

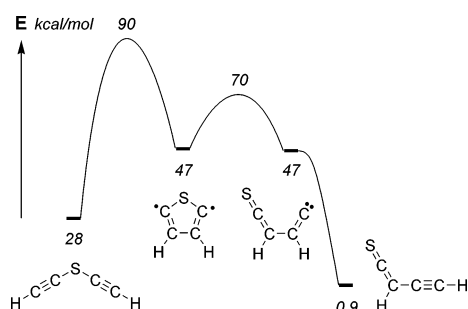
Ring Opening of 2,5-Didehydrothiophene: Structures and Rearrangements of C₄H₂S Isomers

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Electronic structures and rearrangement pathways of several C₄H₂S isomers are computationally investigated by methods based on coupled cluster theory and density functional theory. Six singlet C₄H₂S isomers lie within ca. 30 kcal/mol above butatrienethione (**6**), the apparent global minimum. Ethynylthioketene (**7**) lies only 2 kcal/mol higher in energy than cumulene **6**. Two open-chain isomers, butadiynylthiol (**8**) and diethynyl sulfide (**9**), reside ca. 9 and 24 kcal/mol above **6**, respectively. Lying 30 kcal/mol above **6**, two cyclic singlet isomers, ethynylthiirene (**10**) and cyclopropenylidenemethanthione (**11**), are nearly degenerate in energy. Thiophene-2,5-diyl (**12**) lies substantially higher in energy than **6** (ca. 45 kcal/mol) and is predicted to rearrange preferentially by C–S bond cleavage, leading to thioketene **7**, rather than by C–C bond cleavage, leading to diethynyl sulfide (**9**; retro-Bergman cyclization). Accurate spectroscopic properties of these C₄H₂S isomers, as well as an understanding of their rearrangement pathways, should facilitate the detection and characterization of these isomers in the laboratory and the interstellar medium.

Introduction

The current investigation addresses an array of topics relating to the structures, reactions, and spectroscopy of C₄H₂S isomers. The study provides an important perspective on issues of current interest in diverse fields, including organic chemistry, molecular spectroscopy, and astrochemistry. Sulfur-containing carbon cumulenes, C_nS (*n* = 1, 2, 3, and 5), are known to exist in the interstellar medium.^{1–4} Although C₄S has not been detected in space, its formation has been suggested to occur in dense interstellar clouds in reactions between S⁺ and hydrocarbons.⁵ Neutral and ionic forms of C₄S have been

investigated experimentally^{6,7} and computationally.⁸ Hydrogenated thiocumulenes, H_xC_nS, may also exist at detectable levels in the hydrogen-rich interstellar medium.^{9–12} Recent microwave studies by Gordon et al. report that a series of radicals HC_nS (*n* ≤ 8) and cumulenes H₂C_nS (*n* ≤ 7) are present in a supersonic molecular beam, formed from a low-current discharge of a diacetylene (HC≡C–C≡CH) and CS₂ mixture.^{11,12}

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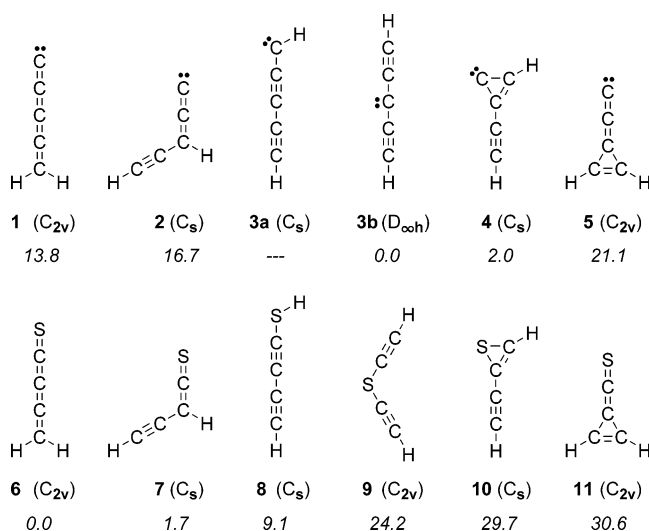
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SCHEME 1^a

^a CCSD(T)/cc-pVTZ energy (kcal/mol, ZPVE corrected) in italics. C_5H_2 isomers from ref 18.

