SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ENANTIOPURE CAMPHOR-BASED DI-, TRI- AND TETRASULFIDES ‡

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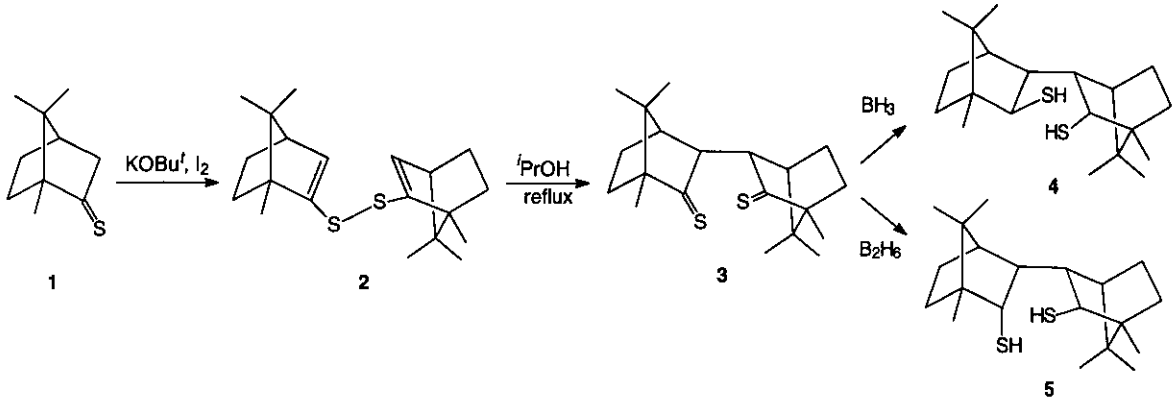
Abstract –The dithiane (**6**) was synthesized by bromine oxidation of the dithiol (**5**), despite the significant steric strain in the pentacyclic system. In the presence of elemental sulfur the oxidation of **5** gave selectively the 1,2,3-trithiacycloheptane (**7**), while from the diastereomeric dithiol (**4**) under the same conditions the 1,2,3,4-tetrathiacyclooctane (**8**) was obtained in good yield. The geometry of the molecules was determined by X-Ray analysis.

INTRODUCTION

Enantiopure 3-*exo*,3'-*exo*-(1*R*,1'*R*)-bithiocamphor (**3**) has become an interesting intermediate for the synthesis of 2,2'-difunctional 3,3'-dibornane derivatives in the last years.[1] Although Sen described a synthesis of **3** in 1937,[2] only few publications[3] focused on the chemistry of this compound appeared until Schroth's paper[4] in 1994. Recently, an efficient way to the C_2-symmetric **3** from (1*R*)-thiocamphor (**1**) was described. Oxidation of the enethiolate of **1** with iodine in toluene yielded **2** which on subsequent dithia-Cope-rearrangement in refluxing isopropanol gave **3** (70% overall yield).[5]



‡ *Dedicated to Professor Dr. Werner Schroth on the occasion of his 70th birthday.*

The X-Ray structural analysis of compound (**3**) shows the thiocamphor units only slightly twisted. The steric repulsion of the methyl groups at C-7 stabilizes the conformation of **3** and the thioxo groups have a sulfur-sulfur distance of 4.05 Å in the most stable conformer.[4] Due to this small distance the thioxo groups influence each other in further reactions. By way of example the reduction with $NaBH_4$ occurred only at one of the thiocarbonyl groups. Due to the proximity, the initially formed thiolate group adds intramolecularly to the remaining C=S group to afford an α-mercaptotetrahydrothiophene derivative.[1b] On the other hand reduction of the thioxo groups by the $BH_3 \cdot SMe_2$ complex was reported by Le Corre *et al.* to be strongly dependent on the reaction conditions. Heating of a toluene solution of **3** with one equivalent of $BH_3 \cdot SMe_2$ from room temperature to reflux gave a 70:30 mixture of the *exo,exo*-thiol (**4**) and the *endo,exo*-thiol (**5**), while addition of a solution of **3** to 2 equivalents of $BH_3 \cdot SMe_2$ at 100°C gave a 10:90 mixture of these compounds.[5] Several more reactions of bithiocamphor (**3**) have been described recently.[6]
In order to synthesize corresponding cyclic disulfides as potential new saturated enantiopure auxiliaries for syntheses we became interested in mild selective oxidations of these thiols.

