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Nanotube Formation Favored by Chalcogen−Chalcogen Interactions

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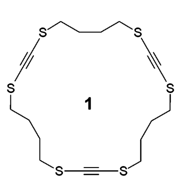
Concepts of supramolecular chemistry have enabled chemists to construct host molecules with large cavities.[1,2] Among others tubular structures were also obtained by self-association. The study of these processes has shown that directional forces are needed to build three-dimensional networks. The most important forces are hydrogen bonds, $\pi-\pi$ stacking, and interactions between soft acids and bases.[2,3]

Self-assembled arrays of organic nanotubes which are based on amino acids[4] and calixarenes[5] have been reported. Common to all of them are hydrogen bonds between the building blocks. Another protocol uses macrocyclic rings with a rigid frame of alternating triple bonds and phenyl rings to maintain planarity.[6] Hydrogen bonding between phenolic OH groups and $\pi-\pi$ interactions of aromatic rings were used to stack the rings on top of each other.[6]

Besides nonbonding interactions between π systems, weak interactions between halogen centers[7] or chalcogen atoms[8] also play an important role in packing of molecules in crystals. van der Waals interactions between sulfur centers have been encountered at various occasions, especially in crystal engineering of organic conductors such as tetrathiafulvalene (TTF).[9]

We found recently[10] that directional forces between chalcogen centers may also lead to columnar structures when the chalcogen atoms were incorporated into fairly rigid ring systems. However, due to their medium ring size no inclusion of guests is possible.

In this report we present four examples of tubular structures which are able to host molecules as guests by applying two different principles. In the cases of **1**−**3** the pre-made rings are stacked on top of each other via van der Waals forces between the chalcogen centers. van der Waals forces are also used for the self-association of 2,7-ditelluraocta-3,5-diyne (**4**). Systems **3** and **4** contain the hitherto unknown structural units of a 1,4-donor-substituted butadiyne with selenium and tellurium, respectively, as donors.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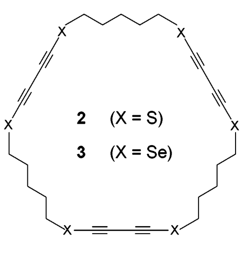
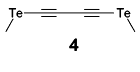

2 (X = S)
3 (X = Se)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The C_3-symmetric 24-membered ring of **1** contains three S−C≡C−S units oriented in a sloping position (Figure 1). This arrangement of the building blocks allows a *zigzag* arrangement of the CH_2 groups of the chain and a torsion angle between the CH_2-S groups of one $CH_2-S-C{\equiv}C-S-CH_2$ moiety of ca. 103°. The sulfur atoms form close contacts with the neighbors, stacked on top of each other (Figure 1).

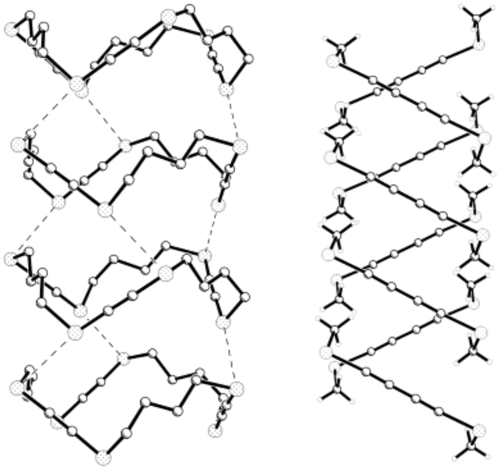

Figure 1. (Left) Side view, showing the stacking of **1**; the short S···S contacts (3.52 Å) are indicated. (Right) Side view, showing the helical arrangement of **4**. Chalcogen atoms are stippled.

The S···S distances amount to 3.52 Å. The diameter of the tubes built by this stacking measures approximately 6 Å. By recrystallizing **1** from *n*-hexane we found that the solvent was included in the tubes as evidenced by the X-ray structure analysis.[11]

Due to the extended rigid building blocks even larger cavities were found for the cyclohexaynes **2** and **3** as compared to those for **1**. Recrystallization of both from *n*-hexane leads to similar structures as found for **1**, including disordered *n*-hexane.[11] By recrystallization of **2** and **3** from toluene the tubes contain one molecule solvent per cycle in an ordered fashion (Figure 2). We ascribe this regularity to a C−H···π interaction between the alkane chains and the π system of toluene. The C−H···π distances amount to 2.78 Å (**2**) and 2.80 Å (**3**), respectively. Similar values were found in a database study.[12] If hexane is included in the tubes, the rings show C_3 symmetry with intertubular chalogen chalcogen distances of 3.83 Å (**2**) and 3.82 Å (**3**), respectively. In the case of toluene as guest the C_3 symmetry is lifted, and some of the intertubular chalcogen−chalcogen distances become slightly shorter, and some of them become slightly longer. The tubes of **3** tolerate also chlorobenzene, *p*-xylene, and even the polar nitrobenzene as guests.

