1,2,5-Trithiepin: A 10π-Electron Heteroaromatic System

Shou-Nan Ueng, Michael Blumenstein, and Klaus G. Grohmann*

Department of Chemistry, Hunter College, CUNY Graduate Center, 695 Park Avenue, New York, New York 10021

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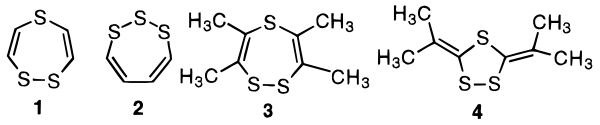
The unsubstituted 1,2,5-trithiepin (**1**) has been synthesized from the known 1,2,5-trithiepane (**6**) through two consecutive Pummerer rearrangements. Proton and carbon NMR spectra were completely analyzed, assigned, and correlated. The protons in **1** are shifted downfield by $\Delta\delta$ = 0.57 ppm for H_3/H_7 (δ = 6.57 ppm) and by 1.10 ppm for H_4/H_6 (δ = 7.24 ppm) relative to the 6,7-dihydro-1,2,5-trithiepin (**7**). These downfield shifts are comparable to thiophene, thus characterizing 1,2,5-trithiepin (**1**) as the first multisulfur 10π-aromatic diatropic molecule incorporating a disulfide linkage. 6,7-Dihydro-1,2,5-trithiepin (**7**) is a dynamic system. Variable-temperature ^{1}H-NMR measurements of **7** yielded an estimated free energy of activation at the coalescence temperature (227 K) of $\Delta G^{\ddagger}$ = 9.83 kcal/mol.

Introduction

1,2,5-Trithiepin (**1**) and its 1,2,3-isomer **2** are of interest as neutral polysulfur isosteres of cyclodecapentaene. Together with thionin and the dithiocins, the trithiepins form a series of heterocyclic analogs of cyclodecapentaene in the same way that thiophene is the monosulfur isostere of benzene.[1,2] Theoretical calculations by Zahradnik et al. using HMO theory predict for the trithiepins high-lying HOMO's and a narrow HOMO−LUMO gap but state that **1** might be more stable than isomer **2**.[3]



1 **2** **3** **4**

Several tetrasubstituted and benzoannelated derivatives of 1,2,5-trithiepin have been reported in the literature;[4,5] however, many of these structures were later found to be incorrect. Boberg, during his detailed study on the alkaline cleavage of 5-amino-4-chloro-1,2-dithiacyclopenten-3-ones, appears to have been the first to report the formation of several tetrasubstituted 1,2,5-trithiepins.[6] Schaumann and Grabley described the formation of tetramethyl-1,2,5-trithiepin **(3)** from phosphorus ylides and carbon disulfide;[7] however, an X-ray structure determination by Kunze et al.[8] established the unique 3,5-bis(isopropylidene)-1,2,4-trithiolane structure **(4)** for this compound. 3,7-Dimethyl-4,6-dicarbomethoxy-1,2,5-trithiepin has been claimed as one of the products of the gas-phase photolysis of 5-methyl-4-carbomethoxy-1,2,3-thiadiazole.[9] Tetramethylmercapto-1,2,5-trithiepin has been reported as one of the methylation products obtained from the tetrathiaoxalate dianion and methyl iodide,[10] but again, clear structural evidence is missing.

In this paper, we wish to report the synthesis and characterization of the unsubstituted l,2,5-trithiepin **(1)**.[11] As part of our continuing investigation of potentially aromatic 10π-sulfur heterocycles,[12] we were interested in the parent 1,2,5-trithiepin **(1)**, in order to investigate this molecule as a potentially 10π-heteroaromatic system. A comparative proton NMR study of **1** and its dihydrocompound **7** should establish the theoretically predicted diatropicity of the molecule, in analogy to the comparison between thiophene and 2,3-dihydrothiophene. 1,2,5-Trithiepin **(1)** would thus represent the first neutral molecule containing a conjugated system of 10π-electrons in the form of two double bonds and three sulfur atoms including a disulfide unit. An interesting related molecule with a conjugated system of 8π-electrons and a disulfide unit is the known 1,2-dithiin **(5)**, first reported by W. Schroth[13] in 1965.

