

The Structure of New Host Molecules that form Channel Inclusion Compounds

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Abstract

1,3-Benzenediamine, N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl) and 1,3,5-Triazine, 2,2'-[2-methyl-1,3-phenylenebis(oxy)]bis(4,6-dichloro) were synthesized as host molecules. The inclusion compound of 1,3-Benzenediamine, N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl) crystallizes in the monoclinic crystal system in space group C2/c. The host molecule occupies the space group 2-fold special position and packed in the crystal lattice in such a manner as to leave channels running along the *c* axis of a rectangular cross-section. It crystallizes with two molecules of acetone that are hydrogen bonded to the amino nitrogen atoms. Molecules of 1,3,5-Triazine, 2,2'-[2-methyl-1,3-phenylene bis(oxy)]bis(4,6-dichloro) are packed in the crystal in such a manner as to leave channels of a trapezoid cross-section that are running along the *a* axis. Guest molecules such as metanol, ethanol, and ethyl acetate can be used to fill the channels. The crystal structures of two inclusion compounds are described.

Introduction

During the second half of the 19th century the field of non-covalent chemistry received momentum especially since the introduction of the notion "Supramolecular Chemistry." Supramolecular chemistry was defined as chemistry based on non-covalent interactions, such as hydrogen bond, dipole-dipole, dipole-induced dipole, electrostatic, charge-transfer, hydrophobic, dispersive Van der Waals, coordination interactions, or in short as "soft bonds"[1]. Preceding to the use of the notion "Supramolecules," other words have been used such as "inclusion compounds," "host-guest compounds" etc. Several books were written and the record was in 1996 when eleven volumes of Comprehensive Supramolecular Chemistry were published [2]. In the narrower subject of host-guest chemistry most of the effort was devoted to the understanding of the interaction between the host and guest molecules, the physicochemical aspects [3], and to the design of new host compounds for possible applications [4]. The host compounds may be classified into two main groups: (i) host molecule that has a shape that enables the accommodation of a guest molecule. Examples for such host molecules are cyclodextrins, cyclophanes, calixarenes, polyethers etc., and (ii) host molecules that can form inclusion through packing in a lattice in such a way that cavities, channels, or layers are being occupied by guest molecules. The inclusion compounds obtained from the first type of host molecules are also called

"cavitates" and the inclusion compounds obtained from the second type of host molecules are also called "clathrates" [5]. Among the solid-state clathrates of organic hosts the channel clathrates are very interesting and they have been thoroughly studied because of their potential applications in separation between guest molecules. For example the inclusion compounds of urea [6], or trimesic acid [7], both providing channels with hexagonal cross-section, alicyclic diols [8], and tri-*o*-timotide [9], that provide channels with triangle cross-section.

The interactions between the guest and the host molecules may be weak (Van der Waals interactions) or strong (hydrogen bonds). In the present work we describe the synthesis and the crystal structure of inclusion compounds made up from two new host molecules based on cyanuric chloride: 1,3-Benzenediamine, N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl) (**1**) with acetone, and 1,3,5-Triazine, 2,2'-[2-methyl-1,3-phenylene bis(oxy)]bis(4,6-dichloro) (**2**) with ethyl acetate (Scheme 2).

Experimental section

NMR data were collected on a Bruker AC400 instrument at 25 °C.

Synthesis

1,3,5-Triazine, 2,2'-[2-methyl-1,3-phenylenebis(oxy)]bis(4,6-dichloro)(**1**)^{1/2}(ethyl acetate). To a stirred mixture

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of 1.84 g (10 mmol) of cyanuric chloride in 20 ml of acetone, cooled in an ice bath, was added dropwise over 10 min, 0.62 g (5 mmol) of 2-methylresorcinol in 5 ml of acetone and 1.33 g (5 mmol) of 2,4,6-collidine. A mixture was stirred at 0 °C for two hours. The mixture was filtered from collidine chloride, the solution was diluted with 20 ml of ice water. The solution was treated with chloroform to extract the product. The solution was dried over MgSO₄. The resulted mixture was allowed to remain at room temperature overnight. The chloroform extract was filtered and concentrated to dryness in vacuo. Cream-white solid was purified by silica gel chromatography with CH₂Cl₂ and isolated in 66 % yield. Recrystallization from ethyl acetate gave the inclusion complex (guest-ethyl acetate, m.p. 178 °C, ¹H NMR (CDCl₃) δ 7.41 (t, H), 7.13 (d, 2H), 2.02 (s, 3H).

