Synthesis of 3,7-Disubstituted 9-Thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol Derivatives and Crystal Structure of Tetramethyl 3(4a*H*)-Oxo-1,4-dihydrophenanthro[9,10-*a*]pentalene-1,2,4,4a-tetracarboxylate

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A simple and efficient approach to the 9-thiatricyclo[3.3.1.0^{3,7}]nonane ring system (**5**) has been found by treating *cis*-bicyclo[3.3.0]octane-3,7-diones (**1**) with Lawesson's reagent or phosphorus pentasulfide. When dione **1** is treated with Lawesson's reagent tetramethyl 3(4a*H*)-oxo-1,4-dihydrophenanthro[9,10-*a*]pentalene-1,2,4,4a-tetracarboxylate (**6**) is obtained as a by-product as shown by X-ray structural analysis.

Lawesson's reagent is widely used for the thionation of organic molecules[1] and as a starting material for the synthesis of phosphorus-containing rings since the first work of Lecher et al.[2]. It is an efficient and selective thionation agent for aldehydes and ketones, the reaction is successful with amides, esters, thioesters, lactones and lactams, and substituents are often not affected[1][3][4].

Thioketones[5][6] may be prepared in high yield by heating the appropriate ketone with Lawesson's reagent in either boiling benzene, xylene, or toluene until the evolution of hydrogen sulfide gas has ceased.

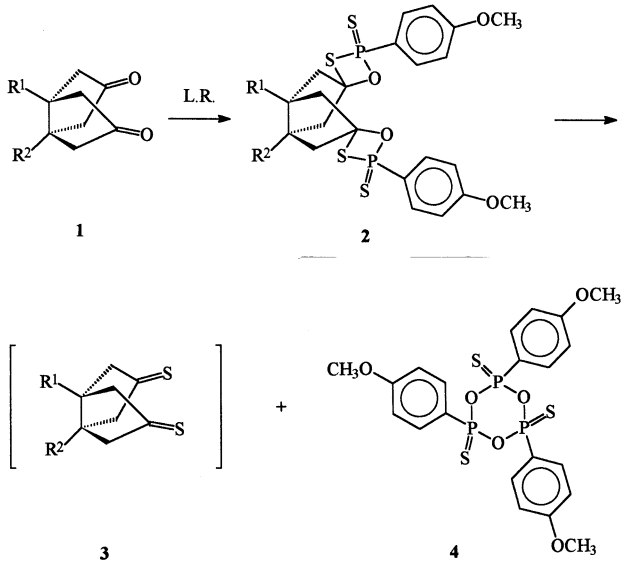
Aliphatic thioketones containing α-hydrogen atoms often exist as equilibrium mixtures with the colourless enethiols, which may form stable dimers by attack on the thioketone under elimination of hydrogen sulfide[4].

In previous studies concerning the reaction of *cis*-bicyclo[3.3.0]octane-3,7-diones **1a−c**[7][8] with Lawesson's reagent enethiolization seems to have strong influence, and so the expected bicyclic dithiones **3** were not obtained.

We now report that the interaction of Lawesson's reagent with bicyclic diones **1** under mild conditions provides a convenient method for the synthesis of the 9-thiatricyclo[3.3.1.0^{3,7}]nonane derivatives **5**. The reaction presumably involves the formation of the 3,7-dithioxo compounds **3** as intermediates which undergo spontaneous in situ cyclization to give a tricyclic system. It is likely that anchimeric assistance of one of the transient thiocarbonyl groups leads to the creation of this cage structures **5**.

As a result of this anchimeric effect we obtain the 9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiols **5** by intramolecular attack on the electrophilic thiono carbon atom by enethiol sulfur followed by addition of hydrogen sulfide. The structure of products **5a−c** was confirmed by microanalyses, IR, ^{1}H-, ^{13}C-NMR spectroscopy, and mass spectrometry.