RESULTS AND DISCUSSION

According to the published procedures[5] we reproduced the syntheses of **4** and **5**. However, in our hands this reaction gave practically pure **5**. Only traces of **4** have been detected in the crude product. In order to get a deeper insight into the structure and its consequences on the reactivity of these compounds we determined the geometry of *endo,exo*-(1*R*,3*S*)-1,7,7-trimethyl-3-((2*S*,4*R*)-4,7,7-trimethyl-3-sulfanylbicyclo[2.2.1]hept-2-yl)bicyclo[2.2.1]heptane-2-thiol (**5**) by X-Ray analysis (Figure 1). Comparison of the X-Ray structures of **3**[4] and **5** proves the suggestion[5] that the latter is formed *via* a simultaneous "diborane" reduction of both thiocarbonyl groups from one side of the molecule, while **4** should be formed by a stepwise reduction. This explanation is supported by the fact that the equilibrium between the monomeric $BH_3 \cdot SMe_2$ and its dimer is temperature dependent. Similar to all borane-adducts the stability increases at lower temperature.[7] Under the conditions of the reduction to **5** the equilibrium changes to the "free" $BH_3 \cdot SMe_2$, which stabilizes its electron deficiency by dimerization to B_2H_6, which is the reactive species at high temperature.

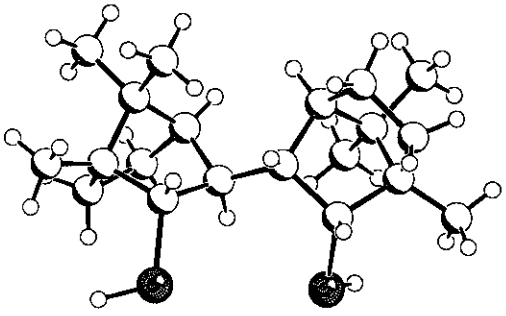


Figure 1. X-Ray crystal structure of *endo,exo*-(1*R*,3*S*)-1,7,7-Trimethyl-3-((2*S*,4*R*)-4,7,7-trimethyl-3-sulfanyl-bicyclo[2.2.1]hept-2-yl)bicyclo[2.2.1]heptan-2-thiol (**5**).

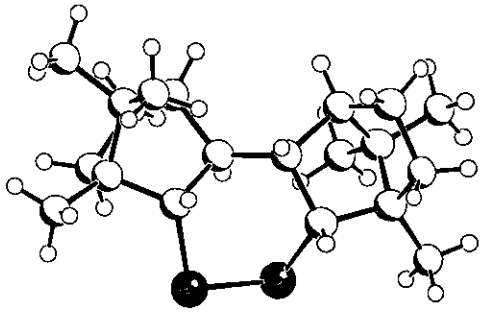
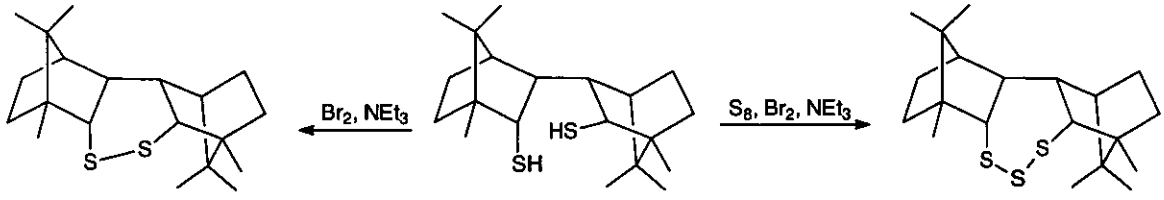


Figure 2. X-Ray crystal structure of *endo,exo*-(7*R*,8*S*,11*R*,12*R*)-7,12,15,15,16,16-hexamethyl-9,10-dithiapentacyclo[11.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadecane (**6**).

