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SYNTHESIS AND STRUCTURAL ANALYSIS OF 3,6,8,11,16-HEXAHYDRODICYCLOHEPTA[*c,h*][1,6]DITHIECIN

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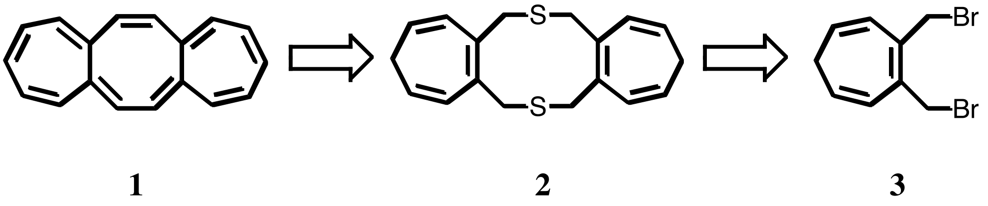
Abstract – The cycloaddition reaction of 3,6,9-trihydrocyclohepta[*c*][1,2]dithiin (**5**), prepared from 3,4-bis(bromomethyl)-1,3,5-cycloheptatriene (**3**) in two steps, with 3,4-dimethylene-1,5-cycloheptadiene (**6**) in the presence of boron trifluoride-etherate gave 3,6,8,11,16-hexahydrodicyclohepta[*c,h*][1,6]dithiecin (**2**). The temperature-dependent NMR study indicated that **2** possesses the fluxional tetrahydrodithiecin moiety in solution at room temperature. The X-Ray crystal structure analysis showed that **2** has an S-letter shape which was supported as the most stable conformer by DFT molecular orbital calculations.

INTRODUCTION

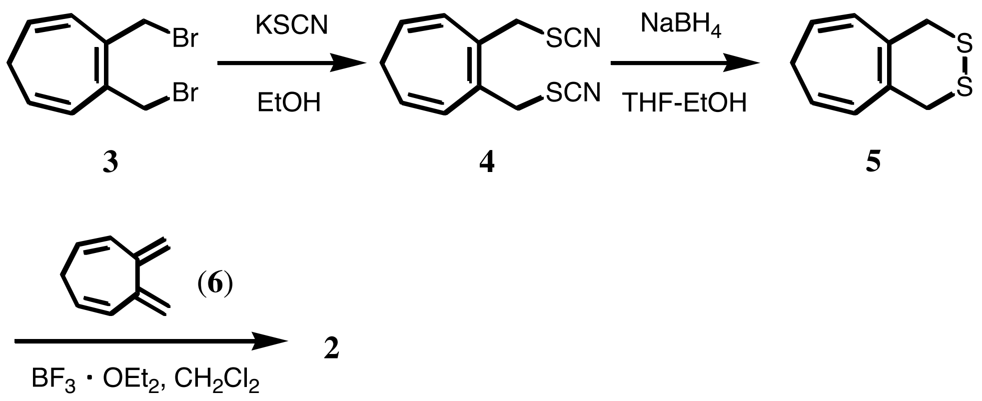
Structural and conformational analysis of medium- to large-sized flexible heterocycles has been studied for the past three decades.[1] Results of the analysis are of great importance to interpret and predict their physical and chemical behavior such as the transannular nonbonding contact between heteroatoms and the chelating ability of the core site.[2] Meanwhile, in our synthetic program toward dicyclohepta-[*a,e*]cyclooctene (**1**),[3] a nonalternant tricyclic unsaturated hydrocarbon which consists of seven- and eight-membered rings and potentially is aromatic with a perimetrical 18π-electron array, we envisage that desulfurization of the title dithiecin, 3,6,8,11,14,16-hexahydrodicyclohepta[*c,h*][1,6]dithiecin (**2**), is one promising route to construct the carbon framework of **1**. In this note we report the synthesis and the structural and conformational analysis of **2**.



