Helically chiral thia- and diselena-quinquephenylophanes

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Helically chiral thia- and diselena-quinquephenylophanes have been synthesized starting from suitable benzene derivatives *via* an 8-step synthesis path. Helical thiaquinquephenylophane **9** was obtained from bis(bromomethyl)quinquephenyl **8** in cyclisation with thioacetamide under high-dilution conditions in 10% yield. The corresponding diselenaquinquephenylophane was obtained in 17% yield by using KSeCN and reduction. The *M*- and *P*-enantiomers of the thiaphane were separated by HPLC using the Okamoto resin. The CD and UV spectra of the pure *M*- and *P*-enantiomers of the thiaphane were recorded. X-Ray structure analyses of the racemic crystals were performed for both compounds. Unit-cell parameters: **9**, a = 10.952(1), b = 11.896(2), c = 9.804(1) Å, α = 104.19(1), β = 111.71(1), γ = 80.19(1)°, V = 1146.0(3) Å^3; **10**, a = 10.304(2), b = 15.204(4), c = 9.128(1) Å, α = 105.08(2), β = 113.72(1), γ = 93.41(2)°, V = 1242.2(5) Å^3. In addition, a dimeric selena-bridged [3.3]quinquephenylophane was observed, and its presence confirmed by FAB-MS and ^{77}Se NMR spectroscopy.

The synthesis of helical compounds has been an area of interest since Newman's helicenes.[1] A family of helically chiral oligophenylophanes have been prepared earlier by Vögtle *et al*,[2] but the enantiomers have not been separated. Several examples of helically chiral [2.2]heteraphanes have also been presented by Vögtle[3] and some of these phanes have been resolved into their enantiomers. CD spectra and X-ray diffraction studies have been presented earlier and the correlation between the CD spectra and the structures has been discussed, although not fully interpreted, in some explicit examples.[4] Over the past few years the interest in helical compounds has been expanded into the field of supramolecular chemistry, where attention is focused on the double-helical metal complexes. The helical supramolecular complexes result from the molecular recognition and self-assembly of non-helical ligands around a metal ion. This type of helicate formation was first discovered by Lehn[5] and later applied by Constable,[6] Scowen[7] and several other groups.

The synthesis of helically chiral cyclophanes implies a ring closure, normally under high-dilution conditions, of a non-chiral open-chain precursor molecule. The ring closure produces a racemic mixture of left- and right-handed enantiomers. In some cases the *M*(minus)- and *P*(plus)-isomers can be separated with HPLC using a chiral column. The CD spectra can give information about the spatial orientation of the chromophores, but the experimental and theoretical correlation between the absolute configuration and the CD spectra is not straightforward and only in cases with structurally very similar compounds can some generalisations be made.[8]

Our aim in this study was to synthesize a helically chiral cyclophane and resolve it into its *M*- and *P*-enantiometers using HPLC with a chiral phase in the column. The compound was designed to contain an atom with enough anomalous scattering power (normally an S, Cl or P atom is enough) to allow reliable determination of absolute configuration using X-ray diffraction analysis. In spite of our vigorous attempts to grow crystals from the HPLC-resolved enantiomers no crystal of optical purity was obtained. Owing to our failure to reach our final goal we report here the resolution of the enantiomers of the title thiaphane and their CD spectra, and in addition the X-ray structures of the racemic crystals of both title compounds.