Mild oxidation of **5** with elemental bromine in the presence of triethylamine leads to the expected intramolecular coupling to the disulfide (**6**) in 51% yield. Additionally, also the trisulfide (**7**) was isolated under these reaction conditions (21%). The disulfide (**6**) is an interesting molecule due to its highly strained sulfur-sulfur bond. The X-Ray crystal structure analysis of the 1,2-dithiane (**6**) (Figure 2) shows a twisted sulfur-sulfur bond with a C-S-S-C torsion angle of 41.2(2)°. This is to the best of our knowledge the most distorted sulfur-sulfur bond in a dithiane structure, which has ever been observed in a crystal.[8] Related sulfur compounds with high strain energy are well known for their biological activity.[9]



6 **5** **7**

The interest in the higher homologues of dithiane (**6**) and in their structural details led us to treat **5** with elemental sulfur, bromine and triethylamine. In this way **5** was selectively transformed to **7** in 58% yield. Compound (**7**) was formed with <95% selectivity by treatment of **5** with sulfur and triethylamine or even without the base. The conversion of **6** into **7** on a direct way could not be achieved with elemental sulfur, perhaps due to the high dissociation energy of the S-S bond in saturated systems. The X-Ray structure of **7** shows much less distorted S-S bonds with torsion angles of 69.5(1)° and 89.6(1)°. The latter one is close to the ideal value for S-S bonds (90°).[9b]

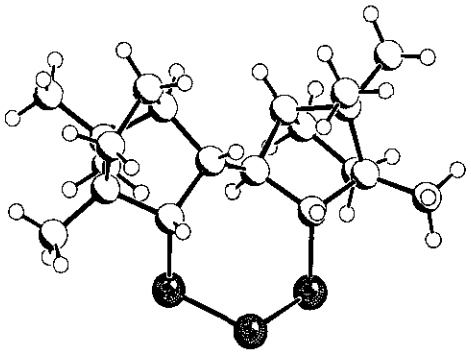


Figure 3. X-Ray crystal structure of *endo,exo*-(7*R*,8*S*,12*R*,13*R*)-7,13,16,16,17,17-hexamethyl-9,10,11-trithiapentacyclo[10.2.1.1^{4,7}.0^{2,12}.0^{3,8}]heptadecane (**7**).

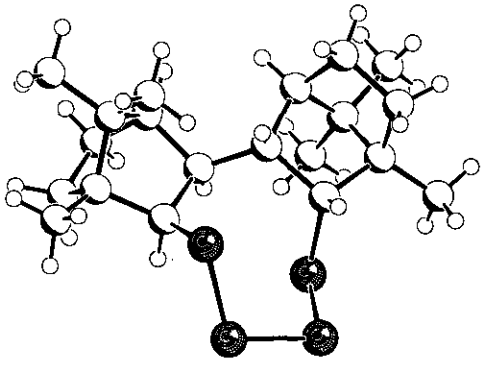
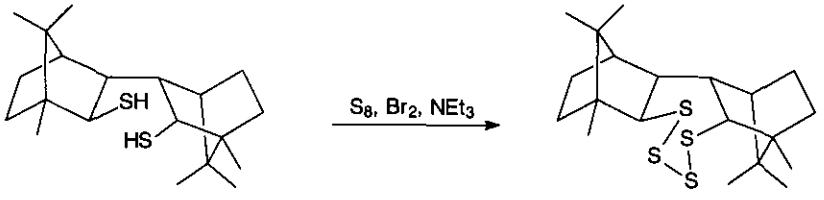


Figure 4. X-Ray crystal structure of *exo,exo*-(7*R*,8*R*,13*R*,14*R*)-7,14,17,17,18,18-hexamethyl-9,10,11,12-tetrathiapentacyclo[12.2.1.1^{4,7}.0^{2,13}.0^{3,8}]octadecane (**8**).