Scheme 1

RESULTS AND DISCUSSION

The 3,4-bis(bromomethyl)-1,3,5-cycloheptatriene (**3**)[4] was reacted with potassium thiocyanate in refluxing ethanol to give a quantitative yield of bisthioisocyanate (**4**), which was transformed to 3,6,9-trihydrocyclohepta[*c*][1,2]dithiin (**5**) in 70% yield by treatment with sodium borohydride in a mixture of ethanol and THF. Reaction of **5** with 3,4-dimethylene-1,5-cycloheptadiene (**6**),[4] which can be prepared from **3** by reduction with activated zinc powder, in the presence of boron trifluoride-etherate in



Scheme 2

Table 1. Reaction between **5** and **6** with various Lewis acids

entry	Lewis acid	conditions	yield (%) of **2**
1	Et_2AlCl	rt, 72 h, $CHCl_3$	1
2	$AlCl_3$	0 °C, 24 h, CH_2Cl_2	8
3	$SnCl_4$	0 °C, 48 h, CH_2Cl_2	6
4	$BF_3 \cdot OEt_2$	rt, 24 h, $CHCl_3$	15
5	$BF_3 \cdot OEt_2$	rt, 18 h, CH_2Cl_2	18
6	$BF_3 \cdot OEt_2$	rt, 22 h, Et_2O	11
7	$TiCl_4$	0°C, 24 h, CH_2Cl_2	4

dichloromethane gave **2** as colorless prisms in 18% yield.[5] The cycloaddition under other reaction conditions with various Lewis acids, such as stannic chloride, titanium chloride, and aluminum chloride gave lower yields of **2** accompanied with a gummy substance, probably due to the slightly acid-sensitive nature of **6** (Table 1).

Compound (**2**) was characterized well by spectroscopic and combustion analyses. In the ^{1}H NMR spectrum of **2** in a tetrachloroethane-d_2 solution at room temperature, signals of both methylene protons at the seven-membered and the tetrahydro[1,6]dithiecin rings were observed broadened. The seven-membered ring protons appeared as a triplet and the tetrahydrodithiecin ring protons as a singlet at 110 °C. Both the signals coalesced simultaneously at 29 °C, and the former appeared as two doublets and the latter as two doublets of a triplet at –30 °C (Figure 1). On the basis of these results, free energy of activation

