Synthesis of Pentathiepanes and Isolation of the Conformers Based on High Inversion Barrier of the Pentathiepane Ring

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Acenaphtho[1,2-*a*]acenaphthylene (**1**) was sulfurated with elemental sulfur to give a pentathiepane derivative (**2**). A dynamic NMR spectrum analysis revealed that the two naphthalene rings of **2** are chemically nonequivalent up to 100 °C. The pentathiepane ring of **2** was shown to adopt a chair conformation both in solution and crystals. In accordance with the NMR spectrum analysis, the sulfuration of 5-phenylacenaphtho[1,2-*a*]acenaphthylene (**12**) gave a pair of conformers (**16a** and **16b**), which were isolated in pure form. The Friedel–Crafts acetylation of **2**, followed by dithioacetalization with 1,2-ethanedithiol, also gave a pair of isolable conformers (**18a** and **18b**). These two pairs of conformers isomerized, as a result of the ring inversion, to each other in solution at room temperature in the first-order kinetics. The activation parameters for this process, E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, were determined. Based on the experimental observations, a probable mechanism for the inversion process is proposed.

Introduction

Recently, much attention has been paid to the chemistry of cyclic oligosulfides from a standpoint of physical and chemical properties as well as that of biological activities.[1,2] Particularly, since the isolation of naturally occurring benzopentathiepins, varacins and lissoclinotoxins,[3,4] from marine organisms, the chemistry of 1,2,3,4,5-pentathiepins, which consist of five sulfur atoms and two vicinal sp^2 carbons, has been under brisk investigation.[2] The conformation of 1,2,3,4,5-pentathiepins in crystals was found to be a chair by X-ray analysis.[5] Molecular mechanics[4e] and ab initio molecular orbital[6] calculations also revealed that the chair conformation is the most stable. Varacins and lissoclinotoxins were claimed to be chiral because of slow inversion of the pentathiepin ring on the NMR time scale.[4d,4e] Indeed, recently, the conformers due to the slow inversion of the benzopentathiepin ring were isolated, and the activation parameters for the ring inversion were determined by analysis of the NMR spectra.[7] Meanwhile, although the chemistry of 1,2,3,4,5-pentathiepanes, a saturated analog of pentathiepins, has been also studied mainly from interest in syntheses and reactions,[1,8−12] their conformational study has been limited. Pentathiepanes are generally labile and decompose to 1,2,3-trithiolanes and elemental sulfur during purification procedures such as silica-gel column chromatography[12] and distillation (80°C/0.05 mmHg).[9] In addition, an equilibrium of a pentathiepane with the corresponding trithiolane and elemental sulfur is rapidly attained in polar solvents, whilst the reverse process is slow.[9a] In these cases, the equilibrium lies to the trithiolane side. This will explain that the conformational analysis of 1,2,3,4,5-pentathiepanes has not been examined in detail. We report here the synthesis of pentathiepanes, which are so thermally stable and have such a high inversion barrier that they enabled us to isolate a pair of conformers in pure form and to characterize their conformation by NMR spectroscopy and X-ray single-crystal analysis.[13]

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Results and Discussion

Three methods are available for preparation of 1,2,3,4,5-pentathiepanes; 1) sulfuration of alkenes with elemental sulfur in the presence or absence of a catalyst,[9a,10,11] 2) reactions of 1,2-bis(chlorothio)ethanes with S_3^{2-} reagents,[12] and 3) the Diels−Alder reaction of the parent 1,2,3,4,5-pentathiepin with cyclopentadiene.[8] Among them, sulfuration of alkenes is apparently the simplest, and thus the method of our choice, although it often produces mixtures of pentathiepanes and trithiolanes. The alkene of our choice is acenaphtho[1,2-*a*]acenaphtylene (**1**).[14] The D_{2h} symmetry of **1** would not only make a product analysis easier but also enable us to do a conformational study of the sulfuration product.[15,16] Thus, the sulfuration was carried out by heating **1** with elemental sulfur (1 equivalent as S_8) in DMF at 130°C. The reaction gave the pentathiepane (**2**), with a [5.3.3]propellane structure,[17] as the sole product in 88% yield. The formation of trithiolane (**3**), often noted in sulfuration of other alkenes, was not observed. The pentathiepane (**2**), obtained as colorless crystals, decomposed at 248°C to form **1** and sulfur. The pentathiepane (**2**) showed two doublets of doublets at δ = 7.61 and 7.66 and four doublets at δ = 7.73, 7.76, 7.77, and 7.82 in the ^{1}H-NMR spectrum, and twelve peaks due to the aromatic carbons in the range δ = 120.9−143.4 and one peak due to the bridgehead carbons at δ = 96.7 in the ^{13}C-NMR spectrum, revealing the nonequivalency of the two naphthalene rings. The dynamic NMR spectra in [D_8]toluene, monitored from 25°C to 100°C, showed that neither the coalescence nor the broadening of the signals took place. These observations

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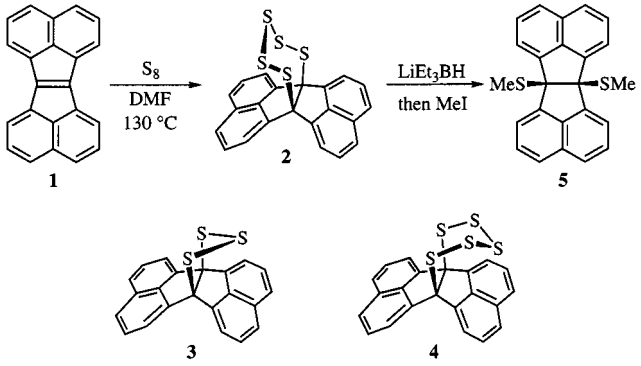
hint that the ring inversion of the pentathiepane ring did not occur at least up to 100°C on the NMR time scale. Reduction of **2** with $LiEt_3BH$, followed by treatment with MeI, gave a 66% yield of the bis-sulfide (**5**). As expected, the two naphthalene rings of **5** are equivalent. Thus, the ^1H NMR spectrum of **5** showed a doublet of doublets at δ = 7.55, two doublets at δ = 7.63 and 7.77, and one singlet at δ = 1.92. The ^{13}C-NMR spectrum showed six peaks due to the aromatic carbons in the range δ = 121.1−145.0, one peak due to the benzylic carbon at δ = 77.0, and one peak due to the methyl carbon at δ = 16.0. Therefore, the above NMR data can best be explained by assuming the chair structure of **2** with a C_S symmetry, in which the two naphthalene rings are placed in a different environment. The boat conformation (**4**), although it can also explain the NMR data, would be unfavorable because of steric and electronic repulsive interactions between the sulfur ring and the naphthalene ring.[15]



Scheme 1

The molecular structure of **2** was determined by single crystal X-ray analysis. An ORTEP drawing of **2** is given in Figure 1 and the selected bond lengths and angles data are listed in Table 1. In agreement with the prediction by the NMR analysis, **2** adopts a typical chair conformation in which the pentathiepane ring is fixed over one of the naphthalene rings. Interestingly, the C(1)−C(2) bond length of **2**, 1.63 Å, is much longer than those of common carbon-carbon single bonds. It is also much longer than the corresponding C−C bond length of the previously reported 6-trimethylsilyl-1,2,3,4,5-pentathiepane (**6**, 1.52 Å) that exists in a twist-boat conformation.[10] Also noteworthy is that the S(1)−C(1)−C(naph2) and S(5)−C(2)−C(naph4) bond angles of 112.9° and 113.0°, are much larger than S(1)−C(1)−C(naph1) and S(5)−C(2)−C(naph3), 102.3° and 102.8°, probably due to the repulsive interactions between the pentathiepane ring and the naphthalene ring containing the C(naph2) and C(naph4) atoms.

