

# Sulfur-Bridged *peri*-Naphthalenes: Synthesis, Conformational Analysis, and Photoelectron Spectroscopy of the Mono-, Di-, and Trisulfides of 1,8-Dimethylnaphthalene<sup>1</sup>

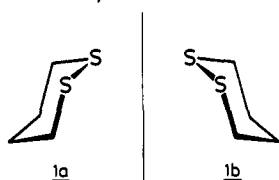
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**Abstract:** The sulfur-bridged 1,8-*peri*-naphthalenes 3*H*,7*H*-naphtho[1,8-*de*]-1,2-dithiepin (**8**) and 4*H*,8*H*-naphtho[1,8-*ef*]-1,2,3-trithiocin (**9**) have been prepared. Their variable-temperature <sup>1</sup>H NMR spectra reveal the presence of conformations undergoing rapid equilibration. For the disulfide (**8**) line-shape analysis yields a single interconversion with  $\Delta H^\ddagger = 9.3$  kcal/mol and  $\Delta S^\ddagger = -1.2$  cal/(mol K). Two processes are resolvable for the trisulfide (**9**), a relatively rapid one with  $\Delta H^\ddagger = 15.4$  kcal/mol and  $\Delta S^\ddagger = -1.1$  cal/(mol K) and a slower exchange with  $\Delta G^\ddagger = 17.9$  kcal/mol. Interpretation of the DNMR data was assisted by molecular mechanics calculations and photoelectron spectroscopic measurements. It is concluded that the disulfide (**8**) exists as an unsymmetrical twist-boat conformer with an S-S dihedral angle of ca. 40°. On the NMR time scale, racemization occurs via a boat conformation (*C*<sub>2</sub> symmetry) with a predicted barrier of  $\Delta E = 7.5$  kcal/mol. The calculations suggest, however, an accompanying but lower energy transformation ( $\Delta E = 5.4$  kcal/mol) which interconverts superimposable enantiomers by way of a twist transition state of *C*<sub>2</sub> symmetry. For the trisulfide (**9**) the force field calculations indicate the boat structure to be 0.6 kcal/mol more stable than the chair conformation. Boat-boat interchange is suggested to take place through an intermediate twist form ( $\Delta E = 13.6$  kcal/mol) and is lower in energy than the corresponding boat-chair equilibration.

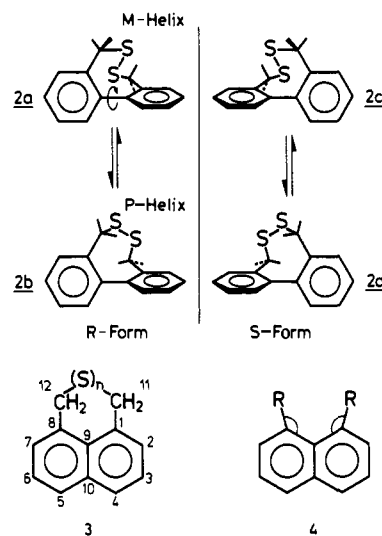
Unstrained disulfides are found as a racemic mixture with a CS-SC dihedral angle of 80-90°.<sup>2</sup> In principle the optical antipodes are separable, if the energy barrier to rotation about the S-S bond is high enough to prevent rapid interconversion. Enantiomeric exchange for acyclic systems requires an energy expenditure of 7-9 kcal/mol,<sup>3</sup> while constraining the S-S bond to a ring increases the cost by several kilocalories per mole. For example, the first demonstration of the existence of rapidly equilibrating optical isomers focused on 1,2-dithane (**1**) and derived a value of  $\Delta G^\ddagger = 11.6$  kcal/mol.<sup>4</sup>



A number of subsequent studies,<sup>2a</sup> notably by Lüttringhaus and co-workers,<sup>5</sup> have routinely yielded  $\Delta G^\ddagger$ 's for the inversion of cyclic disulfides of 9-15 kcal/mol, far too low to permit isolation of the individual mirror image forms. Unequal enantiomer populations may, however, result from the presence of a chiral center elsewhere in the molecule.<sup>2a,c,6</sup> Forced conformational rigidity, a tactic employed by nature, also leads to a mirror image preference.<sup>2a,c,7</sup>

The single known case of resolution of a disulfide lacking an asymmetric atom is due to Lüttringhaus, Hess, and Rosenbaum.<sup>5</sup> Dithiacyclooctadiene (**2**) is configurationally stable up to 130 °C and possesses a barrier to racemization of  $\Delta G^\ddagger = 28.8$  kcal/mol. Nonetheless, the compound owes its enantiomeric stability not to the S-S rotational barrier but to resistance to rotation about the C1-C1' bond in the biphenyl moiety. Equilibration between diastereomers **2a** and **2b** on the one hand and **2c** and **2d** on the other is rapid even at -80 °C, indicating that the S-S torsional barrier is less than  $\Delta G^\ddagger = 10$  kcal/mol.

In an attempt to design a disulfide in which chirality is conferred exclusively by the S-S bridge, but one with a sufficiently high S-S rotational barrier, we considered the *peri*-naphthalene system **3**.



Naphthalenes with substituents in the 1,8-positions have been extensively investigated and have been shown to experience con-

(1) Molecules with a Helix Structure. 3. For part 2 see: H. J. Bestmann and W. Both, *Chem. Ber.*, **107**, 2926 (1974); *Organo-Sulfur Mechanisms*. 13. For part 12 see: G. Rindorf, F. S. Jørgensen, and J. P. Snyder, *J. Org. Chem.*, in press. Part 11: J. P. Snyder and T. A. Halgren, *J. Am. Chem. Soc.*, **102**, 2861 (1980).

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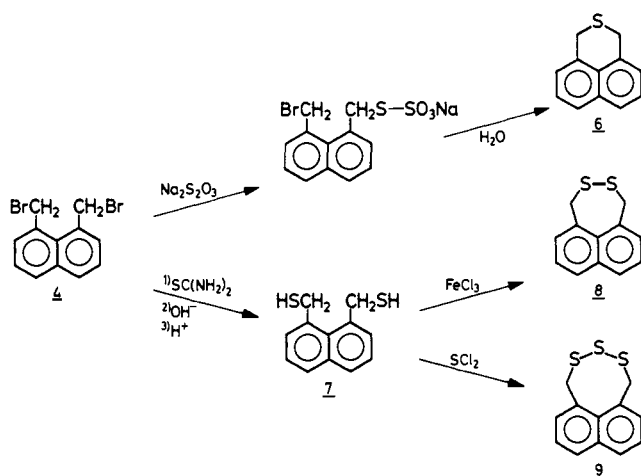
(4) G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **82**, 4428 (1960); *ibid.*, **83**, 4357 (1961).

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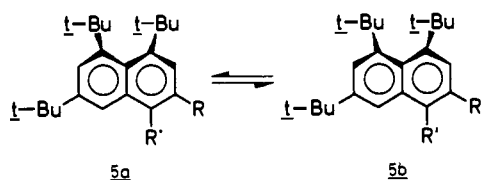
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Scheme 1



siderable distortion under conditions of high strain.<sup>8</sup> For example, 1,8-dimethylnaphthalene<sup>9</sup> (4, R =  $\text{CH}_3$ ) responds to steric repulsion between the methyl groups by a widening of each of the bridgehead  $\text{C}=\text{C}-\text{CH}_3$  bond angles by  $4^\circ$  relative to naphthalene.<sup>10</sup> The 1,8-bis(dimethylamino) derivative (4, R =  $\text{N(CH}_3)_2$ ) relieves the strain both by in-plane ( $4^\circ$ ) and out-of-plane bending.<sup>11</sup> The C1 and C8 atoms are shifted by 0.15 Å to opposite sides of the mean plane of the ring system. Similar behavior is evidenced by 4 (R =  $\text{CH}_2\text{Br}$ )<sup>12</sup> and other sterically congested 1,8-disubstituted naphthalenes.<sup>13</sup>

An extreme situation is exemplified by the tetra-*tert*-butylnaphthalene 5 ( $\text{R}' = \text{H}$ , R = *t*-Bu). Not only are the inner  $\text{C}=\text{C}-\text{C}$  angles seriously expanded as shown in 4 ( $8.5^\circ$ ) but also the benzenoid rings are distorted into flattened half-chairs.<sup>14</sup> The C1 and C8 atoms are consequently bent out of the mean molecular plane by  $21-22^\circ$ . An important outcome of the introduction of bulky groups of this kind is that the resulting ground states possess  $\text{C}_2$  symmetry and exist as racemic mixtures.<sup>8</sup> In compound 5 ( $\text{R}' = \text{CH}_2\text{C}_6\text{H}_5$ , R = H), whereas the barrier to rotation of the 1,8-*tert*-butyl groups is only 6.5 kcal/mol, the barrier to enantiomer interconversion occasioned by the flipping from 5a to 5b has been estimated to be greater than 24 kcal/mol.<sup>15</sup> Other *peri*-naphthalene systems show similar but attenuated dynamic behavior.<sup>8,16</sup>



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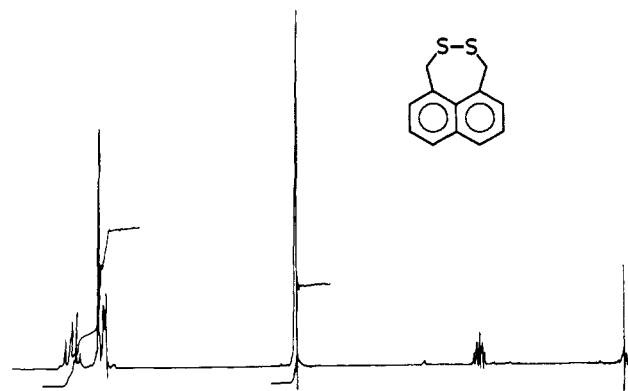


Figure 1. 60-MHz  $^1\text{H}$  NMR spectrum of disulfide 8 in  $\text{CD}_3\text{COCD}_3$  with  $\text{Me}_4\text{Si}$  as the internal standard at ambient conditions.

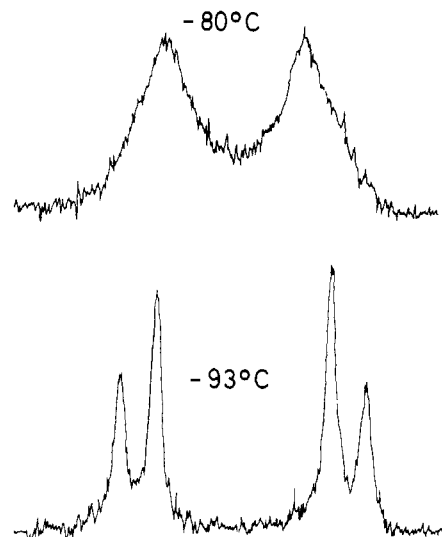


Figure 2. 100-MHz  $^1\text{H}$  NMR spectra of the  $\text{CH}_2$  protons of disulfide 8 in acetone- $d_6$  at  $-80$  and  $-93^\circ\text{C}$ .

