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# Self-Organization of Chalcogen-Containing Cyclic Alkynes and Alkenes To Yield Columnar Structures

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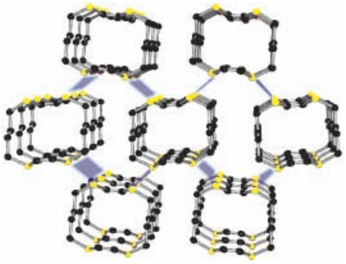
## ABSTRACT



**Close contacts between chalcogen atoms in cyclic dienes and diynes are used to create columnar structures in the solid state. Rigid and fairly planar cycles with chalcogen centers are the preconditions for forming those columnar structures.**

Isotropic forces between molecules cause the closest packings as the extensive study of crystal structures has shown. In the solid state, directional forces are needed to build three-dimensional structures with voids, channels, helices, or networks. These forces are, among others, hydrogen bonds, $\pi-\pi$ stacking and interactions between soft acids and bases.[1,2]

Molecular aggregation by means of hydrogen bonding and $\pi-\pi$ stacking was used to construct channel-like structures. Moore et al. used macrocyclic rings with a rigid frame of alternating triple bonds and phenyl rings to maintain planarity.[3] Hydrogen bonding between phenolic OH groups and $\pi-\pi$ stacking of aromatic rings were used to place the rings on top of each other. Ghadiri et al.[4] built flat cyclic peptides composed of an even number of D- and L-amino acids. Adopting a flat conformation, these cycles associate in stacks in an antiparallel fashion by forming hydrogen bonds between neighboring rings within one column. Both strategies produced molecular tubes. Close contacts between chalcogen centers in the solid state have been reported,[5−10] above all during the investigation of organic conductive

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materials.[7-9] Examples are tetrathiafulvalene (TTF), bis(ethylenedithio)tetra-fulvalene (BEDT-TTF), and tetramethyltetraselenafulvalene (TMTSF) to name but a few of them. In these species and their related derivatives, other interactions also contribute significantly to the formation of two- and three-dimensional networks besides close chalcogen contacts.[7-9] Close C−H···S contacts, C−H···$\pi$ contacts, and $\pi$−$\pi$ stacking cause these interactions.[11,12] In this communication, we demonstrate that close contacts between chalcogen centers alone are able to create columnar structures if rigid and fairly planar ring systems are used.

During our studies of the properties of electron-rich cyclic diynes and dienes (Figure 1), we found structures in which the rings are stacked on top of each other showing close chalcogen−chalcogen contacts. To understand the motifs of the van der Waals contacts, we consider first the packing of 1-thiacyclododeca-3,10-diyne (**1**).[13]

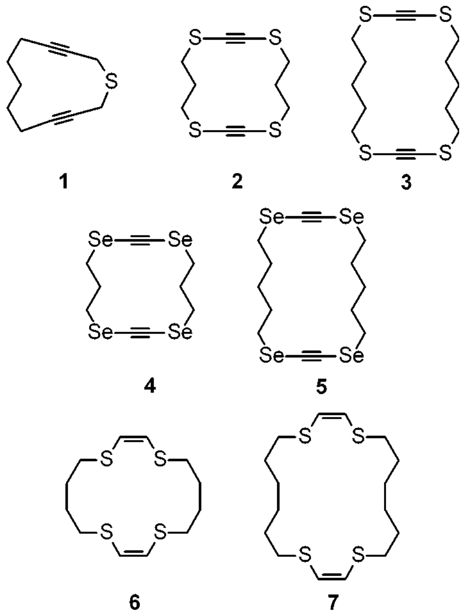

**Figure 1.**

This molecule provides a rather flat ring structure with one sulfur center. 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 (which are stacked on top of each other). As a result, a zigzag arrangement of the chalcogen atoms arises. This is outlined in Figure 2.

The close contacts between the sulfur centers (*a* and *b* in Figure 2) and the S···S distances inside a stack are listed in Table 1. In Figure 3, the resulting columns are shown. The two contacts generate a pair of columns as shown in Figure 3.

