Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Complexation with Diol Host Compounds. Part 35: Inclusion Compounds of 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol with CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3CN

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To cite this Article Caira, M. R. , Jacobs, A. , Nassimbeni, L. R. and Toda, F.(2004) 'Complexation with Diol Host Compounds. Part 35: Inclusion Compounds of 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol with CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3CN', Supramolecular Chemistry, 16: 2, 107 — 112

To link to this Article: DOI: 10.1080/10610270310001607807

URL: http://dx.doi.org/10.1080/10610270310001607807

Supramolecular Chemistry, March 2004, Vol. 16 (2), pp. 107–112

Complexation with Diol Host Compounds. Part 35: Inclusion Compounds of 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol with CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3CN

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Received (in Southampton, UK) 15 May 2003; Accepted 24 July 2003

Inclusion compounds were formed with 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (H) and carbon tetrachloride, chloroform, dichloromethane and acetonitrile. 1 ($H\cdot 1/2CCl_4$), 2 ($H\cdot 1/2CHCl_3$) and 3 ($H\cdot 1/2CH_2Cl_2$) are true clathrates with the guest molecules situated in cages created by the host. 4 ($H\cdot 2CH_3CN$) exhibits a different packing arrangement with the guest molecules located in channels. The crystal structures and stability of these inclusion compounds were investigated.

Keywords: Inclusion compounds; Clathrates; Kinetics; Isostructurality

INTRODUCTION

Diol hosts have been shown to be highly versatile in the preparation of a large variety of inclusion compounds. This particular host, 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (**H**), is an example of a wheel-and-axle compound and includes a large number of different guests. The structure of the non-porous form of the host compound, the apohost, has been elucidated [1] and the kinetics of complexation with acetone and the solid-state reaction with benzophenone have been described. The host–guest complexes obtained with apolar molecules cyclohexane and the xylene isomers have been studied [2]. The structures of its inclusion compounds with the lutidine [3] and picoline [4] isomers have been solved and its selectivity of aminobenzonitrile isomers both from solution and by solid–solid reaction has been studied [5]. The dynamics of guest exchange occurring between this host and the guests tetrahydrofuran (THF) and thiophene (THIO) have been discussed, and a mechanism for the exchange reaction has been proposed [6]. We now present the results of the structural analyses and kinetics of desorption obtained from the inclusion of carbon tetrachloride, chloroform, dichloromethane and acetonitrile by the host, (**H**). The atomic numbering is shown in Scheme 1 (all hydrogens except the host hydroxyl hydrogens have been omitted for clarity).

STRUCTURE DETERMINATION AND REFINEMENT

Suitable crystals of **1** ($\mathbf{H}\cdot 1/2CCl_4$) and **4** ($\mathbf{H}\cdot 2CH_3CN$) were obtained by slow evaporation of dilute solutions of the host **H** in the liquid guest at room temperature, while inclusion compounds **2** ($\mathbf{H}\cdot 1/2CHCl_3$) and **3** ($\mathbf{H}\cdot 1/2CH_2Cl_2$) were grown at 4°C. Preliminary cell dimensions and space group symmetry were determined photographically. These unit cell dimensions were subsequently refined on a Nonius Kappa CCD diffractometer using graphite-monochromated MoKα radiation. The strategies for the data collections were evaluated using the COLLECT [7] software. The data were scaled and reduced using DENZO-SMN [8]. The crystal data and important experimental details of the data collections are given in Table I. All four structures were solved by direct methods using

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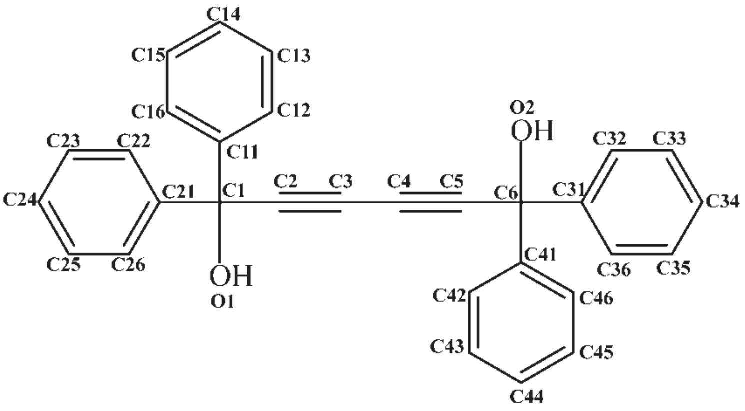
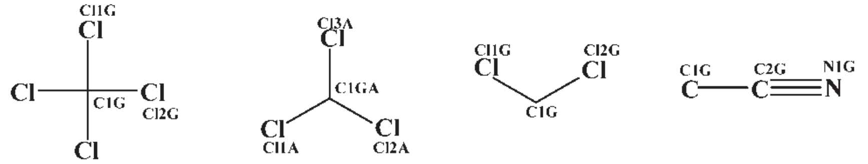
ISSN 1061-0278 print/ISSN 1029-0478 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/10610270310001607807