Scheme 1



Camps et al. described a synthesis of 3,7-disubstituted tricyclo[3.3.0.0^{3,7}]octane-1,5-diols by intramolecular pinacol reduction of *cis*-1,5-disubstituted bicyclo[3.3.0]octane-3,7-diones with low-valent titanium species[8]. This simple approach was first published by H. M. R. Hoffmann et al. using samarium(II) diiodide as pinacol coupling reagent[9]. Other polycyclic derivatives are described[10].

UV irradiation of 9-thiabicyclo[6.1.0]nona-2,4,6-triene in ether in the presence of a sensibilizator gave 9-thiabarbaral-

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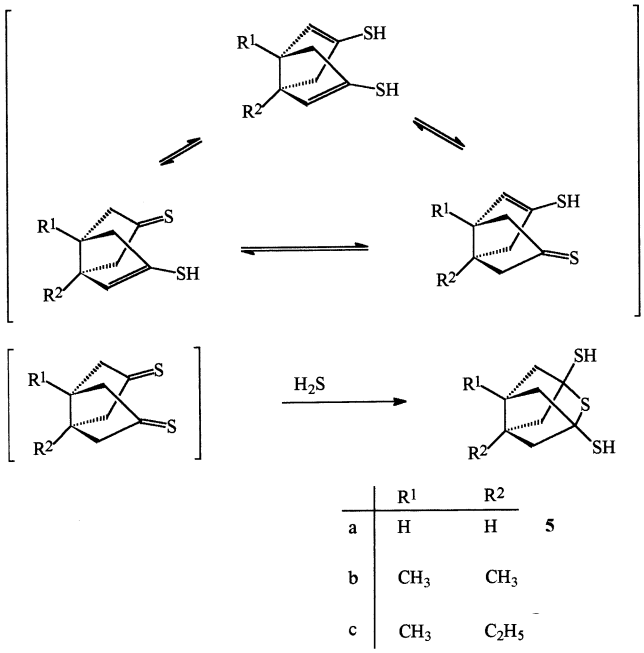
Scheme 2



	R1	R2	
a	H	H	5
b	CH_3	CH_3	
c	CH_3	C_2H_5	

ane (9-thiatricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene) by C−S bond scission[11].

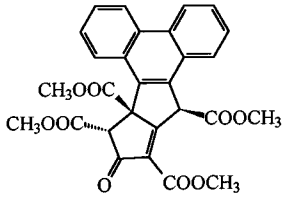
In connection with our efforts to prepare sulfur-containing derivatives of bicyclic diketones[12], we were able to isolate also the phosphorus-containing by-products and to identify them as the 2,4,6-tris(*p*-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphorinane 2,4,6-trisulfide (**4**) and the spiro compound **2**.

The trimeric (*p*-methoxyphenyl)thionophosphane oxide (**4**) was characterized for the first time by Lawesson et al.[13]. But nothing was reported until now about the isolation of labile spiro compounds like **2**.

All reaction mixtures contained an unknown by-product which could be isolated by column chromatography. The spectroscopic data did not allow its unequivocal structure assignment. Therefore, a suitable crystal of the by-product was subjected to an X-ray crystal structure analysis. As a result, the substance could be identified as tetramethyl-3(4*aH*)-oxo-1,4-dihydrophenanthro[9,10-α]pentalene-1,2,4,4a-tetracarboxylate (**6**, Scheme 3). But **6** could not be obtained by treatment of **1** with phosphorus pentasulfide. To our surprise, the treatment of cyclopentanone with Lawesson's reagent in boiling toluene[14] gave not a trace of this product (TLC detection). We conclude that four molecules of (*p*-methoxyphenyl)thionophosphane oxide in connection with **1** in a sequence of transformations (demethylation, aromatic cycloaddition, dimerization, ring contraction etc.) form **6** without incorporation of any atom of **1** into the resulting molecule **6**. The mechanism is not yet known.

