

Two Tautomeric Trihetero[9](9,10)anthracenophanes

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Thiacrown ethers stand apart from their aza- and oxacrown counterparts for a number of reasons, some that have hindered their development and others that promise unique future applications. The facility of the soft sulfides to complex cations of Ag, Cu, and Au for example opens up new possibilities in the coordination chemistry of macrocycles with multiple sulfide linkages. On the other hand, the tendency of SCH₂CH₂S subunits to favor *anti* arrangements leads to preferred conformations having sulfurs arrayed poorly with regard to cooperative binding to an ion.^{1–3} An additional barrier to thiacycrown chemistry has probably been the lack of satisfactory methods of preparation.⁴

We are interested in preparing thiacycrown ethers that incorporate a tautomeric spacer within the thiacycrown macrocycle since this feature creates the added potential for distinct spatial arrangements of sulfurs (and therefore differential ligating ability) in the various tautomeric forms of the host. Such a combination might find use, for example, in signaling the presence of a particular ion, *i.e.* as a sensor for that ion, if the tautomeric forms are fairly close in energy and have distinguishable spectroscopic properties. The anthracene–methylenedihydroanthracene tautomeric pair fits these requirements. Anthracenes substituted with an alkyl group at the 9 position have a methylenedihydroanthracene (MDA) tautomer that is generally less stable than the anthracene form. In the case of 9-methylanthracene^{5–7} the energy difference is *ca.* 40 kJ mol⁻¹. However, in some sterically crowded anthracenes the gap is smaller, and the MDA has been shown to be the more stable tautomer.⁸ Also, for 9,10-bridged anthracenes ([*n*](9,10)-anthracenophanes) there is substantial experimental^{9–11} and computational¹² evidence that the energies of the

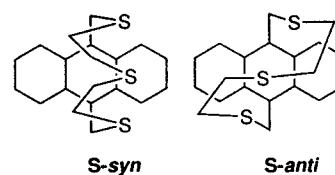
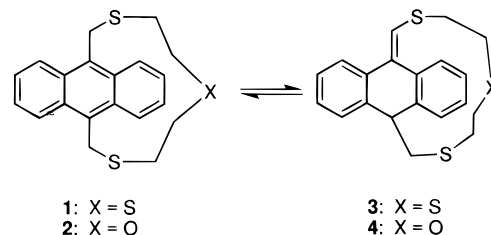


Figure 1. Stylized drawings of the two families of conformations of **1**.

tautomeric partners are close and that as bridge length is decreased, the MDA tautomer becomes the more stable member of the pair. In all-carbon systems it is at a bridge length of 7 or 8 that this transition occurs, the principal cause being the increasingly large torsional strain contribution due to bending of the anthracene ring in the cyclophane tautomer. As a beginning in establishing the effects of multiple heteroatoms and larger bridge sizes on the tautomeric equilibrium and on bridge conformation, we have prepared two trihetero[9](9,10)-anthracenophanes, **1** and **2**, which are capable of existing as their MDA tautomers **3** and **4**.



Results and Discussion

Through a global search of conformations of **1** using molecular mechanics methods, followed by semiempirical MO (AM1) minimization of structures, two unique conformations falling within a 3 kcal mol⁻¹ window were located. The conformers are distinguishable in part by the disposition of the sulfurs connected to the benzylic positions, either *S-syn* or *S-anti* as shown in Figure 1. These geometries have *C*_s and *C*₂ symmetry, respectively, and are qualitatively similar to the structures calculated previously for [9]paracyclophane^{13,14} and 2,8-dithia[9](9,10)anthracenophane.^{9a,15} The lowest energy conformer (ΔH_f 65.73 kcal mol⁻¹) is *S-anti*, and the sulfurs within