On this basis it was reasoned that the *peri*-naphthalene substituent pattern and the disulfide characteristics might combine to yield a conformationally rigid disulfide with chiral properties stemming from the  $\text{S}-\text{S}$  unit alone. Structure 3 ( $n = 2$ ) suggested itself with the additional advantage that the  $\text{CH}_2$  groups  $\alpha$  to sulfur would be useful for barrier evaluation by DNMR. Thus we report the synthesis of the sulfur-enhanced series 3 ( $n = 1, 2, 3$ ) and their structural and conformational characteristics.

**Synthesis.** Preparation of the compounds forming the basis for our studies is outlined in Scheme I. The common precursor is the readily available 1,8-bis(bromomethyl)naphthalene (4, R =  $\text{CH}_2\text{Br}$ ). Treatment of the dibromide with sodium thiosulfate in ethanol-water provided sulfide 6 in 65–70% yield, presumably by way of the intermediate mono-Bunte salt. Dimercaptan 7 was obtained by combining the dibromide and thiourea to give the corresponding bis(thionium bromide) followed by the action of strong base and acid workup (70–75%). The disulfide bridge was closed by oxidation of the thiol with  $\text{FeCl}_3$  (8, 70–80%), and the trisulfide link formed by mixing sulfur dichloride and 7 (9, 40–48%). Compounds 6–9 are all crystalline and give correct composition by combustion analysis and mass spectroscopy.

**Dynamic NMR.** Kinetic data for each conformer were obtained by NMR line-shape analysis as prescribed by density matrix theory.<sup>17,18</sup> The spectroscopic parameters such as chemical shifts,

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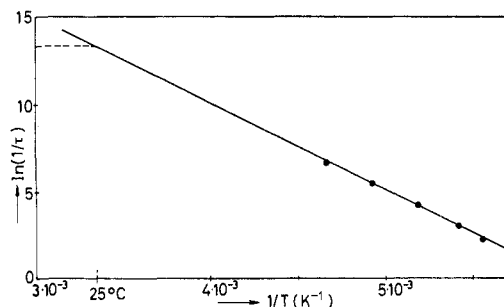


Figure 3. The NMR half-life ( $\ln(1/\tau)$ ) vs. temperature ( $1/T$ ) dependence for disulfide 8. The slope provides the activation energy for inversion,  $E_a$ .

Table I. Rate Measurements and Activation Parameters for Ring Inversion of Various Conformations of Sulfide 6, Disulfide 8, and Trisulfide 9

compd	$T_c, ^\circ\text{C}$	$k(25^\circ\text{C}), \text{s}^{-1}$	$\Delta G^\ddagger, \text{kcal/mol}$	$E_a, \text{kcal/mol}$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{cal/mol K}$	$T_2, \text{s}^{-1}$
6	$<-90^a$		$<8$				
8	$-73^a$	$5.7 \times 10^5$	9.5	9.9	9.3	-1.2	0.18 <sup>c</sup>
9a	$35^a, 52^b$	22	15.8	16.0	15.4	-1.1	0.18
9b	$75^b$		17.9 <sup>d</sup>				

<sup>a</sup> Acetone- $d_6$ . <sup>b</sup> Pyridine- $d_5$ . <sup>c</sup> Assumed to be identical with that for trisulfide 9. <sup>d</sup> Calculated with the assumptions:  $\Delta\delta_{AB} = 43$  Hz and  $J_{AB} = 15.6$  Hz.

coupling constants, and natural line widths were gathered from low-temperature measurements and extrapolated to higher temperatures where kinetic line broadening occurs. The only fitting parameter for simulating the kinetic line shape was the lifetime. From the temperature dependence of the reciprocal lifetimes the Arrhenius activation energy can be calculated. Eyring theory subsequently yields the activation enthalpy  $\Delta H^\ddagger$  and the activation entropy  $\Delta S^\ddagger$ .

The 60-MHz  $^1\text{H}$  NMR spectrum of the tricyclic sulfide 6 at room temperature shows a sharp singlet at 4.0 ppm corresponding to the  $\text{CH}_2$  protons  $\alpha$  to sulfur. Cooling the sulfide to  $-80^\circ\text{C}$  causes no change in the methylene absorption, although some broadening has been previously noted between  $-80$  and  $-100^\circ\text{C}$ .<sup>19</sup> Unfortunately the substance proved too insoluble for further temperature reduction. The absence of single decomposition into an AB quartet is indicative of rapid ring inversion for the non-planar<sup>20</sup> sulfide. An upper limit of  $\Delta G^\ddagger = 10$  kcal/mol can be placed on the interconversion.

Disulfide 8 delivers an ambient proton NMR spectrum which likewise consists of a  $\text{CH}_2$  singlet (Figure 1). However, the 100-MHz trace at  $-90^\circ\text{C}$  (acetone- $d_6$ ) yields a well-resolved symmetrical AB quartet at 4.45 ppm which coalesces upon warming to  $-77^\circ\text{C}$  (Figure 2). The inverses of the resulting half-lives,  $\tau$ , were plotted against  $1/T$  (Figure 3) to give  $E_a = 9.9$  kcal/mol. The corresponding Eyring parameters and rate constant are specified in Table I.

The richest NMR spectra were provided by trisulfide 9. At room temperature and at 100 MHz the methylene protons appear as a pair of overlapping AB quartets in the ratio of 10:1 (pyridine- $d_5$ ) at 4.95 ppm ( $J_{AB} = 15.2$  Hz) and 4.85 ppm ( $J_{AB} \approx 14$  Hz), respectively. The outer more intense bands coalesce around  $35^\circ\text{C}$  (acetone- $d_6$ ) as shown in the composite of Figure 4. Line-shape analysis gives  $E_a = 16.0$  kcal/mol for the process

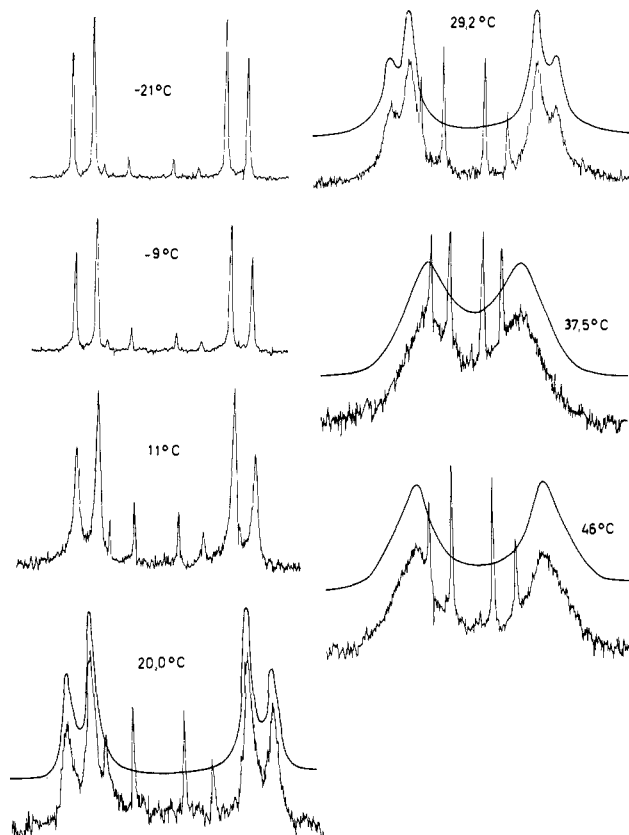


Figure 4. Temperature dependence of the 100-MHz  $^1\text{H}$  NMR spectrum of the trisulfide 9  $\text{CH}_2$  protons. At higher temperatures ( $T_{\text{eff}} = 20$ – $40^\circ\text{C}$ ) the calculated spectra of the outer AB quartet ( $T_c = 35^\circ\text{C}$ ) are superimposed with the experimental curves; the solvent is  $\text{CD}_3\text{COCD}_3$ .

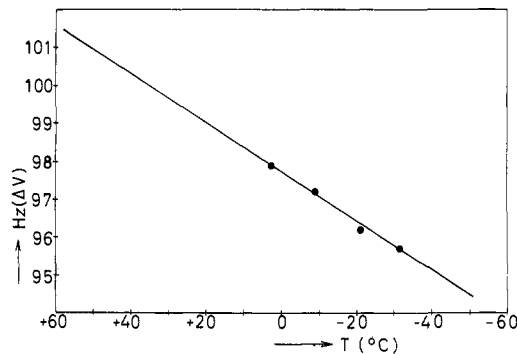


Figure 5. Temperature dependence of the 100-MHz proton chemical shift of the  $\text{CH}_2$  outer AB quartet ( $T_c = 35^\circ\text{C}$ , cf. Figure 4) in trisulfide 9.

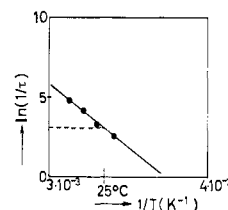


Figure 6. The NMR half-life ( $\ln(1/\tau)$ ) vs. temperature dependence for the outer AB quartet ( $T_c = 35^\circ\text{C}$ , cf. Figure 4) in trisulfide 9. The slope provides  $E_a$  for inversion.

associated with the more abundant trisulfide conformer 9a (Figure 6). The remaining activation values are listed in Table I.

**Molecular Symmetry Considerations.** The DNMR measurements permit the specification of the minimum symmetry requirements for the molecular geometries of compounds 6, 8, and 9. For example, the temperature-independent  $\text{CH}_2$  singlet for sulfide 6 formally implies chemically equivalent protons ( $H_A =$

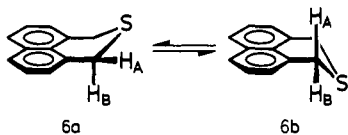
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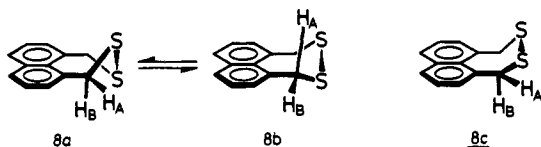
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H<sub>B</sub>) as either a consequence of planarity in the six-membered sulfur-containing ring or rapid equilibration between nonplanar forms, i.e., actual or average C<sub>s</sub> symmetry. The X-ray analysis of **6** is in accord with intuitive expectations for a folded structure.<sup>20</sup> Thus the spectra are easily rationalized by invoking equilibrium between **6a** and **6b** on the NMR time scale.