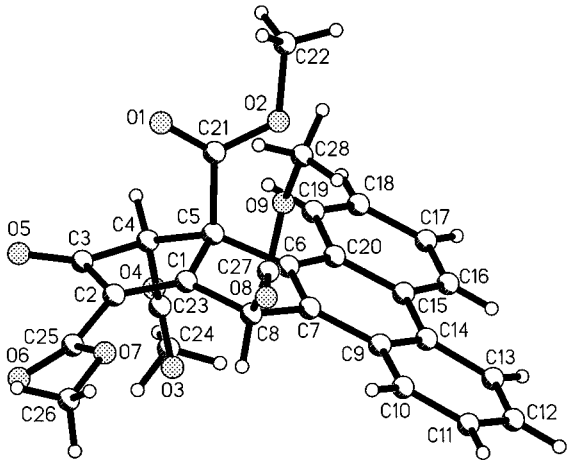
The molecular structure of **6** is shown in Figure 1. It has no unusual peculiarities from the geometric point of view. The phenanthrene fragment is planar in good approximation, the rms deviation of fitted atoms amounts to 0.024 Å. As expected, C6−C7 [1.361(3) Å] and C14−C15

Scheme 3



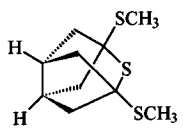
[1.459(3) Å] are the shortest and longest C−C bonds, respectively, within that fragment. The interatomic distances C1−C2 [1.332(3) Å] and C3−O5 [1.198(3) Å] agree well with the empirical average bond lengths for the C=C double bond in cyclopentenes [1.323(13) Å] and C=O double bond in cyclopentanones [1.208(7) Å], respectively, which have been retrieved from the Cambridge Structural Database[15].

Figure 1. Molecular structure and atom numbering of 3(4a*H*)-oxo-1,4-dihydrophenanthro[9,10-*a*]pentalene-1,2,4,4a-tetracarboxylate (**6**)

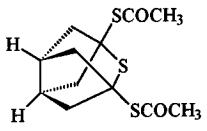


9-Thiatricyclo[3.3.1.$0^{3,7}$]nonane-1,5-dithiol (**5a**) reacts with iodomethane in the presence of potassium *tert*-butoxide to the 1,5-bis(methylthio) derivative **7** in good yield. Compound **5a** can be diacetylated to the corresponding bis(acetylmercapto) compound **8** by treating with acetic anhydride in boiling pyridine.

Scheme 4



7



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In conclusion, our experiments demonstrate that substituted *cis*-bicyclo[3.3.0]octane-3,7-diones **1a−c** react with Lawesson's reagent or phosphorus pentasulfide by intramolecular sulfide formation, rather than by intermolecular reaction known for a series of aliphatic ketones.

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Experimental Section

General: All reactions were carried out under argon. Melting points were determined with a Kofler hot stage microscope and are uncorrected. − IR: Perkin−Elmer FTIR spectrometer Spectrum 1000. − UV/Vis: Perkin−Elmer Lambda 14. − NMR: Bruker WP 200, AC 80 or Varian Gemini 200 or Unity 500. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ as solvent. − MS: AMD 402 of the AMD Intectra GmbH (70 eV). − Reactions were monitored by TLC using Merck DC Alufolien Kieselgel 60 F_{254} plates and were visualized under UV irradiation. − Column chromatography was performed with Kieselgel 60 (Merck; particle size 0.063−0.2 mm). − The elemental analyses were performed with the elementary analyser Vario El Foss Heraeus of Elementar Analysen Systeme GmbH. − *cis*-Bicyclo[3.3.0]octane-3.7-dione (**1a**)[7], *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**1b**)[7], and *cis*-1-ethyl-5-methylbicyclo[3.3.0]octane-3,7-dione (**1c**)[16][17] were prepared according to known literature procedures. − We were not able to find spectroscopic data for compound **1c** and so we describe this compound in detail.

