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Cyclic Tetraselenadiynes: Rigid Cycles with Long-Range van der Waals Forces between Chalcogen Centers

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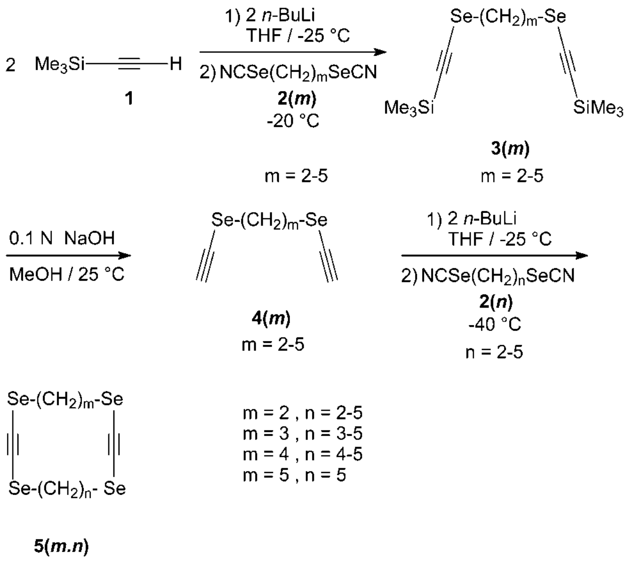
The synthesis of cyclic tetraselenadiynes could be achieved by a stepwise approach. Key steps were the reaction of the lithium salt of trimethylsilylacetylene (**1**) with α,*ω*-diselenocyanatoalkanes **2**(*m*) (*m* = 2−5). By treating the bis-lithium salt of the resulting α,*ω*-diselenaalkadiynes **4**(*m*) (*m* = 2−5) again with **2**(*n*) (*n* = 2−5) the cyclic tetraselenadiynes **5**(*m.n*) resulted, with methylene chains of length *m* and *n* between the SeC≡CSe units. The structures of seven ring systems could be investigated in the solid state. These investigations reveal that the molecular structures are determined by the rigid SeC≡CSe units, which try to adopt torsion angles of the CH_2−Se *σ*-bonds between 60° and 90°. In the solid state, the systems **5**(*3.3*) and **5**(*5.5*) show columnar structures that can be traced back to close contacts between Se atoms of neighboring rings.

Introduction

In host−guest chemistry, directional forces are of crucial importance.[1,2] These forces are necessary to build three-dimensional structures with voids, channels, helices, or networks. Directional forces are also the basic requirements for bonding between guests and hosts. Hydrogen bonds and *π*−*π* stacking are the most important ones in pure organic host−guest chemistry. If we extend our view also to metal complexes, the interactions between soft acids and bases have to be named too.[3]

Channel-like structures have been generated by utilizing hydrogen bonding and *π*−*π* stacking. Moore et al.[4] used macrocyclic rings with a rigid frame of alternating triple bonds and phenyl rings to maintain planarity. Hydrogen bonding between phenolic OH groups and *π*−*π* stacking of the aromatic rings provided the directional forces within one column. Ghadiri et al.[5] constructed flat cyclic peptides composed of an even number of D- and L-amino acids. These cycles associate in stacks in an antiparallel fashion by forming hydrogen bonds between neighboring rings within one column.

Scheme 1



In this paper, we provide examples for directional forces between chalcogen centers in cyclic tetrathiadiynes and cyclic tetraselenadiynes that may lead to columnar structures in the solid state. We also will present a protocol for preparing cyclic tetraselenadiynes with Se atoms in the position α to the triple bonds.

Results

Synthesis. To prepare cyclic tetraselenadiynes, we make use of a protocol closely related to that recently applied for the synthesis of cyclic tetrathiadiynes.[6] Our route is summarized in Scheme 1.

The lithium salt of trimethylsilylacetylene, prepared from **1** and butyllithium,[7] was reacted at −20 °C with α,*ω*-diselenocyanatoalkanes[8−10] **2**(*m*) (*m* = 2−5) to afford

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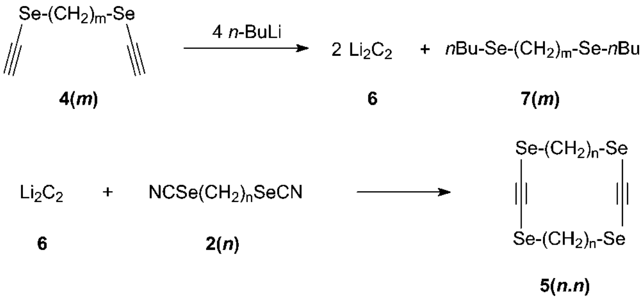
Table 1. Most Relevant Distances and Angles of the Tetraselenacyclodiynes[a]

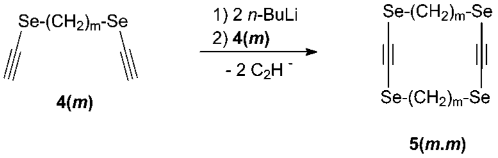
compd	t_1, t_2 (pm)	α_1, α_2 (deg)	α_3, α_4 (deg)	β (deg)	γ_1, γ_2 (deg)
5(*2.2*)	471, 471	179, 179	179, 179	11	25, 25
5(*2.4*)	461, 490	178, 171	176, 175	62	84, 65
5(*2.5*)	479, 506	178, 177	175, 176	25	76, 88
5(*3.3*)	567, 567	176, 177	177, 176	0	63, 63
5(*3.5*)	561, 578	175, 174	174, 175	0	73, 73
5(*4.4*)[b]	527, 528	180, 176	177, 179	82	88, 87
	523, 528	179, 175	177, 178	80	88, 83
5(*5.5*)	827, 827	176, 176	176, 176	0	61, 61

[a] For the definition of the distances and angles see Figure 2. [b] Two independent molecules exist in the unit cell; one of them is slightly disordered.

Scheme 2



Scheme 3



the bis(trimethylsilyl)diselenaalkadiynes **3**(m) ($m = 2-5$) in good yields. The protecting groups were removed with catalytic amounts of dilute NaOH at ambient temperature. The isolated diynes **4**(m) ($m = 2-5$) were lithiated and reacted again with α,ω-diselenocyanatoalkanes **2**(n) ($n = 2-5$) to produce the desired cyclic tetraselenadiynes **5**($m.n$). It is interesting to look at the obtained yields. With the exception of **5**(*2.2*), the smallest ring that was synthesized, we notice the highest yields (35−45%) for those rings with $m = n$. One reason for the lower yields in the case of rings with different chain lengths between the SeC≡CSe building units were side reactions that led to products with equal chain lengths as shown in Schemes 2 and 3. Treatment of the diselenaalkadiynes **4**(m) with an excess of butyllithium and subsequently with **2**(n) to generate **5**($m.n$) yields in a side reaction the dilithium acetylide **6** and α,ω-bis(butylselena)alkane (**7**(m)). The reaction of **6** with 2 equiv of **2**(n) produces **5**($n.n$) as a side product together with **5**($m.n$). The mixture of **5**($m.n$) and **5**($n.n$) is difficult to separate; therefore, the purification of **5**($m.n$) is tedious and reduces the obtained yield. Evidence for the occurrence of this side reaction was found during the synthesis of **5**(*4.5*). Next to the desired product we also isolated **5**(*4.4*) and **5**(*5.5*).