The above observations suggest that introduction of a proper substituent of one of the naphthalene rings of **2** would result in the formation of a pair of separable conformers. We therefore first attempted to introduce an ethyl group into the 5-position of **2**. Thus, 3-ethylacenaphtho[1,2-*a*]acenaphthylene (**7**) was prepared starting from 5-acetylacenaphthene (**8**) (Scheme 2). The acenaphthene (**8**) was treated with 1,2-ethanedithiol in the presence of $BF_3 \cdot OEt_2$

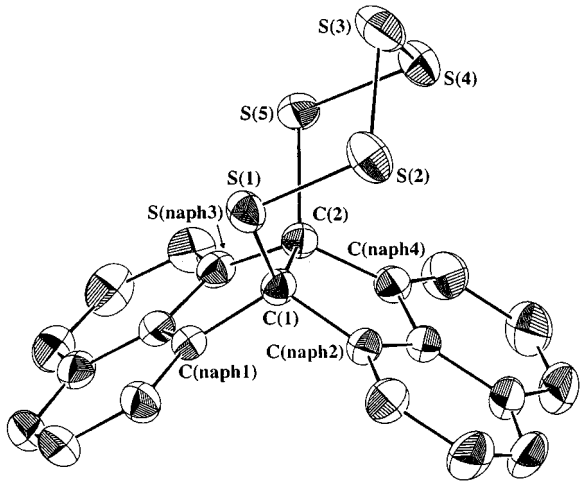


Figure 1. An ORTEP drawing of **2** (50% probability ellipsoids, hydrogen atoms omitted for clarity)

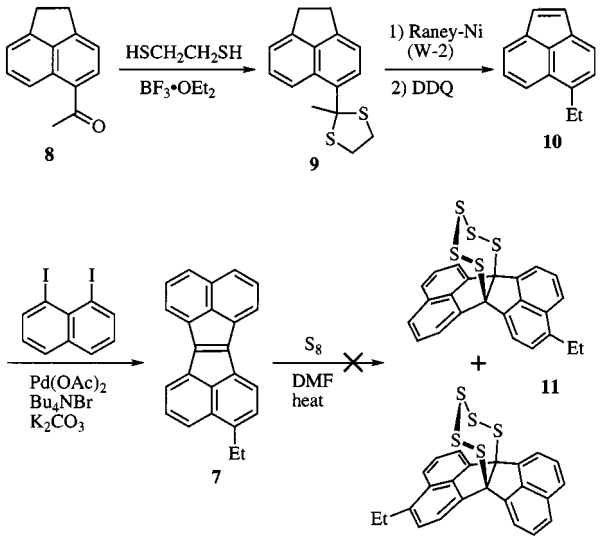
Table 1. Selected bond lengths [Å] and bond angles [°] of **2**

Bond lengths		Bond angles	
C(1)−C(2	1.633(3)	C(1)−C(2)−S(5)	119.4(2)
C(1)−S(1)	1.842(3)	C(2)−C(1)−S(1)	119.6(2)
C(2)−S(5)	1.838(3)	C(1)−S(1)−S(2)	106.4(1)
S(1)−S(2)	2.037(1)	C(2)−S(5)−S(4)	105.1(1)
S(2)−S(3)	2.059(1)	S(1)−S(2)−S(3)	103.8(1)
S(3)−S(4)	2.051(2)	S(2)−C(3)−S(4)	104.1(1)
S(4)−S(5)	2.038(1)	S(3)−S(4)−S(5)	104.4(1)
		S(1)−C(1)−C(naph1)	102.3(2)
		S(1)−C(1)−C(naph2)	113.0(2)
		S(5)−C(2)−C(naph3)	102.8(2)
		S(5)−C(2)−C(naph4)	112.9(2)

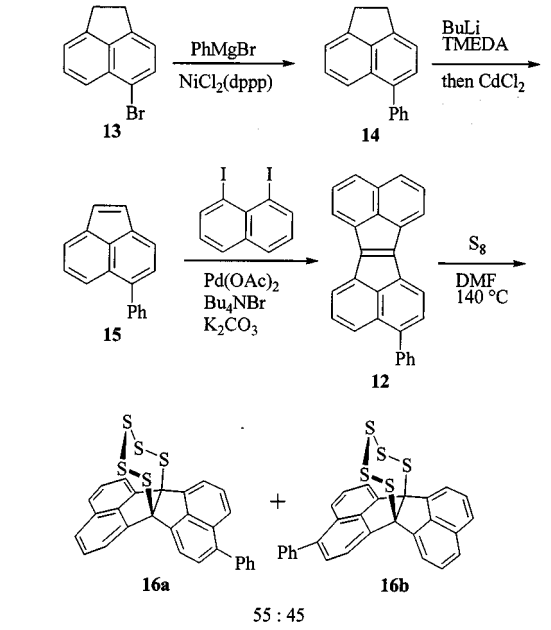
to give the dithioacetal (**9**) in 74% yield.[17] Desulfuration of **9** with Raney-Ni,[18] followed by dehydrogenation with DDQ,[19] gave 5-ethylacenaphthylene (**10**) in 31% overall yield. Coupling of **10** with 1,8-diiodonaphthalene in the presence of $Pd(OAc)_2$ provided **7** in 30% yield. Disappointingly, however, the sulfuration of **7** with elemental sulfur (1 equivalent as S_8) led to a complex mixture which does not contain the expected pentathiepane. The ^1H-NMR spectrum of the reaction mixture did not show any signals that indicate the presence of the ethyl group, probably because the reaction of **7** with sulfur took place much faster at the benzylic position than at the C=C bond.[20]

The above unsuccessful results prompted us to introduce a phenyl group, rather than an alkyl group, into **2**. The $[NiCl_2(dppp)]$-catalyzed coupling of **13** with PhMgBr gave 5-pheneylacenaphthene (**14**) in 79% yield.[21] Dehydrogenation of **14** by treatment with BuLi and TMEDA and then with $CdCl_2$ gave 5-phenylacenaphthylene (**15**) in 61% yield.[22] Coupling of **15** with 1,8-diiodonaphthalene yielded the expected **12** in 44% yield (Scheme 3).

Sulfuration of **12** with elemental sulfur gave the expected pentathiepane (**16**) in 60% yield with recovery of **12** in 23% yield. As expected, **16** was formed as a mixture of two conformers, **16a** and **16b**, in the equilibrium ratio of 55:45. The two isomers, **16a** and **16b**, were isolated in pure form by



Scheme 2



Scheme 3

HPLC separation as colorless crystals, and decomposed at 150°C and 144°C, respectively, to form **12** and sulfur. Single crystals for X-ray analysis of **16b** were obtained by crystallization from a hexane/CS_2 mixture at −40°C. The stereochemistry of **16b** in which the pentathiepane ring and the phenyl group are placed in *syn* orientation was determined by X-ray analysis at −120°C (Figure 2).[23]

The ^{1}H-NMR assignments for **16a** and **16b**, given in Table 2, were performed by ^{1}H-^{1}H COSY and NOESY experiments. The four signals due to H(1), H(6), H(8), and H(11) in **16a** appeared at lower fields than the corresponding signals in **16b**. In contrast, the four signals due to H(2), H(5), H(7), and H(12) in **16a** appeared at higher fields than those in **16b**. The phenyl group is remote from H(7), H(8), H(11), and H(12) and hence would not much affect their chemical shift values. Accordingly, the above sizable upfield

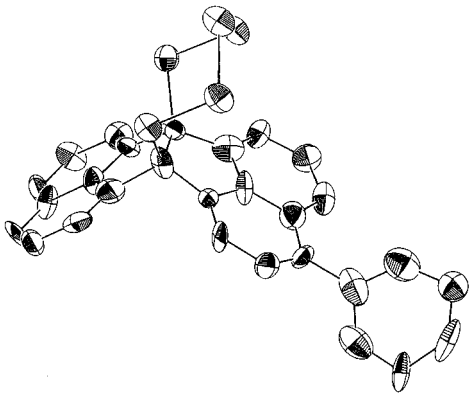


Figure 2. An ORTEP drawing of **16b** (50% probability ellipsoids, hydrogen atoms omitted for clarity)

or downfield shifts would be caused by the ring sulfur atoms.[9a,12] Therefore, these shifts would serve as a criterion of distinguishing *syn*- and *anti*-pentathiepanes, if the assignment of the relevant hydrogens can be unambiguously made for the both conformers. The ^{13}C-NMR spectrum of **16a** showed twenty-two peaks due to the sp^2 carbon atoms in the range δ = 121.1−143.5 and two peaks due to the bridgehead carbons at δ = 96.0 and 96.5, while that of **16b** showed twenty-one peaks in the range δ = 121.0−143.6 and two peaks at δ = 96.1 and 96.5; the chemical shift values of the bridgehead carbons are comparable with that of **2** (δ = 96.7). The UV/Vis absorption spectra of **16a** and **16b** are similar to each other.