cis-1-Ethyl-5-methylbicyclo[3.3.0]octane-3,7-dione (**1c**): Yield: 8.25 g (50%), colourless crystals, m.p. 51−53°C, R_f = 0.54 (silica gel, ethyl acetate/methanol 1:1), b.p. 150−170°C (0.7 Torr, kugelrohr distillation). − IR (capillary): $\tilde{\nu}$ = 1744 cm^{-1}, 1708 (C=O); in $CHCl_3$ solution: $\tilde{\nu}$ = 1742, 1706 (C=O); in CCl_4 solution: $\tilde{\nu}$ = 1746, 1716 (C=O). − ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.52 (q, 2 H, CH_2), 2.33 (s, 2 H, CH_2), 2.34 (s, 2 H, CH_2), 2.35 (s, 2 H, CH_2), 2.36 (s, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 9.7, 21.3, 26.9, 45.7, 47.5, 49.3, 51.2, 218.6. − MS (70 eV); *m/z* (%): 180 [M$^+$] (81), 165 (4), 138 (3), 111 (11), 95 (40), 83 (94), 67 (7), 55 (100). − $C_{11}H_{16}O_2$ (180.25): calcd. C 73.30, H 8.95; found C 73.42, H 9.07.

9-Thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiols **5** (Scheme 2). − *Typical Procedure:* 12 mmol (4.8 g) of Lawesson's reagent was added to a solution of 10 mmol of the bicyclic diketone **1a** in 50 ml of anhydrous toluene. The reaction mixture was heated at reflux under argon for 3 h, cooled to room temp. and extracted three times with 15 ml of 10% aqueous sodium hydroxide. The extracts were acidified with 2 N hydrochloric acid. The colourless crystalline product of **5a** was separated, washed with water and recrystallized several times from methanol/*n*-butanol (1:3). The organic layer was dried with anhydrous sodium sulfate. Solvent evaporation and silica-gel chromatography of the residue [elution with *n*-hexane/ethyl acetate (1:1), ethyl acetate, ethyl acetate/methanol (1:1)] gave three other products. The first fraction contained 2,4,6-tris(4-methoxyphenyl)-1,3,5,2,4,6-trioxatriphosphorinane 2,4,6-trisulfide (**4**)[13]. The second eluate contained a colourless solid, which could be identified as substance **2a**. Tetramethyl 3(4a*H*)-oxo-1,4-dihydrophenanthro[9,10-*a*]pentalene-1,2,4,4a-tetracarboxylate (**6**) was isolated from the third fraction.

Yield of **5a**: 650 mg (32%), colourless crystals, R_f = 0.73 [silica gel, *n*-hexane/ethyl acetate (1:1)], m.p. 140−142°C. − IR (KBr): $\tilde{\nu}$ = 1102 cm^{-1}, 1179, 1256, 1298, 1442, 1498, 2509 (SH), 2852, 2955. − UV/Vis (dichloromethane): λ_{max} (lg ε) = 374 nm (5.55), 469 (5.33). − ^{1}H NMR ($CDCl_3$): δ = 2.16 (m, 8 H, C-2,4,6,8), 2.32 (s, 2 H, 2 SH), 2.87 (m, 2 H, C-3,7). − ^{13}C NMR ($CDCl_3$): δ = 55.7 (C-1,5), 53.5 (C-2,4,6,8), 41.4 (C-3,7). − MS (70 eV); *m/z* (%): 204 [M$^+$] (89), 171 [M$^+$ − SH] (100), 137 (91), 111 (23), 97 (40). − $C_8H_{12}S_3$ (204.31): calcd. C 47.03, H 5.92, S 47.08; found C 48.10, H 5.54, S 46.17.