1,3-Benzenediamine,N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl)(2)*2(acetone). To a cooled 20 ml of water in an ice bath was added boiled mixture of 1.84 g (10 mmol) of cyanuric chloride in 15 ml of acetone, the mixture was cooled in an ice bath at 0 °C. 1.08 g (10 mmol) of 1,3-phenylenediamine was added dropwise over 10 min. The mixture was stirred at 0 °C for 1.5 h and after 0.5 h at room temperature. The mixture was diluted with 100 ml of ice water. The cream-white solid was filtered. Recrystallization from mixture of (1:1) ethyl acetate and acetone gave the product in 76.1% yield, m.p. 210 °C, ¹H NMR (CDCl₃) δ 8.1 (s, H), 7.45 (d, 2H), 7.38 (t, H).

Crystal structure determination

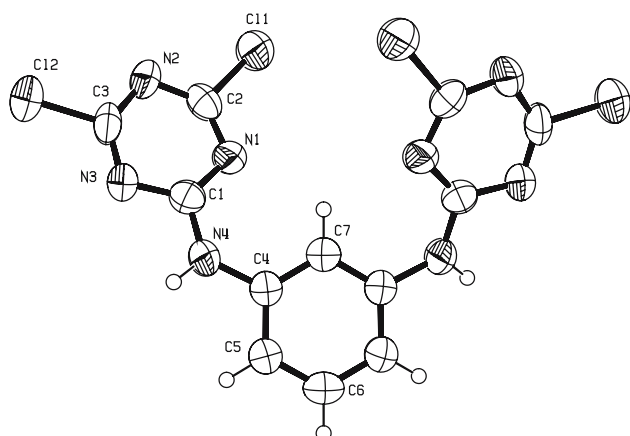
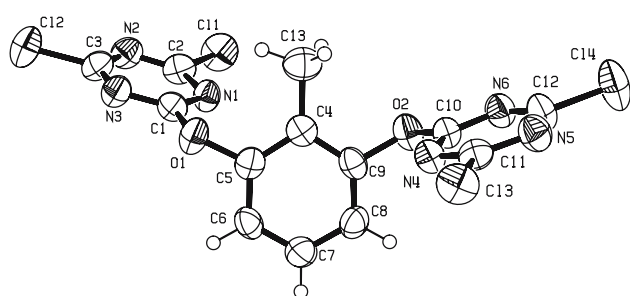
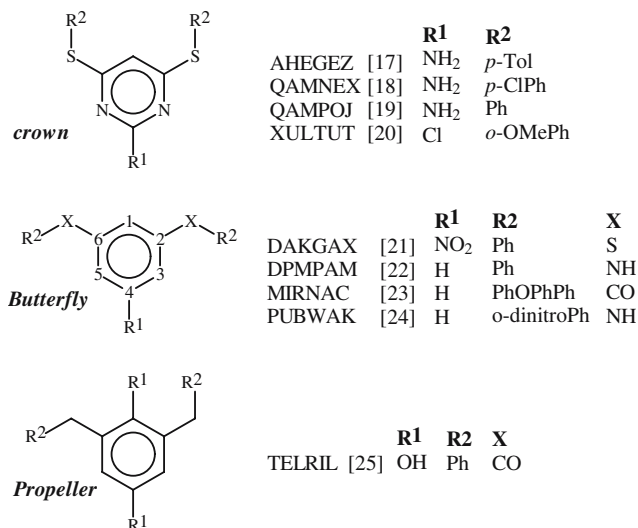
Relevant details of data collection and refinement of the crystal structures of (1)*(ethyl acetate) and (2)*(acetone)₂ are collected in Table 1. The crystal structures were solved and refined with *SHELXL93* [10], using anisotropic displacement parameters for non-hydrogen atoms. All H atoms were located from difference Fourier maps and refined isotropically. The ethyl acetate is disordered and was refined isotropically without the hydrogen atoms.