Results and Discussion

The starting material in our synthesis of **1** was the known 1,2,5-trithiepane **(6)**,[14] obtained in 58% yield through the $FeCl_3$ oxidation of bis(2-mercaptoethyl) sulfide (Scheme 1). The 60 MHz proton NMR spectrum of 1,2,5-trithiepane **(6)** is deceptive, as it exhibits only a broad singlet at δ = 3.05 ppm ($CDCl_3$). However, the 300 MHz spectrum showed a narrow ABCD multiplet. The ^{13}C-NMR spectrum displayed the expected two resonances at δ = 37.6 ppm (C_3/C_7) and at 31.2 ppm (C_4/C_5). The signal assignment is based on the long-range carbon−proton coupling constants.[15] Oxidation of **6** with 1 mol of *m*-chloroperoxybenzoic acid in chloroform at 0

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) For a review see: Field, L.; Tuleen, D. L. *The Chemistry Of Heterocyclic Compounds*; Rosowsky, A., Ed.; Wiley-Interscience: New York, 1972; Vol. 26, Chapter X, D, p 623.

(2) (a) Pauling, L.; Schomaker, V. *J. Am. Chem. Soc.* **1939**, *61,* 1769. (b) Bradlow, H. L.; Vanderwerf, C. A.; Kleinberg, J. *J. Chem. Educ.* **1947**, *24,* 433. (c) Longuet-Higgins, H. C. *Trans. Faraday Soc.* **1949**, *45,* 173.

(3) Zahradnik, R.; Párkányi, C. *Collect. Czech. Chem. Commun.* **1965**, *30,* 3016. Zahradnik, R. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1965; Vol. 5, p 1 ff.

(4) Lust, S.; Mueller, O. W.; v. Schoor, A.; Jacobi, E. German Patent 1095582, U.S. Patent 3000780, 1962; *Chem. Abstr.* **1962**, *56* 5162. Sasaki, Y. Japan JP, 48/1494 [73/1494], 18 Jan 1973, 2 pp. Brass, K.; Pfluger, R.; Hornsberg, K. *Chem. Ber.* **1936**, *69B,* 80.

(5) Simmons, H. E.; Vest, R. D.; Blomstrom, D. C.; Roland, J. R.; Cairns, T. L. *J. Am. Chem. Soc.* **1962**, *84,* 4746.

(6) Boberg, F. *Liebigs Ann. Chem.* **1965**, *683,* 132.

(7) Schaumann, E.; Grabley, F. F. *Liebigs Ann. Chem.* **1979**, 1702.

(8) Kunze, U.; Merkel, R.; Winter, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21,* 291.

(9) Müller, E.; Meier, H.; Zeller, K. P. *Liebigs Ann. Chem.* **1972,** *766,* 32.

(10) Jeroschewski, P.; Hansen, P. *Z. Chem.* **1982**, *22*(6), 223.

(11) Ueng, S.-N. Ph.D. Thesis, CUNY Graduate Center, 1978.

(12) Grohmann, K.; Semmelhack, C.; Chiu, I.-C. *Tetrahedron Lett.* **1976**, 1251; *J. Am. Chem. Soc.* **1976**, *98,* 2005; 169th National Meeting of the American Chemical Society, April 1975, Philadelphia; American Chemical Society: Washington, DC, 1975; ORGN 94, Abstract.

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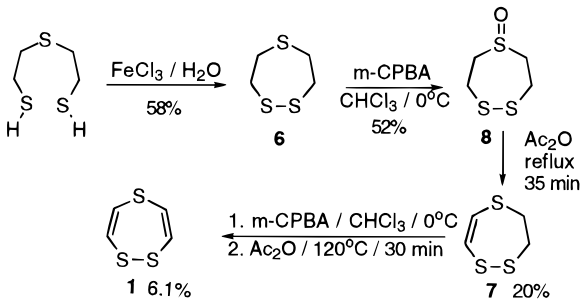
Scheme 1



°C formed a crystalline sulfoxide **8** (mp 95−96 °C) in 52% yield. Pummerer rearrangement[16] of the sulfoxide **8** in refluxing distilled acetic anhydride for 35 min gave the 6,7-dihydro-1,2,5-trithiepin **(7)** in 20% yield (bp 61.5 °C/ 0.06 mm Hg). The same compound was obtained in 17% yield upon treatment of 1,2,5-trithiepane **(6)** with *N*-chlorosuccinimide in CCl_4 at 5 °C followed by triethylamine in dry benzene at 80 °C. 6,7-Dihydro-1,2,5-trithiepin **(7)** is a stable colorless oil with the following spectral characteristics.