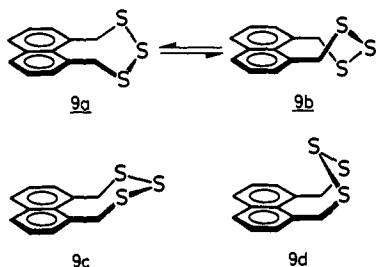


The analysis and subsequent conformer designation for the sulfur homologues **8** and **9** is not so unambiguously carried out. The low-temperature AB spectrum of disulfide **8** suggests the presence of either a chiral C<sub>2</sub> twist conformer **8a/8b** or a C<sub>s</sub> half-boat form **8c**. Molecular models indicate a dihedral angle



of ~90° for the former, whereas that for the latter is necessarily 0°. Since disulfide substituents and lone electron pairs prefer a near gauche orientation,<sup>2,21</sup> a tentative interpretation of the variable-temperature NMR spectra is that the disulfide exists in the relatively S-S unstrained C<sub>2</sub> conformation **8a/8b**, but the enantiomers are equilibrated above -75 °C.

The overlapping pair of AB quartets observed for trisulfide **9** demands the presence of at least two energetically nonequivalent rotamers that are interconverted above 75 °C. Candidates are the C<sub>2</sub> enantiomeric pair **9a/9b** and the C<sub>s</sub> chair and boat geometries **9c** and **9d**, respectively.



All of the above-mentioned structures fulfill the requirements of the DNMR data but are not necessarily sufficient to describe the actual stereochemical situation. That is, each of the structures **8a-9d** is in principle equivalent to a pair of equilibrating, chiral C<sub>1</sub> geometries and therefore potential transition states for an interchange between them. In the sequel we employ principally a combination of force field calculations and photoelectron spectroscopy measurements to identify the underlying equilibria and to specify the torsional angle about the S-S bond for disulfide **8**. The calculations were performed with Allinger's 1973 force field (MMPI) shown to be capable of treating both aromatic compounds<sup>22</sup> and polysulfides.<sup>1,23-25</sup>

**Molecular Mechanics Calculations for 6, 8, and 9.** The *perinaphthalene* sulfide **6** has been the subject of an X-ray crystallographic study.<sup>20</sup> In order to gauge MMPI's reliability for the

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Table II. Molecular Mechanics Calculated and Experimental Data for 2*H*,6*H*-Naphtho[1,8-*cd*]thiin (**6**)<sup>a</sup>

symmetry	C <sub>s</sub>	C <sub>2v</sub>	
E <sub>rel</sub> (kcal/mol)	0.0	5.3	exptl <sup>b</sup>
Bond Lengths (Å)			
S-C11	S-C12	1.812	1.797
C1-C11	C8-C12	1.509	1.504
C1-C9	C8-C9	1.433	1.430
C1-C2	C7-C8	1.382	1.385
C2-C3	C6-C7	1.419	1.417
C3-C4	C5-C6	1.376	1.375
C4-C10	C5-C10	1.426	1.426
C9-C10		1.417	1.420
Nonbonded Distances (Å)			
C11-C12		2.66	2.84
C1-C8		2.50	2.50
C4-C5		2.47	2.46
H11-H12		2.55	
S out-of-plane		0.98 <sup>c</sup>	0.94
Bond Angles (Deg)			
C11-S-C12		94.7	104.3
S-C11-C1	S-C12-C8	111.5	121.5
C9-C1-C11	C9-C8-C12	122.2	125.3
C1-C9-C8		121.7	122.2
Dihedral Angles (Deg)			
C11-S-C12-C8	C12-S-C11-C1	59.1	0.0
S-C11-C1-C9	S-C12-C8-C9	35.9	0.0
C8-C9-C1-C11	C1-C9-C8-C12	0.6	0.0

<sup>a</sup> Numbering of atoms as given in structure 3. <sup>b</sup> Reference 20. <sup>c</sup> This value corresponds to an angle of 53.1° between the C11-S-C12 plane and the average plane of the rest of the molecule.

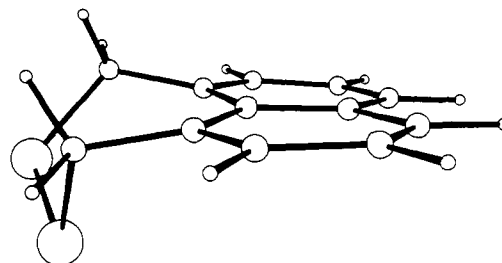


Figure 7. ORTEP<sup>28</sup> drawing of the minimum energy conformation of 3*H*,7*H*-naphtho[1,8-*de*]-1,2-dithiepin (**8**) as determined by molecular mechanics.

class of compounds represented by **3**, we have optimized the geometry of **6** without restriction to give the C<sub>s</sub> conformation **6a/6b** (cf. Table II). Agreement between the experimental data and the calculated quantities is generally quite good. Significantly both determinations yield a folded thiopyran ring with the sulfur atom out of the plane by 0.94 and 0.98 Å, respectively.

The transition state for interconversion of **6a** and **6b** was assumed to possess a planar C<sub>2v</sub> geometry (cf. Table II). Its energy is only 5.3 kcal/mol above that of the C<sub>2</sub> form in accord with an actual inversion barrier of <10 kcal/mol.<sup>19</sup>

To begin the investigation of disulfide **8**, we fully optimized the twist (**8a/8b**) and the half-boat (**8c**) shapes under the constraints of C<sub>2</sub> and C<sub>s</sub> symmetries, respectively. The final structures were then reoptimized without restriction. The energy of both the C<sub>2</sub> and C<sub>s</sub> forms dropped considerably to give a common structure with C<sub>1</sub> symmetry, **8d**. In the latter, both sulfurs lie on the same side of the naphthalene ring giving a twist-boat structure (Figure 7). The calculated energies of the disulfide isomers **8a/8b** (C<sub>2</sub>) and **8c** (C<sub>s</sub>) relative to **8d** (C<sub>1</sub>) are 5.4 and 7.5 kcal/mol, respectively.

The differences in energy can be rationalized by a comparison of molecular geometries with particular emphasis on the S-S dihedral angles and heavy-atom bond angles. The MMPI structures are listed in Table III. By design the C<sub>s</sub> form incorporates an energy maximum with respect to the disulfide bridge: θ(CSSC) = 0°. Simultaneously for steric repulsion between

Table III. Molecular Mechanics Calculated Data for 3*H*,7*H*-Naphtho[1,8-*de*]-1,2-dithiepin (8)<sup>a</sup>

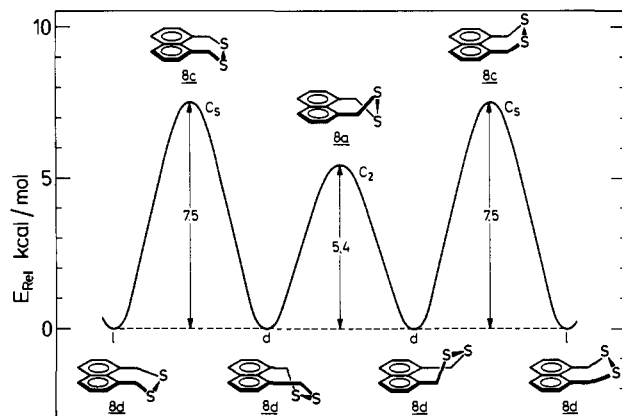
symmetry	<i>C</i> <sub>1</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>s</sub>
<i>E</i> <sub>rel</sub> (kcal/mol)	0.0	5.4	7.4
Bond Lengths (Å)			
S-S	2.015	2.005	1.998
S-C11	1.812	1.819	1.797
S-C12	1.819	1.797	1.793
C1-C11	1.816	1.519	1.521
C8-C12	1.521	1.506	1.506
C1-C9	1.445	1.446	1.453
C8-C9	1.446	1.453	1.426
C1-C2	1.386	1.385	1.392
C7-C8	1.385	1.392	1.395
C2-C3	1.416	1.416	1.412
C6-C7	1.416	1.412	1.408
C3-C4	1.373	1.372	1.369
C5-C6	1.372	1.369	1.369
C4-C10	1.427	1.427	1.426
C5-C10	1.427	1.426	1.422
C9-C10	1.423	1.433	1.429
Nonbonded Distances (Å)			
C11-C12	3.05	2.90	2.98
C1-C8	2.57	2.61	2.58
C4-C5	2.44	2.40	2.38
H11-H12	2.29		2.22
Bond Angles (Deg)			
S-S-C11	102.0	101.5	99.2
S-S-C12	101.5	99.2	105.9
S-C11-C1	118.5	105.2	123.0
S-C12-C8	105.2	123.0	107.5
C9-C1-C11	125.9	125.5	132.6
C9-C8-C12	125.5	132.6	122.9
C1-C9-C8	125.1	127.9	129.3
Dihedral Angles (Deg)			
C11-S-S-C12	43.5	82.2	0.0
S-S-C11-C1	40.9	98.8	70.0
S-S-C12-C8	98.8	70.0	76.3
S-C11-C1-C9	74.2	53.4	31.0
S-C12-C8-C9	53.4	31.0	73.4
C8-C9-C1-C11	10.7	9.9	2.6
C1-C9-C8-C12	9.9	2.6	6.6
α			66.0 <sup>b</sup>

<sup>a</sup> Numbering of atoms as given in structure 3. <sup>b</sup> This value corresponds to the angle between the plane C11-S-S-C12 and the average plane of the rest of the molecule.

the *peri*-CH<sub>2</sub> groups to be avoided, the naphthalene bridgehead angle (CH<sub>2</sub>)C-C-C(CH<sub>2</sub>) with a value of 121–122° in the unsubstituted parent<sup>10</sup> has expanded to 129.3°. Likewise the pair of angles ∠SSC = 105.9° is enlarged relative to the normal values of 102–104°. <sup>2,22–24,26</sup>

For the *C*<sub>2</sub> species (8*a*/8*b*), θ(CSSC) = 82.2° well within the range observed for unstrained dialkyl disulfides (80–90°).<sup>2,22–24,26</sup> However, the cost for maintaining *C*<sub>2</sub> symmetry lies in the 3–15° expansion of bond angles within the sulfur-containing seven-membered ring and in the 3–4° reduction of the C-S-S angles (cf. Table III). A compromise between the extremes shown in 8*a*/8*b* and 8*c* is found in the structure of 8*d*. The S-S dihedral angle is predicted to be 43.5°, and the C-C-S angles are calculated at 105.2 and 118.5°. Otherwise the seven-membered bond angles are much closer to the unstrained quantities than found for 8*a*-*c*. Finally it can be mentioned that all of the structures contain the anticipated steric repulsion across the *peri* positions. The calculated nonbonded C...C and H...H distances of 2.4–3.1 and 2.2–2.3 Å, respectively (cf. Table III), are under the corresponding sums of the van der Waals radii (3.4 and 2.4 Å, respectively<sup>27</sup>).