A second side reaction that produces again a product with equal chain lengths occurs during the lithiation step of **4**(m) and subsequent reaction with **2**(n) (Scheme 3). It is due to a disproportionation reaction and was first described by Brandsma.[7] He found that ethynyl selenides readily disproportionate in the presence of base into bis(alkylselena)acetylenes and acetylene. The reaction might be rationalized by assuming that displacement of ethynyl anion from selenium takes place in a manner similar to the displacement of cyanide ion (cf. Scheme 1). This leads in the case of **4**(m) to **5**($m.m$) and acetylene as a side product during the preparation of **5**($m.n$) as shown in Scheme 3. Both side reactions as summarized in Schemes 2 and 3 contribute to a reduction of yields during the synthesis and purification of **5**($m.n$) ($m \neq n$).

Structural Investigations. (a) Molecular Structures. We were able to grow single crystals of **4**(*2*), **5**(*2.2*), **5**(*2.4*), **5**(*2.5*), **5**(*3.3*), **5**(*3.5*), **5**(*4.4*), and **5**(*5.5*). As examples, we show in Figure 1 the molecular structures of **5**(*2.2*), **5**(*2.4*), **5**(*3.3*), and **5**(*3.5*). In Table 1, we list the most relevant distances and angles found in the solid state. These are the transannular distances t_1 and t_2 as well as the angles describing the bending of the triple bonds ($\alpha_1-\alpha_4$) and the torsion angles (β, γ_1, γ_2) as defined in Figure 2. Not compiled in Table 1 are the lengths of the triple bonds and the distances between the sp centers and the selenium atoms, which vary only slightly. The former modulate between 118 and 121 pm, values that were also encountered for cyclic mono- and diynes.[11] The latter vary between 181 and 184 pm. The distances between opposite triple bonds, t_1 and t_2, spread from 461 to 827 pm. This diversity was anticipated insofar as larger chains imply larger separations. The angles $\alpha_1-\alpha_4$ vary only slightly between 171° and 179°, indicating that the SeC≡CSe unit is a rigid building block. The torsion angle β between the triple bonds was found to be 0° in the cases of those rings where the SeC≡CSe units are connected by an odd number of methylene groups (**5**(*3.3*), **5**(*3.5*), **5**(*5.5*)), and therefore, chair conformations of the rings are adopted.

A comparison among the torsional angles γ_1 and γ_2 between the CH_2-Se σ-bonds reveals values close to 60° for the rings with chair conformation ($\beta = 0$). This was expected and observed for many of the corresponding carbon compounds.[11] In the other cases, with the exception of **5**(*2.2*), values for γ_1 and γ_2 vary between 65° and 89°. These angles result as a compromise between the fact that the CH_2-Se σ-bonds try to adopt a torsion angle of approximately 90° and the alkane chains try to adopt a zigzag arrangement with a staggered conformation.[12] To substantiate these arguments, we have calculated the torsion angles for $H_3CXC{\equiv}CXCH_3$ (X = S, Se, O) by using the DFT (B3LYP) method[13] applying a 6-311G* basis set.[14] The computations were carried out with the Gaussian 98 program[15] by optimizing all geometrical parameters. Frequency calculations were carried out to characterize the nature of the stationary points. For the Se

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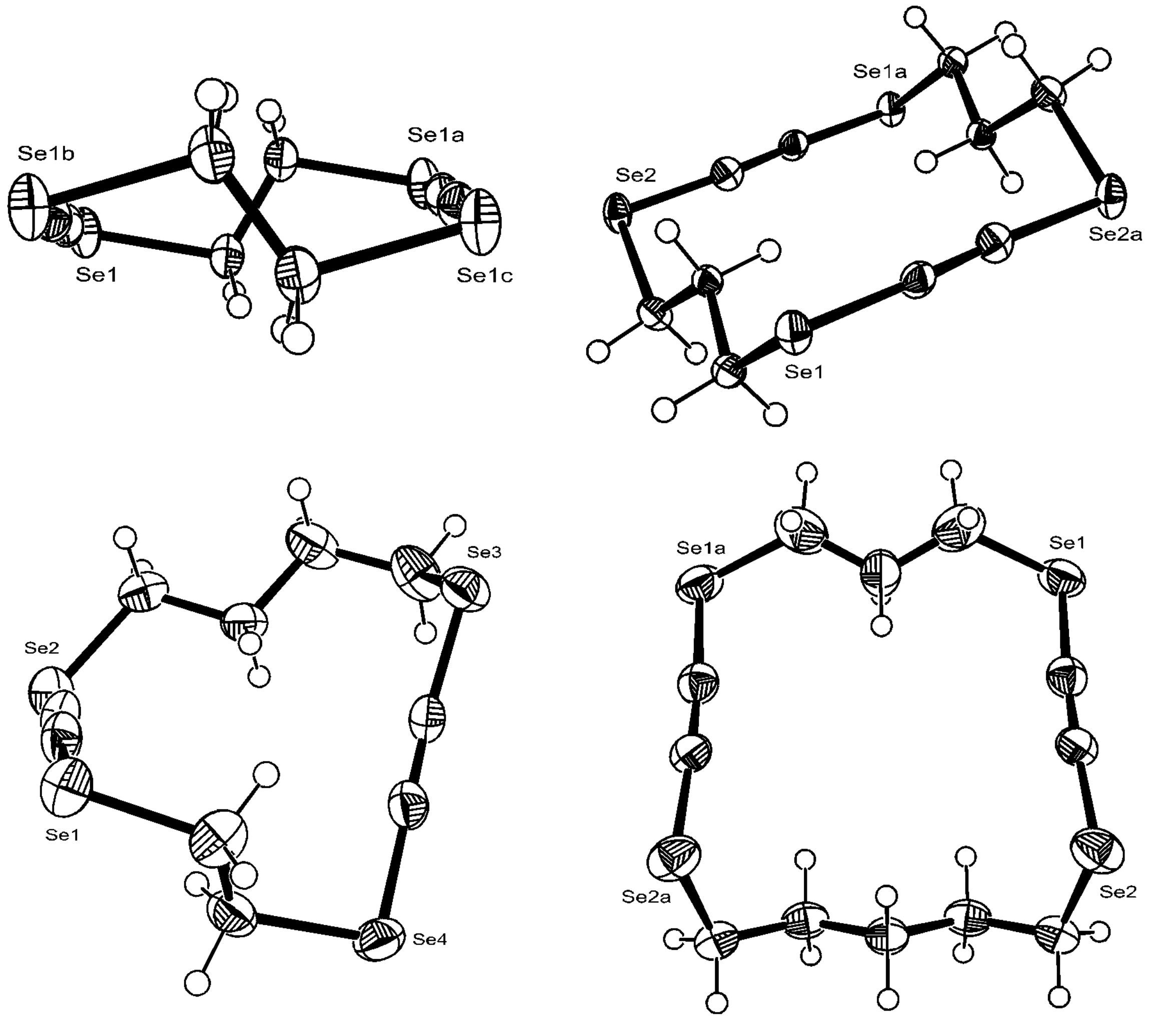

Figure 1. ORTEP plots (50% ellipsoid probability) of the molecular structures of **5**(*2.2*), **5**(*3.3*), **5**(*2.4*), and **5**(*3.5*).