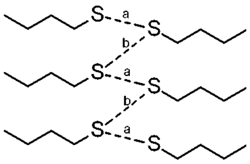

**Figure 2.** Schematic plot of chalcogen atoms of two neighboring rings yielding a zigzag arrangement and the definition of the intermolecular chalcogen−chalcogen distances *a* and *b*.

**Table 1.** Distances within a Zigzag Arrangement of Two Stacks and Distances within a stack for compounds **1**−**7**

| | distances (Å) within a zigzag arrangement of chalcogenes between two stacks | | | | | | |
|---|---|---|---|---|---|---|---|
| compd | a | b | a′ | b′ | a″ | b″ | distance (Å) within a stack |
| **1** | 3.53 | 3.53 | | | | | 4.74 |
| **2** | 3.75 | 3.89 | 3.66 | 4.18 | 3.96 | 5.59 | 4.55 |
| **3** | 3.63 | 3.86 | 4.49 | 4.54 | | | 4.61 |
| **4** | 3.80 | 3.83 | 3.75 | 4.31 | 3.90 | 5.65 | 4.56 |
| **5** | 3.68 | 3.84 | 4.37 | 4.59 | | | 4.63 |
| **6** | 3.47 | 4.13 | | | | | 5.22 |
| **7** | 4.07 | 4.07 | 4.18 | 4.18 | | | 5.24 |

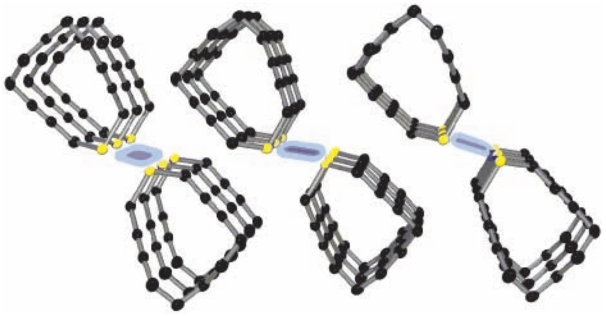

**Figure 3.** POV-Ray plot of the columnar structure of **1**. Sulfur atoms are indicated by the yellow color, and H atoms have been omitted for the sake of clarity. The blue color shows close distances between the sulfur atoms.

A rectangle-like structure with four chalcogen atoms placed at the corners of the rectangle is common to 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (**2**), 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (**3**),[14] and the corresponding selena congeners[15] **4** and **5**.

For **3** and the isomorphous **5** (see Figure 4), a zigzag arrangement of the chalcogen atoms is found similar to that

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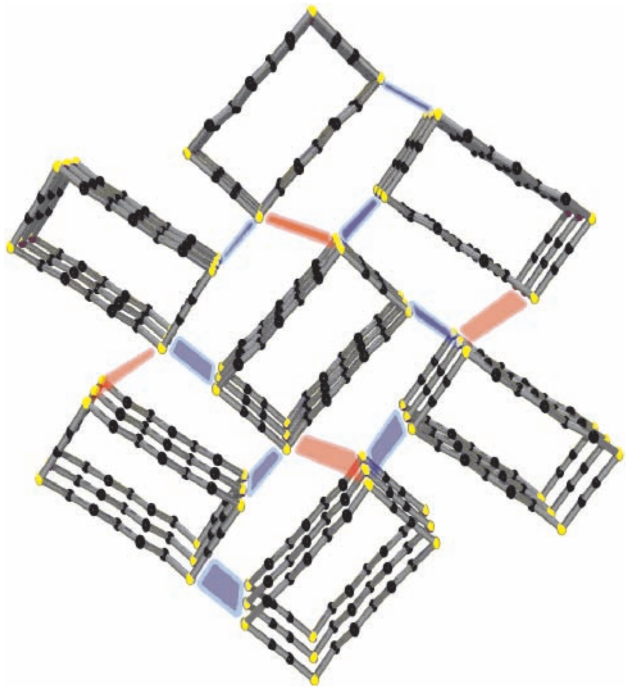

**Figure 4.** POV-Ray plot of the columnar structure of **3**. Sulfur atoms are indicated by the yellow color, and H atoms have been omitted for the sake of clarity. The blue color between the sulfur atoms shows close distances ($a$, $b$), and the red color shows the longer ones ($a'$, $b'$).

of **1**. In **3** and **5**, there are two crystallographically different types of chalcogen centers. Chalcogen atoms of the first type show two longer contacts ($a'$, $b'$ in Table 1; red in Figure 4) to chalcogen atoms of the same type and two shorter contacts to chalcogen atoms of the other type ($a$, $b$ in Table 1; blue in Figure 4). In addition, each type shows long contacts (4.61 Å in **3** and 4.63 Å in **5**) within the stacks. These contacts correspond to the $a$-axis of the unit cell. Thus, the first type of chalcogen atoms shows six contacts, whereas the second type shows only four.

