JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NORDMAN, C. E. & SCHILLING, J. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 115–123. Copenhagen: Munksgaard.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1984). C**40**, 1721–1723

Structure of the Clathrate Inclusion Compound Tetraphenylene–Carbon Tetrachloride (2/1), $2C_{24}H_{16}.CCl_4$

BY HENRY N. C. WONG,* TIEN-YAU LUH AND THOMAS C. W. MAK†

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

(*Received* 18 *April* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 762{\cdot}61$, tetragonal, $P4_2/n$, $a = 9{\cdot}930\,(2)$, $c = 18{\cdot}948\,(4)$ Å, $V = 1868{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}356$, D_m (flotation in KI/H_2O) = $1{\cdot}355$ g cm^{-3}, $F(000) = 788$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 3{\cdot}52$ cm^{-1}, $T = 295$ K, final $R_F = 0{\cdot}097$ and $R_{wF} = 0{\cdot}079$ for 1047 observed reflections. There are no unusual bond distances or angles. The encaged CCl_4 species exhibits orientational disorder within a nearly spherical cavity of free diameter 7·2–7·4 Å.

Introduction. Tetraphenylene (tetrabenzo[*a,c,e,g*]-cyclooctatetraene) (I) was observed to form addition compounds with small solvent molecules such as CH_3COCH_3, $CHCl_3$, CCl_4, C_5H_5N, C_6H_6, and dioxan over four decades ago (Rapson, Shuttleworth & van Niekerk, 1943). These molecular adducts were recently 're-discovered' and shown to be clathrate inclusion compounds of the general formula $2C_{24}H_{16}.G$, where *G* is a guest species ranging in size from methylene chloride to cyclohexane (Huang & Mak, 1982). Unlike neat tetraphenylene (I), which crystallizes from ethanol in space group $C2/c$ (Irngartinger & Reibel, 1981), the clathrates constitute an isomorphous series belonging to space group $P4_2/n$ with $Z = 2$. X-ray analysis of the $2C_{24}H_{16}.CHCl_3$ clathrate (II) revealed that the host tetraphenylene molecule utilizes crystallographic C_2 symmetry in the construction of the cagework, generating nearly spherical clathration cavities of free diameter‡ 7·0–7·2 Å and site symmetry $\bar{4}$ which accommodate the disordered $CHCl_3$ guest species (Huang & Mak, 1982). A subsequent study of the benzene and cyclohexane clathrates [formulae (III) and (IV), respectively] has established that the tetraphenylene host lattice is capable of adapting itself to the subtle steric requirements of the enclosed guest molecules (Herbstein, Mak, Reisner & Wong, 1984). In order to circumvent the disorder problem, we decided to employ an 'ideal guest species', namely CCl_4 as reported in the present clathrate (V), which fully matches the optimal size and required $\bar{4}$ symmetry of the clathration cavity.

Experimental. Tetraphenylene (I) was prepared by the pyrolysis of biphenylene in the liquid phase (Friedman & Lindow, 1968). Slow evaporation of a solution of (I) in re-distilled carbon tetrachloride at ambient laboratory temperature (295 K) yielded well formed plates of the $2C_{24}H_{16}.CCl_4$ clathrate (V), which gradually turned opaque on exposure to air. A single crystal of (V) was removed from the mother liquor, quickly covered with petroleum jelly, cut to a suitable size (0·4 × 0·4 × 0·3 mm), and sealed in a 0·5 mm

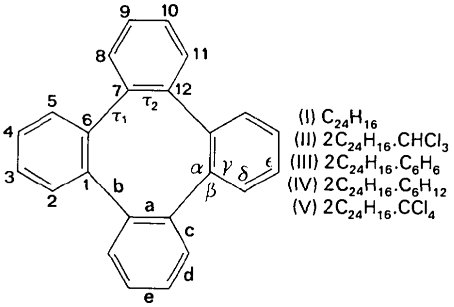

Fig. 1. Structural formula of tetraphenylene (I) showing the numbering system used and labelling of the chemically equivalent bond lengths, bond angles, and torsion angles.

---

* Also known as N. Z. Huang.

