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Solid-state tubular assemblies of thiolactones: synthesis and structural characterization

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Abstract—The synthesis of cyclic thiolactones, 2,5,8-trithiacyclododecane-1,9-dione (**4**), 2,5,8,14,17,20-hexathiacyclotetracosane-1,9,13,21-tetraone (**5**), 2,5,8-trithiacyclotetradecane-1,9-dione (**6**) and 2,5,8,16,19,22-hexathiacyclooctacosane-1,9,15,23-tetraone (**7**) was achieved by tin-template reaction of 2,2-dibutyl-2-stanna-1,3,6-trithiacyclooctane (**1**) with corresponding diacyl chlorides. The structures of 12-, 14-, 24- and 28-membered ring systems of **4**, **6**, **5**, and **7**, respectively, were investigated by X-ray structure analysis. These investigations revealed that, in the solid-state, thiolactones **4** and **7** form tubular assemblies. However, the crystal structure of **5** forms layered packing dominated by CH···O hydrogen bonds whereas **6** forms three-dimensional network via CH···O hydrogen bonds and van der Waals interactions.

1. Introduction

The chemistry of macrocycles has initiated the development of supramolecular chemistry, in which not only monomeric but also dimeric and oligomeric structures play a central role.[1] Tubular molecular structures have attracted the attention of chemists due to their occurrence in nature and their potential in materials science. Tailor-made tubular assemblies have an important impact on many areas of research, in particular, drug development, molecular electronics and materials science. Recent scientific literature reports inorganic and organic tubular assemblies such as graphite,[2] boron nitride nanotubes,[3] zeolites,[4] polymeric lipid-based tubules,[5] carbohydrate-based nanotubes,[6] cyclic chalcogen alkynes[7] or cyclic peptide nanotubes.[8]

As an extention of our interest in the synthesis and characterization of novel macrocyclic polythiaethers that contain one or more cage moieties within the crown ether framework[9] we have turned to the preparation of macrocyclic polythiolactones.[10a] Our in-depth studies on polythiolactones revealed that some of the molecules form tubular assemblies in the solid-state through weak C–H···O interactions. Thus, we report the synthesis and molecular and crystal structures of the 12-, 14-, 24- and 28-membered cyclic thiolactones determined by X-ray structure analysis.

2. Results and discussion

2.1. Synthesis

To prepare cyclic polythiolactones, we used the strategy via ring-opening condensation of stannapolythiane with diacyl chloride,[10] as shown in Scheme 1.

Stannathiane **1**, prepared from dibutyltin oxide and 2,2′-thiadiethanthiole,[10a] was reacted with glutaryl chloride **2** or pimeloyl chloride **3** to afford di- and tetra-polythiolactones **4**–**7** in good to moderate yields. Table 1 shows that in the reaction of **2** ($n=3$) the product yield is lower than that of **3** ($n=5$). Since all of the products **4**–**7** have large rings, it is likely that the difference in the obtained yields could be due to difference in the reactivity between **2** and **3**. It should be pointed out that efficient macrocyclization can be achieved by proper adjustment of experimental conditions.[11] The reaction conditions were adjusted to favour the formation of dimers.[12] However, the ratio of the products **4**:**5** and **6**:**7** depends on the ring size, Table 1. Thus, the 14-membered di-thiolactone **6** is formed as a major ring product in preference to the 28-membered tetra-thiolactone **7**. On the contrary, the 12-membered di-thiolactone **4** competes equally with the 24-membered tetra-thiolactone **5**, to give

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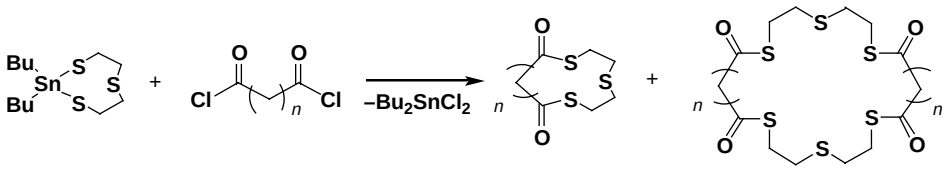

1 **2** $n=3$, **3** $n=5$ **4** $n=3$, **6** $n=5$ **5** $n=3$, **7** $n=5$

Scheme 1. Reagents and conditions: $CHCl_3$ reflux, 2,2′-bipyridyl, rt.

Table 1. Reaction of stannathiane **1** with diacyl chlorides **2** and **3**

Diacyl chloride	Products	Mp (°C)[a]	Ring size	Product ratio[b]	(k'_n)[c]	Yield (%)[d]
2	**4**	113–117	12	1:1	0.03	44
	5	108–109	24		0.28	
3	**6**	118–119	14	3:1	0.20	80
	7	98–100	28		0.70	

[a] Melting points are not corrected.
[b] Determined by HPLC.
[c] HPLC capacity factor of the eluted compound ($k'_n=t_n-t_0/t_0$).
[d] The yield of pure isolated products.

a mixture of products in a 1:1 ratio. The observed formation of thiolactones **4**–**7** from cyclic stannapolythiane **1** and diacyl chloride **2** and **3** is in accord with the results obtained for the formation of macrocyclic lactones, which is a kinetically controlled cyclization type of reaction.[13] Inspection of Table 1 also reveals that there are striking regularities in the melting points of thiolactones **4**–**7**. Dimers **5** and **7** exhibit lower melting points than monomers **4** and **6**. This is in accord with crystal packing densities of the compounds in the solid-state: dimers **5** and **7** have lower crystal packing density than the corresponding monomers **4** and **6**, (see Section 2, Table 4).

All new compounds were characterized by analysis of their respective IR, ^1H and ^{13}C NMR spectra, elemental microanalysis and/or HRMS (see Section 3).

