetraphenylene molecule showing the numbering system used and the chemically equivalent bond lengths and angles.

Table III. Comparison of averaged bond lengths, angles and torsion angles of tetraphenylene as defined in Figure 1.

Bond/Angle	Present work		Irgartinger & Reibel [6]
	(I)	(II)	
<i>a</i>	1.41(1)	1.399(7)	1.400(3)
<i>b</i>	1.48(1)	1.491(10)	1.494(3)
<i>c</i>	1.39(1)	1.398(9)	1.397(3)
<i>d</i>	1.37(1)	1.380(9)	1.381(4)
<i>e</i>	1.35(1)	1.372(9)	1.373(4)
α	122.3(8)	122.6(5)	122.5(2)
β	119.6(9)	118.8(5)	118.6(2)
γ	117.9(9)	118.5(6)	118.8(2)
Torsion angles ($^\circ$)			
C1 – C6 – C7 – C12	64(1)	62.6(7)	
C7 – C12 – C12' – C7' ^a	– 68(1)	– 67.9(7)	
C6' – C1' – C1 – C6	– 67(1)	– 70.4(7)	
Mean ($ \tau $)	66(1)	67.0(7)	66.1(3)
C6 – C7 – C12 – C12'	2(1)	1.6(8)	
C7 – C6' – C1' – C1	– 1(1)	– 3.1(9)	
Mean ($ \tau $)	1.5(1)	2.3(9)	1.0(3)

^a Atoms labelled with primes are related to the reference atoms by twofold symmetry.

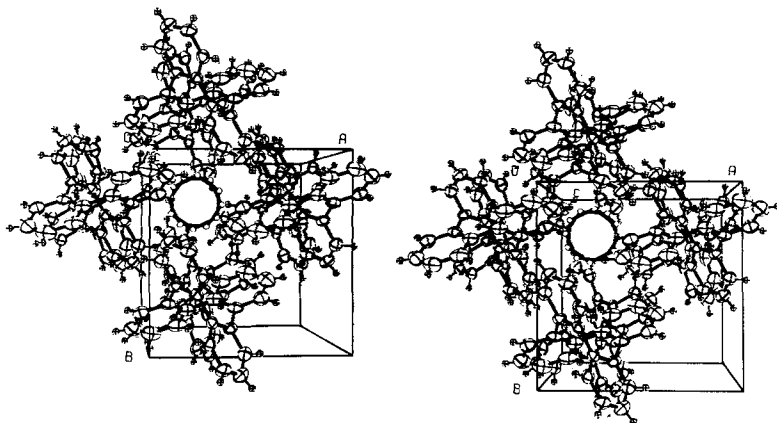


Fig. 2. ORTEP [14] stereodiamgram of the unit cell showing the cavity around $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. Both disordered benzene positions are included. The ellipsoids are of 50% probability.

4.3. GUEST; CYCLOHEXANE

We find four crystallographically independent peaks around $\frac{1}{4} \frac{1}{4} \frac{1}{4}$. This can formally be interpreted in terms of both disordered chair and/or boat conformations. However, in view of the fact that the lowest energy conformation is the familiar chair, we consider the four independent peaks to represent disordered chair conformations.

4.4. THE CAVITY

This has the general shape of an oblate spheroid with its minor axis parallel to [001]; the limiting shape is a sphere of free diameter 7.0–7.2 Å in the CCl_4 clathrate. As noted earlier [2] the dimensions of the cavity undergo slight, but significant, changes with the various guests; the tetraphenylene cagework adapts itself to the not-very-different steric requirements of the guests. This behavior can be observed in Table IV where the various clathrates are ordered according to their unit-cell volumes. This table also presents a comparison between the volume of the cavity (calculated by subtracting the volume of the tetraphenylene [6] from