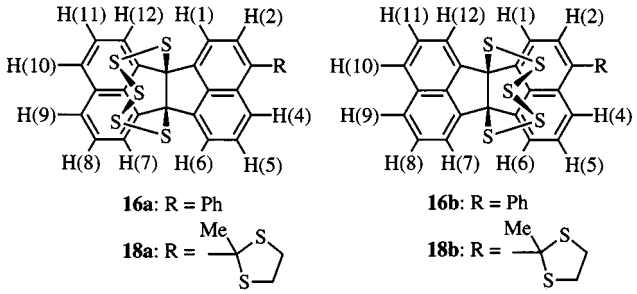
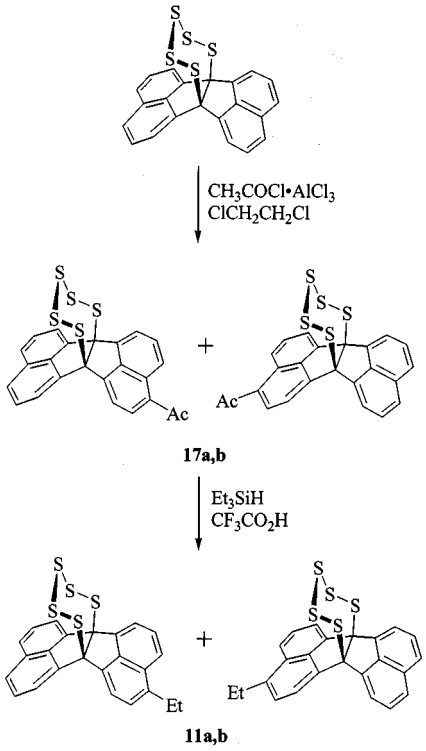


Table 2. Selected ^{1}H-NMR spectroscopic data of **16a** and **16b**

Protons	**16a** (*J* values in Hz)	**16b** (*J* values in Hz)
H(1)	7.93 (7.8)	7.83 (7.3)
H(2)	7.62 (7.8)	7.66 (7.3)
H(4)	7.93 (8.5)	7.91 (8.5)
H(5)	7.64 (7.0 and 8.5)	7.67 (7.0 and 8.5)
H(6)	7.88 (7.0)	7.80 (7.0)
H(7)	7.78 (7.0)	7.86 (7.2)
H(8)	7.70 (7.0 and 7.8)	7.66 (7.2 and 8.4)
H(9)	7.82 (7.8)	7.82 (8.4)
H(10)	7.82 (7.6)	7.82 (8.3)
H(11)	7.72 (6.5 and 7.6)	7.66 (6.8 and 8.3)
H(12)	7.80 (6.5)	7.88 (6.8)

Next, electrophilic aromatic substitutions of **2** were examined to prepare a pair of conformers. The S−S bonds of cyclic oligosulfides are often cleaved heterolytically by the action of electrophiles. For instance, an S−S bond of the benzopentathiepin is cleaved by treatment with Lewis

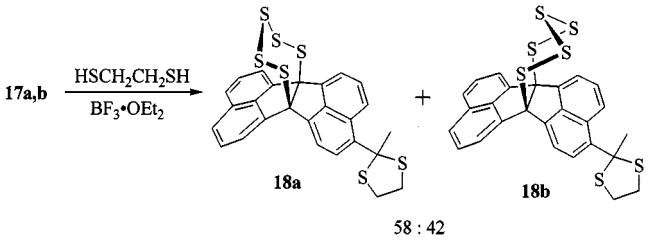
acids[24,25] and that of a trithiolane with sulfuryl chloride.[12] Therefore, the reaction of **2** with electrophiles must be performed under mild conditions. Disappointingly, nitration of **2** with NO_2BF_4 gave an inseparable mixture of mono- and dinitrated products with recovery of **2** in 69% yield.[26] Friedel–Crafts acylations of **2** in the usual manner were also unsatisfactory. Satisfactory results were attained by adding a suspension of a $CH_3COCl \cdot AlCl_3$ complex in $Cl(CH_2)_2Cl$ to a solution of **2** in the same solvent at room temperature. In this way, the desired monoacetylated pentathiepane (**17**) was obtained in 30% yield together with the desulfuration product **1** (19%) and elemental sulfur (16%) with recovery of **2** in 42% yield. As expected, **17** was formed as a mixture of two conformers, **17a** and **17b**, in the ratio of 62:38 (Scheme 4). Although **17a** and **17b** were inseparable by HPLC, the major coformer **17a** was isolated in pure form, though only in a small amount, by washing the mixture with hot ethanol. The conformer (**17b**) could not be isolated in pure form. The stereochemistry of **17a** and **17b** could not be determined by ^{1}H-NMR analysis because full assignments of the aromatic hydrogens were not attained for these compounds. Single crystals of **17a** for X-ray analysis were not obtained despite many attempted crystallizations from a variety of solvents. We therefore examined the conversion of the acetyl group of **17** to other groups next.



Scheme 4

Reduction of **17** with Et_3SiH in CF_3CO_2H furnished the expected mixture of two conformers of **11** in 76% yield.[27] However, two conformers, **11a** and **11b**, were not separated by HPLC, GPC, preparative TLC, or crystallization.

The $BF_3 \cdot OEt_2$-catalyzed dithioacetalization of **17** with 1,2-ethanedithiol gave a mixture of two conformers, **18a** and **18b**, in the equilibrium ratio of 58:42 (Scheme 5). The conformers, **18a** and **18b**, could be separated by HPLC as colorless crystals and decomposed at 159°C and 161°C, respectively. Although attempted preparation of single crystals of **18a** and **18b** for X-ray analyses was unsuccessful, their stereochemistry was determined by ^{1}H-NMR spectrum analyses. Both **18a** and **18b** showed eight doublets and three doublets of doublets in the aromatic region. The selected ^{1}H NMR data for **18a** and **18b** are shown in Table 3. The four signals due to H(1), H(6), H(8), and H(11) in **18a** showed downfield shifts relative to those in **18b**, and the four signals due to H(2), H(5), H(7), and H(12) in **18a** showed upfield shifts relative to those in **18b**. Therefore, in analogy to the assignment of **16a** and **16b**, the stereochemistry of **18a** and **18b** was determined to be *anti* and *syn*, respectively.