1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (H)



carbon tetrachloride chloroform dichloromethane acetonitrile

SCHEME 1

SHELXS-97 [9] and refined using full-matrix least-squares with the program SHELXL-97 [10] refining on F^2. The non-hydrogen atoms were treated anisotropically and the aromatic hydrogens were geometrically constrained with a common temperature factor. All the hydroxyl hydrogens were located in the difference electron density maps and were refined with a simple bond length restraint and independent isotropic thermal parameters.

Compounds **1** and **2** crystallize in the space group $C2/c$ with $Z = 8$. In both structures the host was located in general positions with the guest molecules situated on a twofold axis at Wyckoff position e. For **2** the carbon and chlorine atoms of the guest are disordered over two positions with site occupancy factors of 50% and the hydrogen atoms were omitted from the final model.

Compound **3** crystallizes in the space group $P2_1/n$ with $Z = 8$. Consequently the asymmetric unit consists of two host molecules and one guest molecule with both the hosts and guest in general positions.

Compound **4** crystallizes in the space group $P2_1/n$ with $Z = 2$. The host molecule was located on a centre of inversion at Wyckoff position a, with the guest in general positions. Crystallographic data for compounds **1** to **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC nos 209472 (**3**), 209473 (**4**), 209474 (**2**) and 209475 (**1**). Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

THERMAL ANALYSIS

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a Perkin-Elmer PC7-series system. TG analyses were used to determine accurate host:guest ratios, while DSC measurements yielded the onset temperatures of guest release and allowed the monitoring of any phase changes that may occur in the structures during heating. Crystals were blotted dry and crushed before analysis. Experiments were performed over a temperature range of 30–200°C at a heating rate of $10°\mathrm{C\,min}^{-1}$ with a purge of dry nitrogen at $40\,\mathrm{ml\,min}^{-1}$.

DISCUSSION

Structures **1**, **2** and **3** exhibit a distinctive host conformation in that the hydroxyl moieties are *gauche*. The torsion angles O(1)–C(1)···C(6)–O(2) for these three compounds were calculated as: **1** — 57.7(3)°, **2** — 56.1(2)° and **3**—54.3(2)°, 57.2(2)°. The host molecules self-assemble to form a tetrameric hydrogen bond network and guests are trapped in the resultant cavities. This is illustrated in Fig. 1. Similar packing

TABLE I Crystal data, experimental and refinement parameters

	1	**2**	**3**	**4**
Compound	$C_{30}H_{22}O_2 \cdot 1/2CCl_4$	$C_{30}H_{22}O_2 \cdot 1/2CHCl_3$	$C_{30}H_{22}O_2 \cdot 1/2CH_2Cl_2$	$C_{30}H_{22}O_2 \cdot 2CH_3CN$
M_W, g mol^{-1}	491.38	473.66	456.94	496.58
Temperature, K	200(2)	173(2)	173(2)	200(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
a, Å	22.190(10)	22.270(5)	17.083(3)	10.847(2)
b, Å	13.775(3)	13.869(3)	13.629(3)	8.251(2)
c, Å	17.38(3)	16.934(3)	22.274(5)	15.364(3)
α, °	90	90	90	90
β, °	107.49(7)	107.71(3)	108.02(3)	91.05(3)
γ, °	90	90	90	90
V, Å^3	5067(9)	4982.2(2)	4931(2)	1374.8(5)
Z	8	8	8	2
Absorption coefficient, mm^{-1}	0.282	0.232	0.180	0.075
$F(000)$	2040	1972	1912	524
Crystal size, mm	0.31 × 0.25 × 0.47	0.44 × 0.30 × 0.22	0.61 × 0.51 × 0.33	0.28 × 0.39 × 0.31
Index ranges	h: 26,25; k: 0,16; l: 0,20	h: −26,20; k: ±16; l: −19,17	h: ±22; k: −17,15; l: −26,28	h: ±12; k: 0,9; l: −5,18
Reflections collected/unique	4628/4465	12323/4356	23752/11091	2577/2416
Data/restraints/parameters	4465/4/320	4356/4/333	11091/8/620	2416/2/177
Goodness-of-fit	0.923	1.052	1.045	0.991
ρ_{calc}, g cm^{-3}	1.288	1.263	1.231	1.200
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0637$ $wR_2 = 0.1687$	$R_1 = 0.0668$ $wR_2 = 0.1691$	$R_1 = 0.0742$ $wR_2 = 0.1928$	$R_1 = 0.0479$ $wR_2 = 0.1243$
R indices (all data)	$R_1 = 0.1530$ $wR_2 = 0.1906$	$R_1 = 0.1148$ $wR_2 = 0.1956$	$R_1 = 0.1088$ $wR_2 = 0.2192$	$R_1 = 0.0780$ $wR_2 = 0.1338$
Largest difference peak and hole, e Å^{-3}	0.340 and −0.321	0.460 and −0.451	0.843 and −1.155	0.163 and −0.258