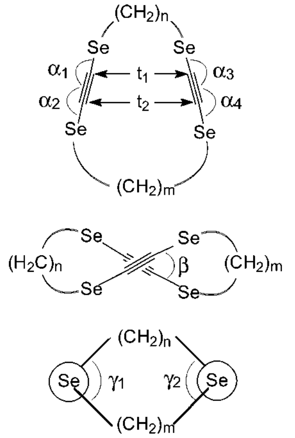

Figure 2. Definitions of transannular distances t_1 and t_2, angles α_1−α_4, and torsion angles β and γ_1, γ_2 in **5**(*m.n*).

congener, the conformation of minimum energy has a torsion angle of 91.3°. Bock supposed a similar value by means of photoelectron spectroscopy.[16] It was also found that the rotational barrier for X = Se is between the barrier for the sulfur and oxygen congeners as shown in Figure 3. A natural bond orbital (NBO) analysis reveals that the magnitude of the rotational barriers results essentially as a compromise of two effects: The orbital overlap between the lone pairs at the chalcogen atoms and the π^* orbitals of the triple bond decreases from oxygen to selenium, whereas the energy differences of these orbitals decrease from oxygen to selenium. The result is the highest rotational barrier of the three for the sulfur congener.

If one compares the torsion angles β and γ_1, γ_2 of the cyclic tetrathiadiynes and tetraselenadiynes one finds a close similarity with the exception for the systems with ethano bridges between the XC≡CX units. In the sulfur case, the system adopts a chair conformation ($\beta = 0$, γ_1, $\gamma_2 = 99.3°$, $t_1 = t_2 = 356$ pm), with the ethano bridges almost in an eclipsed conformation. In the selenium

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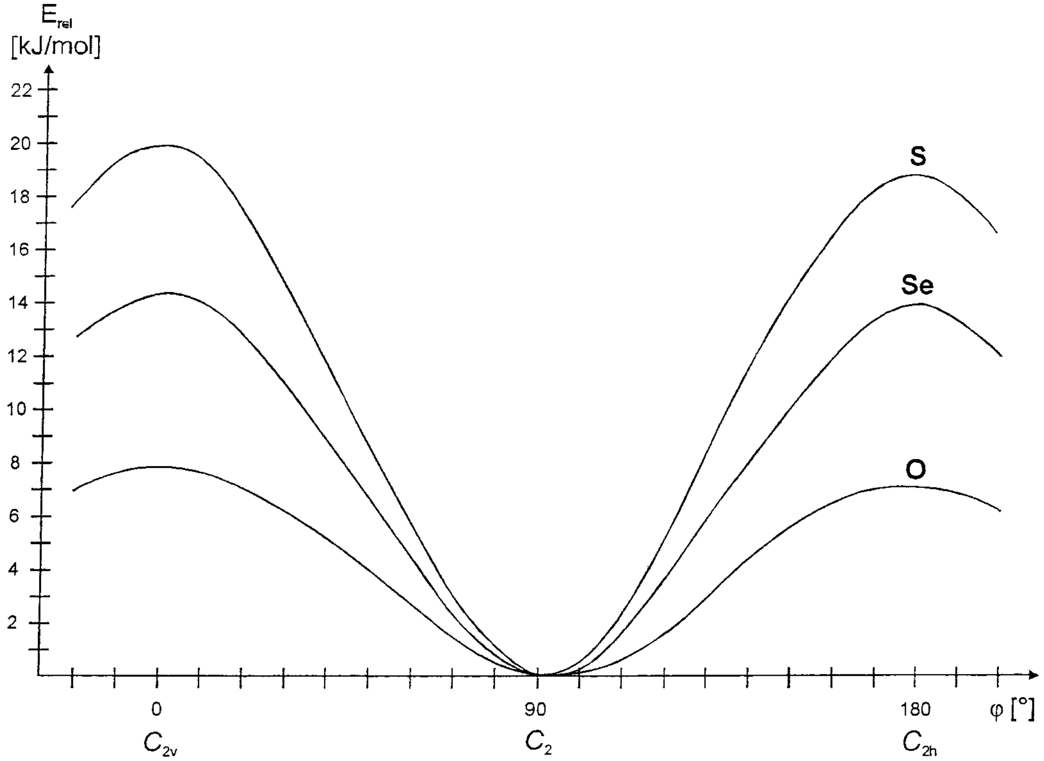

Figure 3. Relative rotational barriers for $H_3CXC{\equiv}CXCH_3$ for X = O, S, Se. The energies are based on B3LYP/6-311G* calculations.

congener **5**(*2.2*) (Figure 1), a twist-like conformation with D_2-symmetry is preferred. This allows a longer distance between the chalcogen centers (4.69 Å (Se), 3.56 Å (S)[6]) and a staggered conformation of the ethano bridges. To achieve that, small torsion angles γ_1 and γ_2 (24.9°) at the selenium atoms have to be tolerated.

Analogous to the sulfur systems, we found that the alkane chains between the SeC≡CSe units try to adopt a strain-free conformation. This is approached by reduction of the torsional angles γ from 90° down to approximately 60° for **5**(*3.3*), **5**(*3.5*), and **5**(*5.5*) and even to 25° for **5**(*2.2*). From Figure 3, it is seen that a deviation of the torsion angle from the minimum at 90° by 30° costs only 4 kJ/mol.

(b) Packing in Crystal. In the case of **5**(*3.3*) and **5**(*5.5*), we noticed the appearance of columnar structures in the solid state.[17] These structures arise by stacking the almost planar rigid rings on top of each other. Checking the corresponding sulfur systems again we found isomorphous structures.[6,17] In Figure 4a, we show as an example the packing of **5**(*5.5*). Common to all these rings is a rectangular structure. The short sides of the rectangle are spanned by the rigid SC≡CS and SeC≡CSe units, respectively, whereas the long sides are formed by the alkane chains, adopting a zigzag conformation. The chalcogen atoms are located at the four edges of the rather flat rectangle.

All selenium atoms keep close contacts with pairs of chalcogen atoms of neighboring stacks. As a result, a zigzag arrangement of the selenium atoms occurs. This is shown schematically in Figure 4b. In the case of **5**(*5.5*), we encounter two crystallographic different types of chalcogen atoms. The first type of selenium atoms shows two longer contacts (d_2 = 4.37, 4.59 Å) to selenium atoms

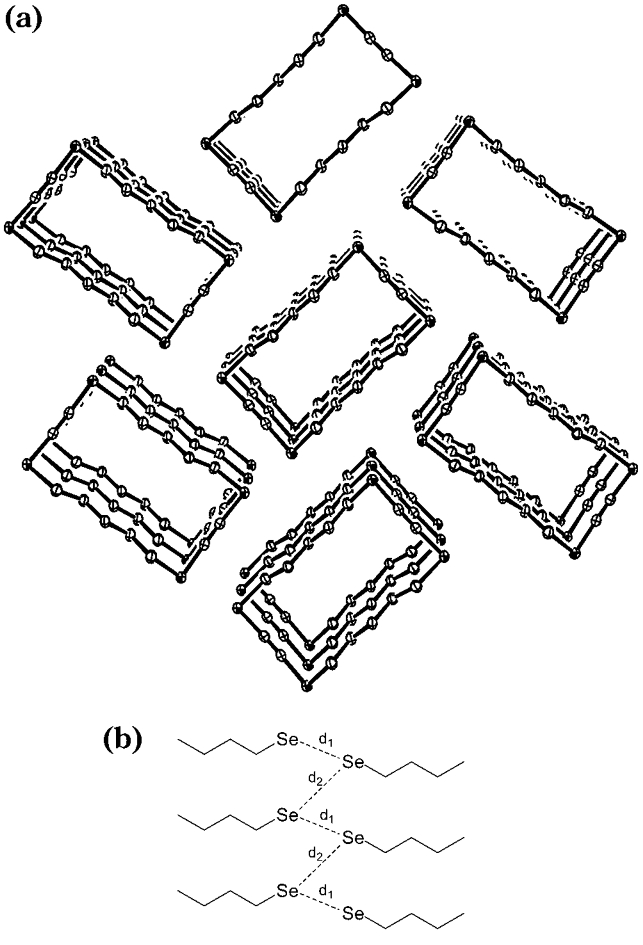

Figure 4. (a) Columnar structures of **5**(*5.5*) in the solid state (50% ellipsoid probability, H atoms have been omitted for the sake of clarity). (b) Schematic plot of selenium atoms of two neighboring rings yielding a zigzag arrangement and the definition of the intermolecular selenium selenium distances d_1 and d_2.

