

Syntheses and solid state structures of cyclic diynes with two chalcogen centres – a competition between weak interactions

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In this paper we report the synthesis of cyclic diynes of the general formula mX_n . The letters m and n indicate the lengths of chains between two $C\equiv C-X$ units where X indicates S, Se, or Te. The lengths of the bridges vary between $m = 4-8$ and $n = 2-6$. Structural investigations by means of X-ray diffraction reveal for most systems a chair-like conformation in the solid state. For $5S_2$, $5S_2$, $7S_2$, $5Se_2$ and $5Te_2$ tubular structures were encountered. These structures can be traced back to weak $X \cdots X$ or weak $C-H \cdots \pi$ interactions.

Introduction

Supramolecular chemistry is based on so-called noncovalent bonding interactions. This term includes as major contributions hydrogen bonding, ion-ion interactions, ion-dipole interactions, dipole-dipole interactions, cation- π interactions and π - π stacking.^{1,2} The energy range of these forces varies from 5–200 kJ mol⁻¹ with the strongest interactions provided by the Coulombic forces and hydrogen bonding. The weakest forces result from interactions involving π -units.^{1,2} Close contacts between chalcogen centres in the solid state have been reported most notably during the investigation of organic conductive materials.³⁻⁶ However, in these compounds other directional forces besides close chalcogen contacts also contribute significantly to the formation of two and three dimensional networks,^{4,5} where the most important contributions arise from close $C-H \cdots S$ contacts, $C-H \cdots \pi$ interactions and π - π stacking.^{7,8}

Recently, we found that cyclic alkynes,⁹ alkenes¹⁰ and alkanes¹¹ containing chalcogen atoms organise themselves in columnar structures. As a common building motif we discovered that in these columns chalcogen atoms of neighbouring stacks yield a *zig-zag* arrangement in which the intermolecular distances between the chalcogen centres are shorter than the sum of the van der Waals radii (Fig. 1). In many cases we found that the interactions between the chalcogen centres can be described as an interplay between the occupied p-type orbital of one chalcogen centre (X) and the empty $X-C \sigma^*$ orbital³ of the other, as shown in Fig. 1. Furthermore, correlation effects contribute significantly.⁶

Our first examples were cyclic tetrathia- and tetraselenaalkynes of type A. We thought it of interest to reduce the

number of chalcogen centres to find out if short interactions still prevail or if other weak interactions such as $C-H \cdots \pi$ interactions⁷ take place. For this purpose we prepared cyclic diynes of type B in which X represents sulfur, selenium or tellurium. In this paper we report the syntheses and the structures of B. (We will use the representation mX_n for rings of type B. In these formulae m and n represent the chain lengths and X the chalcogen type).

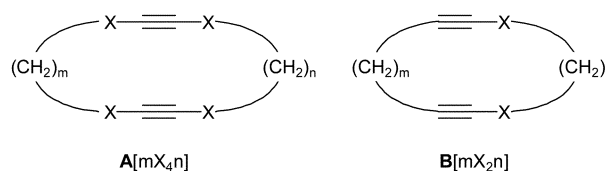
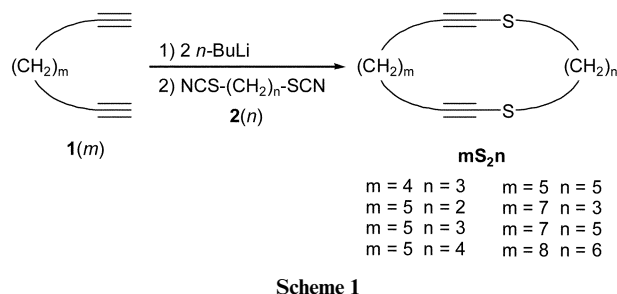


Fig. 2 Cyclic diynes of type A and B.

Results

Syntheses

To prepare the desired cyclic dithiadynes mS_2n and diselenadynes mSe_2n we made use of a protocol that was used to prepare the corresponding cyclic tetrathiadynes¹² and tetraselenadynes.¹³ We commenced our synthesis with the bis-lithium salts of the corresponding α,ω -alkadiynes (**1**(m)) which were prepared in THF from the hydrocarbons with two equivalents of *n*-butyllithium. To this solution α,ω -dithiocyanate (**2**(n)) (Scheme 1) or α,ω -diselenocyanate (**3**(n)) (Scheme 2) was added. This one pot procedure afforded the cyclic diynes mS_2n and mSe_2n in 20–50% yield as white to yellow coloured solids.



To obtain the corresponding ditellura rings we treated the bis-lithium salts of the α,ω -alkadiynes (**1**(m)) with freshly ground tellurium metal and α,ω -diiodoalkanes (**4**(n)) (Scheme 3).¹⁴ This one pot reaction produced the cyclic diynes mTe_2n in 40% yield as pale yellow coloured solids.

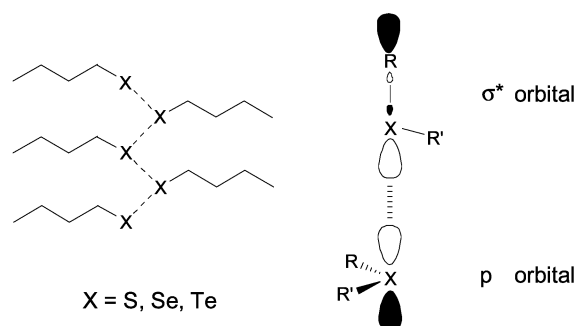
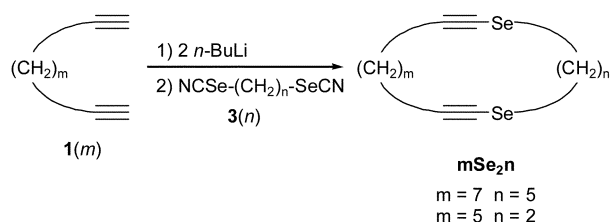


Fig. 1 Schematic plot of a *zig-zag* type arrangement of the chalcogen-chalcogen interactions between two stacks of rings (left). Interaction of the occupied p-orbital of a chalcogen centre X (S, Se, Te) with the σ^* orbital of a $X-C$ bond (right).