† To whom correspondence should be addressed.

‡ As defined by Barrer (1964, p. 318).

0108-2701/84/101721-03$01.50

Table 1. *Atomic coordinates* (× 10⁴) *and thermal parameters* ($\text{Å}^2 \times 10^3$)

$U_{eq} = \frac{1}{3}$trace **U**.

	x	y	z	U_{eq}	Site occupancy
Host molecule					
C(1)	7123 (4)	1849 (4)	1346 (2)	37 (1)	1
C(2)	7322 (5)	987 (5)	1917 (2)	46 (2)	1
C(3)	6598 (5)	−191 (5)	1993 (3)	55 (2)	1
C(4)	5631 (5)	−507 (5)	1503 (2)	55 (2)	1
C(5)	5396 (5)	342 (5)	934 (3)	50 (2)	1
C(6)	6148 (4)	1521 (4)	841 (2)	36 (2)	1
C(7)	5833 (4)	2413 (4)	226 (2)	38 (1)	1
C(8)	4493 (5)	2855 (5)	132 (3)	49 (2)	1
C(9)	4141 (5)	3646 (5)	−434 (3)	58 (2)	1
C(10)	5081 (5)	4014 (5)	−920 (3)	56 (2)	1
C(11)	6403 (5)	3569 (4)	−851 (2)	47 (2)	1
C(12)	6788 (4)	2766 (4)	−279 (2)	36 (1)	1
Guest species					
C(13)	2500	2500	2500	50 (3)	1
Cl(1)	3272 (13)	3579 (10)	1985 (7)	197 (6)	0·500
Cl(2)	819 (9)	2292 (24)	2339 (11)	170 (10)	0·251 (12)
Cl(3)	1606 (23)	2369 (38)	1786 (8)	281 (15)	0·249 (12)

Lindemann-glass capillary partly pre-filled with carbon tetrachloride at its tip portion. The crystal was thus enclosed in a carbon tetrachloride atmosphere, and the petroleum jelly held it stationary against the wall of the capillary.

Nicolet *R*3*m* four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Orientation matrix and unit-cell parameters from established procedure (Sparks, 1976). ω–2θ variable scan (2·55 to 8·37° min⁻¹) technique, range 1° below $K\alpha_1$ to 1° above $K\alpha_2$, background counting for one-half of scan time on each side of intensity maximum. $2\theta_{\max} = 54°$, collection range $0 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq l \leq 25$. Three standard reflections monitored every 50 measurements, intensity variation ±2%. 2055 unique data measured, 1008 observed with $I > 1{\cdot}5\sigma(I)$. Lorentz and polarization factors applied, no absorption correction. Raw intensities processed by learnt-profile procedure (Diamond, 1969).

Structure analysis of (V) commenced with the atomic coordinates of carbon atoms C(1)–C(12), which define a half-molecule of (I) in the asymmetric unit of the chloroform clathrate (II) (Huang & Mak, 1982). A subsequent difference Fourier map showed that the CCl_4 guest molecule, which occupies Wyckoff position 2(*a*), has several preferred orientations of unequal population centered at the C(13) atom. Three electron density maxima lying 1·62–1·72 Å from the fixed C(13) atom had peak heights in the approximate ratio 2:1:1; these were assigned as Cl atoms Cl(1), Cl(2) and Cl(3) with site occupancy factors of $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{4}$, respectively. In the structure refinement, all 16 non-hydrogen atoms in the asymmetric unit were refined anisotropically, C—Cl bond-distance constraints of 1·70 ± 0·01 Å being applied by the method of observational equations (Rollett, 1970). The six H atoms were generated geometrically (C—H fixed at 0·96 Å) assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent C atoms. In the last least-squares cycles, the site occupancy factor of Cl(1) was held at 0·500 while those of Cl(2) and Cl(3) were varied as g and $(0{\cdot}500-g)$, respectively.