Embracing the current interest in hydrogenated thiocumulenes, along with related interests in dehydroaromatic species¹³ and cycloaromatization reactions,^{14,15} we decided to study isomers on the C_4H_2S potential energy surface (PES),¹⁶ with a focus on their spectroscopic properties and relevant rearrangement pathways.

Previously, we demonstrated the successful application of coupled-cluster methods in studying highly unsaturated species such as C_3H_2 isomers,¹⁷ C_5H_2 isomers,¹⁸ and a series of enediynes¹⁹ and ene-nitriles,²⁰ to levels where spectroscopic properties predicted by theory and measured by experiment agree quite satisfactorily. As a framework for thinking about the C_4H_2S potential energy surface, we adopted the perspective that formal “replacement” of the divalent (carbene) carbon in the low-energy C_5H_2 isomers with divalent sulfur would probably guide us to the corresponding low-energy C_4H_2S isomers (Scheme 1).²¹ After describing the structures of several low-energy C_4H_2S isomers in some detail, we consider their rearrangement pathways relevant to ongoing experimental efforts in our laboratory and elsewhere.

Computational Methods

Initially, all C_4H_2S stationary points were subject to geometry optimization at the B3LYP/6-31G* level of density func-

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tional theory (DFT), using Becke’s three-parameter hybrid exchange functional²² and the correlation functional²³ of Lee, Yang, and Parr (B3LYP), with a split-valence basis set, 6-31G*, and incorporation of the “guess = mix” keyword for open-shell calculations. Subsequently, harmonic vibrational frequencies were calculated to characterize the stationary points as true minima or transition states. An Intrinsic Reaction Coordinate (IRC) on each transition state was further employed to recognize the minima to which the transition state connects.

DFT methods overestimate bond delocalization,^{18,24,25} and this well-established problem is a serious issue in computing structures and energies for the types of highly unsaturated molecules encountered in the current investigation. Therefore, the DFT structures were then applied to successive optimizations based on coupled cluster theory, including all single and double excitations iteratively (CCSD)²⁶ and triple excitation perturbatively (CCSD(T)),²⁷ with Dunning’s correlation-consistent, polarized-valence basis sets, cc-pVDZ and cc-pVTZ.²⁸ The basis sets for C_4H_2S utilize 84 and 182 contracted Gaussian functions, respectively. Electron correlation included both valence and core. Harmonic vibrational frequencies for each optimized structure were calculated up to the level of CCSD(T)/cc-pVDZ. The computed frequencies have not been scaled. Singlet 2,5-didehydrothiophene (**12**) and the transition states for its two modes of ring opening (**TS**_{12–9}, **TS**_{12–13}) pose challenging computational problems because of singlet diradical character.^{29,30} Following the recommendation of Crawford et al.,³¹ who studied these problems in great detail in the case of *p*-benzyne, we employed an unrestricted wave function (UHF-CCSD(T)/cc-pVDZ) in the optimization of **12**, **TS**_{12–9}, and **TS**_{12–13}.^{32–36} Harmonic vibrational frequencies for these species were determined at the UHF-B3LYP/6-31G* level of theory, but not at UHF-CCSD(T)/cc-pVDZ. Coupled-cluster calculations were performed with a local version of the ACESII program system;³⁷ DFT calculations were performed with Gaussian 98.³⁸

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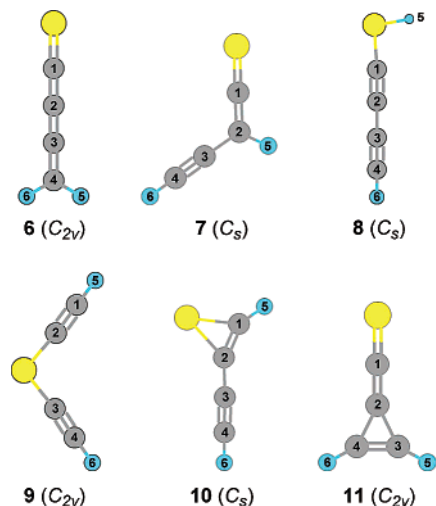


FIGURE 1. Equilibrium structures (CCSD(T)/cc-cc-pVTZ) and atom numbering for C_4H_2S isomers **6**–**11**.

