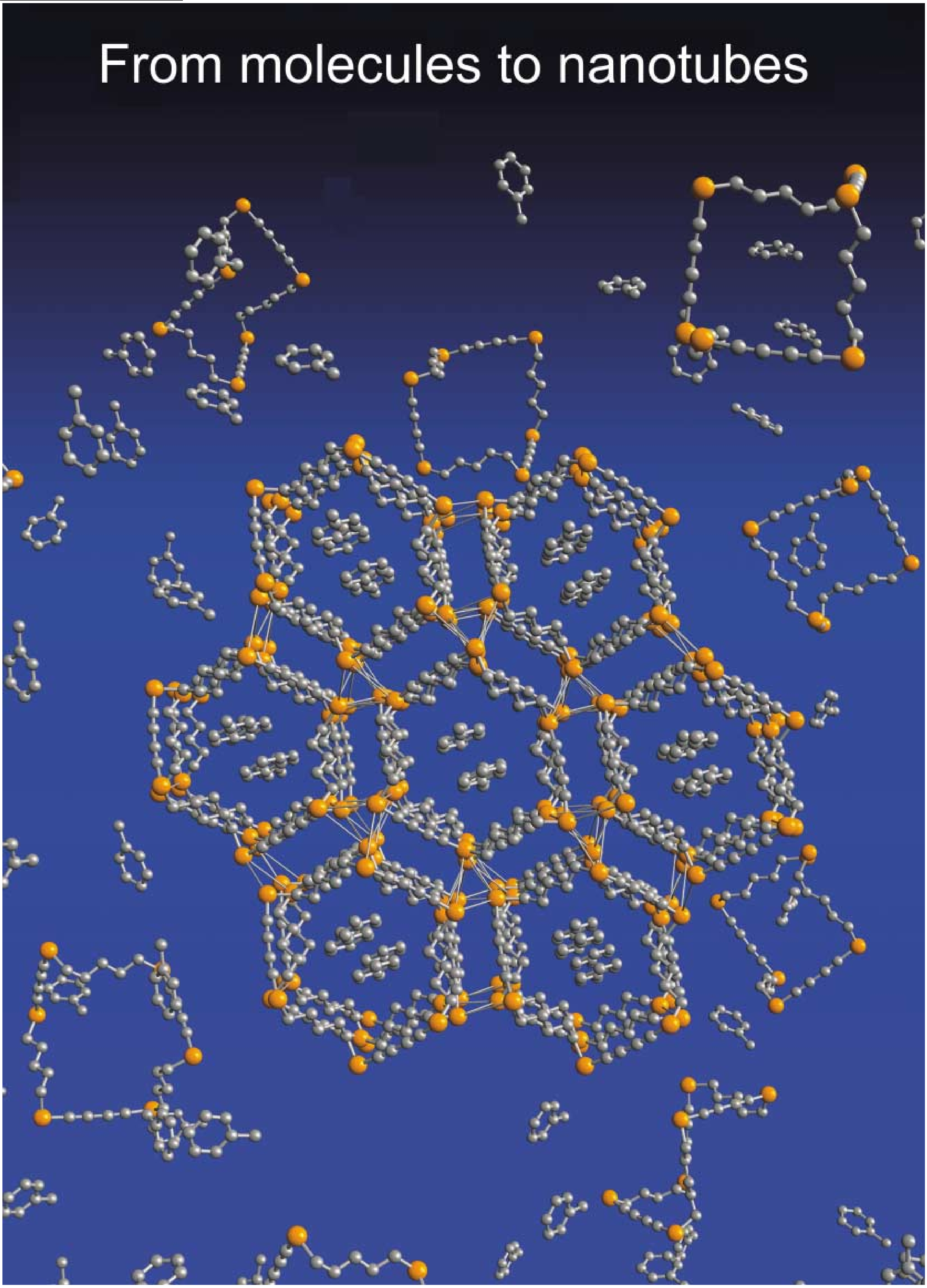

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A World Beyond Hydrogen Bonds?—Chalcogen–Chalcogen Interactions Yielding Tubular Structures

Rolf Gleiter,* Daniel B. Werz, and Bernhard J. Rausch[a]

Abstract: It is shown that tubular structures arise in the solid state through close chalcogen–chalcogen ($X\cdots X$) contacts. As examples a variety of cyclic systems containing sulfur and selenium centers is presented. Common to all of them are close contacts between the chalcogen centers of neighboring stacks giving rise to a zigzag or ladder-type arrangement. In the case of cyclic systems of ring size 24–33 the resulting tubes are able to include hydrocarbons as guest molecules. For 2,7-ditelluraocta-3,5-diyne (**17**) the close contacts between the tellurium centers of the acyclic C_2 symmetric building blocks generate a helical arrangement in which *n*-hexane was included. The favored $X\cdots X$ contacts can be traced back to $n\mathrm{p}(X)-\sigma^*(X-C)$ interactions.