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(3) For a general discussion of the affect of replacement of oxygen by sulfur in crown ethers on structure and complexation see Goldberg, I. In *Crown Ethers and Analogues*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Ch. 7.
(4) For a short review of the thiacycrown synthesis and chemistry see Kellog, R. M., Ch. 14 In *Crown Compounds: Toward Future Applications*; Cooper, S. R., Ed.; VCH Publishers, Inc.: New York, 1992.
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each ethylene subunit of the bridge are *anti* to each other. The second conformer is *S-syn* (ΔH_F 66.96 kcal mol⁻¹), also with sulfurs within each ethylene subunit of the bridge *anti* to each other. A similar search for **3** afforded five conformations within a 3 kcal window (ΔH_F 65.37, 65.90, 65.91, 66.12, 68.07 kcal mol⁻¹), and several are quite similar in energy to the lowest energy conformation of **1**. At the AM1 level, therefore, it appears that the two tautomeric forms are very close in energy and that each has a number of conformations of similar energy.

For **2**, a global search analogous to that done for **1** afforded three low energy conformations (ΔH_F 24.61, 26.45, 27.24 kcal mol⁻¹). The lowest energy conformation is *S-anti* (C_2 symmetry), and the heteroatoms in both ethylene subunits are *anti*. The three lowest energy MDA conformers have ΔH_F 24.08, 24.09, and 24.19 kcal mol⁻¹. So once again, this sort of analysis suggests that the tautomers are of similar energy.

Both **1** and **2** were prepared in fair yield (unoptimized crude yields are **1**: 54%; **2**: 69%) without recourse to the usual high-dilution conditions that are commonly used for cyclizations of this sort and without aid of the use of the cesium salt methods that have proven so successful for macrocyclic polythioether synthesis.¹⁶ Both were prepared by refluxing a suspension of 9,10-bis(chloromethyl)anthracene in an ethanolic potassium hydroxide solution containing 2-mercaptoethyl sulfide (or 2-mercaptoethyl ether for **2**) under an atmosphere of nitrogen for 3 h.

The X-ray crystal structure of **1**,¹⁷ though disordered, reveals that **1** crystallizes as the anthracene tautomer, and that the benzylic sulfurs are *neither S-syn* nor *S-anti* but rather are essentially contained in a plane bisecting the 9,10 positions and perpendicular to the anthracene ring. There is slight folding of the anthracene ring as evidenced by an angle of 5.3° between the least-squares planes of the outer six-member rings of the anthracene subunit. Also, the sulfurs within each ethylene subunit are *anti* to each other as they are in the lowest energy calculated structure of this tautomer. In fact, energy minimization (AM1) using this as the starting structure afforded a conformation identical to the lowest energy conformation located via the global search. Apparently, crystal packing forces are sufficient to overcome the peri interactions that contribute to the canting of the benzylic methylene groups in calculated structures. A comparison of bridge dihedral angles from the crystal structure with those established by calculation is presented in Table 1.

The solid state structure for **2** is also the anthracene tautomer and in this case it has the *S-anti* conformation with the sulfurs within each ethylene subunit *anti* to the oxygen as in the lowest energy calculated structure for **2**. The dihedral angle between the least-squares planes of the outer six-member rings is 3.8°. Energy minimization (AM1) using the X-ray structure as starting geometry afforded a conformation that was identical to the lowest energy calculated structure. A comparison of bridge dihedral angles from the crystal structure with those established by calculation is presented in Table 2.

Proton NMR spectra of **1** and **2** reveal that both exist

Table 1. Dihedral Angles (deg) for **1 from the Crystal Structure, Semiempirical MO (AM1), and Molecular Mechanics (MMX) Calculations**

dihedral angles	crystal structure	AM1	MMX
S ₁ -C ₁ -C ₂ -S ₂	177.23	179.26	176.14
H ₁ -C ₁ -C ₂ -H ₂	61.83	54.38	59.85
H ₁ -C ₁ -C ₂ -H ₄	178.84	173.48	177.25
H ₃ -C ₁ -C ₂ -H ₂	177.25	174.19	177.33
H ₃ -C ₁ -C ₂ -H ₄	65.73	66.70	65.27
S ₂ -C ₃ -C ₄ -S ₃	175.49	179.22	178.53
H ₅ -C ₃ -C ₄ -H ₆	59.86	54.43	59.41
H ₇ -C ₃ -C ₄ -H ₆	174.51	173.53	177.12
H ₅ -C ₃ -C ₄ -H ₈	177.22	174.24	177.25
H ₇ -C ₃ -C ₄ -H ₈	68.13	66.66	64.97