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Results and discussion

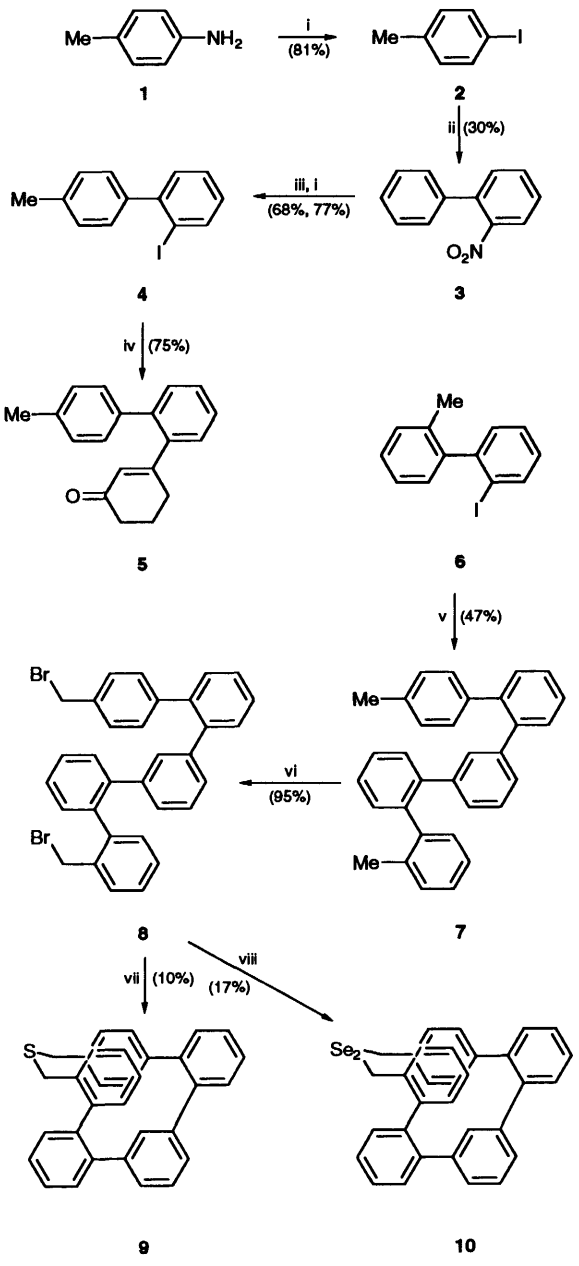
The helically chiral quinquephenylophanes were synthesized as shown in Scheme 1. In the cyclisation steps vii and viii (see Scheme 1) of 2,4‴-bis(bromomethyl)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenyl **8** produced 2-thia[3](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenylophane **9** and 2,3-diselena-[4](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenylophane **10**.[9]

The crystal structures of compounds **9** and **10** were determined by X-ray diffraction analysis. The structures show that the thiaphane **9** and diselenaphane **10** are relatively strained (Figs. 1 and 2). Despite distortion, all phenyl rings retain planarity, the largest deviation from the least-squares (LS)-planes being 0.02 Å. The more spacious ring of diselenaphane **10** allows one phenyl ring [C(11)–C(16)] to twist more out from the whole phane. This is the only fundamental difference in structures **9** and **10**. The torsion angles between the phenyl rings C(10)–C(15) and C(16)–C(21) in thiaphane **9** and C(11)–C(16) and C(17)–C(22) in the corresponding diselenaphane **10** differ by 35°. This can be observed by comparing Figs. 1 and 2. All other torsion angles between the phenyl rings do not differ more than a few degrees.

Owing to sterical requirements the hydrogens of methylene bridges are pointing out from C(1) and partly inside, into the small cavity, at C(3) [C(4) in **10**]. This causes chemical-shift and coupling-constant differences between protons at the methylene carbons C(1) and C(3)/C(4). An inner hydrogen at C(3)/C(4) lies only 2.76 Å away from C(31) in structure **9** and 3.35 Å from C(32) in structure **10**, respectively. Also, an upfield shift for the proton at C(21) [C(22) in **10**] is interpreted by its location in a shielding area of another phenyl ring [C(28)–C(33)]; C(29)–C(34) in **10**]. The distance from the same *meta*-proton to C(28) in structure **9** is 2.73 Å and to C(29) in structure **10** is 2.71 Å.

The organisation of the oligophenyl chain causes overlapping and rigidity in the cycle, thus preventing inversion of the thiaphane even at moderate temperatures. This was calculated earlier in a study of related compounds by Hammerschmidt.[11] In the diselenaphane the selena bridge joining the ends of the phenyl chain is longer but rigidity is still retained. As can be seen from the space-filling models in Figs. 1 and 2 the cavities are too small to accommodate any guest molecules.