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Table 2. The Shortest (d_1) and Second Shortest (d_2) Intermolecular Se···Se Distances in the Solid-State Structures of the Tetraselenacyclodiynes

compd	d_1 (pm)	d_2 (pm)
5(*2.2*)	370	412
5(*2.4*)	387	390
5(*2.5*)	358	378
5(*3.3*)	375	380
5(*3.5*)	390	400
5(*4.4*)	363	381
5(*5.5*)	368	384

of the same type and two shorter contacts to selenium atoms of the other types (d_1 = 3.68, 3.84 Å) of the neighboring rings. In addition, each type of chalcogen atoms shows long contacts (4.63 Å) within the stacks. These contacts correspond to the short crystallographic axis. The first type of selenium atoms shows six contacts, whereas the second type shows only four.

A further variation of the intermolecular interactions found for **5**(*5.5*) is found in the 14-membered rings of **5**(*3.3*). We observe for a first set of selenium atoms close contacts yielding to a zigzag motif, but the distances d_1 and d_2 vary more than for **5**(*5.5*). The second set of selenium centers forms also a zigzag (d_1', d_2') and a ladder-type arrangement.

Other cyclic systems (**5**(*2.2*), **5**(*2.4*), **5**(*2.5*), **5**(*3.5*), and **5**(*4.4*)) investigated also revealed short intermolecular Se···Se distances in the solid state. In Table 2, we have listed the two shortest Se···Se distances (d_1, d_2) recorded in the solid state for all cyclic tetraselenadiynes investigated in this paper. All intermolecular Se···Se distances are shorter than the van der Waals distance between two selenium centers (4.0 Å).[18] The short Se···Se contact is a determinant element for the packing in the solid state. However, a columnar structure is only adopted for **5**(*3.3*) and **5**(*5.5*). We ascribe this to the fact that the other rings are puckered too strongly. The 12-membered rings of **5**(*2.2*) establish a close packing by perpendicular orientation to each other. This seems to be more efficient than a columnar stacking.

Discussion

Our investigations reveal close contacts between the selenium atoms in the various structures (Table 2). Those between neighboring rings are closer than the van der Waals distances (Se···Se 4.0 Å),[18] others, especially those within the stacks, are longer. However, taking the van der Waals potential of noble gases[19] like argon as an example one finds that at 4.5 Å the stabilization energy amounts to 50% of that of 3.8 Å.[19] In the case of S···S contacts, recent calculations estimate a stabilization of 1.5 kJ/mol at the minimum.[20]

Close contacts between chalcogen centers have been noticed at various occasions,[21−25] especially during the investigations of electron-transfer based conducting and superconducting materials such as tetrathiafulvalene (TTF), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), and tetramethylselenafulvalene (TMTSF), to name but a few.[21,23] In these species and their related derivatives, other interactions besides close chalcogen chalcogen contacts such as $\pi-\pi$ stacking, close C−H···Se, and C−H···π interactions[26,27] contribute significantly to the formation of two- and three-dimensional networks.

Our investigations reveal that a rigid ring with chalcogen atoms at the periphery leads in many cases to columnar structures wherein the rings can adopt a zigzag motif with the neighbors. In the given examples, other directional forces such as $\pi-\pi$ stacking and C−H···donor interactions play at most a minor role, and therefore, the Se···Se contacts dominate. In most cases (**5**(*2.4*), **5**(*2.5*), **5**(*3.5*) and **5**(*4.4*)), the contacts show directional preference that roughly the 4p lone pair of one Se center is directed to the σ*(Se−C) orbital of the neighboring ring.[24,25]

Conclusions

We were successful in synthesizing cyclic tetraselenadiynes by applying a similar protocol as used for the preparation of the sulfur congeners. It was found that the bond between the selenium centers and the alkyne units was cleaved easier than the sulfur-alkyne bond by strong bases giving rise to unintentional side reactions. We found a great similarity between the molecular structures of the selenium and the sulfur rings if the rings consist of more than 12 members. The most interesting result were the columnar structures found for **5**(*3.3*) and **5**(*5.5*). This finding let us conclude that for larger rings with enough stiff building elements there should be a possibility for inclusions.

Experimental Section

General Methods. All reactions were conducted in oven-dried glassware under an argon atmosphere with magnetic stirring. THF was dried with sodium/benzophenone and distilled under argon before use. Melting points are uncorrected. Material used for column chromatography: silica gel 60 (Macherey-Nagel). ^{1}H NMR and ^{13}C NMR were recorded either at 300 and 500 MHz (^{1}H NMR) or 75.5 and 125.8 MHz (^{13}C NMR), respectively, using the solvent as internal standard. The IR spectra were recorded with a FT-IR instrument. The high-resolution mass spectra (HRMS) were recorded in the EI (70 eV) mode. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Trimethylsilylacetylene (**1**) and the diselenocyanatoalkanes **2**(n) were prepared according to literature methods.[7−10]

General Procedure for the Preparation of Bis(trimethylsilyl)diselenaalkadiynes 3(m). To a solution of trimethylsilylacetylene (**1**) in 250 mL of anhydrous THF was added n-butyllithium (1.6 M solution in hexane) dropwise at −25 °C over a period of 20 min. The solution was stirred for 1−2 h at −25 °C. The diselenocyanatoalkane **2**(m) dissolved in 100 mL of anhydrous THF was added dropwise over a period

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of 30 min keeping the temperature below −20 °C to yield a yellow solution. The reaction mixture was then allowed to stirr for 1 h at −15 °C. Fifty milliliters of saturated NH_4Cl solution and 100 mL of light petroleum were added, the layers were separated, and the aqueous layer was extracted three times with light petroleum. The combined organic extracts were washed with brine and dried with $MgSO_4$. After evaporation of the solvent, the resulting residue was filtered rapidly through silica gel with a mixture of light petroleum/diethyl ether (10:1) yielding the bis(trimethylsilyl)diselenaalkadiynes **3**(*n*).

1,8-Bis(trimethylsilyl)-3,6-diselenaocta-1,7-diyne (3(*2*)). Starting materials: 0.99 g (10.1 mmol) of TMSA (**1**), 6.3 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.20 g (5.0 mmol) of 1,2-diselenocyanatoethane (**2**(*2*)). Filtration afforded 1.62 g (84.2%) of **3**(*2*) as a yellow solid: mp 51 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 18H, C*H*$_3$), 3.18 (s, 4H, SeC*H*$_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 0.14 (*C*H$_3$), 28.24 (Se*C*H$_2$), 84.57 (≡*C*Se), 109.23 (≡*C*Si); IR (film) 2958, 2901, 2085, 1249, 854, 763 cm^{-1}; MS (EI, 70 eV) 382 [M$^+$], 354, 205, 179, 162, 123, 97, 73; HRMS (EI, 70 eV) calcd for $C_{12}H_{22}Si_2{}^{78}Se^{82}Se$ 381.9600, found 381.9597.