Table IV. Crystal data ordered according to unit-cell volumes

Guest	Volume (Å ³)			Ref.
	Cell	Cavity	Guest	
CH_2Cl_2	1806	77.7	82.0 (–120 °C)	[7]
Acetone	1813.0	81.2		
Tetrahydrofuran	1815.7	82.6		
CH_2Br_2	1830.6	90.0	95.1 (–90 °C)	[8]
CHCl_3	1831.5	90.5	103.8 (–88 °C)	[9]
Dioxan	1843.5	96.5		
Pr^iBr	1853.3	101.4		
Pr^nBr	1866.2	107.8		
CCl_4	1866.8	108.2	116.6 (10 Kbar)	[10]
Benzene	1868.6	109.0	118.5 (–135 °C)	[11]
Cyclohexane	1898.6	124.1	140.3 (–158 °C)	[12]

the total volume) and the volume of the guest as found in the literature. A remarkably good agreement was found, although we note that the volume of the guest (taken from the literature) is consistently slightly larger than that of the cavity. Thus, we may be tempted to conclude that the packing in the clathrate is more efficient than in the crystals of the neat guest. These results should, however, be viewed with some caution, since all our calculations were based on the assumption that the volume of tetraphenylene in the clathrate is identical to that of the neat crystal. For some of the guests, the volume of the cavity agrees well with that of the guest at high pressures (in the case of the benzene guest, for example, the volume of the cavity is 109.0 \AA^3 while that in benzene-phase (II) at 21°C and 12 kbar is 103.1 \AA^3 [13]).

In order to relate the changes in the volume of the clathrate unit cell to those in the two crystallographically independent axes Table V is presented. The various clathrates were divided into three groups according to the three main families of guests. For group (I) we observe an increase in the a axis when we switch from the five-membered ring of tetrahydrofu-

Table V. Crystal data ordered according to groups of guest molecules

Group	Guest	$a(\text{\AA})$	$c(\text{\AA})$
I	Tetrahydrofuran	9.906(1)	18.503(5)
	Dioxane	9.968(1)	18.553(5)
	Benzene	10.069(1)	18.431(5)
	Cyclohexane	10.073(1)	18.712(2)
II	CH_2Cl_2	9.892(5)	18.46(1)
	CH_2Br_2	9.935(2)	18.546(6)
	CHCl_3	9.925(2)	18.593(3)
	Pr^fBr	9.973(1)	18.633(5)
	CCl_4	9.930(2)	18.932(6)
III	CH_3COCH_3	9.902(2)	18.491(6)
	Pr^rBr	10.004(1)	18.647(4)

ran to the six-membered ring of dioxane. A further increase occurs when changing from dioxane to cyclohexane, no doubt due to the additional hydrogens present in cyclohexane. Since the guest molecules are located essentially in planes parallel to (001) no drastic changes in the c axis are expected for these three non-planar guests. The relatively small changes which do occur are consistent with the degree of nonplanarity of the guests; the c axis being shortest for tetrahydrofuran and longest for cyclohexane. On the other hand, a significant contraction in the c axis is observed in the case of the planar benzene guest.

Several general trends can be discerned in group (II). For instance, there is a slight increase in both axes when switching from CH_2Cl_2 to the bulkier CH_2Br_2 . A similar pattern is observed when changing from CHCl_3 to the larger CCl_4 , the increase in c being, however, more dramatic. This significant change in c would be consistent with an in-plane disorder of the chlorine atoms in CHCl_3 (with the hydrogen being located above and below the plane). Taking into account the fact that the size of the methyl group is close to that of chlorine, the Pr^fBr guest was located (in size) between CHCl_3 and CCl_4 . The c axis for the Pr^fBr guest is virtually identical to that of CHCl_3 , again suggesting an in-plane disorder of the methyl and bromine groups. Consequently, the bulky Br atom causes a significant increase in a . In the CCl_4 clathrate, there is an increase of $\sim 0.4 \text{ \AA}$ in c , which could suggest that the CCl_4 molecule

is located such that the fourth C–Cl bond points along [001], with in-plane disorder of the rest of the molecule; however experimental work in progress (Mak *et al.*) shows that this is an oversimplification.

Finally, in group (III), there is an expected increase in both axes when switching from acetone to the bulkier Pr^{III}Br.

In conclusion, we may summarize that the tetraphenylene cagework is able to adjust itself to the subtle steric requirements of the various guests. This can easily be observed from the changes in the volume of the cavity and even more distinctly by comparing the dimensions of the individual crystallographic axes.

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