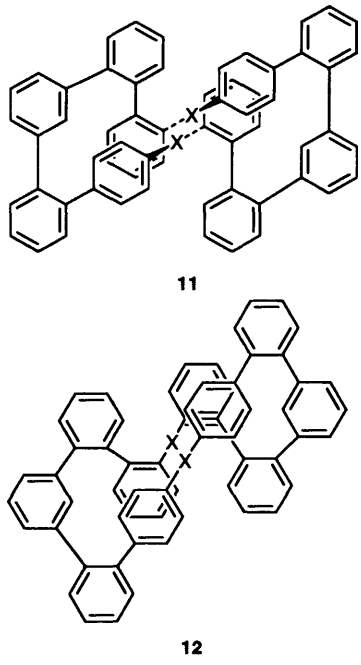
The enantiomers of the thiaphane **9** were separated by HPLC using (+)-poly(triphenylmethylmethacrylate) resin. The UV spectrum of the racemic mixture and the CD spectra of the *M*



Scheme 1 Synthesis of helically chiral thia- and diselena-quinquephenylophanes. *Reagents and conditions:* i, $NaNO_2$ followed by KI, aq. HCl, 0 °C; ii, 2-nitrobenzoic acid, Cu_2O, quinoline, reflux; iii, N_2H_4, Raney-Ni, EtOH, reflux; analogously synthesis of compound **6**; iv, BuLi followed by addition of 3-ethoxycyclohex-2-enone and hydrolysis, Et_2O, 0 °C, Ar; v, (i) BuLi followed by addition of compound **5** and hydrolysis, Et_2O, 0 °C, Ar, (ii) DDQ, abs toluene, reflux; vi, NBS, CCl_4, reflux, *hv*; vii, TAA, KOH, benzene, reflux in high dilution; viii, (i) KSeCN, acetone, room temp., (ii) $NaBH_4$, THF–EtOH, room temp., dilute solution (NBS = *N*-bromocuccinimide, DDQ = 2,3-dicyano-5,6-dichloro-*p*-benzoquinone, TAA = thioacetamide).

and *P* enantiomers are shown in Fig. 3. The spectra confirm the existence of enantiomers of the same helically chiral molecule.

The dimeric compounds that were separated from the reaction mixtures of steps vii and viii did not produce any crystals suitable for X-ray analysis. However, ^1H, ^{13}C, ^{77}Se NMR and MS spectra of a fraction from step viii confirmed the existence of the *mono*selena-bridged dimers. Also, ^{13}C NMR spectroscopic analysis of a fraction from the thia-bridged cyclophane synthesis refers to dimeric forms. In principle the 'double' ring closure produces a racemic mixture of four pairs of diastereoisomers. The terminal phenyl rings of quinquephenyl chain **8** are *ortho*-substituted in the one and *para*-substituted in the other end. During cyclisation, the new bonds can be formed between the similarly or differently substituted terminal phenyls. Additional isomerism is created by the preorganisation of joining quinquephenyls that can be either *M*- or *P*-enantiomers. This results in altogether eight possible combinations of quinquephenyl moieties forming a [3.3]quinquephenylophane. Two of the four diastereoisomeric enantiomer pairs (pairs 1 and 2, see explanation below) are in fact *meso*-forms, thus reducing the number of different dimers to six. The four pairs of diastereoisomers can be categorised according to the substitution patterns of adjoining phenyl rings. (*e.g.*, *o-p* or *p-p*) and the helicity (*M* or *P*) of the quinquephenyl moieties: (i) *o-p*/*o-p*: *M-P*/*P-M*; (ii) *p-p*/*o-o*: *M-P*/*P-M*; (iii) *o-p*/*o-p*: *M-M* and *P-P*; (iv) *p-p*/*o-o*: *M-M* and *P-P*. Two enantiomers are presented in structures **11** and **12**.



Scheme 2 A schematic presentation of two [3.3]quinquephenylophane enantiomers. X = $-CH_2SCH_2-$ or $-CH_2SeSeCH_2-$. Compound **11**: *o-p* and *o-p*-connected moieties, chiral helicities of the moieties *P* and *P*. This enantiomer with its *M-M* enantiomer are the only ones which are expected to wind and form an 'eight loop'. Compound **12**: *p-p* and *o-o*-connected moieties, chiral helicities of moieties are *P* and *P*. A macrocycle consisting of a *para*-substituted phenyl chain and a meandering *ortho*-substituted phenyl chain.

