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New Carbon Sulfides Based on 4,5-Dimercapto-1,2-dithiole-3-thione (β-$C_3S_5^{2-}$): $[C_3S_5]_n$, C_6S_8, and C_5S_7

Daniel D. Doxsee, Collin P. Galloway, Thomas B. Rauchfuss,* Scott R. Wilson, and Xiaoguang Yang

School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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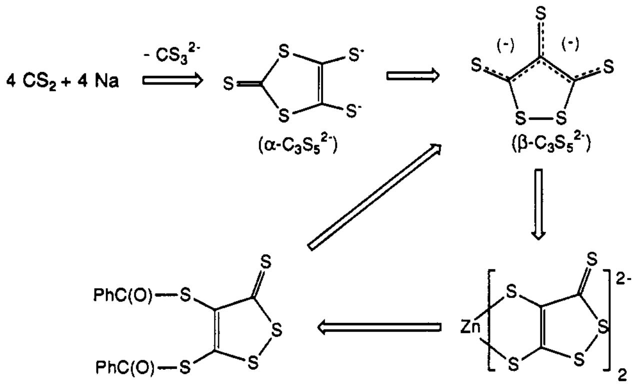
This investigation centers on the preparation of new binary carbon sulfides based on the 1,2-dithiole-3-thione subunit as found in the precursor dithiolate $C_3S_5^{2-}$. Tricyclic C_6S_8, **1**, was obtained in high yield by thermal elimination of H_2S from the dimercaptan β-$C_3S_5H_2$. A crystallographic study confirmed a tricyclic structure of idealized D_{2h} symmetry containing an unusual planar 1,4-dithiin unit. The crystals of **1** are monoclinic, space group $P2_1/c$, with $a = 8.046(2)$, $b = 9.797(3)$, $c = 13.818(4)$ Å, $V = 1048.3(9)$ Å^3, and $Z = 4$. The final R and R_w values were 0.036 and 0.042, respectively. The bicyclic carbon sulfide C_5S_7, **3**, was prepared from reduction of C_4S_6, **2**, with $LiBEt_3H$, followed by addition of thiophosgene. Oxidation of $Cp_2Ti(\beta$-$C_3S_5)$ or $Zn(\beta$-$C_3S_5)_2^{2-}$ with SO_2Cl_2 afforded $[\beta$-$C_3S_5]_n$, **4**, an orange insoluble solid. Degradation of $[\beta$-$C_3S_5]_n$ with dimethyl acetylenedicarboxylate (DMAD) afforded C_3S_5·2DMAD, **5**, together with small amounts of C_3S_5·3DMAD, **6**. The single-crystal X-ray structure of C_3S_5·2DMAD revealed a folded 1,4-dithiin linked to a planar 1,3-dithiole. Crystals of **5** are monoclinic, space group Cc, with $a = 18.760(4)$, $b = 13.664(3)$, $c = 7.880(2)$ Å, $V = 1957(2)$ Å^3, and $Z = 4$. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.036$ and $R_w = 0.047$. The DMAD treatment proceeds in a similar manner with $[M(\beta$-$C_3S_5)_2]^{2-}$ (M = Zn, Ni) to yield $[M(C_3S_5$·$DMAD)_2]^{2-}$. The C_3S_5·DMAD ligand can subsequently be removed from the zinc complex by reaction with thiophosgene giving bicyclic C_4S_6·DMAD, which can also be obtained via $Cp_2Ti(C_3S_5$·DMAD).

Introduction

Binary phases are fundamentally important substances by virtue of their simple stoichiometries. This is especially true when the new compositions are derived from abundant resources. Given the breadth of the chemistry of carbon, it is somewhat surprising that binary molecular carbon compounds remain to be discovered, especially when they are derived from an element as widely studied as sulfur. On the other hand, we are mindful that most of the molecular allotropes of sulfur have been discovered since 1970[1] and the first molecular allotrope of carbon, C_{60}, is only a few years old.[2]

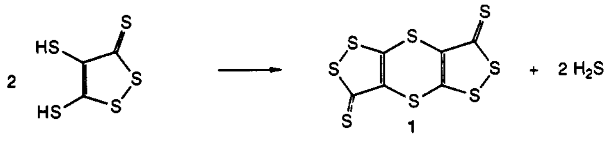
When we began our studies on binary carbon sulfides, only four molecular compounds with the formula C_xS_y could be considered well characterized.[3] Additionally, the polymeric materials $(CS_2)_n$ and $(CS)_n$ have long been known.[3b] Aside from CS_2, the only commercially available carbon sulfide is one isomer of C_4S_6, although convincing supporting characterization data have never been reported for this species.[4b] A variety of stoichiometrically simple carbon sulfides can be synthesized by treatment of carbon sulfide anions with various electrophilic reagents such as protons, sulfur halides, and oxidants. This topic has been briefly reviewed.[3b] Previously we have reported the generation of several new binary carbon sulfides derived from 4,5-dimercapto-1,3-dithiole-2-thione ("dmit"[3e]), referred to herein as α-$C_3S_5^{2-}$. Hoyer and co-workers have shown that α-$C_3S_5^{2-}$ thermally rearranges to give 4,5-dimercapto-1,2-dithiole-3-thione, or β-$C_3S_5^{2-}$.[5] The latter species has been isolated as zinc and nickel salts $(NR_4)_2[M(\beta$-$C_3S_5)_2]$ (Scheme I). The diester β-$C_3S_5(COPh)_2$ is a more conveniently isolable source of the β-$C_3S_5^{2-}$ unit,[5] which we have converted to the new carbon sulfides C_6S_8, C_5S_7, and $[C_3S_5]_n$. As part of this effort, we demonstrate the utility of an electrophilic acetylene for functionalizing β-C_3S_5 derivatives.