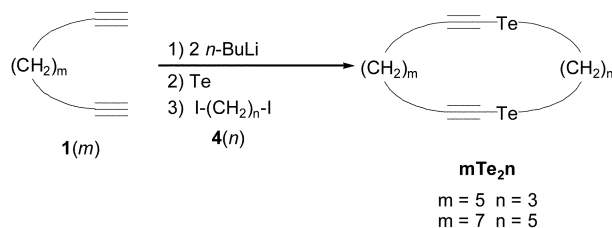
Table 1 Most relevant distances (pm) and angles (deg) of mS_2n , mSe_2n and mTe_2n ^a

Comp.	t_1 t_2	a_1 a_2	a_3 a_4	β	γ_1 γ_2
4S₂3	431.6	175.6	175.7	24.9	12.2
	462.4	179.0	178.0		52.5
5S₂2	488.9	173.2	174.6	11.6	32.9
	468.6	176.8	177.8		18.4
5S₂3	531.1	177.8	178.8	0.7	57.9
	539.1	177.0	178.2		57.0
5S₂4	534.1	178.7	177.5	9.9	62.2
	553.4	178.5	172.8		99.9
5S₂5	535.2	177.8	177.8	0.0	107.9
	556.6	174.9	174.9		107.3
7S₂3	555.2	178.2	177.2	6.6	45.1
	550.9	176.6	178.1		56.2
7S₂5	787.4	177.9	178.5	1.8	58.8
	795.2	177.2	178.6		57.0
5Se₂2	505.3	175.4	176.8	6.7	36.5
	497.4	177.2	176.8		14.2
5Te₂3	551.4	177.2	177.4	1.8	58.8
	574.1	179.4	177.6		58.0

^a For the definition of the distances and angles see Fig. 4.



Scheme 2



Scheme 3

Structural investigations

Our main impetus for carrying out these syntheses was the structure elucidation of the ring systems. In most cases we were able to isolate single crystals which allowed us to carry out X-ray diffraction studies. As examples we show in Fig. 3 the molecular structures of **5S₂3**, **5S₂5**, **5Se₂2** and **5Te₂3**. In order to characterise the molecular structures the most relevant distances and angles found in the solid state are summarised in Table 1. These include the transannular distances t_1 and t_2 as well as the angles describing the bending of the triple bonds (a_1 – a_4) and the torsion angles β , γ_1 and γ_2 as defined in Fig. 4.

Not listed in Table 1 are the lengths of the triple bonds and the distances between the sp centres and the chalcogen atoms, which vary only slightly. The former range between 118 pm and 120 pm. Similar values were found for cyclic mono- and diynes.¹⁵ The distances between the sp centres and the chalcogen atoms vary between 169 pm and 170 pm for C(sp)–S, 183 pm and 184 pm for C(sp)–Se, and 206 pm and 207 pm for C(sp)–Te. The values reported for the C(sp)–S and C(sp)–Se distances of cyclic tetrathia-¹² and tetraselenadiynes¹³ resemble these numbers. The same can be said for the C(sp)–Te values recorded for bis(methyltelluro)alkynes.¹⁴ The distances between opposite triple bonds vary between 431 pm and 795 pm. This variation was anticipated since larger chains between the rigid units imply larger separations. The angles a_1 – a_4 vary only slightly between 173° and 179° indicating that the CH₂–C≡C–X