Table 2. Dihedral Angles (deg) for **2 from the Crystal Structure, Semiempirical MO (AM1), and Molecular Mechanics (MMX) Calculations**

dihedral angles	crystal structure	AM1	MMX
S ₁ -C ₁ -C ₂ -O	176.40	177.94	178.07
H ₁ -C ₁ -C ₂ -H ₂	52.70	50.03	54.12
H ₁ -C ₁ -C ₂ -H ₄	172.41	171.31	172.86
H ₃ -C ₁ -C ₂ -H ₂	170.08	168.96	170.90
H ₃ -C ₁ -C ₂ -H ₄	70.22	69.76	70.35
O-C ₃ -C ₄ -S ₂	179.59	177.87	177.34
H ₅ -C ₃ -C ₄ -H ₆	55.48	49.97	53.51
H ₇ -C ₃ -C ₄ -H ₆	173.77	171.25	172.21
H ₅ -C ₃ -C ₄ -H ₈	172.87	168.89	170.28
H ₇ -C ₃ -C ₄ -H ₈	68.84	69.83	71.02

preferentially as the anthracene tautomer in solution as well; no signals other than those attributable to this tautomer are detectable. (This is true in a variety of solvents over a wide polarity range.) These spectra also suggest that the bridge in both compounds is conformationally mobile on the NMR time scale since the AA'BB' pattern for the ethylene subunits (two multiplets, each due to two protons of a single methylene group: ¹H, ¹H COSY and ¹H, ¹³C COSY) is confined to a narrow shift range in contrast with the expectation that some protons would be shifted to very high field by the anisotropic shielding effect of the anthracene ring given their proximity to that ring plane in the calculated structures. Moreover, the benzylic methylene protons appear as a singlet rather than the AB quartet expected for any of the individual conformations in the absence of rapid conformational interconversion. Carbon NMR spectra for both compounds are entirely consistent with this picture since only 7 signals (3 aliphatic) are observed in the broad-band decoupled spectra.

The AA'BB' patterns of the SCH₂CH₂S subunits in **1** and SCH₂CH₂O subunits in **2** specify the solution phase bridge conformation further. The vicinal coupling constants of **1** were extracted through a full-lineshape fit of the calculated spectrum to the room temperature experimental spectrum yielding the coupling constants in Table 3. For comparison, the analogous couplings for the crystal structure and the lowest energy calculated structure (both molecular mechanics, MMX force field, and semiempirical MO, AM1, methods), generated using the Karplus equation modified to accommodate the effects of sulfur substitution,¹⁸ are also presented. If one assumes that the spectrum is produced by enantiomeric (*S-anti*) or identical (*S-syn*) conformations interconverting rapidly on the NMR time scale, then the coupling constants extracted through spectrum simulation should

(16) Dijkstra, G. D. H.; Kellogg, R. M. *J. Org. Chem.* **1987**, *52*, 4230 and references therein.

(17) The authors have deposited atomic coordinates for **1** and **2** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

(18) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783-2792.