2.2. Molecular structures and ring conformations

Crystal and molecular structures of 12-, 14-, 24-, and 28-membered polythiolactones were determined and their conformations are shown in Figures 1–4. Their conformations defined by characteristic S–C–C–S fragments are listed in Table 2. The influence of the ring size and steric strain on the conformation is analysed by extending data extracted from the Cambridge Structural Database.[14]

The 12-membered ring of compound **4** (Fig. 1) reveals an unusual 'heart-shape' conformation with the sulfur atoms positioned somewhere between *endo*- and *exo*-orientation. The conformation of the two S–C–C–S moieties is

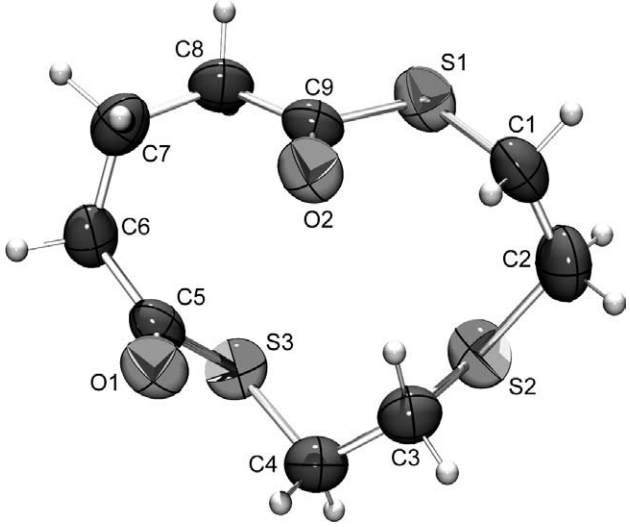

Figure 1. Molecular structures of **4**. Torsion angles defining the ring conformation are (clockwise from S1–C1 bond): $^{+}g\ ^{-}g\ a\ ^{-}g\ ^{-}g\ a\ ^{-}g\ ^{+}g\ ^{-}g\ a\ a$.

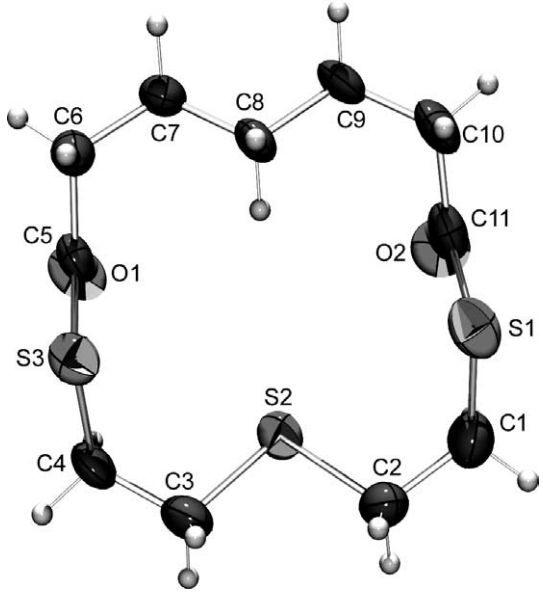

Figure 2. Molecular structure of **6**. The unit cell comprises two similar conformers, one of them is shown. Torsion angles defining the ring conformation are (clockwise from S1–C4 bond): $^{-}g\ ^{+}g\ a\ a\ ^{-}g\ ^{+}g\ a\ a\ ^{-}g\ a\ a\ ^{+}g\ ^{-}g\ a$.

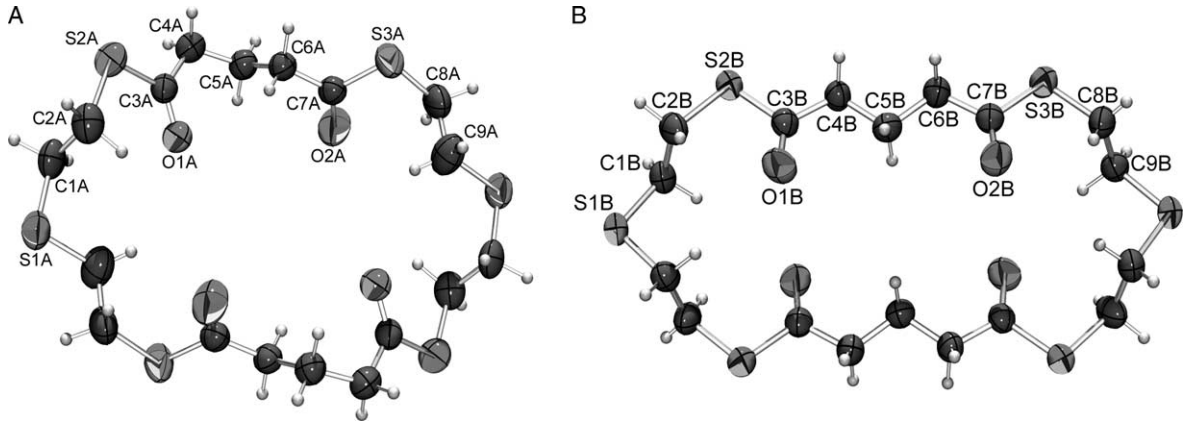

Figure 3. There are two conformers in the crystal of **5**: the molecules A and B. Both rings exhibit C_i molecular symmetry. Torsion angles defining conformations are: (for A clockwise from S1A–C1A bond) $^{-}g\ a\ ^{-}g\ a\ a\ ^{-}g\ a\ a\ a\ ^{-}g\ a\ a$ and (for B clockwise from S1B–C1B bond) $^{+}g\ a\ ^{+}g\ a\ a\ a\ a\ a\ a\ ^{-}g\ a\ ^{-}g$.