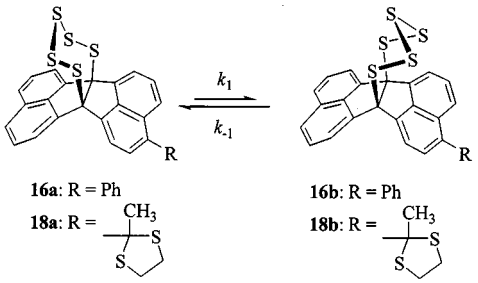
Scheme 5

Table 3. Selected ^{1}H-NMR spectroscopic data of **18a** and **18b**

Protons	**18a** (*J* values in Hz)	**18b** (*J* values in Hz)
H(1)	7.74 (7.3)	7.64 (7.6)
H(2)	8.26 (7.3)	8.28 (7.6)
H(4)	8.32 (8.6)	8.31 (8.2)
H(5)	7.70 (7.1 and 8.6)	7.73 (6.9 and 8.2)
H(6)	7.86 (7.1)	7.77 (6.9)
H(7)	7.73 (7.3)	7.81 (7.0)
H(8)	7.68 (7.3 and 8.0)	7.62 (7.0 and 7.6)
H(9)	7.79 (8.0)	7.79 (7.6)
H(10)	7.79 (8.0)	7.79 (7.6)
H(11)	7.68 (7.3 and 8.0)	7.62 (6.7 and 7.6)
H(12)	7.74 (7.3)	7.81 (6.7)

The two pairs of conformers, **16a** and **16b**, and, **18a** and **18b**, isomerized slowly into each other in solution, even at room temperature (Scheme 6). This was unexpected since the two naphthalene rings of **2** are chemically nonequivalent up to 100°C. In a 2.0 mM $CHCl_3$ solution, the isomerization between **16a** and **16b** exactly obeyed first-order kinetics. The rate constants for the isomerization from **16a** to **16b** were 0.73, 1.54, 2.99, and 4.03 $\times 10^{-5}$ s^{-1} and those from **16b** to **16a** were 0.90, 1.76, 3.65, and 4.86 $\times 10^{-5}$ s^{-1} at 20, 25, 30, and 35°C, respectively. The final equilibrium ratio of **16a** to **16b** was about 55:45 in this temperature range. In a 1.8 mM $CHCl_3$ solution, the isomerization between **18a** and **18b** also showed first-order kinetics. The rate constants were 0.36, 1.17, 2.54, and 5.44 $\times 10^{-5}$ s^{-1} for from **18a** to **18b**, and 0.51, 1.65, 3.46, and 7.14 $\times 10^{-5}$ s^{-1} for from **18b** to **18a** at 17, 25, 30, and 36°C, respectively. The final equilibrium ratio of **18a/18b** was about 58:42 in this temperature range. These observations reveal that the

syn-pentathiepanes are thermodynamically slightly less stable than the *anti*-ones, presumably due to the repulsive interactions between the substituent on the naphthalene ring and the sulfur ring in *syn*-conformers.

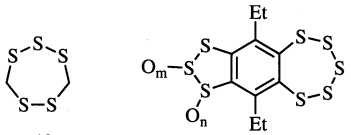


Scheme 6

The above kinetic data led to the activation parameters, E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, given in Table 4. All activation parameters are larger for the isomerization between **18a** and **18b** are large than those for the **16a/16b** equilibration. The activation energies E_a for the isomerization of these pentathiepanes are much larger than that of lenthionine (**19**) (E_a = 54 kJ·mol^{-1}),[28] which has an S−C−S−C−S unit, and not an −S−C−C−S− unit, while they are slightly smaller than those of benzopentathiepin derivatives (**20**) (E_a = 107−116 kJ·mol^{-1}).[7]

Table 4. Activation parameters for isomerization of pentathiepanes

	16a	16b	18a	18b
E_a (kJ·mol^{-1})	103.9	103.8	108.5	105.6
$\Delta H^{\neq}$ (kJ·mol^{-1})	101.4	101.3	106.0	103.1
$\Delta S^{\neq}$ (J·K^{-1}·mol^{-1})	2.9	4.2	16.2	9.0



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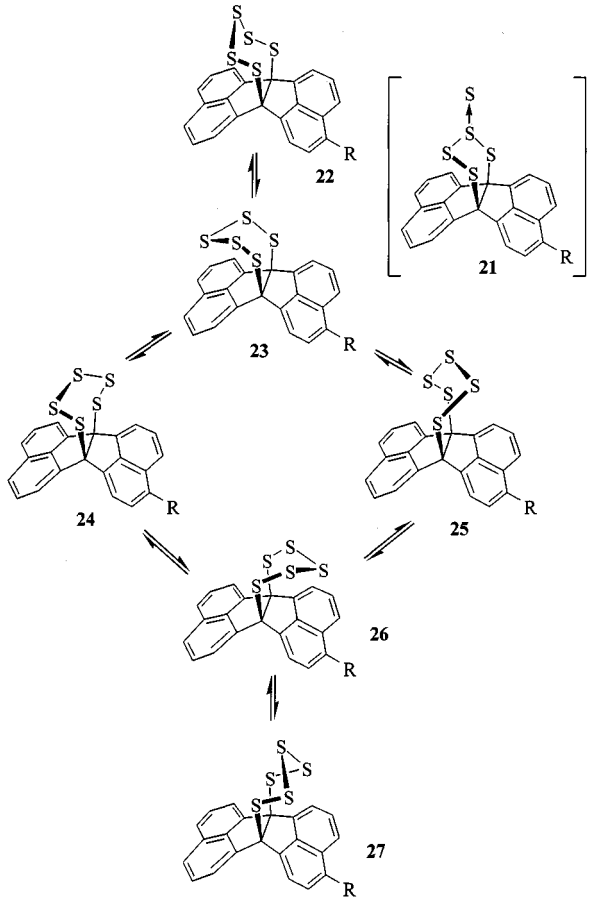
20: m = 1, n = 0
m = 0, n = 1

We have also obtained the following kinetic data for these isomerizations. In 1.8 mM solutions at 25°C, the rate constants from **18a** to **18b** were 1.33 in C_6H_6, 1.17 in $CHCl_3$, and 1.18·10^{-5} s^{-1} in CH_3CN, and those from **18b** to **18a** were 1.72 in C_6H_6, 1.65 in $CHCl_3$, and 1.63·10^{-5} s^{-1} in CH_3CN, respectively. Thus, the isomerization rates were practically not influenced by the solvent polarity, though they decreased slightly in the more polar solvents. This indicates that the isomerization does not involve either heterolytic cleavage of an S−S bond, yielding an ionized species, or formation of a polar intermediate such as tetrathiane *S*-sulfides (**21**).[29] Tris(trimethylsilyl)silane is known to serve as a hydrogen donor for sulfur radicals.[30] The isomerization rate of **18a** in a 1.8 mM $CHCl_3$ solution at 25°C was also not influenced by the addition of a large excess of this reagent with k = 1.24·10^{-5} s^{-1}. Thus, a mechanism involving homolytic cleavage of an S−S bond yielding a radical intermediate, appears to be ruled out. The isomerization therefore proceeds probably by a process, not involving cleavage of an S−S bond (Scheme 7). The most likely mechanism involves the initial inversion of the chair (**22**) to the boat conformation (**23**). Then, **23** undergoes a pseudorotation to give **24** and/or **25**. These two twist-boat conformers are diasteromeric to each other, and would afford another boat form (**26**) by one more pseudorotation. Finally, ring-inversion of **26** completes the isomerization to **27**. The rate-determining step of the isomerization would be the conversion of **22** to **23**, which requires the planarity of the five sulfur atoms in the transition state, and hence results in an increase of repulsive interactions between lone-pair electrons on adjacent sulfur atoms.[6,31] The observed small $\Delta S^{\neq}$ values are in agreement with this mechanism.



