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Silyl-Substituted Tetrathia[7]helicenes: Synthesis, X-ray Characterization and Reactivity

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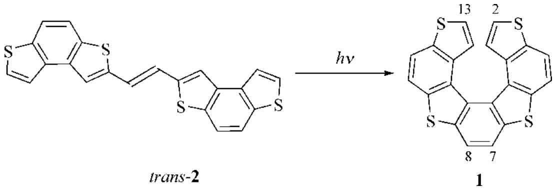
We describe the synthesis of trialkylsilyl-substituted *trans*-1,2-bis(thieno[3,2-*e*]benzothiophene-2-yl)ethenes as suitable soluble precursors for the preparation of the corresponding silylated tetrathia[7]helicenes, which, in turn, can be desilylated or transformed into dihalogen-substituted derivatives through electrophilic substitution of silyl substituents. X-ray structural studies showed that the presence of the two triisopropylsilyl groups on the terminal thiophene rings accounts for the high solubility of the alkene and for the very large dihedral angle in the helicene.

Introduction

Helicenes[1] are very interesting helical-shaped aromatic systems, and they possess great potential for the use in the development of new materials with optoelectronic properties. In fact, theoretical and experimental studies conducted both on carbo- and heterohelicenes pointed out that they possess peculiar characteristics related to their optical and electronic properties.[1h]

Heterohelicenes,[1b,1g,2] in which heteroaromatic units are incorporated into an extended aromatic π system, have received less attention than carbohelicenes, but they can provide some advantages due to the presence of heterocyclic rings, which may allow regioselective functionalization of the aromatic system.[2e,2g,3] Among the various heterohelicenes known, tetrathia[7]helicene (**1**, [7]TH, Scheme 1) is one of the most interesting owing to the alternate presence of thiophene and benzene rings. In this system, the regioselective functionalization of the terminal thiophene rings should, in principle, be easy and versatile, allowing, through the introduction of different functional groups, the tuning of specific properties, such as the nonlinear optical (NLO) response or the entry to new chiral ligands for catalysis.[4,5]



Scheme 1. Photochemical cyclization of alkene **2** to [7]TH **1**.

We have recently undertaken a research project focused on the study of the chemico–physical properties of tetrathia[7]helicene (**1**) and its derivatives, for which theoretical and experimental studies conducted by some of us and other authors, have shown that these compounds have great potential as new chiral molecules for advanced materials in NLO.[6,7] Therefore it is of interest to develop new synthetic methodologies to make an easier and wider access to the starting materials.

The multistep synthesis of tetrathia[7]helicene (**1**) although improved by some of us,[2e] still finds limitation in the oxidative photocyclization of the insoluble *trans* alkene **2** (Scheme 1), which, to be isomerized to the corresponding *cis* isomer and then transformed into helicene **1**, requires a highly diluted reaction mixture, a huge amount of solvent and long reaction times. This is due to the planar structure of *trans* alkene **2**, which, in the solid state, is arranged in close packed planes with high nonbonding interactions. To solve this solubility problem, we tried to prevent the packed arrangement in the solid state of *trans* alkene **2** through the introduction of appropriate substituents.

In this paper we report an approach that consists in the design and synthesis of 1,2-bis(thieno[3,2-*e*]benzothiophene-2-yl)ethenes bearing alkylsilyl substituents,

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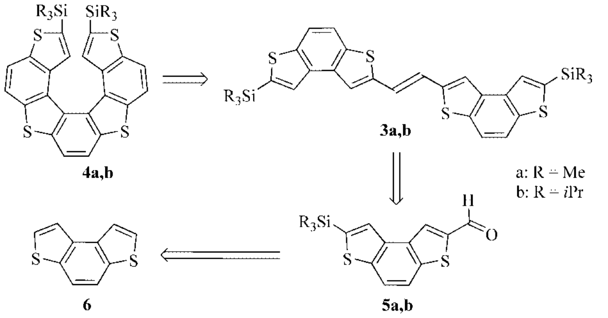
which should increase the solubility of *trans* alkene **2** and, under appropriate conditions, should be replaced with several electrophilic reagents.[8] We now report our results on the synthetic protocols for introducing trialkylsilyl groups on the above-mentioned alkenes and on the study of the reactivity of the new silylated helicenes.

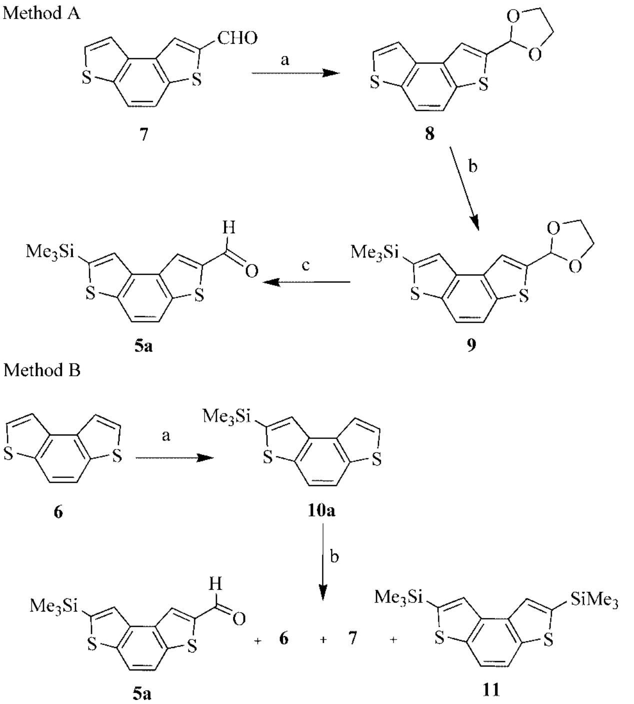
Results and Discussion

For this study, we selected trialkylsilyl-substituted alkenes **3a**,**b** as suitable helicene precursors. The presence of the silyl moieties in the α positions of the terminal thiophene rings should, in fact, lead to 2,13 silyl-substituted helicenes **4a**,**b** (Scheme 2), which can be studied in electrophilic silyl substitution reactions.



Scheme 2. Retrosynthetic pathway for the synthesis of helicenes **4a**,**b**.

In addition, we expected higher solubilities in organic solvents for **3a**,**b** and therefore a more convenient transformation into helicenes **4a**,**b**. Retrosynthetic analysis suggested that compounds **3a**,**b** could be synthesized from the corresponding silylated aldehydes **5a**,**b** by following a procedure set up by us,[2e] which involves McMurry reductive coupling. Compounds **5a**,**b** in turn could be prepared from the parent precursor thieno[3,2-*e*]benzothiophene **6**. We synthesised aldehyde **5a** (R = CH_3) by using two different strategies (Scheme 3 methods A and B). In method A, aldehyde **7**[2e] was protected as an acetal by using PTSA as the catalyst to afford **8**; the trimethylsilyl group was then introduced by treating the anion, selectively generated from **8** with *n*BuLi at –78 °C, with trimethylsilyl chloride. Quantitative deprotection of silylated acetal **9** to give **5a** was then achieved by treatment with $FeCl_3·6H_2O$ at room temperature in dry CH_2Cl_2.[9] In this way, compound **5a** was obtained in 61% overall yield. In method B we started from **6**, and we inverted the order in which the functional groups were introduced by first introducing the silyl and then the formyl group. In this way we reduced the number of steps and no protection/deprotection strategy was necessary. The trimethylsilyl group was introduced upon selective deprotonation at the 2-position of **6** with *n*BuLi at –78 °C, followed by the addition of trimethylsilyl chloride. The formylation of compound **10a** to give **5a** required some optimization studies, because in addition to compound **5a**, we observed the formation of variable amounts of byproducts, **6**, **7** and **11** (Scheme 3, Table 1).