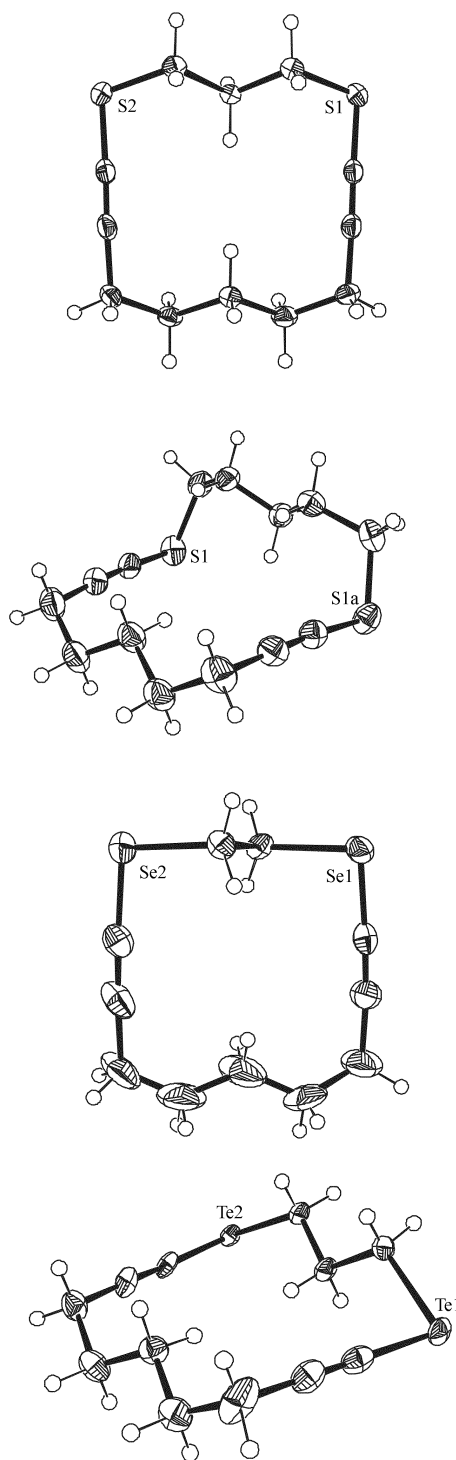


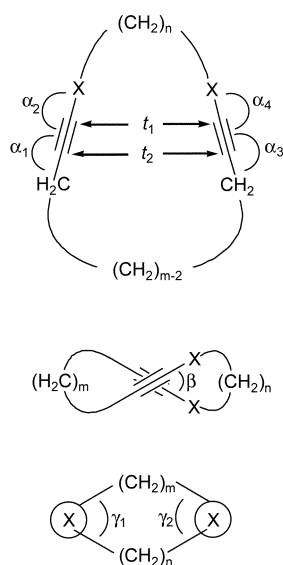
Fig. 3 ORTEP plots (50% ellipsoid probability) of the molecular structure of **5S₂3**, **5S₂5**, **5Se₂2** and **5Te₂3** (from top to bottom).

unit is a rigid building block and almost linear. The torsion angle β is small, especially for those molecules with an uneven number of methylene groups in the chain (**5S₂3**, **5S₂5**, **7S₂5** and **5Te₂3** (see Fig. 3)). This allows a chair-like conformation of these rings.

A comparison of the torsion angles γ_1 and γ_2 between the CH₂–X and CH₂–CH₂ σ -bonds reveals in the case of **5S₂3**, **7S₂3**, **7S₂5** and **5Te₂3** values around 60°. Similar values were encountered for rings with four sulfur or four selenium centres.^{12,13} Quantum chemical calculations suggest^{12,13} that these values can be interpreted as a compromise between the fact that the CH₂–X bonds try to adopt approximately 90° whereas the alkane chains try to adopt a zig-zag arrangement within a staggered conformation.¹⁶ The value of γ_1 and γ_2 found

Table 2 Comparison of short intermolecular distances (pm) between various rings with two alkyne and two chalcogen units

Cycle	$d_{\min} X \cdots X$	$d_{\min} C-H \cdots X$	$d_{\min} C-H \cdots \pi$	Mol. struct.	Columnar stacking
4S₂3	476.6	304.1	286.8	Dist. chair	–
5S₂2	376.0	297.7	289.2	Dist. chair	+
5S₂3	418.6	293.1	288.7	Chair	+
5S₂4	365.3	292.7	283.2	Chair	–
5S₂5	428.6	301.1	288.0	Chair	–
7S₂3	378.9	302.0	286.5	Boat	–
7S₂5	499.7	289.3	285.4	Chair	+
5Se₂2	364.1	309.7	282.0	Plane	+
5Te₂3	381.4	283.2	334.9	Chair	+

**Fig. 4** Definitions of transannular distances (t_1 , t_2), angles (α_1 – α_4) and torsion angles (β , γ_1 , γ_2).

for **5S₂5** (107.3°) is encountered whenever a chair conformation is found.¹²

Packing in the solid state

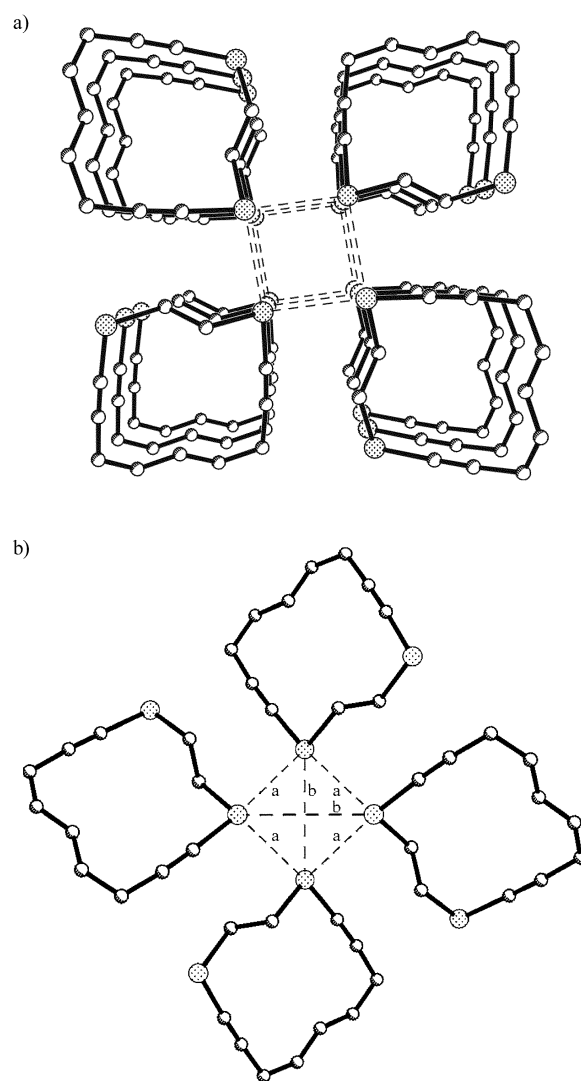
As pointed out in the beginning, the expected p – σ^* interactions between the rings (*cf.* Fig. 1) might be replaced by $C-H \cdots \pi$ or $C-H \cdots X$ interactions when the number of chalcogen atoms is reduced. We find close contacts between the chalcogen centres for **5S₂2**, **5S₂4**, **7S₂3**, **5Se₂2** and **5Te₂3**. For these species we encountered $X \cdots X$ distances (see Table 2) which are in the order of the van der Waals distances ($S \cdots S = 370$ pm, $Se \cdots Se = 400$ pm, $Te \cdots Te = 440$ pm)¹⁷ or below. In the cases of **5S₂2**, **5Se₂2** and **5Te₂3** the rings are stacked on top of each other to yield a tubular structure. For **5S₂2** and **5Se₂2** the rings in one plane are grouped in blocks of four in which the chalcogen atoms of neighbouring rings form a distorted tetrahedron (Fig. 5). The distances between the Se centres are $a = 364$ pm and $b = 421$ pm.