^{77}Se NMR experiment

Measured values of the selenium nuclei shifts in the diselena compound **10** and the corresponding dimers **11**/**12** are in correlation with the normal values presented in the literature.[12] ^{77}Se is a very sensitive NMR nucleus and it is easily influenced by its chemical environment. The coupling constants $J(^{77}Se,^{13}C)$ and $J(^{77}Se,^1H)$ are reported to be dependent on stereochemical relationships.[12]

Two peaks for two different selenium nuclei appear in the proton-decoupled spectrum of diselena compound **10**. As was described above there are six different possible dimers. The centrosymmetric *meso* forms both produce one signal and two pairs of enantiomers produce two signals per pair resulting in a total of six signals over the chemical-shift scale δ_{Se} 300–400 ppm. The differences in the Se nuclei are caused mainly by spatial arrangements while the helical chirality does not affect the NMR spectrum. The ^{77}Se NMR spectra are presented in Fig. 4. The coupling constants are presented in the Experimental

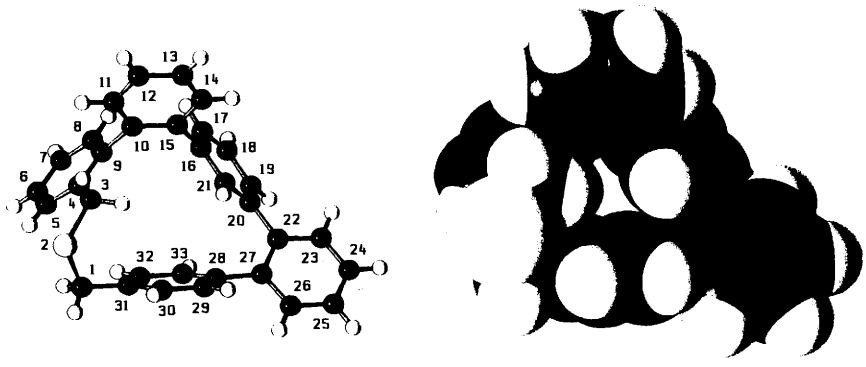


Fig. 1 SCHAKAL[10] plot for compound **9**

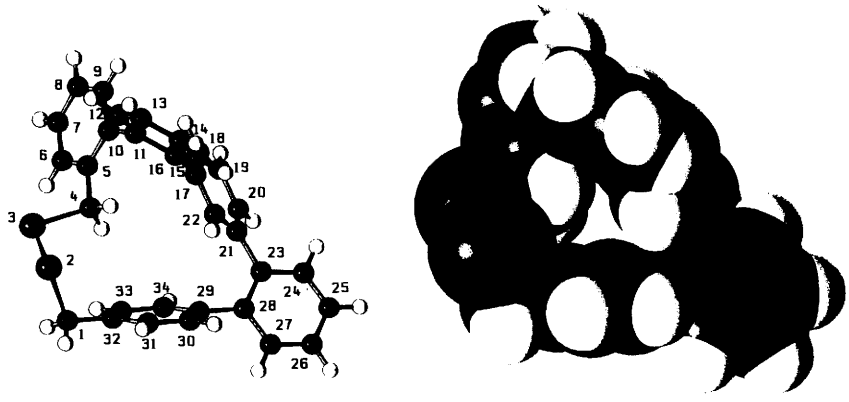


Fig. 2 SCHAKAL[10] plot for compound **10**