In order to place structures 8*a*-*d* on a relative potential energy surface, we have interconverted them computationally by incrementing values of θ(CSSC) and optimizing all other internal coordinates with respect to the energy. Thus by altering the S-S torsional angle from 45 to 0° in 15° steps, we smoothly transformed the twist-boat 8*d* into boat 8*c* without passing through intervening energy minima or maxima. Likewise by changing the adjacent dihedral angle, θ(SSCC), of the *C*<sub>1</sub> conformation 8*d* stepwise from +74 to -31°, we obtained the *C*<sub>2</sub> rotamer 8*a*/8*b* without complication. These results allow one to sketch a hypersurface for the interconversion of the disulfide geometries (cf. Figure 8). The *C*<sub>1</sub> enantiomers are consequently found by the force field to equilibrate via a *C*<sub>2</sub> transition state with an energy barrier of 5.4 kcal/mol. It should be noted that the chirality of the *C*<sub>1</sub> species is not altered along this pathway, *R* → *R* and *S*

Figure 8. The hypersurface of 3*H*,7*H*-naphtho[1,8-*de*]-1,2-dithiepin (8) as determined by molecular mechanics.Table IV. Molecular Mechanics Calculated Data for 4*H*,8*H*-Naphtho[1,8-*ef*]-1,2,3-trithiocin (9)<sup>a</sup>

symmetry	<i>C</i> <sub>s</sub> (boat)	<i>C</i> <sub>s</sub> (chair)	<i>C</i> <sub>2</sub>
<i>E</i> <sub>rel</sub> (kcal/mol)	0.0	0.6	13.6
Bond Lengths (Å)			
S-S	2.020	2.021	2.029
S-C11	1.819	1.819	1.811
C1-C11	1.519	1.519	1.521
C1-C9	1.450	1.448	1.452
C1-C2	1.388	1.388	1.388
C2-C3	1.415	1.415	1.415
C3-C4	1.371	1.371	1.370
C4-C10	1.427	1.427	1.427
C9-C10	1.427	1.427	1.427
Nonbonded Distances (Å)			
S-S	3.15	3.12	3.13
C11-C12	3.17	3.18	3.32
C1-C8	2.59	2.58	2.60
C4-C5	2.41	2.42	2.42
H11-H12	2.06	2.10	
H2-H11	2.27	2.26	2.25
Bond Angles (Deg)			
S-S-S	102.4	101.3	101.1
S-S-C11	103.5	103.3	102.9
S-C11-C1	113.4	110.7	116.7
C9-C1-C11	128.0	128.3	128.4
C1-C9-C8	126.2	126.2	127.2
α	114.0 <sup>b</sup>	111.4 <sup>b</sup>	
β	111.4 <sup>c</sup>	110.1 <sup>c</sup>	
Dihedral Angles (Deg)			
S-S-S-C11	73.3	74.7	45.3
S-S-C11-C1	40.8	115.2	122.7
S-C11-C1-C9	84.9	84.7	75.0
C8-C9-C1-C11	0.5	0.0	14.9

<sup>a</sup> Numbering of atoms as given in structure 3. <sup>b</sup> This value corresponds to the angle between the C11-S-S-C12 and the average plane of the rest of the molecule. <sup>c</sup> This value corresponds to the angle between the S-S-S and the plane C11-S-S-C12.

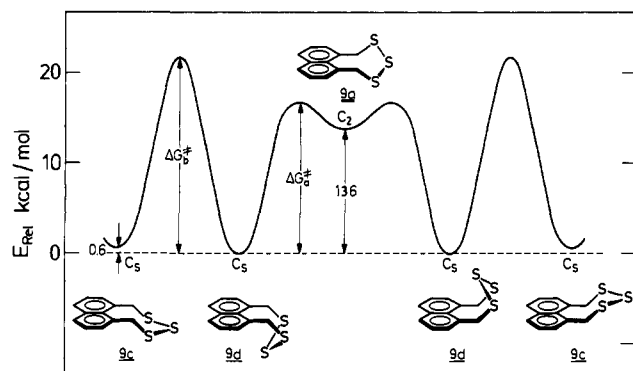
→ *S*. An alternative and more costly racemization route (7.5 kcal/mol) utilizes the *C*<sub>s</sub> form as its saddle point structure. Here, mirror images are interconverted, *R* → *S*.

Finally trisulfide 9 was investigated by first calculating structures 9*a*/9*b* and 9*c*/9*d* within the point groups *C*<sub>2</sub> and *C*<sub>s</sub>, respectively. Subsequent removal of the symmetry restrictions did not lead to energy lowerings or to changes in molecular geometry. We conclude that the calculated structures (cf. Table IV) therefore represent true potential energy minima.

The molecular mechanics calculations suggest that the two *C*<sub>s</sub> conformations are nearly isoenergetic, Δ*E* = 0.6 kcal/mol, and 13 kcal/mol more stable than the twist boat form 9*a*/9*b*. Although the latter optical isomers show expanded S-C-C angles (by 3–6°) relative to the *C*<sub>s</sub> structures, their destabilization appears to reside largely in the compressed S-S dihedral angles. Like disulfides,

(26) J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, **99**, 2931 (1977).

(27) A. J. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).



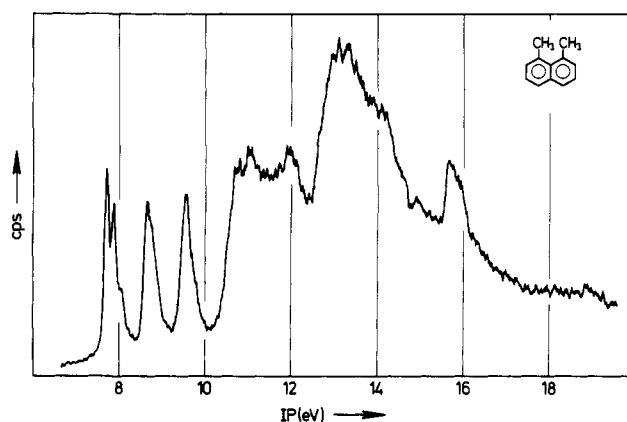
**Figure 9.** The hypersurface of 4*H*,8*H*-naphtho[1,8-*ef*]-1,2,3-trithiocin (**9**) as determined by molecular mechanics. The heights of the barriers  $\Delta G_s^\ddagger$  and  $\Delta G_c^\ddagger$  are estimated by analogy with the behavior of disulfide **8** (cf. Figure 8).

trisulfides prefer the gauche arrangement around the S-S bond with  $\theta(\text{CSSC}) = 80\text{--}90^\circ$  in acyclic, unstrained structures.<sup>2c,25b,28</sup> Accordingly the boat and chair conformations **9c** and **9d** sustain S-S torsions of 73–75°, while the twist-boat **9a/9b** exhibits a value of 45° (cf. Table IV). Potential surface calculations have not been performed for the trisulfides, but by analogy with the dynamics of the disulfides a hypersurface as depicted in Figure 9 is suggested. This point is discussed further in the final section.

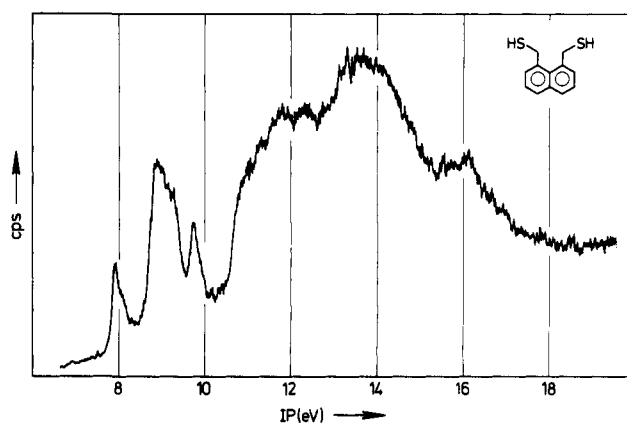
**Experimental Verification of the Ground-State Structure of Disulfide 8.** The DNMR measurements for disulfide **8** at  $-90^\circ\text{C}$  display a well-resolved AB quartet for the CH<sub>2</sub> protons (Figure 2) indicative of a system with C<sub>2</sub> or C<sub>s</sub> symmetry; i.e., **8a/8b** or **8c**, respectively. On the contrary the force field calculations suggest the latter species to be transition states separating enantiomers of the low-energy C<sub>1</sub> conformation **8d** (Figure 8). We have attempted to investigate the disulfide at temperatures below  $-90^\circ\text{C}$  in the NMR, but its low solubility has prevented the gathering of information for interpreting the AB quartet as a static pattern or a dynamic average.<sup>29</sup>

The molecular shapes in question differ significantly in the MMPI predicted degree of twist about the S-S bond: **8a/8b**,  $\theta(\text{CSSC}) = 82^\circ$ ; **8c**,  $0^\circ$ ; **8d**,  $44^\circ$ . In this spirit we have considered the possible utility of correlations between  $\theta(\text{CSSC})$  and various spectroscopic quantities (Raman<sup>30</sup> ( $\nu(\text{S-S})$ ), UV<sup>31,32</sup> ( $\lambda_{\text{max}}$ ), and PES<sup>31,33</sup> ( $\Delta\text{IE}(n_+ - n_-)$ ). Unfortunately, although disulfide **8** shows a Raman absorption in the region associated with the S-S stretching frequency ( $510\text{ cm}^{-1}$ , solid phase), the presence of sp<sup>2</sup> carbons in the molecule  $\beta$  to sulfur renders it ineligible for analysis by the  $\alpha,\beta$ -dialkyl disulfide correlation of  $\theta(\text{CSSC})$  and  $\nu(\text{S-S})$ . Furthermore a possible comparison with dithiocin **2** ( $\theta(\text{CSSC}) = 56^\circ$ <sup>34</sup>) is ruled out by the difficulty of making an unambiguous assignment of  $\nu(\text{S-S})$ .<sup>30</sup>