Table 3. Predicted Vicinal Coupling Constants (Hz) in 1 Determined from the Dihedral Angles in the Crystal Structure, Two Computational Methods, and Experimental Values Established through Spectrum Simulation

dihedral angles	crystal structure	AM1	MMX	simulated
S ₁ -C ₁ -C ₂ -S ₂	—	—	—	—
H ₁ -C ₁ -C ₂ -H ₂	2.23	4.19	3.26	4.64
H ₁ -C ₁ -C ₂ -H ₄	13.13	12.97	13.10	13.19
H ₃ -C ₁ -C ₂ -H ₂	13.10	13.01	13.10	13.19
H ₃ -C ₁ -C ₂ -H ₄	2.85	2.09	2.34	4.64
S ₂ -C ₃ -C ₄ -S ₃	—	—	—	—
H ₅ -C ₃ -C ₄ -H ₆	1.88	4.18	3.19	4.64
H ₇ -C ₃ -C ₄ -H ₆	13.02	12.98	13.10	13.19
H ₅ -C ₃ -C ₄ -H ₈	13.10	13.01	13.11	13.19
H ₇ -C ₃ -C ₄ -H ₈	3.18	2.09	2.30	4.64

be compared to the average of *gauche* (H1C1C2H2, H3C1C2H4 for example) or *anti* (H1C1C2H4, H3C1C2H2 for example) vicinal couplings in the crystal structure or calculated structure of **1**. The *anti* vicinal coupling constants agree within 0.2 Hz for the crystal structure and both calculated structures. The *gauche* vicinal couplings afforded by simulation of the experimental spectrum agree most closely with the AM1 result but are still 1.5 Hz higher.

The assumption of rapid chemical exchange for both **1** and **2** was confirmed through examination of their spectra at lower temperatures; low temperature (400 MHz) proton NMR spectra for both compounds exhibited reversible broadening of all peaks and at the lowest temperatures that we were able to achieve (*ca.* -119 °C; CD₂Cl₂/ethanol-*d*₆), the benzylic methylene protons appeared as an AB quartet as is expected for slowly interconverting *S-anti* or *S-syn* conformers. For **1**, the ΔG^\ddagger for the exchange process¹⁹ at the coalescence temperature (T_c -86 °C) of the AB quartet is 8.44 kcal mol⁻¹. At -119°, the other bridge protons in **1** are resolved into broad multiplets at δ 2.05 (1H), 1.43 (2H), and -0.25 (1H) ppm.²⁰ We were unable to extract accurate coupling constants through full lineshape analysis of these peaks.

Conclusions

In summary, we have found that the trihetero[9](9,-10)anthracenophanes **1** and **2** are easily prepared without recourse to high-dilution techniques. Each compound was found (computationally) to have a tautomeric partner of similar energy: The lowest energy calculated structures for **1** and **3** at the AM1 level are within *ca.* 0.4 kcal mol⁻¹ of each other. The gap for **2** and **4** is less than 0.6 kcal mol⁻¹. (In both compounds the MDA tautomer is the lowest energy structure.) Nonetheless, only the anthracene tautomer in each pair is represented in the NMR spectra of these compounds, and both crystallize in this form as well. The X-ray crystal structure for **1** has the same pattern of staggering in the bridge as the lowest energy calculated structure though the benzylic methylene groups are not canted in the same fashion. For **2**, the crystal structure has essentially the same conformation as the lowest energy calculated geometry.

(19) The free energy of activation at coalescence was calculated as follows: $\Delta G_c^\ddagger = aT[9.972 + \log(T(\delta\nu/2 + 6J_{AB}^2)^{1/2})]$ where $a = 4.575 \times 10^{-3}$, $J_{AB} = 12.7$ Hz, and $\delta\nu = 236$ Hz: Sandstrom, J. *Dynamic NMR Spectroscopy*, Academic Press: New York, 1982.

(20) The behavior of **2** at low temperatures is similar though the T_c is approximately 20 °C higher corresponding to an approximate free energy of activation that is 1 kcal mol⁻¹ higher than that found for **1**.

Both **1** and **2** are conformationally mobile on the NMR time scale at room temperature, and both show reversible broadening at lower temperatures indicative of the slowed interconversion of enantiomeric or identical conformations. Finally, although larger members of this series with more binding sites will be required for most efficient binding, preliminary experiments indicate that compound **1** does form Ag⁺ complexes while **2** does not.