By treatment of the dithiol (**4**) under the same reaction conditions as **5**, no di- or trisulfides derived from **4** were found. Instead the first crystalline enantiopure tetrathiacyclooctane (**8**) was formed with high selectivity which was isolated in 59% yield after chromatographic purification.



4 **8**

The geometry of **8** was also investigated by X-Ray structural analysis and the S-S torsion angles were found to be 86.3(2)° and 88.7(2)° (figure 4).

These results can be informal explained by the minimum of strain energy in each compound. The calculated (AM1) structures of **7** and **8** show only minimal divergence from the measured torsion angles in the X-Ray structures (Table 1). We compared the different torsion angles of the measured molecules *endo,exo*-**7** and *exo,exo*-**8** and their hypothetical (calculated) diastereomers *exo,exo*-**7*** and *endo,exo*-**8***. These values suggest the reason why from **4** no *exo,exo*-trisulfide (**7***) and from **5** no *endo,exo*-tetrasulfide (**8***) was formed under the reaction conditions mentioned above.

Table 1: Calculated (AM1) and measured (X-Ray) torsion angles of the diastereomers of molecules (**7**) and (**8**).

C-S-S-S torsion angles	*endo,exo*-**7**	*exo,exo*-**8**	*exo,exo*-**7***	*endo,exo*-**8***
Found (X-ray)	69.5(1)° / 88.6(1)°	86.3(2)° / 88.7(1)°	-	-
Calculated (AM1)	66° / 84°	89° / 89°	44° / 45°	39° / 93°

* hypothetical molecules

EXPERIMENTAL

General Remarks: Bithiocamphor (**3**) and the dithiols (**4**) and (**5**) were prepared according to literature methods.[5] All other starting materials were obtained from Acros, Merck and Fluka chemicals.

Melting and boiling points are uncorrected. – ^{1}H- (600 MHz) and ^{13}C NMR (150 MHz): Varian 600 MHz apparatus Unity Plus. TMS was used as standard for ^{1}H- and $CDCl_3$ for ^{13}C NMR spectroscopy. $CDCl_3$ was used as solvent. The resonance signals were assigned to the atoms by 2D measurements (GCOSY, *1DTOXSY, GHSQC and GHMBC*) – MS spectra (70 eV): GC/MS coupling: Varian GC 3400/MAT 8230 and data system SS 300 of Finnigan MAT and Varian GC 3400/Varion Saturn IT (Ion Trap) and data system NIST. – Elemental analysis: Mikroanalytisches Laboratorium, OC, Universität Münster. X-ray data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92.