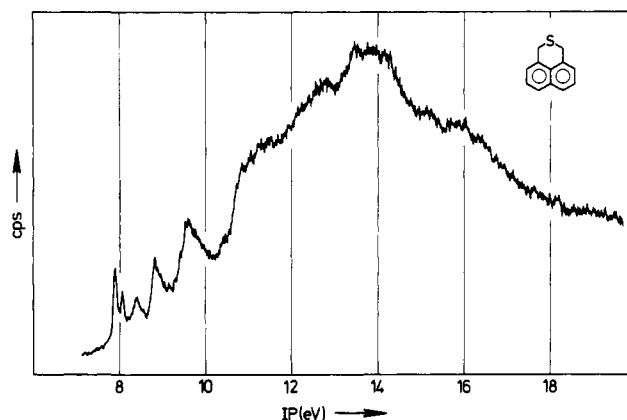
The UV/ $\theta(\text{CSSC})$  correlation arises from a predictable red shift of the dialkyl disulfide first absorption maximum as the S-S dihedral angle closes from  $90^\circ$  ( $\lambda_{\text{max}} \approx 250\text{ nm}$ ) to  $0^\circ$  ( $\lambda_{\text{max}} \approx 350\text{ nm}$ ).<sup>31,32</sup> The  $\lambda_{\text{max}}$  in question is weak, however,  $\epsilon = 300\text{--}500$ , and its observation depends on the absence of interfering absorption. Naphthalene itself displays a broad structured band from 240 to 290 nm ( $\epsilon = 5800$ , CH<sub>3</sub>CN) that is red-shifted by the



**Figure 10.** Photoelectron spectrum of 1,8-dimethylnaphthalene.



**Figure 11.** Photoelectron spectrum of 1,8-bis(mercaptomethyl)naphthalene (**7**).



**Figure 12.** Photoelectron spectrum of 2*H*,6*H*-naphtho[1,8-*cd*]thiin (**6**).

introduction of methyl groups at the peri positions (1,8-dimethylnaphthalene:  $\lambda_{\text{max}} = 250\text{--}330\text{ nm}$  ( $\epsilon = 8000$ , CH<sub>3</sub>CN)). The transition energy shift ( $\Delta\lambda_{\text{max}}$ ) in benzenoid hydrocarbons in response to alkyl substitution is a well-known phenomenon for which there is a solid theoretical basis.<sup>8,35</sup> The sulfur-containing derivatives **6**, **8**, and **9** exhibit precisely the same behavior and thereby eliminate the UV spectra from consideration as a source of structural information.

The remaining  $\theta(\text{CSSC})$  indicator, photoelectron spectroscopy, requires a knowledge of  $\Delta\text{IE}(n_+ - n_-)$ . From an MO viewpoint, the  $p\pi$ -type lone electron pairs on sulfur interact to form a bonding ( $n_+$ ) and an antibonding ( $n_-$ ) combination.<sup>31–33</sup> The degree of interaction or the magnitude of the resulting energy level split is a function of the value of  $\theta(\text{CSSC})$ ; maxima at  $0$  and  $180^\circ$ ,

(28) J. Donohue, *J. Am. Chem. Soc.*, **72**, 2701 (1950); F. Lemmer, F. Feher, A. Gieren, S. Hechtischer, and W. Hoppe, *Angew. Chem.*, **82**, 319 (1970).

(29) We are appreciative to Professor J. Sandström (University of Lund) for assistance in attempts to obtain suitable low-temperature spectra.

(30) H. W. Van Wart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1823 (1976).

(31) Cf. ref 26, and references therein.

(32) D. B. Boyd, *J. Am. Chem. Soc.*, **94**, 8799 (1972); J. Webb, R. W. Strickland, and F. S. Richardson, *ibid.*, **95**, 4775 (1973).

(33) H. Bock and G. Wagner, *Angew. Chem.*, **84**, 119 (1972); G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974); M. F. Guimon, C. Guimon, and G. Pfister-Guillouzo, *Tetrahedron Lett.*, 441 (1975).

(34) G. H. Wahl, Jr., J. Bordner, D. N. Harpp, and J. G. Gleason, *J. Chem. Soc., Chem. Commun.*, 985 (1972); *Acta Crystallogr., Sect. B*, **B29**, 2272 (1973).

(35) J. W. Dodd, *J. Chem. Soc. B*, 2427 (1971); E. Heilbronner, T. Hoshi, J. L. v. Rosenberg, and K. Hafner, *Nouv. J. Chim.*, **1**, 105 (1977) and references therein.

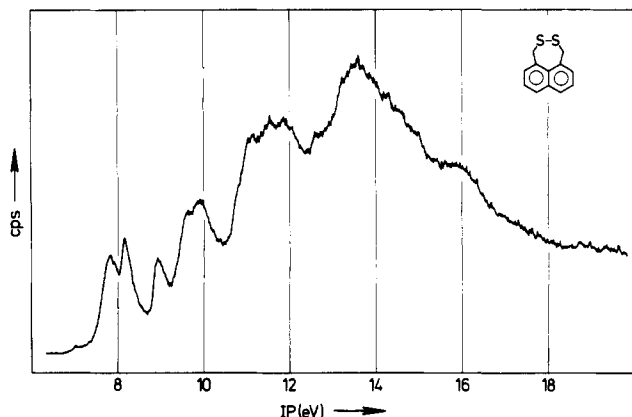


Figure 13. Photoelectron spectrum of 3H,7H-naphtho[1,8-de]-1,2-dithiopin (8).

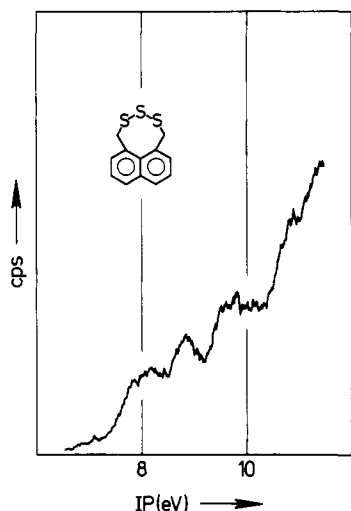


Figure 14. Photoelectron spectrum of 4H,8H-naphtho[1,8-ef]-1,2,3-trithiocin (9).

a minimum at  $90^\circ$ . Assuming the validity of Koopmans' theorem,<sup>36</sup> one is obligated to assign the ionization energies to the MO's in question in order to apply the torsional correlation. In the following sections we employ model compound comparisons and finally MO calculations to distinguish the sulfur lone pair MO's from the naphthalene orbitals of similar energy. The resulting  $\Delta IE$  permits an estimate of  $\theta(\text{CSSC})$  for disulfide 8.

**Photoelectron Spectra.** The He I PE spectra of 1,8-dimethylnaphthalene, dithiol 7, sulfide 6, disulfide 8, and trisulfide 9 are displayed in Figures 10–14. Specific IE's are given in Figure 15 and have been correlated as indicated by the solid lines in the following manner.

Naphthalene and its methyl derivatives deliver photoelectron spectra that yield to interpretation in terms of the hyperconjugative interaction of  $\text{CH}_3$  with the aromatic rings dependent on the position of substitution.<sup>35,37,38a</sup> The first three ionization potentials of 1,8-dimethylnaphthalene, cleanly separated and of equal intensity (Figure 10), are thereby unambiguously assigned to the lowest lying delocalized MO's  $\pi_1$ – $\pi_3$  (7.71, 8.67, and 9.53 eV, Figure 15).

(36) Cf.: H. Bock and B. G. Ramsey, *Angew. Chem.*, **85**, 773 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 734 (1973). J. W. Rabalais, "Principles of Ultraviolet Photoelectron Spectroscopy", Wiley, New York, 1977, pp 99–103.

(37) E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, **55**, 289 (1972); C. Utsonomiya, T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **48**, 1852 (1975); R. Gleiter, R. Haider, I. Murata, and R. M. Pagni, *J. Chem. Res., Synop.*, 72 (1979).

(38) (a) J. P. Maier, *Helv. Chim. Acta*, **57**, 994 (1974); C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Am. Chem. Soc.*, **94**, 1466 (1972). (b) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, 1970.

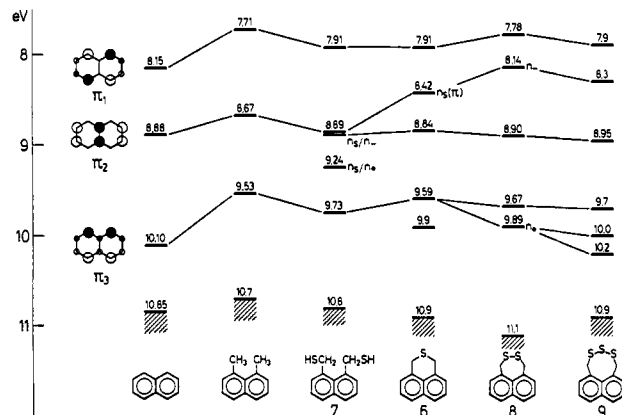


Figure 15. Energy level correlation diagram for some 1,8-peri-naphthalenes assuming the validity of Koopmans' theorem. The numerical values refer to the experimentally determined PES ionization potentials (eV, cf. Figures 10–14).

The trace for the dimercaptan 7 shows two sharp peaks at 7.91 and 9.73 eV assignable to the  $\pi_1$  and  $\pi_3$  MO's, respectively. Each of these values falls between the corresponding ionizations for naphthalene and the 1,8-dimethyl derivative.  $IE_1$  exhibits vibrational fine structure ( $1335 \text{ cm}^{-1}$ ) very similar to that found for the hydrocarbons ( $1400$ – $1450 \text{ cm}^{-1}$ <sup>38</sup> and  $1350 \text{ cm}^{-1}$ , respectively). The broad band found at 8.89 eV is particularly intense and possesses a shoulder at 9.24 eV. It may be assumed that the former corresponds to two ionizations, one of which is attributable to  $\pi_2$ . The other is clearly a sulfur lone pair IE as is the 9.24-eV value. The latter fortuitously coincides with that for benzyl mercaptan ( $IE(n_S) = 9.24 \text{ eV}$ <sup>39</sup>). The nondegeneracy of the sulfur nonbonding electrons in 7 may originate from the existence of a weak  $\text{S}\cdots\text{S}$  interaction (i.e.,  $(n_-/n_+)$  or from a hydrogen bond between the SH groups.<sup>40,41</sup>

It is noteworthy that the IE's  $\pi_1$ – $\pi_3$  for dithiol 7 are 0.2 eV lower in energy than for 1,8-dimethylnaphthalene. This is nearly 1 order of magnitude larger than the corresponding increase for the  $\text{CH}_3 \rightarrow \text{CH}_2\text{SH}$  change in toluene (0.04 eV<sup>39,42</sup>). We surmise that the unsymmetrical  $\text{CH}_2$  disposition with respect to the aromatic ring and the overall out-of-plane distortion experienced by 4 ( $\text{R} = \text{CH}_2\text{Br}$ )<sup>12</sup> likewise obtains for 7 ( $\text{R} = \text{CH}_2\text{SH}$ ). The increased relative cost of removing an electron from 7 vs.  $\text{C}_6\text{H}_5\text{—CH}_2\text{SH}$  may then be rationalized as a destabilization of the corresponding nonplanar cation ( $7^+$ ) to a difference in geometry between the neutral and the ionized species or perhaps to a reduced hyperconjugative interaction between  $\text{CH}_2$  and the aromatic rings as a result of restricted rotation about the ring  $\text{CH}_2$ – $\text{C—C}$  bonds.<sup>8,35,44</sup>

(39) D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Chem. Phys.*, **76**, 1030 (1972).