Scheme I



Results

Preparation of C_6S_8. Samples of C_6S_8 (**1**) were first isolated as a minor product of the oxidation of acetonitrile solutions of $(NEt_4)_2[Zn(\beta$-$C_3S_5)_2]$ with $SOCl_2$. The material obtained in this way afforded the specimen used in the crystallographic analysis (see below). A more efficient route to this novel carbon sulfide involves refluxing toluene solutions of the dimercaptan β-$C_3S_5H_2$ (eq 1). This simple method allows for the easy isolation



(1)

® Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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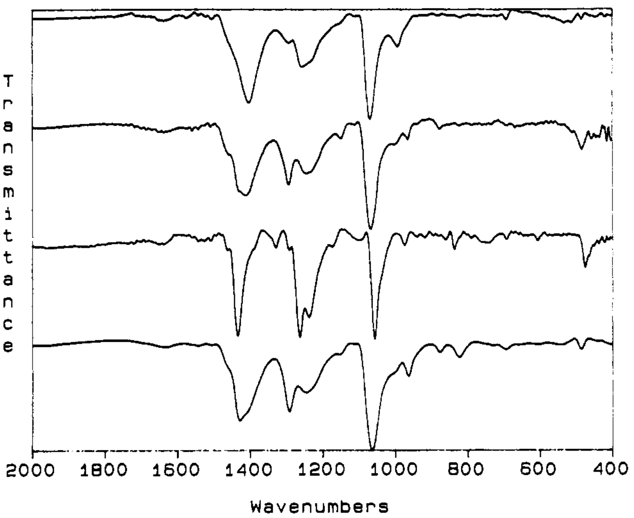


Figure 1. Infrared spectra for C_5S_7 (**3**)(top), C_4S_6 (**2**), C_6S_8 (**1**), and $[C_3S_5]_n$ (**4**).

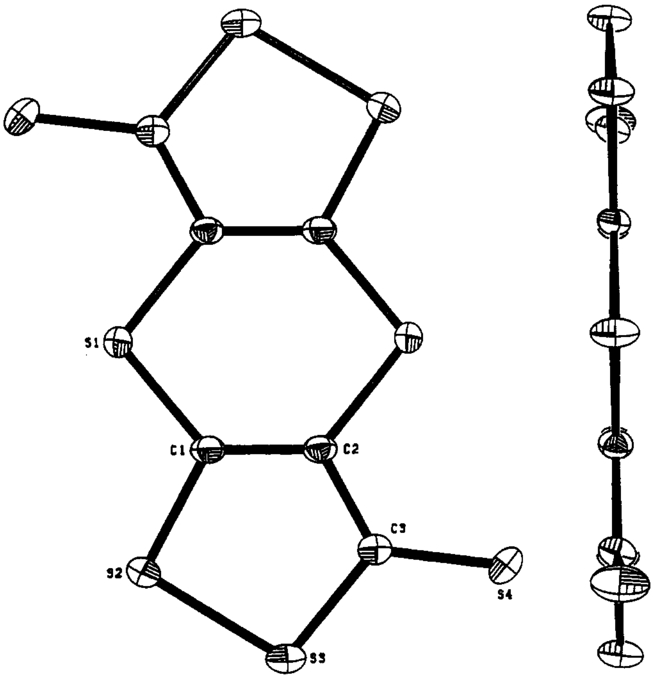


Figure 2. ORTEP drawings (35% probability ellipsoids) of C_6S_8 (**1**).

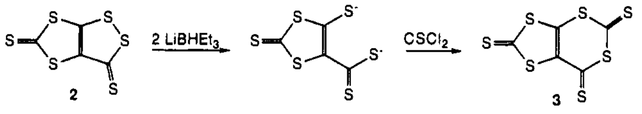
and purification of multigram quantities of this red-brown, air-stable solid. The retention time for C_6S_8 on reverse-phase HPLC is shorter than other carbon sulfides,[3a–3d] suggesting that it is relatively polarizable (hence poorly soluble in the nonpolar stationary phase). The EIMS of the new compound exhibits an intense molecular ion current with the appropriate isotopic distribution. Peaks for S_8^+, $C_3S_8^+$, and $C_3S_6^+$ were not observed. The IR spectrum (Figure 1) exhibits bands at 1435 ($\nu_{c=c}$), 1263, 1240, 1055 ($\nu_{c=s}$), and 477 (ν_{s-s}), consistent with the observed structure. Compound **1** only slightly colorizes CS_2; hence, we were unable to record its ^{13}C NMR spectrum.

Structure of C_6S_8. Single crystal X-ray diffraction (Figure 2) reveals that there are two very similar, but crystallographically independent, molecules in the asymmetric unit. Noteworthy is the fact that, unlike other 1,4-dithiins,[6] **1** is almost planar with a S···S fold angle (within the dithiin) of less than 2.1°. The S–S bond distances of 2.057 Å are unexceptional; cf. orthorhombic S_8 (2.051 Å)[1] and S_6 (2.057 Å).[1] The S(1)–S(4′) and S(4)–S(1′) distances of 3.089(2) and 3.099(2) Å are significantly shorter than the sum of the van der Waals radii (3.630 Å)[14] and conceivably contribute to the stability of the planar dithiin ring. The angles at sulfur within the dithiin are 101.9 Å. The C(1)–C(2) bond length (1.368 Å) is slightly longer than in C_6S_{12} (1.342 Å)[3d] and C_6S_{10} (1.349 Å)[3c] (see Table I).