(7*R*,8*S*,11*R*,12*R*)-7,12,15,15,16,16-Hexamethyl-9,10-dithiapentacyclo[10.2.1.1^{4,7}.0^{2,11}.0^{3,8}]hexadecane (**6**): In an argon flushed vessel *triethylamine (3.48 mL, 25 mmol) was added to a solution of exo,endo-*dithiol (**5**) (2.5 g, 7.4 mmol) in dry dichloromethane (100 mL) at 0°C. The stirred solution was treated dropwise with a solution of bromine (0.38 mL, 7.4 mmol) in dry dichloromethane (25 mL). After 12 h of stirring the mixture was quenched on ice, the aqueous phase was separated and extracted twice with dichloromethane (50 mL). The combined organic layers were dried over $MgSO_4$, concentrated and the residue was purified by column chromatography (ether/petroleum ether 1:50). Yield: 1.26 g (51 %); mp 151°C (isopropanol); $[\alpha]_D^{20}$ +238.3° (c =1.0, ether); ^{1}H NMR: δ 3.80 (d, 1H, $^3J_{HH}$ = 8.6 Hz, 2'-H), 3.05 (dd, 1H, $^3J_{HH}$ = 9.5 Hz, $^4J_{HH}$ = 2.5 Hz, 2-H), 2.34 (dd, 1H, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 9.5 Hz, 3-H), 2.00-2.05 (m, 1H, 6-H_{exo}), 1.74-1.78 (m, 1H, 3'-H), 1.72-1.77 (m, 1H, 5'-H_{exo}), 1.71-1.72 (m, 1H, 4'-H), 1.70-1.74 (m, 1H, 5-H_{exo}), 1.68-1.69 (m, 1H, 4-H), 1.57-1.62 (m, 1H, 6'-H_{exo}), 1.30-1.35 (m, 1H, 6'-H_{endo}), 1.27-1.32 (m, 1H, 6-H_{endo}), 1.18-1.22 (m, 1H, 5-H_{endo}), 1.06-1.11 (m, 1H, 5'-H_{endo}), 1.33 (s, 3H, 8'-H_3), 0.96 (s, 3H, 8-H_3), 0.92 (s, 3H, 10'-H_3), 0.84 (s, 3H, 9-H_3), 0.80 (s, 3H, 9'-H_3), 0.75 (s, 3H, 10-H_3); ^{13}C NMR: δ 64.7 (d, C-2'), 55.7 (d, C-3'), 55.5 (d, C-2), 51.2 (s, C-1', C-7'), 50.9 (s, C-1, C-7), 50.8 (d, C-3), 50.2 (s, C-1, C-7), 48.7 (d, C-4'), 48.5 (s, C-1', C-7'), 46.1 (d, C-4), 38.4 (t, C-6'), 31.5 (t, C-5), 30.6 (t, C-5'), 27.9 (t, C-6), 22.9 (q, C-9'), 22.7 (q, C-8'), 22.6 (q, C-9), 20.5 (q, C-8), 13.5 (q, C-10'), 13.4 (q, C-10); GC/MS m/z (%) 336 (23) [M^+], 304 (4) [M^+ - S], 271 (100) [M^+ -HS_2], 243 (2), 215 (11). Anal. Calcd for

$C_{20}H_{32}S_2$: C 71.37, H 9.58. Found C 69.38, H 9.64. (Some amount of elemental sulfur could not be removed by chromatography).

(7*R*,8*S*,12*R*,13*R*)-7,13,16,16,17,17-Hexamethyl-9,10,11-trithiapentacyclo[11.2.1.1^{4,7}.0^{2,12}.0^{3,8}]heptadecane (7): In an argon flushed vessel sulfur (7.8 g, 30.4 mmol) and triethylamine (3.48 mL, 25 mmol) was added to a solution of *exo,endo*-dithiol (**5**) (10.0 g, 29.6 mmol) in dry dichloromethane (200 mL) at 0°C. The stirred solution was treated dropwise with a solution of bromine (1.52 mL, 29.6 mmol) in dry dichloromethane (50 mL). After 16 h of stirring at rt the mixture was quenched on ice, the aqueous phase was separated and extracted twice with dichloromethane (50 mL). The combined organic extracts were dried over $MgSO_4$, concentrated and the residue was purified by column chromatography (pentane). Yield: 6.33 g (58 %); mp 121-126°C (isopropanol); $[\alpha]_D^{20}$ +144.8° (c =1.2, ether); ^{1}H NMR: δ 3.45 (d, 1H, $^3J_{HH}$ = 9.0 Hz, 2'-H), 3.35 (q, 1H, $^3J_{HH}$ = 5.2 Hz, 2-H), 2.52 (dd, 1H, $^3J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 5.2 Hz, 3-H), 2.12 (dd, 1H, $^3J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 9.0 Hz, 3'-H), 1.96 (d, 2H, $^3J_{HH}$ = 4.3 Hz, 4-H, 4'-H), 1.80-1.86 (m, 1H, 6-H), 1.73-1.79 (m, 1H, 5'-H_{exo}), 1.68-1.74 (m, 1H, 5-H_{exo}), 1.58-1.64 (m, 1H, 6'-H), 1.31-1.37 (m, 1H, 6'-H), 1.28-1.35 (m, 1H, 5-H_{endo}), 1.26-1.31 (m, 1H, 6-H), 1.06-1.11 (m, 1H, 5'-H_{endo}), 0.98 (s, 3H, 8'-H_3, 9'-H_3), 0.98 (s, 3H, 8-H_3, 9-H_3), 0.94 (s, 3H, 10-H_3, 10'-H_3), 0.93 (s, 3H, 10-H_3, 10'-H_3), 0.87 (s, 3H, 8-H_3, 9-H_3), 0.75 (s, 3H, 8'-H_3, 9'-H_3); ^{13}C NMR: δ 75.6 (d, C-2), 71.2 (d, C-2'), 58.7 (d, C-3'), 57.9 (d, C-3), 51.6 (s, C-1'), 51.2 (s, C-1), 49.5 (d, C-4, C-4'), 49.3 (d, C-4, C-4'), 47.7 (s, C-7'), 47.6 (s, C-7), 38.7 (t, C-6'), 30.9 (t, C-6), 30.1 (t, C-5), 29.8 (t, C-5'), 22.1 (q, C-8', C-9'), 21.4 (q, C-8', C-9'), 21.0 (q, C-8, C-9), 20.2 (q, C-8, C-9), 14.5 (q, C-10, C-10'), 14.4 (q, C-10, C-10'); GC/MS m/z (%) 368 (30) [M^+], 304 (35) [M^+ -S_2], 303 (42) [M^+ -HS_2], 271 (100) [M^+ -HS_3], 265 (5), 194 (9), 135 (14). Anal. Calcd for $C_{20}H_{32}S_3$: C 65.16, H 8.75. Found C 63.51, H 8.84. (Some amount of elemental sulfur could not be removed by chromatography).