In **5Te₂3** the rings are arranged in such a way that the Te centres oppose each other which leads to the formation of stacks of pairs (Fig. 6) with additional interactions between the stacks.

For **4S₂3**, **5S₂3**, **5S₂5** and **7S₂5** we find relatively short distances for $C-H \cdots \pi$ and $C-H \cdots X$ contacts whereas the contacts between the sulfur centres vary between 400 and 500 pm (see Table 2). Nevertheless, we encountered for **5S₂3** and **7S₂5** stacking of the rings as shown in Fig. 7 for **7S₂5**. The $C-H \cdots \pi$ distances recorded for these two ring systems (285 and 289 pm) compare well with other weak hydrogen bonds with alkyne units.⁷

Discussion

In Table 2 we have compiled the closest intermolecular $X \cdots X$, $C-H \cdots \pi$ and $C-H \cdots X$ distances for all the cycles

**Fig. 5** a) Columnar structure of **5Se₂2** in the solid state (H atoms have been omitted for the sake of clarity). b) Enlarged arrangement of four neighbouring rings indicating the tetrahedral arrangement of the Se centres.

we have investigated in the solid state. It is seen that only in five cases do we find that the chalcogen–chalcogen contacts are below the van der Waals distances whereas in four other cases the intermolecular interactions are dominated by weak $C-H \cdots \pi$ and $C-H \cdots X$ interactions. In these cases the $C-H \cdots X$ and $C-H \cdots \pi$ distances are close to 290 pm. These values are in the same order of those found for other systems.⁷ The comparison of the data compiled in Table 2 shows that the contributions of the $X \cdots X$ interactions increase in the sequence S – Se – Te , whereas the other weak interactions decrease from S and Se towards Te . We also find that the formation of tubular structures is more likely in those cases where the chalcogen–chalcogen interactions dominate.

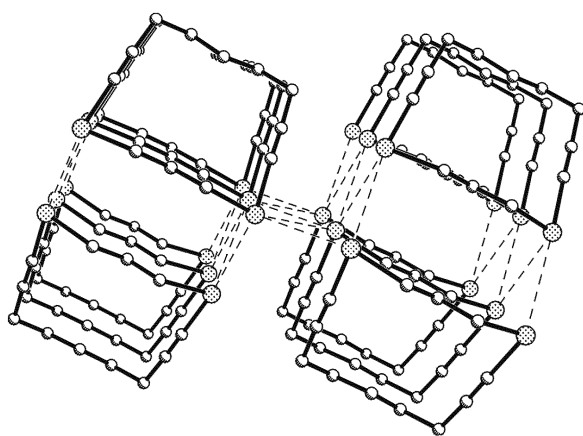


Fig. 6 Columnar structure of $5\text{Te}_2.3$ in the solid state (H atoms have been omitted for the sake of clarity).

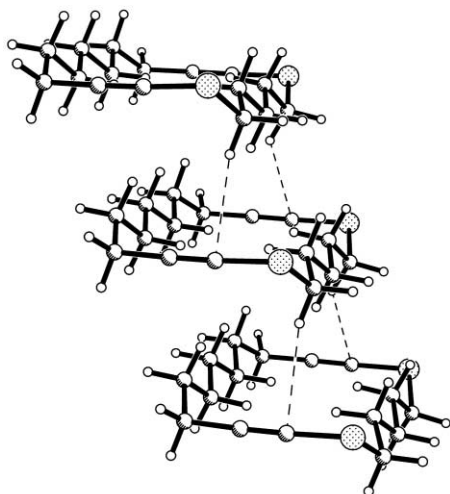


Fig. 7 Structure of $7\text{S}_2.5$ in the solid state. The C–H \cdots π interactions are indicated.

Conclusion

We were able to synthesise a series of cyclic diynes with one sulfur, selenium and tellurium atom in the α -position to each of the triple bonds. The structural investigations of single crystals reveal that in nearly all samples the rings adopt a chair or chair-like conformation. The solid state investigations furthermore reveal in five cases a stacking of the rings on top of each other. This could be traced back to weak intermolecular interactions of the p - σ^* type or C–H \cdots π interaction.

Experimental

General methods

All melting points are uncorrected. Elemental analyses were carried out by Mikroanalytisches Laboratorium der Universität Heidelberg. IR spectra were recorded with a Bruker Vector 22. The NMR spectra were measured with a Bruker WH 300 (^{13}C NMR at 75.47 MHz) and a Bruker Avance 500 (^{13}C NMR at 125.77 MHz) using the solvent as internal standard (δ). The high-resolution mass spectra (HRMS) were recorded in the EI (70 eV) and positive-ion FAB mode in *m*-nitrobenzyl alcohol. All reactions were carried out in dried glassware under nitrogen or argon atmosphere using dried and oxygen-free solvents. Materials used for column chromatography were: silica gel (Macherey-Nagel), Celite (Fluka). Acyclic diynes^{18–20} and dithiocyanatoalkanes^{21–25} were prepared according to literature methods.