Scheme 3. Method A: (a) ethylene glycol, PTSA, toluene, reflux, 96%; (b) *n*BuLi, TMSCl, –78 °C, dry THF, 64%; (c) $FeCl_3·6H_2O$, dry CH_2Cl_2, room temp., 99%; overall yield 61%. Method B: (a) *n*BuLi, TMSCl, dry THF, –78 °C, 87%; (b) *t*BuLi, dry DMF, dry THF, –78 °C, 89%; overall yield 77%.

Table 1. Ratio of compounds obtained in the formylation of **10a**.

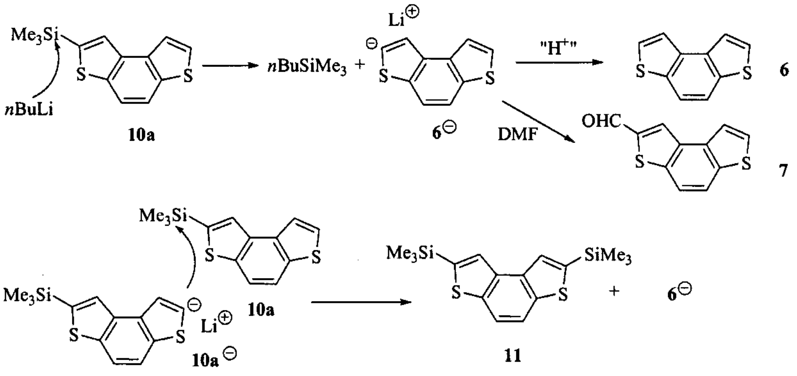
Entry	RLi	**5a** [%]	**10a** [%]	**6** [%]	**7** [%]	**11** [%]
1[a]	*n*BuLi	30	24	20	20	9
2[b]	*n*BuLi	34	26	26	18	–
3[a]	*t*BuLi	–	49	20	–	25
4[b]	*t*BuLi	89	–	2	3	6

[a] After the addition of the alkyllithium, the anion was warmed to room temp. for 20 min. [b] After the addition of the alkyllithium, the mixture was stirred at –78 °C for 3 h.

In particular, we found that the success of the formylation of **10a** was strongly dependent on the type of base (*n*BuLi or *t*BuLi) as well as on the temperature of the reaction. As reported in Table 1, the best conditions to isolate compound **5a** in high yields (89%) were the use of *t*BuLi as a base at –78 °C (Table 1, Entry 4). By using method B, the overall yield for the synthesis of compound **5a** was 77%.

In Scheme 4, we propose a mechanism for the formation of byproducts **6**, **7** and **11**.

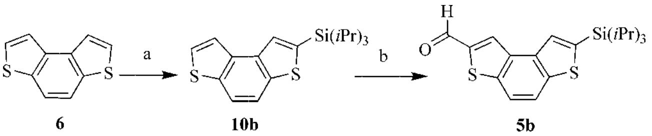
The formation of compounds **6** and **7** can be rationalized by taking into account the nucleophilicity of *n*BuLi, which can displaces the trimethylsilyl group of **10a**, thus generating anion **6**$^-$, which, in turn, can either be quenched to give **6** or can react with DMF to give **7**. In analogy, the nucleophilicity of anion **10a**$^-$ is responsible for the displacement of the trimethylsilyl group from **10a**, with the formation of bis(trimethylsilyl)thieno[3,2-*e*]benzothiophene **11** and anion **6**$^-$, which can be quenched to give **6** or **7**. The proposed mechanism supports the best experimental conditions



Scheme 4. Proposed mechanism for the formation of byproducts **6**, **7** and **11**.

found for the formylation of **10a**; specifically, the use of *t*BuLi as a nonnucleophilic base at –78 °C for the generation of the anion (Table 1, Entry 4).

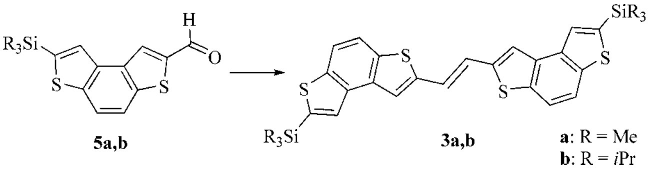
The synthesis of compound **5b** (Scheme 5) was accomplished by using method B (Scheme 3); namely, by silylation of the anion generated from **6** and formylation of the anion derived from **10b**.



Scheme 5. Reaction conditions: (a) *n*BuLi, (iPr)$_3$SiCl (TIPSCl), dry THF, 0 °C, 72%; (b) *n*BuLi, dry DMF, dry THF, –78 °C, 98%.

However, as in the trimethylsilyl case, some work for the optimization was necessary. In particular, the silylation of the anion of **6** to give **10b** was performed at 0 °C instead of –78 °C at which temperature the bulky (iPr)$_3$SiCl was not reactive enough. Quite interestingly, we found that this bulky, and more stable group, allowed the use of *n*BuLi for the subsequent formylation reaction and, in this case, we did not observe any desilylation, as was found in the synthesis of **5a**.

Aldehydes **5a**,**b**, previously unreported in the literature, were submitted to standard McMurry coupling conditions to give the corresponding alkenes **3a**,**b** in 77 and 99% yields, respectively (Scheme 6).[2e]



Scheme 6. McMurry coupling for the synthesis of alkenes **3a**,**b**. Reaction conditions: TiCl$_4$, Zn, pyridine, dry THF.

As expected, **3a**,**b** were isolated as the *E* isomers, but thanks to the presence of the trialkylsilyl substituents, they were very soluble in organic solvents and could be recovered and purified by standard techniques. Moreover, contrary to the case of the previously reported alkene **2**, we could perform complete spectroscopic characterization of these compounds in terms of ^{1}H NMR, ^{13}C NMR and UV/Vis spectroscopy.[10]

Also, to better understand the reason of its high solubility, we submitted a single crystal of compound **3b** to X-ray analysis. An ORTEP view of compound **3b** is shown in Figure 1. The most important bond lengths and angles are collected in the caption. The molecule presents with crystallographically imposed *C*i symmetry, and the inversion centre is located at the midpoint of the C7–C7′ double bond [1.347(4) Å]. It is noteworthy to mention that in the benzene ring the C3–C4 bond length [1.428(2) Å] is significantly longer than the C9–C10 one [1.372(3) Å]. The molecule, except for the triisopropylsilyl groups, is planar, and in the

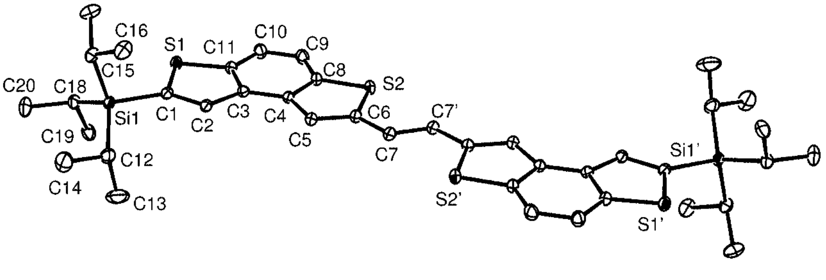


Figure 1. ORTEP view of compound **3b** with the atomic numbering scheme. Ellipsoids are drawn at their 30% level. Selected bond lengths [Å] and angles [°]: C7–C7′ 1.347(4), C3–C4 1.428(2), C4–C5 1.429(2), C9–C10 1.372(3); C7′–C7–C6 125.2(2).

crystal packing, the molecules lie on planes at a distance of 3.488(2) Å (see Figure 2), which is not suggestive of any remarkable intermolecular interaction. This long interplanar distance, which is due to the presence of the bulky triisopropylsilyl groups, could justify the greater solubility of **3b** with respect to that of the unsubstituted compound **2**.