Results and Discussion

A. Structural Properties of Individual Isomers.

Equilibrium structures of six singlet C_4H_2S isomers (Figure 1) are calculated in the series of coupled-cluster methods with Dunning basis sets: CCSD/cc-pVDZ, CCSD(T)/cc-pVDZ, and CCSD(T)/cc-pVTZ. The structural properties of each molecule, including dipole moments and rotational constants, are tabulated in Tables 1–6, along with harmonic vibrational frequencies calculated at the level of CCSD(T)/cc-pVDZ.

Butatrienethione (6). The equilibrium structure of **6** (C_{2v} symmetry), optimized in the series of coupled-cluster calculations, is consistent with a reported microwave spectrum¹² and with a DFT calculation at the level of BLYP/6-311G**.³⁹ The C–C bond lengths of **6** display slightly less bond-length alternation than the all-carbon analogue $H_2C=C=C=C$: (**1**).¹⁸ The structures computed for **6** sensibly reflect the computational method employed: the distance across the heavy atom framework, $r(SC_4)$, increases upon inclusion of the triples correction (5.496 Å at CCSD/cc-pVDZ vs 5.521 Å at CCSD(T)/cc-pVDZ) but decreases with a larger basis set (5.521 Å at CCSD(T)/cc-pVDZ vs 5.436 Å at CCSD(T)/cc-pVTZ) (Table 1). The computed rotational constants B_e and C_e fall within ca. 4 MHz (0.3%) of the experimental values, while the major rotational constant A_e along the heavy atom skeleton deviates by ca. 5.5%.¹² The computed, equilibrium rotational constants are not precisely

TABLE 1. Structural Properties of Butatrienethione (**6**)^a

Structures, Rotational Constants, and Dipole Moments				
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	exptl (r_o) ^b
$r(SC_1)$	1.5803	1.5878	1.5688	
$r(C_1C_2)$	1.2935	1.2985	1.2768	
$r(C_2C_3)$	1.2946	1.2989	1.2763	
$r(C_3C_4)$	1.3278	1.3357	1.3140	
$r(C_4H_5)$	1.0947	1.0964	1.0784	
$\theta(C_3C_4H_5)$	120.59	120.55	120.54	
A_e	282376	281278	290657	275400
B_e	1360	1348	1391	1395
C_e	1354	1342	1384	1388
μ	1.576	1.409	1.560	

Harmonic Frequencies and Infrared Intensities at the Level of CCSD(T)/cc-pVDZ

mode	symmetry	freq (exptl ^c)	intensity (exptl ^c)
ω_1	a_1	3158.9 (3018)	6.1 (2)
ω_2	a_1	2136.4 (2089)	942.3 (100)
ω_3	a_1	1804.5 (1783)	70.4 (8)
ω_4	a_1	1425.6 (1380)	18.9 (6)
ω_5	a_1	1175.4 (1170)	72.8 (8)
ω_6	a_1	587.3	7.0
ω_7	b_1	744.9 (759)	58.3 (5)
ω_8	b_1	435.6	0.3
ω_9	b_1	347.2	0.1
ω_{10}	b_1	117.8	1.8
ω_{11}	b_2	3259.9	0.2
ω_{12}	b_2	978.6	0.5
ω_{13}	b_2	508.5	0.0
ω_{14}	b_2	338.3	0.1
ω_{15}	b_2	123.8	0.9

^a Bond lengths (Å), bond angles (deg), dipole moments (D), harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1. ^b From ref 12. ^c Detected in an Ar matrix, ref 16; IR band intensities are reported in relative % of the strongest band intensity.