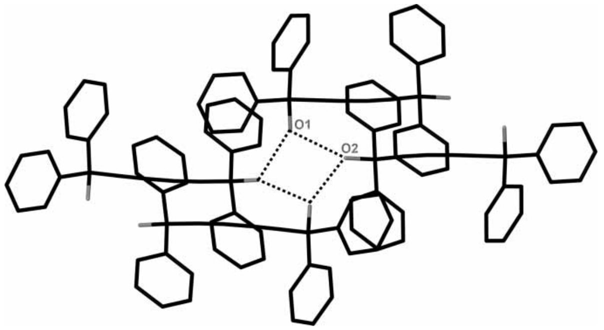


FIGURE 1 Hydrogen bonding scheme for **1**.

motifs have been observed in the crystal structures of this host and cyclohexane, the isomers of xylene [2] and furan [6]. The cavities have been mapped using the program SECTION [11] and were found to have approximate dimensions of: (**1**) 9.8 × 9.5 × 6.7 Å, (**2**) 6.5 × 6.3 × 5.5 Å and (**3**) 5.2 × 6.1 × 6.7 Å. Although there is no host–guest hydrogen bonding, structures **1**, **2** and **3** are stabilized by short aromatic C–H···π contacts [12] less than 3.05 Å between certain aromatic C–H bonds of one host and the phenyl rings of a neighbouring host molecule. Compound **3** also has an extra (Guest)–C–H···π-(Host) interaction of 3.26 Å. Structures **1** and **2** are isostructural with respect to the host framework and **3** exhibits an analogous molecular packing arrangement.

The lengths of the hydrogen bonds are similar, with O···O distances of: (**1**) 2.721(4), 2.710(4); (**2**) 2.689(1), 2.702(1); (**3**) 2.711(1), 2.689(1), 2.677(1) and 2.673(1) Å. For **4**, symmetry requirements dictate that the host hydroxyl groups adopt the *trans* conformation. The guest molecules are located in channels parallel to [010], as shown in Fig. 2a, and are stabilized by (Host)–O–H···N-(Guest) hydrogen bonds. A perspective of the host–guest system is shown in Fig. 2b.

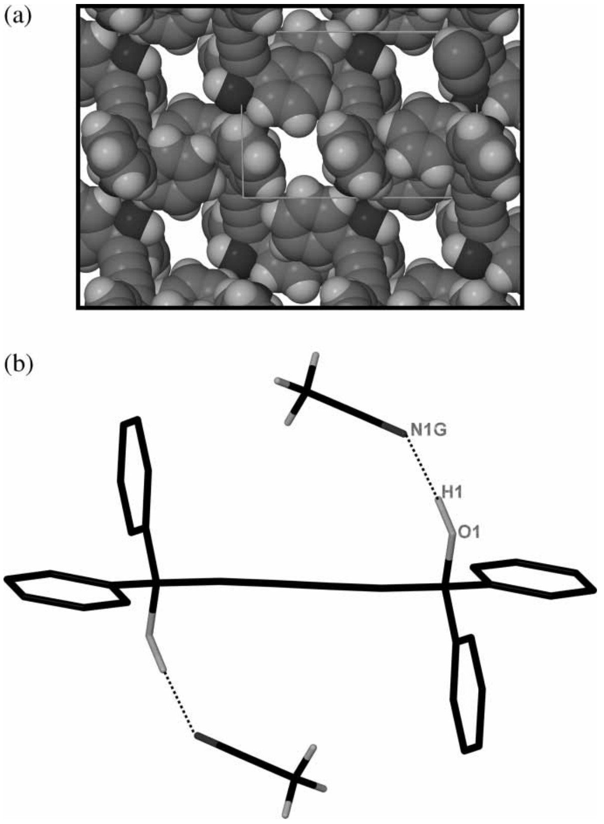


FIGURE 2 (a) Space-filling projection of **4** along [010] with guests omitted, showing the open channels. (b) Perspective of **4**.