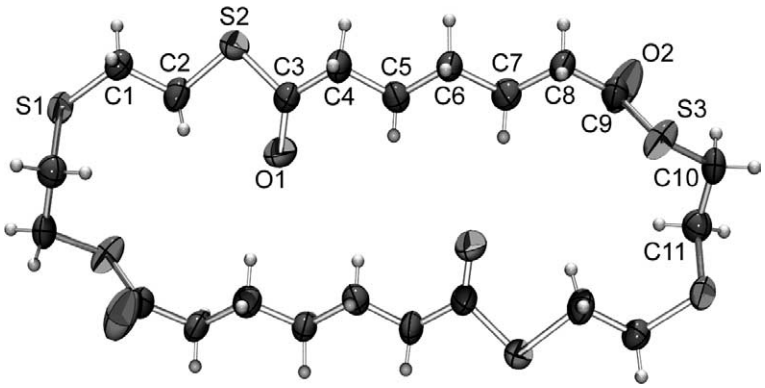

Figure 4. Tetra-thiolactone **7** in the solid-state is of the C_i molecular symmetry. The crystallographically independent unit is a half of the molecule. Torsion angles defining the ring conformation are (clockwise from S1–C1 bond): $^{-}g\ a\ a\ a\ a\ a\ a\ a\ a\ ^{+}g\ a\ ^{+}g\ ^{+}g\ a$.

$^{-}$*gauche* (Table 2, Fig. 5a). Compounds **5** and **6** comprise two crystallographically independent molecules in the unit cells (Table 2). Thus, the 14-membered ring of compound **6** occurs as two conformers of similar conformations (Figs. 2 and 5b): in both rings the conformations of S–C–C–S moieties are $^{+}$*gauche*, $^{-}$*gauche*. One sulfur atom adopts the *endo*-orientation whereas the other two have orientations somewhere between *endo* and *exo*. Both conformers of compound **5** (Fig. 3), in the solid-state, exhibit C_i molecular symmetry (Table 2); conformer A is in a crown-like conformation (Fig. 5c) whereas conformer B appears in a twisted conformation (Fig. 5d). In both rings, sulfur and oxygen atoms are *exo*-oriented. The 24-membered ring of compound **7** (Fig. 4) also reveals C_i molecular symmetry (Table 2). The conformation is illustrated in Figure 5e with four sulfur atoms *exo*-oriented whereas two of them exhibit geometry somewhere between *endo* and *exo*. The present data support *exo*-orientation of sulfur atoms to be sterically favored in large rings (24- and 28-membered ones).

To examine possible steric strain on the ring conformation we have focused on the ring systems involving the Csp^2 atoms that affect the flexibility of the S–C–C–S moieties.[15] In the present analysis, based on our data and data extracted from the Cambridge Structural Database,[14] special attention

Table 2. The conformations of S–C–C–S fragments in cyclic structures **4–7**

Compound	Molecular symmetry	No. of atoms in the ring	S–C–C–S torsion angle (°)[a]			
			1	2	3	4
4	C_1	12	−50.4(5)	−63.9(4)	—	—
6A[b]	C_1	14	73.6(5)	−68.1(5)	—	—
6B[b]	C_1	14	65.2(5)	−69.5(5)	—	—
5A[b]	C_i	24	−174.8(3)	168.3(3)	174.8(3)	−168.3(3)
5B[b]	C_i	24	−172.0(3)	175.9(3)	172.0(3)	−175.9(3)
7	C_i	28	−175.5(4)	69.3(3)	175.5(4)	−69.3(3)

[a] The numbering of torsion angles 1–4 is in agreement with the atom numbering given in Figures 1–4.
[b] Two crystallographically independent molecules.

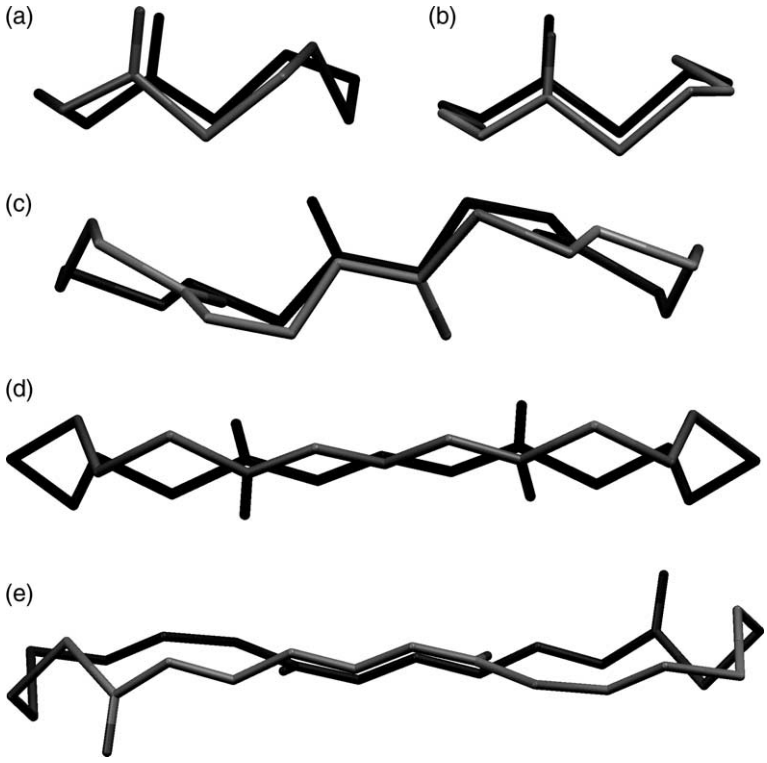

Figure 5. Side-views of the molecules **4**–**7** illustrating different ring conformations: (a) **4**, (b) **6**A, (c) **5**A (d) **5**B, (e) **7**. Conformations of **6**A and **6**B are similar; thus **6**A is shown, only.