1,9-Bis(trimethylsilyl)-3,7-diselenanona-1,8-diyne (3(*3*)). Starting materials: 1.17 g (11.9 mmol) of TMSA (**1**), 7.4 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.49 g (5.9 mmol) of 1,3-diselenocyanatopropane (**2**(*3*)). Filtration afforded 1.30 g (55.5%) of **3**(*3*) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 18H, C*H*$_3$), 2.32 (quint, ^3J = 6.8 Hz, 2H, SeCH$_2$C*H*$_2$), 2.95 (t, ^3J = 6.8 Hz, 4H, SeC*H*$_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 0.15 (*C*H$_3$), 28.30 (Se*C*H$_2$), 29.84 (SeCH$_2$*C*H$_2$), 85.67 (≡*C*Se), 108.02 (≡*C*Si); IR (film) 2958, 2898, 2088, 1412, 1249, 860, 843, 760 cm^{-1}; MS (EI, 70 eV) 394 [M$^+$], 202, 179, 162, 113, 97, 73; HRMS (EI, 70 eV) calcd for $C_{13}H_{24}Si_2{}^{78}Se^{80}Se$ 393.9755, found 393.9755.

1,10-Bis(trimethylsilyl)-3,8-diselenadeca-1,9-diyne (3(*4*)). Starting materials: 1.84 g (18.7 mmol) of TMSA (**1**), 11.7 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 2.50 g (9.4 mmol) of 1,4-diselenocyanatobutane (**2**(*4*)). Filtration afforded 2.81 g (73.3%) of **3**(*4*) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 18H, C*H*$_3$), 1.95 (m, 4H, SeCH$_2$C*H*$_2$), 2.81 (m, 4H, SeC*H*$_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 0.15 (*C*H$_3$), 28.53 (SeCH$_2$*C*H$_2$) 29.41 (Se*C*H$_2$), 85.89 (≡*C*Se), 107.89 (≡*C*Si); IR (film) 2958, 2897, 2088, 1448, 1249, 860, 843, 760 cm^{-1}; MS (EI, 70 eV) 410 [M$^+$], 281, 233, 216, 179, 162, 97, 73; HRMS (EI, 70 eV) calcd for $C_{14}H_{26}Si_2{}^{80}Se_2$ 409.9904, found 409.9902.

1,11-Bis(trimethylsilyl)-3,9-diselenaundeca-1,10-diyne (3(*5*)). Starting materials: 4.20 g (42.8 mmol) of TMSA (**1**), 26.8 mL of *n*-butyllithium (1.6 M in *n*-hexane) and 6.00 g (21.4 mmol) of 1,5-diselenocyanatopentane (**2**(*5*)). Filtration afforded 7.42 g (82.2%) of **3**(*5*) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 18H, C*H*$_3$), 1.56 (m, 2H, SeCH$_2$CH$_2$C*H*$_2$), 1.85 (m, 4H, SeCH$_2$C*H*$_2$), 2.80 (t, ^3J = 7.3 Hz, 4H, SeC*H*$_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 0.19 (*C*H$_3$), 28.98 (SeCH$_2$CH$_2$*C*H$_2$), 29.07 (Se*C*H$_2$), 29.39 (SeCH$_2$*C*H$_2$), 86.08 (≡*C*Se), 107.78 (≡*C*Si); IR (film) 2958, 2935, 2897, 2087, 1417, 1249, 860, 842, 760 cm^{-1}; MS (EI, 70 eV) 424 [M$^+$], 274, 247, 230, 179, 162, 97, 73; HRMS (EI, 70 eV) calcd for $C_{15}H_{28}Si_2{}^{78}Se^{80}Se$ 422.0068, found 422.0055.

General Procedure for the Preparation of the Diselenaalkadiynes 4(*m*). To a solution of the bis(trimethylsilyl)diselenaalkadiyne **3**(*m*) in 150 mL of methanol and 20 mL of THF was added 0.1 N aqueous NaOH dropwise over a period of 15 min. The reaction mixture was stirred for 2 h at room temperature. The mixture was poured into 300 mL of ice/water, and 300 mL of diethyl ether was added. The layers were separated and the aqueous layer was extracted five times with diethyl ether. The combined organic layers were washed with NH_4Cl solution and brine and dried with $MgSO_4$. After rotary evaporation, the product was isolated by column chromatography on silica gel, eluting with mixtures of light petroleum/diethyl ether.

3,6-Diselenaocta-1,7-diyne (4(*2*)). Starting materials: 8.60 g (22.6 mmol) of **3**(*2*) and 22.6 mL (2.26 mmol) of 0.1 N NaOH. Column chromatography afforded 3.83 g (71.8%) of **4**(*2*) as a colorless solid: mp 62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.86 (s, 2H, ≡C*H*), 3.22 (s, 4H, SeC*H*$_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 27.78 (Se*C*H$_2$), 64.07 (≡*C*Se), 89.60 (≡*C*H); IR (film) 2933, 2022, 1412, 1221, 1163, 693, 619, 571 cm^{-1}; MS (EI, 70 eV) 238 [M$^+$], 210, 160, 133, 105; HRMS (EI, 70 eV) calcd for $C_6H_6{}^{78}Se^{80}Se$ 235.8807, found 235.8788. Anal. Calcd for $C_6H_6Se_2$: C, 30.53; H, 2.56. Found: C, 30.63; H, 2.62.

3,7-Diselenanona-1,8-diyne (4(*3*)). Starting materials: 2.27 g (5.8 mmol) of **3**(*3*) and 5.8 mL (0.58 mmol) of 0.1 N NaOH. Column chromatography afforded 1.08 g (74.5%) of **4**(*3*) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (quint, ^3J = 6.8 Hz, 2H, SeCH$_2$C*H*$_2$), 2.79 (s, 2H, ≡C*H*), 2.95 (t, ^3J = 6.8 Hz, 4H, SeC*H*$_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 27.63 (Se*C*H$_2$), 29.88 (SeCH$_2$*C*H$_2$), 64.79 (≡*C*Se), 88.63 (≡*C*H); IR (film) 2936, 2849, 2029, 1439, 1224, 680, 574 cm^{-1}; MS (EI, 70 eV) 252 [M$^+$], 224, 210, 160, 119, 105; HRMS (EI, 70 eV) calcd for $C_7H_8{}^{80}Se_2$ 251.8956, found 251.8920. Anal. Calcd for $C_7H_8Se_2$: C, 33.62; H, 3.22. Found: C, 33.57; H, 3.27.

3,8-Diselenadeca-1,9-diyne (4(*4*)). Starting materials: 5.50 g (13.5 mmol) of **3**(*4*) and 13.5 mL (1.35 mmol) of 0.1 N NaOH. Column chromatography afforded 2.30 g (64.7%) of **4**(*4*) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (m, 4H, SeCH$_2$C*H*$_2$), 2.79 (s, 2H, ≡C*H*), 2.83 (m, 4H, SeC*H*$_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 27.93 (*C*H$_2$), 29.64 (*C*H$_2$), 65.10 (≡*C*Se), 88.46 (≡CH); IR (film) 2933, 2852, 2027, 1444, 1261, 1213, 680, 574 cm^{-1}; MS (EI, 70 eV) 266 [M$^+$], 224, 210, 160, 133, 119, 105; HRMS (EI, 70 eV) calcd for $C_8H_{10}{}^{80}Se_2$ 265.9113, found 265.9077.