comparable to the experimental rotational constants, which contain contributions from the coupling of vibration and rotation. The discrepancies observed between the computed and experimental rotational constants for **6**, however, are qualitatively similar to those observed for $H_2C=C=C=C$: (**1**): A (5.3%), B (0.08%), and C (0.04%).^{18,40} The somewhat “less outstanding” agreement of the computed and experimental B and C rotational constants for cumulene **6** vs carbene **1** likely reflects the greater computational difficulty introduced by the sulfur atom in **6**. The large deviation between the computed and experimental values of the A rotational constant of both cumulene **6** and carbene **1** is likely attributed to zero-point vibrational effects, as discussed previously for $H_2C=C=C=C$: (**1**)^{18,40} and $H_2C=C=C=C=O$.⁴¹ The computed vibrational spectrum reveals two low-frequency bending vibrations ($<150\text{ cm}^{-1}$) of the heavy atom framework, which may significantly perturb the A rotational constant from the value computed for the equilibrium geometry. Optimization attempts seeking a bent structure failed, as nonplanar C_s structures (initial C1–

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C2–C3 angle 148° or 162° or 175°; bent out-of-plane) restore back to linearity in the course of the optimization (CCSD/cc-pVDZ). DFT calculations, by us⁴² and by others,³⁹ also predict a linear heavy atom skeleton for **6**, but we do not consider these calculations to be decisive in light of the tendency of DFT methods to overemphasize bond delocalization,^{18,24,25} which may bias the calculation toward the linear structure. By comparison, the structure for the oxygen analogue, butatrienone (H₂C=C=C=C=O), remains a subject of uncertainty. The microwave rotational spectrum has been interpreted in terms of a semirigid bender model and a single minimum on the potential energy surface.⁴¹ Calculations uniformly predict a shallow potential energy surface, although the prediction of a single minimum or a double minimum varies with the computational method employed.^{43–45} Radom favors a bent equilibrium structure with a very low barrier (ca. 15 cm⁻¹) to linearity.⁴³ Qualitatively, the deviation of the cumulene chain from linearity has been ascribed to the contribution of the resonance structure that places vinyl anion character at the β -carbon.^{43–45} The importance of this resonance contributor is apparently diminished in the case of H₂C=C=C=C=S (**6**).

Butatrienethione (**6**) arises as an exclusive product upon photodissociation of 3,4-thiophenedicarboxylic acid anhydride in an argon matrix.¹⁶ As tabulated in Table 1, theoretical vibrational frequencies and corresponding intensities are in good agreement with experimental counterparts, particularly for three cumulenic stretching modes: relative computed IR intensities of ω_3 and ω_5 , with respect to ω_2 , are almost identical to experimental values. The computed dipole moment of **6** (1.56 D) at the level of CCSD(T)/cc-pVTZ fits the trend of alternating experimental dipole moments in the cumulenic thione series³⁹ as: H₂C=S, 1.65 D;⁴⁶ H₂C=C=S, 1.02 D;⁴⁷ H₂C=C=C=S, 2.06 D;⁴⁸ H₂C=C=C=C=S, 1.56 D (this work). The dipole moment for **6** is dramatically smaller than that of the corresponding carbon-chain compound H₂C=C=C=C=C: (**1**) (5.8 D).¹⁸

Ethynylthioketene (7). Ethynylthioketene (**7**) bears a close structural resemblance to the all-carbon analogue, ethynylpropadienyliene (**2**),¹⁸ apart from the significant difference in the terminal C=S vs C=C: bond lengths (1.558 Å vs 1.286 Å; CCSD(T)/cc-pVTZ; Table 2). Although ethynylthioketene (**7**) lies close in energy to butatrienethione (**6**), and is likely to be formed along with **6** in an electrical discharge, **7** is less polar than **6** (0.38 D vs 1.56 D) and therefore represents a less attractive candidate for detection by rotational spectroscopy in the laboratory or in space. In the context of the alternating trend of dipole moments described earlier for butatrienethione (**6**), the dipole moment for ethynylthioketene (**7**; 0.38 D) is expected to be smaller than that of propyne-thial (HC≡CCHS, 1.88 D),^{49,50} an adjacent member of the