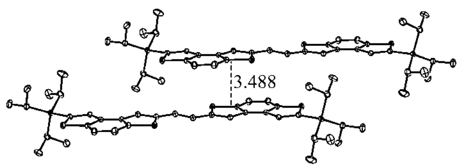
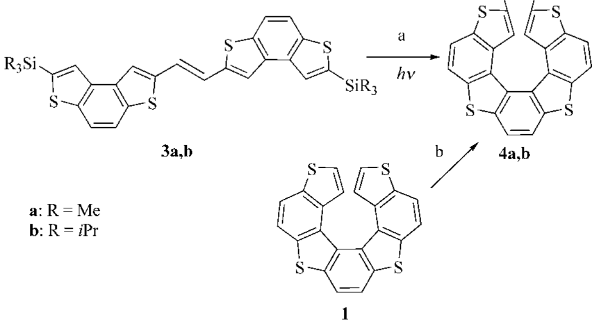


Figure 2. A perspective drawing of stacked molecules of **3b**.

The improved solubility of compounds **3a**,**b** allowed their easy photocyclization to the corresponding 2,13-difunctionalized [7]THs, **4a**,**b**, by using an unfiltered medium pressure, 150 W Hg lamp in only 5 h at 40 °C for **3a** and 6 h at 50 °C for **3b** (Scheme 7) instead of the 24 h required for the photocyclization of **2** to [7]TH **1**.[2e]



Scheme 7. Reaction conditions: (a) I_2, C_6H_6, yield **4a** 69%; yield **4b** 50%; (b) *n*BuLi, TMSCl, dry THF, –78 °C, yield **4a** >99%.

The two enantiomers of helicene **4a** were separated by HPLC by using a Chiralcel OD analytical column {$[\alpha]_D^{20}$ = ±870 (*c* = 0.016, $CHCl_3$)}. Figure 3 shows the CD spectra of the two enantiomers; the first enantiomer (Figure 3, 1a) has an $[\alpha]_D^{20}$ = +870 (*c* = 0.016, in $CHCl_3$),[11] and the second (Figure 3, 1b) has an $[\alpha]_D^{20}$ = –860 (*c* = 0.016, in $CHCl_3$). The CD spectrum of (+)-**4a** (Figure 3, 1a) between 250 and 350 nm and near 400 nm was similar to the CD spectra of the dextrorotatory enantiomers of the two thiahelicenes **12**[12a] ($[\alpha]_D^{20}$ = 2050) and **13**[12b] {$[\alpha]_D^{20}$ = 2720 (*c* = 0.0557)} (Figure 4), which are known to have (*P*)-, or right-handed, helicity. Accordingly, it is likely that (+)-**4a** also has (*P*)-helicity and (–)-**4a** has (*M*)-helicity.[13]

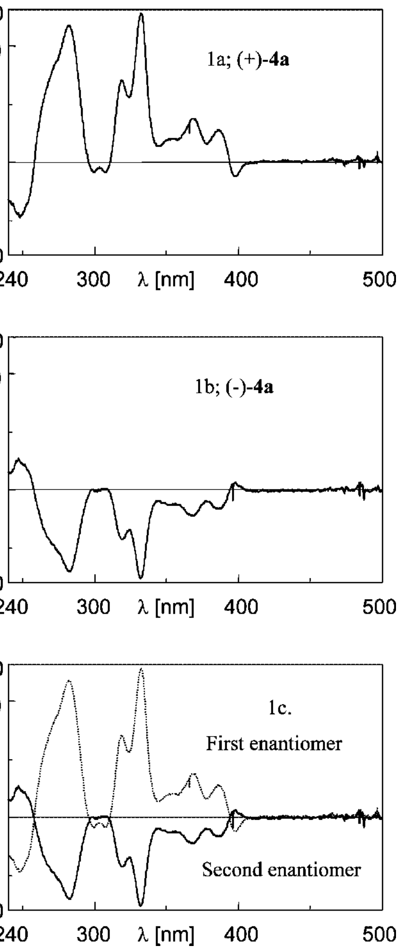
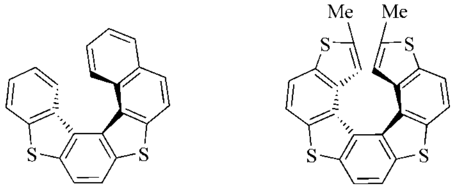


Figure 3. CD spectra of enantiomers of helicene **4a**.



(*P*)-**12** (*P*)-**13**

Figure 4. Configuration of (*P*)-heterohelicenes.

The ^1H NMR spectrum of helicene **4b** showed a multiplicity of the signals related to the diastereotopic methyl groups of the (*i*Pr)$_3$Si moiety, as two doublets at δ = 0.76 ppm (*J* = 6.8 Hz). Variable temperature ^1H NMR spectroscopic experiments recorded at 213 K showed no effect on the multiplicity of the signals, whereas by increasing the temperature up to 383 K, the two doublets showed better resolution (see NMR spectra in Supporting Information).

The relatively low yield in the cyclization step to give **4b** (50%, Scheme 7), and the formation of a significant amount of byproducts, among which aldehyde **5b** was identified, suggested that the bulky (*i*Pr)$_3$Si groups could cause a large distortion in the dihedral angle of helicene **4b**. This was confirmed by the X-ray diffraction analysis of a single crystal of **4b**, which shows a very large dihedral angle of 59.1(1)°.[14]

The crystal structure of compound **4b** was determined to elucidate its molecular geometry and crystal packing. The obtained structural parameters were compared with those of the tetrathia[7]helicene, **1** (see Table 2).[15] A view of the molecule is shown in Figure 5, together with the atomic labelling scheme. The C–C outer core bonds of **4b** are shorter and the C–C inner core bonds are longer than the expected 1.39 Å, as already observed in the unsubstituted helicene and in several carbo- and heterohelicenes[15] as well as in its precursor **3b**. All seven fused rings are deviated from planarity as evidenced in Table 3 and there is an increase in the deformation passing from the external A and A′ rings to the central D ring (see Scheme 8 for nomenclature of fused rings).

Table 2. Selected bond lengths [Å] for compound **4b** compared with those of the racemate of **1**.

	4b	**1**
C12–C13	1.367(5)	1.376(7)
C16–C17	1.359(7)	1.356(7)
C20–C21	1.343(7)	1.376(7)
C3–C4	1.417(5)	1.426(5)
C5–C6	1.419(5)	1.443(6)
C7–C8	1.434(4)	1.426(5)

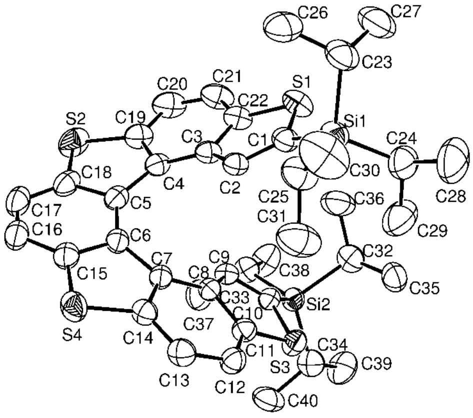
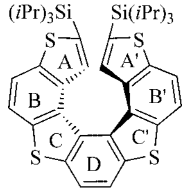


Figure 5. View of the molecular structure of **4b** with the atomic numbering scheme. Ellipsoids are drawn at their 30% level.

Table 3. Mean deviations [Å] of the ring atoms from the least-squares planes of the rings for compound **4b** compared with those of the racemate of **1**.

	4b	**1**
A	0.015(3)	0.013(3)
A′	0.013(4)	0.013(3)
B	0.034(4)	0.030(3)
B′	0.036(4)	0.030(3)
C	0.040(4)	0.035(3)
C′	0.036(4)	0.035(3)
D	0.058(5)	0.055(3)



Scheme 8. Nomenclature of fused rings for helicene **4b**.