Keywords: alkynes • chalcogens • host–guest systems • noncovalent interactions • self-assembly

Introduction

Channel-like structures have captured the interest of chemists for many years. The most prominent channels are ionic channels,[1] zeolites,[2] and carbon nanotubes.[3] Ionic channels are responsible for the transport of sodium and potassium ions through the lipophilic cell walls. Numerous investigations reveal that these channels are formed by proteins. The dimensions are about 30–80 Å in length and 8–12 Å in diameter.[3] X-ray investigations revealed that both ends of the anionic channel are surrounded by negatively charged amino acids; this gives rise to a high local concentration of cations. The large diameter allows the migration of cations with their hydration sphere into the polar cavity created by the peptide. Essential for the tubular structure are hydrogen bonds between the amino acid units.

Zeolites are silicates with regular rigid three-dimensional frameworks made up of silicon, aluminium, and oxygen centers. This covalently bound framework contains cavities and channels. The inside of a zeolite is covered with negatively charged oxygen centers and with OH groups, providing a hydrophilic environment inside that is similar to the ionic channels. These cavities allow the inclusion of metal ions and larger molecules, such as dyes, that can be anchored by hydrogen bonds or dipole–dipole interactions.[2]

Carbon nanotubes are formed from graphite sheets in which the carbon atoms are connected by covalent bonds.[3] The material properties such as electronic,[4] optical,[5] and mechanical[6] behavior of these carbon nanotubes are of particular interest.

The various channels, especially the naturally occuring tubes, have stimulated chemists to design artificial ones using similar building motifs to those found in nature. In this conceptual paper we will follow up the question: Is it possible to construct tubular structures by using noncovalent interactions that avoid the use of hydrogen bonding? Before discussing the possibilities, we will first look at some building motifs that use hydrogen bonds and other stabilizing effects to generate tubes and channels. Due to the limited space, we have omitted coordinative interactions between Lewis-acidic metal centers and bases, instead we just refer to recent reviews in this field.[7–9]

Hydrogen Bonds

There are a number of ways to generate tubular structures from proteins that have been reviewed in detail.[10–12] We would like to pick out only two whose building motifs are related to those discussed later.

Ghadiri showed that the 24-membered ring formed from *cyclo*[-(D-Ala-L-Glu-D-Ala-L-Glu)$_2$][10, 11, 13] adopts a flat conformation in which all backbone amide functionalities lie approximately perpendicular to the plane of the structure. In this conformation the various rings are able to stack in such a way that they are connected with hydrogen bonds to produce a contiguous β-structure (Figure 1).

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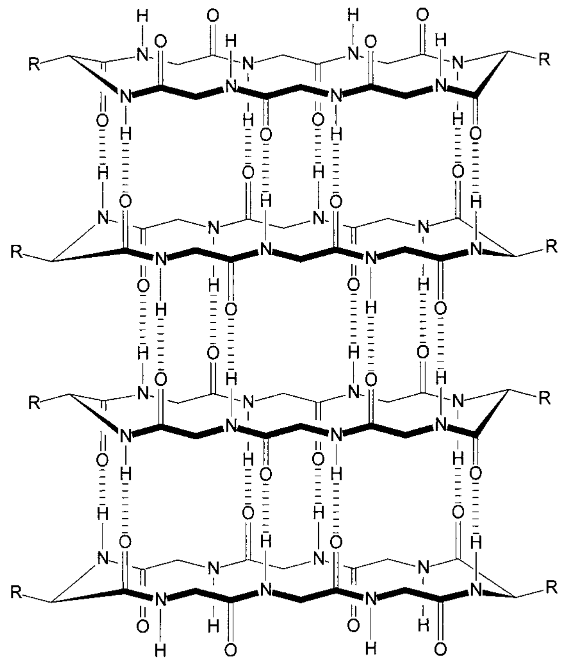


Figure 1. Self-assembled peptide *cyclo*[-(D-Ala-L-Glu-D-Ala-L-Glu)$_2$] to yield a tubular configuration. For the sake of clarity only the backbone structure is represented.

Also dipeptides such as L-Leu-L-Val are bound head-to-tail by hydrogen bonding to form helices with six dipeptide molecules per turn.[12, 14] As a result, channels about 5 Å in diameter are formed that are distinctly hydrophilic in nature (Figure 2). For brevity, we just mention that the tubular inclusion complexes of urea,[15, 16] starch,[16, 17] and cyclodextrines[18] have been characterized.