Experimental Section

General Procedures. All solvents and organic reagents were used as acquired and were obtained from Aldrich Chemical Company, except bis(chloromethyl)anthracene (Eastman). NMR spectra were run at 400 MHz (¹H) or 100 MHz (¹³C) in CDCl₃ (TMS reference) unless otherwise specified. For low temperature NMR experiments, the probe temperature was calibrated using a neat methanol sample. UV-vis spectra were obtained on chloroform solutions.

2,5,8-Trithia[9](9,10)anthracenophane (1). 2-Mercaptoethyl sulfide (0.200 mL, 1.53 mmol) was added to a stirred suspension of 0.173 g of potassium hydroxide (3.06 mmol) and 0.413 g of 9,10-bis(chloromethyl)anthracene (1.50 mmol) in 95% ethyl alcohol (65 mL), and the resulting mixture was refluxed for 3 h under dry nitrogen. The reaction mixture was cooled to room temperature, and the precipitated product was removed by vacuum filtration and washed with water on the filter. Additional product was isolated by addition of water to the filtrate followed by vacuum filtration and washing with water resulting in a 54% yield. A recrystallized sample of **1** (65% recovery from CHCl₃/hexanes; mp > 210 °C) gave the following data: ¹H NMR δ 0.84 (m, 4H), 1.87 (m, 4H), 4.99 (s, 4H), 7.64 (m, 4H), 8.43 (m, 4H); ¹³C NMR δ 26.81, 29.54, 32.35, 125.42, 126.52, 128.06, 130.45 ppm; UV-vis λ_{max} 260, 350, 368, 388, 410 nm; IR (KBr pellet) 1445, 1422, 1188, 1183, 772, 668, 614 cm⁻¹. Compound **1** reacted instantly with AgBF₄ in CHCl₃, affording a yellow precipitate that was insoluble in toluene, acetone, acetonitrile, and methanol. This material dissolved slowly in DMSO-*d*₆, and the ¹H NMR spectrum was identical to the spectrum of **1**. Apparently, **1** forms an oligomeric complex with Ag⁺ that is decomposed by DMSO.

5-Oxa-2,8-dithia[9](9,10)anthracenophane (2). Compound **2** was prepared in 69% yield (crude) with the same procedure as **1** but using 2-mercaptoethyl ether. A recrystallized sample of **2** (59% recovery after two recrystallizations from CHCl₃/petroleum ether; mp 195–199 °C) gave the following data: ¹H NMR δ 1.65 (m, 4H), 1.82 (m, 4H), 4.95 (s, 4H), 7.62 (m, 4H), 8.38 (m, 4H); ¹³C NMR δ 26.56, 27.20, 67.93, 125.28, 126.32, 128.59, 130.71 ppm; UV-vis λ_{max} 235, 265, 368, 388, 411; IR (Nujol mull) 1065, 770, 722, 613 cm⁻¹. Trace amounts of a second compound crystallized separately during recrystallization of **2**. ¹H NMR δ 2.73 (m), 3.51 (m), 4.55 (s), 7.15 (m), 8.09 (m) ppm. This compound was tentatively assigned a [9.9](9,10)-anthracenophane structure in which each nine atom bridge contains two sulfurs and one oxygen, i.e. the likely dimeric structure from reaction of 2-mercaptoethyl ether and 9,10-bis(chloromethyl)anthracene.

Calculations. Minimum energy structures were located by using the global search program GMMX (Serena Software, Bloomington, IN), employing primarily a statistical search on coordinates. Unique minimum energy structures within 3 kcal mol⁻¹ of the lowest energy structure located in this fashion were then subjected to molecular mechanics minimization using the MMX force field²¹ in the computer program PCMODEL, version 4.5 (Serena Software). Finally, these molecular mechanics structures were reminimized using the AM1 model in the program Spartan, version 4 (Wavefunction, Inc.).