X-Ray crystallography and structure solution †

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200 K. Relevant crystal and data collection parameters are given in Table 3. The structures were solved by using direct methods, least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with the SHELXTL (5.10) software package.²⁶ In some of the structures ($4\text{S}_2.3$, $5\text{S}_2.2$, $5\text{S}_2.4$, $5\text{S}_2.5$, $5\text{Se}_2.2$) parts of the alkyl chains were found to be disordered. In all cases this could be refined as superposition of two different orientations. The occupancy factors of the minor components refined to values between 12% and 29%. The crystal needles of $7\text{S}_2.5$ could not be cut without damaging the crystals. Therefore an intact long needle of 3 mm length was used for the structure analysis. The introduced error of varying diffracting volumes was corrected with SADABS.²⁶ Table 3 contains 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 Farrugia.²⁷

General procedure for the preparation of dithiacycloalkadiynes and diselenacycloalkadiynes

To a solution of the alkadiyne (10 mmol) in anhydrous THF (200 ml) was added *n*-butyllithium (20 mmol, 2.5 M in hexane) at -25°C over a period of 15 min. The solution was stirred for 1 h at -25°C and then allowed to warm up to room temperature. To 1000 ml of anhydrous THF were added solutions of the dilithiated alkadiyne in THF (250 ml) and the dithiocyanatoalkane (diselenocyanatoalkane) (10 mmol) in THF (250 ml) dropwise at -40°C over a period of 5 h. After complete addition, the reaction mixture was allowed to warm up to room temperature overnight. After rotary evaporation of the solvent the crude product was absorbed on Celite. Polymers and salts were removed by flash filtration { SiO_2 [3% NEt_3 (v/v)], toluene}. The solvent was removed by rotary evaporation and the cyclic diyne was isolated by column chromatography { SiO_2 [3% NEt_3 (v/v)], mixtures of *n*-hexane and toluene}.

1,5-Dithiacyclotrideca-6,12-diyne ($4\text{S}_2.3$). The general procedure starting from octa-1,7-diyne and 1,3-dithiocyanatopropane yielded 379 mg (30%) of $4\text{S}_2.3$ as a colourless solid. Mp 70°C (from CH_2Cl_2) (Found: C, 63.02; H, 6.66; S, 30.22. $\text{C}_{11}\text{H}_{14}\text{S}_2$ requires C, 62.81; H, 6.71; S, 30.49%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2918, 2859, 1627, 1454, 1434, 1417; $\delta_{\text{H}}(300\text{ MHz, CDCl}_3)$ 1.49–1.70 (6 H, m, CH_2), 1.91–1.99 (2 H, m, CH_2), 2.11–2.41 (4 H, m, CH_2), 2.81 (2 H, m, CH_2); $\delta_{\text{C}}(75\text{ MHz, CDCl}_3)$ 17.7 (CH_2), 19.4 (CH_2), 27.4 (CH_2), 33.2 (CH_2), 68.3 (C), 93.8 (C); m/z (EI-HRMS) 210.0520 (M^+). $\text{C}_{11}\text{H}_{14}\text{S}_2$ requires 210.0537.

1,4-Dithiacyclotrideca-5,12-diyne ($5\text{S}_2.2$). The general procedure starting from nona-1,8-diyne and 1,2-dithiocyanatoethane yielded 442 mg (35%) of $5\text{S}_2.2$ as a colourless solid. Mp 105°C (from CH_2Cl_2) (Found: C, 62.81; H, 6.77; S, 30.37. $\text{C}_{11}\text{H}_{14}\text{S}_2$ requires C, 62.81; H, 6.71; S, 30.49%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2941, 2856, 2187, 1637, 1414, 679; $\delta_{\text{H}}(300\text{ MHz, CDCl}_3)$ 1.41–1.52 (4 H, m, CH_2), 1.65–1.79 (2 H, m, CH_2), 2.32–2.40 (4 H, m, CH_2), 3.05 (4 H, s, CH_2); $\delta_{\text{C}}(75\text{ MHz, CDCl}_3)$ 19.3 (CH_2), 25.7 (CH_2), 26.7 (CH_2), 36.8 (CH_2), 68.9 (C), 94.2 (C); m/z (EI-HRMS) 210.0500 (M^+). $\text{C}_{11}\text{H}_{14}\text{S}_2$ requires 210.0537.

1,5-Dithiacyclotetradeca-6,13-diyne ($5\text{S}_2.3$). The general procedure starting from nona-1,8-diyne and 1,3-dithiocyanatopropane yielded 1.00 g (45%) of $5\text{S}_2.3$ as a colourless solid. Mp 115°C (from CH_2Cl_2) (Found: C, 64.14; H, 7.18; S, 28.55. $\text{C}_{12}\text{H}_{16}\text{S}_2$ requires C, 64.23; H, 7.19; S, 28.58%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$

† CCDC reference numbers 207497–207505. See <http://www.rsc.org/suppdata/ob/b3/b303653g/> for crystallographic data in .cif or other electronic format.

Table 3 Crystal data and structure refinement for **4S₂3**, **5S₂2**, **5S₂3**, **5S₂4**, **5S₂5**, **7S₂3**, **7S₂5**, **5Se₂2** and **5Te₂3^a**