In Figure 3 we display a top view of the solid-state structure of **4** when recrystallized from *n*-hexane. The 2,7-ditelluraocta-3,5-diyne units form a rectangular cavity which is large enough to include solvent as evidenced by the residual electron density in the center.[11] The distance between opposite sides within the rectangular cavity amounts to 7 Å. Due to the torsion of the methyl groups (53°) the molecules orient themselves in helical stacks (side view, Figure

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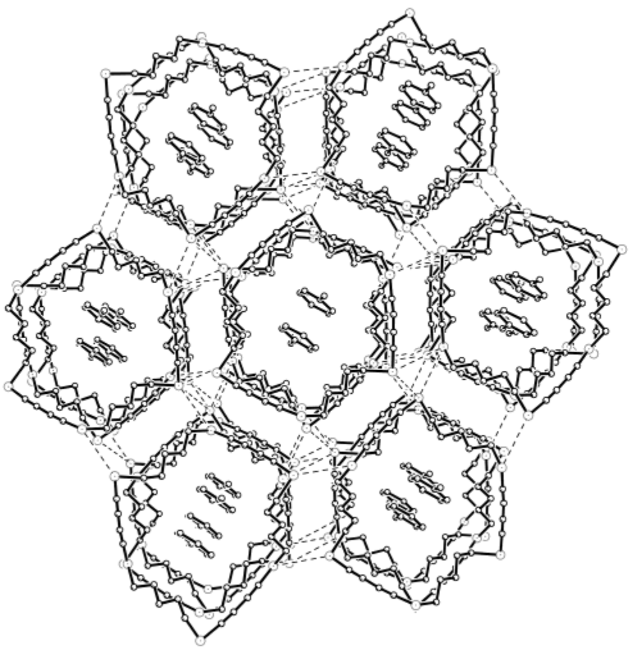

Figure 2. Top view of the structure of **3**, indicating the short Se···Se distances and the included toluene molecules. The hydrogens are ommitted for clarity.

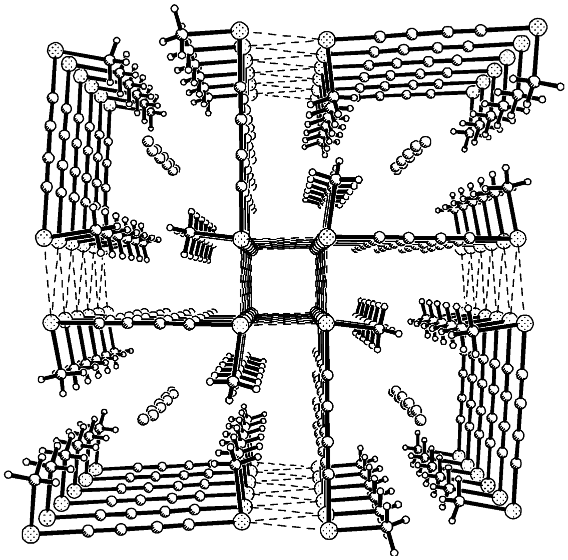

Figure 3. Top view of the structure of **4**, indicating close Te···Te contacts and the included *n*-hexane molecules. Tellurium atoms are stippled.

1). The solid-state structure of **4** is dominated by close Te···Te contacts: each Te atom, placed at the edge of a stack, keeps in close contact with four Te atoms in (the two) neighboring stacks. As a result each Te forms *zigzag* like contacts (3.74 and 3.82 Å) to two neighboring stacks (Figure 3). Together with one diagonal contact (4.30 Å) and two contacts within the stack (4.46 Å) each tellurium atom experiences seven close contacts.

Several of the chalcogen−chalcogen distances in our tubular structures are longer than the van der Waals distances (S···S = 3.7 Å, Se···Se = 4.0 Å, Te···Te = 4.4 Å).[13] However, the van der Waals potential is far reaching. In the case of argon one finds that at 4.5 Å the stabilization energy amounts to 50% and even at 5.5 Å to 15% of that found at the minimum (3.8 Å).[14] Due to the fact that each chalcogen atom in the ring provides several close chalcogen−chalcogen contacts, the small contributions add up. Recent calculations on S···S contacts estimate a stabilization energy of 1.5 kJ/mol at the minimum.[15]

In conclusion, we present here the first examples in which close contacts between sulfur, selenium, and tellurium centers, respectively, favor the formation of tube-like structures in the solid state that are able to host other molecules.

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Supporting Information Available: Experimental details, spectra data, X-ray data and stacking plots for all new compounds (PDF). X-ray data and details of the refinement procedure in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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