Table I. Selected Bond Lengths (Å) and Angles (deg) for C_6S_8 (**1**)

S(1)–C(1)	1.749(4)	C(3)–C(2)	1.427(5)
C(1)–S(2)	1.719(4)	C(2)–C(1)	1.364(5)
S(2)–S(3)	2.059(2)	C(3)–S(4)	1.646(4)
S(3)–C(3)	1.733(4)	S(1)···S(4′)	3.089(2)
S(1)–C(1)–C(2)	129.7(3)	C(3)–C(2)–C(1)	118.5(4)
S(1)–C(1)–S(2)	112.8(2)	C(1)–C(2)–S(1′)	128.3(3)
C(1)–S(2)–S(3)	94.2(1)	C(2)–S(1′)–C(1′)	101.9(2)
S(2)–S(3)–C(3)	97.1(1)	S(1)–C(1)–C(2)–S(1′)	178.9(3)
S(3)–C(3)–S(4)	121.8(4)	C(2)–C(1)–S(1)–C(2′)	2.1(4)
S(3)–C(3)–C(2)	112.8(3)	C(1)–S(1)–C(2′)–C(1′)	−2.0(4)

Scheme II



1,4-Dithiins normally adopt a boat structure in which the two sulfur atoms are tilted toward one another.[6] However various molecular orbital calculations have indicated that the energy barrier between planar and boat conformers is very small.[7–12] The observed structural trends for 1,4-dithiins[6] suggest that the planar structure is stabilized by electron-withdrawing substituents.[13]

Preparation of C_5S_7. The reaction of β-$C_3S_5^{2-}$ with $CSCl_2$ is known to give the unsymmetrical C_1 isomer C_4S_6 (**2**) although characterization data have not been reported.[4a,15] This species is isomeric with the D_{2h} bis(dithiole) derived from α-$C_3S_5^{2-}$ and $CSCl_2$ and the claimed C_{2h} dithiole containing four contiguous carbon atoms.[4b] The ^{13}C NMR spectrum of the brown CS_2-soluble C_1-isomer compound shows resonances at 216.3, 200.0, 161.1, and 148.8 ppm which are assigned to the two thiocarbonyls[16] and the nonequivalent olefinic carbon centers. Distinctive IR bands are observed at 1416 ($\nu_{c=c}$) and 1070 ($\nu_{c=s}$), as well as medium-intensity absorptions in the 1250–1300-cm^{-1} region. Collectively this information is consistent with the structure observed crystallographically for the I_2 adduct of this carbon sulfide.[4a]

The new carbon sulfide C_5S_7 (**3**) was prepared from *unsym*-C_4S_6 via the reaction of $CSCl_2$ and $Li_2C_4S_6$ (Scheme II). The latter was generated in situ by reduction of **2** with 2 equiv of $LiHBEt_3$. In addition to microanalysis and FDMS (which displays the molecular ion in the expected isotopic distribution), the formulation of C_5S_7 is based on its IR spectrum, which is very similar to that of **2** but lacking bands in the ν_{s-s} region. Like **1**, this species proved to be too insoluble for ^{13}C NMR characterization.

Preparation of $[\beta$-$C_3S_5]_n$. The sulfuryl chloride oxidation of acetonitrile solutions of $[Zn(\beta$-$C_3S_5)_2]^{2-}$ afforded a bright orange-yellow precipitate analyzing approximately as $[C_3S_5]_n$ (**4**). Unlike

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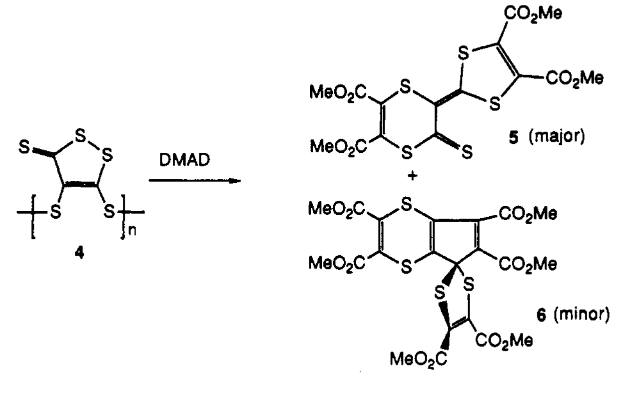
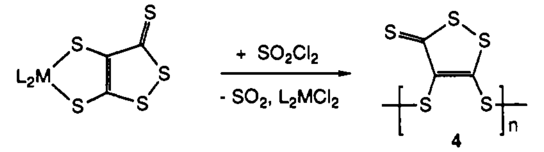
(16) Copeland, C.; Conway, R. J.; Patroni, J. J.; Stick, R. V. *Aust. J. Chem.* **1981**, *34*, 555.

Scheme III



other carbon sulfides,[3a-d] the new species is totally insoluble in CS_2; for this reason it is assumed to be polymeric (eq 2).