The 300 MHz proton NMR spectrum of the dihydrotrithiepin **7** displayed an interesting feature. The two CH_2 groups, expected to appear as two triplets, were observed as a triplet at 3.11 ppm (J = 6 Hz) and as a broad multiplet at 3.83 ppm.[17] A ^{1}H-DNMR study confirmed our assumption that **7** is a dynamic system. At −95 °C the signals for both CH_2 groups changed into two separate, well-resolved AB systems with further coupling (Figure 1). On the basis of the decoalescence for the δ = 3.83 ppm signal at 227 K, one can estimate a free energy of activation for this process of approximately 9.8 kcal/mol.[18] Sulfoxidation of 6,7-dihydro-1,2,5-trithiepin **(7)** gave an uncharacterized sulfoxide that upon Pummerer rearrangement in distilled acetic anhydride under argon at 100 °C yielded 1,2,5-trithiepin **(1)** in 6.1% yield as an unstable yellow oil. 1,2,5-Trithiepin **(1)** was

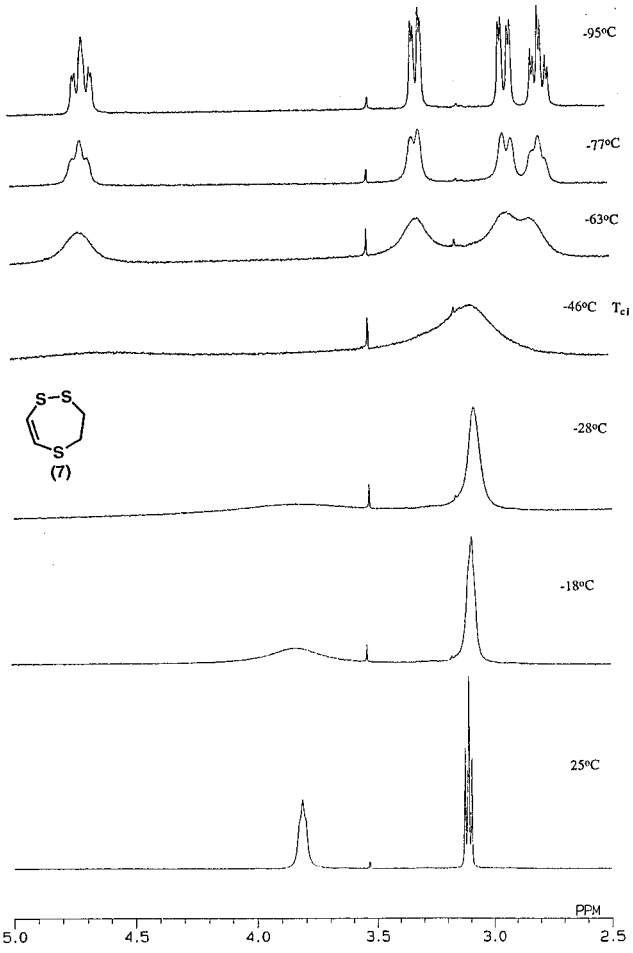


Figure 1. Variable-temperature ^{1}H-NMR spectrum of 6,7-dihydro-1,2,5-trithiepin (**7**) in CD_2Cl_2.

purified by low-temperature preparative TLC under argon. It proved to be pure by GC and GC/MS. The compound can be stored in dilute solutions under argon in the freezer. The high-resolution mass spectrum showed an ion at m/z = 147.9474 (calcd for $C_4H_4S_3$ = 147.947 52). The mass spectrum exhibited in addition to the molecular ion m/e = 148 (30%) significant fragmentation peaks at 116 (29, M − 32), 103 (100, M − 45), 84 (46, M − 64), 64 (15, M − 84), 58 (92, M − 90), 57 (49, M − 91), 45 (86, M − 103). The UV spectrum in ethanol showed three maxima at λ_{max} = 263 nm (ϵ = 2250), 296 (1720), 353 (1400).

The proton NMR spectrum of **1** exhibits an AA′XX′ system with H_A = 7.24 ppm (J_{AX} = 9 Hz) and H_X = 6.57 ppm (J_{AX} = 9 Hz). The ^{13}C-NMR spectrum showed the expected two signals at δ = 128.6 ppm and at 131.5 ppm.

