A New Inclusion Compound between 2,4,5,7,9,10-hexachloro-1,3,6,8-tetrakis (4-methoxyphenylthio)pyrene Host and Cyclohexane Guest Stabilized by C–H···π and C–H···Cl Interaction

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Abstract

Crystal structure analysis shows the 2,4,5,7,9,10-hexachloro-1,3,6,8-tetrakis-(4-methoxyphenylthio) pyrene host and its cyclohexane guest in the *P*nma crystal lattice. The crystal data and refinement parameter for the title compound are: $a = 15.864(3)$, $b = 30.455(6)$, $c = 9.231(5)$ Å, $V = 4459.2$ (14) Å^3. For $Z = 4$ and $M_w = 1045.76$, the calculate density $Dcal = 1.558$ g/cm^3. The C–H···π interaction and C–H Cl interaction stabilized the inclusion of cyclohexane molecules. The S···Cl weak interaction assembled the host molecules into a two-dimensional layer structure, and a three-dimensional structure was obtained by connecting the layers with C–H···O hydrogen bonding.

Introduction

It is well known that highly symmetrical molecule has potential to be host precursor of solvent inclusion compounds [1]. David D. MacNicol and his co-workers [1–3] developed a series of spider-like host molecules to investigate the host–guest interaction between host and guest solvent molecules, such as ether, alcohol, ketone and halocarbon. Keiki Kishikawa and his co-workers [4] summarized that five features should be required to construct the guest–host–guest sandwich structure. According to these assumptions, we synthesized a new C$_{2h}$ symmetric compound, 2,4,5,7,9,10-hexachloro-1,3,6,8-tetrakis(4-methoxyphenylthio)pyrene host molecules, for inclusion of guest molecules and obtained a host–guest–host structure with weak interaction. In crystal structure three kinds of intermolecular weak interaction are involved: S···Cl weak interaction, C–H···Cl interaction and C–H···O hydrogen bonding. The inclusion of guest cyclohexane molecules was accomplished by both C–H···Cl interaction and C–H···π interaction. And the 3-dimentional structure was assembled by S···Cl weak interaction and C–H···O hydrogen bonding.

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Experimental

Synthesis

The title compound was obtained by stirring the mixture of perchlorinated pyrene (C$_{16}$Cl$_{10}$) and sodium salt of 4-methyloxythiophenol (1:12 molar equivalents), in 1,3-dimethyl-2-imidazolidin-one (DMEU) solvent, at ambient temperature for 5 days. The products were purified by column chromatography on Al$_2$O$_3$ eluted with toluene/cyclohexane (1:3). Suitable crystals were obtained from toluene/cyclohexane (1:3) solution for X-ray diffraction in about 2 weeks.

Crystallography

Preliminary examination and data collection were performed with Mo-K$_\alpha$ radiation on the Bruker Smart Apex 2000 diffractometer equipped with a graphite crystal incident beam monochromator ($\lambda = 0.71073$ Å) in ω scan mode at 223 K. The data were corrected for absorption by SADABS program in BrukerAXS program package. The structure of the title inclusion compound was solved by direct methods and refined by full-matrix least-squares on F^2. About 3671 observations with $I > 2\sigma(I)$, out of 3809 unique reflections measured ($R_{int} = 0.0689$) were used in the analysis. About 292 parameters have been refined. All non-hydrogen atoms were treated anisotropically. All hydrogen atoms were

Table 1. Crystal data and structure refinement for p1b

Identification code	p1b
Empirical formula	C50 H40 Cl6 O4 S4
Formula weight	1045.76
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Pnma
Unit cell dimensions	a = 15.864(3) Å α = 90°
	b = 30.455(6) Å β = 90°
	c = 9.2298(17) Å γ = 90°
Volume	4459.2(14) Å^3
Z, Calculated density	4, 1.558 Mg/m^3
Absorption coefficient	0.621 mm^{-1}
$F(000)$	2152
Crystal size	0.32 × 0.03 × 0.24 mm
Theta range for data collection	1.34–23.00°
Limiting indices	$-17 \leq h \leq 17$, $-33 \leq k \leq 33$, $-10 \leq l \leq 10$
Reflections collected/unique	25393/3154 [R(int) = 0.0595]
Completeness to θ = 23.00	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3154/0/292
Goodness-of-fit on F^2	1.175
Final R indices [$I > 2$sigma(I)]	R1 = 0.0944, w$R2$ = 0.2168
R indices (all data)	R1 = 0.0976, w$R2$ = 0.2191
Largest diff. peak and hole	2.576 and −0.725 eÅ^{-3}

positioned at their calculated positions and were assigned common isotropic temperature factors. All calculations have been performed on a personal computer with the SHELX program package [5]. A summary of the data collection and structure refinement information is provided in Table 1.