(2)

The EIMS fragmentation pattern of **4** is a superposition of the mass spectra of C_6S_8 (see below) and S_8. The observation of the S_8 fragmentation peaks suggests the presence of exocyclic S–S bonds. Its IR spectrum (Figure 1) exhibits bands at 1429 ($\nu_{C=C}$), 1292, 1063 cm^{-1} ($\nu_{C=S}$), and 480 (ν_{S-S}) indicating the presence of 1,2-dithiole-3-thione groups. Compared with C_6S_{10},[3c] the band assigned to $\nu_{C=S}$ is weaker and occurs at lower frequency while the $\nu_{C=C}$ band is more intense. Bands at intermediate frequencies are assigned to ν_{C-C} and ν_{C-S}.

Degradation of 4 with Dimethyl Acetylenedicarboxylate. This effort was initiated to obtain information on the structural subunits of $[\beta\text{-}C_3S_5]_n$ via degradation with the highly electrophilic dimethyl acetylenedicarboxylate (DMAD). This process gave high yields of red C_3S_5·2DMAD, **5**, together with small amounts of a species with the formula C_3S_4·3DMAD, **6**, (Scheme III). These and other DMAD reactions (see below) are accelerated by the addition of small amounts of PBu_3, although the mechanism of this effect was not investigated. The ^1H NMR spectrum of **5** showed four equally intense OCH_3 peaks, and EIMS revealed the molecular ion. The ^1H NMR spectrum of **6** shows five OCH_3 resonances with relative intensities of 1:1:1:1:2. Aside from elemental analysis, this formulation is supported by both FDMS and EIMS, both of which showed the strong molecular ion peak.

Structure of C_3S_5·2DMAD (5). The structure of **5** was confirmed by single-crystal X-ray diffraction (Figure 3; Table II). The 1,3-dithiole (C_3S_2) ring is nearly planar, while the 1,4-dithiin (C_4S_2) ring is strongly folded along the S···S vector (44.8 and 41.2°) as is usually observed.[6] The 1,4-dithiin ring is further distorted by virtue of the asymmetry arising from the thiocarbonyl and 1,3-dithiole substituents. The two C–C bonds within the 1,4-dithiin are 1.337(10) and 1.417(8) Å.

Reactions of Coordinated $\beta\text{-}C_3S_5^{2-}$ with DMAD. In light of the high reactivity of $[\beta\text{-}C_3S_5]_n$ toward DMAD, we investigated the addition of DMAD to coordinated $\beta\text{-}C_3S_5^{2-}$. Solutions of $(NEt_4)_2[M(\beta\text{-}C_3S_5)_2]$ (M = Zn, Ni) react smoothly with DMAD at room temperature to give salts of the intensely colored addition compounds $(NEt_4)_2[M(C_3S_5\text{·}DMAD)_2]$ (Scheme IV). The zinc, nickel, and titanocene (see below) C_3S_5·DMAD compounds all display two methyl resonances in their ^1H NMR spectra, indicating the presence of unsymmetrical dithiole groups.

Preparation of $Cp_2Ti(\beta\text{-}C_3S_5)$. The green complex $Cp_2Ti(\beta\text{-}C_3S_5)$ was prepared by the chelate transfer reaction of $(NEt_4)_2[Zn(\beta\text{-}C_3S_5)_2]$ and Cp_2TiCl_2. The Cp rings in this species appear nonequivalent in the low-temperature NMR spectrum.

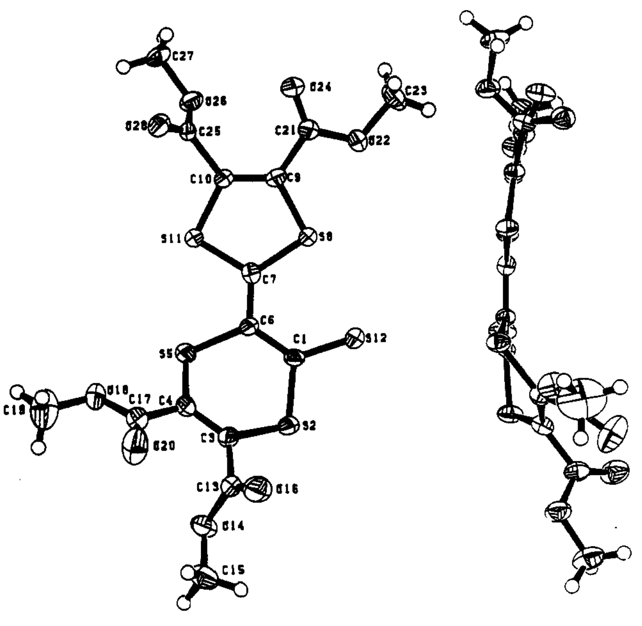
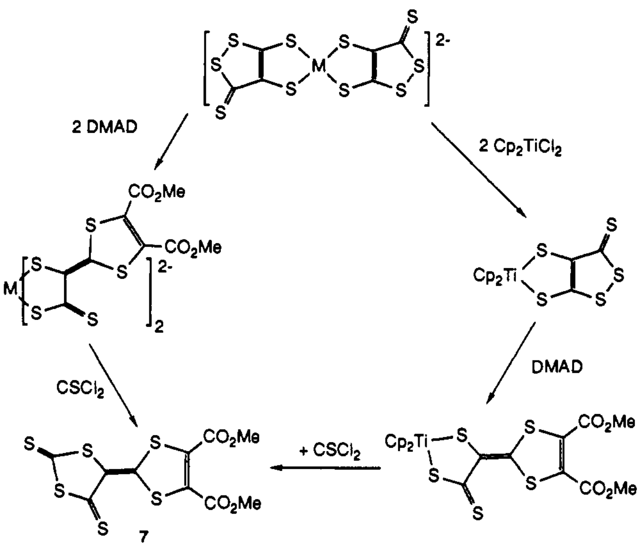


Figure 3. ORTEP drawings (35% probability ellipsoids) of C_3S_5·2DMAD (**5**).