Chemical Shift Assignments

A decision as to whether the proton signal at δ = 6.57 ppm corresponds to the protons H_3 and H_7 while the signal at δ = 7.24 ppm corresponds to protons H_4 and H_6 or vice versa and in the same way the assignment of the ^{13}C-NMR signal at δ = 131.4 ppm to C_3/C_7 and at δ = 128.6 ppm to C_4/C_6 can be reached on the basis of the

(13) Schroth, W.; Billig, F.; Langguth, H. *Z. Chem.* **1965**, *5*, 353. Schroth, W.; Billig, F.; Reinhold, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 689. See also: (a) Behringer H.; Meinetsberger E. *Liebigs Ann. Chem.* **1981**, 1729. (b) Hartke, K.; Pfleging, E. *Liebigs Ann. Chem.* **1988**, 933. (c) Schroth, W.; Hintzsche, E.; Spitzner, R.; Irngartinger, H.; Siemund, V. *Tetrahedron Lett.* **1994**, *35*, 1973. (d) Block, E.; Guo, C.; Thiruvazhi, M.; Toscano, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 9403. (e) Koreeda, M.; Yang, W. *Synlett* **1994**, 201. (f) Freeman, F.; Kim, D. S. H. L.; Rodriguez, E. *Sulfur Rep.* **1989**, *9*, 207. (g) Schroth, W.; Hintzsche, E.; Viola, H.; Klose, H.; Boese, R.; Kempe, R.; Sieler, J. *Chem. Ber.* **1994**, *127*, 401. (h) Koreeda, M.; Yang, W. *J. Am. Chem. Soc.* **1994**, *116*, 10793 and references therein.

(14) (a) Field, L.; Barbee, R. B. *J. Org. Chem.* **1969**, *34*, 36. (b) Field, L.; Foster, C. H. *J. Org. Chem.* **1970**, *35*, 749. (c) Schoberl, A.; Grafie, A. *Liebigs Ann. Chem.* **1958**, *614*, 66.

(15) The gated decoupled ^{13}C-NMR spectrum of trithiepan **(6)** shows for the high-field signal (31.2 ppm) a triplet of multiplets with J = 140 Hz, while the low-field signal at 37.6 ppm appears as a triplet of triplets with J = 140 and 2.6 Hz. The observed low-field coupling pattern is attributed to the coupling of carbons 3 and 7 next to the disulfide linkage with the hydrogens attached to them and the hydrogens on the neighboring carbons. There is no coupling across the disulfide functionality. In contrast to that, the triplet of multiplets observed for C4/C6 is the result of an additional long-range $^3J_{CH}$ coupling across the sulfide group.

(16) (a) Pummerer, R. *Chem. Ber.* **1910**, *43*, 1401. (b) Parham, W. E.; Bharsar, M. D. *J. Org. Chem.* **1963**, *28*, 2686. (c) Johnson, C. R.; Phillips, W. G. *J. Am. Chem. Soc.* **1969**, *91*, 682. For recent reviews on the Pummerer rearrangement see: Oae, S.; Numatat, T. *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier Sci. Publ. Co.: New York, 1980; Vol. 5, pp 45−102. Russel, G. A.; Mikoi, G. J. *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Interscience Publ.: New York, 1968; Vol. 1, pp 157−207. DeLucchi, O.; Miotti, U.; Modena, G. *Organic Reactions*; Paquette, L. A., Ed.; John Wiley: New York, 1991; Vol. 6, p 909.

(17) The 60 MHz ^{1}H NMR of **7** exhibited two clear triplets with J = 6 Hz.

(18) Using a decoalescence temperature of 227 K (−46 °C) for the δ = 3.83 ^{1}H NMR signal and a chemical shift difference between the H_{4a}/H_{4b} of $\Delta\delta$ = 712 Hz, one obtains for **7** $\Delta G^{\ddagger}$ = 9.83 kcal/mol based on $\Delta G^{\ddagger} = 4.57T_c[9.97 + \log(T_c/\Delta\delta)]$; see: *NMR-Spektroskopie*; Günther, H., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1973; p 248.