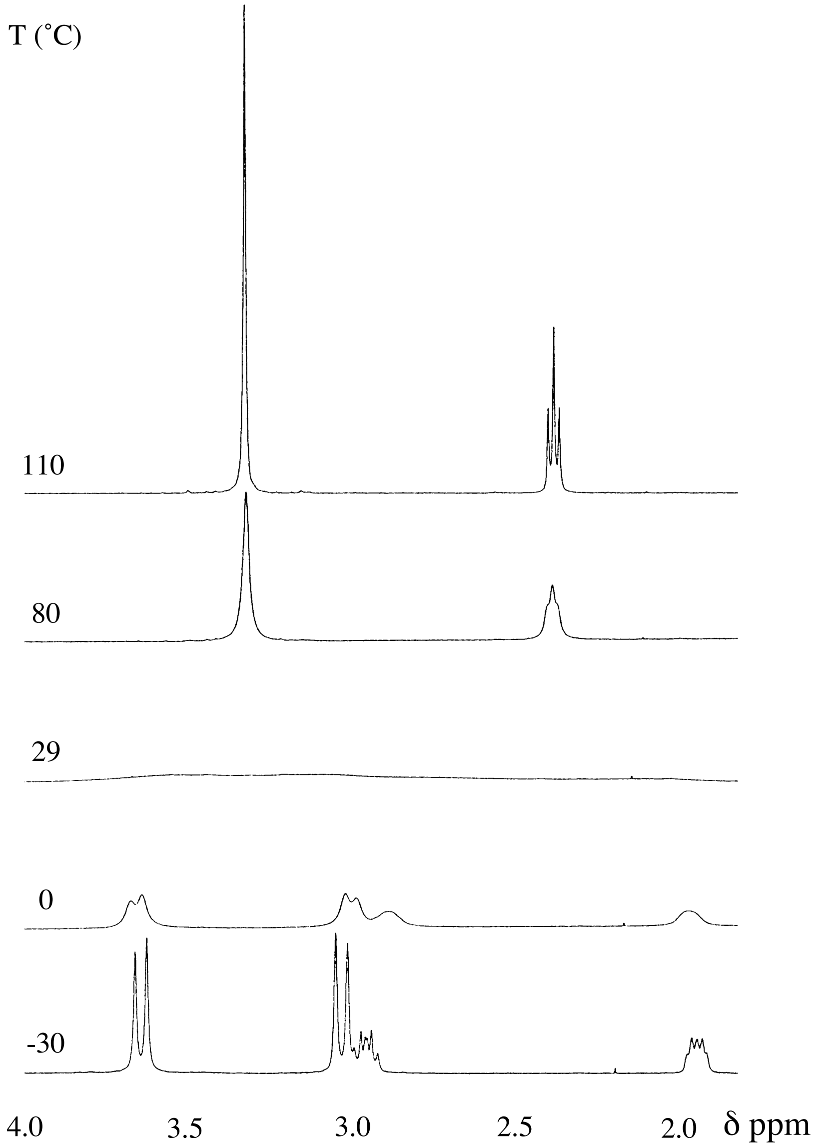


Figure 1. Variable temperature ^{1}H NMR spectra of **2** in tetracholoethane-d_2

for the dynamic process was estimated to be approximately 13.5 kcal mol^{-1}.[6] Since ring inversion of cycloheptatrienes is known as a fast process with activation energy of less than 6 kcal mol^{-1},[7] this observed dynamic process in **2** can be attributed to inversion of the central tetrahydrodithiecin ring. Lehn et al. previously reported that the ring inversion process of deuterated 2,5,7,10-tetrahydro[1,6]dithiecin has the comparable activation energy of 12.6 kcal mol^{-1} with the coalescence temperature (–24 ˚C).[8] Selegue et al. described the fluxional nature of the tetrahydro[1,6]dithiecin ring in its 3,4,8,9-tetrachloro derivative,[9] though its dynamic behavior has not been clarified because of its low solubility.

The crystal structure of **2** was elucidated by X-Ray crystallographic analysis. Selected crystal data for **2** are shown in Table 2 and the ORTEP drawing and crystal packing are in Figure 2. The crystal structure of **2** shows symmetry of an inversion center and two halves of the molecule are occupied in a unit cell. The S1-S1* atom distance is 5.341 Å. The tetrahydro[1,6]dithiecin ring possesses a puckered form with the chair-like conformation and two cycloheptatrienes have a boat form with an anti configuration to each other. Thus, two bows of the cycloheptatrienes bend in the opposite direction to each other toward the inner side of this molecule. Thus, a side view of the structure from the shorter molecular axis appears as an S-letter shape. The structure of the cycloheptatriene part of **2** in crystal state is very similar to that of 1,3,5-cycloheptatriene (**8**) itself in the vapor phase analyzed by the microwave method.[10,11] The bending angles[12] of the bow and stern of the cycloheptatriene part in **2** and **8** are similar as shown in Table 3. Although there are reported crystal structures of many cycloheptatriene derivatives,[13] only one derivative without a substituent at the 7 position, 2,5-dimethyl-3,4-diphenylcycloheptatriene (**9**), was documented in the literature so far.[14] The bending of **9** is clearly greater than those of **2** and **8**, probably because of steric

