# SYNTHESIS OF A CYCLIC TETRASELENADIYNE CONTAINING AROMATIC BUILDING BLOCKS

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The synthesis of a tricyclic tetraselenadiyne, **5**, was achieved by reacting the bis lithium salt of bis((ethynylselenyl)methyl)benzene (**4a**) with 1,2-bis(selenocyanatomethyl)benzene (**2**). X-ray analysis reveals channel like structures in the solid state. The packing of **5** in the crystal is due to short distances between the selenium atoms which alternate between 348 pm and 352 pm.

Hydrogen bonding between molecules is the most important and most spread non-covalent force in supramolecular chemistry.[1,2] Other directional forces which can lead to supramolecular assemblage of molecules are interactions between Lewis acids and bases,[3] ion-dipol interactions[4] and π-π stacking[5] to name the most important ones. The most appealing supramolecular structures resulting from these forces are helices and tubes. The tubular structures can be subdivided into those whose skeletons are determined by covalent bonding and those which aggregate by non-covalent bonding. Representative examples for the former type are carbon nanotubes[6] and zeolites.[7]

Hydrogen bonding between various molecules plays the major role in building tubes via non-covalent interactions. Examples are the stacks of cyclodextrins,[8] polymer lipid-based tubes,[9] cyclic peptides[10] or shape persistent cycles with phenolic units.[11]

The idea of using the chalcogen–chalcogen interactions as directional forces to obtain tubular structures was validated during recent studies in which cyclic aliphatic diynes and dienes containing chalcogen atoms organized themselves in columnar structures.[12,13]

The common features of these solid-state structures are chalcogen atoms containing rings which are stacked on top of each other. In the solid state the rings associate in such a way that the chalcogen center of one ring keeps in close contact with two chalcogen centers of two neighbouring rings that are stacked on top of each other. As a result a zig-zag arrangement of chalcogen atoms arises as shown in Figure 1a. The interaction between two chalcogen centers can be described as a secondary interaction between an occupied p-type orbital of one chalcogen center (X) and the empty X-C σ* orbital of the other[14] (Figure 1b) together with induction and dispersion forces.[15]
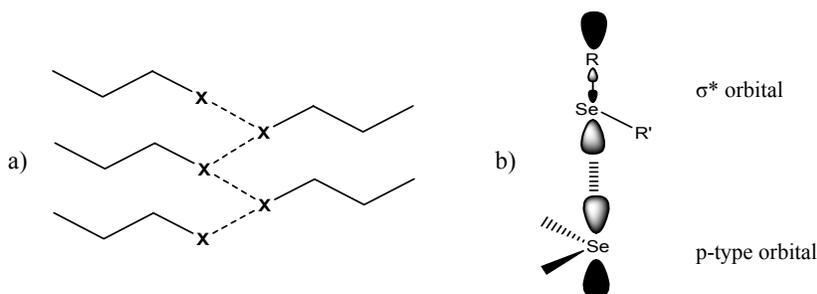


Fig. 1 – a) Schematic plot of a zig-zag type arrangement of the chalcogen-chalcogen interaction in solid state; b) Interaction of the occupied p orbital with the unoccupied σ * orbital in selenaethers.

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The cycles investigated so far consisted of rigid units (e.g. X-C≡C-X, X= S,Se,Te) and methylene chains as flexible parts.[12,13] The inclusion of benzene rings into the methylene chains adds more rigidity to this part and opens the possibility of π-π stacking. To investigate the results of this idea we synthesized a tricyclic tetraselenadiyne containing the building block mentioned. We analysed its solid-state structure characteristics in our larger effort to understand the nature of chalcogen-chalcogen non-bonding interactions.