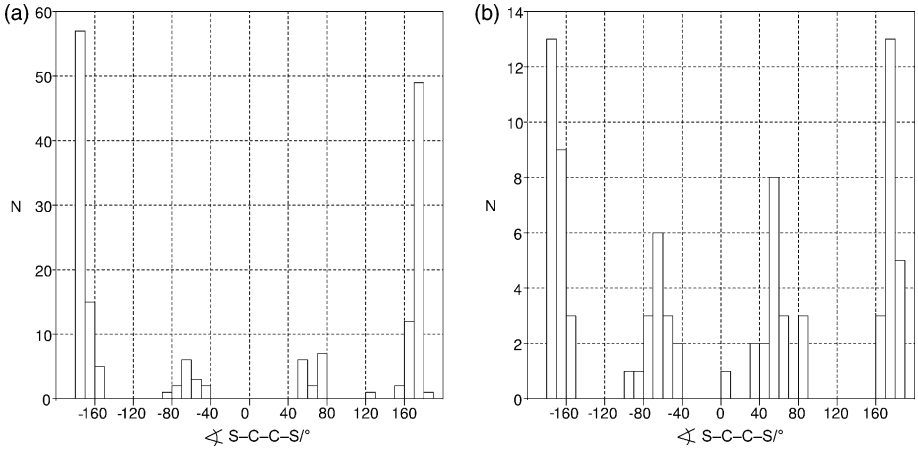

Figure 6. (a) Highly populated $\pm$*anti* conformation of torsion angles S–C–C–S for moieties CH_2–S–CH_2–CH_2–S–CH_2 of macrocyclic compounds found in the CSD; (b) distribution of torsion angles S–C–C–S for moieties Csp^2–S–CH_2–CH_2–S–Csp^2 of macrocyclic compounds found in the CSD show both *anti* and *gauche* conformations.

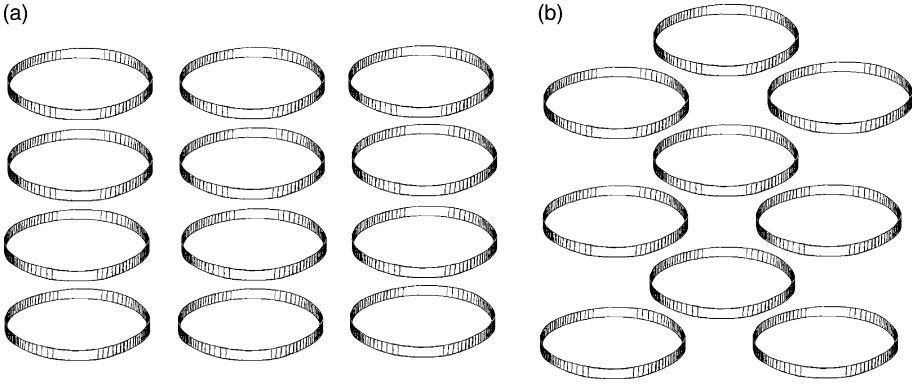

Figure 7. Two ways of stacking rings in tubular assemblies: (a) discrete tubes, (b) partially overlapping tubes.

Table 3. C–H···O interactions generating tubular assemblies in compounds **4** and **7**

Compound	Hydrogen bond	C–H (Å)	H···O (Å)	C···O (Å)	C–H···O (°)	Symmetry operation on acceptor
4	C1–H1B···O1	0.97(5)	2.53(5)	3.464(5)	162(3)	$1+x, y, z$
	C6–H6A···O1	0.92(4)	2.54(4)	3.293(4)	140(3)	$1+x, y, z$
	C8–H8A···O1	1.02(4)	2.71(4)	3.366(3)	132(3)	$1+x, y, z$
	C8–H8B···O2	0.92(4)	2.68(7)	3.335(4)	129(5)	$-x, 1-y, 1-z$
7	C8-H8B···O1	1.05(5)	2.69(5)	3.703(4)	162(4)	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
	C10–H10A···O2	0.96(6)	2.53(6)	3.225(5)	132(4)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$