Chart 1

Data Set 1: One Bond Correlations	Data Set 2: Long-Range Correlations
δ = 119.1 ppm with δ = 6.00 ppm	δ = 6.00 ppm with δ = 126.6 ppm
δ = 126.6 ppm with δ = 6.14 ppm	δ = 6.14 ppm with δ = 119.1 ppm
δ = 33.0 ppm with δ = 3.83 ppm	δ = 6.14 ppm with δ = 33.0 ppm
δ = 35.7 ppm with δ = 3.13 ppm	δ = 3.13 ppm with δ = 33.0 ppm

following measurements and considerations: The proton-coupled ^{13}C-NMR spectrum of 1,2,5-trithiepin **(1)** consists of a doublet centered at $\delta = 131.4$ ppm with $^1J_{CH} = 179.7$ Hz and a doublet of doublets of doublets centered at $\delta = 128.6$ ppm with $^1J_{CH} = 170.4$ Hz, $^2J_{CH} = 10.3$ Hz, and $^3J_{CH} = 6.8$ Hz. It is reasonable to assume that $^3J_{CH} = 6.8$ Hz is the long-range coupling between C_4 or C_6 and H_6 or H_4 across the sulfide part of the molecule.[19] With the further assumption that the corresponding long-range coupling $^4J_{CH}$ across the disulfide part between C_3 and H_7 or C_7 and H_3 is zero and that $^2J_{CH}$ between C_3/C_7 and H_4 or H_6 is close to zero, while $^3J_{CH}$ for C_4 to $H_6 = 6.8$ Hz,[20] we assign to carbons 3 and 7, next to the disulfide part of **1** $\delta = 131.4$ ppm, and to carbons 4 and 6, α to the sulfide section of **1**, $\delta = 128.6$ ppm. Partial off-resonance decoupling experiments identified the protons attached to C_3/C_7 and C_4/C_6 via their ^{13}C−H coupling constants, thus allowing a unambiguous chemical shift assignment for all protons and carbons.

The chemical shift assignments for the 6,7-dihydro-1,2,5-trithiepin **(7)** were complicated by the fact that the molecule was dynamic on the basis of variable temperature proton NMR measurements. The proton-coupled ^{13}C-NMR spectrum of 6,7-dihydro-1,2,5-trithiepin **(7)** consists of a doublet of quartets centered at $\delta = 126.6$ ppm with $^1J_{CH} = 171$ Hz and $^2J_{CH} = {}^3J_{CH} = 5.8$ Hz, a doublet of doublets centered at 119.1 ppm with $^1J_{CH} = 176$ Hz and $^2J_{CH} = 3.7$ Hz, a triplet of narrow triplets with $^1J_{CH} = 140$ Hz and $^2J_{CH} = 2.1$ Hz, and a triplet of doublets of narrow triplets with $^1J_{CH} = 142$ Hz, $^2J_{CH} = 2.0$ Hz, and $^3J_{CH} = 6.1$ Hz.

A room-temperature ^{13}C−^{1}H one-bond correlation experiment, HMQC,[21] connected the carbon signals with the respective proton resonances as shown in data set 1 (Chart 1). Long-range correlations obtained through an HMBC[22] experiment are summarized in data set 2 (Chart 1).

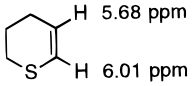
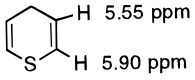
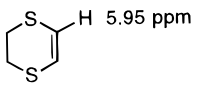
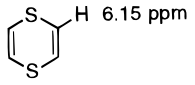
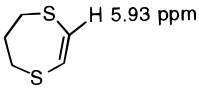
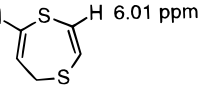
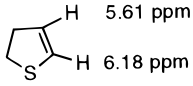
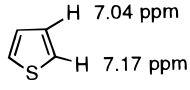
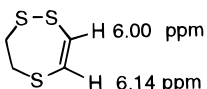
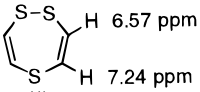
Due to the width of the ^{1}H-NMR signal at $\delta = 3.83$ ppm, no long-range correlations to these protons are observed in the HMBC experiment.