Table 2. Selected crystal data and details of structure determination of **2**

Empirical formula	$C_{18}H_{20}S_2$
Crystal color, habit	colorless, prismatic
Crystal dimensions	0.40 × 0.40 × 0.40 mm
Crystal system	triclinic
Lattice type	primitive
Omega scan peak width at half-height	0.25°
Lattice parameters	a = 7.233 (2) Å, b = 8.348 (2) Å, c = 6.583 (3) α = 105.96 (2)°, β = 95.45 (3)° γ = 92.79 (2)° V = 379.3 (2) $Å^3$
Space group	$P\bar{1}$ (#2)
Z value	1
D_{calc}	1.315 g/cm^3
F_{000}	160.00
μ(MoKα)	3.38 cm^{-1}
Residuals: R1	0.032
Goodness of fit indicator	1.39

hindrance between the methyl and the phenyl substituents. Therefore, the bending observed in the crystal structure of **2** is surprisingly an example revealing the least perturbed form of the cycloheptatriene part.[15]

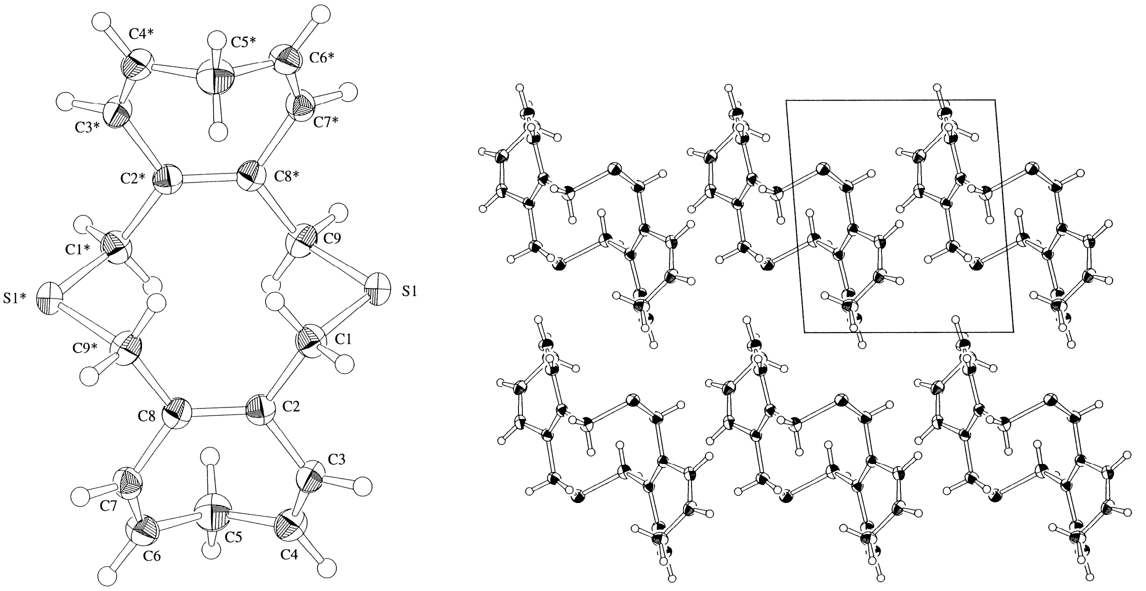
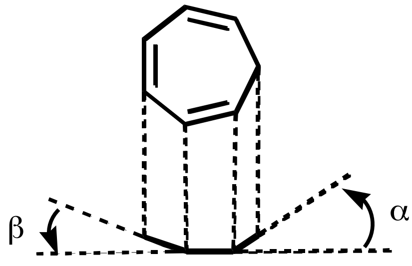


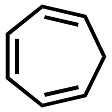
Figure 2. An ORTEP drawing and crystal packing along the *c* axis in the crystal of **2** showing our numbering system

Table 3. Bending angles of cycloheptatrienes.

compound	α (in degree)	β (in degree)
2[a]	51.6	28.8
8	50 ± 5[b] 49.5[c]	29.5 ± 4[b] 28[c]
9[d]	52.6	34.3

[a] Results of this study. [b] Taken from ref 10. [c] Results of MM2 calculations. Taken from ref 11. [d] Taken from ref 14.