Figure 1 shows the ORTEP diagram of the title inclusion compound. The atomic coordinates, equivalent isotropic displacement parameters and selected geometric parameters are given in Supplementary section. The distance and angles from donor to acceptor are shown in Table 2.

Results and discussion

As shown in Figure 1, four chlorine atoms (at C16, C16A, C20, C20A positions of pyrene rings) were displaced by 4-methoxyphenylsulfanyl groups with the four substituent groups pointing to opposite orientation in *aabb* type where *a* and *b* denote side chains projecting above and below the mean plane of pyrene core, respectively. The dihedral angle between the four benzene rings and the central 'pyrene ring plane' (C17, C17A, C18, C18A, C19, C19A, plane deviation 0.005 Å) are 61.9° and 62.3°, respectively. Mainly caused by the steric hindrance, the pyrene ring is not coplanar. The C atoms which bonded with Cl atoms (C15, C22, C21) deviated from the 'pyrene ring plane' 0.12, 0.22 and −0.30 Å, respectively, and C20 and C16 which bonded with S atoms deviated from the 'pyrene ring plane' −0.14 and 0.28 Å, respectively.

In the inclusion compound, a 'cavity' can be found built up by two pyrene rings and four benzene rings of substituent groups (Figure 2). The guest cyclohexane

Table 2. C–H···π Interaction and Hydrogen bands [Å and deg.]

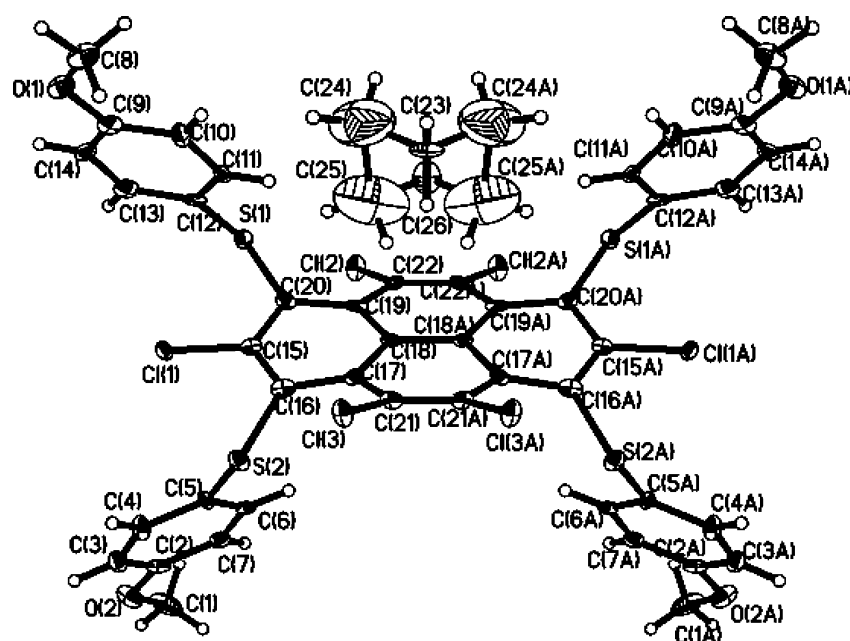| D–H···A	d(D–H)	d(H–A)	d(D···A)	<(DHA)
C26–H26B···π	0.97	2.81	3.75	161.6
C24–H24A···Cl2B	0.97	2.89	3.71	143.0
C1B–H1AB···Cl1A	0.96	2.87	3.31	109.5
C3A–H3AB···O2B	0.93	2.45	3.35	162.5