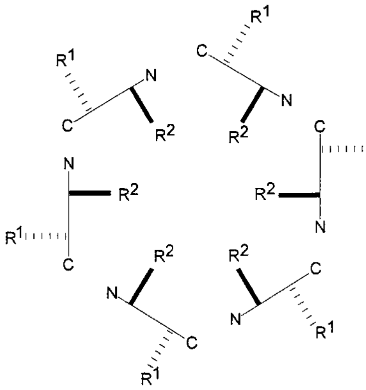
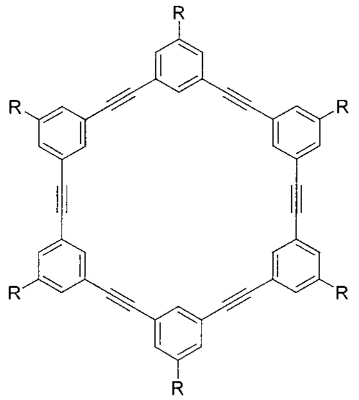


Figure 2. Schematic representation of the self-assembly of six dipeptides per turn.

π – π Stacking

X-ray investigations on extended π-systems such as [18]annulene,[19] kekulene,[20] or porphyrins[21] show that these systems adopt a cofacial arrangement in which the centers are offset. These facts have been rationalized recently by an attractive interaction between the positively charged σ-frame and the negatively charged π-system.[22] This attraction outweighs the repulsive interaction between the π-electrons, and the slipping of the centers can be reduced by diminishing the electron density within the π-systems. This simple model predicts that even extended π-systems, such as kekulene, are not suited to build columnar stacks.

The slipping of the centers of larger centrosymmetric π-systems might be overcome by additional directive forces such as hydrogen bonds. This concept was used by Moore and others[23] to generate channels between macrocycles in which the slipping was reduced. Rigid macrocycles, for example, **1a**, are hydrogen bonded to each other to form a two-dimensional closest packed sheet with two types of holes: the 9 Å hole due to the macrocycle and a 9.3 Å hole due to the hydrogen bonds (Figure 3). Without these directive forces of the hydrogen bonding (e.g., **1b**), no tubular arrangements are found in the solid state.



R = OH **1a**
R = *t*Bu **1b**

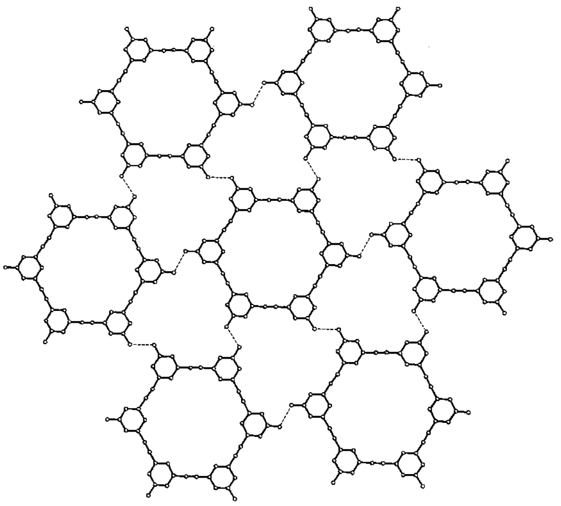


Figure 3. Single layer of the crystal structure of **1a** parallel to the 001 plane showing a two-dimensional hexagonal closest packing of **1a** stabilized by hydrogen bonds.

To achieve the observed columnar structure, the sheets are aligned in such a way that channels are built. This has been ascribed to electrostatic interactions and van der Waals forces. Probably, the electron-withdrawing effect of the triple bonds reduces the repulsive π – π interaction[22] and thus makes stacking possible.

Van der Waals Forces

Numerous structures are known in which halogen atoms bound to other fragments, or in which chalcogen species of the type R-S-R′, have intermolecular X···X distances that are significantly shorter (0.1–0.4 Å) than the sum of their van der Waals radii.[24, 25] The close contacts are based on attractive forces on the order of 2–9 kJ mol^{-1};[26] these might take the place of hydrogen bonds, if there are enough "nonbonding interactions" possible.

An analysis of the halogen–halogen interactions in the solid state by Desiraju[27] reveals that the close contacts can be subdivided into two types (I and II) depending upon the size of the angles θ_1 and θ_2 defined in Figure 4.

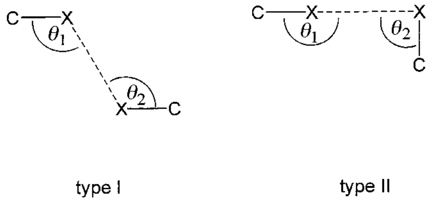


Figure 4. Definition of angles θ_1 and θ_2 for type I and type II of halogen–halogen interaction of two C–X units.