These measurements together with the considerations that long-range coupling across the sulfide part of the molecule is significant while there is no coupling across the disulfide section yielded the following chemical shift assignments for the 1,2,5-trithiepin **(1)** and the 6,7-dihydro-1,2,5-trithiepin **(7)** as shown in Table 1. Additional support for these assignments comes from the

Table 1. Proton and Carbon Chemical Shifts for 1,2,5-Trithiepin (1) and Its Dihydro Derivative 7

	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
	7.24 (H_4/H_6) 6.57 (H_3/H_7)	128.6 (C_4/C_6) 131.4 (C_3/C_7)
	6.14 (H_6) 6.00 (H_7) 3.83 (H_4) 3.11 (H_3)	126.6 (C_6) 119.1 (C_7) 33.0 (C_4) 35.7 (C_3)

Table 2. Proton Chemical Shifts of Selected Sulfur Heterocycles

		Δδ ppm
		- 0.13
		- 0.11
		0.2
		0.08
		1.43
		0.99
 (7)	 (1)	0.57
		1.10

observations that sp^3—^{13}C chemical shifts for carbons adjacent to a sulfide functionality are generally upfield from those of carbons next to a disulfide functionality.[23] This has also been observed for the 1,2,5-trithiepane **(6)**.[15]

Most significant are the observed ^{1}H-chemical shift changes upon going from the 6,7-dihydro-1,2,5-trithiepin **(7)** to 1,2,5-trithiepin **(1)**. For comparison, the proton chemical shifts for a series of related cyclic sulfur compounds are presented in Table 2.

As is apparent from these data, only very *minor* proton chemical shift changes are being observed upon going from dihydrothiopyran to thiopyran,[24] from dihydro-1,4-dithiin to 1,4-dithiin,[25] or from 1,4-dithia-2-cycloheptene to 1,4-dithia-2,5-cycloheptadiene.[26] However, introduc-

(19) For comparison the same $^3J_{CH}$ for thiophene is 5.2 Hz: *Nuclear Magnetic Resonance*; Atta-ur-Rahman, Eds.; Springer Verlag: New York, 1986; Table 4.31.

(20) (a) Gassmann, P.; Drewen, H. *J. Am. Chem. Soc.* **1974**, *95*, 3002. (b) Wilson, G.; Albert, R. *J. Org. Chem.* **1973**, *38*, 2160. (c) Vilsmeier, R.; Sprugel, W. *Tetrahedron Lett.* **1972**, 625.

(21) Heteronuclear Multiple Quantum Correlation: Muller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481.

(22) Heteronuclear Multiple Bond Correlation: Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

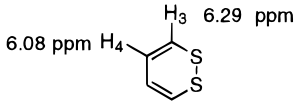
(23) Barbarella, G.; Dembach, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 108.

(24) *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press Oxford, New York, Toronto, 1984; Vol. 3, Part 2B, p 885.

(25) Butler, B. S.; Read, J. M., Jr.; Goldstein, J. H. *J. Mol. Spectrosc.* **1970**, *35*, 83.

(26) Chiu, I.-C. Ph.D. Thesis, CUNY Graduate Center, 1977.

tion of the second double bond into 2,3-dihydrothiophene, a cyclic vinyl sulfide, which leads to thiophene, the archetype of aromatic sulfur heterocycles, causes downfield shifts of 1.43 ppm for the β-protons and 0.99 ppm for the α-protons.[27] The same magnitude of downfield shifts are observed for the 6,7-dihydro-1,2,5-trithiepin **(7)**/1,2,5-trithiepin **(1)** pair. Protons H_3/H_7, next to the disulfide unit, experience a downfield shift by *0.57* ppm, while protons H_4/H_6, are shifted downfield by *1.10* ppm. These data strongly suggest a diamagnetic ring current, thus characterizing 1,2,5-trithiepin **(1)** as the first neutral 10π-aromatic multisulfur heterocycle containing a disulfide unit as part of the cyclic conjugated system. A comparison with the 8π-electron, potentially antiaromatic 1,2-dithiin **(5)**, first reported by Schroth[13] in 1965, is of interest. This fascinating deep red molecule exhibits proton chemical shifts at 6.08 and 6.29 ppm.[28]



1,2-Dithiin **(5)**[13]

On the basis of these data it could be classified as a nonaromatic sulfur heterocycle.