3,7-Dimethyl-9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol (**5b**): 1.66 g (10 mmol) of *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**1b**) was used according to the general procedure. Yield of **5b**: 510 mg (22%), colourless crystals, m.p. 157−158°C (ethanol), R_f = 0.74 (silica gel, *n*-hexan/ethyl acetate). − IR (KBr): $\tilde{\nu}$ = 1029 cm^{-1}, 1104, 1178, 1252, 1291, 1443, 1499, 2546, 2866, 2958. − ^{1}H NMR ($CDCl_3$): δ = 1.05 (s, 3 H, CH_3), 2.06 (s, 1 H, CH), 2.21 (s, 4 H, 2 CH_2). − ^{13}C NMR ($CDCl_3$): δ = 22.6 (CH_3), 49.1 (C-3,7), 55.1 (C-2,4,6,8−H_2), 57.2 (C-1,5). − MS (70 eV); *m/z* (%): 232 (70), 204 (55), 171 (100), 155 (57), 139 (38), 108 (22). − $C_{10}H_{16}S_3$ (232.42): calcd. C 51.69, H 6.94, S 41.39; found C 51.01, H 7.24, S 41.74.

3-Ethyl-7-methyl-9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol (**5c**): 1.80 g (10 mmol) of *cis*-1-ethyl-5-methylbicyclo[3.3.0]octane-3,7-dione (**1c**) was used according to the general procedure. Yield of **5c**: 599 mg (24%), pale yellow oil (colourless crystals after treatment with cold petroleum ether), m.p. 56−58°C, R_f = 0.70 [silica gel, *n*-hexane/ethyl acetate (1:1)]. − IR (KBr): $\tilde{\nu}$ = 1192 cm^{-1}, 1233, 1317, 1440, 2501, 2851, 2954. − ^{1}H NMR ($CDCl_3$): δ = 0.80 (q, 2 H, CH_2), 0.98 (s, 3 H, CH_3), 1.23 (t, 3 H, CH_3), 2.08 (s, 2 H, CH_2), 2.12 (s, 2 H, CH_2), 2.21 (s, 2 H, 2 SH), 2.28 (s, 2 H, CH_2), 2.31 (s, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 10.7 (CH_3CH_2), 22.7 (CH_3CH_2), 25.9 (CH_3), 46.1 (C-7), 50.6 (C-3), 51.1, 52.1, 58.2 (CSH). − MS (70 eV); *m/z* (%): 246 (76), 232 (42), 204 (83), 171 (100), 138 (90), 104 (68). − $C_{11}H_{18}S_3$ (246.46): calcd. C 53.61, H 7.36, S 39.03; found C 53.42, H 7.62, S 38.94.

Compound **2a** (R^1, R^2 = H, Scheme 1): Yield: 1.25 g (19%), R_f = 0.72 (silica gel, ethyl acetate), m.p. 146−148°C (methanol). − ^{1}H NMR ($CDCl_3$): δ = 2.03 (m, 10 H, C-2,4,6,8−H_2, C1,5−H), 3.88 (s, 6 H, 2 OCH_3), 6.98−7.04 (m, 4 H, CH), 8.08−8.11 (m, 4 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 40.1 (CH); 50.6, 53.6 (CH_2); 55.5 (OCH_3); 95.2 (C-3,7); 113.7, 113.9, 114.1, 114.3 (*m*-C_{aryl}); 133.81, 133.98, 134.13, 134.27 (*o*-C_{aryl}); 164.1 (*p*-C_{aryl}). − MS (70 eV); *m/z* (%): 542 (69), 526 (42), 510 (17), 419 (17), 356 (26), 340 (27), 217 (9), 202 (100), 186 (24), 170 (30), 139 (90). − $C_{22}H_{24}O_4P_2S_4$ (542.62): calcd. C 48.49, H 4.46, S 23.64; found C 48.63, H, 4.34, S 23.55.

Compound **2b** (R^1, R^2 = CH_3, Scheme 1): Yield: 0.90 g (14%), R_f = 0.70 (silica gel, ethyl acetate), m.p. 160−162°C (methanol). − MS (70 eV); *m/z* (%): 570 (53), 554 (53), 538 (18), 463 (19), 447 (73), 399 (64), 367 (34), 356 (26), 352 (18), 293 (61), 261 (67), 166 (100), 151 (26), 136 (84). − $C_{24}H_{28}O_4P_2S_4$ (570.69): calcd. C 50.51, H 4.95, S 22.47; found C 49.95, H, 4.64, S 22.58.