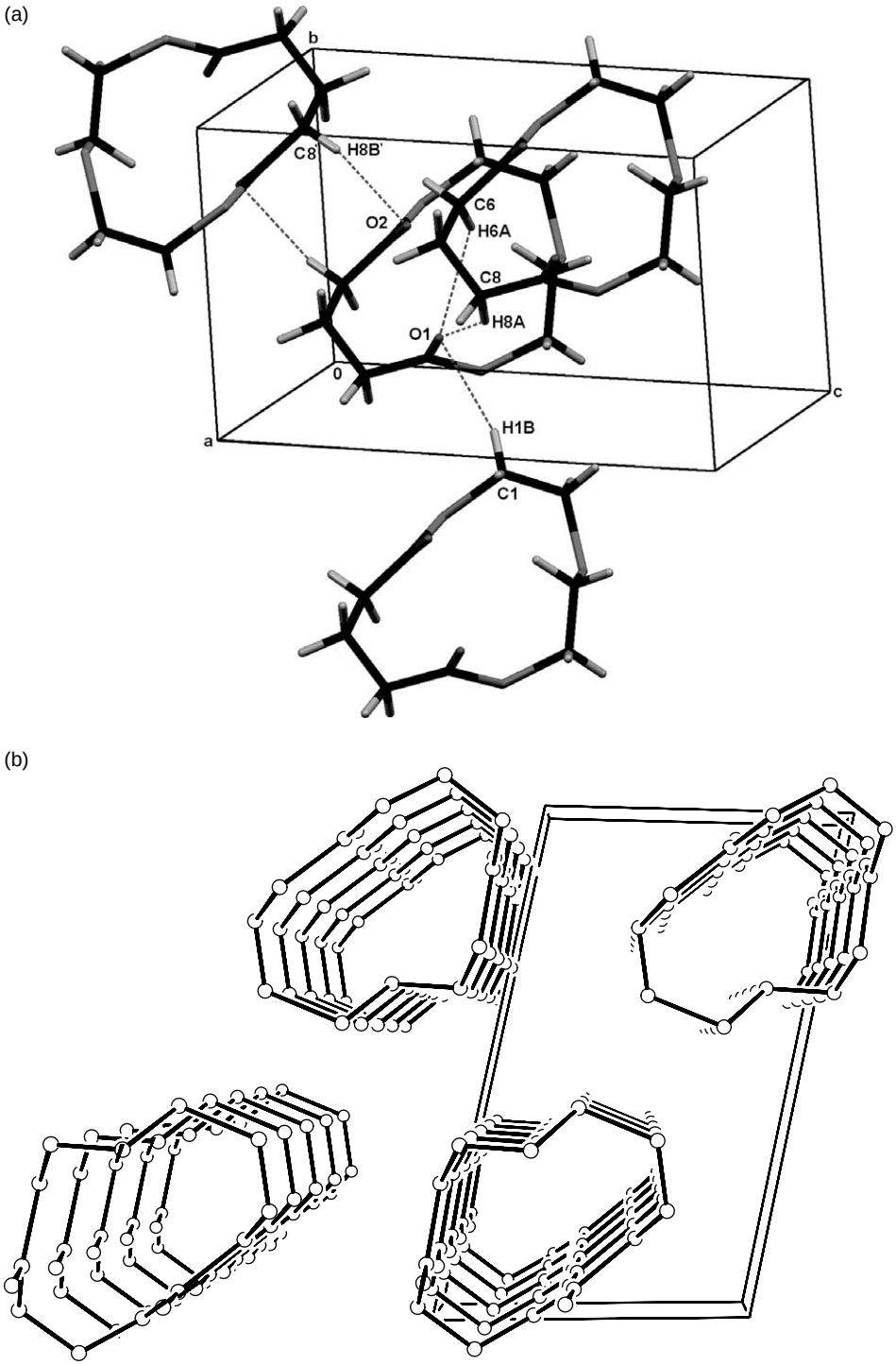

Figure 8. (a) The three-dimensional crystal packing of **4** with details of intratubular (C6–H6A···O1 and C8–H8A···O1) and intertubular (C1–H1B···O1 and C8–H8B···O2) hydrogen bonding. The atom O1 acts as a triple acceptor (Table 3). (b) The rings are stacked along [100] forming tubular assemblies.

is paid to the hybridization of the terminal carbon atoms of the Cα–S–CH_2–CH_2–S–Cα moiety. In the structures reported, one of the Cα(S) atoms is a methylene carbon and the other is a carbonyl carbon. The Cambridge Structural Database only reveals structures with both Cα(S) having the same hybridization: both Cα(S) are Csp^3 (methylene) or both Cα(S) are Csp^2 (carbonyl). As Csp^3 atoms do not impose steric strain, the moiety S–CH_2–CH_2–S predominantly has the *anti* conformation (Fig. 6a). The presence of the Csp^2 atoms imposes steric strain on the ring and hence the *gauche* conformation of the S–C–C–S moiety is more common (Fig. 6b) although the *anti* conformation does occur.

The analysis of about 900 structures (CSD)[14] including up to 11-membered rings reveals a preference for $^{\pm}$*gauche* conformation for the atom sequence S–C–C–S and *endo*-orientation of the sulfur atoms. However, the analysis for 12-membered and larger rings of macrocyclic polythianes (CSD, 137 entries) reveals that in most cases, sulfur atoms are *exo*-oriented as we have observed for the 24- and 28-membered rings of **5** and **7**, respectively. Rings with 12 or more atoms having no steric strain on the atom sequence S–CH_2–CH_2–S prefer the *anti* conformation. Compounds **4** and **6** having 12- and 14-membered rings, respectively, reveal *gauche* conformation for the sequence S–C–C–S due to the presence of Csp^2 (carbonyl) atoms.

2.3. Crystal structures and tubular assemblies

Hydrogen bonding is utilized extensively in the supramolecular chemistry due to its directionality and well defined donor and acceptor sites, which enable recognition and copying with high fidelity. These non-covalent interactions with appropriately crafted macrocycles can lead to tubular structures. Macrocyclic molecules can form topologically different tubular arrays.[7,8,16] A preference to form a tube-like stacking is found in oligopeptides[8b] and chalcogen alkynes.[7] The Cambridge Structural Database (137 entries selected of 12-membered rings and larger with at least one S–CH_2–CH_2–S moiety) was used to analyze assembly of such molecules. The analysis revealed that over 40% of the structures comprise tubular assemblies with the topology shown in Figure 7a whereas only a small portion generate partially overlapping tubes (Fig. 7b).

However, macrocyclic polythianes are less studied and there are no data about polythiolactones. Among the four structures presented in this work, polythiolactones **4**–**7**, two of them, **4** and **7**, reveal tubular structures in the solid-state with similar topology as shown in Figure 7a.

The crystal packing of reported macrocyclic polythianes is governed by weak C–H···O and van der Waals interactions that connect molecules into two-dimensional (**5** and **7**)