(40) The PES detection of hydrogen bonding between two first row atoms,  $\text{A—H}\cdots\text{B}$  routinely results in a stabilization of the lone pair participating in the H bond ( $\Delta B$ , 0.05–0.6 eV) and a destabilization of the lone pair on the atom to which hydrogen is bound (A).<sup>41</sup> By reference to  $\text{C}_6\text{H}_5\text{—CH}_2\text{SH}$ , the IE shift pattern is not maintained for 7. If a hydrogen bond is the structural element responsible for unequal  $IE(n_S)$ 's, the severe steric crowding in the 1,8-dithiol may engender the superposition of the  $\Delta IE$  factors.

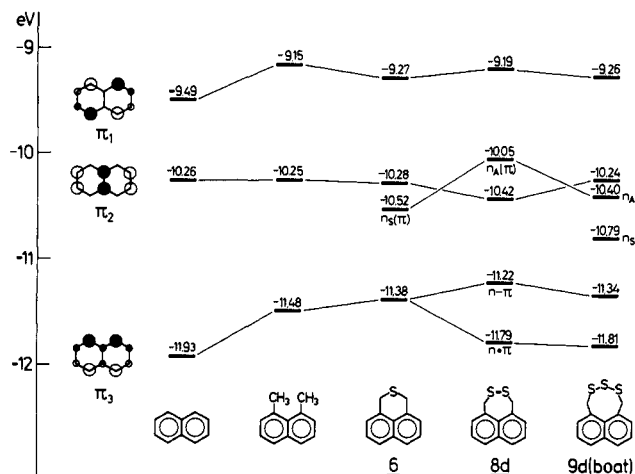
(41) R. S. Brown, *Can. J. Chem.*, **54**, 642, 1929, 3203, 3206 (1976); R. S. Brown and R. W. Marcinko, *J. Am. Chem. Soc.*, **99**, 6500 (1977).

(42) For monosubstituted benzene systems the replacement of methyl by larger alkyl groups causes a small but persistent decrease in the ionization energy of the  $\pi$  levels.<sup>43</sup> For example  $\text{CH}_3 \rightarrow \text{CH}_2\text{CH}_3$  results in a reduction in IE from 8.82 to 8.76 eV.

(43) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962); B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc. B*, 790 (1971); M. Klessinger, *Angew. Chem.*, **84**, 544 (1972); T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **47**, 2563 (1974); C. Párkányi, B. W. Levitt, and L. S. Levitt, *Chem. Ind.*, 356 (1977).

(44) Optimal hyperconjugative interaction between  $\text{CH}_2\text{R}$  and an adjacent  $\pi$  center requires the  $\pi$ -bonded atoms to lie in a plane bisecting the  $\text{H—C—H}$  angle.<sup>45</sup>

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**Figure 16.** CNDO/S molecular orbital correlation diagram for some 1,8-*peri*-naphthalenes. Where possible, correlation lines have been drawn between heavily mixed MO's which retain dominant contributions from either the sulfur bridge or the naphthalene moieties, respectively. Numerical values refer to the calculated MO energies in electronvolts.

The PE spectrum of sulfide **6** (Figure 12) contains four IE's below 10.5 eV. The bands can be assigned to the three naphthalene  $\pi$  orbitals and the sulfur lone pair. The first band at 7.91 eV is attributable to  $\pi_1$ . Support for this allotment is the observed vibrational fine structure of 1330  $\text{cm}^{-1}$  indicative of the lowest energy  $\pi$  orbital. We assign the ionization at 8.42 eV to the sulfur lone pair  $n_s(\pi)$ . The value corresponds closely to the IE's measured for cyclic and alicyclic sulfides: tetrahydrothiophene, 8.42 eV;<sup>46</sup> tetrahydrothiopyran, 8.45 eV;<sup>47</sup> and dimethyl sulfide, 8.44 eV.<sup>33</sup> Finally a rather broad fourth band is reasonably deconvoluted into two ionizations. The maximum lies at 9.59 eV and the shoulder at 9.9 eV. By analogy with the first three members of the series in Figure 15, the former would appear to correspond to  $\pi_3$  and the latter to the  $\sigma$ -sulfur lone-pair  $n_s(\sigma)$ .

Disulfide **8** provides five bands in its PE spectrum from 7.7 to 10.5 eV. Two of these most certainly correspond to the bonding ( $n_+$ ) and antibonding ( $n_-$ ) combinations of the sulfur lone electron pairs, the remaining three belonging to the aromatic nucleus. The first and third maxima can be assigned to the  $\pi_1$  and  $\pi_2$  naphthalene orbitals as they follow unexceptionally the pattern established by the prior members of the series (Figure 15). The second band at 8.14 eV is then identified with  $n_-$ . Endorsement for this view is found in the half-width of the first three bands in Figure 13.  $\pi$  orbitals often lead to broader peaks than lone-pair energy levels.<sup>48</sup> Accurate designation of the remaining two ionizations is difficult. Since the IE's for  $\pi_3$  of 1,8-dimethylnaphthalene, **6** and **7** fall between 9.50 and 9.75 eV, it is consistent to tentatively place this MO at 9.67 eV and  $n_+$  at 9.89 eV.

The PES measurement for trisulfide **9** yields no well-resolved bands below 10.5 eV (Figure 14). It can be anticipated that at least six IE's may be located in this region, namely, the three aromatic  $\pi$  orbitals and a minimum of three sulfur lone-pair combinations. Furthermore, if the DNMR evaluation and the force field calculations are regarded as reasonable approximations to the gas-phase equilibrium populations, the PES sample may have contained from 10 to 25% of the less stable conformation. The spectrum is complicated accordingly. With these reservations in mind the three broad bands in Figure 14 have been decomposed as indicated in Figure 15. A high degree of reliance has been placed on maintaining the correlation of aromatic  $\pi$  levels. Consequently the IE's at 8.3, 10.0, and 10.2 eV are regarded as lone-pair orbitals.

**Table V.** Calculated Electronic Spectra of Sulfide **6**, Disulfide **8**, and Trisulfide **9** ( $\lambda_{\text{max}}$ , nm) (CNDO/S-CI)

sulfide 6	disulfide 8	trisulfide 9
300 (A')	299	297 (A')
H $\rightarrow$ L+1 (0.76)	H $\rightarrow$ L (0.83)	H $\rightarrow$ L (0.84)
H-1 $\rightarrow$ L (0.58)	H-2 $\rightarrow$ L+1 (0.46)	H-1 $\rightarrow$ L+1 (0.44)
H-2 $\rightarrow$ L (0.22)	H-1 $\rightarrow$ L+1 (0.21)	H-3 $\rightarrow$ L+1 (0.24)
H-3 $\rightarrow$ L+5 (0.12)	H-1 $\rightarrow$ L (0.11)	
H-7 $\rightarrow$ L+2 (0.11)		
295 (A')	295	290 (A')
H $\rightarrow$ L (0.83)	H $\rightarrow$ L+1 (0.78)	H $\rightarrow$ L+1 (0.78)
H-1 $\rightarrow$ L+1 (0.49)	H-2 $\rightarrow$ L (0.54)	H-1 $\rightarrow$ L (0.53)
H-2 $\rightarrow$ L+1 (0.18)	H-1 $\rightarrow$ L (0.25)	H-3 $\rightarrow$ L (0.28)
H-3 $\rightarrow$ L+2 (0.14)	H-1 $\rightarrow$ L+1 (0.13)	
266 (A'')	284	258 (A'')
H-2 $\rightarrow$ L+3 (0.84)	H-1 $\rightarrow$ L+2 (0.80)	H-3 $\rightarrow$ L+2 (0.63)
H-1 $\rightarrow$ L+3 (0.40)	H-1 $\rightarrow$ L+3 (0.32)	H-1 $\rightarrow$ L+2 (0.53)
H-2 $\rightarrow$ L (0.26)	H $\rightarrow$ L+2 (0.32)	H-2 $\rightarrow$ L+3 (0.46)
H-3 $\rightarrow$ L+3 (0.15)	H-2 $\rightarrow$ L+2 (0.27)	H $\rightarrow$ L+3 (0.13)
H-1 $\rightarrow$ L (0.12)	H $\rightarrow$ L+3 (0.17)	H-2 $\rightarrow$ L+4 (0.13)
H-5 $\rightarrow$ L+3 (0.12)	H-4 $\rightarrow$ L+3 (0.11)	H-2 $\rightarrow$ L+7 (0.13)
231 (A')	263	255 (A')
H $\rightarrow$ L+2 (0.79)	H-1 $\rightarrow$ L+3 (0.68)	H-2 $\rightarrow$ L+2 (0.74)
H-3 $\rightarrow$ L (0.51)	H $\rightarrow$ L+3 (0.35)	H-3 $\rightarrow$ L+3 (0.37)
H-1 $\rightarrow$ L+5 (0.16)	H-1 $\rightarrow$ L+4 (0.34)	H-1 $\rightarrow$ L+3 (0.28)
H-2 $\rightarrow$ L (0.16)	H-1 $\rightarrow$ L+2 (0.30)	H $\rightarrow$ L+2 (0.21)
H-7 $\rightarrow$ L+1 (0.12)	H-2 $\rightarrow$ L+2 (0.21)	H-5 $\rightarrow$ L+3 (0.18)
H-2 $\rightarrow$ L+5 (0.10)	H-3 $\rightarrow$ L+2 (0.18)	H-2 $\rightarrow$ L+5 (0.18)
H-1 $\rightarrow$ L (0.10)	H-2 $\rightarrow$ L+2 (0.12)	H-2 $\rightarrow$ L+10 (0.15)
	H-3 $\rightarrow$ L+5 (0.12)	H-2 $\rightarrow$ L (0.14)
	H-2 $\rightarrow$ L+4 (0.11)	H-4 $\rightarrow$ L+3 (0.11)
	H-4 $\rightarrow$ L+2 (0.11)	
	H-1 $\rightarrow$ L (0.11)	
	H-4 $\rightarrow$ L+5 (0.10)	