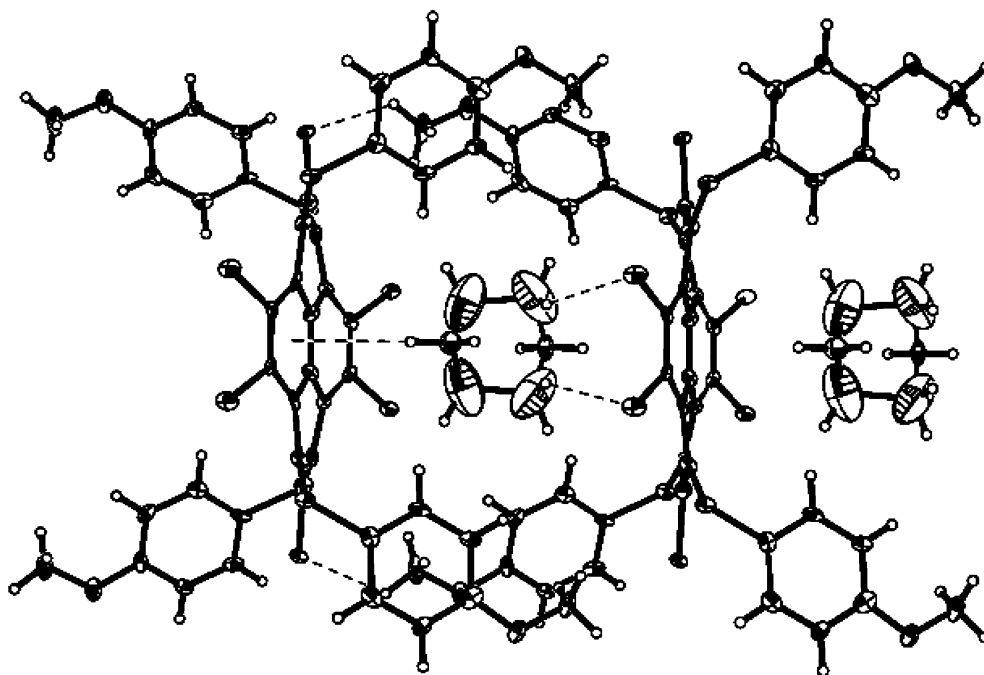*Figure 1. ORTEP* diagram of the title inclusion compound (ellipsoids at 50% probability).

Figure 2. The cavity built up by two pyrene rings and four benzene rings. The dish lines show the C–H⋯Cl and the C–H⋯π interaction stabilizing the inclusion structure. Viewed along **a** axis.

molecule was included in this cavity with chair form. As shown in Figure 2, two neighboring host molecules were linked by C–H⋯Cl interaction with the distance of 2.87 Å (Cl1⋯H1AB and Cl1A⋯H1AC). Freytag and Jones [6] considered that these C–H⋯Cl non-classical hydrogen bonds should be essentially liner and appreciably shorter than the sum of their van der Waals radius. The value, compared with the sum of their van der Waals radius (2.95 Å) [7], shows the occurrence of intermolecular C–H⋯Cl weak interaction. In addition, in the title inclusion compound, two different interaction were included between the 'cavity' and the guest molecules: (i) C–H⋯Cl interaction between the chlorine atoms (Cl2C or Cl2D) of the host molecule and hydrogen atoms (H24A or H24C) of the cyclohexane guest molecule (C–H⋯Cl distance 2.89 Å, see Fig-

ure 2).(ii) C–H⋯π interaction between the guest and the pyrene ring. The centroids of the pyrene (C17, C17A, C18, C18A, C21, C21A and C19B, C19C, C18B, C18AB, C22B, C22C) are apart from the hydrogen atoms of cyclohexane (H26B and H23A) with distance of 2.81 and 2.96 Å, respectively. The former values agree well with those expected for common C–H⋯π interaction [8–10], demonstrating C–H⋯π interaction in the inclusion compound. Different from the classic hydrogen and other no-covalent force, C–H⋯Cl bonding and C–H⋯π interaction in the title compound were rather weak, however, they played a significant role in maintaining the 'cavity' and increasing the stability of the title compound.