The synthesis of 7,8,17,18-tetradehydro-5,10,15,20-tetrahydro-dibenzo[*f,n*][1,4,9,12]tetraselena-cyclohexadecine (**5**) was achieved using a stepwise approach, as shown in Scheme 1.
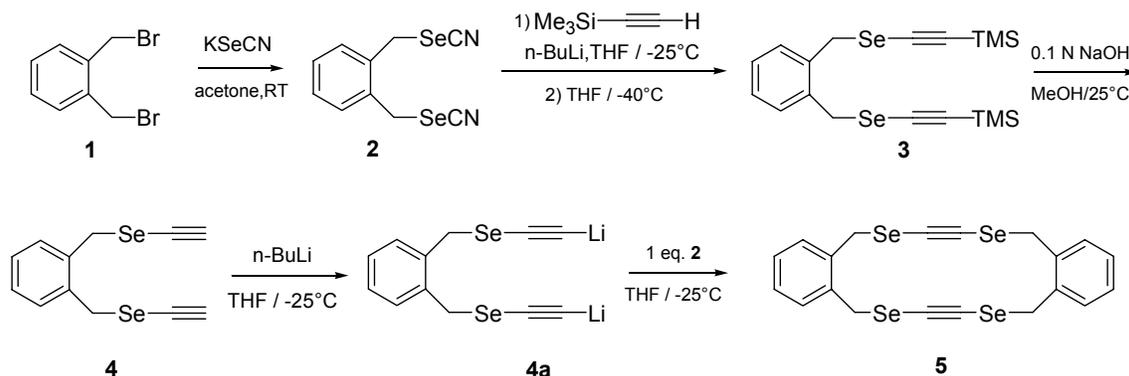


Scheme 1

1,2-bis(selenocyanatomethyl)benzene (**2**) was prepared according to literature[16], the intermediates **3** and **4** were synthesized analogous to related species[12b] and their analytic data are given.[17a,17b] The target molecule could be prepared from **4** and **2**.[17c]

## DISCUSSION

The NMR spectra of **5** in solution show only one signal for the four selenium atoms, one for the four CH$_2$ carbon atoms and a broad singlet for the four aromatic protons, between −80°C and room temperature indicating $D_{2n}$ symmetry due to very rapid motion.

Single crystals suitable for X-ray diffraction studies[20] of **5** were obtained from a solution of *n*-hexane/dichloromethane at 20°C. The most striking features of the molecular structure of **5** (Figure 2) are the twisting of the planes of the two benzene rings by 87° along the common axis and differences in the bending of the two Se-C≡C-Se units. The twisting of the two benzene rings we ascribe to the fact that the torsion angles γ of the two CH$_2$-Se bonds[12b] of each CH$_2$-Se-C≡C-Se-CH$_2$ unit in a cyclic system tries to adopt values between 60° and 90°, depending on the size of the ring[12b]. In the case of **5**, γ amounts to 75° (C1-Se1-Se2-C4) and 92° (C11-Se3-Se4-C14). The observation that one Se-C≡C-Se unit of **5** is bent stronger than the other will be discussed below.

In Figure 3 we show a section of the columnar structures which arise in the solid state by stacking the rings on top of each other. A remarkable feature of the structure of **5** is that only one Se-C≡C-Se unit of each ring is involved in the intermolecular bonding. This gives the impression that the various rings are threaded like pearls on a string made of ⋯Se-C≡C-Se⋯Se-C≡C-Se⋯ units (Figure 4).

To optimize the Se⋯Se interaction, the angles at the *sp* centers have been altered. Those units which are involved in the string formation show a stronger bending (167.1(2)° and 168.7(2)°) than those angles of the *sp* centers of the Se-C≡C-Se units which are not a member of the intermolecular thread (176.2(3)° and 178.2(3)°). The inter-ring distances between the Se atoms are 348 pm and 352 pm. Both values are considerably smaller than the sum of the Van-der-Waals radii for Se (380 pm)[24].