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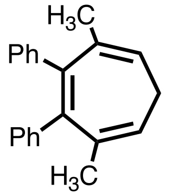
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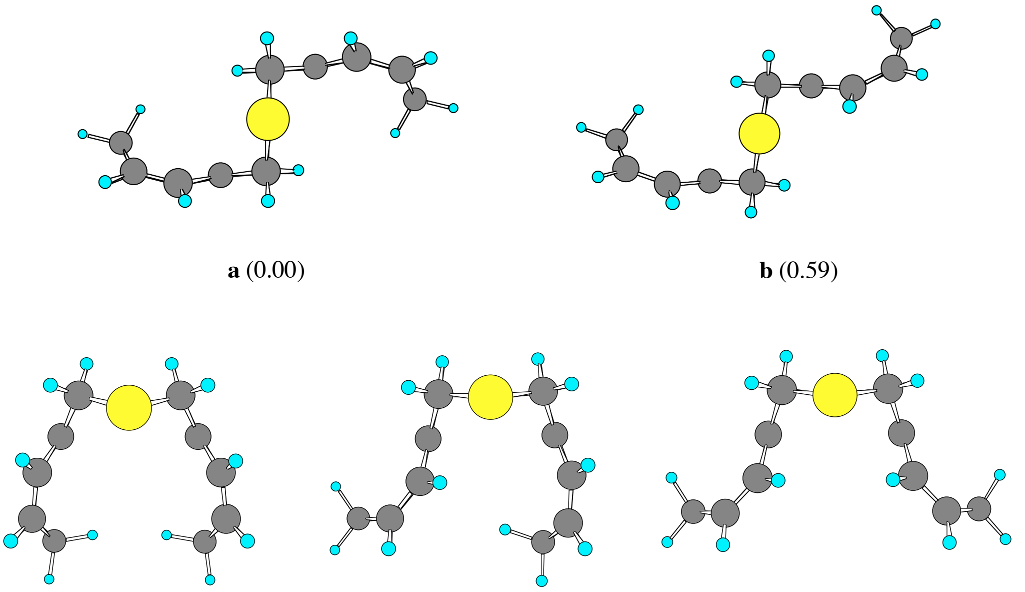
DFT calculations of **2** at the B3LYP/6-31G (d) level of theory predict many conformations, among which five conformers (**a**–**e**), shown in Figure 3, were more stable than others.[16] The tetrahydrodithiecin ring can have mainly puckered and folded conformations. The conformers (**a** and **b**), whose tetrahydrodithiecin ring appears as a Z-letter shape when viewed from the short molecular axis, belong to the former and the conformers (**c**,**d** and **e**) to the latter. The conformers (**a** and **b**) have less angle strain in the ring, thus are more stable than the latter. The most stable conformer (**a**), whose gross shape appears as an S-letter when viewed from the short molecular axis, is quite similar to the crystal structure. The differences in bond lengths and bond angles between the calculated and crystal structures are less than 0.033 Å and 1.54°, respectively, suggesting that results of DFT calculations at the level are valuable also for conformational analysis of a medium-sized ring containing heteroatoms.



a (0.00) **b** (0.59)

c (4.63) **d** (2.93) **e** (4.10)

Figure 3. The conformers (Chem 3D output) generated by B3LYP/6-31G (d) calculations for **2.** Their relative total energies (in kcal mol^{-1}) to that of the conformer (**a**) are in parentheses.

SUMMARY

We have synthesized a novel tetrahydro[1,6]dithiecin derivative (**2**) fused with two cycloheptatriene rings by the cycloaddition between the [1,2]dithiin (**5**) and (**6**). The variable temperature NMR study of **2** indicates the fluxional nature of the [1,6]dithiecin ring and the solid state structure obtained by X-Ray crystallographic analysis reveals the puckered chair-like conformation of the tetrahydrodithiecin ring and the boat conformation of the cycloheptatriene rings.