TABLE 2. Structural Properties of Ethynylthioketene (**7**)^a

Structures, Rotational Constants, and Dipole Moments			
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ
$r(\text{SC}_1)$	1.5703	1.5767	1.5578
$r(\text{C}_1\text{C}_2)$	1.3360	1.3432	1.3219
$r(\text{C}_2\text{C}_3)$	1.4397	1.4390	1.4190
$r(\text{C}_3\text{C}_4)$	1.2241	1.2312	1.2092
$r(\text{C}_2\text{H}_5)$	1.0959	1.0979	1.0797
$r(\text{C}_4\text{H}_6)$	1.0766	1.0781	1.0582
$\theta(\text{SC}_1\text{C}_2)$	+179.51	+179.58	+179.37
$\theta(\text{C}_1\text{C}_2\text{H}_5)$	118.02	118.04	117.55
$\theta(\text{H}_5\text{C}_2\text{C}_3)$	119.57	119.74	119.41
$\theta(\text{C}_2\text{C}_3\text{C}_4)$	+178.65	+178.61	+178.27
$\theta(\text{C}_3\text{C}_4\text{H}_6)$	-179.46	-179.38	-179.16
A_e	22406.7	22128.5	23571.6
B_e	1718.5	1709.7	1743.8
C_e	1596.1	1587.1	1623.7
μ	0.344	0.331	0.377

Harmonic Frequencies and Infrared Intensities at the Level of CCSD(T)/cc-pVDZ			
mode	symmetry	freq	intensity
ω_1	a'	3462.0	77.1
ω_2	a'	3184.5	13.4
ω_3	a'	2149.6	13.8
ω_4	a'	1799.0	273.4
ω_5	a'	1267.8	21.2
ω_6	a'	1035.3	8.4
ω_7	a'	834.3	13.6
ω_8	a'	627.5	30.7
ω_9	a'	541.3	4.1
ω_{10}	a'	325.9	2.0
ω_{11}	a'	108.6	0.3
ω_{12}	a''	622.7	7.9
ω_{13}	a''	523.4	60.5
ω_{14}	a''	365.5	2.8
ω_{15}	a''	329.0	4.9

^a Bond lengths (Å), bond angles (deg; (+/-) notions representing clockwise/counterclockwise directions from the first atoms), dipole moments (D), harmonic vibrational frequencies (cm⁻¹), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1.

homologous series. The magnitude of the difference, however, seems unexpectedly large. Laboratory IR detection of **7** would be evidenced by the signature of a typical thioketene IR spectrum, a relatively intense S=C=C stretching vibration (ω_4 , 1800 cm⁻¹, 273 km/mol) (Table 2).

Butadiynylthiol (8). Bearing the equivalent heavy-atom framework as the global minimum **6**, the equilibrium structure of butadiynylthiol (**8**) uniformly converged in C_s symmetry in the series of coupled-cluster calculations. In contrast to H₂C=C=C=C=S (**6**), thiol **8** exhibits pronounced bond-length alternation, with C≡C distances of 1.215 and 1.211 Å and a C–C distance of 1.366 Å (Table 3). The two soft skeletal bending vibrations (<150 cm⁻¹) in thiol **8** are quite similar to those of butatrienethione (**6**). In the computed infrared spectrum of **8**, the C–H stretch (ω_1 , 3460 cm⁻¹, 94.9 km/mol) is dramatically more intense than the S–H stretch (ω_2 , 2696 cm⁻¹, 2 km/mol). The C≡C stretching vibration acquires modest intensity (ω_3 , 2255 cm⁻¹, 28 km/mol) by virtue of the

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TABLE 3. Structural Properties of Butadiynylthiol (8)^a