<sup>a</sup> The 75 lowest energy singly excited configurations were included. The singlet transition symmetries ( $C_g$ ) are indicated in parentheses after the  $\lambda_{\text{max}}$  values. The CI state composition is to the right of the indicated excitation. For orbital nomenclature see ref 57. <sup>b</sup> Selected MO symmetries (A or S with respect to the  $C_g$  mirror plane) and electron distributions as measured by the squares of the wave function coefficients are as follows (N = naphthalene ring): **6**, H-2 (S,  $n_S$  (70%)/N (21%)), H-1 (S,  $n_S$  (14%)/N (84%)), H (A, N (96%)); **8**, H-2 ( $n_{SS}$  (10%)/N (88%)), H-1 ( $n_{SS}$  (72%)/N (18%)), H ( $n_{SS}$  (8%)/N (86%)); **9**, H-3 (S,  $n_{SSS}$  (56%)/N (31%)), H-2 (A,  $n_{SSS}$  (80%)), H-1 (S,  $n_{SSS}$  (27%)/N (68%)), H (A,  $n_{SSS}$  (4%)/N (92%)).

**CNDO/S Calculations.** In order to obtain additional confirmation of the orbital assignments indicated by Figure 15, we have performed CNDO/S calculations<sup>49</sup> on the MMPI determined geometries of the 1,8-*peri*-naphthalene structures. The CNDO/S procedure employs sulfur d orbitals and is specifically parameterized to yield UV-vis transitions comparable with experiment. When applied to simple dialkyl disulfides, it is capable of providing a quantitative evaluation of electronic transitions and a qualitative estimate of S-S ionization potentials as a function of  $\theta(\text{CSSC})$ .<sup>26</sup>

The low-energy ionization potentials predicted by CNDO/S are shown in Figure 16. In all cases the calculated values are overestimated by 1–1.5 eV. The qualitative correspondence with experiment is nonetheless quite good. Within the  $D_{2h}$  point group, the three lowest IE's of naphthalene are correctly given as the  $A_u$ ,  $B_{1u}$ , and  $B_{3g}$   $\pi$  orbitals.<sup>50</sup> These are calculated to be lifted in energy by the addition of methyl at the 1- and 8-positions.<sup>8,35</sup> Sulfur bridging as in **6**, **8**, and **9** introduces the sulfur lone-pair orbitals, which in the CNDO/S approximation are stabilized relative to the naphthalene  $\pi$  orbitals. The displacement is evident in Figures 15 and 16 where the low-energy  $n_S$  MO's are shown

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to rise and then fall along the sulfur-homologated series. One outcome of the relative ordering of the two orbital sets is that  $\pi_2$  and  $n_S$  are similar in energy and are consequently strongly mixed in some cases by the CNDO/S calculation. The orbital correlation (Figure 16) takes this into account by connecting energy levels in which the coefficients of the CNDO/S wave functions are centered largely on the naphthalene or the sulfur centers. Qualitatively the calculations support the assignments derived from comparisons of the PE spectra. Most important they confirm that the second and fourth or fifth MO's for disulfide **8** should be regarded as the sulfur  $n_-$  and  $n_+$  combinations, respectively.

The long wavelength UV spectra predicted by CNDO/S-CI for the naphthalene derivatives are tabulated along with the experimental quantities in Table V. In acetonitrile 1,8-dimethylnaphthalene, **6**, **8**, and **9** all exhibit moderately intense, broad bands (65–75 nm wide at base line) at  $\lambda_{\max} = 287, 289, 288,$  and  $300$  nm ( $\epsilon$  6–8000), respectively. Likewise each shows a vibrational fine structure characteristic of the naphthalene nucleus. The CNDO/S-CI calculations quantitatively reproduce the band maxima and indicate that, although there is considerable configurational mixing, the excitations can be characterized essentially as  $\pi-\pi^*$  in nature and localized largely in the aromatic moiety. Much weaker absorption is located at 266 (**6**), 284 (**8**), and 258 nm (**9**) corresponding to the  $n_S \rightarrow \sigma^*(S-C)$  and  $\sigma(S-S) \rightarrow \sigma^*(S-S)$  transitions, respectively. Utilization of the analogous experimental quantities as indicators of molecular geometry about the S–S bonds is clearly precluded by the low intensities and unfavorable  $\lambda_{\max}$ 's relative to the  $\pi$  bands.

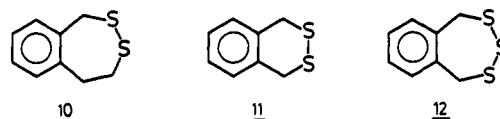
### Discussion and Conclusions

The preparation of *peri*-naphthalene disulfide **8** has, unfortunately, not provided a solution to the problem of creating under ambient conditions a pair of conformationally rigid helical disulfide enantiomers. As revealed by DNMR, however, the compound exists as a mixture of conformers interconvertible over an energy barrier of  $\Delta H^\ddagger = 9.3$  kcal/mol (Table I). At  $-90^\circ\text{C}$  this process is slowed down to such an extent that a well-resolved AB pattern for the  $\text{CH}_2$  protons (Figure 2) is observed. Our force field calculations, summarized in Figure 8, suggest that the latter is itself an average spectrum. The chiral twist-boat ground states **8d** ring invert through the  $C_2$  energy maximum **8a/8b**. In this way the  $\text{CH}_2$  groups appear equivalent on the NMR time scale. As mentioned above, attempts to freeze out this dynamic were frustrated by technical difficulties. For the second higher energy process a barrier of 7.5 kcal/mol is calculated. Thus the racemization of **8d** over the  $C_2$  boat transition state (**8c**) can be identified with the experimental NMR barrier of 9.3 kcal/mol (Table I).

The structure of the molecular mechanics disulfide ground state can be confirmed by reference to the PES measurements and the previously reported correlation between  $\theta(\text{CSSC})$  and  $\Delta E(n_+ - n_-)$ .<sup>33</sup> As discussed above,  $n_-$  is easily assigned to  $IE = 8.14$  eV, while  $n_+$  is either at 9.67 or 9.89 eV. The respective  $\Delta E(n_+ - n_-)$  values are 1.53 and 1.75 eV. These, in turn, may be translated into an S–S torsional angle of either  $43$  or  $37^\circ$  by means of the experimental relationship. This provides reasonable agreement with the MMPI value of  $\theta(\text{CSSC}) = 44^\circ$  for the twist-boat shape **8d** (Table III). The chiral twist  $C_2$  structure **8a/8b** with a calculated S–S dihedral angle of  $82^\circ$  is thereby eliminated as the ground-state species.

The related seven-membered ring disulfide **10** has likewise been studied by variable-temperature NMR.<sup>2a,51</sup> Below  $0^\circ\text{C}$  two forms are evident in the ratio of 7:3. These have been assigned to the chair and the twist-boat conformations, respectively. Two coalescence temperatures are observed at  $-60$  and  $0^\circ\text{C}$  ( $\Delta G^\ddagger = 10.4$  and  $13.5$  kcal/mol, respectively). The former was attributed to pseudorotation between boat and twist-boat forms, whereas the latter was identified with chair–chair interconversion. Consideration of molecular models suggest that the boat–twist-boat

transformation in **10** requires passage of  $\theta(\text{CSSC})$  through  $0^\circ$  as is the case for the MMPI predicted racemization of twist **8d** via the boat transition-state **8c** ( $\Delta G^\ddagger(-73^\circ\text{C}) = 9.5$  kcal/mol, Table I). Likewise the half-chair ground state of enantiomers of the benzodithiin **11** equilibrates presumably by way of a half-boat form ( $\theta(\text{CSSC}) = 0^\circ$ ) with an energy barrier of  $\Delta G^\ddagger(T_c < -80^\circ\text{C}) \sim 8.5$  kcal/mol.<sup>52</sup> The similarity in energy barriers for **8**, **10**, and **11** may well be indicative of a resemblance in transition-state structure.



For the trisulfide **9** the experimental NMR data can also be rationalized by molecular mechanics. The boat conformers are predicted to be more stable than the chair forms by 0.6 kcal (Figure 9). Thus we assign the more intense outer AB quartet to the former and the inner, less intense quartet to the latter (Figure 4). Interconversion between the boat conformations by way of a twist-boat  $C_2$  structure (**9a/b**) is predicted to take place with a barrier somewhat larger than 13.6 kcal/mol (Figure 9). The experimental NMR value for this process is  $\Delta H^\ddagger = 15.4$  kcal/mol. We assume boat–chair interconversion to show the higher barrier of  $\Delta G^\ddagger(75^\circ\text{C}) = 18$  kcal/mol (Table I). For comparison the dynamic  $^1\text{H}$  NMR behavior of **12** can be cited.<sup>51</sup>

At room temperature two forms assigned the chair and the "flexible" conformations are present in the ratio of 85:15. Ring inversion between them requires  $\Delta G^\ddagger(114^\circ\text{C}) = 17.4$  kcal/mol, while pseudorotation between boat and twist geometries was estimated to be  $\Delta G^\ddagger(-80^\circ\text{C}) = 10$  kcal/mol. No attempt was made to specify the relative stability of the latter conformations, but force field calculations of the type employed in the present work suggest the boat of **12** to be more stable than the twist by 7.7 kcal/mol and less stable than the chair by 2.3 kcal/mol. Furthermore the relative experimental magnitudes of ring inversion and pseudorotation are likewise matched by calculation.<sup>53</sup> Thus the seven-membered ring trisulfides **9** and **11** appear to be similar in their equilibrium composition ( $\Delta G(\text{chair/boat}, 25^\circ\text{C}) = 1.4$  and  $1.0$  kcal/mol, respectively) and ring inversion barrier ( $\Delta G^\ddagger = 17.9$  ( $75^\circ\text{C}$ ) and  $17.4$  ( $83^\circ\text{C}$ ) kcal/mol, respectively) but somewhat divergent in pseudorotation energy requirements ( $\Delta G^\ddagger = 15.8$  ( $35^\circ\text{C}$ ) and  $10$  ( $-80^\circ\text{C}$ ) kcal/mol, respectively).