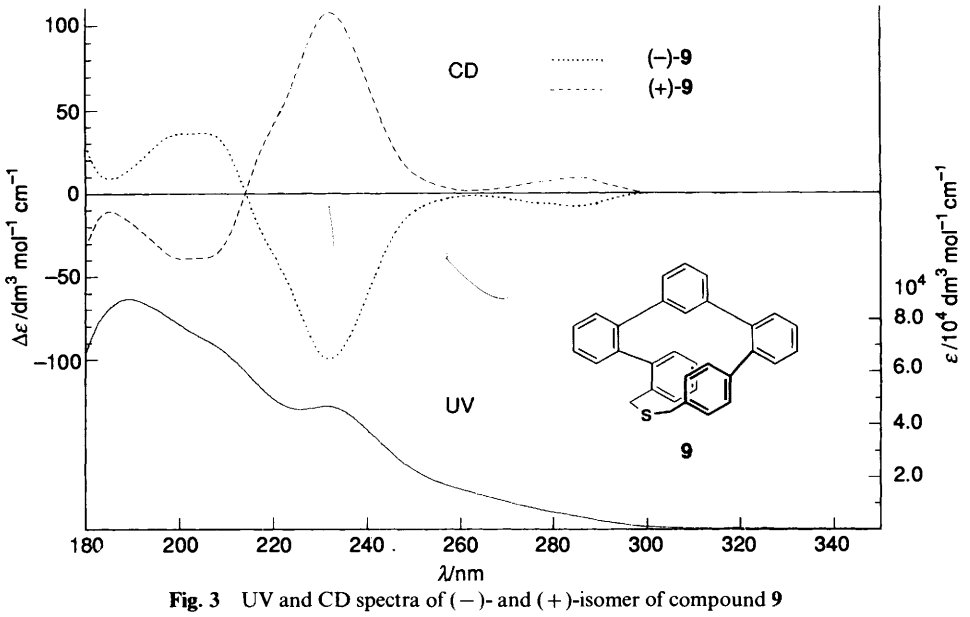


Fig. 3 UV and CD spectra of (−)- and (+)-isomer of compound **9**

section. No attempts to assign the independent signals in the ^{77}Se spectra were made.

Experimental

General

NMR spectra were recorded on JEOL FT 270 and Bruker AM400 instruments, for samples in $CDCl_3$ and CCl_4 solutions. *J*-Values are given in Hz. Mass spectra were run on a VG AutoSpec HRMS instrument, and FAB-MS on a Kratos Concept 1 H. Separation of enantiomers was performed on HPLC with poly(triphenylmethyl methacrylate) (PTrMA) supported on silica gel. CD and UV spectra were recorded on a JASCO J-720 and MR (molar rotation) on a Perkin-Elmer 241 LC instrument. Crystal data were collected on an Enraf-Nonius CAD4 diffractometer. TLC was carried out on silica gel 60 F_{254} (Riedel-de Haën), and column chromatography on silica gel 60 F_{254} (63–200 μm) Merck.

The precursor of both cycles, 2,4‴-bis(bromomethyl)-1:1′, 2′:1″,3″:1‴,2‴:1⁗-quinquephenyl **8**, was prepared according to Hammerschmidt and Vögtle with slightly improved yields in steps iv, vii and viii (see Scheme 1).[13]

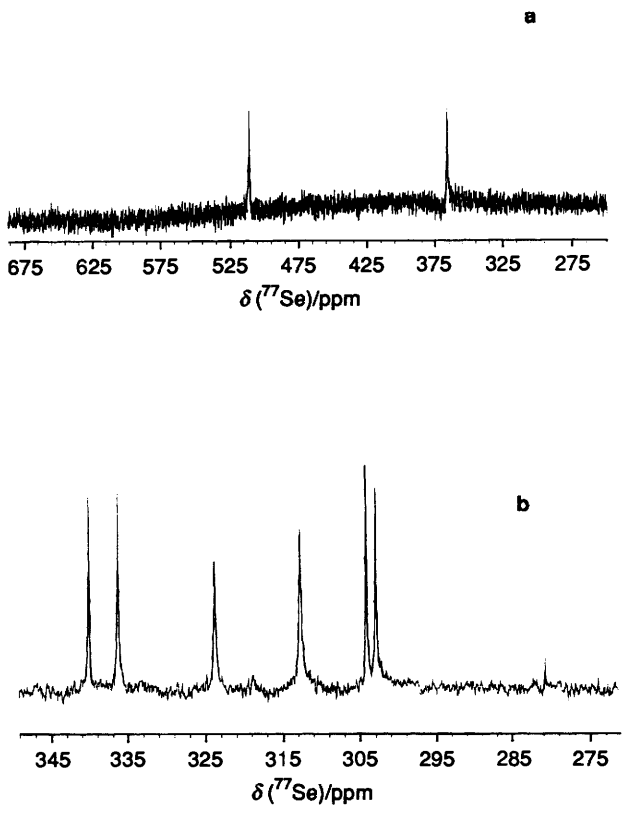


Fig. 4 ^{77}Se NMR spectra of compounds **10** (a) and **11**/**12** (b)

