# Clathrate Inclusion Compounds of Tetraphenylene

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Crystallization and *X*-ray studies have revealed the existence of a new class of clathrates in which the host tetraphenylene molecule uses crystallographic $C_2$ symmetry in the construction of the cagework; the clathration cavity of point symmetry $S_4$ can accommodate guest species ranging in size from methylene chloride to cyclohexane.

Ever since the pioneering crystallographic research of Powell[1] over three decades ago, interest in clathrate compounds and molecular inclusion phenomena has expanded at a rapid pace.‡ A major advance in recent years has been the rational design and synthesis of novel host lattices. MacNicol and co-workers[2,3] have skilfully exploited the trigonal symmetry of 'hexa-host' molecules, and it was subsequently recognized[4,5] that two-fold molecular symmetry also plays a dominant role in the architecture of many clathration lattices consolidated by van der Waals' attraction and/or hydrogen bonding. In the present work, we report the discovery of a new class of clathrate compounds in which the host tetraphenylene (tetrabenzo[*a*,*c*,*e*,*g*]cyclo-octatetraene) molecule ($C_{24}H_{16}$, idealized point group $D_{2d}$) uses crystallographic $C_2$ symmetry in the construction of the cagework.

An early electron diffraction study[6] established that tetraphenylene has a tub configuration like that of cyclo-octatetraene.[7] Tetraphenylene crystallizes from ethanol in the monoclinic form (space group $C2/c$), and a detailed *X*-ray analysis has recently been reported.[8] In the course of our studies on benzannelated eight-membered ring systems,[9,10] we discovered that the crystallization of tetraphenylene in chloroform yielded tetragonal plates which gradually turned opaque on exposure to air. The density of the crystallized product as measured by flotation in aqueous potassium iodide solution considerably exceeds that expected for a solid hydrocarbon. These findings are indicative of guest–host interaction in the crystalline solvate and prompted us to undertake a systematic crystallization and *X*-ray study employing a wide variety of potential guest species.

Tetraphenylene was prepared by the pyrolysis of biphenylene in the liquid phase.[11] Clathrate crystals obtained by slow evaporation of solutions of tetraphenylene in 'guest' solvents (G) conform to the general formula $2C_{24}H_{16}\cdot G$ in space group $P4_2/n$ with $Z = 2$. Single crystals were mounted in 0.5 mm Lindemann glass capillaries and unit-cell dimensions were measured on a Nicolet R3 diffractometer with graphite-monochromatised Mo-$K_\alpha$ radiation. The crystal data are

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‡ The first international symposium devoted solely to this field was held in Warsaw in 1980 (contributions dealing with molecular structure were published as *J. Mol. Struct.*, 1981, **75**, 1), and a second meeting has been organised to take place in Parma, Italy in September 1982.

**Table 1.** Crystal data for clathrate inclusion compounds of tetraphenylene.

| Guest solvent, G | Molecular diameter[a]/Å | $a$/Å | $c$/Å | $U$/Å$^3$ | $D_c$/g cm$^{-3}$ | $D_m$[b]/g cm$^{-3}$ |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 6.08 | 9.892(5) | 18.46(1) | 1806 | $1.27_6$ | 1.285 |
| MeCOMe | | 9.902(2) | 18.491(6) | 1813.0 | 1.233 | 1.231 |
| Tetrahydrofuran | | 9.906(1) | 18.503(5) | 1815.7 | 1.245 | 1.258 |
| $CH_2Br_2$ | | 9.935(2) | 18.546(6) | 1830.6 | 1.420 | 1.408 |
| $CHCl_3$ | 6.44 | 9.925(2) | 18.593(3) | 1831.5 | 1.320 | 1.318 |
| Dioxan | | 9.968(1) | 18.553(5) | 1843.5 | 1.255 | 1.262 |
| Pr$^i$Br | | 9.973(1) | 18.633(5) | 1853.3 | 1.311 | 1.309 |
| Pr$^n$Br | *ca.* 6.8 | 10.004(1) | 18.647(4) | 1866.2 | 1.302 | 1.286 |
| $CCl_4$ | 6.68 | 9.930(2) | 18.932(6) | 1866.8 | 1.357 | 1.355 |
| Benzene | 6.90 | 10.069(1) | 18.431(5) | 1868.6 | 1.221 | 1.221 |
| Cyclohexane | | 10.073(1) | 18.712(2) | 1898.6 | 1.212 | 1.229 |

[a] Taken from the tabulation of ref. 13. [b] The measured densities are subject to larger errors for the less stable clathrates.

tabulated in Table 1. Ordering of the clathrates according to their unit-cell volumes provides a rational scale of effective molecular size for the encaged guest species, which seems preferable to one based on the measurement of Stuart-type space-filling models.[12] Like ethanol, some solvents such as methyl iodide (molecular diameter 5.70 Å on the scale[13] adopted in Table 1), acetonitrile, carbon disulphide (molecular diameter 6.20 Å), diethyl ether, and toluene do not form clathrates and simply yield monoclinic tetraphenylene crystals.

Intensity data ($2\theta \leqslant 47°$) were collected for the $2C_{24}H_{16}\cdot CHCl_3$ clathrate by the $\theta$–$2\theta$ scan technique. The structure determination and refinement were carried out using 664 unique reflections [$I > 3\sigma(I)$]. With the unit-cell origin at $\bar{1}$, the host $C_{24}H_{16}$ and guest G molecules occupy Wyckoff positions 4(*e*) of point symmetry 2 and 2(*a*) of point symmetry $\bar{4}$, respectively. The crystallographic $C_2$ axis passes through the centres of a pair of single bonds in the eight-membered ring. The enclosed $CHCl_3$ species is necessarily disordered in its cavity; treatment of the resulting electron density maxima as C and Cl atoms with fractional occupancy factors yielded a final $R$ of 0.113.§ The guest–host interaction is of the van der Waals' type. The clathration cavity is very nearly spherical with a free diameter[14] of 7.0—7.2 Å.

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§ The atomic co-ordinates for this work may be obtained from the Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Any request should be accompanied by the full literature citation for this communication.

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