Noteworthy is the observation that while 6,7-dihydro-1,2,5-trithiepin **(7)** is perfectly stable over many years in the cold, the 1,2,5-trithiepin **(1)** is rather unstable, rapidly decomposing (polymerizing) neat as well as in solutions. The reduced thermal stability of 1,2,5-trithiepin **(1)** compared to its dihydro derivative **7** might be attributed to a more planar geometry of **1** as suggested from Dreiding models. The planarization of the molecule leading to a cyclic conjugated 10π-electron-system might result in a strong splitting of the nonbonding in-plane orbitals of the disulfide unit in **1**, thus generating a high energy HOMO with a narrow HOMO/LUMO gap.[29] Similar arguments have been presented in order to explain the instability of thioctic acid compared to its six- and seven-membered analogs. Further studies on the chemistry of this interesting system, 1,2,5-trithiepin **(1)** will be reported.

Experimental Section

General Comments. Proton and carbon NMR spectra were measured in $CDCl_3$ at 300 MHz. The variable-temperature data were obtained at 400 MHz. HMQC and HMBC experiments were performed at room temperature at 500 MHz. GC−MS were measured at 70 eV under electron impact conditions. All solvents and reagents were purified prior to use according to established procedures. Analytical thin layer chromatography (TLC) was conducted on "Polygram" Sil G/UV_{254} plates (0.25 mm). Flash chromatography was performed using Merck silica gel 60 (230−400 mesh).

1,2,5-Trithiepane 5-*S*-Oxide (8): (a) With *m*-Chloroperbenzoic Acid. A solution of 5.70 g of *m*-CPBA (33 mmol) in 30 mL of $CHCl_3$ was added dropwise to a stirred solution of 4.56 g of 1,2,5-trithiepane **(6)**[14] (30 mmol) in 80 mL of $CHCl_3$. The temperature of the reaction was kept between 0 and 4 °C. Stirring was continued at this temperature for 2 h. The reaction mixture was added to 150 mL of an ice-cold saturated $NaHCO_3$ solution containing 2 mL of a saturated $NaHSO_3$ solution. Extraction with two portions of 100 mL of $CHCl_3$, washing the organic extracts with 50 mL of a saturated ice-cold NaCl solution, and drying the chloroform layer over anhydrous $MgSO_4$ followed by evaporation under reduced pressure gave 4.1 g of a white solid. Recrystallization from CCl_4 gave 2.52 g (50%) of white crystals, mp 95−96 °C (lit.[14] mp 95−96 °C).

^{1}H-NMR ($CDCl_3$, ppm) δ: 2.9−3.1 (m, 4 H), 3.35−3.4.5 (m, 2 H), 3.55−3.7 (m, 2 H). IR(CCl_4): 1420, 1390, 1025, 1005, 840 cm^{-1}.

b. With Sodium *m*-Periodate. A solution of $NaIO_4$ (2.31 g, 13.2 mmol) in 55 mL of water was added slowly (20 min) to a stirred solution of 1,2,5-trithiepane (**6**) (2.0 g, 13.2 mmol) in 150 mL of tetrahydrofuran. The temperature of the reaction mixture was maintained at 0−3 °C. Stirring was continued for 3 h at this temperature and for 5 h at room temperature. An additional 50 mL of THF was added, the suspension was cooled to 0 °C and filtered, and the solid was washed with two portions of 50 mL of THF. The filtrate was evaporated under vacuum yielding a two-phase watery−oily mixture. Extraction with 50 mL of $CHCl_3$, drying of the organic layer over $MgSO_4$, and evaporation of the solvent gave a pale yellow crude sulfoxide **8**, which after recrystallization from CCl_4 melted at 95−96 °C. Yield of recrystallized material: 0.87 g (40%).

6,7-Dihydro-1,2,5-trithiepin (7) via Pummerer Rearrangement. A solution of 1,2,5-trithiepane 5-*S*-oxide **(8)** (1.52 g, 10 mmol) in 25 mL of distilled acetic anhydride was refluxed for 35 min. The dark brown mixture was poured into 150 mL of ice−water, stirred for 1 h to hydrolyze the acetic anhydride, extracted twice with 100 mL of ether, carefully neutralized with 150 mL of an ice-cold saturated $NaHCO_3$ solution, washed with ice-cold saturated NaCl solution, and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the dark oily residue was chromatographed on SiO_2 with hexane, giving 0.29 g (20%) of 6,7-dihydro-1,2,5-trithiepin **(6)**, $bp_{0.06}$ = 61.5 °C.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm) δ: 3.11(2 H, t, J = 6 Hz), 3.85 (2 H, broad m), 5.99 (1 H, d, J = 9 Hz), 6.17 (1 H, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 33 (t), 35.7 (t), 119.1 (d), 126.6 (d). IR (neat): 3020, 2920, 1530, 790 cm^{-1}. UV (EtOH): λ_{max} = 263 nm (ϵ = 2500), 321 nm (ϵ = 2700). MS (EI/70 eV) m/z: 150 (M, 69),122, 105 (100), 58, 45 (100).