Scheme 7

Experimental Section

General: All reactions were carried out under argon. Acenephtho[1,2-*a*]acenaphthylene (**1**) was synthesized according to ref.[14b] Silica-gel column chromatography: Kieselgel Art 7734 (Merck, 70−230 mesh). − Preparative thin-layer chromatography (PTLC): 20 × 20 cm glass plate coated with silica gel (Merck). Preparative HPLC was performed on a Hitachi 655 unit equipped with a Hitachi 638-41 UV detector (254 nm), using GL Science Inertsil SIL (∅ 10 mm × 50 mm + ∅ 10 mm × 250 mm) column, and the column was eluted with 5% $CHCl_3$/hexane (for separation of **16a**

and **16b**) and 6.3% $CHCl_3$/hexane (for separation of **18a** and **18b**) at a flow rate of 4.0 mL·min^{-1}. Analytical HPLC for the determination of kinetics was performed on the same equipment, using a GL Science Inert-SIL column (∅ 4.6 mm × 150 mm), and the column was eluted with hexane (for **16a** and **16b**) and 6.3% $CHCl_3$/hexane (for **18a** and **18b**) at a flow rate of 1.0 mL·min^{-1}. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 equipped with a JAI UV-254 detector and a JAI RI-5 RI detector, using a JAIGEL-H column which was eluted with $CHCl_3$ at a flow rate of 3.5 mL·min^{-1}. Melting points are uncorrected. − NMR: Bruker ARX400, AC300P, AC200 (400, 300, and 200 MHz for ^{1}H, and 100.6, 75.5, and 50 MHz for ^{13}C, respectively). For ^{1}H NMR, $CDCl_3$ as solvent, TMS as internal standard; for ^{13}C NMR, $CDCl_3$ δ_C = 77.0, CD_2Cl_2 δ_C = 53.8. − IR: Hitachi 270-50. − UV/Vis: JASCO V-560. − MS: JEOL JMS-DX303 (70 eV). − Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

6b,12b-Epipentathioacenaphtho[1,2-*a*]acenaphthylene (2): A mixture of **1** (501 mg, 1.81 mmol) and elemental sulfur (464 mg, 1.81 mmol as S_8) in DMF (10 mL) was heated at 130°C for 36 h. The reaction mixture was cooled to room temp. The resulting crystals were collected by filtration, washed with a small amount of CH_2Cl_2, and crystallized from toluene to give 694 mg (88%) of **2**. The washings and the mother liquor of the crystallization were combined and purified to give 30 mg (6%) of the unreacted **1**. Compound **2**: colorless crystals, m.p. 248°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.0 Hz, 2 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 7.0 Hz, 2 H), 7.66 (dd, *J* = 7.0, 8.1 Hz, 2 H), 7.61 (dd, *J* = 7.0, 8.1 Hz, 2 H). − ^{13}C NMR (100.6 MHz, 20% CS_2−$CDCl_3$): δ = 143.4, 140.9, 136.5, 134.5, 131.0, 130.9, 128.55, 128.46, 125.8, 124.8, 121.2, 120.9, 96.7. − IR (KBr): $\tilde{\nu}$ = 3056, 2391, 2352, 1936, 781 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 223 nm (4.48), 227 (4.49), 231.5 (4.56), 300.5 (4.20), 318.5 (4.13), 332.5 (4.14). − MS (EI); *m*/*z*: 436 (M^+). $C_{22}H_{12}S_5$ (436.67): calcd. C 60.51, H 2.77, S 36.72; found C 60.64, H 2.71, S 36.80.

***cis*-7,14-Bis(methylthio)acenaphtho[1,2-*a*]acenaphthene (5):** To a suspension of **2** (50 mg, 0.12 mmol) in THF (2.0 mL) was added slowly a 1.0 M THF solution of $LiEt_3BH$ (0.95 mL, 0.95 mmol) (Aldrich) at 0°C. After the mixture had been stirred at 0°C for 1 h, MeI (163 mg, 1.2 mmol) was added. The mixture was stirred at 0°C for 2 h and the reaction was quenched by addition of cold water (5 mL). The mixture was extracted with ether (10 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (20 g) and the column was eluted with 17% of benzene/hexane to give 28 mg (66%) of **5**, colorless needles (hexane), m.p. 243−247°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.0 Hz, 4 H), 7.63 (d, *J* = 8.1 Hz, 4 H), 7.55 (dd, *J* = 7.0, 8.1 Hz, 4 H), 1.92 (s, 6 H). − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 145.0, 135.4, 131.7, 128.9, 124.9, 121.1, 77.0, 16.0. − IR (KBr): $\tilde{\nu}$ = 3040, 2916, 1590, 1418, 1215, 969, 938, 819. − MS (EI); *m*/*z*: 370 [M^+]. − $C_{24}H_{18}S_2$ (370.54): calcd. C 77.80, H 4.90, found C 77.75, H 4.87.

Crystal Structure Determination of 2: Single crystals of **2** of suitable quality and size were obtained by crystallization from a mixture of $CHCl_3$ and CS_2. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the diffractometer by using Mo-K_α radiation (λ = 0.71073 Å) and the data collection was made by the MAC DENZO program system. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR in the CRYSTAN-GM program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full matrix least squares. $C_{22}H_{12}S_5$ (436.67), monoclinic, space group *C*2/*c*, *a* = 25.545(8), *b* = 9.880(2), *c* = 16.427(5) Å, β = 114.77(3)°, *V* = 3753.0(12) Å^3, *Z* = 8, *d* = 1.54 Mgm^{-3}, μ = 5.963 mm^{-1}, crystal dimension: 0.22 × 0.16 × 0.14 mm, θ_{max}: 28.87°, number of measured reflections: 4929 [3657 observed with $I > 3\sigma(I)$], refined parameters: 244, goodness of fit: 2.388, *R* = 0.041, *wR* = 0.051, $\Delta\rho_{max}$ = 0.33 eÅ^{-3}, $\Delta\rho_{min}$ = −0.39 eÅ^{-3}.

5-Acetylacenaphthene (8): AcCl (1.13 g, 14.0 mmol) was added to a suspension of $AlCl_3$ (2.35 g, 17.0 mmol) in $Cl(CH_2)_2Cl$ (20 mL) at 0°C. To this mixture was added a solution of acenaphthene (1.70 g, 11 mmol) in $Cl(CH_2)_2Cl$ (10 mL) at 0°C. After having been stirred at room temp for 3 h, the mixture was poured onto ice water (30 mL). The organic layer was separated, washed with a saturated aqueous Na_2CO_3 solution (10 mL) and water (10 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (50 g) and the column was eluted with 25% Et_2O/hexane to give 1.32 g (63%) of **8**, pale yellow crystals (hexane), m.p. 66.5−68.5°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 8.5 Hz, 1 H), 8.08 (d, *J* = 7.3 Hz, 1 H), 7.60 (dd, *J* = 7.0, 8.5 Hz, 1 H), 7.37 (d, *J* = 7.0 Hz, 1 H), 7.31 (d, *J* = 7.3 Hz, 1 H), 3.42 (broad s, 4 H), 2.73 (s, 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 200.0, 153.0, 145.9, 139.5, 132.7, 130.3, 129.9, 129.1, 122.4, 120.2, 117.9, 30.3, 28.8. − IR (KBr): $\tilde{\nu}$ = 3040, 2924, 1662, 1600, 1500, 1466, 1398, 1354, 1270, 1232, 1202, 964, 842, 776 cm^{-1}. − MS (EI); *m*/*z*: 196 [M^+]. − $C_{14}H_{10}O$ (196.25): calcd. C 85.68, H 6.16, found C 85.60, H 6.11.