Table II. Selected Bond Lengths (Å) and Angles (deg) for C_3S_5·2DMAD (**5**)

C(1)–S(12)	1.650(6)	C(6)–C(7)	1.390(8)
C(1)–S(2)	1.769(6)	C(7)–S(8)	1.73(1)
S(2)–C(3)	1.74(1)	S(8)–C(9)	1.756(6)
C(3)–C(4)	1.337(10)	C(9)–C(10)	1.34(1)
C(4)–S(5)	1.762(8)	C(10)–S(11)	1.728(8)
S(5)–C(6)	1.78(1)	S(11)–C(7)	1.730(8)
C(6)–C(1)	1.417(8)	S(8)···S(12)	2.906(7)
S(12)–C(1)–C(6)	126.8(4)	C(7)–S(8)–C(9)	94.4(4)
C(6)–C(1)–S(2)	119.9(4)	C(4)–S(5)–C(6)	102.2(4)
C(1)–S(2)–C(3)	105.9(3)	C(10)–S(11)–C(7)	95.7(5)
S(2)–C(3)–C(4)	124.7(6)	S(11)–C(7)–S(8)	115.4(4)
C(3)–C(4)–S(5)	121.4(7)	S(2)–C(1)–C(6)–S(5)	−11.6(7)
S(5)–C(6)–C(1)	121.6(4)	C(1)–C(6)–S(5)–C(4)	44.8(7)
S(5)–C(6)–C(7)	115.1(5)	C(6)–S(5)–C(4)–C(3)	−41.2(8)

Scheme IV



This behavior is characteristic of dithiolene derivatives of titanocene.[17] In several cases this titanium species was employed as a reagent in exploring the preparation of these new carbon sulfides, but invariably we later found other simpler reagents to

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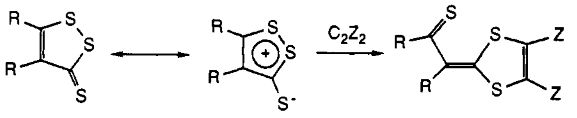
[17] Köpf, H. *Angew. Chem.* **1971**, *83*, 146. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 134.

accomplish the transformation of interest. This titanium complex also efficiently adds DMAD to give a brown adduct which does not exhibit a dynamic structure by NMR. $Cp_2TiC_3S_5$·DMAD reacts readily with thiophosgene to give golden crystals of C_4S_6·DMAD, 7. This bicyclic species was characterized by its ^1H NMR, IR, and EIMS data. It is perhaps more convenient to use $(NR_4)_2[Zn(C_3S_5\cdot DMAD)_2]$ as a souce of $C_3S_5\cdot DMAD^{2-}$ (Scheme IV).

Conclusions

Salts of the easily available dianion β-$C_3S_5^{2-}$ have been employed in the preparation of three new carbon sulfides, $[\beta\text{-}C_3S_5]_n$, C_5S_7, and C_6S_8. C_6S_8 is a tricyclic planar 1,4-dithiin. Its synthesis exploits the H_2S elimination pathway originally employed in the preparation of another isomer of C_6S_8 from α-$C_3S_5H_2$.[3a] The decreased acidity of the β-$C_3S_5H_2$ is evidenced by the higher temperatures required for the H_2S elimination reaction. This type of coupling reaction is also precedented in the chemistry of $S_2C_2(CN)_2^{2-}$ (mnt^{2-}).[18] Further studies of C_6S_8 could exploit the reactivity inherent in the pair of S–S bonds.

The apparently polymeric $[\beta\text{-}C_3S_5]_n$ was examined primarily through its degradation products derived from the addition of dimethyl acetylenedicarboxylate (DMAD). In this transformation the DMAD cleaves both S–S bonds without modification of the C–C and C–S skeleton. This addition of DMAD to the 1,2-dithiole-3-thiones was generalized to include the coordinated β-C_3S_5 ligands. Together with previous findings in our laboratory,[19] this work illustrates the effectiveness of DMAD as a reagent in the chemistry of sulfur. These results indicate that β-$C_3S_5^{2-}$ chelates might exhibit more extensive ligand-based reactivity. We suggest that the ease of addition of DMAD to β-C_3S_5 derivatives is a consequence of the dipolar character of 1,2-dithiole-3-thiones (eq 3). This polarization by the 1,2-dithiole group also provides a mechanism for charge delocalization from the 1,4-dithiin ring in C_6S_8, thus stabilizing its planar conformation.



(3)

The preparation of C_5S_7 from the unsymmetrical isomer of C_4S_6 illustrates once again the versatility and selectivity of the $LiBHEt_3$ as a reagent for the reductive cleavage of S–S bonds.[20] The intermediate species $Li_2C_4S_6$ merits further scrutiny as a ligand precursor. The connectivity of the C and S atoms within the bicyclic structure of C_5S_7 parallels the connectivity of C and N atoms in purines.