2-Thia[3](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗- quinquephenylophane 9

The ring closure to the sulfide was carried out with thioacetamide (TAA) under high-dilution conditions. A solution of compound **8** (1.2 g, 2.1 mmol) and TAA (0.15 g, 2.1 mmol) in benzene (150 cm^3) was dropped simultaneously with a solution of KOH (0.27 g, 4.75 mmol) in water–ethanol (1:50) into refluxing solvent [benzene (800 cm^3) and ethanol (400 cm^3)] in a 2-CV-apparatus during 8 h and the mixture was refluxed additionally for 2 h. The solution was filtered and evaporated to dryness. Chromatography on silica gel with benzene–light petroleum (distillation range 60–80 °C) (1:1) as eluent yielded 2-thia[3](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenylophane **9** (90 mg, 10%), R_f 0.47; δ_H (270 MHz; $CDCl_3$) 2.56 (2 H, q, $^2J_{H,H}$ −17.1, CH_2), 3.81 (2 H, q, $^2J_{H,H}$ −12.8, CH_2), 5.70–5.87 (3 H, m, ArH) and 6.21–6.83 (17 H, m, ArH); δ_C 30.70, 34.98, 125.45, 126.98, 127.11, 127.40, 127.52, 127.64, 128.36, 128.49, 128.78, 128.99, 129.70, 129.97, 130.69, 130.83, 130.88, 134.20, 135.97, 138.84, 139.88, 140.51, 140.61, 140.66, 140.80, 141.45 and 142.12; partial overlap showing only 27 signals of the 31 possible; *m/z* 440 (M^+, 100%), 407 (61), 391 (8), 239 (14), 215 (6), 204 (15), 197 (24) and 165 (22). Continued separation yielded a mixture of thia-bridged dimers (see Fig. 3) (145 mg, 15%), R_f 0.20; δ_C 20.09, 22.72, 29.38, 29.72, 34.58, 34.68, 35.20, 35.59, 125.37, 126.44, 127.01, 127.35, 127.69, 127.93, 128.29, 128.56, 128.60, 129.10, 129.20, 129.90, 130.07, 130.33, 130.60, 130.68, 130.77, 130.88, 131.02, 135.58, 135.66, 135.77, 135.96, 136.12, 136.24, 136.35, 138.65, 138.79, 138.94, 139.07, 140.21, 140.23, 140.37, 140.49, 140.56, 140.69, 140.76, 140.76, 140.91, 140.95, 141.07, 141.39 and 141.43.

2,3-Diselena[4](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenylophane 10

To a solution of compound **8** (0.6 g, 1.06 mmol) in argon-degassed acetone–CH_2Cl_2 (1:1; 40 cm^3) was added dropwise a solution of KSeCN (0.4 g, 2.6 mmol) in argon-degassed acetone (20 cm^3) under argon during 4 h at room temperature. The formed KBr was filtered off and the filtrate was added dropwise during 24 h to a solution of $NaBH_4$ (0.3 g, 0.8 mmol) in tetrahydrofuran (THF)–ethanol (5:1; 300 cm^3) at room temperature.[14] Evaporation of solvents, and chromatography of the residue on silica gel with benzene–light petroleum as eluent, yielded 2,3-diselena[4](2,4‴)-1:1′,2′:1″,3″:1‴,2‴:1⁗-quinquephenylophane **10** (100 mg, 17%), R_f 0.46; δ_H (270 MHz; CCl_4) 2.92 (2 H, q, $^2J_{H,H}$ −12.8, CH_2), 4.04 (2 H, q, $^2J_{H,H}$ −11.9, CH_2), 6.34–6.37 (1 H, m, ArH) and 7.39–6.76 (19 H, m, ArH); δ_C 29.46, 32.35, 126.51, 126.71, 126.77, 126.85, 126.85, 127.04, 127.13, 127.24, 127.43, 127.47, 127.77, 127.87, 129.73, 129.44, 129.68, 129.84, 130.18, 130.65, 131.35, 138.03, 138.28, 138.59, 139.32, 139.69, 139.80, 140.39, 140.56, 140.76 and 141.85; ^{1}H-decoupled ^{77}Se NMR spectroscopy with Me_2Se_2 (δ_{Se} 275 ppm) as external standard: δ_{Se} 510.31 and 366.01; *m/z* 568.