5-[2-(2-methyl-1,3-dithiolanyl)]acenaphthene (9): A mixture of **8** (4.0 g, 21 mmol), 1,2-ethanedithiol (3.92 g, 42 mmol), and $BF_3 \cdot OEt_2$ (3.0 mL, 21 mmol) in CH_2Cl_2 (50 mL) was stirred at room temp for 20 h. The reaction was quenched by addition of water (20 mL) at 0°C. The organic layer was separated, washed with 1 M KOH (20 mL) and water (20 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (100 g) and the column was eluted with 50% CH_2Cl_2/hexane to give 4.20 g (74%) of **9**, pale green crystals (hexane), m.p. 128−129°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.2 Hz, 1 H), 8.02 (d, *J* = 7.3 Hz, 1 H), 7.48 (dd, *J* = 7.3, 8.2 Hz, 1 H), 7.28 (d, *J* = 7.3 Hz, 1 H), 7.17 (d, *J* = 7.3 Hz, 1 H), 3.50−3.43 (m, 2 H), 3.36−3.31 (m, 6 H), 2.35 (s, 3 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 146.4, 146.3, 140.3, 136.4, 128.5, 126.8, 125.8, 122.2, 118.9, 118.0, 69.1, 39.3, 33.7, 30.4, 29.3. − IR (KBr): $\tilde{\nu}$ = 3032, 2964, 2924, 1602, 1444, 1426, 1376, 1356, 1332, 1287, 1078, 1062, 842, 774, 750 cm^{-1}. − MS (EI); *m*/*z*: 272 [M^+]. − $C_{16}H_{16}S_2$ (272.44): calcd. C 70.54, H 5.92, found C 70.59, H 5.91.

5-Ethylacenaphthene: A suspension of **9** (4.0 g, 15 mmol) and a large excess of Raney Ni (W-2) (prepared from 8 g of nickel-aluminum alloy) in EtOH (40 mL) was heated at reflux for 24 h. The nickel catalyst was removed by filtration and the filtrate was evaporated. The residue was chromatographed on a column of silica gel (80 g) with hexane as the eluent to give 1.48 g (55%) of 5-ethylacenaphthene, yellow oil. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 1 H), 7.44 (dd, *J* = 7.0, 8.3 Hz, 1 H), 7.26 (d, *J* = 7.0 Hz, 2 H), 7.19 (d, *J* = 7.0 Hz, 1 H), 3.39−3.33 (m, 4 H), 3.03 (q, *J* = 7.5 Hz, 2 H), 1.35 (t, *J* = 7.5 Hz, 3 H). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 146.4, 143.8, 139.5, 136.1, 130.2, 127.4, 126.2, 119.2, 119.1, 118.9, 30.6, 29.7, 25.0, 15.2. − IR (neat): $\tilde{\nu}$ = 3032, 2928, 2860, 1608, 1506, 1458, 1372, 838, 770 cm^{-1}.

5-Ethylacenaphthylene (10): A mixture of 5-ethylacenaphthene (100 mg, 0.55 mmol) and DDQ (187 mg, 0.82 mmol) in benzene (3.0 mL) was heated at reflux for 20 h. The mixture was diluted with hexane (10 mL) and the resulting precipitate was removed by fil-

tration. The filtrate was evaporated and the residue was chromatographed on a column of silica gel (15 g) with hexane as the eluent to give 56 mg (56%) of **10**, yellow oil. − ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 142.6, 140.1, 137.8, 129.1, 128.5, 127.2, 126.2, 126.1, 124.4, 123.9, 123.68, 123.65, 25.1, 16.6.

3-Ethylacenaphtho[1,2-*a*]acenaphthylene (7): A mixture of **10** (610 mg, 2.4 mmol), 1,8-diiodonaphthalene (839 mg, 2.2 mmol), Bu_4NBr (784 mg, 2.4 mmol), K_2CO_3 (762 mg, 5.5 mmol), and palladium(II) acetate (25 mg, 0.11 mmol) in DMF (10 mL) was heated at 100°C for 23 h. The reaction mixture was filtered with a pad of Celite and the solid on the pad was washed with ether (20 mL). The filtrate and the washings were combined, washed with water (3× 15 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (40 g) and the column was eluted with hexane to give the crude **7**, which was crystallized from hexane to give 202 mg (30%) of pure **7**, violet plates, m.p. 169−170°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99−7.95 (m, 4 H), 7.89 (d, *J* = 7.0 Hz, 1 H), 7.79 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 8.3 Hz, 1 H), 7.61−7.56 (m, 3 H), 7.39 (d, *J* = 7.0 Hz, 1 H), 3.20 (q, *J* = 7.6 Hz, 2 H), 1.44 (t, *J* = 7.6 Hz, 3 H). − IR (KBr): $\tilde{\nu}$ = 3040, 2926, 2872, 1481, 1454, 1442, 1201, 820, 766 cm^{-1}. − MS (EI); *m/z*: 304 (M^+). − $C_{24}H_{16}$ (304.39): calcd. C 94.70, H 5.30, found C 94.64, H 5.30.

Reaction of 7 with Elemental Sulfur: A mixture of **7** (100 mg, 0.33 mmol) and elemental sulfur (84 mg, 0.33 mmol as S_8) in DMF (5.0 mL) was heated at 140°C for 23 h. The insoluble materials were removed by filtration and washed with ether (20 mL). The filtrate and the washings were combined, washed with water (3× 10 mL), dried with $MgSO_4$, and evaporated. The residue consisted of more than seven components and failed to give any identifiable pure products on purification with crystallization and GPC.

5-Phenylacenaphthene (14): To a mixture of 5-bromoacenaphthene (466 mg, 2.0 mmol) and [1,3-bis(diphenylphosphanyl)propane]-nickel(II) chloride (25 mg, 0.046 mmol) in ether (10 mL) was added a 1.5 M ether solution of PhMgBr (4.0 mL, 6.0 mmol) at 0°C. The resulting mixture was heated at reflux for 4 h. The reaction was quenched by addition of an aqueous solution of NH_4Cl (5 mL). The organic layer was washed with water (10 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (50 g) with hexane as the eluent to give 330 mg (72%) of **14**, yellow oil, − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.4 Hz, 1 H), 7.55 (d, *J* = 7.3 Hz, 2 H), 7.47 (dd, *J* = 7.3, 7.6 Hz, 2 H), 7.37 (m, 3 H), 7.32 (d, *J* = 7.1 Hz, 1 H), 7.29 (d, *J* = 6.8 Hz, 1 H), 3.42 (m, 4 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 146.0, 145.4, 140.4, 139.5, 135.5, 129.7, 129.6, 128.4, 128.3, 127.9, 126.9, 120.7, 119.2, 119.0, 30.4, 29.9. − IR (neat): $\tilde{\nu}$ = 3060, 3032, 2924, 2884, 2840, 1604, 1494, 1448, 1428, 1368, 838, 776, 764 cm^{-1}. − $C_{18}H_{14}$ (230.31): calcd. C 93.87, H 6.13, found C 93.73, H 6.11.

5-Phenylacenaphthylene (15): To a solution of **14** (123 mg, 0.54 mmol) and TMEDA (1.6 mL) in THF (4.0 mL) was added a 1.53 M hexane solution of BuLi (1.37 mL, 2.01 mmol) at room temp. After the mixture had been heated at reflux for 1 h, $CdCl_2$ (196 mg, 1.1 mmol) was added while hot. The mixture was cooled to room temp and the reaction was quenched by addition of water (10 mL). The mixture was extracted with ether (20 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (20 g) with hexane as the eluent to give 75 mg (61%) of **15**, yellow oil. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.1 Hz, 1 H), 7.84 (dd, *J* = 8.0, 8.1 Hz, 2 H), 7.74 (d, *J* = 7.9 Hz, 2 H), 7.68−7.63 (m, 5 H), 7.60−7.56 (m, 1 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 140.9, 139.7, 139.6, 138.9, 130.4, 129.4, 129.0, 128.5, 128.24, 128.21, 127.7, 127.3, 126.6, 126.3, 124.04, 124.00. − IR (neat): $\tilde{\nu}$ = 3028, 2920, 1722, 1602, 1492, 1472, 766, 702 cm^{-1}. − $C_{18}H_{12}$ (230.31): calcd. C 94.70, H 5.30, found C 94.71, H 5.32.