3,9-Diselenaundeca-1,10-diyne (4(*5*)). Starting materials: 1.43 g (3.4 mmol) of **3**(*5*) and 3.4 mL (0.34 mmol) of 0.1 N NaOH. Column chromatography afforded 0.72 g (76.6%) of **4**(*5*) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (quint, ^3J = 7.5 Hz, 2H, SeCH$_2$CH$_2$C*H*$_2$), 1.86 (m, 4H, SeCH$_2$C*H*$_2$), 2.77 (s, 2H, ≡C*H*), 2.81 (t, ^3J = 7.3 Hz, 4H, SeC*H*$_2$CH$_2$CH$_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 28.53 (Se*C*H$_2$), 28.95 (SeCH$_2$CH$_2$*C*H$_2$), 29.50 (SeCH$_2$*C*H$_2$), 65.30 (≡*C*Se), 88.26 (≡*C*H); IR (film) 2931, 2853, 2027, 1449, 1208, 678, 572 cm^{-1}; MS (CI+) 279 [MH$^+$]. Anal. Calcd for $C_9H_{12}Se_2$: C, 38.87; H, 4.35. Found: C, 38.58; H, 4.39.

General Procedure for the Preparation of the Tetraselenacycloalkadiynes 5(*m.n*). To a solution of the diselenaalkadiyne **4**(*m*) in 70 mL of anhydrous THF was added *n*-butyllithium at −25 °C over a period of 15 min. The solution was stirred for 1 h at −25 °C and then allowed to warm to room temperature. To 600 mL of anhydrous THF were added solutions of the dilithiated diselenaalkadiyne in THF and the diselenocyanatoalkane **2**(*n*) in THF dropwise at −40 °C over a period of 5 h. After complete addition, the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed by rotary evaporation, and the resulting residue was filtered through silica gel [3% NEt_3 (v/v)] with toluene as eluent to remove salts and polymers. After rotary evaporation, the product was isolated by column chromatography [silica gel [3% NEt_3 (v/v)], *n*-hexane/toluene, 3:1].

1,4,7,10-Tetraselenacyclododeca-2,8-diyne (5(*2.2*)). Starting materials: 1.00 g (4.2 mmol) of 3,6-diselenaocta-1,7-diyne (**4**(*2*)), 5.3 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.01 g (4.2 mmol) of 1,2-diselenocyanatoethane (**2**(*2*)). Column chromatography afforded 26 mg (1.5%) of **5**(*2.2*) as a colorless solid: mp 114 °C dec; ^{1}H NMR (500 MHz, $C_6D_5CD_3$) δ 2.60 (s, 8H, SeC*H*$_2$); ^{13}C NMR (125.77 MHz, $C_6D_5CD_3$) δ 31.38 (Se*C*H$_2$), 79.71 (≡*C*); IR (KBr) 2923, 2083, 1639, 1405, 1261, 1222 cm^{-1}; MS (EI, 70 eV) 422 [M$^+$], 394, 366, 208, 184; HRMS (EI, 70 eV) calcd for $C_8H_8{}^{78}Se^{80}Se_3$ 421.7295, found 421.7277.

1,4,7,10-Tetraselenacyclotrideca-2,8-diyne (5(*2.3*)). Starting materials: 1.10 g (4.7 mmol) of 3,6-diselenaocta-1,7-diyne (**4**(*2*)), 5.9 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.17 g (4.7 mmol) of 1,3-diselenocyanatopropane (**2**(*3*)). Column chromatography afforded 457 mg (22.6%) of **5**(*2.3*) as a colorless solid: mp 142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (quint, ^3J = 7.4 Hz, 2H, SeCH$_2$C*H*$_2$), 2.83 (t, 4H, ^3J = 7.4 Hz, SeC*H*$_2$CH$_2$), 3.25 (s, 4H, SeC*H*$_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 28.42 (SeCH$_2$*C*H$_2$), 29.84 (Se*C*H$_2$), 30.73 (Se*C*H$_2$CH$_2$), 79.59 [≡C(s)], 79.75 [(≡C(l)]; IR (KBr) 2928, 2052, 1630, 1410, 1229, 742 cm^{-1}; MS (EI, 70 eV) 436 [M$^+$], 408, 364, 328, 250, 202, 184; HRMS (EI, 70 eV) calcd for $C_9H_{10}{}^{78}Se^{80}Se_3$ 435.7451,

Table 3. Crystal Data and Structure Refinement for Compounds 4(*2*), 5(*2.2*), 5(*2.4*), and 5(*2.5*)

compd	**4**(*2*)	**5**(*2.2*)	**5**(*2.4*)	**5**(*2.5*)
emp formula	$C_6H_6Se_2$	$C_8H_8Se_4$	$C_{10}H_{12}Se_4$	$C_{11}H_{14}Se_4$
formula wt	236.03	419.98	448.04	462.06
cryst system	monoclinic	tetragonal	orthorhombic	monoclinic
space group	$P2_1/c$	$P4_22_12$	$P2_12_12_1$	$P2_1/n$
unit cell dimens				
a (Å)	7.9609(7)	8.1476(1)	9.5047(2)	8.4424(7)
b (Å)	6.1598(5)	8.1476(1)	9.8962(2)	9.9088(7)
c (Å)	8.5406(7)	8.3466(2)	14.1523(2)	17.3432(13)
α (deg)	90	90	90	90
β (deg)	117.585(2)	90	90	95.310(2)
γ (deg)	90	90	90	90
Z	2	2	4	4
V (Å^3)	371.20(5)	554.076(16)	1331.17(4)	1444.60(19)
D_{calcd} (g/cm^3)	2.11	2.52	2.24	2.12
absorp coeff	9.86	13.19	10.99	10.13
θ range for data coll (deg)	2.9−32.1	3.5−27.5	2.5−27.5	2.4−25.3
index ranges	$-10 \le h \le 11$	$-10 \le h \le 10$	$-12 \le h \le 12$	$-6 \le h \le 10$
	$-9 \le k \le 6$	$-10 \le k \le 10$	$-12 \le k \le 12$	$-10 \le k \le 7$
	$-12 \le l \le 12$	$-10 \le l \le 10$	$-18 \le l \le 18$	$-20 \le l \le 19$
reflns collected	3179	5646	13749	4068
ind reflns	1286	639	3061	2515
reflns obsd	1017	621	2591	1863
obsd data/param	1286/38	639/36	3061/127	2515/136
goodness-of-fit on F^2	1.06	1.22	1.04	0.99
$R(F)$	0.058	0.020	0.032	0.033
$R_w(F^2)$	0.159	0.052	0.069	0.068
($\Delta\rho$)max, ($\Delta\rho$)min (e Å^{-3})	1.33, −1.42	0.43, −0.48	0.94, −0.62	0.39, (−0.66)

found 435.7498. Anal. Calcd for $C_9H_{10}Se_4$: C, 24.91; H, 2.32. Found: C, 25.08; H, 2.51.

1,4,7,10-Tetraselenacyclotetradeca-2,8-diyne (5(*2.4*)). Starting materials: 1.10 g (4.2 mmol) of 3,8-diselenadeca-1,9-diyne (**4**(*4*)), 5.2 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.00 g (4.2 mmol) of 1,2-diselenocyanatoethane (**2**(*2*)). Column chromatography afforded 103 mg (5.5%) of **5**(*2.4*) as a colorless solid: mp 99 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.07 (m, 4H, $SeCH_2C\mathit{H}_2$), 2.79 (m, 4H, $SeC\mathit{H}_2CH_2$), 3.20 (s, 4H, $SeC\mathit{H}_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 28.71 ($Se\mathit{C}H_2$), 29.77 ($Se\mathit{C}H_2CH_2$), 30.44 ($SeCH_2\mathit{C}H_2$), 79.47 [$\equiv\mathit{C}$(s)], 82.01 [($\equiv\mathit{C}$(l)]; IR (KBr) 2962, 2928, 2053, 1631, 1412, 1161, 766 cm^{-1}; MS (EI, 70 eV) 450 [M$^+$], 422, 367, 341, 314, 286, 264, 216, 184; HRMS (EI, 70 eV) calcd for $C_{10}H_{12}{}^{78}Se^{80}Se_3$ 449.7608, found 449.7619. Anal. Calcd for $C_{10}H_{12}Se_4$: C, 26.81; H, 2.70. Found: C, 27.10; H, 2.87.