A typical thermal analysis result is shown in Fig. 3. In all four compounds the TG shows a two-step desolvation but the individual steps do not correspond to a simple stoichiometry. Overall there is good agreement between the experimental and calculated host:guest ratios, with 1:0.5 the host:guest ratio for compounds **1**, **2** and **3** and 1:2 the host:guest ratio for **4**. The DSC curves show three distinct endotherms, corresponding to the loss of guest and the host melt. A summary of the thermal analysis results is given in Table II, where T_{on}, the endotherm onset temperature, is compared with T_b, the normal boiling point for each guest. Note that the highest

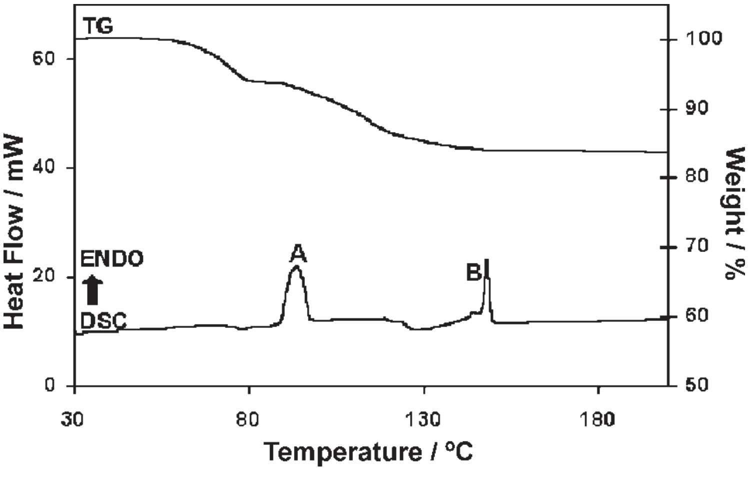


FIGURE 3 Thermal analysis results for **4**.

TABLE II Thermal analysis data

			1	2	3	4
H:G ratio			1:0.5	1:0.5	1:0.5	1:2
TG results	Calc. % mass loss		15.7	12.6	9.3	16.5
	Exp. % mass loss		16.2	12.6	9.3	16.2
DSC results	T_{on} (K)	A*	380.1	366.9	369.5	361.9
		B*	420.1	420.5	420.6	419.6
Normal boiling points T_b (K)			349.7	334.5	312.8	354.6
T_{on}/T_b			1.087	1.097	1.181	1.021

*A and B refer to the endotherms as indicated in Fig. 4.

value of T_{on}/T_b is obtained for compound **3**, which shows a stronger affinity of the host compound for dichloromethane than for carbon tetrachloride or chloroform. This is not totally unexpected due to the additional C–H···π interaction that exists between the host and the dichloromethane guest. It has been observed that C–H···π interactions enhance the stability of inclusion compounds [13].

