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Self-organization of cyclic selenaethers to yield columnar structures

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Abstract—The previously published X-ray structures of five cyclic selenaethers (**1**–**5**) revealed columnar arrangements in the solid state. In most cases (**1**–**4**) the distances between the chalcogen centers of neighboring stacks are shorter than the sum of the van der Waals radii. This is the first time that rather flexible saturated cyclic compounds were reported to form three-dimensional columnar structures due to non-bonding chalcogen–chalcogen interactions in the solid state. © 2002 Elsevier Science Ltd. All rights reserved.

Recently, we found that cyclic alkenes and cyclic alkynes containing chalcogen atoms organize themselves into columnar structures.[1–3] As a common building motif we discovered that in these columns chalcogen atoms of neighboring stacks yield a zigzag arrangement ($a \approx b$) via van der Waals forces as presented schematically in Fig. 1. In some cases this building motif is changed to a ladder type arrangement ($a \ll b$).

The common feature of the unsaturated cyclic compounds is that most of the intermolecular distances between the different chalcogen atoms are shorter than the sum of the corresponding van der Waals radii. In many cases we found that the so called non-bonding interactions between the chalcogen centers can be described as an interplay of the occupied p-type orbital of one chalcogen center (X) and the empty X–C σ^* orbital of the other[4,5] as shown in Fig. 2 for Se···Se contacts. It was believed to be essential that the cyclic chalcogen substituted compounds reveal a rather flat and rigid geometry—provided by the π-system building blocks—to pile up in stacks and to form a three-dimensional columnar arrangement.

In the course of our in-depth study of chalcogen interactions, we scrutinized the published data on the X-ray

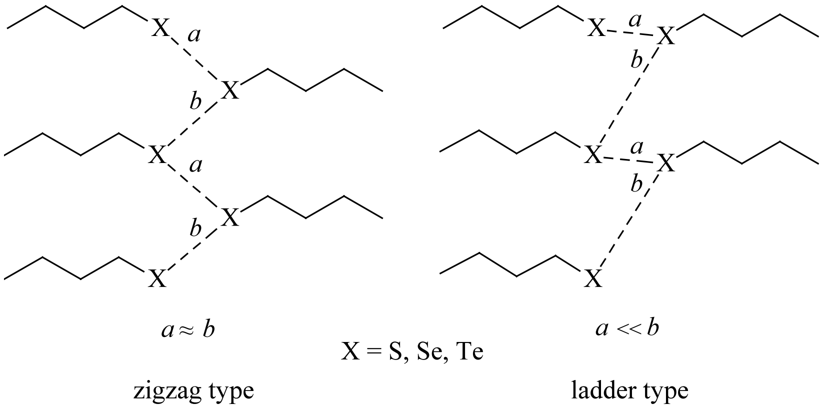

Figure 1. Schematic plot of a zigzag (left) and ladder (right) type arrangement of the chalcogen–chalcogen interaction in the solid state.

Keywords: crownethers; selenium; self-organization; tubular structures.

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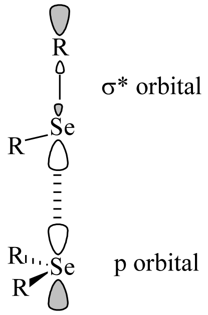


Figure 2. Interaction of the occupied p orbital with the unoccupied σ* orbital in selenaethers.

structures of some selenium coronands. We found that even saturated cyclic compounds like 1,5,9-triselenacyclododecane (**1**),[6] 1,3,7,9-tetraselenacyclododecane (**2**),[7] 1,4,8,11-tetraselenacyclotetradecane (**3**),[7] 1,3,7,9,13,15-hexaselenacyclooctadecane (**4**)[7] and 1,5,9,13,17,21-hexaselenacyclotetraeicosane (**5**)[7] are able to form three-dimensional tubular networks in the solid state despite the lack of any rigid building block in the cyclic moieties.

In Figs. 3 and 4 we show as representative examples the X-ray structures of **4** and **2**,[7] respectively. As in the unsaturated congeners, the selenium substituted cyclodiynes,[2] the cyclic selenaethers form tubular structures with relatively short contacts between the chalcogen atoms of neighboring columns. These distances (*a*, *b*, *a*′, *b*′) are listed in Table 1. Also the distances between the chalcogen centers within one stack are given. In Figs. 3 and 4 the contacts between the selenium atoms in **4** and **2** are indicated by broken lines. It is seen that the motifs presented in Fig. 1 are also maintained in this three-dimensional network.