Experimental Section

Materials and Methods. Procedures and instrumentation have been previously described.[21] The compounds $(NR_4)_2[Zn(\beta\text{-}C_3S_5)_2]$,[5] $(NR_4)_2[Ni(\beta\text{-}C_3S_5)_2]$,[5] β-$C_3S_5H_2$,[5] β-$C_3S_5(COPh)_2$,[5] and $(MeCp)_2Ti(CO)_2$[22] were prepared according to literature methods. The reagents DMAD, SO_2Cl_2, Cp_2TiCl_2, Cl_2CS, PhCOCl, $LiBHEt_3$, and PBu_3 were purchased from Aldrich and used without purification.

C_6S_8 (1). A yellow orange slurry of 2.014 g of β-$C_3S_5H_2$ (10.2 mmol) in 150 mL of toluene was refluxed with stirring under a slow purge of nitrogen. The solution quickly became deep red/brown and H_2S evolved (detected with moist lead acetate paper). After 20 h the slurry was filtered and the red-brown solid was washed with 5 × 30 mL portions of toluene. Yield: 1.551 g (93%). Anal. Calcd for C_6S_8: C, 21.93; S, 78.07. Found: C, 22.77; S, 77.83. EIMS (70 eV): m/z 328 (M^+). IR (KBr): 1436 (s), 1268 (s), 1058 (s), 474 cm^{-1} (w).

Table III. Crystallographic Data for C_6S_8 and $C_3S_5(DMAD)_2$

formula	C_6S_8	$C_{15}H_{12}S_5O_8$
mol wt	328.55	480.56
a, Å	8.046(2)	18.760(4)
b, Å	9.797(3)	13.664(3)
c, Å	13.818(4)	7.880(2)
α, deg	90.0	90.0
β, deg	105.76(1)	104.31(1)
γ, deg	90.0	90.0
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	Cc
V, Å^3	1048.3(9)	1957(2)
Z	4	4
ρ_{calcd}, g/cm^3	2.082	1.631
cryst dimens, mm	0.1 × 0.1 × 0.4	0.2 × 0.2 × 0.5
collcn temp, °C	25	25
radiation (λ, Å)	Mo Kα (0.717 073)	Mo Kα (0.717 073)
2θ range, deg	3–46	3–50
measd reflcns	2696	2054
unique reflcns	1967	1805
obsd reflcns ($I > 2.58\sigma(I)$)	1517	1621
R,[a] %	3.6	3.6
R_w,[b] %	4.2	4.7

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The sample of C_6S_8 used for the crystallographic analysis (see below) was obtained by treatment of a slurry of 0.98 g of $(NEt_4)_2[Zn(\beta\text{-}C_3S_5)_2]$ (1.37 mmol) in 50 mL of CH_3CN with a solution of 200 μL of $SOCl_2$ (2.73 mmol) in 10 mL of CH_3CN at –40 °C over the course of 30 min. A yellow precipitate formed during the addition. After the addition, the reaction mixture was allowed to warm to room temperature and the mixture was filtered in air. The yellow solid was washed with 10 mL of CH_3CN, 10 mL of acetone, and 20 mL of DMF to give an orange filtrate from which orange microcrystals formed upon standing. Yield: 10 mg (2%).

C_4S_6 (2). A solution of 0.945 g (41.1 mmol) of Na in 50 mL of MeOH was added to a slurry of 8.350 g (20.5 mmol) of β-$C_3S_5(COPh)_2$ in 100 mL of MeOH. The initial tan slurry soon intensified to very deep red-brown. After 2.5 h the volatiles were removed at 50 °C and 100 mL of dry THF was added to the residue. Addition of 1.57 mL (20.6 mmol) of Cl_2CS to the slurry via syringe resulted in an immediate color change to dark red/brown. After 16 h, the solution was diluted with 50 mL of MeOH, and the brown precipitate was filtered off and washed with H_2O and MeOH. Yield: 4.21 g (85%). Anal. Calcd for C_4S_6: C, 19.98; S, 80.02. Found: C, 20.42; S, 79.07. ^{13}C NMR (CS_2, $Cr(acac)_3$): δ 216.3, 200.0, 161.1, 148.8. FDMS: m/z 240 (M^+). IR (KBr): 1416 (s), 1294 (m), 1244 (m), 1070 (vs), 486 cm^{-1} (w).

C_5S_7 (3). A solution of 2.62 mL of 1 M $LiBHEt_3$ (2.62 mmol) was added to a 0 °C slurry of 0.315 g of C_4S_6 (1.31 mmol) in 70 mL of THF. After 15 min, the reaction solution was allowed to warm to room temperature. After a further 20 min, the deep red colored reaction solution was treated with 100 μL of $CSCl_2$ (1.31 mmol). After 5 h the slurry was diluted with 30 mL of MeOH. The dark brown solid was filtered off and washed with H_2O, MeOH, and CH_2Cl_2. Yield: 0.335 g (90%). Anal. Calcd for C_5S_7: C, 21.11; S, 78.89. Found: C, 21.29; S, 78.03. FDMS: m/z 284 (M^+). IR (KBr): 1402 (s), 1293 (w) and 1257 (m), 1069 (s), 992 cm^{-1} (w).[23]

$[\beta\text{-}C_3S_5]_n$ (4). A solution of 226 μL of SO_2Cl_2 (2.8 mmol) in 100 mL of acetonitrile was added dropwise to a slurry of 1.006 g of $(NEt_4)_2[Zn(\beta\text{-}C_3S_5)_2]$ (1.4 mmol) in 40 mL of CH_3CN at ca. –40 °C. After the addition, the solution was allowed to warm to room temperature, stirred an additional 1 h and filtered. The yellow precipitate was washed with CH_3CN, H_2O, MeOH, and Et_2O. Yield: 490 mg (89%, assuming C_3S_5). Anal. Calcd for C_6S_{10}: C, 18.37; S, 81.63. Found: C, 19.3; S, 75.3. EIMS (70 eV): m/z 328 ($M^+ - 2S$), 264 ($C_6S_6^+$), 256 (S_8^+). IR (KBr): 1429 (s), 1292 (s), 1240 (m), 1063 (s), 480 cm^{-1} (w).