1,4,7,10-Tetraselenacyclopentadeca-2,8-diyne (5(*2.5*)). Starting materials: 1.10 g (4.7 mmol) of 3,6-diselenaocta-1,7-diyne (**4**(*2*)), 5.9 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.31 g (4.7 mmol) of 1,5-diselenocyanatopentane (**2**(*5*)). Column chromatography afforded 100 mg (4.7%) of **5**(*2.5*) as a colorless solid: mp 100 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (m, 2H, $SeCH_2CH_2C\mathit{H}_2$), 1.90 (m, 4H, $SeCH_2C\mathit{H}_2CH_2$), 2.80 (t, $^3J = 6.0$ Hz, 4H, $SeC\mathit{H}_2CH_2CH_2$), 3.18 (s, 4H, $SeC\mathit{H}_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 27.18 ($SeCH_2CH_2\mathit{C}H_2$), 28.55 ($SeCH_2\mathit{C}H_2CH_2$), 30.09 ($Se\mathit{C}H_2CH_2CH_2$), 30.30 ($Se\mathit{C}H_2$), 80.34 ($\equiv\mathit{C}$), 81.88 ($\equiv\mathit{C}$); IR (KBr) 2927, 2848, 2069, 1632, 1451, 1413, 1284, 1216, 769 cm^{-1}; MS (EI, 70 eV) 464 [M$^+$], 436, 355, 278, 230, 184; HRMS (EI, 70 eV) calcd for $C_{11}H_{14}{}^{78}Se^{80}Se_3$ 463.7764, found 463.7781. Anal. Calcd for $C_{11}H_{14}Se_4$: C, 28.60; H, 3.05. Found: C, 28.71; H, 3.12.

1,4,8,11-Tetraselenacyclotetradeca-2,9-diyne (5(*3.3*)). Starting materials: 0.63 g (2.52 mmol) of 3,7-diselenanona-1,8-diyne (**4**(*3*)), 3.2 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 0.64 g (2.52 mmol) of 1,3-diselenocyanatopropane (**2**(*3*)). Column chromatography afforded 408 mg (36.1%) of **5**(*3.3*) as a colorless solid: mp 188 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.47 (quint, $^3J = 8.0$ Hz, 4H, $SeCH_2C\mathit{H}_2$), 2.79 (t, $^3J = 8.0$ Hz, 8H, $SeC\mathit{H}_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 28.57 ($SeCH_2\mathit{C}H_2$), 32.09 ($Se\mathit{C}H_2$), 80.36 ($\equiv\mathit{C}$); IR (KBr) 2928, 2083, 1629, 1446, 1410, 1227, 764 cm^{-1}; MS (EI, 70 eV) 450 [M$^+$], 409 [M$^+$ − C_3H_5], 328, 250, 202, 184. HRMS (EI, 70 eV) calcd for $C_{10}H_{12}{}^{78}Se^{80}Se_3$ 449.7608, found 449.7621. Anal. Calcd for $C_{10}H_{12}Se_4$: C, 26.81; H, 2.70. Found: C, 27.06; H, 2.76.

1,4,8,11-Tetraselenacyclopentadeca-2,9-diyne (5(*3.4*)). Starting materials: 1.10 g (4.2 mmol) of 3,8-diselenadeca-1,9-diyne (**4**(*4*)), 5.2 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 1.05 g (4.2 mmol) of 1,3-diselenocyanatopropane (**2**(*3*)). Column chromatography afforded 340 mg (17.4%) of **5**(*3.4*) as a colorless solid: mp 150 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (m, 4H, $SeCH_2C\mathit{H}_2C\mathit{H}_2CH_2$), 2.43 (quint, $^3J = 7.4$ Hz, 2H, $SeCH_2C\mathit{H}_2CH_2$), 2.77 (t, $^3J = 7.4$ Hz, 4H, $SeC\mathit{H}_2CH_2C\mathit{H}_2$), 2.80 (m, 4H, $SeC\mathit{H}_2CH_2CH_2C\mathit{H}_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 28.22 ($SeCH_2\mathit{C}H_2CH_2$), 29.65 ($Se\mathit{C}H_2CH_2CH_2\mathit{C}H_2$), 30.31 ($SeCH_2\mathit{C}H_2\mathit{C}H_2CH_2$), 32.29 ($Se\mathit{C}H_2CH_2CH_2$), 80.19 [$\equiv\mathit{C}$(s)], 81.84 [$\equiv\mathit{C}$(l)]; IR (KBr) 2928, 2854, 2061, 1629, 1445, 1410, 1264, 1223, 767, 721 cm^{-1}; MS (EI, 70 eV) 464 [M$^+$], 423, 409, 367, 328, 286, 250, 208, 184; HRMS (EI, 70 eV) calcd for $C_{11}H_{14}{}^{78}Se^{80}Se_3$ 463.7764, found 463.7759. Anal. Calcd for $C_{11}H_{14}Se_4$: C, 28.59; H, 3.05. Found: C, 28.64; H, 3.04.

1,4,8,11-Tetraselenacyclohexadeca-2,9-diyne (5(*3.5*)). Starting materials: 0.75 g (3.0 mmol) of 3,7-diselenanona-1,8-diyne (**4**(*3*)), 3.8 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 0.84 g (3.0 mmol) of 1,5-diselenocyanatopentane (**2**(*5*)). Column chromatography afforded 150 mg (10.5%) of **5**(*3.5*) as a colorless solid: mp 100 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.65 (quint, $^3J = 8.0$ Hz, 2H, $SeCH_2CH_2C\mathit{H}_2$), 1.93 (m, 4H, $SeCH_2C\mathit{H}_2CH_2$), 2.39 (quint, $^3J = 8.0$ Hz, 2H, $SeCH_2C\mathit{H}_2$), 2.76 (m, 8H, $SeC\mathit{H}_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 28.10 ($SeCH_2CH_2\mathit{C}H_2$), 28.60 ($Se\mathit{C}H_2$), 29.13 ($Se\mathit{C}H_2$), 29.41 ($SeCH_2\mathit{C}H_2CH_2$), 32.37 ($SeCH_2\mathit{C}H_2$), 80.24 ($\equiv\mathit{C}$), 81.32 ($\equiv\mathit{C}$); IR (KBr) 2927, 2851, 1631, 1435, 1415, 1297, 1226, 758 cm^{-1}. MS (EI, 70 eV) 478 [M$^+$], 408, 328, 250, 202, 184; HRMS (EI, 70 eV) calcd for $C_{12}H_{16}{}^{77}Se_2{}^{82}Se_2$ 477.7985, found 477.8051. Anal. Calcd for $C_{12}H_{16}Se_4$: C, 30.27; H, 3.39. Found: C, 30.32; H, 3.60.