SHELXTL program system (Sheldrick, 1982) on Data General Corporation Nova 3/12 minicomputer. Nicolet Zeta 1553 digital plotter. Analytic expressions of neutral-atom scattering factors, anomalous-dispersion corrections incorporated (*International Tables for X-ray Crystallography*, 1974). Refinement by 'blocked-cascade' least squares (Schilling, 1970) with $\sum w(|F_o|-|F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + 0{\cdot}0005|F_o|^2]^{-1}$; g converged to 0·251 (12); final $R_F = 0{\cdot}097$, $R_{wF} = 0{\cdot}079$, $S = 1{\cdot}67$ for 140 parameters and 1047 observed data; $(\Delta/\sigma)_{\max} = 0{\cdot}15$, residual extrema in final difference map +0·42 to −0·49 e Å⁻³.

Discussion. Atomic parameters are listed in Table 1 (origin of space group at $\bar{1}$).* Bond distances, bond angles, and selected torsion angles in the tetraphenylene moiety (I) are displayed in Table 2, in accordance with the numbering scheme given in its structural formula (Fig. 1). A crystallographic C_2 axis passes through the centers of the C(1)—C(1′) and C(12)—C(12′) single bonds of the eight-membered ring. The averaged molecular dimensions in Table 2 are in good agreement with corresponding values reported for uncomplexed tetraphenylene (Irngartinger & Reibel, 1981) and the chloroform, benzene, and cyclohexane clathrates (see Table III in Herbstein *et al.*, 1984), except that the τ_1 values show a wider spread and the

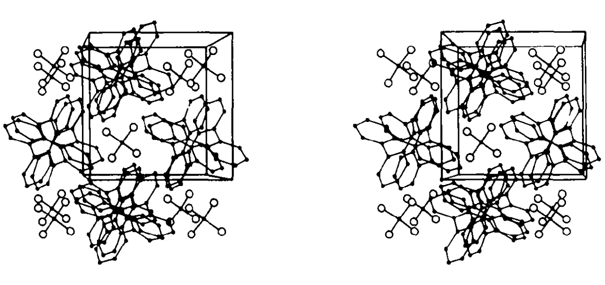

Fig. 2. Stereoview of the molecular packing in the $2C_{24}H_{16}.CCl_4$ clathrate (V), illustrating the environment of a guest species located at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). The disordered CCl_4 molecule is shown in its preferred orientation, and H atoms have been omitted for clarity. The unit-cell origin lies at the upper left corner, with **a** pointing from left to right, **b** downwards, and **c** away from the reader.

---

* Lists of anisotropic temperature factors, structure factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39527 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°), *and selected torsion angles* (°)

Type*	Measured values				Average value
a	C(1)–C(6)	1·400 (6)	C(7)–C(12)	1·392 (6)	1·396 (6)
b	C(1)–C(1′)	1·494 (8)	C(6)–C(7)	1·496 (6)	1·499 (8)
	C(12)–C(12′)	1·508 (8)			
c	C(1)–C(2)	1·394 (6)	C(5)–C(6)	1·399 (6)	1·401 (8)
	C(7)–C(8)	1·413 (6)	C(11)–C(12)	1·399 (6)	
d	C(2)–C(3)	1·380 (7)	C(4)–C(5)	1·389 (7)	1·383 (8)
	C(8)–C(9)	1·373 (7)	C(10)–C(11)	1·391 (7)	
e	C(3)–C(4)	1·372 (7)	C(9)–C(10)	1·362 (7)	1·367 (7)
α	C(6)–C(1)–C(1′)	123·3 (3)	C(1)–C(6)–C(7)	122·6 (4)	123·0 (4)
	C(6)–C(7)–C(12)	122·8 (4)	C(7)–C(12)–C(12′)	123·4 (3)	
β	C(2)–C(1)–C(1′)	117·4 (3)	C(5)–C(6)–C(7)	118·8 (4)	118·0 (9)
	C(6)–C(7)–C(8)	118·6 (4)	C(11)–C(12)–C(12′)	117·1 (3)	
γ	C(2)–C(1)–C(6)	119·1 (4)	C(1)–C(6)–C(5)	118·5 (4)	118·9 (4)
	C(8)–C(7)–C(12)	118·5 (4)	C(7)–C(12)–C(11)	119·3 (4)	
δ	C(1)–C(2)–C(3)	121·8 (4)	C(4)–C(5)–C(6)	121·1 (4)	121·2 (4)
	C(7)–C(8)–C(9)	121·1 (4)	C(10)–C(11)–C(12)	120·8 (4)	
ε	C(2)–C(3)–C(4)	119·2 (5)	C(3)–C(4)–C(5)	120·2 (5)	120·2 (6)
	C(8)–C(9)–C(10)	120·5 (5)	C(9)–C(10)–C(11)	119·9 (5)	
τ_1	C(1)–C(6)–C(7)–C(12)	60·2 (5)	C(6)–C(1)–C(1′)–C(6′)	-70·3 (5)	66·6 (5)†
	C(7)–C(12)–C(12′)–C(7′)	-69·3 (5)			
τ_2	C(7)–C(6)–C(1)–C(1′)	3·9 (5)	C(6)–C(7)–C(12)–C(12′)	3·2 (5)	3·6 (5)