Continued separation yielded a mixture of selena-bridged dimers (see structures **11** and **12**) (99 mg, 19%), R_f 0.19; δ_H (270 MHz; $CDCl_3$) 3.15–3.79 (m, CH_2), 6.28–6.32 (m, ArH) and 6.47–7.20 (m, ArH); δ_C 25.56, 26.40, 26.90, 27.01, 27.74, 28.09, 28.58, 30.31, 126.58, 126.62, 126.76, 127.27, 127.47, 127.61, 127.74, 127.93, 128.10, 128.25, 128.43, 128.67, 128.83, 129.10, 129.13, 129.98, 130.05, 130.32, 130.43, 130.48, 130.63, 130.79, 130.84, 130.95, 131.20, 131.34, 131.40, 131.51, 131.75, 137.35, 137.54, 137.67, 137.72, 137.79, 139.34, 139.44, 139.53, 139.80, 140.03, 140.09, 140.46, 140.63, 140.72, 140.80, 140.87, 140.91, 140.98, 141.02, 141.11, 141.22, 141.29, 141.33, 141.42, 141.49 and 141.51; H-coupled ^{77}Se NMR spectroscopy with Me_2Se_2 (δ_{Se} 275 ppm) as external standard: δ_{Se} 303.01 (t, $^2J_{Se,H}$ 10), 304.19 (t, $^2J_{Se,H}$ 10), 312.78 (m), 323.79 (m), 336.29 (t, $^2J_{Se,H}$ 12) and 340.13 (t, $^2J_{Se,H}$ 12).

Enantiomeric separation, molar rotation and CD and UV spectra of compound 9

The enantiomeric separation was achieved by HPLC with (+)-PTrMA[15] supported on silica gel (10 μm) (125 × 4.7 mm) and hexane–propan-2-ol (95:5; 1 cm^3 min^{-1}) at room temperature. The enantiomeric purity (ee ≥99% for each) was determined by HPLC: t_R (+)$_D$-**9** (7.2 min); (−)$_D$-**9** (13.2 min). The CD and UV spectra were recorded on a JASCO-J720 spectrometer (cell length 0.5 mm; hexane; λ 180–350 nm), the MR on a Perkin-Elmer 241 LC spectrometer (cell length 9.999 cm; hexane). λ_{max} (hexane)/nm: ε/dm^3 mol^{-1} cm^{-1} × 10^{-4}) 189.5 (8.79), 198.2 (8.04), 204.4 (7.34), 214.2 (5.98), 226.0 (4.58), 228.7 (4.64), 231.6 (4.70) and 242.3 (3.41); (+)$_D$-**9** CD (hexane) λ (Δδ) 185.2 (−10.7), 204.0 (−38.5), 214.1 (0.0), 232.0 (107.3), 263.0 (1.6), 284.9 (9.1) and 303.9 (0.0). For (+)$_D$-**9** MR (hexane) λ([Φ]^{30}) 302 (+17.65 ± 148), 365 (+5.531 ± 55), 436 (+2.557 ± 39), 546 (+1.106 ± 31), 578 (+959 ± 30) and 589 (+934 ± 30). For (−)$_D$-**9** CD (hexane): λ(Δδ) 185.2 (8.8), 204.0 (36.2), 214.0 (0.0), 232.0 (−99.0), 263.7 (−1.5), 284.9 (−8.0) and 302.0 (0.0). For (−)$_D$-**9** MR (hexane) λ([Φ]^{30}) 302 (−17.753 ± 244), 365 (−5.432 ± 68), 436 (−2.458 ± 47), 546 (−1.093 ± 38), 578 (−941 ± 37) and 589 (−910 ± 37).