The dihedral angles between adjacent rings range from 10.5(1) to 12.5(1)°, whereas the A–A′ dihedral angle is 59.1(1)°, which is notably larger than that observed in unsubstituted helicene **1** (see Table 4). As regards the packing, **4b** crystallizes together with cyclohexane molecules of solvation in the ratio 2:1. The solvent is located around the inversion centre in the voids left by the packed molecules. The crystal symmetry ($P\bar{1}$) allows each couple of molecules to be stacked around the inversion centre. The D and C rings of two centrosymmetric molecules are almost parallel [dihedral angle 10.5(1)°] and the distance between their centroids is 3.820(1) Å, which suggests that there are no intermolecular interactions (see Figures 6 and 7).

Table 4. Selected dihedral angles [°] between the least-squares planes of the rings for compound **4b** compared with those of the racemate of **1**.

	4b	**1**
A–B	10.7(1)	8.8(2)
A′–B′	11.7(1)	8.8(2)
B–C	11.1(1)	8.6(1)
B′–C′	12.5(1)	8.6(1)
C–D	11.9(1)	11.3(1)
C′–D	10.5(1)	11.3(1)
A-A′	59.1(1)	48.6(1)

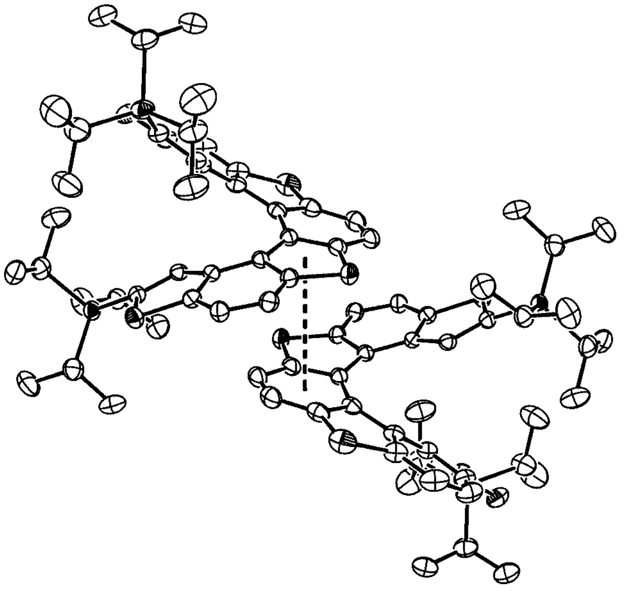


Figure 6. A perspective drawing of the stacked molecules of **4b**.

Functionalization of tetrathia[7]helicenes was an important goal of our research in that it could allow the obtainment of a series of new compounds on which to study their physical properties[2g] in view of the application as new materials with optoelectronic properties. Substituted thiahelicenes can, in principle, be synthesized starting from functionalized precursors,[16] but this strategy represents a

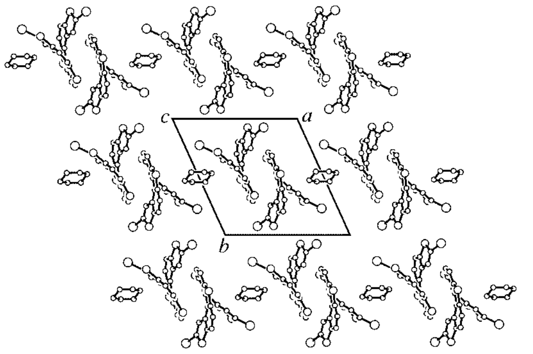
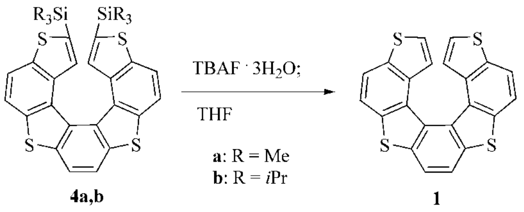


Figure 7. Crystal packing of **4b** viewed along the *c* axis.

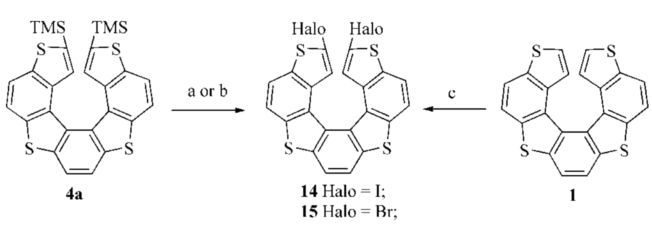
limitation to the variety of functional groups that can be used that, for example, have to be stable to photochemical conditions. The direct and possibly selective functionalization of helicenes seems of most general usefulness. We previously reported the monoformylation of parent [7]TH **1**[2e] in the 2-position to give the 2-formyl-[7]TH. Here we report the transformation of [7]TH **4a**,**b** into new halogen derivatives **14** and **15** as well as a desilylation reaction to give **1**.

It is well known that alkylsilyl groups on aromatic systems can be either eliminated or substituted with electrophilic reagents.[8] The treatment of **4a**,**b** with TBAF provided [7]TH **1**, in quantitative yield, but whereas **4a** underwent fast desilylation at room temperature, **4b** needed to be heated at reflux according to the reduced reactivity of the TIPS group towards fluoride ion (Scheme 9).[17]



Scheme 9. Cleavage of the trialkylsilyl groups from helicenes **4a**,**b**. R = Me; yield ≥98%; R = *i*Pr; yield ≥98%.

The treatment of **4a** with bromine[18] or ICl[19] (Scheme 10) furnished 2,13-dihalo[7]TH **14** and **15** in high yield and in a facile manner. In fact, the corresponding halogenated products could be recovered by filtration from the reaction mixture and no chromatographic purification was necessary. It is worthwhile to note that the direct electrophilic bromination of unsubstituted helicene **1** with bromine led to an intractable mixture of products. However, the iodination of **1** through the formation of the dianion and subsequent reaction with iodine also cleanly gave the corresponding diiodo helicene **14**.



Scheme 10. Regioselective electrophilic substitution of the TMS moieties of helicene **4a**. Reaction conditions: (a) ICl 0.1 M, dry CH_2Cl_2, yield of **14** 66%; (b) Br_2, dry CH_2Cl_2, yield of **15** 79%; (c) *n*BuLi, I_2, dry THF, –78 °C, yield of **14** 76%.

Conclusions

In this paper we described the synthesis of functionalized *trans*-1,2-bisthieno[3,2-*e*]benzothiophenylalkenes **3a**,**b** as well as new substituted tetrathia[7]helicenes **4a**,**b**, **14** and **15**. We showed that the presence of silylated substituents on the thiophene rings of alkenes **3** renders them very soluble in organic solvents, which allows their easy spectroscopic characterization and facilitates their photochemical cyclization to the corresponding helicenes. X-ray analysis of alkene **3b** showed that, in the solid state, the presence of the bulky TIPS groups strongly influences the molecular packing. Analogously, X-ray analysis of diTIPS-helicene **4b** showed a large dihedral angle between the two terminal thiophene rings of 59.1°, which allows the possibility of modulating the helix pitch by inserting appropriate substituents on the terminal thiophene rings. Helicene **4b** can be easily separated into its individual enantiomers by chiral HPLC techniques. The NLO response of silylhelicenes, even in the enantiomeric pure form, is currently under investigation.

In addition to acting as solubilizing groups, trialkylsilyl substituents of helicenes **4a**,**b** can be easily replaced with bromine and iodine. The new halogen-substituted helicenes are interesting molecules, and they are susceptible to further transformations, such as metal-mediated C–C couplings. We are currently studying these reactions with the aim to achieve more extended conjugated systems. In this way, it will be possible to greatly increase the number of new derivatives that can be designed and synthesized as potentially useful new functional molecules for nonlinear optics.