EXPERIMENTAL

IR spectra were recorded on a JASCO IR-810 spectrophotometer. UV spectra were measured on a Shimadzu UV-256FS spectrophotometer. ^{1}H (400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded with tetramethylsilane as an internal standard on a JEOL α400 spectrometer. MS spectra were measured on a JEOLJMS-D-300 mass spectrometer. Potassium thiocyanate was purchased from Wako Chem. Co., and sodium borohydride and boron trifluoride-etherate were from Tokyo Kasei Industry, Inc. Column chromatography was done with Merck Kieselgel 60 Art 7734. The starting materials (**3**) and (**6**) were prepared by the literature method.[4] Density functional calculations were conducted using the Gaussian 98 package[17] on an HPC-AlphaUP264/667FF-1024U computer. Total energies used were the values corrected by zero-point energies obtained in the frequency calculations.

3,4-Bis(bromomethyl)-1,3,5-cycloheptatriene (3):[4] a colorless oil. ^{1}H NMR ($CDCl_3$) δ = 2.29 (t, *J*= 6.8 Hz, 2H), 4.31 (s, 4H), 5.59 (dt. *J*= 9.5, 6.8 Hz, 2H), 6.15 (d, *J*= 9.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ = 27.4, 31.5, 124.6, 128.3, 138.8. MS (70 eV) *m/z* (rel intensity): 278 (M^+, 7), 199 (35), 185 (16), 183 (16), 1185 (45), 117 (100), 115 (29), 91 (37), 51 (16). HRMS calcd for $C_9H_{10}{}^{79}Br^{81}Br$: 277.9310, found: 277.9291. *Caution: This compound is a potent lachrymator.*

3,4-Dimethylene-1,5-cycloheptadiene (6):[4] an air-sensitive colorless oil. ^{1}H NMR ($CDCl_3$) δ = 3.02 (m, 2H), 4.90 (d, *J*= 1.6 Hz, 2H), 5.40 (d, *J* =1.6 Hz, 2H), 5.57 (dt. *J*= 11.2, 4.9 Hz, 2H), 6.02 (dm, *J* = 11.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ = 31.4, 115.7, 127.3, 129.8, 145.8. MS (70 eV) *m/z* (rel intensity): 118 (M^+, 29), 117 (49), 91 (35), 43 (51), 28 (100). HRMS calcd for C_9H_{10}: 118.0781, found: 118.0776. A 1:1 TCNE adduct: mp 146-149 °C. Anal. Calcd for $C_{15}H_{10}N_4$: C, 73.16; H, 4.09; N, 22.75%. Found: C, 73.36; H, 4.40; N, 22.72%.

3,4-Bis(thioisocyanomethyl)-1,3,5-cycloheptatriene (4).

A mixture of 3.39 g (12.2 mmol) of **3** and 4.80 g (49.4 mmol) of potassium thiocyanate in 200 mL of ethanol was refluxed for 4 h. Solids formed were removed by suction filtration and the filtrate was evaporated. The residue was diluted with 200 mL of water and extracted with ether (60 mL×3). The combined organic layer was washed with brine and was dried with $MgSO_4$. The solvent was removed and the residue was purified by recrystalization from ether-hexane to give 2.83 g (99% yield) of **4** as colorless needles. mp 100-102 °C. ^{1}H NMR ($CDCl_3$) δ = 2.41 (t, *J*= 6.8 Hz, 2H), 4.02 (s, 4H), 5.71 (dt. *J*= 9.3, 6.8 Hz, 2H), 6.15 (d, *J*= 9.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ = 27.6, 36.4, 111.3, 126.9, 127.5, 135.9. IR (KBr) 2950w, 2145s, 1455m, 1430w, 1390w, 1120m, 1200w, 890w, 860w, 805w, 770w, 710m, 635m cm^{-1}. MS (70 eV) *m/z* (rel intensity): 234 (M^+, 3), 176 (9), 175 (39), 172 (15), 162 (6), 148 (17), 118 (43), 117 (100), 59 (35). HRMS calcd for $C_{11}H_{10}N_2S_2$: 234.0284, found: 234.0340. Anal. Calcd for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95%. Found: C, 56.52; H, 4.43; N, 11.89%.