* Types as defined in Fig. 1. Atoms labelled with primes are related to reference atoms by twofold rotation symmetry.

† Average of absolute values.

average τ_2 value is significantly larger. In all instances the bond lengths and bond angles follow the trends: $b >> a \sim c \sim d > e$, $\alpha >> \beta \sim \gamma$, and $\delta > \varepsilon > \gamma$.

The most notable feature in the present structure is that the encaged CCl_4 molecule exhibits orientational disorder, despite the fact that its size and shape ideally conform to the specifications for an ordered guest species. In the model adopted for structure refinement, the guest molecule has a principal orientation of 50% population generated from Cl(1) [C—Cl = 1·64 (1) Å, Cl—C—Cl from 107·0 (8) to 110·7 (4)°]; atoms Cl(2) [C—Cl = 1·71 (1) Å] and Cl(3) [C—Cl = 1·62 (2) Å] together correspond to the superposition of two or more minor molecular orientations making up the remaining 50% population. This description is undoubtedly a gross simplification, and its inadequacy is reflected in the comparatively large estimated standard deviations for the parameters of the Cl atoms (Table 1) as well as their apparent pronounced anisotropy.

Fig. 2 provides a stereoview of the molecular packing in (V) with the CCl_4 guest species shown in its preferred orientation. The significant Cl···C intermolecular distances under 3·80 Å are: 3·53, 3·57 and 3·78 Å for Cl(1); 3·58, 3·64, 3·65, 3·75 and 3·79 Å for Cl(2); and 3·33, 3·43 and 3·45 Å for Cl(3). Based on these van der Waals separations, the clathration cavity in (V) can be considered as nearly spherical with an estimated free diameter of 7·2–7·4 Å. The principal molecular orientation associated with Cl(1) may be rationalized in terms of the smaller number and longer length of the resulting host–guest contacts.

References

Barrer, R. M. (1964). *Non-stoichiometric Compounds*, edited by L. Mandelcorn. New York: Academic Press.

Diamond, R. (1969). *Acta Cryst.* A**25**, 43–55.

Friedman, L. & Lindow, D. F. (1968). *J. Am. Chem. Soc.* **90**, 2324–2333.

Herbstein, F. H., Mak, T. C. W., Reisner, G. M. & Wong, H. N. C. (1984). *J. Inclusion Phenom.* In the press.

Huang, N. Z. & Mak, T. C. W. (1982). *J. Chem. Soc. Chem. Commun.* pp. 543–544.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99, 149. Birmingham: Kynoch Press.

Irngartinger, H. & Reibel, W. R. K. (1981). *Acta Cryst.* B**37**, 1724–1728.

Rapson, W. S., Shuttleworth, R. G. & van Niekerk, J. N. (1943). *J. Chem. Soc.* pp. 326–327.

Rollett, J. S. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 167–191. Copenhagen: Munksgaard.

Schilling, J. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 201–204. Copenhagen: Munksgaard.

Sheldrick, G. M. (1982). *Computational Crystallography*, edited by D. Sayre, pp. 506–514. New York: Oxford Univ. Press.

Sparks, R. A. (1976). *Crystallographic Computing Techniques*, edited by F. R. Ahmed, pp. 452–467. Copenhagen: Munksgaard.