Besides the intermolecular selenium-selenium interactions, other intramolecular and intermolecular interactions involving selenium centers are important in generating the solid state columnar structures of **5**. An interesting fact is observed when analysing intramolecular selenium-hydrogen interactions (see Table 1). The two longest interactions (Se1-H14A and Se2-H11A with values of 305 pm and 306 pm), involve the Se

centers that are also interacting with other Se centers, while the shortest two interactions (Se3-H4A and Se4-H1A with lengths of 283 pm, 296 pm respectively) relate to the Se centers not involved in other selenium-selenium interactions. This could be a further proof of the competition between selenium-selenium and selenium-hydrogen interactions.[15]

*Table 1*

Most relevant short intra- and intermolecular selenium-hydrogen
contacts of **5** ($Se_x$ - $H_z$). All values in pm.

| $Se_x$ | Intramolecular | Intermolecular | |
|---|---|---|---|
| | $H_z$ (distance) | $H_z$ (distance) | |
| Se1 | H14A (305) | H'1B (330) | H'19 (328) |
| Se2 | H11A (306) | H''4B (318) | H''6 (310) |
| Se3 | H4A (296) | - | - |
| Se4 | H1A (283) | - | - |

In conclusion, we synthesised a cyclic tetraselenadiyne, containing benzene rings as building blocks, which despite its rather flexible structure still forms tubular structures in the solid state. This columnar structure is based on interactions of the selenium atoms like selenium-selenium intermolecular interactions as well as inter- and intramolecular selenium-hydrogen bonding. The competition between the selenium-selenium interaction and selenium-hydrogen bonding that we experimentally observe in this case is in conformity with theoretical studies.[15]

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17. a) ***Analytic properties of 1,2-bis(((trimethylsilyl)ethynyl-selanyl)methyl)benzene(3). ¹H-NMR spectrum***[18] (500MHz, CDCl₃, δ, ppm, TMS as internal standard): 0.16 (s, 18H, Si(CH₃)₃); 4.21 (s, 4H, CH₂); 7.23 (m, 2H, H_arom); 7.26 (m, 2H, H_arom). ***¹³C-NMR spectrum***[18] (125 MHz, CDCl₃, δ, ppm): -0.10 (6C, Si(p-CH₃)₃); 30.07 (2C, s-CH₂); 86.14 (2C, q-Se≡CSi); 109.73 (2C, q-Se≡CSi);