Experimental Section

General: Reagents obtained from commercial sources were used without further purification. Before use, THF was dried by distillation over sodium wires/benzophenone; CH_2Cl_2 was dried by distillation over P_2O_5; butyllithium solutions were titrated. Trimethylsilyl chloride (TMSCl) and triisopropylsilyl chloride (TIPSCl) were distilled prior to use over CaH_2. To monitor the progress of the reactions, thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 precoated plates. Flash chromatography was performed with Merck silica gel 60, 230–400 mesh. Melting points were determined with a Büchi 510 apparatus and are uncorrected or with a Mettler Toledo 820 DSC. The IR spectra were recorded with a Perkin–Elmer FT-IR 1725X. High-resolution mass spectra were recorded with a Vg Analytical 7070 EQ. Agilent 1100 series HPLC, equipped with DAD analyzer, was used for the resolution of compound **4a**; a Chiralcel OD chiral column was purchased from Daicel Chemical Industries. ^1H and ^{13}C NMR were recorded with Bruker AC200, Bruker AC300 or Bruker AMX-300 spectrometers. Unless otherwise stated, all of the operations were performed under a nitrogen atmosphere in flame-dried glassware.

Thieno[3,2-*e*]benzothiophen-2-carbaldehyde Ethylene Acetal (8): A solution of **7** (833 mg, 3.82 mmol), ethylene glycol (0.54 mL, 9.45 mmol) and *p*TsOH monohydrate (28.4 mg) in toluene (16 mL) was stirred and heated at reflux in a Dean Stark apparatus for 9 h; the progress of the reaction was monitored by TLC (light petroleum/AcOEt, 1:1). The solution was treated with a saturated aqueous sodium carbonate solution (25 mL). The organic phase was washed twice with distilled water and dried with Na_2SO_4, and the solvent was removed under reduced pressure to afford, without further purification, 965.2 mg (3.68 mmol, 96.3%) of compound **8** as a yellow-orange solid. M.p. 103–104 °C (*i*Pr_2O/acetone, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.14 (m, 4 H, CH_2), 6.29 (s, 1 H, CH-Ar), 7.55 (d, J = 5.4 Hz, 1 H), 7.67 (d, J = 5.4 Hz, 1 H), 7.76 (d, J = 8.6 Hz, 1 H), 7.77 (s, 1 H), 7.82 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.4 (CH_2), 100.5 (CH-Ar), 118.7, 119.2, 120.8, 121.7, 126.6 (CHar), 134.1, 134.8, 136.4, 136.7, 142.7 (Cq) ppm. IR (nujol): $\tilde{\nu}$ = 3099 (CH st), 1527 (γ CH), 1214, 1142, 1067 cm^{-1}. MS (EI): m/z (%) = 262 (35) $[M]^+$, 218 (100) $[M - C_2H_4O]^+$, 190 (80) $[M - 72]^+$, 145 (60), 91 (65). HRMS: calcd. for $C_{13}H_{10}O_2S_2$ 262.0122; found: 262.0092.

7-Trimethylsilylthieno[3,2-*e*]benzothiophene-2-carbaldehyde Ethylene Acetal (9): A solution of *n*BuLi (1.42 M in hexane, 1.56 mL, 2.2 mmol, 1.1 equiv.) was added dropwise whilst stirring to a solution of **8** (516.2 mg, 1.98 mmol) in dry THF (20.5 mL) at –78 °C. The solution was stirred for 5 min at –78 °C and for 15 min at room temp. The resulting light-blue suspension was cooled to –78 °C, treated with TMSCl (0.53 mL, 7.36 mmol) and the progress of the reaction was monitored by TLC (light petroleum/AcOEt, 9:1). After 40 min at –78 °C, the solution was warmed to room temp. (the colour of the solution changed to pale yellow) and quenched with water (21.5 mL). THF was removed under reduced pressure, the crude material was taken up with CH_2Cl_2 (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 8 mL). The organic phases were dried with Na_2SO_4, the solvent was removed under reduced pressure and the crude material was purified by flash chromatography on silica (light petroleum/ethyl acetate, 9:1) to give title compound **9** as a yellow-orange solid (418.0 mg, 63.6%), **5a** (47.5 mg, 8.4%) and unreacted **8** (6%). M.p. 98–100 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.40 (s, 9 H, CH_3Si), 4.14 (m, 4 H, -CH_2-O), 6.29 (s, 1 H, CH-Ar), 7.72 (d, J = 8.6 Hz, 1 H), 7.78 (s, 1 H), 7.80 (s, 1 H), 7.81 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2 (CH$_3$Si), 65.4 (-CH$_2$-O), 100.6 (CH-Ar), 118.6, 119.1, 120.9, 128.4 (CHar), 134.0, 136.2, 136.6, 140.6, 142.6 (Cq) ppm. IR (nujol): $\tilde{\nu}$ = 3051 (CH st), 1245 ($SiCH_3$), 1140, 1066 cm^{-1}. MS (EI): m/z (%) = 334 (8) $[M]^+$, 319 (5) $[M - CH_3]^+$, 290 (83) $[M - C_2H_4O]^+$, 275 (100) $[M - 59]^+$, 262 (6) $[M - 72]^+$. HRMS: calcd. for $C_{16}H_{18}O_2S_2Si$ 334.0518; found 334.0497.

Synthesis of 2-Formyl-7-trimethylsilylthieno[3,2-*e*]benzothiophene (5a)

Method A: To a solution of compound **9** (376.4 mg, 1.125 mmol) in dry CH_2Cl_2 (31 mL) at room temp. was added $FeCl_3 \cdot 6H_2O$ (1.0442 g, 3.85 mmol, 3.42 equiv.). The resulting suspension, monitored by TLC (light petroleum/AcOEt, 9:1), was stirred for 20 min and quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was washed with brine and dried with Na_2SO_4, and the solvent was removed under reduced pressure to afford, without further purification, 323.8 mg (1.115 mmol, ≥99%) of compound **5a** as a yellow solid.

Method B: A solution of *t*BuLi (1.5 M in pentane, 2.55 mL, 3.82 mmol, 1.67 equiv.) was added dropwise whilst stirring and under an argon atmosphere to a solution of **10a** (599 mg, 2.282 mmol) in dry THF (23 mL) at –78 °C. The solution was stirred for 3 h at –78 °C. The resulting dark-green solution was treated with dry DMF (0.36 mL, 4.66 mmol), and the progress of the reaction was monitored by TLC (hexane/AcOEt, 9.5:0.5). After 2 h at –78 °C, the solution was quenched with a saturated aqueous solution of NH_4Cl (3 mL). THF was removed under reduced pressure, the crude material was taken up with CH_2Cl_2 (10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 7 mL). The organic phase was dried with Na_2SO_4, the solvent was removed under reduced pressure and the crude material was purified by flash chromatography on silica (hexane/AcOEt, 9.5:0.5) to give compound **5a** as yellow solid (589.4 mg, 88.9%).

5a: M.p. 133–134 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.43 (s, 9 H, CH_3Si), 7.77 (d, J = 8.7 Hz, 1 H), 7.87 (s, 1 H), 7.97 (d, J = 8.7 Hz, 1 H), 8.42 (s, 1 H), 10.15 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2 (CH$_3$Si), 118.8, 122.6, 128.1, 131.8 (CHar), 133.6, 137.3, 140.4, 141.2, 142.9, 144.9 (Cq), 184.2 (CHO) ppm. IR (nujol): $\tilde{\nu}$ = 3060 (CH st), 1667 (C=O), 1246 ($SiCH_3$) cm^{-1}. MS (EI): m/z (%) = 290 (83) $[M]^+$, 275 (100) $[M - CH_3]^+$. HRMS: calcd. for $C_{14}H_{14}O_2S_2Si$ 290.0255; found 290.0245.