C_3S_5·2DMAD (5). A slurry of 0.24 g $[\beta\text{-}C_3S_5]_n$(0.61 mmol) in 20 mL of CH_2Cl_2 was treated with 2 drops of PBu_3 followed by 151 μL of DMAD

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Table IV. Atomic Coordinates for C_6S_8

	x/a	*y/b*	*z/c*
S(1)	–0.0802(2)	–0.0926(1)	0.58936(7)
S(2)	0.0124(2)	0.1502(1)	0.71064(8)
S(3)	0.1193(2)	0.3279(1)	0.67524(9)
S(4)	0.1950(2)	0.3852(1)	0.48165(9)
S(1′)	0.4825(2)	0.9102(1)	0.38425(7)
S(2′)	0.3492(2)	0.6902(1)	0.48335(8)
S(3′)	0.3140(2)	0.6897(1)	0.62523(8)
S(4′)	0.3920(2)	0.9167(1)	0.76992(8)
C(1)	0.0060(6)	0.0723(4)	0.5982(3)
C(2)	0.0648(5)	0.1450(4)	0.5300(3)
C(3)	0.1266(6)	0.2803(4)	0.5557(3)
C(1′)	0.4302(5)	0.8545(4)	0.4929(3)
C(2′)	0.4432(5)	0.9225(4)	0.5814(3)
C(3′)	0.3903(6)	0.8527(4)	0.6586(3)

Table V. Atomic Coordinates for $C_3S_5{\cdot}2DMAD$

	x/a	*y/b*	*z/c*
C(1)	0.5156(3)	–0.1327(4)	–0.0124(1)
S(2)	0.4753(3)	–0.2501(1)	–0.0526(8)
C(3)	0.3814(5)	–0.2333(4)	–0.072(1)
C(4)	0.3437(5)	–0.1530(5)	–0.136(1)
S(5)	0.3853(3)	–0.0563(1)	–0.2244(8)
C(6)	0.4733(5)	–0.0482(4)	–0.074(1)
C(7)	0.4993(5)	0.0464(4)	–0.033(1)
S(8)	0.5858(3)	0.0757(1)	0.0932(8)
C(9)	0.5682(5)	0.2020(4)	0.092(1)
C(10)	0.5028(5)	0.2331(4)	–0.002(1)
S(11)	0.4430(3)	0.1450(1)	–0.1124(8)
S(12)	0.6022	–0.1358(1)	0.01013(8)
C(13)	0.3483(5)	–0.3191(4)	0.002(1)
O(14)	0.3068(4)	–0.3730(3)	–0.124(1)
C(15)	0.2722(6)	–0.4583(6)	–0.067(2)
O(16)	0.3609(5)	–0.3382(4)	0.156(1)
C(17)	0.2646(5)	–0.1447(5)	–0.139(1)
O(18)	0.2309(4)	–0.0801(4)	–0.258(1)
C(19)	0.1521(5)	–0.0721(6)	–0.282(2)
O(20)	0.2351(5)	–0.1911(5)	–0.050(1)
C(21)	0.6241(5)	0.2643(4)	0.208(1)
O(22)	0.6870(4)	0.2160(3)	0.2621(10)
C(23)	0.7461(5)	0.2668(6)	0.382(1)
O(24)	0.6129(4)	0.3451(3)	0.252(1)
C(25)	0.4732(5)	0.3369(4)	–0.011(1)
O(26)	0.5089(4)	0.3965(3)	–0.090(1)
C(27)	0.4830(5)	0.4973(5)	–0.103(1)
O(28)	0.4218(4)	0.3571(3)	0.0492(10)

(1.22 mmol). The solid dissolved to give a dark red solution. After 2 h, the soluble portion of the reaction was concentrated and chromatographed on silica gel, eluting with CH_2Cl_2, which gave a major red band which crystallized upon the addition of hexanes. Yield: 195 mg (69% based on DMAD). ^1H NMR ($CDCl_3$): singlets at δ 3.95, 3.94, 3.89, 3.84. Anal. Calcd for $C_{15}H_{12}O_8S_5$: C, 37.50; H, 2.50. Found: C, 37.73; H, 2.63. EIMS (70 eV): δ 480 (M^+). Elution with acetone afforded a yellow fraction, which was evaporated to give ca. 50 mg of yellow-orange crystals of $C_3S_4{\cdot}3DMAD$, **6**. FDMS: *m/z* 590 (M^+). ^1H NMR ($CDCl_3$): singlets at δ 3.95 (3H), 3.93 (3H), 3.90 (3H), 3.87 (3H), and 3.81 (6H). Anal. Calcd for $C_{21}H_{18}O_{12}S_4$: C, 42.71; H, 3.05. Found: C, 42.81; H, 3.10.