In the category of type I, the two angles are equal and around 160°. In the category of type II, θ_1 amounts to approximately 180° and θ_2 to approximately 90°. The analysis shows that type II is encountered in those cases in which the polarizability of the halogen is sizeable, that is, for higher halogens and unsymmetrical interactions. It has been shown for Cl···Cl interactions that a realistic anisotropic model for the repulsion, dispersion, and electrostatic forces has to be used to describe the nonbonding interactions properly.[28]

With the discovery of superconductivity of complexes of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ), the solid-state structure of these and related species have been investigated thoroughly.[29] These studies revealed that close S···S contacts play an important role in the formation of two- and three-dimensional networks in the solid state. It was found that besides close S···S contacts, C–H···S, C–H···π and π–π stacking contribute to the solid-state structures.[30]

The examination of the S···S distances and the resulting configurations of a series of compounds belonging to the type R-S-R′ with R,R′≠H could be rationalized in terms of electrophilic–nucleophilic interactions of different sulfur centers, or by considering the corresponding frontier orbitals (Figure 5).[25, 31]

In most cases the arrangement of the planes, defined by R, S, and R′, was that one R-S-R′ unit (say the electrophile) approaches the other R-S-R′ unit (the nucleophile), in such a way that both planes are nearly perpendicular to each other (Figure 5). In terms of frontier orbital theory, the occupied 3p orbital on one unit interacts with the empty σ* orbital of either the R–S or R′–S bonds. Recent quantum chemical model calculations (HF) confirm this view.[26] It was found that the np(X)–σ*(X–C) interaction increases in the series S, Se, Te and that the acceptor capability of an X–C(sp) σ bond is stronger than that of a X–C(sp^3) bond. In the case of Te, the total energy was decreased by about 2.8 kJ mol^{-1} for an X···X–C(sp^3) interaction and about 9.2 kJ mol^{-1} for an X···X–C(sp) interaction.[26]

During our studies on cyclic tetrathiadiynes we found three structures (**3**–**5**)[32] in which the rings are stacked on top of each other, with close contacts between the sulfur centers of neighboring stacks. The prevailing motifs of the van der Waals contacts can best be seen when considering the structure of **2**,[33] which contains only one sulfur center. This molecule provides a rather flat ring system with one sulfur center pointing outward. In the solid state, the rings associate in such a way that the sulfur center of one ring keeps in close contact with two sulfur centers of two neighboring rings that are stacked on top of each other. As a result a zigzag arrangement of the sulfur atoms arises as shown in Figure 6. In some cases this building motif is changed to a ladder-type arrangement ($a \ll b$).

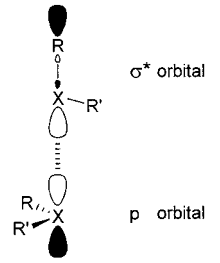
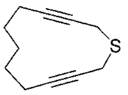


Figure 5. Directional bonding of two chalcogen centers in R-X-R′ units by interaction of an occupied p orbital with an unoccupied σ* orbital.



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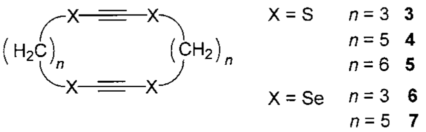


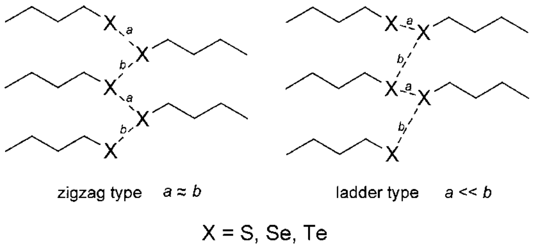


Figure 6. Schematic drawing of a zigzag (top) and a ladder (bottom) type arrangement of the chalcogen–chalcogen interaction in the solid state.

The contacts between the sulfur centers (a, b = 3.53 Å) of the neighbors are closer than the van der Waals radius (S···S = 3.7 Å).[34] The distances within the stack of **2** are longer (4.74 Å). In Figure 7 the resulting columns observed in the solid state of **2** are shown.

It is seen that the two contacts of one sulfur center generates a pair of columns. The 3p lone pair of the sulfur in **2** coincides with the direction of one C–S bond of the neighboring ring that contains chalcogen centers (c.f. Figure 5).