2-Trimethylsilylthieno[3,2-*e*]benzothiophene (10a): A solution of *n*BuLi (1.6 M in hexane, 0.64 mL, 1.024 mmol, 1.1 equiv.) was added dropwise whilst stirring to a solution of **6** (174.6 mg, 0.918 mmol) in dry THF (9.5 mL) at –78 °C. The solution was stirred for 5 min at –78 °C and for 15 min at room temp. The resulting yellow solution was cooled to –78 °C and treated with TMSCl (0.24 mL, 1.85 mmol), and the progress of the reaction was monitored by TLC (light petroleum/AcOEt, 9.5:0.5). After 30 min at –78 °C, the solution was warmed to room temp. (the colour of the solution changed to pale yellow), and quenched with water (5 mL). THF was removed under reduced pressure, the crude material was taken up with CH_2Cl_2 (10 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried with Na_2SO_4, the solvent was removed under reduced pressure and the crude material was purified by flash chromatography on silica (hexane) to give compound **10a** as white solid (209.6 mg, 87%). M.p. 69–71 °C (pentane). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.42 (s, 9 H, CH_3Si), 7.55 (d, J = 5.4 Hz, 1 H), 7.74 (d, J = 5.4 Hz, 1 H), 7.78 (d, J = 8.7 Hz, 1 H), 7.82 (s, 1 H), 7.83 (d, J = 8.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2 (CH$_3$Si), 118.5, 118.6, 121.9, 126.2, 128.5 (CHar), 134.4, 136.0, 136.2, 140.5, 142.3 (Cq) ppm. MS (EI): m/z (%) = 262 (80) $[M]^+$, 247 (100) $[M - CH_3]^+$, 231, 217, 190. UV/Vis (CH_2Cl_2): λ (ε) = 344 (19400), 284 (7860), 266 (9000) nm. HRMS: calcd. for $C_{13}H_{14}S_2Si$ 262.0306; found 262.0335.

2-Triisopropylsilylthieno[3,2-*e*]benzothiophene (10b): A solution of *n*BuLi (1.48 M in hexane, 4.5 mL, 6.66 mmol, 1.05 equiv.) was added dropwise whilst stirring to a solution of **6** (1.207 g, 6.343 mmol) in dry THF (55 mL) at 0 °C. The solution was stirred for 5 min at 0 °C and for 20 min at room temp. The resulting yellow solution was cooled to 0 °C and treated with TIPSCl (2.24 mL, 10.47 mmol, 1.65 equiv.), and the progress of the reaction was monitored by TLC (light petroleum). After 1.5 h at 0 °C, the solution was warmed to room temp. and quenched with distilled water (20 mL). THF was removed under reduced pressure, the crude material was taken up with CH_2Cl_2 (20 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried with Na_2SO_4, the solvent was removed under reduced pressure and the oily material was purified by flash chromatography (light petroleum/AcOEt, 9.5:0.5) to afford 1.627 g (74%) of **10b**. M.p. 60 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.17 (d, 18 H, CH_3CH), 1.46 (m, 3 H, CHSi), 7.56 (d, J = 5.4 Hz, 1 H), 7.76 (d,

J = 5.4 Hz, 1 H), 7.78 (d, J = 8.5 Hz, 1 H), 7.85 (s, 1 H), 7.83 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 12.1 (*C*HSi), 19.0 (*C*H$_3$CH), 118.4, 118.5, 122.1, 126.4, 130.1 (CHar), 134.4, 136.0, 136.2, 136.9, 140.7 (Cq) ppm. MS (EI): *m*/*z* (%) = 346 (66) [M]$^+$, 303 (100) [M – C$_3$H$_7$]$^+$, 275, 261, 247, 190. HRMS: calcd. for $C_{19}H_{26}S_2Si$ 346.1245; found 346.1212.

2-Formyl-7-triisopropylsilylthieno[3,2-*e*]benzothiophene (5b): A solution of *n*BuLi (1.39 M in hexane, 3.3 mL, 4.58 mmol, 1.1 equiv.) was added dropwise whilst stirring and under a nitrogen atmosphere to a solution of **10b** (1.42 g, 4.09 mmol) in dry THF (50 mL) at –78 °C. The solution was stirred for 1 h 45 min at –78 °C. The solution was treated with dry DMF (0.7 mL, 9.08 mmol), and the progress of the reaction was monitored by TLC (light petroleum/AcOEt, 9.5:0.5). After 30 min at –78 °C, the solution was quenched with a saturated aqueous solution of NH$_4$Cl (18 mL). THF was removed under reduced pressure, the crude material was taken up with CH$_2$Cl$_2$ (40 mL) and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 11 mL). The organic phase was dried with Na$_2$SO$_4$, the solvent was removed under reduced pressure and the crude material was purified by flash chromatography on silica (light petroleum/AcOEt, 9.5:0.5) to afford 1.61 g of compound **5b** as pale-rose solid in 98% yield. M.p. 132.5–133.2 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.17 (d, J = 7.2 Hz, 18 H, C*H*$_3$), 1.46 (m, 3 H, C*H*CH$_3$), 7.80 (d, J = 8.7 Hz, 1 H), 7.89 (s, 1 H), 7.99 (d, J = 8.7 Hz, 1 H), 8.48 (s, 1 H), 10.17 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.8 (*C*HCH$_3$), 18.6 (*C*H$_3$), 118.6, 122.5, 129.6, 131.8 (CHarom), 133.5, 137.1, 139.4, 140.4, 141.3, 142.9 (Cq), 184.1 (CHO) ppm. IR (nujol): $\tilde{\nu}$ = 2998 (CH st), 1666 (C=O), 883.2 (Si–C) cm^{-1}. HRMS: calcd. for $C_{20}H_{26}OS_2Si$ 374.1194; found 374.1116.

1,2-Bis(7-trimethylsilylthieno[3,2-*e*]benzothiophen-2yl)ethene (3a): Pure TiCl$_4$ (0.135 mL, 1.23 mmol, 1.24 equiv.) was carefully added to dry THF (8.2 mL) at 0 °C to afford a bright-yellow mixture as a result of the formation of the TiCl$_4$·2THF complex. After stirring the mixture at 0 °C for 5 min, powdered zinc (154.0 mg, 2.36 mmol, 2.37 equiv.) was added, and the mixture was heated at reflux for 1 h 35 min. (the colour changed from yellow to dark blue), after which pyridine (0.085 mL, 1.05 mmol, 1.06 equiv.) was added, and the mixture was heated at reflux for another 30 min. After cooling the mixture to room temp. **5a** (289.1 mg, 0.995 mmol) was added, and the reaction mixture was heated at reflux for another 1 h 15 min. The progress of the reaction was monitored by following the disappearance of **5a** by TLC (light petroleum/CH$_2$Cl$_2$, 7:3). The mixture was pored into ice–water (50 mL) and left overnight. The mixture was then decanted, and the resulting solid was collected by filtration and washed with water. The resulting brown solid was than extracted in soxhlet with toluene and then washed with hexane to afford 209.7 mg of compound **3a** as a yellow solid (77%). M.p. 332 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.42 (s, 18 H, C*H*$_3$Si), 7.31 (s, 2 H), 7.68 (d, J = 8.7 Hz, 2 H), 7.71 (s, 2 H), 7.78 (s, 2 H), 7.80 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = –0.2 (*C*H$_3$Si), 118.3, 119.2, 122.0, 124.0, 128.5 (CHar), 135.0, 135.6, 135.8, 140.9, 142.4, 143.0 (Cq) ppm. MS (EI): *m*/*z* (%) = 548 (100) [M]$^+$, 73 (43) [Si(CH$_3$)$_3$]$^+$. UV/Vis (CH$_2$Cl$_2$): λ = 424, 399, 378, 360 nm. HRMS: calcd. for $C_{28}H_{28}S_4Si_2$ 548.06124; found 548.06140.