As indicated in Figure 3, the title compound forms a one-dimensional chain by C–H⋯Cl weak interaction
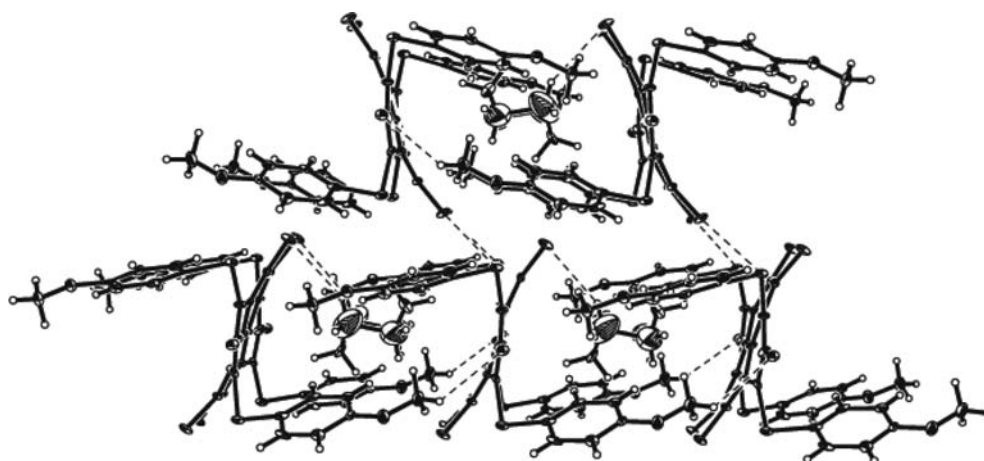

Figure 3. The view of the packing diagram shows the layer structure and the guest molecules are included in the net lattice. The weak interaction between S atoms and Cl atoms are shown to construct the two-dimensional layer structure. Viewed along **b** axis.
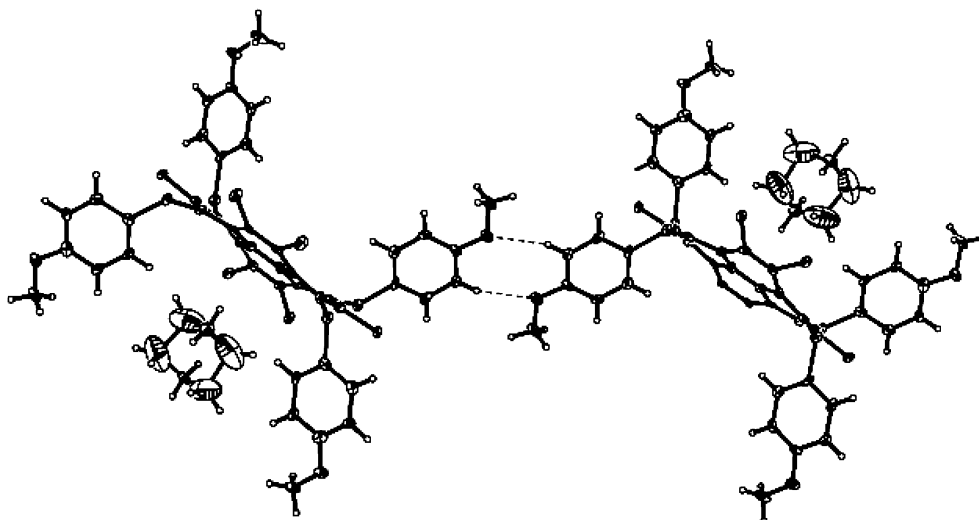
Figure 4. The C–H···O hydrogen bonding linked two host molecules that belong to different layers so as to assemble the neighboring layers. Viewed along **a** axis.

(with H···Cl distance of 2.87 Å), viewed along **b** axis. Moreover, S···Cl weak interaction can be observed between two neighboring 'chains.' Han-Dong Yin and his co-workers [11] reported the S···Cl weak interaction with S···Cl distance of 3.487 Å in the complex of organotin (IV) with dithiomorpholinocarbamate ligand. In our work the S···Cl distance is 3.49 Å implying the occurrence of weak interaction. As a result, a layer with two-dimensional network structure was obtained. Furthermore, the layers were connected by C–H···O hydrogen bonding (O2A···H3AB and O2B···H3AA) with distance of 2.45 Å (see Figure 4) to give a three-dimensional structure.

In conclusion, we have prepared a new compound based on C–H···Cl interaction (with distance of 2.89 Å) and C–H···π interaction (with distance of 2.81 Å). The crystal structure exhibits that the C–H···Cl interaction and C–H···π interaction played a vital role in stabilizing the 'cavity' structure and the inclusion of guest molecules. Furthermore, molecules of the title compound are connected by intermolecular S···Cl contacts (with distance of 3.49 Å) and C–H···O hydrogen bonding (with distance of 2.45 Å) to give a three-dimensional network. The result indicated that intermolecule weak interaction should be considered for the molecule design, likely leading to unusual supramolecular structure.

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