6,7-Dihydro-1,2,5-trithiepin (7) via Chlorination/Dehydrochlorination. Recrystallized NCS (16.3 g, 0.12 mol) was added in small portions to a stirred solution of 1,2,5-trithiepane (**8**) (15.4 g, 0.1 mol) in 300 mL of distilled anhydrous CCl_4 at 0 °C over a period of 30 min. Stirring was continued at 10−15 °C for 3 h. The suspension was cooled, the succinimide was filtered, and the solution was concentrated at 18−20 °C under vacuum. The oily residue was dissolved in 350 mL of anhydrous benzene. To the cooled benzene solution was added freshly distilled anhydrous triethylamine (20.2 g, 0.2 mol) dissolved in 50 mL of anhydrous benzene over a 30 min period. The mixture was subsequently heated at 80 °C for 12 h, cooled, and poured onto 150 mL of ice-cold 3 N HCl. The layers were separated, and the aqueous layer was extracted with 100 mL of benzene. The organic layer was washed with 100 mL of saturated NaCl solution and 100 mL of a saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, and evaporated, and the residue was distilled. The yield of distilled 3,4-dihydro-1,2,5-trithiepin **(7)** was 2.59 g (17%, $bp_{0.06}$ = 61−62 °C).

1,2,5-Trithiepin (1). A solution of *m*-CPBA (1.81 g, 10.5 mmol) in 30 mL of $CHCl_3$ was added dropwise to a stirred solution of 6,7-dihydro-1,2,5-trithiepane **(7)** (1.5 g, 10 mmole) in 10 mL of $CHCl_3$ under argon. The temperature of the reaction was maintained between 0 and 4 °C. Stirring was continued at this temperature for 1 h. The reaction mixture was evaporated under vacuum, and 30 mL of freshly distilled acetic anhydride was added. The reaction flask was placed in an oil bath preheated to 120 °C and kept at this temperature under argon for 30 min. The dark reaction mixture was poured onto 100 mL of ice/water containing some pieces of dry

(27) *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, New York, Toronto, 1984; Vol. 4, Part 3, 3.01.4.1 Table 7.

(28) However, a definite chemical shift assignment is not given.

(29) (a) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655 and references therein. (b) Affleck, J. G.; Dougherty, G. *J. Org. Chem.* **1950**, *16*, 865.

ice. After being stirred for 1 h, the mixture was extracted with ether (2 × 75 mL). The ether layer was neutralized with saturated ice-cold $NaHCO_3$ solution, washed with saturated NaCl solution, and dried over anhydrous $MgSO_4$. The crude material was chromatographed under argon with hexane on a cooled preparative plate (EM SiO_2) yielding a yellow band of 1,2,5-trithiepin **(1)**. Concentration gave 90 mg of an unstable yellow oil (6.1%). The compound is stable in dilute solution in the refrigerator but decomposes rapidly at room temperature neat or in solution to insoluble probably polymeric materials.

1. ^{1}H-NMR ($CDCl_3$, ppm) δ: 7.24, 6.57 (AA′XX′, J_{AX} = 9 Hz). ^{13}C-NMR ($CDCl_3$, ppm) δ: 128.6, 131.5. IR (CCl_4): 3100, 1560, 1290, 805, 825 cm^{-1}. UV (ethanol) λ_{max}: 263 nm (ϵ = 2250), 296 (1720), 353 (1400). MS (EI/70 eV) m/z: 148 (30), 116 (29, M − 32), 103 (100, M − 45), 84 (46, M − 64), 64 (15, M − 84), 58 (92, M − 90), 57 (49, M − 91), 45 (86, M − 103). HR-MS m/z: 147.9474 (calcd for $C_4H_4S_3$ = 147.947 52).

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