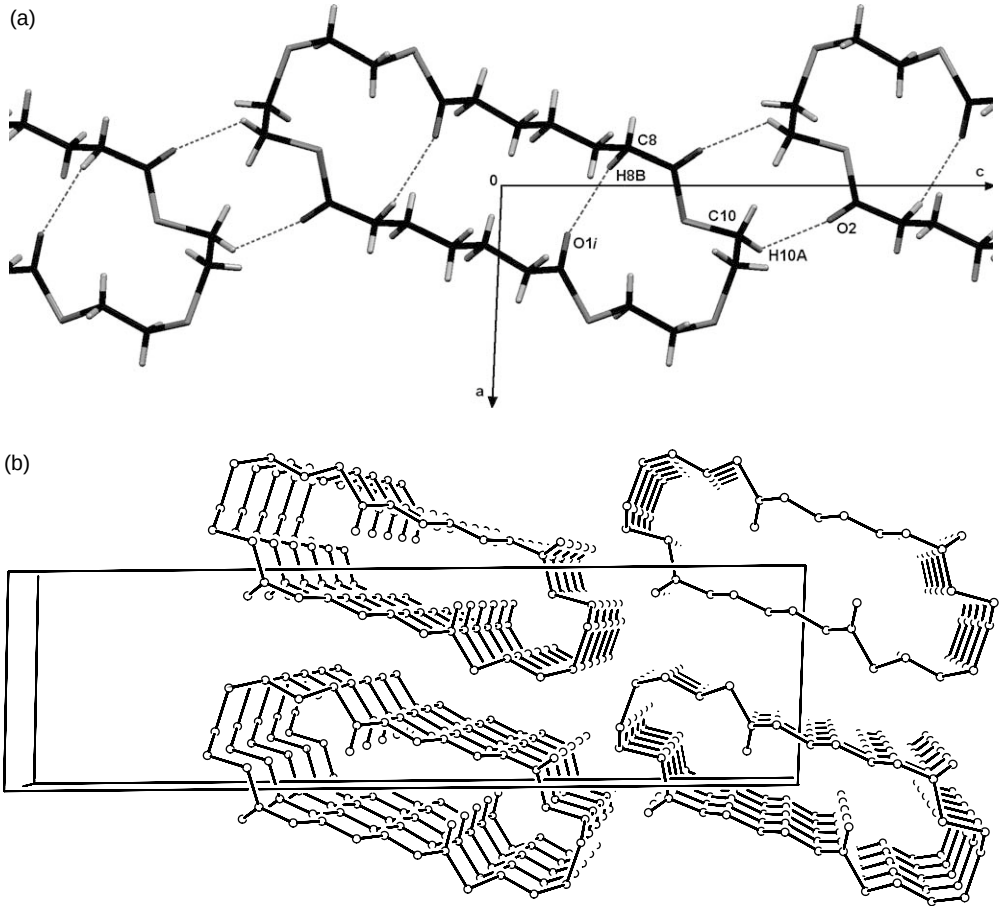

Figure 9. (a) The structure of **7** with intratubular [C8–H8B···O1^i ($i=-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)] and intertubular (C10–H10A···O2) hydrogen bonds. (b) Tubular assemblies are generated along [010] direction.

Table 4. Crystallographic parameters, data collection and structure refinement data for polythiolactones **4**, **5**, **6** and **7**

Compound	**4**	**5**	**6**	**7**
Empirical formula	$C_9H_{14}O_2S_3$	$C_{18}H_{28}O_4S_6$	$C_{11}H_{18}O_2S_3$	$C_{22}H_{36}O_4S_6$
Formula wt (g mol^{-1})	250.38	500.76	278.43	556.87
Crystal dimensions (mm)	0.15×0.15×0.10	0.8×0.3×0.18	0.4×0.4×0.05	0.25×0.20×0.10
Space group	*P*-1	$P2_1/a$	$P2_12_12_1$	$P2_1/c$
a (Å)	5.5049(5)	9.7259(3)	9.2304(5)	8.4793(4)
b (Å)	8.244(4)	9.7267(4)	9.3203(5)	5.3034(3)
c (Å)	13.479(7)	25.8877(9)	31.281(2)	30.716(1)
α (°)	77.64(4)	90	90	90
β (°)	84.39(4)	100.544(3)	90	92.446(4)
γ (°)	78.9(3)	90	90	90
Z	2	4	8	2
V (Å^3)	585.3(4)	2407.7(1)	2691.1(3)	1380.0(2)
D_{calc} (g cm^{-3})	1.421	1.381	1.374	1.340
μ (mm^{-1})	5.582	5.428	4.911	4.788
Θ range (°)	3.36–76.52	1.74–76.61	2.83–76.42	2.88–76.3
Range of *h*, *k*, *l*	$-6>h>6$; $0>k>10$; $-16>l>16$	$-12>h>0$; $-12>k>0$; $-32>l>32$	$-11>h>0$; $-11>k>0$; $-39>l>0$	$-10>h>10$; $-6>k>0$; $-38>l>0$
Reflections collected	2918	5674	3553	2952
Independent reflections	2443	5070	3229	2894
Observed reflections ($I\geq 3\sigma$)	1794	3031	3049	1434
R_{int}	0.1921	0.0782	0.1424	0.0351
$R(F)$	0.055	0.0624	0.0677	0.0620
$R_w(F^2)$	0.1674	0.1878	0.1799	0.1699
Goodness of fit	0.874	1.020	1.083	0.981
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.504; −0.401	0.457; −0.457	0.447; −0.665	0.389; −0.338

and three-dimensional networks (**4** and **6**). The reported C–H···O hydrogen bonds in Table 3 satisfied their function in crystal packing and the geometric parameters using liberal cut-off criteria as suggested by Desiraju and Steiner.[17] However, open-ended tubular molecular assemblies are generated in two structures: di-thiolactone **4**, of the 12-membered ring skeleton (Fig. 8) and tetra-thiolactone **7** of the 28-membered ring (Fig. 9). In both structures the placement of a pair of self-complementary hydrogen bonding functions, that is, C–H and O=C of neighbouring rings favours non-covalent interactions and ring stacking (Table 3).

In general, the governing principle for creating tubular assemblies can be attributed to complementary requirements producing the stacking of the ring. It should be pointed out that cyclic thiolactones **4** and **7**, which both form tubular structures, do not exhibit twisted conformations (Fig. 5a and e). The more chair-like conformations in **4** and **7** have carbonyl groups accessible for hydrogen bonding CH···O between the rings (Table 3). Thus, stacked rings can be connected into a tubular array of molecules. In both structures, **4** and **7** stacked rings are related by translation along the axis *a* (5.5049 Å) and *b* (5.3034 Å), respectively (Table 4).