A further variation of the intermolecular interactions discussed so far is found in the 14-membered rings of **2** and the isomorphous **4**. We find for a first set of chalcogen atoms close contacts yielding to a zigzag motif, but the distances vary more than in **3** and **5** ($a'$, $b'$ in Table 1). The second set of chalcogen centers forms a zigzag ($a$, $b$) and a ladder type ($a''$, $b''$) of contacts with stacks of the first type. This produces a total amount of seven contacts for one type of chalcogen atom and five contacts for the other.

Similar columnar structures were also found for (2*Z*,10*Z*)-1,4,9,12-tetrathiacyclohexadeca-2,10-diene (**6**) and (2*Z*,12*Z*)-1,4,11,14-tetrathiacycloeicosa-2,12-diene (**7**)[16] as shown in Figure 5. The rings of **6** and **7** adopt a chairlike conformation with rigid S−CH═CH−S units anti to each other. In **6**, the contacts between neighboring rings form an asymmetric zigzag arrangement with a close and a wider contact ($a$, $b$ in Table 1). The S···S distance within the stacks amounts to 5.22 Å.

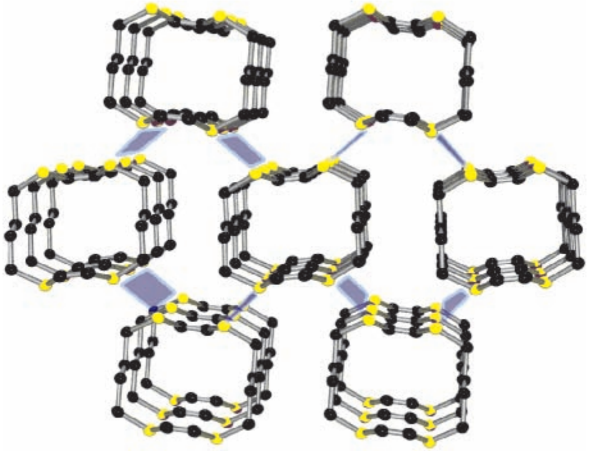

**Figure 5.** POV−Ray plot of the columnar structure of **6**. Sulfur atoms are indicated by the yellow color, and H atoms have been omitted for the sake of clarity. The blue color shows close distances between the sulfur atoms.

For **7**, we observed again a zigzag interaction of the sulfur centers. Two types of sulfur atoms show symmetric interactions ($a = b$; $a' = b'$) of similar distance ($a$, $b$ and $a'$, $b'$ in Table 1).

In light of previous investigations on close S···S contacts,[5,10] we examined the directionality of the interactions in our examples. The 3p lone pair of the sulfur in **1** coincides with the direction of the S−C bond of the neighboring ring. The same holds for the shortest contact ($a$ in Table 1) for **3** and **5**. We could not detect a clear-cut preference in the other examples.

Our investigations show that close contacts between chalcogen atoms incorporated in a rigid ring system may excert a similar steering effect as reported for hydrogen bonds and $\pi-\pi$ stacking to obtain columnar structures in the solid state. Several of the distances between the chalcogen atoms found in our columnar structures, especially inside the stacks, are longer than the van der Waals distances (S···S = 3.7 Å, Se···Se = 4.0 Å).[17] However, taking the van der Waals potential of noble gases,[18] like argon as an example, 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. In the case of S···S contacts, recent calculations estimate a stabilization energy of 1.5 kJ/mol at the minimum.[9] Each chalcogen atom in the ring provides several close chalcogen−chalcogen contacts. This seems sufficient to pile up columnar structures. As we anticipated, our results reveal various columnar structures but no inclusion of guests because the sizes of the rings in our examples are too small. With larger rings containing rigid units and chalcogen centers, one might

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be able to form larger tubes that are tailored to host other molecules.