1,2-Bis[7-(triisopropylsilyl)thieno[3,2-*e*]benzothiophene-2yl]ethene (3b): Pure TiCl$_4$ (0.48 mL, 4.38 mmol, 1.28 equiv.) was added carefully in dry THF (29 mL) at 0 °C (the colour of the solution changed to bright yellow). After stirring the mixture at 0 °C for 5 min, powdered zinc (537 mg, 8.225 mmol, 2.40 equiv.) was added, and the mixture was heated at reflux for 1 h 35 min. (the colour changed from yellow to dark blue), after which pyridine (0.30 mL, 3.73 mmol, 1.09 equiv.) was added. The mixture was heated at reflux for another 30 min. After cooling the mixture to room temp., **5b** (1.28 g, 3.43 mmol) was added, and the reaction mixture was heated at reflux for another 1 h 30 min. The progress of the reaction was monitored by TLC (light petroleum/CH$_2$Cl$_2$, 8:2). The mixture was pored into ice–water (100 mL), THF was removed under reduced pressure and the crude material was taken up with CH$_2$Cl$_2$ (400 mL). After filtration and phase separation, the aqueous phase was extracted with CH$_2$Cl$_2$ (100 mL). The organic phase was dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure to afford **3b** as a yellow solid (1.22 g, 99%). The product was recrystallized from 1,2-dichloroethane for analytical proposes. M.p. 289.7–291.5 °C (1,2-dichloroethane). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.19 (d, J = 7.41 Hz, 36 H, C*H*$_3$CH), 1.44 (m, 6 H, C*H*Si), 7.34 (s, 2 H), 7.50 (d, J = 8.7 Hz, 2 H), 7.75 (s, 2 H), 7.82 (d, J = 8.7 Hz, 2 H), 7.84 (s, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.9 (*C*HSi), 18.7 (*C*H$_3$CH), 118.2, 119.1, 122.0, 124.0, 128.5 (CHar), 135.0, 135.8, 136.0, 137.5, 141.0, 142.4 (Cq) ppm. MS (EI): *m*/*z* (%) = 716 (100), 673 (10), 631 (10). UV/Vis (CH$_2$Cl$_2$): λ (ε) = 424 (47200), 400 (57460), 380 (39350), 360 (26660), 320 (17600), 304, (18880), 238 (59800) nm. HRMS: calcd. for $C_{40}H_{52}S_4Si_2$ 716.24904; found 716.2467.

Synthesis of 2,13-Bis(trimethylsilyl)tetrathia[7]helicene (4a)

Method A: Compound **3a** (161.4 mg, 0.294 mmol) and iodine (8.2 mg, 0.032 mmol, 0.11 equiv.) were dissolved in benzene (250 mL) at room temp. The stirred solution was irradiated with a 150-Watt unfiltered Hg medium-pressure lamp, equipped with a quartz jacket. During the first 2.5 h, the solution temperature was maintained at 40 °C, after which it was cooled to 30 °C, and the solution was irradiated for another 2.5 h. The course of the reaction was followed by TLC (light petroleum/CH$_2$Cl$_2$, 8:2). The reaction mixture was evaporated at reduced pressure, and the residue was dissolved in dichloromethane (50 mL) and then extracted with a saturated aqueous solution of Na$_2$SO$_3$ (10 mL); the aqueous phases were extracted with CH$_2$Cl$_2$ (3 × 10 mL). The organic phases were collected and dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure to afford 203.5 mg of a solid residue, which was purified by flash chromatography (light petroleum/CH$_2$Cl$_2$, 8:2) to give 110.2 mg of compound **4a** as a pale-yellow solid in 68.5% yield.

Method B: A solution of *n*BuLi (1.6 M in hexane, 0.31 mL, 0.491 mmol, 2.2 equiv.) was added dropwise whilst stirring to a solution of **1** (89.9 mg, 0.223 mmol) in dry THF (7 mL) at –78 °C. The solution was stirred for 40 min at –78 °C (and the colour turned brown) and treated with TMSCl (0.114 mL, 0.893 mmol, 4 equiv.); the progress of the reaction was monitored by TLC (light petroleum/CH$_2$Cl$_2$, 7:3), and the solution turned yellow. After 50 min at –78 °C, the solution was warmed to room temp. and quenched with water (7 mL). THF was removed under reduced pressure, the crude material was taken up with CH$_2$Cl$_2$ (10 mL) and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 3 mL). The organic phase was washed with water and dried with Na$_2$SO$_4$, and the solvent was removed under reduced pressure to afford, without further purification, compound **4a** in quantitative yield.

Compound 4a: M.p. 318.5 °C (toluene/light petroleum, 1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ = –0.74 (s, 18 H, C*H*$_3$Si), 6.38 (s, 2 H), 7.94 (d, J = 8.3 Hz, 2 H), 8.02 (s, 2 H), 8.03 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = –0.6 (*C*H$_3$Si), 118.6, 120.3, 120.9, 132.4 (CHar), 130.3, 130.9, 136.5, 137.4, 137.7, 140.2, 141.0 (Cq) ppm. MS (EI): *m*/*z* (%) = 546 (100) [M]$^+$, 531 [M – CH$_3$]$^+$, 400 [M – 2 (CH$_3$)$_3$Si]$^+$, 73 (43) [Si(CH$_3$)$_3$]$^+$. UV/Vis

(CH_2Cl_2): λ (ε) = 398 (16300), 378 (13600) nm. HRMS: calcd. for $C_{28}H_{26}S_4Si_2$ 546.0456; found 546.0452.

2,13-Bis(triisopropylsilyl)tetrathia[7]helicene (4b): Compound **3b** (220.0 mg, 0.306 mmol) and iodine (7.8 mg 0.030 mmol, 0.10 equiv.) were dissolved in benzene (250 mL) at room temp. The stirred solution was irradiated with a 150-Watt unfiltered Hg medium pressure lamp, equipped with a quartz jacket. The solution was irradiated for 6 h at 50 °C. The progress of the reaction was followed by TLC (light petroleum). The solution was filtered and washed with a saturated aqueous solution of Na_2SO_3 (2 × 100 mL). The aqueous phases were extracted with CH_2Cl_2 (2 × 100 mL). The organic phases were collected and dried with Na_2SO_4, and the solvent was removed under reduced pressure to afford 297.7 mg of a solid residue, which was purified by flash chromatography (light petroleum) to give 106.3 mg of **4b** (50%). M.p. 250–252 °C (hexane/cyclohexane, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82 (d, CH_3, J = 4.87 Hz, 6 H), 0.84 (d, CH_3, J = 4.83 Hz, 12 H), 0.88 (m, CHCH$_3$, 6 H), 7.25 (s, 1 H), 7.94 (d, J = 8.6 Hz, 1 H), 7.96 (s, 1 H), 8.02 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1 (CHCH$_3$), 19.0 (CH$_3$), 119.0, 120.4, 121.3, 133.4 (CHar), 130.8, 131.6, 136.7, 136.9, 137.9, 138.2, 142.0 (Cq) ppm. UV/Vis (CH_2Cl_2): λ (ε) = 396 (29400), 378 (24900), 316 (23200), 302 (24670), 250 (55360) nm. $C_{40}H_{50}S_4Si_2$ (715.25): C 67.17, H 7.05, S 17.93, Si 7.85; found C 67.22, H 7.21, S 17.92, Si 7.65.