Compound	4S₂3	5S₂2	5S₂3	5S₂4	5S₂5
Chemical formula	C ₁₁ H ₁₄ S ₂	C ₁₁ H ₁₄ S ₂	C ₁₂ H ₁₆ S ₂	C ₁₃ H ₁₈ S ₂	C ₁₄ H ₂₀ S ₂
Formula weight	210.34	210.34	224.37	238.39	252.42
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal shape	Polyhedron	Needle	Polyhedron	Polyhedron	Polyhedron
Crystal size/mm ³	0.42 × 0.30 × 0.09	0.44 × 0.16 × 0.13	1.00 × 0.14 × 0.11	0.34 × 0.30 × 0.17	0.35 × 0.30 × 0.16
Temperature/K	200	200	200	200	200
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 4̄	<i>Pc</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>
<i>Z</i>	4	8	2	8	4
Unit cell dimensions					
<i>a</i> (Å)	13.5954(2)	20.0210(17)	4.5402(1)	18.2162(2)	9.1023(2)
<i>b</i> (Å)	9.5961(1)	20.0210(17)	13.4819(2)	9.0748(1)	16.8216(3)
<i>c</i> (Å)	9.1230(2)	5.6850(6)	9.7130(2)	16.3181(2)	9.1905(2)
<i>a</i> (°)	90	90	90	90	90
<i>β</i> (°)	108.318(1)	90	96.274(1)	103.177(1)	90
<i>γ</i> (°)	90	90	90	90	90
<i>V</i> (Å ³)	1129.90(3)	2278.8(4)	590.98(4)	2626.49(5)	1407.21(5)
<i>D</i> _{calc} /g cm ⁻³	1.240	1.230	1.260	1.210	1.191
Absorpt. coeff. μ/mm ⁻¹	0.43	0.42	0.41	0.37	0.352
θ range for data coll. (°)	1.6–27.5	2.9–27.5	1.5–27.5	1.1–24.1	2.4–27.5
Index ranges	–17 ≤ <i>h</i> ≤ 17 –12 ≤ <i>k</i> ≤ 12 –11 ≤ <i>l</i> ≤ 11	–25 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 25 –5 ≤ <i>l</i> ≤ 7	–5 ≤ <i>h</i> ≤ 5 –17 ≤ <i>k</i> ≤ 17 –12 ≤ <i>l</i> ≤ 12	–20 ≤ <i>h</i> ≤ 20 –10 ≤ <i>k</i> ≤ 10 –18 ≤ <i>l</i> ≤ 18	–11 ≤ <i>h</i> ≤ 11 –21 ≤ <i>k</i> ≤ 21 –11 ≤ <i>l</i> ≤ 11
Reflections collected	11416	3482	6006	20189	13285
Independent reflections	2592	2261	2671	4164	1669
Observ. data/parameters	2062/150	1655/155	2579/128	3200/290	1382/92
Goodness-of-fit on <i>F</i> ²	1.03	1.02	1.06	1.06	1.03
<i>R</i> (<i>F</i>)	0.043	0.040	0.024	0.038	0.034
<i>R</i> _w (<i>F</i> ²)	0.109	0.076	0.062	0.093	0.088
(Δρ) _{max} , (Δρ) _{min} (eÅ ⁻³)	0.60, –0.44	0.22, –0.17	0.20, –0.13	0.41, –0.29	0.24, –0.32

Compound	7S₂3	7S₂5	5Se₂2	5Te₂3
Chemical formula	C ₁₄ H ₂₀ S ₂	C ₁₆ H ₂₄ S ₂	C ₁₁ H ₁₄ Se ₂	C ₁₂ H ₁₆ Te ₂
Formula weight	252.42	280.47	304.14	415.45
Crystal colour	Colourless	Colourless	Colourless	Pale yellow
Crystal shape	Polyhedron	Needle	Needle	Needle
Crystal size/mm ³	0.32 × 0.30 × 0.26	3.00 × 0.16 × 0.06	0.70 × 0.20 × 0.12	0.60 × 0.07 × 0.02
Temperature/K	200	200	200	200
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pc</i>	<i>P</i> 4̄	<i>P</i> 2 ₁
<i>Z</i>	4	2	4	2
Unit cell dimensions				
<i>a</i> (Å)	14.4829(2)	4.5938(2)	15.4224(13)	9.8259(3)
<i>b</i> (Å)	10.9233(2)	17.1826(9)	15.4224(13)	4.7316(1)
<i>c</i> (Å)	9.0174(3)	9.9664(5)	4.8824(6)	14.5466(4)
<i>a</i> (°)	90	90	90	90
<i>β</i> (°)	94.972(1)	93.166(1)	90	103.726(1)
<i>γ</i> (°)	90	90	90	90
<i>V</i> (Å ³)	1421.19(4)	785.48(7)	1161.3(2)	656.99(3)
<i>D</i> _{calc} , g cm ⁻³	1.180	1.186	1.740	2.100
Absorpt. coeff. μ/mm ⁻¹	0.348	0.322	6.322	4.404
θ range for data coll. (°)	2.3–27.5	1.2–27.5	1.9–26.4	2.1–27.5
Index ranges	–18 ≤ <i>h</i> ≤ 18 –14 ≤ <i>k</i> ≤ 14 –11 ≤ <i>l</i> ≤ 11	–5 ≤ <i>h</i> ≤ 5 –22 ≤ <i>k</i> ≤ 22 –12 ≤ <i>l</i> ≤ 12	–2 ≤ <i>h</i> ≤ 19 –9 ≤ <i>k</i> ≤ 17 –2 ≤ <i>l</i> ≤ 6	–12 ≤ <i>h</i> ≤ 12 –6 ≤ <i>k</i> ≤ 6 –18 ≤ <i>l</i> ≤ 18
Reflections collected	14396	7873	2215	6353
Independent reflections	3258	3532	1965	2966
Observ. data/parameters	2831/146	3127/164	1666/137	2464/127
Goodness-of-fit on <i>F</i> ²	1.04	1.04	1.07	1.00
<i>R</i> (<i>F</i>)	0.031	0.033	0.043	0.034
<i>R</i> _w (<i>F</i> ²)	0.080	0.079	0.103	0.079
(Δρ) _{max} , (Δρ) _{min} , (eÅ ⁻³)	0.39, –0.33	0.25, –0.15	0.99, –0.74	1.93, –1.13

^a For the definition of the representation *mX₂n* see Fig. 2.

2941, 2859, 1627, 1420, 1262, 731; δ_H(300 MHz, CDCl₃) 1.39–1.51 (4 H, m, CH₂), 1.52–1.79 (2 H, m, CH₂), 2.25–2.41 (6 H, m, CH₂), 2.53–2.77 (4 H, m, CH₂); δ_C(75 MHz, CDCl₃) 19.6 (CH₂), 26.7 (CH₂), 27.2 (CH₂), 29.5 (CH₂), 32.9 (CH₂), 67.5 (C), 94.8 (C); *m/z* (EI-HRMS) 224.0691 (M⁺). C₁₂H₁₆S₂ requires 224.0693.