X-ray Structure Determination. Single crystals of **1** and **2** were grown by vapor diffusion (CHCl₃/hexanes). Data collection for both was done at ambient temperature on a Rigaku AFC6S diffractometer with graphite-monochromated molybde-

(21) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press Inc.: Greenwich, CT, 1993; Vol. 2, p 65–92.

num K_{α} radiation ($\lambda = 0.71069 \text{ \AA}$). Both structures were solved by direct methods.^{22,23} Neutral atom scattering factors were taken from Cromer and Waber.²⁴ Crystal data for **1**: Twenty-five reflections were used for the unit cell determination, corresponding to a triclinic cell in the space group $P1$ bar (no. 2) with the following lattice parameters: $a = 12.233(2) \text{ \AA}$, $b = 14.996(1) \text{ \AA}$, $c = 10.185(2) \text{ \AA}$, $\alpha = 94.29(1)^{\circ}$, $\beta = 94.98(1)^{\circ}$, $\gamma = 108.483(7)^{\circ}$, $V = 1754.9(4) \text{ \AA}^3$. For $Z = 2$ and formula weight 352.5, the calculated density was 1.334 g cm^{-3} . Of the 6468 reflections collected 6156 were unique. $R = 0.057$ ($R_w = 0.074$). The two molecules in the unit cell are very similar except that molecule A is disordered at the third, fourth, sixth, and seventh atoms of the bridge, C16, C17, C18, and C19.²⁵ The ORTEP²⁶ drawing included with the supporting information shows the positions of highest occupancy for the disordered atoms. Crystal data for **2**: Twenty-five reflections were used for the unit cell determination, corresponding to a monoclinic cell in the space

(22) Compound **1**: (a) Gilmore, C.J. MITHRIL, an integrated direct methods computer program. *J. Appl. Crystallogr.* **1984**, *17*, 42. (b) Beurskens, P. T. "DIRDIF: Direct Methods for Difference Structures—An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors"; Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands. Compound **2**: (c) SHELX: Sheldrick, G. M.; Kruger, C.; Goddard, R. In *Crystallographic Computing 3*; Oxford University Press: New York, 1985; pp 175–189.

(23) All calculations were performed by using the TEXSAN, TEXRAY Structure Analysis Package, version 2.1, of Molecular Structure Corporation, The Woodlands, TX.

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.3.1 and 2.2A.

(25) Actual mol wt = 356.6. Formula weight reflects the missing hydrogens on disordered carbon atoms in molecule A. The occupancies for the disordered region are as follows: C16A (0.6498), C16B (1.0000), C16C (0.3067), C17A (0.6498), C17B (1.0000), C17C (0.3502), C18A (0.6846), C18B (1.0000), C18C (0.3154), C19A (0.6819), C19B (1.0000), C19C (0.3181).

(26) Johnson, C. K., 1965, ORTEP Report ORNL-3794. Oakridge National Laboratory, TN.

group $P2_1/a$ (no. 14) with the following lattice parameters: $a = 7.853(3) \text{ \AA}$, $b = 16.062(4) \text{ \AA}$, $c = 13.667(3) \text{ \AA}$, $\beta = 105.32(2)^{\circ}$, $V = 1662.5(7) \text{ \AA}^3$. For $Z = 4$ and formula weight 340.50, the calculated density was 1.024 g cm^{-3} . Of the 4243 reflections collected 3964 were unique. $R = 0.039$ ($R_w = 0.031$).

NMR Spectrum Simulation. The program gNMR (version 3.6, Cherwell Scientific) was used to conduct full-lineshape analysis calculations. Experimental spectra were edited, primarily to remove solvent peaks, prior to initial attempts at locating a solution. However, a final least squares analysis was run on unedited spectra in order to obtain accurate error limits. The variance-covariance matrices and the singular value decomposition matrices showed that the parameters were well determined by the data for the room temperature spectrum of **1**.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **1** and **2**, ^1H NMR spectrum of **1** taken at low temperature, ORTEP drawings of **1** and **2** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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