3-Phenylacenaphtho[1,2-*a*]acenaphthylene (12): A mixture of **15** (49 mg, 0.32 mmol), 1,8-diiodonaphthalene (102 mg, 0.27 mmol), Bu_4NBr (87 mg, 0.27 mmol), K_2CO_3 (93 mg, 0.67 mmol), and $Pd(OAc)_2$ (3 mg, 13 μmol) in DMF (2.0 mL) was heated at 100°C for 20 h. The reaction mixture was filtered with a pad of Celite and the solid on the pad was washed with ether (10 mL). The filtrate and the washings were combined, washed with water (3× 5 mL), dried with $MgSO_4$, and evaporated. The residue was purified by GPC and then crystallization from hexane to give 33 mg (44%) of **12**, violet plates, m.p. 239.5−240.0°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02−7.97 (m, 4 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.63−7.52 (m, 8 H), 7.48−7.44 (m, 1 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 144.5, 144.1, 141.3, 139.6, 134.3, 134.2, 134.1, 133.7, 133.5, 133.4, 130.5, 129.2, 128.4, 128.3, 127.8, 127.74, 127.72, 127.6, 127.5, 127.4, 126.7, 123.14, 123.07, 123.0. − IR (KBr): $\tilde{\nu}$ = 3048, 2912, 1480, 1450, 1436, 842, 820, 764, 702 cm^{-1}. − $C_{28}H_{16}$ (352.44): calcd. C 95.42, H 4.58, found C 95.50, H 4.53.

***anti*-3-Phenyl-6b,12b-epipentathioacenaphtho[1,2-*a*]acenaphthylene (16a) and *syn*-3-Phenyl-6b,12b-epipentathioacenaphtho[1,2-*a*]acenaphthylene (16b):** A mixture of **12** (18 mg, 51 μmol) and elemental sulfur (14 mg, 55 μmol as S_8) in DMF (1.0 mL) was heated at 140°C for 43 h. The insoluble materials were removed by filtration and washed with ether (10 mL). The filtrate and the washings were combined, washed with water (3× 5 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (15 g) and the column was eluted with 20% CH_2Cl_2/hexane to give a 55:45 mixture of **16a** and **16b** (17 mg, 65%). The conformers, **16a** and **16b**, were separated by HPLC (retention time; 45.7 min for **16a** and 51.1 min for **16b**).

16a: colorless crystals (hexane), m.p. 150°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88−7.84 (m, 3 H), 7.78−7.73 (m, 4 H), 7.69−7.57 (m, 4 H), 7.47−7.41 (m, 5 H) − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 143.49, 143.47, 140.9, 140.0, 139.1, 138.8, 136.3, 134.7, 130.6, 129.6, 129.3, 129.1, 128.82, 128.75, 128.4, 127.5, 125.1, 124.7, 121.5, 121.3, 121.12, 121.10, 96.5, 96.0. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 225 nm (3.93), 229 (4.00), 232.5 (4.11), 233.5 (4.11), 236.5 (4.17), 244 (4.22), 311.5 (3.94), 343.5 (4.01). − MS (FAB); *m/z*: 513 [$(M+1)^+$].

16b: colorless crystals (hexane), m.p. 144°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02−7.97 (m, 4 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.63−7.52 (m, 8 H), 7.48−7.44 (m, 1 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 143.6, 142.7, 140.8, 139.0, 138.1, 136.7, 134.4, 130.9, 129.7, 129.5, 128.9, 128.7, 128.6, 128.4, 127.4, 126.0, 123.8, 121.36, 121.34, 121.2, 121.0, 96.5, 96.1. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 222.5 nm (4.03), 224.5 (3.74), 226 (3.81), 233 (4.06), 237 (4.12), 244 (4.19), 307 (3.94), 342 (3.90). − MS (FAB); *m/z*: 513 [$(M+1)^+$]. − $C_{28}H_{16}S_5$ (512.77): calcd. C 65.59, H 3.15, found C 65.83, H 3.13 (performed on a mixture of **16a** and **16b**).

Crystal Structure Determination of 16b: Single crystals of **16b** were obtained by crystallization from a mixture of hexane and CS_2 at −40°C: these crystals included one CS_2 molecule in each formula unit. Crystal data for **16b**·CS_2: $C_{29}H_{16}S_7$ (588.91), triclinic, space group *P*1bar, *a* = 8.611(4), *b* = 10.779(8), *c* = 15.269(9) Å, α = 99.45(4), β = 100.38(4), γ = 110.12(4)°, *V* = 1269.1(13) Å^3, *Z* = 2, *d* = 1.54 Mgm^{-3}, μ = 4.525 mm^{-1}, crystal dimensions: 0.12 × 0.04 × 0.04 mm, *T* = 153 K, θ_{max}: 28.55°, number of measured

reflections: 4800 [1238 observed with $I > 3\sigma(I)$], refined parameters: 291, goodness of fit: 3.094, $R = 0.089$, $wR = 0.096$, $\Delta\rho_{max} = 0.48$ eÅ^{-3}, $\Delta\rho_{min} = -0.74$ eÅ^{-3}.

Nitration of 2: To a solution of **2** (87 mg, 0.20 mmol) in CH_2Cl_2 (2.0 mL) was added a 0.2 M sulfolane solution of NO_2PF_6 (0.3 mL, 0.06 mmol) at −78°C. The mixture was warmed to room temp gradually and stirred for 1 h. The reaction was quenched by adding ice water (1 mL). The resulting precipitate was collected and washed with a small amount of CH_2Cl_2 to give 60 mg of the unreacted **2** (69%). The organic layer was dried with $MgSO_4$ and evaporated. Although the residue contained small amounts of mono- and dinitrated pentathiepanes (IR and ^{1}H-NMR analyses), they could be separated neither by silica-gel column chromatography nor HPLC.

Friedel−Crafts Acetylation of 2: To a suspension of $AlCl_3$ (40 mg, 0.30 mmol) in $Cl(CH_2)_2Cl$ (2.0 mL) was added AcCl (26 mg, 0.33 mmol) at 0°C. After the mixture had been stirred at 0°C for 3 h, a solution of **2** (131 mg, 0.30 mmol) in $Cl(CH_2)_2Cl$ (20 mL) was added at 0°C. The resulting mixture was stirred for 3 h and poured onto ice water (30 mL). The organic layer was separated, washed with a saturated aqueous Na_2CO_3 solution (10 mL) and water (10 mL), dried with $MgSO_4$, and evaporated. The residue was purified by silica-gel column chromatography to give 12 mg of elemental sulfur, 16 mg (19%) of **2**, and the crude **17**. The crude **17** was purified by GPC and then crystallization to give 43 mg (30%) of **17** as a mixture of two conformers. **17**: pale brown crystals (CH_2Cl_2/hexane), m.p. >130°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 233 K): δ = 8.84−8.80 (m, 1 H), 8.25 (d, J = 7.5 Hz, 0.62 × 1 H), 8.17 (d , J = 7.5 Hz, 0.38 × 1 H), 7.89−7.60 (m, 9 H), 2.73 (s, 0.62 × 3 H), 2.70 (s, 0.38 × 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 199.8, 199.7, 149.5, 146.6, 144.0, 143.5, 143.0, 141.2, 140.9, 140.3, 137.3, 136.7, 135.1, 134.5, 132.9, 132.8, 132.5, 132.2, 131.31, 131.29, 131.1, 131.0, 128.86, 128.82, 128.78, 128.73, 128.6, 127.7, 127.5, 126.3, 126.2, 126.1, 125.5, 125.4, 125.3, 122.3, 122.2, 121.5, 121.30, 121.26, 120.2, 120.1, 96.8, 96.6, 96.2, 29.0. − IR (KBr): ṽ = 3052, 2920, 1668, 1590, 1498, 1466, 1420, 1400, 1350, 1266, 1228, 1202, 1080, 962, 832, 814, 784 cm^{-1}. − MS (EI); *m*/*z*: 478 [M$^+$]. − $C_{24}H_{14}OS_5$ (478.70): calcd. C 60.22, H 2.95, found C 60.46, H 3.23.