In conclusion, the synthesis of cyclic di- and tetra-thiolactones **4**–**7** was achieved via ring-opening condensation of corresponding stannapolythiane **1** with diacyl chlorides **2** and **3**. The molecular structures of cyclic ring systems **4**, **6**, **5**, and **7**, were investigated by X-ray structure analysis. In the crystal structures of **5** and **6** there are crystallographically independent molecules. In **5** there are two different conformers where each of them generates a layer. In **6** two conformers are very similar and they are connected by C–H···O hydrogen bonds generating the three-dimensional pattern of hydrogen bonding. However, thiolactones **4** and **7** form tubular assemblies governed by CH···O hydrogen bonding between the stacked rings. To the best of our knowledge, these are the first columnar structures of polythiolactone systems reported.

3. Experimental

3.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 300 and 600 MHz spectrometers using TMS or $CDCl_3$ as the internal standard. HPLC-analyses were performed on an instrument equipped with a UV detector operated at $\lambda=$ 230 nm. An OmniSpher C18 (250×4.6 mm) chromatography column was employed by eluting with CH_3CN at a flow rate of 1 mL/min. Dibutyltin oxide and 2,2′-thiadiethanthiol were used as obtained from commercial sources. The diacyl chlorides **2** and **3** were prepared according to the standard procedure.[18] For the single crystals of polythiolactones **4**–**7**, all polythiolactones were recrystallized from a mixture of $CHCl_3$/MeOH in a 1:1 ratio.

3.2. General procedure for the synthesis of the di-thiolactones and tetra-thiolactones 4–7

A solution of stannathiane **1** (2.5 mmol) in dry $CHCl_3$ (40 mL) was heated to reflux, and a solution of corresponding diacyl chloride **2** or **3** (2.5 mmol) in dry $CHCl_3$ (10 mL) was added dropwise over 4 h with stirring. After the addition of reagents had been completed, the resulting mixture was refluxed during 1 h, cooled to ambient temperature and then was treated with 2,2′-bipyridyl (2.5 mmol). The resulting mixture was filtered through small pad of silica, and the filtrate was concentrated in vacuo. A gross mixture of products was separated on a Florisil column (60–100 mesh) by using a 0→20% of

EtOAc–CH_2Cl_2 gradient elution scheme to afford the corresponding products.

3.2.1. 2,5,8-Trithiacyclododecane-1,9-dione (4). White solid (20% yield); mp 113–117 °C. IR (KBr) 2937, 2912, 1694, 1426, 1395, 1079, 1016, 976, 824, 675 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.15–2.24 (m, 2H), 2.66–2.74 (m, 4H), 2.81–2.89 (m, 4H), 3.17–3.24 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 20.8, 28.5, 29.6, 43.5, 197.6. Anal. Calcd for $C_9H_{14}O_2S_3$: C, 43.17; H, 5.64. Found: C, 43.39; H, 5.93.

3.2.2. 2,5,8,14,17,20-Hexathiacyclotetracosane-1,9,13,21-tetraone (5). White solid (24% yield); mp 108–109 °C. IR (KBr) 2931, 2904, 1686, 1402, 1052, 989, 954, 753 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.98–2.11 (m, 4H), 2.66 (t, 8H, $J=7.3$ Hz), 2.78 (d, 4H, $J=8.9$ Hz), 2.81 (d, 4H, $J=7.8$ Hz), 3.11 (d, 4H, $J=7.8$ Hz), 3.13 (d, 4H, $J=8.9$ Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 21.1, 29.2, 31.9, 42.5, 197.8. Anal. Calcd for $C_{18}H_{28}O_4S_6$: C, 43.17; H, 5.64. Found: C, 43.43; H, 5.84.

3.2.3. 2,5,8-Trithiacyclotetradecane-1,9-dione (6). White solid (60% yield); mp 118–119 °C. IR (KBr) 2910, 2856, 1685, 1431, 1260, 1100, 1036, 948 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 1.45–1.52 (m, 2H), 1.70–1.78 (m, 4H), 2.54–2.61 (m, 4H), 2.81–2.86 (m, 4H), 3.14–3.19 (m, 4H). ^{13}C NMR (600 MHz, $CDCl_3$): δ 25.5, 26.0, 28.6, 33.1, 43.0, 198.9. HRMS calcd for $C_{11}H_{18}O_2S_3$ $[M]^+$ 278.046347, found 278.043494. Anal. Calcd for $C_{11}H_{18}O_2S_3$: C, 47.45; H, 6.52. Found: C, 47.26; H, 6.43.

3.2.4. 2,5,8,16,19,22-Hexathiacyclooctacosane-1,9,15,23-tetraone (7). White solid (20% yield); mp 98–100 °C. IR (KBr) 2935, 2852, 1685, 1467, 1423, 1102, 1017, 969 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 1.34–1.44 (m, 4H), 1.65–1.73 (m, 8H), 2.55–2.61 (m, 8H), 2.74–2.80 (m, 8H), 3.07–3.14 (m, 8H). ^{13}C NMR (600 MHz, $CDCl_3$): δ 25.0, 27.8, 29.1, 32.0, 43.6, 198.5. HRMS calcd for $C_{22}H_{36}O_4S_6$ $[M+H]^+$ 557.101068, found 557.101752. Anal. Calcd for $C_{22}H_{36}O_4S_6$: C, 47.45; H, 6.52. Found: C, 47.14; H, 6.54.

3.3. X-ray diffraction analysis

Data collection was performed on an Enraf Nonius CAD4 diffractometer, using a graphite monochromated Cu Kα (1.54179 Å) radiation at room temperature [293(2) K]. Three standard reflections were measured every 120 min as an intensity control. Absorption correction based on eight ψ-scan reflexions was performed.[19] The WinGX standard procedure was applied for data reduction.[20] Each structure was solved with SHELXS97[21] and refined with SHELXL97.[22] The models were refined using the full matrix least squares refinement on F^2. Hydrogen atoms were refined as free entities. The atomic scattering factors were those included in SHELXL97.[22] Molecular geometry calculations were performed with PLATON,[23] and molecular graphics were prepared using ORTEP-3,[24] and CCDC-Mercury.[25] Crystallographic data can be obtained from the Cambridge Crystallographic Data Centre, deposit@ccdc.cam.ac.uk; CCDC-273292, CCDC-273293, CCDC-273294 and CCDC273407.