Rectangular rings with four chalcogen atoms are present in the thiadiynes **3**–**5** and also in the selenium derivatives **6** and

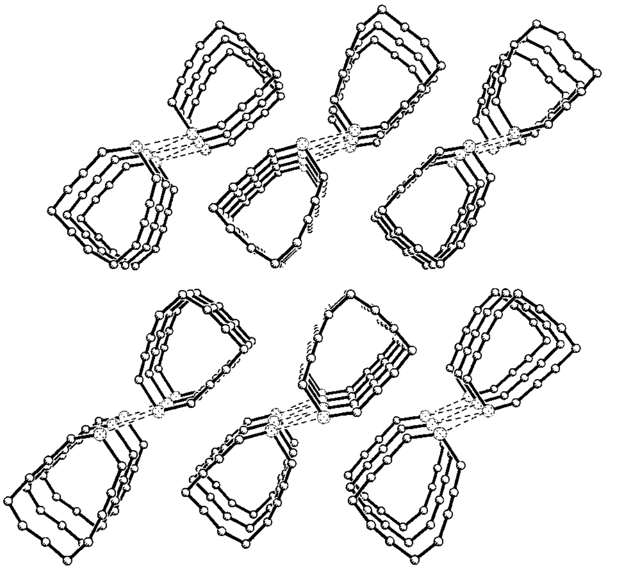


Figure 7. Plot of the columnar structure of **2**. The H atoms have been omitted for the sake of clarity.

7.[35] For all five ring systems the chalcogen centers at the edges of the rectangle keep close contacts to those of neighboring rings in other stacks, as shown in Figure 8 for **7**. In this way the zigzag motif between the sulfur atoms shown in Figure 6 is maintained. In **4** and **7** two crystallographically different types of chalcogen centers are found; these give rise to two shorter and two longer contacts between the chalcogen centers (Figure 6). The chalcogen distances within the stack are clearly longer than the corresponding van der Waals radii.

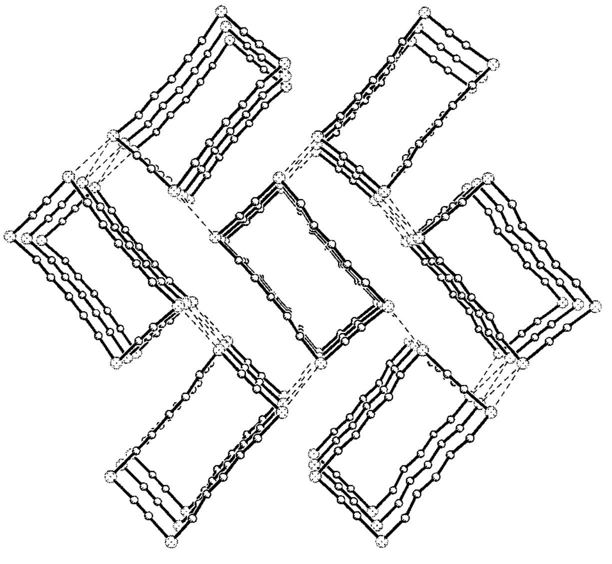
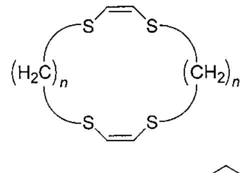


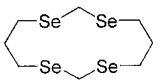
Figure 8. Plot of the columnar structure of the tetraselenacyclodiyne **7**.

However, close contacts between chalcogens are not only limited to alkynes; they are also encountered in the cyclic tetrathiaalkadienes **8** and **9**.[36] The rings adopt a chairlike conformation with rigid S–CH=CH–S units *anti* to each other. Again, in **8** the interaction between neighboring rings forms an asymmetric zigzag arrangement with short ($a = 3.47$ Å) and long ($b = 4.13$ Å) contacts. In **9** the zigzag arrangement is found to be symmetric ($a = b = 4.07$ Å).



$n = 4$ **8**

$n = 6$ **9**



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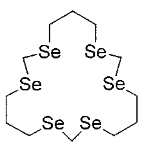

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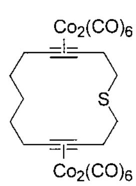
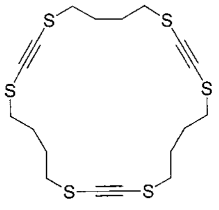


12

Even the fully saturated tetraselena and hexaselena crown ethers (**10** and **11**, respectively)[37] form tubular structures in the solid state.[38] These flexible macrocycles are directed by the interaction of the chalcogen atoms to stack upon each other and to form a columnar arrangement. The distances between the selenium atoms in **10** and **11** are only 3.69 Å and 3.63 Å, respectively.[38]

In the course of this study, we scrutinized our data on the X-ray structures of sulfur-substituted cylic bis(hexacarbonyldicobalt) complexes, which can be conveniently synthesized by the reaction of the corresponsing diyne with octacarbonyldicobalt.[39] We discovered that complex **12** is able to form columnar structures in the solid state with $S\cdots S$ contacts of 3.88 Å and 3.95 Å, despite the presence of the volumnious hexacarbonyldicobalt units in the cyclic moiety.[39]