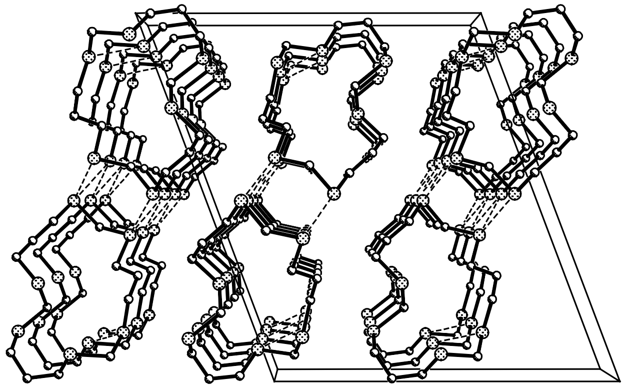


Figure 3. Plot of the columnar arrangements of **4** in the solid state. Broken lines indicate Se···Se distances less than 4 Å. H atoms are omitted for clarity.

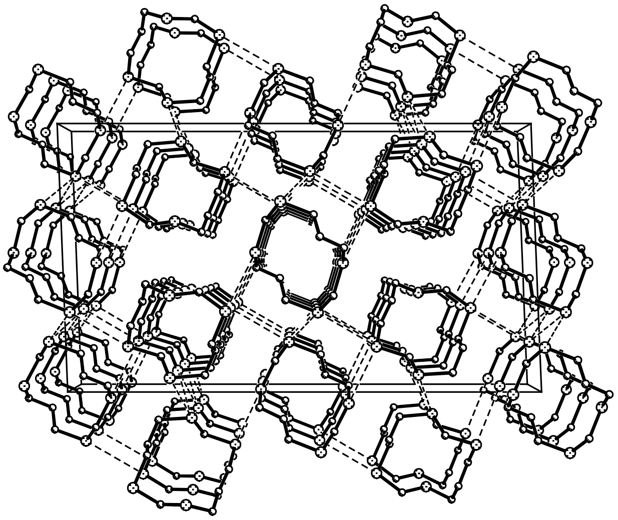
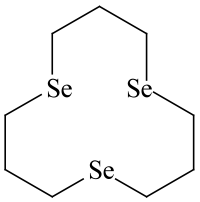
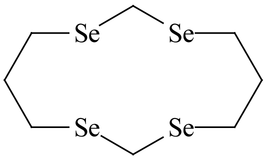


Figure 4. Plot of the columnar arrangements of **2** in the solid state. Broken lines indicate Se···Se distances less than 4 Å. H atoms are omitted for clarity.



1



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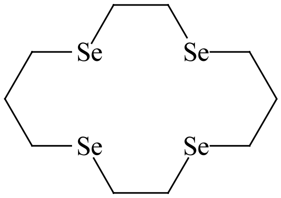

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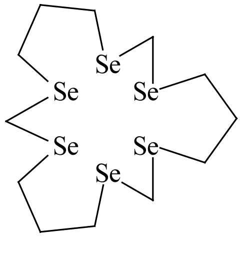

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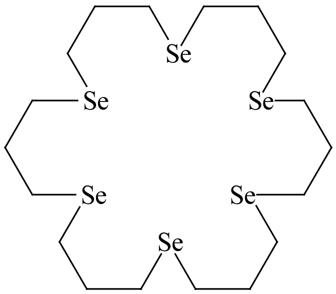

5

Table 1. Se···Se distances between the stacks and within the stacks in **1**–**5** in Å

Compd	Dist. between the stacks				Dist. within the stacks
	a	*b*	*a*′	*b*′	
1[6]	3.77[†]	3.77[†]	3.73[‡]		5.63
2[7]	3.69[†]	3.69[†]	3.77[†]	3.82[†]	5.53
3[7]	3.41[†]	3.94[†]			5.45
4[7]	3.63[†]	3.81[†]			5.43
5[7]	4.25[†]	4.30[†]			5.28

[†] Zigzag type.

[‡] Ladder type (for definition refer to Fig. 1).

A comparison of the intermolecular chalcogen–chalcogen distances with the van der Waals distance for Se···Se (4.0 Å)[8] reveals (Table 1) that in most cases (**1**–**4**) the distances found in the solid state are shorter than the sum of the van der Waals radii. For **5** the intercolumnar distances (*a*, *b*) are larger than the sum of the van der Waals radii as are the chalcogen–chalcogen distances within one stack.

However, taking the van der Waals potential of noble gases,[9] 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% compared to that found at the minimum at 3.8 Å. In the case of chalcogen–chalcogen contacts, recent calculations estimate a stabilization energy of 1.5–2.0 kJ/mol at the minimum.[10,11] Thus, in a columnar arrangement with many short contacts between chalcogen centers the stabilization energy is multiplied. The various non-bonding selenium interactions may direct the coronands **1**–**5** to align in such a way that a three-dimensional network of columns is built in the solid state.

Our literature search revealed that even in saturated cyclic selenaethers tubular structures are formed in the solid state due to close chalcogen–chalcogen interactions. Despite the lack of rigid building blocks like triple- or double-bonds the directive force between the selenium atoms in **1**–**5** is strong enough to stack the rather flexible cyclic systems upon each other.

Acknowledgements

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