A 62:38 mixture of **17a** and **17b** was heated in refluxing EtOH for 1 h. The mixture was filtered, while hot, to give **17a** in a small amount. Attempted separation of **17a** and **17b** by other methods such as silica-gel column chromatography and HPLC was unsuccessful. **17a**: colorless crystals, m.p. >130°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89−8.87 (m, 1 H), 8.32 (d, J = 7.5 Hz, 1 H), 7.88−7.81 (m, 7 H), 7.66 (t, J = 7.7 Hz, 2 H), 2.80 (s, 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 200.5, 149.5, 143.7, 140.5, 139.9, 136.9, 134.3, 133.34, 133.27, 131.55, 131.49, 130.9, 128.8, 128.6, 128.3, 126.4, 126.1, 125.2, 122.2, 121.4, 120.0, 96.3, 95.7, 29.3. − IR (KBr): ṽ = 3044, 2924, 1668, 1588, 1498, 1420, 1348, 1266, 1228, 1172, 1080, 832, 814, 788, 776 cm^{-1}.

3-Ethyl-6b,12b-epipentathioacenaphtho[1,2-*a*]acenaphthylene (11): To a solution of 200 mg (0.42 mmol) of **17** in CF_3CO_2H (2.0 mL) was added Et_3SiH (97 mg, 0.84 mmol) at 0°C. The mixture was warmed to room temp and stirred for 3 h. The reaction was quenched by addition of a 1 M MeOH solution of NaOH (5 mL) at 0°C. The mixture was diluted with CH_2Cl_2 (15 mL) and water (10 mL). The organic layer was separated, washed with water (10 mL), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (30 g) and the column was eluted with 50% $CHCl_3$-hexane to give 147 mg (76%) of **11** as a mixture of two conformers. The conformers could be separated neither by HPLC, GPC, PTLC, nor crystallization. **11**: pale yellow crystals, m.p. 140−141°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84−7.52 (m, 10 H), 7.46 and 7.39 (d and d, J = 7.2 Hz, 1 H), 2.98 and 2.96 (q and q, J = 7.4 Hz, 2 H), 1.29 and 1.27 (t and t, J = 7.4 Hz, 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 144.3, 144.1, 144.0, 141.65, 141.63, 141.5, 141.4, 140.6, 139.4, 139.0, 137.1, 136.9, 135.0, 134.7, 131.4, 131.1, 130.1, 129.8, 128.74, 128.72, 128.67, 128.65, 128.34, 128.30, 127.30, 127.29, 126.0, 125.9, 125.13, 125.07, 123.0, 122.2, 121.5, 121.4, 121.3, 121.24, 121.21, 121.18, 121.1, 121.0, 97.20, 97.17, 96.7, 96.6, 25.13, 25.10, 15.1, 14.9. − IR (KBr): ṽ = 3048, 2920, 1498, 1426, 1264, 1218, 1080, 832, 818, 784, 770 cm^{-1}. − MS (EI); *m*/*z*: 464 [M$^+$]. − $C_{24}H_{16}S_5$ (464.72): calcd. C 62.03, H 3.47, found C 62.11, H 3.75.

***anti*-3-[2-(2-Methyl-1,3-dithiolanyl)]-6b,12b-epipentathioacenaphtho[1,2-*a*]acenaphthylene (18a) and *syn*-3-[2-(2-Methyl-1,3-dithiolanyl)]-6b,12b-epipentathioacenaphtho[1,2-*a*]acenaphthylene (18b):** To a solution of 52 mg (0.11 mmol) of **17** and 1,2-ethanedithiol (52 mg, 0.55 mmol) in CH_2Cl_2 (3.0 mL) was added 3 drops of $BF_3{\cdot}OEt_2$ at room temp. After the mixture had been stirred for 3 h, the reaction was quenched by addition of water (1 mL). The organic layer was separated, washed with a aqueous 1 M KOH (2 mL), dried with K_2CO_3, and evaporated. The residue was crystallized from hexane to give a 58:42 mixture of **18a** and **18b** (59 mg, 99%). The conformers, **18a** and **18b**, were separated by HPLC (retention time; 41.8 for **18a** and 45.9 min for **18b**). **18a**: colorless crystal, m.p. >159°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 233 K): δ = 8.32 (d, J = 8.6 Hz, 1 H), 8.26 (d, J = 7.3 Hz, 1 H), 7.86 (d, J = 7.1 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 2 H), 7.74 (d, J = 7.3 Hz, 2 H), 7.73 (d, J = 7.3 Hz, 1 H), 7.70 (dd, J = 7.1, 8.6 Hz, 1 H), 7.67 (dd, J = 7.3, 8.0 Hz, 2 H), 3.47−3.45 (m, 2 H), 3.29−3.27 (m, 2 H), 2.29 (s, 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 143.5, 143.4, 141.7, 141.2, 140.5, 136.3, 135.8, 130.6, 128.7, 128.0, 127.9, 126.6, 125.7, 125.1, 121.4, 121.0, 120.6, 96.4, 95.3, 68.5, 39.6, 33.1. − IR (KBr): ṽ = 3048, 2920, 1498, 1426, 1264, 1218, 1080, 832, 818, 784, 770 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) 223.5 nm (4.02), 228 (4.07), 229.5 (4.03), 230.5 (4.02), 236 (4.20), 244 (4.28), 307.5 (4.02), 325.5 (4.01), 340.5 (4.06). **18b**: colorless crystal, m.p. >161°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 233 K): δ = 8.31 (d, J = 8.2 Hz, 1 H), 8.28 (d, J = 7.6 Hz, 1 H), 7.81 (d, J = 6.7 Hz, 1 H), 7.80 (d, J = 7.2 Hz, 1 H), 7.79 (d, J = 7.6 Hz, 2 H), 7.78 (d, J = 6.9 Hz, 1 H), 7.73 (dd, J = 6.9, 8.2 Hz, 1 H), 7.64 (d, J = 7.6 Hz, 1 H), 7.62 (dd, J = 7.0, 7.6 Hz, 2 H), 3.53−3.48 (m, 2 H), 3.35−3.29 (m, 2 H), 2.36 (s, 3 H). − ^{13}C NMR (100.6 MHz, $CDCl_3$, 233 K): δ = 144.3, 143.8, 141.7, 140.6, 138.9, 137.6, 137.6, 134.2, 130.7, 128.5, 127.9, 127.6, 126.7, 125.9, 124.6, 121.3, 121.2, 121.0, 120.2, 96.2, 95.2, 68.5, 40.0, 39.1, 33.2. − IR (KBr): ṽ = 3048, 2920, 1498, 1428, 1276, 1216, 1080, 842, 816, 784 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} (lg ε) 224 nm (4.17), 229 (3.98), 231.5 (4.12), 237 (4.21), 244 (4.28), 305.5 (4.06), 326.5 (4.02), 340 (4.04). − $C_{26}H_{18}S_7$ (554.89): calcd. C 56.28, H 3.27, found C 56.73, H 3.45 (performed on a mixture of **18a** and **18b**).

Kinetics for Isomerization between 16a and 16b, and 18a and 18b: A small test tube in which a cold solution of a pure conformer was placed was dipped into a thermostat to initiate the isomerization. Isomerization rates were measured by HPLC: a 20 mL aliquot was taken at regular intervals and the peak intensities of two isomers were determined. The absorption coefficients (ε) at 254 nm, 10 500 (for **16a**), 9 000 (**16b**), 11 200 (**18a**), and 10 700 (**18b**), were used to determine the relative amounts. The activation parameters were obtained by the Eyring treatment of the rate constants at a variety of temperatures.

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