Results and discussion

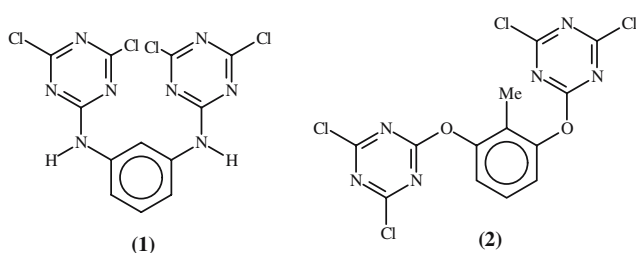
Crystallographic data for the two inclusion compounds 1*2(acetone), and 2*1/2(ethyl acetate) are summarize in Table 1. The molecular structures of **1** and **2** with the atomic numbering are shown in Figures 1, and 2, respectively. The two host molecules adopt different conformations. Comparison of similar molecules shows that they adopt one of three main conformations, *crown*, *butterfly*, and *propeller* as shown in Scheme 1 with their Cambridge Crystallographic Data Center refcodes [11]. The distinction between the three types of conformations is based on the torsion angles about the bonds C–X (Scheme 1) where X is C, N, O, or S. In the conformation *crown*, the absolute value of the torsion angles C3–C2–X–R², and C5–C6–X–R² (Scheme 1) are

Table 1. Crystal data and structure refinement for **1** and **2**

	1	2
Formula	C ₁₂ H ₆ Cl ₄ N ₈ *2(C ₃ H ₆ O)	C ₁₃ H ₆ Cl ₄ N ₆ O ₂ *1/2(C ₄ H ₈ O ₂)
M _r	520.20	454.05
Crystal color, habit	Colorless	Colorless
Crystal dimensions	0.30 × 0.30 × 0.15	0.51 × 0.18 × 0.15
Crystal system	Monoclinic	Orthorhombic
Space Group	C2/c	Pna2 ₁
a [Å]	7.950(1)	7.510(1)
b [Å]	19.450(3)	16.902(3)
c [Å]	15.370(3)	15.286(3)
β [°]	92.18(3)	90.00
V [Å ³]	2374.9(7)	1940.3(6)
Z	4	4
D _{calc} [g cm ⁻³]	1.455	1.554
μ(MoK _α) [cm ⁻¹]	0.0531	0.0639
2θ max [°]	50.98	50.08
Reflection collected	3255	1782
Independent reflections	1973	1782
Observed reflections	679	1568
Largest difference peak [eÅ ⁻³]	0.162	0.286
Largest difference hole [eÅ ⁻³]	-0.170	-0.190
No. of parameters	149	250
R ^a	0.0395	0.0490
WR ^a	0.0708	0.1300
GOF ^b	0.666	1.148

Figure 1. Molecular structure of **1**.Figure 2. Molecular structure of **2**.

Scheme 1.



Scheme 2.

in the range of 158.2–176.2°. The range of the absolute values of the same torsion angles is 1.3–34.8° in the *butterfly* conformation. In the *propeller* conformation the absolute value of one of the torsion angles is above 90°, the other below 90°. 1,3-Benzenediamine,N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl) (**1**) occupies the 2-fold crystallographic special position and adopts the *crown* conformation. 1,3,5-Triazine,2,2'-[2-methyl-1,3-phenylene bis(oxy)]bis(4,6-dichloro) (**2**) on the other hand adopts the *propeller* conformation.