$(NEt_4)_2[Zn(C_3S_5{\cdot}DMAD)_2]$. A solution of 0.21 g of $(NEt_4)_2[Zn(\beta\text{-}C_3S_5)_2]$ (0.292 mmol) in 30 mL of CH_2Cl_2 was treated with 3 drops of PBu_3 followed by 72 μL of DMAD (0.585 mmol). After 1 h the resulting dark red solution was concentrated to 10 mL and diluted with 30 mL of Et_2O to give red microcrystals. Yield: 0.270 g (92%). Anal. Calcd for $C_{34}H_{52}N_2O_8S_{10}Zn$: C, 40.73; H, 5.23; N, 2.79. Found: C, 40.41; H, 5.30; N, 2.76. ^1H NMR (CD_3CN): δ 3.78 and 3.80 (12H, OCH_3); δ 3.13 (quartet, 16H), 1.18 (triplet, 24H).

$(NEt_4)_2[Ni(C_3S_5{\cdot}DMAD)_2]$. A slurry of 0.15 g of $(NEt_4)_2[Ni(\beta\text{-}C_3S_5)_2]$ (0.211 mmol) in 20 mL of CH_2Cl_2 was treated with 3 drops of PBu_3 followed by 64 μL of DMAD (0.516 mmol). After 30 min the solids had dissolved giving a green solution, which was filtered and evaporated. The residue was recrystallized from 30 mL of CH_3CN by the addition of Et_2O. Yield: 120 mg (56%). Anal. Calcd for $C_{34}H_{52}N_2NiO_8S_{10}$: C, 41.00; H, 5.27; N, 2.81. Found: C, 41.15; H, 5.44; N, 2.76. ^1H NMR (CD_3CN): δ 3.80 (6H, OCH_3), 3.82 (6H, OCH_3), 3.16 (quartet, 16H), 1.19 (triplet, 24H).

$(C_5H_5)_2Ti(\beta\text{-}C_3S_5)$. A slurry of 5 g of $(NEt_4)_2[Zn(\beta\text{-}C_3S_5)_2]$ (6.97 mmol) and 3.64 g of Cp_2TiCl_2 (13.93 mmol) in 50 mL of THF was heated under reflux for 4 h. The resulting green solution was cooled to room temperature, filtered, and concentrated. Dilution of the concentrate with 50 mL of Et_2O afforded green crystals. Yield: 4.59 g (88%). Anal. Calcd for $C_{13}H_{10}S_5Ti$: C, 41.72; H, 2.67. Found: C, 41.97; H, 3.00. ^1H NMR (CD_2Cl_2, 23 °C): δ 6.15 (s, C_5H_5). ^1H NMR (CD_2Cl_2, –67 °C): δ 5.89 (s, 5H, C_5H_5), 6.41 (s, 5H, C_5H_5).

$(C_5H_5)_2Ti(C_3S_5{\cdot}DMAD)$. A slurry of 0.5 g of $Cp_2Ti(\beta\text{-}C_3S_5)$ (1.337 mmol) in 20 mL of CH_2Cl_2 was treated with 2 drops of PBu_3 followed by 165 μL of DMAD (1.34 mmol). The bright green reaction mixture assumed a brownish tint, and after 1 h all solids had dissolved. After 2 h 0.18 g of black green crystals was collected. A further crop of 0.25 g was obtained by diluting the filtrate with Et_2O. Combined yield: 62%. Anal. Calcd for $C_{19}H_{16}O_4S_5Ti{\cdot}CH_2Cl_2$: C, 39.95; H, 2.99; S, 26.63. Found: C, 40.87; H, 3.09; S, 25.67. ^1H NMR ($CDCl_3$): 3.91 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 5.30 (CH_2Cl_2), 6.28 (s, 10H, C_5H_5). EIMS (70 eV): *m/z* 516 (M^+).

$C_4S_6{\cdot}DMAD$. A slurry of 0.15 g of $(NEt_4)_2[Zn(C_3S_5{\cdot}DMAD)_2]$ (0.15 mmol) in 30 mL of acetone was treated with 23 μL of $CSCl_2$ (0.30 mmol). The slurry became orange and after 3 h was evaporated to give golden crystals, which were washed with cold ether. Yield: 92 mg (80%). Anal. Calcd for $C_{10}H_6O_4S_6$: C, 31.41; H, 1.57. Found: C, 31.30: H, 1.60. ^1H NMR ($CDCl_3$): δ 3.98 (3H, OCH_3), 3.97 (3H, OCH_3). EIMS (70 eV): *m/z* 381 (M^+), 306 ($M^+ - CO_2$), 262 ($M^+ - CO_2 - CS$).

X-ray Crystallography for C_6S_8. Crystal and data collection parameters are summarized in Table III. The structure was solved by direct methods (SHELXS-86); correct positions for the eight sulfur atoms were deduced from an *E*-map. Subsequent least-squares–difference Fourier calculations revealed positions for the remaining atoms. In the final cycle of least squares, all atomic positions were independently refined with anisotropic thermal coefficients. Successful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors. Atomic coordinates are listed in Table IV.

X-ray Crystallography for $C_3S_5{\cdot}2DMAD$. The structure was solved by direct methods (SHELXS-86); correct positions for the sulfur and ring carbon atoms were deduced from an *E*-map. Subsequent least-squares–difference Fourier calculations gave positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of the least squares, anisotropic thermal coefficients were retained for nonhydrogen atoms and a group isotropic thermal parameter was varied for hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors. Atomic coordinates are listed in Table V.

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Supplementary Material Available: A table of thermal parameters (1 page). Ordering information is provided on any current masthead page.