1,6-Dithiacyclopentadeca-7,14-diyne (5S₂4). The general procedure starting from nona-1,8-diyne and 1,4-dithiocyanatobutane yielded 800 mg (34%) of **5S₂4** as a colourless solid. Mp 55 °C (from CH₂Cl₂); ν_{max}(KBr)/cm⁻¹ 2926, 2855, 1638, 1418, 1299, 744; δ_H(300 MHz, CDCl₃) 1.39–1.52 (4 H, m, CH₂), 1.62–1.79 (2 H, m, CH₂), 1.90–2.03 (4 H, m, CH₂), 2.30–2.40 (4 H, m,

CH₂), 267–2.79 (4 H, m, CH₂); δ_C (75 MHz, CDCl₃) 19.8 (CH₂), 27.0 (CH₂), 27.7 (CH₂), 28.7 (CH₂), 35.2 (CH₂), 68.8 (C), 94.0 (C); m/z (EI-HRMS) 238.0840 (M⁺). C₁₃H₁₈S₂ requires 238.0850.

1,7-Dithiacyclohexadeca-8,15-diyne (5S₂5). The general procedure starting from nona-1,8-diyne and 1,5-dithiocyanatopentane yielded 1.06 g (42%) of 5S₂5 as a pale yellow solid. Mp 59 °C (from CH₂Cl₂) (Found: C, 66.70; H, 8.13; S, 25.59). C₁₄H₂₀S₂ requires C, 66.61; H, 7.99; S, 25.39%; ν_{\max} (KBr)/cm⁻¹ 2936, 2854, 1637, 1455, 1418, 742; δ_H (300 MHz, CDCl₃) 1.41–1.70 (12 H, m, CH₂), 1.76–1.89 (4 H, m, CH₂), 2.32–2.38 (4 H, m, CH₂), 2.53–2.71 (4 H, m, CH₂); δ_C (75 MHz, CDCl₃) 20.0 (CH₂), 25.4 (CH₂), 27.8 (CH₂), 28.3 (CH₂), 28.4 (CH₂), 34.0 (CH₂), 67.6 (C), 94.5 (C); m/z (EI-HRMS) 252.1003 (M⁺). C₁₄H₂₀S₂ requires 252.1006.

1,5-Dithiacyclohexadeca-6,15-diyne (7S₂3). The general procedure starting from undeca-1,10-diyne and 1,3-dithiocyanatopropane yielded 545 mg (22%) of 7S₂3 as a colourless solid. Mp 67 °C (from CH₂Cl₂) (Found: C, 66.72; H, 8.01; S, 25.09). C₁₄H₂₀S₂ requires C, 66.61; H, 7.99; S, 25.39%; ν_{\max} (KBr)/cm⁻¹ 2930, 2852, 1639, 1458, 1432, 719; δ_H (300 MHz, CDCl₃) 1.20–1.65 (12 H, m, CH₂), 1.95–1.99 (2 H, m, CH₂), 2.15–2.25 (2 H, m, CH₂), 2.29–2.35 (2 H, m, CH₂), 2.65–2.71 (2 H, m, CH₂); δ_C (75 MHz, CDCl₃) 19.0 (CH₂), 26.1 (CH₂), 27.0 (CH₂), 28.2 (CH₂), 30.8 (CH₂), 33.7 (CH₂), 67.9 (C), 94.5 (C); m/z (EI-HRMS) 252.0988 (M⁺). C₁₄H₂₀S₂ requires 252.1006.

1,7-Dithiacyclooctadeca-8,17-diyne (7S₂5). The general procedure starting from undeca-1,10-diyne and 1,5-dithiocyanatopentane yielded 1.75 g (50%) of 7S₂5 as a colourless solid. Mp 89 °C (from CH₂Cl₂) (Found: C, 68.41; H, 8.62; S, 22.64). C₁₆H₂₄S₂ requires C, 68.51; H, 8.63; S, 22.86%; ν_{\max} (KBr)/cm⁻¹ 2931, 2849, 1627, 1458, 1321, 731; δ_H (300 MHz, CDCl₃) 1.22–1.59 (12 H, m, CH₂), 1.79–1.92 (4 H, m, CH₂), 2.30–2.39 (4 H, m, CH₂), 2.55–2.67 (4 H, m, CH₂); δ_C (75 MHz, CDCl₃) 19.8 (CH₂), 27.5 (CH₂), 28.1 (CH₂), 28.6 (CH₂), 28.7 (CH₂), 29.6 (CH₂), 34.4 (CH₂), 68.0 (C), 94.6 (C); m/z (EI-HRMS) 280.1322 (M⁺). C₁₆H₂₄S₂ requires 280.1320.

1,8-Dithiaicosa-9,19-diyne (8S₂6). The general procedure starting from dodeca-1,11-diyne and 1,6-dithiocyanatohexane yielded 618 mg (20%) of 8S₂6 as a colourless solid. Mp 45 °C (from CH₂Cl₂); ν_{\max} (KBr)/cm⁻¹ 2929, 2854, 1688, 1462, 731; δ_H (300 MHz, CDCl₃) 1.20–1.60 (16 H, m, CH₂), 1.65–1.87 (4 H, m, CH₂), 2.25–2.40 (4 H, m, CH₂), 2.57–2.69 (4 H, m, CH₂); δ_C (75 MHz, CDCl₃) 19.4 (CH₂), 27.8 (CH₂), 28.2 (CH₂), 28.4 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 35.0 (CH₂), 68.3 (C), 94.3 (C); m/z (EI-HRMS) 308.1631 (M⁺). C₁₈H₂₈S₂ requires 308.1633.