In the cases of **2**–**12** the columnar structures in the solid state provide small tunnels with a lipophilic surface given by the alkane bridges; however, the diameters inside the columns are much too small for the inclusion of other molecules. To provide enough space for the inclusion of host molecules larger rings were investigated such as the 24-membered ring **13**,[40] the 22-membered ring **14**,[41] and the 33-membered rings **15** and **16**.[40]



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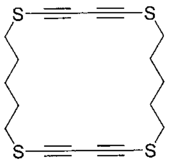

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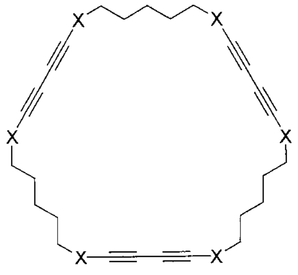
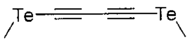


X = S **15**

X = Se **16**



17

The C_3-symmetric ring of **13** contains three $S-C\equiv C-S$ units oriented in a sloping position as shown in Figure 9. Thus three sulfur atoms point upwards and three downwards. An upper

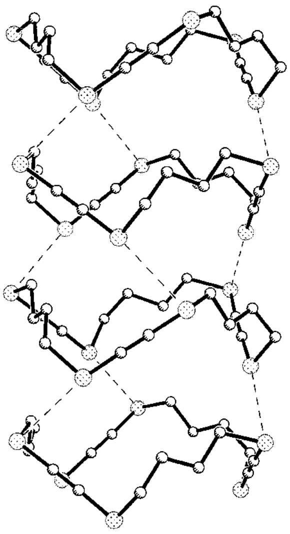


Figure 9. Side view showing the stacking of the rings of **13**. The short S ··· S contacts (3.52 Å) are indicated. Hydrogen atoms are omitted for the sake of clarity.

sulfur atom is connected to a consecutive lower one by a butane chain. These arrangements of the building blocks allow a zigzag conformation of the CH_2 groups of the chain and a torsion angle between the CH_2–S groups of one CH_2–S–C≡C–S–CH_2 unit of approximately 103°. The sulfur atoms form close contacts with those in neighboring rings, stacked on top of each other, and the S ··· S distances amount to 3.52 Å. The diameter of the tubes built by this stacking system measures approximately 6 Å. By recrystallising **13** from *n*-hexane, solvent is included in the tubes.

This building motif very much resembles that reported for *cyclo*[-(D-Ala-L-Glu-D-Ala-L-Glu)$_2$], shown in Figure 1.[13] The hydrogen bonds between the 24-membered rings are now replaced by S ··· S interactions.

In the 24-membered ring of **13** the *n*-hexane molecules are included in a disordered fashion; this shows up in the X-ray analysis as residual electron density in the inside of the tubes. The 22-membered ring of **14** resembles that of **4** and **7** with the exception that the alkyne unit is twice as long in **14** as in **4** and **5**. When we recrystallized **14** from toluene, the tubes contained one molecule of solvent per two cycles in an ordered fashion (Figure 10). We ascribe this regularity to weak C–H ··· π interactions between the alkane chains of **14** and the π-system of toluene.

The 33-membered rings **15** and **16** contain, like **14**, the structural units of a 1,4-donor-substituted butadiyne with sulfur and selenium, respectively, as donors. Due to the extended ring size, the cavities formed by the rings are able to host polar and nonpolar molecules as guests, such as *n*-hexane, toluene, *p*-xylene, bromobenzene, anisole, and nitrobenzene. One molecule of the aromatic guest per cycle is now included in an ordered fashion, as shown in Figure 11 for the hexaselenacyclohexayne **16** with its guest nitrobenzene. If a larger guest like mesitylene is used the tubes are stretched; this is seen by comparing the shape of **16** containing nitrobenzene (Figure 11) and containing mesitylene (Figure 12).[41] Our elastic rings are complemented on the one hand by flexible rings and on the other hand by shape-persistent macrocycles reviewed recently.[42]

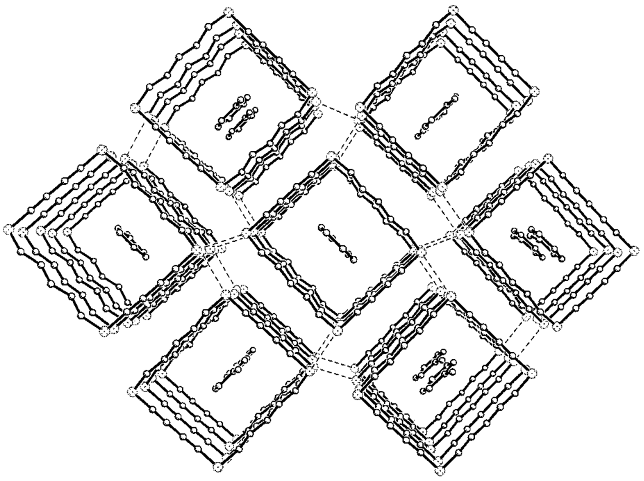


Figure 10. Top view of **14**; the short S ··· S distances and the included toluene molecules are indicated. The hydrogen atoms are omitted for the sake of clarity.