(7*R*,8*R*,13*R*,14*R*)-7,14,17,17,18,18-Hexamethyl-9,10,11,12-tetrathiapentacyclo[12.2.1.1^{4,7}.0^{2,13}.0^{3,8}]octadecane (8): In an argon flushed vessel sulfur (0.46 g, 1.8 mmol) and triethylamine (0.69 mL, 5 mmol) was added to a solution of the *exo,exo*-dithiol (**4**) (0.5 g, 1.5 mmol) in dry dichloromethane (20 mL) at 0°C. The stirred solution was treated dropwise with a solution of bromine (0.076 mL, 1.5 mmol) in dry dichloromethane (5 mL). After 16 h of stirring at room temperature the mixture was quenched on ice, the aqueous phase was separated and extracted twice with dichloromethane (10 mL).

The combined organic extracts were dried over $MgSO_4$, concentrated and the residue was purified by column chromatography (pentane). Yield: 0.35 g (59 %); mp 136°C (isopropanol); $[\alpha]_D^{20}$ +824.3° (c =1.1, ether); ^{1}H NMR: δ 3.54-3.56 (m, 2H, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.8 Hz, 2-H), 2.15-2.23 (m, 2H, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.8 Hz, 3-H), 1.86 (d, 2H, $^3J_{HH}$ = 4.0 Hz, 4-H), 1.72-1.78 (m, 2H, 5-H_{exo}), 1.67-1.72 (m, 2H, 6-H), 1.38-1.43 (m, 2H, 6-H), 1.11-1.16 (m, 2H, 5-H_{endo}), 1.01 (s, 6H, 8-H_3, 9-H_3), 0.87 (s, 6H, 8-H_3, 9-H_3), 0.78 (s, 6H, 10-H_3); ^{13}C NMR: δ 79.3 (d, C-2), 54.6 (d, C-3), 52.7 (s, C-1), 50.5 (d, C-4), 47.7 (s, C-7), 38.2 (t, C-6), 29.9 (t, C-5), 22.4 (q, C-8, C-9), 21.1 (q, C-8, C-9), 15.2 (q, C-10); GC/MS m/z (%) 400 (6) [M^+], 336 (14) [M^+ - S_2], 304 (100) [M^+ - S_3], 272 (13) [M^+ - S_4], 271 (42) [M^+ - HS_4], 215 (8), 194 (50). Anal. Calcd for $C_{20}H_{32}S_4$: C 59.95, H 8.05. Found C 59.30, H 7.89.