The packing of the two inclusion compounds is different. 1,3-Benzenediamine,N,N'-bis(4,6-dichloro-1,3,5-triazine-2-yl) (**1**) crystallizes with two molecules of acetone and are bonded to the guest molecules via N4–H4N O1 hydrogen bonds (H4N O1 distance is 2.029 Å and N4–H4N O1 angle is 170.0°). 1,3,5-Triazine,2,2'-[2-methyl-1,3-phenylene bis(oxy)]bis(4,6-dichloro) (**2**) crystallizes with half a molecule of ethyl acetate (also with methanol and ethanol). The guest molecule is disordered. It is interesting to note that ethyl acetate is found to be disordered in 132 crystal structures out of 277 crystal structures that include ethyl acetate and are deposited in the Cambridge Crystallographic Data Center [11]. The host molecules form dimers between molecules related by translation along the *c* axis with short Cl N and Cl O distances as shown in Figure 3. The geometry of the short contacts are: Cl3 N6 3.175(6) Å, C11–Cl3 N6 170.9(5)°, Cl1 N3 3.340(6) Å, C2–Cl1 N3 155.1(5)°, Cl1 O1 3.157(7) Å, and C2–Cl1 O1 164.6(6)°. Similar short intermolecular contacts between chlorine atom and nitrogen and oxygen separated by one atom was found in only three other compounds (for refcodes see reference [11]).

Tetrachlorothiophene-N-ethoxycarbonylimide-S-oxide (FIZGOK) [12], and Tetradecahydro-dipyrrolo(1,2-a:2,1-i)-1,4,7,10-tetra-azacyclotetradecine-4,9,14,17-tetrone chloroform solvate (QENZOY) [13]. The Cl N distances are 3.415, 3.471, and 3.403 Å in the three compounds respectively. The Cl O distances are 3.224, 3.188, and 3.195 Å in the three compounds, respectively.

P,P'-bis(Tetrachloro-catecholato-O,O')-2,4,6,8-tetramethyl-2,4,6,8-tetra-aza-1,5-diphosphabicyclo(3.3.0)octane-3,7-dione dichloromethane solvate (BIFHON) [14]. The channels formed by the packing of the host molecules in the crystal lattice have different cross-sections, while the cross-section in the lattice of the inclusion compounds of **1** is rectangular with edges of 7.2 × 10.8 Å (Figures 3, 4 and 5), the cross-section of the channel made up by **2** has a trapezoid shape with the size of 10.8 × 6.6 Å (Figure 6). The walls of the channel in **1**(acetone) are made up of chlorine atoms that build the narrower wall boundary of the rectangle, and the face of the phenyl ring which form the wider wall boundary of the rectangle. The inner wall of the rectangle is therefore, rich of electrons. The walls of the channel in **2**(ethyl acetate) are made up from four dichlorotriazine moieties that may be described as two twizers of different opening angle which provides a space between them of a trapezoid shape. It is interesting to note that there are other examples where halo-substituted phenyls may act as

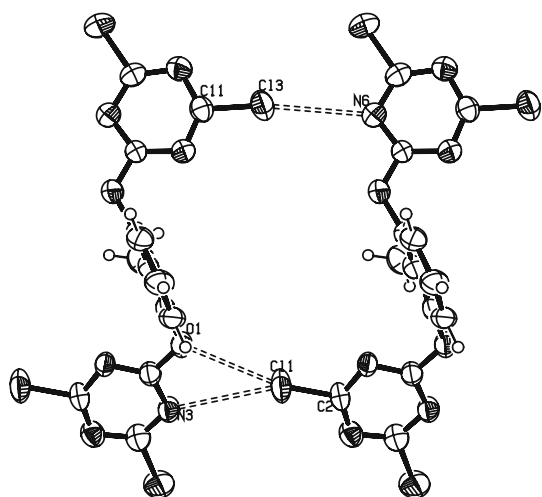


Figure 3. The structure of a dimer of 1,3,5-Triazine,2,2'-[2-methyl-1,3-phenylene bis(oxy)]bis(4,6-dichloro) (**2**).