1,4-Diselenacyclotrideca-5,12-diyne (5Se₂2). The general procedure starting from nona-1,8-diyne and 1,2-diselenocyanatoethane yielded 639 mg (21%) of 5Se₂2 as a colourless solid. Mp 112 °C (from CH₂Cl₂) (Found: C, 43.60; H, 4.73). C₁₁H₁₄Se₂ requires C, 43.44; H, 4.64%; ν_{\max} (KBr)/cm⁻¹ 2943, 2925, 2857, 1638, 1412, 715; δ_H (300 MHz, CDCl₃) 1.41–1.60 (4 H, m, CH₂), 1.65–1.75 (2 H, m, CH₂), 2.34–2.44 (4 H, m, CH₂), 3.20 (4 H, s, CH₂); δ_C (75 MHz, CDCl₃) 19.7 (CH₂), 25.9 (CH₂), 26.9 (CH₂), 30.1 (CH₂), 59.0 (C), 100.4 (C); m/z (EI-HRMS) 305.9439 (M⁺). C₁₁H₁₄Se₂ requires 305.9442.

1,7-Diselenacyclooctadeca-8,17-diyne (7Se₂5). The general procedure starting from undeca-1,10-diyne and 1,5-dithiocyanatopentane yielded 823 mg (22%) of 7Se₂5 as a colourless solid. Mp 90 °C (from CH₂Cl₂) (Found: C, 51.43; H, 6.48). C₁₆H₂₄Se₂ requires C, 51.34; H, 6.46%; ν_{\max} (KBr)/cm⁻¹ 2929, 2847, 1458, 1322, 1266, 729; δ_H (300 MHz, CDCl₃) 1.22–1.64 (10 H, m, CH₂), 1.83–1.99 (4 H, m, CH₂), 2.10–2.22 (2 H, m, CH₂), 2.29–2.37 (4 H, m, CH₂), 2.55–2.79 (4 H, m, CH₂);

δ_C (75 MHz, CDCl₃) 18.1 (CH₂), 20.1 (CH₂), 27.5 (CH₂), 28.2 (CH₂), 28.6 (CH₂), 30.0 (CH₂), 30.4 (CH₂), 57.9 (C), 100.7 (C); m/z (EI-HRMS) 376.0197 (M⁺). C₁₆H₂₄Se₂ requires 376.0208.

General procedure for the preparation of ditelluracycloalkadiynes

To a solution of the alkadiyne in 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 cooled to –40 °C. Then the freshly ground tellurium (200 mesh) was added in the dark. The reaction mixture was stirred overnight to warm up to room temperature. To 500 ml of anhydrous THF were added solutions of the ditellurated alkadiyne in THF and the diiodoalkane in THF dropwise at 0 °C over a period of 4 h. After complete addition, the reaction mixture was allowed to warm up to room temperature overnight. After rotary evaporation of the solvent the crude product was absorbed on Celite. Polymers and salts were removed by flash filtration {SiO₂ [3% NEt₃ (v/v)], toluene}. The solvent was removed by rotary evaporation and the cyclic diyne was isolated by column chromatography {SiO₂ [3% NEt₃ (v/v)], *n*-hexane–toluene = 4 : 1}. All columns were wrapped with aluminium foil to exclude daylight.

1,5-Ditelluracyclotetradeca-6,13-diyne (5Te₂3). The general procedure starting from 6.7 mmol of nona-1,8-diyne, 13.4 mmol of *n*-butyllithium, 13.4 mmol of tellurium and 6.7 mol of 1,3-diiodopropane yielded 1.64 g (59%) of 5Te₂3 as a colourless solid. Mp 143 °C (from toluene) (Found: C, 34.97; H, 3.91). C₁₂H₁₆Te₂ requires C, 34.69; H, 3.88%; ν_{\max} (KBr)/cm⁻¹ 2925, 2884, 2856, 2153, 1638, 1177; δ_H (300 MHz, CDCl₃) 1.52 (4 H, m, CH₂), 1.70 (2 H, m, CH₂), 2.58 (6 H, m, CH₂), 2.71 (4 H, m, CH₂); δ_C (75 MHz, CDCl₃) 9.3 (CH₂), 21.1 (CH₂), 27.4 (CH₂), 28.2 (CH₂), 31.4 (C), 35.8 (CH₂), 113.4 (C); m/z (EI-HRMS) 415.9335 (M⁺). C₁₂H₁₆Te₂ requires 415.9341.

1,7-Ditelluracyclooctadeca-8,17-diyne (7Te₂5). The general procedure starting from 5.7 mmol of undeca-1,10-diyne, 11.4 mmol of *n*-butyllithium, 11.4 mmol of tellurium and 5.7 mol of 1,5-diiodopentane yielded 1.41 g (53%) of 7Te₂5 as a colourless solid. Mp 136 °C (from toluene) (Found: C, 41.04; H, 5.19). C₁₆H₂₄Te₂ requires C, 40.75; H, 5.13%; ν_{\max} (KBr)/cm⁻¹ 2923, 2886, 2852, 2151, 1628, 1466, 1326, 1167; δ_H (300 MHz, *d*₈-toluene) 1.20 (2 H, m, CH₂), 1.34–1.40 (10 H, m, CH₂), 1.80 (4 H, m, CH₂), 2.31–2.41 (8 H, m, CH₂); δ_C (75 MHz, *d*₈-toluene) 7.3 (CH₂), 21.4 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.4 (CH₂), 32.2 (CH₂), 32.5 (C), 34.8 (CH₂), 113.2 (C); m/z (EI-HRMS) 476.0004 (M⁺). C₁₂H₁₆Te₂ requires 476.0002.

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