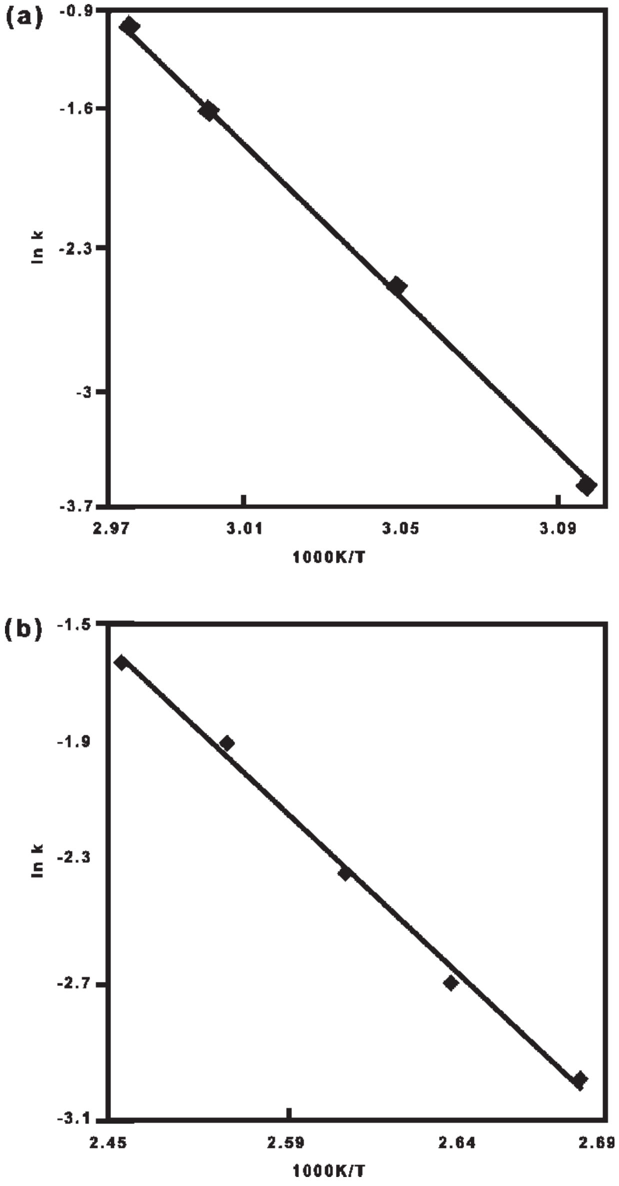


FIGURE 4 Arrhenius plots of **4** for (a) the first desolvation step and (b) the second desolvation step.

KINETICS

For compound **4** the kinetics of desolvation were analysed by carrying out a series of isothermal TG experiments. The two distinct steps in the TG were analysed separately and activation energies obtained for each of them. For step one the mass-time curves were deceleratory and fitted the first-order rate law:

$$-\ln(1-\alpha) = kt$$

where α is the extent of the reaction and k is the rate constant [14].

TG experiments were carried out between 50°C and 63°C. The corresponding Arrhenius plot is shown in Fig. 4a, and yielded an activation energy of 174(6) kJ mol^{-1}.

The second step also yielded deceleratory curves but these followed the three-dimensional diffusion rate law, D3:

$$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2 = kt$$

and the corresponding Arrhenius plot, carried out over a temperature range of 100–120°C, yielded an activation energy of 84(5) kJ mol^{-1} (Fig. 4b).

The higher activation energy obtained for the first desolvation can be explained by the higher diffusion barrier that has to be overcome, possibly as a result of the crystallite size.

CONCLUSION

This study illustrates two different conformations of the host compound 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol. Inclusion of the chlorinated guests results in the guests being situated in cavities with the hydroxyl groups of the host adopting the *gauche* conformation, whereas inclusion of acetonitrile results in the guests being situated in channels with the host hydroxyl groups adopting the *trans* conformation.

References

[1] Bond, D. R.; Johnson, L.; Nassimbeni, L. R. *J. Solid State Chem.* **1991**, *92*, 68.
[2] Nassimbeni, L. R.; Johnson, L.; Toda, F. *Supramol. Chem.* **1993**, *2*, 233.
[3] Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 2681.
[4] Bacsa, J.; Caira, M. R.; Jacobs, A.; Nassimbeni, L. R.; Toda, F. *Cryst. Eng.* **2000**, *3*, 251.
[5] Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D. *J. Am. Chem. Soc.* **2000**, *122*, 9367.

[6] Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D. *J. Chem. Soc., Perkin Trans. 2*, **2001**, 2119.

[7] COLLECT, data collection software, Nonius, Delft, the Netherlands, 1998.

[8] Otinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr, Sweet, R. M., Eds.; Macromolecular Crystallography, Part A, Academic Press: New York, 1997; Vol. 276, pp 307–326.

[9] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[10] Sheldrick, G. M. *SHELX-97, A Program for Crystal Structure Determination*; University of Göttingen: Germany, 1997.

[11] Barbour, L. J. SECTION, a computer program for the graphic display of cross sections through a unit cell*J. Appl. Crystallogr.* **1999**, *32*, 353.

[12] Kim, E.; Paliwal, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 11192.

[13] Cozzi, F.; Siegel, J. S. *Pure Appl. Chem.* **1995**, *67*, 683.

[14] Brown, M. E. *Introduction to Thermal Analysis: Techniques & Applications*; Chapman & Hall: New York, 1988; Chapter 13.