X-Ray analysis §

Crystals of compounds **9** and **10** were grown from CH_2Cl_2 by slow solvent diffusion with acetone.

Crystal data 9. $C_{32}H_{26}S$, M = 440.61, triclinic, a = 10.952(1) b = 11.896(2), c = 9.804(1) Å, α = 104.19(1)°, β = 111.71(1)°,

§ Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See *J. Chem. Soc., Perkin Trans. 1*, Notice to Authors, Issue No. 1.

$\gamma = 80.19(1)°$, $V = 1146.0(3)$ Å^3 (by least-squares refinement on θ-angles 5–12° for 25 automatically centred reflections), λ(Mo-Kα) = 0.7107 Å, space group $P\bar{1}$, $Z = 2$, $D_X = 1.277$ Mg m^{-3}. Crystals. Crystal dimensions 0.2 × 0.2 × 0.3 mm, μ(Mo-Kα) = 0.1516 mm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.5 + 0.35 tan θ, ω scan speed 1–7 deg min^{-1}, graphite-monochromated Mo-Kα radiation, $T = 294(1)$ K, θ-range 2–25° (h −13 ⟶ 12, k −14 ⟶ 13, l 0 ⟶ 11); 4239 reflections measured, 4012 unique (merging $R = 0.008$), DIFABS[16] with minimum and maximum correction coefficients 0.739 and 1.112, giving 3162 with $I > 3\sigma(I)$.

Structure analysis and refinement. Direct methods.[17] Full-matrix least-squares refinement,[18] the scattering factors taken from ref. 19. All non-hydrogen atoms anisotropic. Hydrogens in calculated positions (C–H distance 1.00 Å) and only coordinates refined with fixed isotropic temperature factors ($U = 0.08$ Å^2). The weighting scheme $w = w'\cdot[1.0 - (\Delta F/6\cdot\sigma F)^2]^2$, where w' = Chebychev polynomial function to F_c, with Chebychev values 3.19, 1.00, 2.14. Final R- and R_w-values are 0.0353, 0.0434. Convergence, max. shift/error < 0.01, max. diff. 0.19 e Å^{-3}.

Crystal data 10

$C_{32}H_{26}Se_2$, M = 566.46, triclinic, $a = 10.304(2)$, $b = 15.204(4)$, $c = 9.128(1)$ Å, $\alpha = 105.08(2)°$, $\beta = 113.72(1)°$, $\gamma = 93.41(2)°$, $V = 1242.2(5)$ Å^3 (by least-squares refinement on θ-angles 5–12° for 25 automatically centred reflections), λ(Mo-Kα) = 0.7107 Å, space group $P\bar{1}$, $Z = 2$, $D_X = 1.514$ Mg m^{-3}. Weak crystals. Crystal dimensions 0.15 × 0.2 × 0.4 mm, μ(Mo-Kα) = 3.0100 mm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.5 + 0.35 tan θ, ω scan speed 1–7 deg min^{-1}, Mo-Kα radiation, $T = 294(1)$ K, θ-range 2–25° (h −12 ⟶ 12, k −18 ⟶ 17, l 0 ⟶ 10); 4598 reflections measured, 4335 unique [merging $R = 0.018$], DIFABS[16] with minimum and maximum correction coefficients 0.601 and 1.651, giving 2105 with $I > 3\sigma(I)$.

Structure analysis and refinement. Direct methods.[17] Full-matrix least-squares refinement,[18] the scattering factors taken from ref. 19. All non-hydrogen atoms anisotropic. Hydrogens in calculated positions (C–H distance 1.00 Å) and refined as riding atoms with fixed isotropic temperature factors ($U = 0.08$ Å^2). The weighting scheme $w = w'\cdot[1.0 - (\Delta F/6\cdot\sigma F)^2]^2$, where w' = Chebychev polynomial function on F_c, with Chebychev coefficients 3.22, 0.0409, 2.38. Final R- and R_w-values are 0.0538 and 0.0643. Convergence, max. shift/error < 0.01, max. diff. 0.37 e Å^{-3}.

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