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**Supporting Information Available:** X-ray data[19] and details of the refinement procedure of compounds **4−7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) **Crystal structure determination for 4:** $C_{10}H_{12}Se_4$; MW = 448.04; colorless; polyhedron; 0.18 × 0.14 × 0.06 mm; monoclinic; space group $P2_1/c$; $a$ = 4.5764(1) Å; $b$ = 13.4490(3) Å; $c$ = 10.3777(1) Å; $\beta$ = 95.9390(10)°; $V$ = 635.30(2) Å$^3$; $Z$ = 4; $T$ = 200(2) K; $d_{calc}$ = 2.34 g/cm$^3$; $F(000)$ = 832; $\mu$ = 11.51 mm$^{-1}$; 6451 reflections collected; 1450 independent reflections; 1287 reflections observed; $R(F)$ = 0.021; $R_w(F^2)$ = 0.051; $S$ (GOF) on $F^2$ = 1.11. $(\Delta\rho)_{max}$ = 0.48 e/Å$^3$; $(\Delta\rho)_{min}$ = −0.72 e/Å$^3$. **Crystal structure determination for 5:** $C_{14}H_{20}Se_4$; MW = 504.14; colorless; polyhedron; 0.20 × 0.16 × 0.06 mm; monoclinic; space group $P2_1/c$; $a$ = 4.6252(1) Å; $b$ = 17.2919(2) Å; $c$ = 10.3963(1) Å; $\beta$ = 91.309(1)°; $V$ = 831.26(2) Å$^3$; $Z$ = 2; $T$ = 200(2) K; $d_{calc}$ = 2.01 g/cm$^3$; $F(000)$ = 480; $\mu$ = 8.81 mm$^{-1}$; 8455 reflections collected; 1886 independent reflections; 1641 reflections observed; $R(F)$ = 0.025; $R_w(F^2)$ = 0.058; $S$ (GOF) on $F^2$ = 1.07; $(\Delta\rho)_{max}$ = 0.58 e/Å$^3$; $(\Delta\rho)_{min}$ = −0.87 e/Å$^3$. **Crystal structure determination for 6:** $C_{12}H_{20}S_4$; MW = 292.52; colorless; polyhedron; 0.32 × 0.18 × 0.15 mm; monoclinic; space group $P2_1/c$; $a$ = 5.2225(2) Å; $b$ = 10.3139(4) Å; $c$ = 14.2995(5) Å; $\beta$ = 99.9510(10)°; $V$ = 758.65(5) Å$^3$; $Z$ = 2; $T$ = 200(2) K; $d_{calc}$ = 1.28 g/cm$^3$; $F(000)$ = 312; $\mu$ = 0.60 mm$^{-1}$; 7627 reflections collected; 1740 independent reflections; 1517 reflections observed; $R(F)$ = 0.027; $R_w(F^2)$ = 0.067; $S$ (GOF) on $F^2$ = 1.09; $(\Delta\rho)_{max}$ = 0.26 e/Å$^3$; $(\Delta\rho)_{min}$ = −0.22 e/Å$^3$. **Crystal structure determination for 7:** $C_{16}H_{28}S_4$; MW = 348.62; colorless; polyhedron; 0.42 × 0.21 × 0.04 mm; monoclinic; space group $P2_1/c$; $a$ = 9.8648(3) Å; $b$ = 5.2409(2) Å; $c$ = 18.8504(6) Å; $\beta$ = 100.8330(10)°; $V$ = 957.21(6) Å$^3$; $Z$ = 2; $T$ = 200(2) K; $d_{calc}$ = 1.21 g/cm$^3$; $F(000)$ = 376; $\mu$ = 0.49 mm$^{-1}$; 9373 reflections collected; 2200 independent reflections; 1830 reflections observed; $R(F)$ = 0.029; $R_w(F^2)$ = 0.073; $S$ (GOF) on $F^2$ = 1.08; $(\Delta\rho)_{max}$ = 0.27 e/Å$^3$; $(\Delta\rho)_{min}$ = −0.18 e/Å$^3$.