Compound **2c** could not be isolated due to thermal instability.

Tetramethyl 3(4aH)-Oxo-1,4-dihydrophenanthro[9,10-a]pentalene-1,2,4,4a-tetracarboxylate (**6**, Scheme 3): Yield: 1.41 g (28%), R_f = 0.61 (silica gel, ethyl acetate), m.p. 220−221.5°C subl. (BuOH or toluene). − IR (KBr): $\tilde{\nu}$ = 1435 cm^{-1}, 1505, 1666 (C=O), 1732 (br., 4 COOMe), 2850, 2954. − ^{1}H NMR ($CDCl_3$): δ = 3.13 (s, 3 H, OCH_3-1), 3.63 (s, 3 H, OCH_3-4), 3.69 (s, 3 H, OCH_3-4a), 3.94 (s, 3 H, OCH_3-1a), 4.73 (s, 1 H, HC-4a), 5.99 (s, 1 H, HC-1), 7.59 (m, 1 H, *J* = 15 Hz, CH-5), 7.67 (m, 2 H, *J* = 15 Hz, CH-6,7), 7.71 (m, 2 H, *J* = 9 Hz, CH-10,11), 8.26 (m, 1 H, *J* = 9 Hz, CH-12), 8.73 (m, 2 H, CH-8,9). − ^{13}C NMR ($CDCl_3$): δ = 52.3 (C-4a); 52.4, 52.5, 53.0, 53.8 (4 OCH_3); 65.3 (C-1); 67.0 (C-4); 123.4, 125.3, 126.1 (2 C); 127.1, 127.4, 127.5, 127.6, 127.7, 128.3, 131.4, 131.5, 133.7, 136.1 (C-phenanthrene, C-2); 161.6, 165.5, 168.0, 170.0 (4 $COOCH_3$); 186.5 (C-16); 194.3 (C-20). − MS (70 eV); *m/z* (%): 502 (16), 470 (100), 443(28), 411 (76), 383 (48), 355(7), 325 (18), 297 (7). − $C_{28}H_{22}O_9$ (502.47): calcd. C 66.92, H 4.41; found C 66.43, H 4.63.

Reaction of cis-Bicyclo[3.3.0]octane-3,7-dione with Phosphorus Pentasulfide: 20 mmol (4.44 g) of phosphorus pentasulfide was added to a solution of 10 mmol of *cis*-bicyclo[3.3.0]octane-3,7-dione (**1a**) in 25 ml of diglyme. The mixture was stirred vigorously at 30°C under argon and 80 mmol (6.72 g) of $NaHCO_3$ was added in three portions. After 5 h, the solution was cooled in an ice bath, acidified with 2 N hydrochloric acid, and extracted with three 20-ml portions of diethyl ether. The ether extracts were combined, washed with water and dried with anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 0.99−1.15 g (49−56%) of 9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiole (**5a**).

The analogous reaction of *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (**1b**) gave 825 mg (36%) of 3,7-dimethyl-9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol (**5b**); the corrersponding reaction of **1c** gave **5c** in 33% yield (813 mg).

Treatment of *cis*-bicyclo[3.3.0]octane-3,7-dione with phosphorus pentasulfide in boiling toluene under argon provided besides some polymeric material only 350 mg (17%) of 9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiole (**5a**).