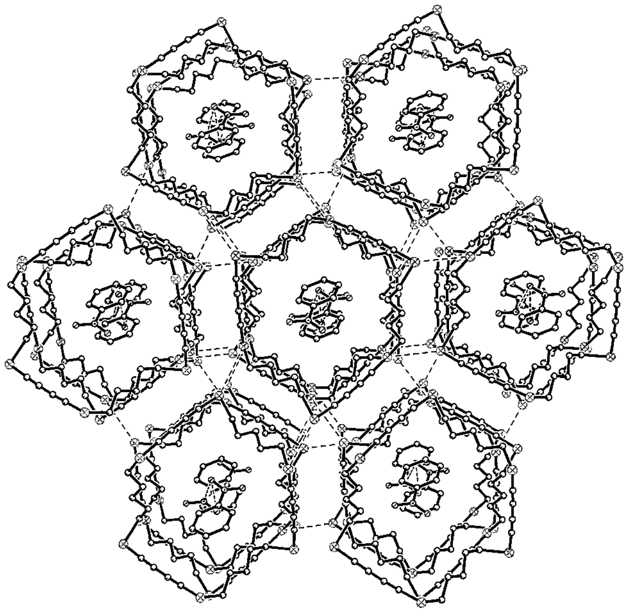


Figure 11. Top view of **16**; short Se ··· Se distances and the included nitrobenzene molecules are indicated. The H atoms are omitted for the sake of clarity.

A further bonding motif was found when the solid-state properties of 2,7-ditelluraocta-3,5-diyne (**17**)[40] were studied. This molecule resembles a rigid rod with two CH_3–Te fragments at the end. The tellurium centers provide the means for forming close intermolecular contacts. For the resulting framework it should be noted that due to the torsion angle between the CH_3–Te bonds (53°), the "rods" show C_2 symmetry.

When **17** is recrystallized from *n*-hexane the 2,7-ditelluraocta-3,5-diyne units form a rectangular cavity that is large enough to include solvent, as evidenced by the residual electron density in the center (Figure 13, top). The distance between opposite triple bonds within the rectangular cavity amounts to approximately 7 Å. Due to the C_2 symmetry of the

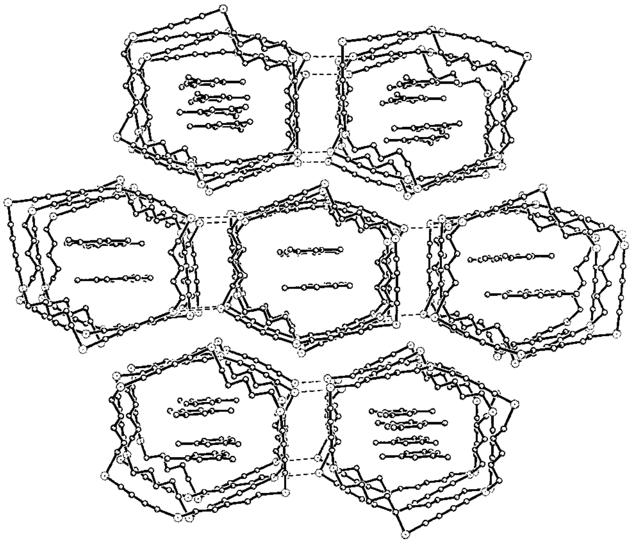


Figure 12. Top view of **16**; the short Se⋯Se distances and the included mesitylene molecules are indicated. The H atoms are omitted for the sake of clarity.

$(CH_3{-}Te{-}C{\equiv}C)_2$ building unit, the molecules orient themselves in helical stacks (see Figure 13, bottom). The solid-state structure of **17** is dominated by close Te⋯Te contacts, whereby 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 atom forms zigzag-like contacts (3.74 Å and 3.82 Å) to two neighboring stacks (cf. Figure 6). Together with one diagonal contact (4.30 Å) and two contacts within the stacks (4.46 Å), each tellurium atom experiences seven close contacts in total.