3,6,9-Trihydrocyclohepta[*d*][1,2]dithiin (5).

To a solution of 0.554 g (2.36 mmol) of **4** in a mixture of THF (70 mL) and ethanol (3 mL) was added 89.0 mg (2.35 mmol) of sodium borohydride. After being stirred at rt for 2.5 h, the reaction mixture was poured into cold diluted hydrochloric acid (200 mL) and extracted with ether (100 mL×5). The combined organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed and the residue was purified by chromatography (SiO_2, hexane) to give 302 mg (70% yield) of **5** as a colorless oil. ^{1}H NMR ($CDCl_3$) $\delta = 2.25$ (t, *J*= 6.8 Hz, 2H), 3.61 (s, 4H), 5.49 (dt. *J*= 9.5, 6.8 Hz, 2H), 5.84 (d, *J*= 9.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) $\delta = 27.4$, 33.7, 123.4, 129.5, 133.4. IR (film) 3010s, 2950s, 2910s, 2875s, 1695w, 1615m, 1560w, 1540w, 1460m, 1435s, 1395s, 1300m, 1215w, 1190w, 860w, 785m, 750m, 710s cm^{-1}. MS (70 eV) *m/z* (rel intensity): 182 (M^+, 16), 149 (16), 118 (43), 117 (100), 115 (28), 103 (14), 91 (32), 77 (15), 64 (38), 39 (21). HRMS calcd for $C_9H_{10}S_2$: 182.0220, found: 182.0220.

3,6,8,11,16-hexahydrodicyclohepta[*c,h*][1,6]dithiecin (2).

To a solution of 0.590 g (3.24 mmol) of **5** and 0.602 g (5.09 mmol) of **6** in 20 mL of dichloromethane was added 0.50 ml (3.95 mmol) of borontrifluoride-etherate under nitrogen atmosphere. After being stirred at rt for 18 h, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane (50 mL×3). The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried with anhydrous $MgSO_4$. The solvent was removed and the residue was purified by chromatography (SiO_2, benzene:hexane = 4:6) to give 179 mg (18% yield) of **2** as colorless prisms and recovery of **5** (0.203 mg, 39%). mp 260-261 °C. ^{1}H NMR (DMSO-d_6, at 110 °C) $\delta = 2.33$ (t, *J*= 6.8 Hz, 4H), 3.33 (s, 8H), 5.55 (dt. *J*= 9.8, 6.8 Hz, 4H), 6.05 (d, *J*= 9.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) $\delta = 28.2$, 31.3, 124.7, 129.5, 133.6. IR (film) 3010w, 2980w, 2960w, 2820w, 1640w, 1435m, 1390m 1308w, 1238w, 980w, 918w, 865w, 800m, 790m, 723m, 698s, 670w, 640w cm^{-1}. MS (70 eV) *m/z* (rel intensity): 300 (M^+, 18), 150 (38), 149 (100), 148, 147, 118 (24), 117 (51), 115 (40), 104 (31), 91 (27), 77 (15), 64 (38), 39 (21). HRMS calcd for $C_{18}H_{20}S_2$: 300.1002, found: 300.0871. Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71%. Found: C, 71.59; H, 6.66%.

X-Ray crystallographic analysis of 2.

A single crystal sample of 2 was prepared by recrystallization from a mixture of acetone, dichloromethane, and hexane. A colorless prismatic crystal having approximate dimensions of 0.40 x 0.40 x 0.40 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squared refinement using the setting angles of 25 (2θ range; 29.5 - 30.0°) carefully centered reflections in the range 300.48, the calculated density is 1.32 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (#2). The data were intensities of three representative reflections measured after every 150 reflections. No decay correction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1600 observed reflections [$I > 3.00\sigma(I)$] and 92 variable parameters: $R = 0.032$, $Rw = 0.058$. Crystallographic data excluding structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 298905 for **2**. A copy of the data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ. UK [DIRECT LINE: +44 1223 762910, Fax: +44 (0) 1223-336033 or e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk.

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