1,5-Bis(methylthio)-9-thiatricyclo[3.3.1.0^{3,7}]nonane (**7**): A three-necked, 100-ml round-bottomed flask was charged under argon with 1 mmol (200 mg) of 9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol (**5a**) and 15 ml of dry DMSO. To this solution, cooled in an ice bath, 2 mmol (224 mg) of potassium *tert*-butoxide was added. Stirring was continued for an additional 30 min and 2 mmol (0.13 ml) of iodomethane was added. The resulting reaction mixture was stirred for a few min, then allowed to stand overnight. The mixture was poured onto crushed ice and the product was isolated by thorough extraction with chloroform. The extracts were combined, washed with water, and dried with sodium sulfate. The solvent was evaporated in a rotary evaporator under reduced pressure and the crude **7** was purified by recrystallization to afford colourless needles. − Yield: 150 mg (65%), m.p. 126−127.5°C (acetonitrile). − ^{1}H NMR ($CDCl_3$): δ = 2.08−2.17 (m, 6 H, 2 CH_2, CH), 2.32 (s, 6 H, 2 SCH_3), 2.72−2.84 (m, 6 H, 2 CH_2, CH). − MS (70 eV); *m/z* (%): 232 (85), 218 (32), 204 (39), 171 (100), 137 (69), 111 (42), 97 (64). − $C_{10}H_{16}S_3$ (232.43) : calcd. C 51.68, H 6.94, S 41.39; found C 51.53, H, 6.70, S 41.50.

1,5-Bis(acetylmercapto)-9-thiatricyclo[3.3.1.0^{3,7}]nonane (**8**): 2 mmol of freshly distilled acetic hydride, 1 mmol (200 mg) of 9-thiatricyclo[3.3.1.0^{3,7}]nonane-1,5-dithiol (**5a**) and 10 ml of dry pyridine were placed in a 50-ml round-bottomed flask and the resulting mixture was refluxed for 5 h producing a clear brown solution. After cooling to room temp., the reaction mixture was poured into 50 ml of ice/water. The precipitate was extracted with dichloromethane and the combined organic layers were washed with 10% hydrochloric acid and water until neutral reaction was reached. The extracts are dried with potassium carbonate. Potassium carbonate was removed by filtration and the solvent was evaporated under reduced pressure. The residue was recrystallized from *n*-butanol to give colourless needles. − Yield: 130 mg (65%), m. p. 154−155°C (*n*-butanol) − IR (KBr): $\tilde{\nu}$ = 1022 cm^{-1}, 1142, 1186, 1275, 1298, 1446, 1508, 1724 (C=O), 2852, 2955. − ^{1}H NMR ($CDCl_3$): δ = 2.28−2.37 (m, 6 H, 2 CH_2, CH), 2.39 (s, 6 H, 2 $COCH_3$), 2.57−2.74 (m, 6 H, 2 CH_2, CH). − $C_{12}H_{16}O_2S_3$ (288.45): calcd. C 49.97, H 5.59, S 33.35; found C 49.63, H, 5.34, S 33.55.

X-Ray Crystallographic Study[18]: Crystal data: $C_{28}H_{22}O_9$; *M* = 502.46; *a* = 10.112(1), *b* = 18.761(2), *c* = 12.806(1) Å, β = 99.14(1)°, *V* = 2398.6(4) Å^3, *Z* = 4, *d* = 1.391 Mg/m^3; crystal system: monoclinic; space group: $P2_1/n$. Data collection: Stoe Stadi4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, crystal size: 0.68 × 0.53 × 0.42 mm, ω/2Θ scanning mode; Θ range: 1.9−30.0°; reciprocal lattice segments: *h*, *k*, *l* ranges from $\overline{14}$, 0, $\overline{17}$ to 14, 26, 0 and $\overline{14}$, $\overline{26}$, 0 to 14, 0, 17; reflections measured: 13929, symmetry-independent reflections: 6964, observed reflections [$I > 2\sigma(I)$]: 4270; μ = 0.105 mm^{-1}. Structure analysis and refinement: structure solution by direct methods; structure refinement by full-matrix least squares on F^2, non-H atoms with anisotropic displacement parameters, H atoms located in a difference Fourier map and refined with isotropic displacement parameters except methyl H atoms which were geometrically positioned and treated as rotating group riding on the corresponding C atom; 6936 F_o/378 parameters in the final refinement; R = 0.0616 (observed data) and R_w (F^2) = 0.1801 (all data). Programmes used: STADI4[19], X-RED[20], SHELXS-86[21], SHELXL-93[22], and XP/PC[23].

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