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References and notes

1. (a) Vögtle, F. *Supramolecular Chemistry*; Wiley: New York, 1991. (b) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995. (c) Schneider, H.-J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, 2000. (d) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, 2000.
2. (a) Iijima, S. *Nature* **1991**, *354*, 56–58. (b) Ajayan, P. M.; Ebbeson, T. W. *Rep. Prog. Phys.* **1997**, *60*, 1025–1062.
3. Chopra, N. G.; Luyken, R. J.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science* **1995**, *269*, 966–967.
4. (a) Dessan, R. M.; Schlenker, J. L.; Higgins, J. B. *Zeolites* **1990**, *10*, 522–524. (b) Calzaferri, G.; Pauchore, M.; Maas, H.; Huber, S.; Khatyr, A.; Schaafsma, T. *J. Mater. Chem.* **2002**, *12*, 1–13.
5. Lee, Y.-S.; Yang, J.-Z.; Sisson, T. M.; Frankel, D. A.; Gleeson, J. T.; Aksay, M.; Keller, S. L.; Gruner, S. M.; O'Brien, D. F. *J. Am. Chem. Soc.* **1995**, *117*, 5573–5578.
6. (a) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516–518. (b) Gattuso, G.; Menzer, S.; Nepogodiev, S. A.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 1451–1454. (c) Benner, K.; Klüfers, P.; Schumacher, J. *Angew. Chem., Int. Ed.* **1997**, *36*, 743–745.
7. (a) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2002**, *67*, 4290–4297. (b) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2004**, *69*, 2945–2952. (c) Gleiter, R.; Werz, D. B. *Chem. Lett.* **2005**, *34*, 126–131.
8. (a) Hartgerink, J. D.; Clark, T. D.; Ghadiri, M. R. *Chem. Eur. J.* **1998**, *4*, 1367–1372. (b) Ranganathan, D.; Lakshmi, C.; Haridas, V.; Gopikumar, M. *Pure Appl. Chem.* **2000**, *72*, 365–372. (c) Reches, M.; Gazit, E. *Science* **2003**, *300*, 625–627. (d) Rozenthal-Aizman, K.; Svensson, G.; Unden, A. *J. Am. Chem. Soc.* **2004**, *126*, 3372–3373.
9. (a) Mlinarić-Majerski, K.; Pavlović, D.; Luić, M.; Kojić-Prodić, B. *Chem. Ber.* **1994**, *127*, 1327–1329. (b) Mlinarić-Majerski, K.; Pavlović, D.; Milinković, V.; Kojić-Prodić, B. *Eur. J. Org. Chem.* **1998**, 1231–1236. (c) Mlinarić-Majerski, K.; Vinković, M.; Škare, D.; Marchand, A. P. *Arkivoc*, **2002**, *IV*, 30–37. [http://www.arkat-usa.org/ark/ARKIVOC/arkivoc_articles.htm]. (d) Marchand, A. P.; Cal, D.; Mlinarić-Majerski, K.; Ejsmont, K.; Watson, W. H. *J. Chem. Crystallogr.* **2002**, *32*, 447–463. (e) Williams, S. M.; Brodbelt, J. S.; Marchand, A. P.; Cal, D.; Mlinarić-Majerski, K. *Anal. Chem.* **2002**, *74*, 4423–4433. (f) Višnjevac, A.; Kojić-Prodić, B.; Vinković, M.; Mlinarić-Majerski, K. *Acta Crystallogr., Sect. C* **2003**, *59*, 314–316.
10. (a) Vujasinović, I.; Veljković, J.; Mlinarić-Majerski, K. *J. Org. Chem.* **2004**, *69*, 8550–8553. (b) Shanzer, A.; Libman, J. *Synthesis* **1984**, 140–141.
11. (a) Chloroform used in the reaction should be freshly washed with water to remove traces of EtOH, and then dried over $MgSO_4$. (b) When CH_2Cl_2 was used as the reaction solvent the NMR spectra showed that the crude mixture of products

contained significant amounts of Bu_2SnCl_2, which makes purification of the products much more difficult. (c) It should be noted that in the reaction of stannathiane **1** with glutaryl chloride **2**, HPLC analysis of reaction mixture revealed the several cyclic oligomers. Column chromatography of the product mixture led to the isolation of the first two, monomer **4** and dimer **5**.

12. Cort, A. D.; Mandolini, L.; Roelens, S. *J. Org. Chem.* **1992**, *57*, 766–768.
13. (a) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95. (b) Cort, A. D.; Ercolani, G.; Iamiceli, A. L.; Mandolini, L.; Mencarelli, P. *J. Am. Chem. Soc.* **1994**, *116*, 7081–7087.
14. (a) CSD version 5.26. (b) Allen, F. H. *Acta Crystallogr., Sect: B* **2002**, *58*, 380–388.
15. (a) Lockhart, J. C.; Thompson, N. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 533–543. (b) Xianming, H.; Kellogg, R. M.; van Bolhuis, F. *J. Chem. Soc., Perkin Trans. 2* **1994**, 707–715.
16. (a) Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049–1052. (b) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, R. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 988–1011.
17. Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999; pp 45–72.
18. Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978; pp 484–485.
19. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect: A* **1968**, *24*, 351–359.
20. Harms, K.; Wocadlo, S. *XCAD-4, Program for Processing CAD4 Diffractometer Data*; University of Marburg: Germany, 1995.
21. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
22. Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997.
23. Spek, A. L. *PLATON98: A Multipurpose Crystallographic Tool*; 120398 Version, University of Utrecht: Utrecht, The Netherlands, 1998.
24. Farrugia, L. J. ORTEP-3 for Windows, *J. Appl. Crystallogr.* **1997**, *30*, 565.
25. Allen, F. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 1, see also pp 31–37.