1,4,9,12-Tetraselenacyclohexadeca-2,10-diyne (5(*4.4*)). Starting materials: 0.45 g (1.7 mmol) of 3,8-diselenadeca-1,9-diyne (**4**(*4*)), 2.1 mL of *n*-butyllithium (1.6 M in *n*-hexane) and 0.45 g (1.7 mmol) of 1,4-diselenocyanatobutane (**2**(*4*)). Column chromatography afforded 284 mg (35.1%) of **5**(*4.4*) as a colorless solid: mp 80 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.06 (m, 8H, $SeCH_2C\mathit{H}_2$), 2.79 (m, 8H, $SeC\mathit{H}_2$); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 29.35 ($Se\mathit{C}H_2$), 29.57 ($SeCH_2\mathit{C}H_2$), 81.02 ($\equiv\mathit{C}$); IR (KBr) 2927, 2840, 1631, 1441, 1409, 1250, 742 cm^{-1}; MS (EI, 70 eV) 478 [M$^+$], 422 [M$^+$ − C_4H_8], 342, 288, 264, 208, 184; HRMS (EI, 70 eV) calcd for $C_{12}H_{16}{}^{78}Se^{80}Se_3$ 477.7921, found 477.7950. Anal. Calcd for $C_{12}H_{14}Se_4$: C, 30.27; H, 3.39. Found: C, 30.39; H, 3.46.

1,4,9,12-Tetraselenacycloheptadeca-2,10-diyne (5(*4.5*)). Starting materials: 1.00 g (3.6 mmol) of 3,9-diselenaundeca-1,10-diyne (**4**(*5*)), 4.5 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 0.96 g (3.6 mmol) of 1,4-diselenocyanatobutane (**2**(*4*)). Column chromatography afforded 121 mg (6.9%) of **5**(*4.5*) as a colorless solid: mp 73 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.61 (m, 2H, $SeCH_2CH_2C\mathit{H}_2$), 1.93 (m, 4H, $SeCH_2C\mathit{H}_2CH_2$), 2.04 (m, 4H, $SeCH_2C\mathit{H}_2$), 2.73 (t, $^3J = 7.5$ Hz, 4H, $SeC\mathit{H}_2CH_2CH_2$), 2.80 (m, 4H, $SeC\mathit{H}_2CH_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 28.82

Table 4. Crystal Data and Structure Refinement for Compounds 5(*3.3*), 5(*3.5*), 5(*4.4*), and 5(*5.5*)

compd	**5**(*3.3*)	**5**(*3.5*)	**5**(*4.4*)	**5**(*5.5*)
emp formula	$C_{10}H_{12}Se_4$	$C_{12}H_{16}Se_4$	$C_{12}H_{16}Se_4$	$C_{14}H_{20}Se_4$
formula wt	448.04	476.09	476.09	504.14
cryst system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	*Pnma*	$P2_1/n$	$P2_1/c$
unit cell dimens				
a (Å)	4.5764(1)	9.1512(1)	10.3006(2)	4.6252(1)
b (Å)	13.4490(3)	17.3619(3)	9.0987(2)	17.2919(2)
c (Å)	10.3777(1)	9.5526(2)	33.8282(5)	10.3963(1)
α (deg)	90	90	90	90
β (deg)	95.9390(10)	90	95.069(1)	91.309(1)
γ (deg)	90	90	90	90
Z	4	4	8	2
V (Å^3)	635.30(2)	1517.74(4)	3158.05(10)	831.26(2)
D_{calcd} (g/cm^3)	2.34	2.08	2.00	2.01
absorp coeff	11.51	9.64	9.27	8.81
θ range for data coll (deg)	2.5−27.5	2.3−24.1	1.2−27.5	2.3−27.4
index ranges	$-5 \leq h \leq 5$	$-10 \leq h \leq 10$	$-13 \leq h \leq 13$	$-5 \leq h \leq 5$
	$-17 \leq k \leq 17$	$-19 \leq k \leq 19$	$-11 \leq k \leq 11$	$-22 \leq k \leq 22$
	$-13 \leq l \leq 13$	$-10 \leq l \leq 10$	$-43 \leq l \leq 43$	$-13 \leq l \leq 13$
reflns collected	6451	11017	31816	8455
ind reflns	1450	1253	7206	1886
reflns obsd	1287	1114	4668	1641
obsd data/param	1450/64	1253/76	7206/298	1886/122
goodness-of-fit on F^2	1.11	1.09	1.02	1.07
$R(F)$	0.021	0.059	0.049	0.025
$R_w(F^2)$	0.051	0.144	0.098	0.058
$(\Delta\rho)$max, $(\Delta\rho)$min (e Å^{-3})	0.48, −0.72	1.69, −1.53	1.56, −1.28	0.58, −0.87

($SeCH_2CH_2CH_2$), 29.08 ($SeCH_2CH_2$), 29.13 ($SeCH_2CH_2CH_2$), 29.27 ($SeCH_2CH_2$), 30.05 ($SeCH_2CH_2CH_2$), 80.78 (≡*C*), 80.86 (≡*C*); IR (KBr) 2928, 2854, 2050, 1632, 1415, 1200 cm^{-1}; MS (EI, 70 eV) 492 [M$^+$], 356, 288, 208, 184, 149; HRMS (EI, 70 eV) calcd for $C_{13}H_{18}{}^{78}Se^{80}Se_3$ 491.8078, found 491.8051. Anal. Calcd for $C_{13}H_{18}Se_4$: C, 31.86; H, 3.70. Found: C, 32.15; H, 3.77.

1,4,10,13-Tetraselenacyclooctadeca-2,11-diyne (5(*5.5*)). Starting materials: 0.37 g (1.3 mmol) of 3,9-diselenaundeca-1,10-diyne (**4**(*5*)), 1.7 mL of *n*-butyllithium (1.6 M in *n*-hexane), and 0.37 g (1.3 mmol) of 1,5-diselenocyanatopentane (**2**(*5*)). Column chromatography afforded 290 mg (44.5%) of **5**(*5.5*) as a colorless solid: mp 146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (quint, $^3J = 7.3$ Hz, 4H, $SeCH_2CH_2CH_2$), 1.92 (m, 8H, $SeCH_2CH_2$), 2.72 (t, $^3J = 7.4$ Hz, 8H, $SeCH_2$); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 29.38 ($SeCH_2$), 29.69 ($SeCH_2CH_2CH_2$), 30.57 ($SeCH_2CH_2$), 80.61 (≡*C*); IR (KBr) 2926, 2851, 2071, 1632, 1454, 1412, 1200, 766 cm^{-1}; MS (EI, 70 eV) 506 [M$^+$], 356, 287, 207, 149; HRMS (EI, 70 eV) calcd for $C_{14}H_{20}{}^{78}Se^{80}Se_3$ 505.8234, found 505.8249. Anal. Calcd for $C_{14}H_{20}Se_4$: C, 33.36; H, 4.00. Found: C, 33.59; H, 4.10.

X-ray Diffraction Analyses. The reflections were collected with a Bruker Smart CCD diffractometer (Mo Kα radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[28] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were either refined isotropically (**5**(*2.2*), **5**(*5.5*)) or calculated according to stereochemical aspects (**4**(*2*), **5**(*2.4*), **5**(*2.5*), **5**(*3.3*), **5**(*3.5*), **5**(*4.4*)). In **5**(*4.4*), two independent molecules exist in the unit cell, one of them is slightly disordered with respect to the conformation of a part of the alkane chain. Structure solution and refinement were carried out with SHELXTL (5.10) software package.[28] Tables 3 and 4 contain the crystallographic data and details of the data collection and the refinement procedure. ORTEP drawings were obtained using the ORTEP-3 for Windows program by L. Farrugia.[29]

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Supporting Information Available: Tables of crystallographic data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters are available for structures **4**(*2*), **5**(*2.2*), **5**(*2.4*), **5**(*2.5*), **5**(*3.3*), **5**(*3.5*), **5**(*4.4*) and **5**(*5.5*). This material is available free of charge via the Internet at http://pubs.acs.org.

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