This concept of building cavities resembles somewhat that encountered for dipeptides such as L-Leu-L-Val, which are bound head-to-tail and form helices with six dipeptides in term (cf. Figure 2).[12]

Conclusion

We have shown that tubular structures can be formed without hydrogen bonding if the building units are arranged properly by van der Waals forces between chalcogen centers. One can either use large rings with rigid building blocks, or stiff open chain building blocks and as many chalcogen units as possible. Several examples of differently sized cyclodiynes and cyclodienes have been presented that reveal close contacts between sulfur and selenium atoms, yielding a three-dimensional columnar arrangement. The synthesis of chalcogen-substituted macrocycles leads to the formation of cavities in the solid state that are able to include various guest molecules. We have demonstrated that the nonbonding chalcogen–chalcogen interactions are the driving forces that may direct cyclic rings to pile up in stacks yielding tubular arrangements. Thus, even saturated selenium-substituted crown ethers are able to form columnar structures despite the lack of $\pi-\pi$ interactions.

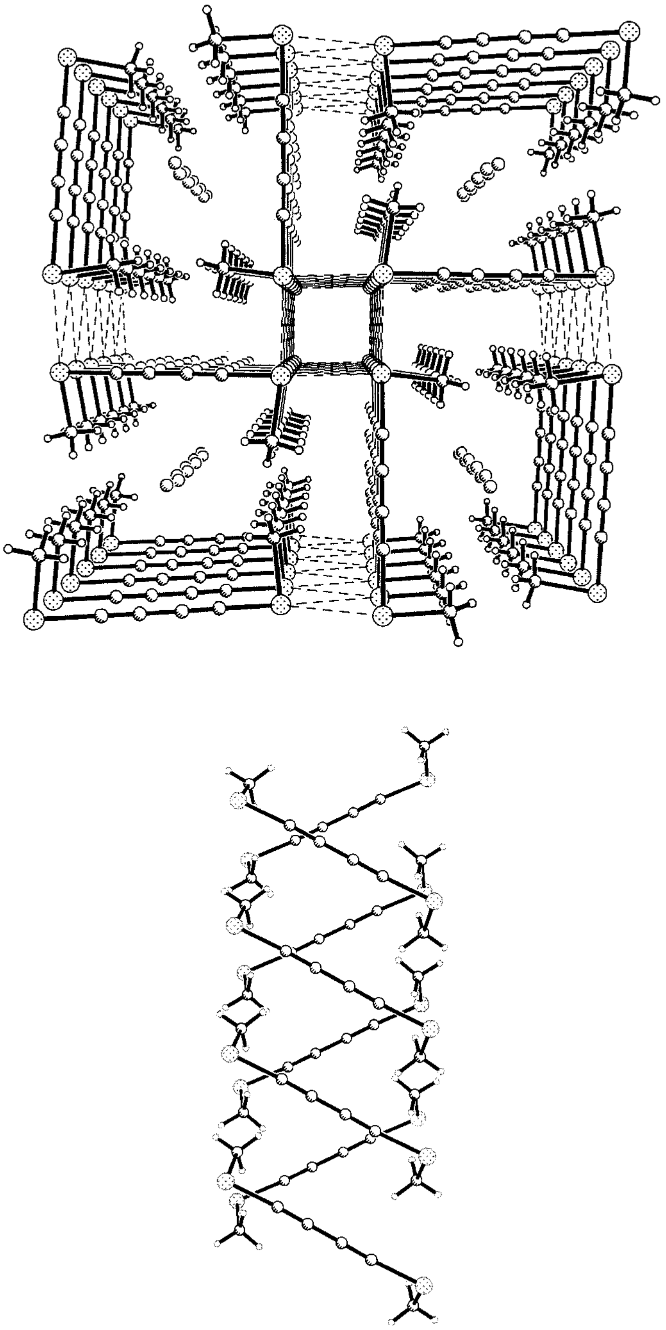


Figure 13. Top: Top view of the structure of **17** with the close Te⋯Te contacts and the included *n*-hexane molecules shown . Bottom: Side view showing the helical arrangement of **17** in the solid state.

To the best of our knowledge there are no channel-like structures available that have short contacts between halogen centers, but in principle this should be possible. A good candidate should be **1** in which the R group is Cl, Br, or I.[43]

The ability to create non-hydrogen-bonded networks, whereby sulfur, selenium, and tellurium provide the cement that binds the superstructure, allows access to new dimensions in stack and cavity design. Such chalcogen–chalcogen interactions may also have been important contributors in the early evolutionary stages of self-organising systems, beyond the very successful world of hydrogen bonds.

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[43] Note added in proof: A paper in which interactions between iodine atoms lead to a stacking of molecules has been published recently: Y. Morita, E. Miyazaki, J. Toyoda, K. Nakasuji, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 205–206.