Synthesis of Tetrathia[7]helicene (1)

Method A: To a stirred solution of **4a** (13.5 mg, 0.0247 mmol) in THF (2 mL) was added a solution of nBu$_4$NF·3H$_2$O (0.1 M in THF, 0.50 mL, 0.05 mmol) at –78 °C, and the reaction was followed by TLC (light petroleum/ethyl acetate, 10:0.5) warming to room temp. After 20 min, water (2 mL) was added, and THF was removed under reduced pressure. The resulting solid was collected by filtration and washed with water (3 × 5 mL) to afford 9.9 mg of compound **1** as a yellow solid (0.0246 mmol, >99%).

Method B: To a stirred solution of **4b** (133 mg, 0.19 mmol) in THF (10 mL) was added nBu$_4$NF·3H$_2$O (206 mg, 0.665 mmol, 3.5 equiv.) at 70 °C, and the reaction was followed by TLC (light petroleum/ethyl acetate, 10:0.5). The mixture was stirred for 2 h and then another aliquot of TBAF (88.3 mg, 1.5e equiv.) was added. After the disappearance of **4b** by TLC, water (20 mL) was added, and THF was removed under reduced pressure. The product was extracted with CH_2Cl_2 (5 mL) and washed with water (3 × 5 mL); the organic phase was dried with Na_2SO_4, and the solvent was removed under reduced pressure to afford, without further purification, 74.7 mg (0.186 mmol, 98%) of compound **1** in quantitative yield.

Compound 1: M.p. 269.26 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.74 (d, J = 5.56 Hz, 2 H), 6.91 (d, J = 5.56 Hz, 2 H), 7.96 (d, J = 8.48 Hz, 2 H), 8.04 (d, J = 8.48 Hz, 2 H), 8.02 (s, 2 H) ppm. MS (EI): m/z (%) = 402 [M]$^+$, 368 (28), 355 (20), 184 (14). UV/Vis (CH_2Cl_2): λ (ε) = 208 (46700), 226 (53700), 246 (54900), 370 (25100), 387 (25700) nm. HRMS: calcd. for $C_{22}H_{10}S_4$ 401.9665; found 401.9682.

Synthesis of 2,13-Diiodotetrathia[7]helicene (14)

Method A: In a dark two-necked round-bottomed flask, a solution of ICl (0.1 M in CH_2Cl_2, 1.8 mL, 0.180 mmol, 2.04 equiv.) was slowly added dropwise over 2 h whilst stirring to a solution of **4a** (48.2 mg, 0.0881 mmol) in CH_2Cl_2 (6 mL) at 0 °C. After 45 min, a white-yellow powder was formed. The suspension was stirred overnight, and the solid compound was filtered and washed with water (3 mL) and CH_2Cl_2 (3 mL) to afford **14** (38 mg) in 66% yield.

Method B: A solution of nBuLi (1.31 M in hexane, 0.31 mL, 0.406 mmol) was added dropwise whilst stirring to a solution of **1** (53.8 mg, 0.134 mmol) in dry THF (7 mL) at –78 °C. The solution was stirred for 30 min at –78 °C (and the colour turned brown) and a solution of I_2 (108.5 mg, 0.428 mmol) in dry THF (1 mL) was added dropwise. The progress of the reaction was monitored by TLC (light petroleum/CH_2Cl_2, 9:1). After 2 h, the solution was warmed to room temp. and quenched with an aqueous solution of Na_2SO_3 (3 mL). THF was completely removed under reduced pressure; the light yellow precipitate material was filtered through an Irsch funnel, washed with water and then twice with pentane (1 mL) to afford **14** (66.3 mg) in 76% yield.

Compound 14: M.p. 345.8 °C (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.95 (s, 2 H), 7.93 (d, J = 8.5 Hz, 2 H), 7.99 (s, J = 8.5 Hz, 2 H), 7.99 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 76.1 (Cq), 118.8, 120.1, 120.7, 136.5 (CHar), 129.0, 129.6, 136.6, 137.1, 137.3, 137.7 141.8 (Cq) ppm. UV/Vis (CH_2Cl_2): λ (ε) = 400 (19280), 382 (18500), 342 (9950), 284 (30800), 246 (48600) nm. MS (EI): m/z (%) = 654 (100) [M]$^+$, 528 [M + I]$^+$, 400 [M – 2 I]$^+$. HRMS: calcd. for $C_{22}H_8I_2S_4$ 653.7598; found 653.7587.

2,13-Dibromotetrathia[7]helicene (15): In a dark two-necked round-bottomed flask, a Br_2 solution (0.166 M in CH_2Cl_2, 1 mL, 0.166 mmol, 2 equiv.) was slowly added dropwise whilst stirring to a solution of **4a** (45.4 mg, 0.0831 mmol) in CH_2Cl_2 (5 mL) at room temp. After 10 min, a white-yellow powder was formed. The solid compound was filtered and washed with CH_2Cl_2 (3 mL) to afford **15** (36.8 mg, 79%). M.p. 345.8 °C (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.76 (s, 2 H), 7.91 (d, J = 8.5 Hz, 2 H), 7.96 (s, J = 8.5 Hz, 2 H), 8.02 (s, 2 H) ppm. UV/Vis (CH_2Cl_2): λ = 384, 336, 316, 248 nm. MS (EI): m/z (%) = 562 (71) [M + 4]$^+$, 560 (100) [M + 2]$^+$, 558 (53) [M]$^+$, 480 (2) [M – Br]$^+$, 400 (18) [M – 2 Br]$^+$. HRMS: calcd. for $C_{22}H_8Br_2S_4$ 557.7876; found 557.7862.

X-ray Data Collection, Structure Solution and Refinement for Compounds 3b and 4b·0.5C$_6$H$_{12}$: The intensity data were collected at 173 K (**3b**) and at room temp. (**4b**·0.5C$_6$H$_{12}$) with a ENRAF NON-

Table 5. Crystal data and structure refinement for compounds **3b** and **4b** 0.5C$_6$H$_{12}$.

Formula	$C_{40}H_{52}S_4Si_2$	$C_{40}H_{50}S_4Si_2 \cdot 0.5C_6H_{12}$
FW	717.24	757.30
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	11.459(4)	14.340(5)
b [Å]	20.821(5)	13.582(4)
c [Å]	8.293(4)	12.938(3)
α [°]		89.07(2)
β [°]	91.785(5)	67.07(2)
γ [°]		67.44(2)
V [Å^3]	1978(1)	2117(1)
Z	2	2
$D_{calcd.}$ [g cm^{-3}]	1.204	1.188
F(000)	768	812
Crystal size [mm]	0.11 × 0.10 × 0.09	0.12 × 0.09 × 0.06
μ [cm^{-1}]	29.78	28.08
Reflections collect	3973	7730
Reflections unique	3714 (R_{int} = 0.024)	7730
Reflections observed [$I > 2\sigma(I)$]	3242	4736
Parameters	228	561
R Indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0392, $wR2$ = 0.1075	$R1$ = 0.0595, $wR2$ = 0.1577
R Indices (all data)[a]	$R1$ = 0.0445, $wR2$ = 0.1126	$R1$ = 0.0964, $wR2$ = 0.1814

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

IUS CAD 4 single-crystal diffractometer (by using graphite monochromated Cu-K_α radiation, $\lambda = 1.54183$ Å). Crystallographic and experimental details are summarized in Table 5. The structures were solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97)[20] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The three isopropyl groups bound to the Si2 atom were found disordered in two positions. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms, except for the aromatic hydrogen atoms in compound **3b**, which were localized on the ΔF map and refined isotropically. CCDC-626079 (for **4b**) and -626080 (for **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Variable-temperature ^{1}H NMR of compound **4b** and ^{1}H and ^{13}C NMR of all synthesized compounds.

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