### Experimental Section

When employed as a solvent, water was first degassed for several hours under aspirator vacuum. All melting points are uncorrected. Spectra were obtained with the following instruments: JEOL A 60 spectrometer (60 MHz,  $^1\text{H}$  NMR), JEOL P FT 100 spectrometer (100 MHz,  $^1\text{H}$  and  $^{13}\text{C}$  NMR), Leitz SP 800 UV spectrometer, Beckman A 3 IR spectrometer, Varian MAT CH-4B mass spectrometer, Cary Krypton Ion Laser (Model 82, Raman), and a Perkin-Elmer PS-18 photoelectron spectrometer.

The PE spectra were calibrated with a mixture of argon and xenon gases introduced into the target chamber simultaneously with the sample. 1,8-Dimethylnaphthalene was injected through the gas inlet at room temperature, whereas a heated probe was employed for the other compounds. The recording temperatures for 1,8-dimethylnaphthalene, **6**, **8**, and **9** were 38–39, 61–66, 73–84, and 90–97  $^\circ\text{C}$ , respectively (experimental resolution, 25–35 meV). The reported ionization energies (Figure 15) are each averages of five determinations.

**1,8-Bis(mercaptomethyl)naphthalene (7).** All operations were carried out under a nitrogen atmosphere. 1,8-Bis(bromomethyl)naphthalene (**4**) ( $R = \text{CH}_2\text{Br}$ )<sup>54</sup> (15.7 g, 50 mmol) and thiourea (8.0 g, 105 mmol) were refluxed for 2 h in a mixture of ethanol (200 mL) and water (50 mL). Evaporation of the solvent from the clear, colorless solution caused the 1,8-bis(methylthioronium bromide)naphthalene to precipitate as a white solid. The latter was dissolved in water (150 mL) and 2-propanol (300

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Table VI. DNMR Quantities for Disulfide 8 and Trisulfide 9

$T, ^\circ\text{C}$	$\Delta\delta, \text{Hz}$	$J, \text{Hz}$	$\delta$
(a) 3 <i>H</i> ,7 <i>H</i> -Naphtho[1,8- <i>de</i> ]-1,2-dithiepin (8) <sup>a</sup>			
-77	86		4.80
-85.5	87.9	15-16	4.80
-90	88.0	15.5	4.80
(b) 4 <i>H</i> ,8 <i>H</i> -Naphtho[1,8- <i>ef</i> ]-1,2,3-trithiocin (9) <sup>b</sup>			
weak AB quartet (4.85 ppm)			
+46	43.0	15.55	5.03
+37.5	43.0	15.60	5.03
+29.2	43.0	15.60	5.03
strong AB quartet (4.95 ppm)			
+20	99.05	13.35	4.96
+12	98.50	13.35	4.96
+4	98.00	13.35	4.96
-6	97.35	13.35	4.96
-18	96.55	13.35	4.96

<sup>a</sup> Figure 2. <sup>b</sup> Figure 4.

mL), the solution was added dropwise to a boiling sodium hydroxide solution (100 mL, 20%) for 2 h, refluxed for 6 h, and finally freed of most of the 2-propanol at reduced pressure. The resulting milky, basic aqueous phase was extracted with benzene to remove some sulfide 6 followed by careful acidification (50% HCl, 400 mL) at 0 °C leading to the precipitation of a white solid. The latter crystallized as colorless needles (*i*-PrOH). By drying at 40 °C in high vacuum and subliming (oil bath temperature 75 °C), we obtained the dimercaptan 7 as white crystals, mp 83–84 °C (3.85–4.10 g, 70–75%). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>S<sub>2</sub>: C, 65.41; H, 5.49. Found: C, 65.24; H, 5.48. <sup>1</sup>H NMR:  $\delta$  (CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.60–7.85 (2 H, m), 7.15–7.45 (4 H, m), 4.40 (4 H, d,  $J$  = 6 Hz, CH<sub>2</sub>), 1.85 (2 H, t,  $J$  = 6 Hz, SH). Mass spectrum,  $m/e$  220 (M<sup>+</sup>), 186 (M – H<sub>2</sub>S), 171, 153, 141, 127, 115. IR:  $\nu_{\text{max}}$  (KBr) 1600, 1440, 830, 780, 2545 (S–H) cm<sup>-1</sup>.

**2*H*,6*H*-Naphtho[1,8-*cd*]thiin (6).** 1,8-Bis(bromomethyl)naphthalene (4) (R = CH<sub>2</sub>Br)<sup>54</sup> (15.7 g, 50 mmol) and sodium thiosulfate pentahydrate (12.4 g, 50 mmol) in ethanol/water (1:1, 100 mL) were heated to 100 °C for 2 h. The solvent was removed at reduced pressure and the residue extracted with boiling benzene (100 mL). The benzene was removed by rotary evaporation, and the residue was dissolved in hot ethanol. By slow cooling, the sulfide 6 crystallized as colorless leaves, mp 98–99 °C (lit. 96–97 °C<sup>55</sup>) (6.05–6.60 g, 65–70%). <sup>1</sup>H NMR:  $\delta$  (CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.75–7.55 (2 H, m), 7.40–7.10 (4 H, m), 4.00 (4 H, s, CH<sub>2</sub>). <sup>13</sup>C NMR:  $\delta$  (CDCl<sub>3</sub>, Me<sub>4</sub>Si) 134.204, 132.083, 128.656 (quaternary aromatic carbons), 127.686, 124.774, 124.133 (tertiary aromatic carbons), 32.520 (CH<sub>2</sub>).

**3*H*,7*H*-Naphtho[1,8-*de*]-1,2-dithiepin (8).** FeCl<sub>3</sub>·6H<sub>2</sub>O (7.0 g, 25 mmol) was dissolved in a mixture of ether (500 mL) and glacial acetic

acid (50 mL). The red-brown mixture was treated with 1,8-bis(mercaptomethyl)naphthalene (7) (1.1 g, 5 mmol) in THF (100 mL) by dropwise addition for 2 h at room temperature. After standing at ambient temperature for 2 days with stirring, the yellow-green solution was extracted twice with water (100 mL). The organic phase was dried over MgSO<sub>4</sub>, the solvent evaporated, and the yellow residue crystallized (EtOH) to give yellow needles, mp 114–115 °C (0.76–0.87 g, 70–80%). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>S<sub>2</sub>: C, 66.01; H, 4.62. Found: C, 65.74; H, 4.51. <sup>1</sup>H NMR:  $\delta$  (CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.70–7.50 (2 H, m), 7.35–7.15 (4 H, m), 4.45 (4 H, s, CH<sub>2</sub>). <sup>13</sup>C NMR:  $\delta$  (CDCl<sub>3</sub>, Me<sub>4</sub>Si) 136.506, 135.592, 133.772 (quaternary aromatic carbons), 129.032, 128.858, 125.230 (tertiary aromatic carbons), 39.976 (CH<sub>2</sub>). Mass spectrum,  $m/e$  218 (M<sup>+</sup>), 186/185 (M – HS), 171 (M – CH<sub>2</sub>S), 152/153/154 (M – 2S), 92, 76. IR:  $\nu_{\text{max}}$  (KBr) 1600, 1580, 1450, 825, 775, 715 cm<sup>-1</sup>. UV:  $\lambda_{\text{max}}$  (CH<sub>3</sub>CN) 232 nm ( $\epsilon$  16800), 288 (8000). Raman:  $\nu_{\text{max}}$  (solid) 510 (S–S) cm<sup>-1</sup>.

**4*H*,8*H*-Naphtho[1,8-*ef*]-1,2,3-trithiocin (9).** 1,8-Bis(mercaptomethyl)naphthalene (7) (1.1 g, 5 mmol) was dissolved in ether (100 mL) and treated dropwise with a solution of sulfur dichloride (0.35 mL) in ether (100 mL) over 1 h. During addition the color of the SCl<sub>2</sub> solution faded and the reaction mixture became acidic. Simultaneously the reaction turned cloudy and finally delivered white crystals. The mixture was stirred at room temperature for 1 h and depleted of ether by rotary evaporation and the residue extracted twice with hot absolute ethanol (100 mL). Upon cooling, the trisulfide 9 crystallized as white needles, mp 173–174 °C (0.50–0.60 g, 40–48%). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>S<sub>3</sub>: C, 57.56; H, 4.02. Found: C, 57.84; H, 4.00. <sup>1</sup>H NMR:  $\delta$  (pyridine-*d*<sub>5</sub>, Me<sub>4</sub>Si) 8.00–7.85 (2 H, m), 7.60–7.40 (4 H, m), 4.70–5.20 (4 H, AB system,  $J$  = 15.2 Hz, CH<sub>2</sub>), 4.30–5.40 (4 H, AB system,  $J$  = 14 Hz, CH<sub>2</sub>). Mass spectrum,  $m/e$  250 (M<sup>+</sup>), 218 (M – S), 186/185 (M – HS<sub>2</sub>), 171, 153/152, 92, 76. IR:  $\nu_{\text{max}}$  (KBr) 1600, 1500, 1470, 830, 775 cm<sup>-1</sup>. UV:  $\lambda_{\text{max}}$  (CH<sub>3</sub>CN) 236 nm ( $\epsilon$  17000), 300 (9050). Raman:  $\nu_{\text{max}}$  (solid) 503 (S–S) cm<sup>-1</sup>.

**Kinetic Measurements.**<sup>56</sup> The polysulfides 8 and 9 were dissolved in acetone-*d*<sub>6</sub> (0.01 mol), and their CH<sub>2</sub> <sup>1</sup>H NMR spectra were taken at various temperatures at a sweep width of 100 MHz (pulse-Fourier technique, 100 MHz), with Me<sub>4</sub>Si as internal standard.  $\Delta\delta$  is the chemical shift difference between the midpoints of the A and B parts of the AB spectra.  $\delta$  corresponds to the shift of the midpoint of the entire AB spectrum from Me<sub>4</sub>Si (cf. Table VI).

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(56) Line-shape analysis was carried out by means of a local computer program on the basis of the expressions given in ref 17 and 18.

(57) For simplicity H = HOMO (highest occupied MO) and L = LUMO (lowest unoccupied MO), H-1, H-2, ... refers to the next highest occupied and the second highest occupied MO's, respectively. Likewise L+1, L+2, ... designate the next lowest, second lowest, and so on virtual orbitals.

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