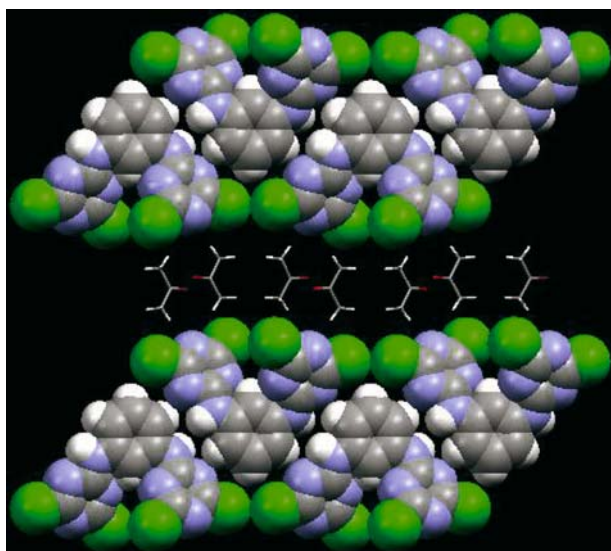


Figure 4. Side view of the channel in **1**. The guest molecules are drawn in stick style and the host molecules are drawn in space-filling style.

host in the formation of channel inclusion compounds. For example the hexagon nanoporous host structure based on 2,4,6-tri-4-(halo-phenoxy)-1,3,5-triazines [15], that crystallize with various substituted benzenes. Another example is the host molecule tetrakis(N-(*p*-Tolyl)-tetrachlorophthalimide [16], that forms channels of ellipsoid cross-section with a width of 3.5 Å which can accommodate only aromatic compounds as guests.

Supporting information available

The crystallographic data for the two inclusion compounds have been deposited with the Cambridge Structural Database in CIF format (CCDC-246138 and CCDC-246139). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Center, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

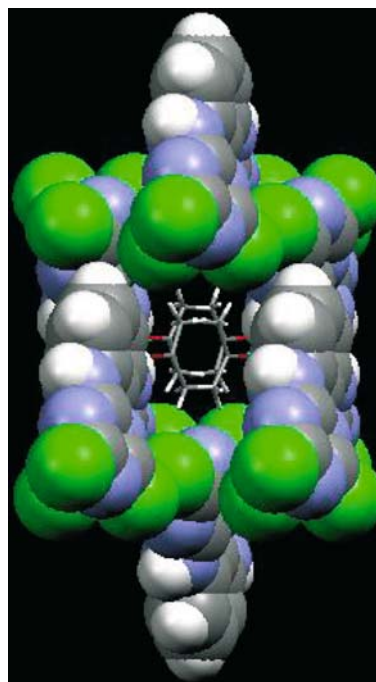


Figure 5. View of the rectangular channel cross-section made of host molecules of **1** (drawn in space-filling style) with the guest molecules (drawn in stick style).

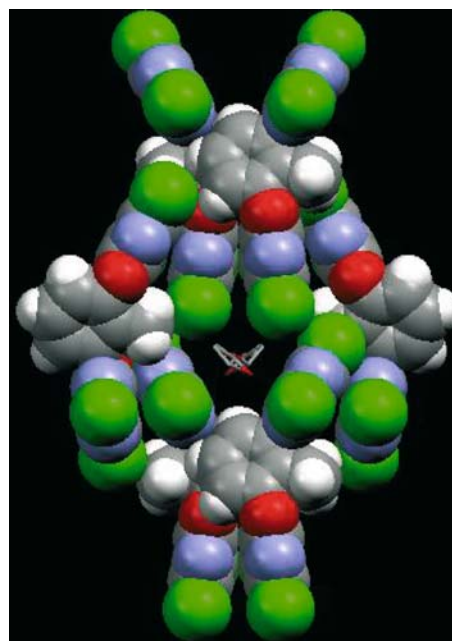


Figure 6. View of the trapezoid channel cross-section made of host molecules of **2** (drawn in space-filling style) with the guest molecules (drawn in stick style).

Graphical Contents entry

The structure of new host molecules that form channel inclusion compounds

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