128.00 (2C, t-C$_{arom}$); 131.07 (2C, t-C$_{arom}$); 135.55 (2C, q-C$_{arom}$). ***$^{77}$Se-NMR spectrum***[18] (95 MHz, CDCl$_3$, δ, ppm): 250.17 (2Se).
b) ***s Analytic properties of 1,2-bis(ethynylselanylmethyl)-benzene (4)***. ***$^{1}$H-NMR spectrum*** (500MHz, CDCl$_3$, δ, ppm, TMS as internal standard): 2.90 (s, 2H, C≡CH); 4.23 (s, 4H, CH$_2$); 7.27 (m, 2H, H$_{arom}$); 7.30 (m, 2H, H$_{arom}$). ***$^{13}$C-NMR spectrum*** (125 MHz, CDCl$_3$, δ, ppm): 29.55 (2C, s-CH$_2$); 65.70 (2C, t-CH); 90.11 (2C, q-SeC≡CH); 128.23 (2C, t-C$_{arom}$); 130.98 (2C, t-C$_{arom}$); 135.32 (2C, q-C$_{arom}$). ***$^{77}$Se-NMR spectrum*** (95 MHz, CDCl$_3$, δ, ppm): 229.13 (2Se). ***IR spectrum***[18] (KBr, cm$^{-1}$): 3277(s); 3061(w); 3020(w); 2954(w); 2028 (w); 1491(m); 1452(m); 1420(w); 1376 (w); 1300(w); 1172(m); 1067(w); 1042(w); 948(w); 875(w); 834(w); 762 (m); 681(m); 592 (m); 436(w). c) ***Synthesis of 7,8,17,18-tetradehydro-5,10,15,20-tetrahydro-dibenzo-[f,n][1,4,9,12]tetraselenacyclohexadecine (5).*** To a solution of **4** (2.81g, 9 mmols) in 250 ml of anhydrous THF, 11ml *n*-BuLi (1.6 M in *n*-hexane, 18 mmols) was added dropwise at –25°C over a period of 15 min, then stirred for 1 h at –25°C. Compound **2** (2.83g, 9 mmols) was also dissolved in 250 ml anhydrous THF. The two solutions were simultaneously added dropwise to 500 ml of anhydrous THF at –40°C over a period of 5h. After complete addition, the reaction mixture was allowed to warm to room temperature overnight. The solvents were removed by rotary evaporation. The resulting residue was filtered through silica gel (3% NEt$_3$) with toluene as eluent to remove salts and polymers. After rotary evaporation, the product was further purified using silica-gel column chromatography. First, a mixture of *n*-hexane and toluene (3:1) was used as eluent and an enriched fraction was further purified through a second column chromatography using a mixture of *n*-hexane and diethylether (10:1). Thin yellow needles were recrystalized from a dichloromethane/*n*-hexane mixture to give the final product (0.182g, 0.32 mmol, 3.6% yield). ***$^{1}$H-NMR spectrum*** (500MHz, CDCl$_3$, δ, ppm, TMS as internal standard): 4.47 (s, 8H, CH$_2$); 7.22 (bs, 8H, H$_{arom}$). ***$^{13}$C-NMR spectrum*** (125 MHz, CDCl$_3$, δ, ppm): 33.05 (4C, s-CH$_2$); 85.92 (4C, q-SeC≡CSe); 128.41 (4C, t-C$_{arom}$); 130.87 (4C, t-C$_{arom}$); 135.46 (4C, q-C$_{arom}$). ***$^{77}$Se-NMR spectrum*** (95 MHz, CDCl$_3$, δ, ppm): 235.04 (4Se). ***IR spectrum*** (KBr, cm$^{-1}$): 3100-3600(s); 1772(w); 1636(m); 1559(w); 1507(w); 1490(w); 1452(w); 1419(w); 1384(w); 1249(w); 1174(w); 1162(w); 1105(w); 845(w); 759(m); 617(w); 536(w); 458(w); 443 (w); 436 (w); 416 (w).

18. $^{1}$H-NMR, $^{13}$C-NMR and $^{77}$Se-NMR spectra were registered on a Bruker AVANCE DRX500 spectrometer at 500.132MHz for $^{1}$H, respectively at 125.76 MHz for $^{13}$C and 95.38 MHz for $^{77}$Se. TMS was used as internal standard for referencing $^{1}$H-NMR spectra, while referencing for $^{13}$C and $^{77}$Se was done using the $\Xi$ scale, following IUPAC recommendations[19]. Both $^{13}$C and $^{77}$Se spectra were recorded with proton decoupling, using a *power-gated decoupling* pulse program from Bruker's XWIN-NMR 3.5 software. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer.

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20. The reflexions were collected with a Bruker Smart CCD diffractometer with graphite monochromator. Compound 5 characterisitics: colorless crystal (polyhedron), dimensions 0.20 x 0.08 x 0.05 mm$^3$, crystal system monoclinic, space group C2/c, Z=8, a=24.293(2) Å, b=5.2235(5) Å, c=30.239(3) Å, alpha=90 deg, beta=92.753(2) deg, gamma=90 deg, V=3832.6(7) Å$^3$, rho=1.983 g/cm$^3$, T=100(2) K, Theta$_{max}$= 28.31 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.3 deg omega-scans with CCD area detector, covering a whole sphere in reciprocal space, 19112 reflections measured, 4744 unique (R(int)=0.0384), 3821 observed (I >2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[21] based on the Laue symmetry of the reciprocal space, mu=7.66mm$^{-1}$, T$_{min}$=0.31, T$_{max}$=0.70, structure solved by direct methods and refined against F$^2$ with a Full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package[22], 217 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.029, wR(F$^2$)=0.058 for observed reflections, residual electron density -0.41 to 0.55 eÅ$^{-3}$. Cambridge Crystallographic Data Centre (CCDC) contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Pictures of crystal structures were obtained using Mercury v1.4 for Windows software package from CSD System[23].

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