X-Ray crystal structure analysis of **5**[10]: Formula $C_{20}H_{34}S_2$, M = 338.59, colorless crystal, 0.50 x 0.30 x 0.20 mm, a = 11.687(2), b = 7.433(1), c = 12.272(1) Å, β = 115.29(1)°, V = 963.9(2) Å^3, ρ_{calc} = 1.167 g cm^{-3}, F(000) = 372 e, μ = 24.40 cm^{-1}, empirical absorption correction *via* φ scan data (0.939 ≤ C ≤ 0.999), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 2226 reflections collected (±h, +k, -l), [(sinθ)/λ] = 0.62 Å^{-1}, 2127 independent and 2075 observed reflections [I ≥ 2 σ(I)], 208 refined parameters, R = 0.036, wR^2 = 0.104, Flack parameter 0.01(2), max. residual electron density 0.43 (-0.37) e Å^{-3}, hydrogens calculated and refined as riding atoms.

X-Ray crystal structure analysis of **6**[10]: Formula $C_{20}H_{32}S_2$, M = 336.58, colorless crystal, 0.50 x 0.30 x 0.10 mm, a = 7.431(1), b = 24.539(6), c = 10.907(2) Å, β = 109.34(1)°, V = 1876.7(2) Å^3, ρ_{calc} = 1.191 g cm^{-3}, F(000) = 736 e, μ = 25.06 cm^{-1}, empirical absorption correction *via* φ scan data (0.943 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 173 K, ω/2θ scans, 4214 reflections collected (-h, -k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 3916 independent and 3746 observed reflections [I ≥ 2 σ(I)], 409 refined parameters, R = 0.051, wR^2 = 0.143, Flack parameter 0.02(2), max. residual electron density 0.93 (-0.44) e Å^{-3}, hydrogens calculated and refined as riding atoms.

X-Ray crystal structure analysis of **7**[10]: Formula $C_{20}H_{32}S_3$, M = 368.64, colorless crystal, 0.60 x 0.50 x 0.20 mm, a = 8.270(1), b = 10.962(1), c = 11.353(1) Å, α = 80.96(1), β = 83.74(1), γ = 75.63(1)°, V = 982.0(2) Å^3, ρ_{calc} = 1.247 g cm^{-3}, F(000) = 400 e, μ = 34.07 cm^{-1}, empirical absorption correction *via* φ scan data (0.871 ≤ C ≤ 0.999), Z = 2, triclinic, space group P1bar (No. 2), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 3473 reflections collected (±h, ±k, -l), [(sinθ)/λ] = 0.59 Å^{-1}, 3286 independent and 3215

observed reflections [$I \geq 2\ \sigma(I)$], 215 refined parameters, $R = 0.041$, $wR^2 = 0.114$, max. residual electron density 0.44 (-0.31) e Å^{-3}, hydrogens calculated and refined as riding atoms.

X-Ray crystal structure analysis of **8**[10]: Formula $C_{20}H_{34}S_4$, $M = 400.70$, colorless crystal, 0.30 x 0.20 x 0.20 mm, $a = 10.625(2)$, $b = 13.376(3)$, $c = 15.405(3)$ Å, $\beta = 106.87(1)°$, $V = 2095.1(7)$ Å^3, $\rho_{calc} = 1.270$ g cm^{-3}, $F(000) = 864$ e, $\mu = 41.43$ cm^{-1}, empirical absorption correction *via* φ scan data ($0.965 \leq C \leq 0.999$), $Z = 2$, monoclinic, space group $P2_1$ (No. 4), $\lambda = 1.54178$ Å, $T = 173$ K, $\omega/2\theta$ scans, 4636 reflections collected ($\pm h$, $+k$, $+l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 4473 independent and 4144 observed reflections [$I \geq 2\ \sigma(I)$], 446 refined parameters, $R = 0.051$, $wR^2 = 0.134$, Flack parameter 0.00(2), max. residual electron density 1.14 (-0.47) e Å^{-3}, hydrogens calculated and refined as riding atoms.

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10. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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