Structures, Rotational Constants, and Dipole Moments			
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ
$r(\text{SC}_1)$	1.7123	1.7129	1.6927
$r(\text{C}_1\text{C}_2)$	1.2276	1.2361	1.2152
$r(\text{C}_2\text{C}_3)$	1.3933	1.3897	1.3661
$r(\text{C}_3\text{C}_4)$	1.2257	1.2337	1.2111
$r(\text{SH}_5)$	1.3531	1.3555	1.3416
$r(\text{C}_4\text{H}_6)$	1.0768	1.0784	1.0576
$\theta(\text{H}_5\text{SC}_1)$	95.89	95.87	96.09
$\theta(\text{SC}_1\text{C}_2)$	-175.89	-175.20	-175.84
$\theta(\text{C}_1\text{C}_2\text{C}_3)$	+179.37	+179.08	+179.37
$\theta(\text{C}_2\text{C}_3\text{C}_4)$	+179.94	+179.98	-179.81
$\theta(\text{C}_3\text{C}_4\text{H}_6)$	-179.82	-179.81	+179.97
A_e	285524.3	283272.1	290365.7
B_e	1331.9	1326.4	1368.1
C_e	1325.7	1320.2	1361.7
μ	0.940	0.942	0.852

Harmonic Frequencies and Infrared Intensities at the Level of CCSD(T)/cc-pVDZ			
mode	symmetry	freq	intensity
ω_1	a'	3460.6	94.9
ω_2	a'	2695.8	2.0
ω_3	a'	2254.7	28.3
ω_4	a'	2084.2	0.9
ω_5	a'	1069.4	1.9
ω_6	a'	959.0	13.4
ω_7	a'	606.8	37.7
ω_8	a'	517.7	0.0
ω_9	a'	492.3	0.0
ω_{10}	a'	279.3	0.4
ω_{11}	a'	123.3	3.7
ω_{12}	a''	563.0	41.0
ω_{13}	a''	438.2	1.2
ω_{14}	a''	302.7	0.8
ω_{15}	a''	130.2	4.8

^a Bond lengths (Å), bond angles (deg; (+/-) notions representing clockwise/counterclockwise directions from the first atoms), dipole moments (D), harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1.

unsymmetrical substitution pattern. The molecular dipole moment of thiol **8** (0.85 D) is roughly aligned with the direction of the S–H bond (S negative, H positive), which is reminiscent of that described for ethynol (hydroxyacetylene; $\text{HC}\equiv\text{COH}$; 1.79 D).⁵¹ The magnitude of the dipole moment is slightly smaller than that computed for ethynthiol ($\text{HC}\equiv\text{CSH}$; 0.93 D, 1.17 D).⁵²

Diethynyl Sulfide (9). Diethynyl sulfide (**9**) is unique among the species included in this investigation; it is amenable to chemical synthesis and isolation, although it is rather reactive and difficult to purify.^{53–55} The molecular structure of sulfide **9** was recently investigated using a combination of microwave spectroscopy and computational methods.⁵⁵ Our results (Table 4) are fully in accord with those described in the earlier study, so

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TABLE 4. Structural Properties of Diethynylsulfide (9)^a

Structures, Rotational Constants, and Dipole Moments				
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	exptl (r_e) ^b
$r(\text{SC}_2)$	1.7196	1.7208	1.7000	1.7209
$r(\text{C}_2\text{C}_1)$	1.2235	1.2304	1.2095	1.2102
$r(\text{C}_1\text{H}_5)$	1.0765	1.0780	1.0575	1.0596
$\theta(\text{H}_5\text{C}_1\text{C}_2)$	+178.90	+178.62	+179.11	+174.99
$\theta(\text{C}_1\text{C}_2\text{S})$	-175.13	-174.72	-175.60	-173.56
$\theta(\text{C}_2\text{SC}_3)$	100.52	100.55	100.58	100.21
A_e	9916.6	9948.4	10081.9	10143.06
B_e	2626.5	2604.4	2696.6	2628.78
C_e	2076.5	2064.0	2127.6	2087.13
μ	0.727	0.683	0.750	0.75

Harmonic Frequencies and Infrared Intensities at the Level of CCSD(T)/cc-pVDZ			
mode	symmetry	freq	intensity
ω_1	a ₁	3465.3	41.4
ω_2	a ₁	2109.5	0.2
ω_3	a ₁	692.1	21.2
ω_4	a ₁	663.7	22.6
ω_5	a ₁	458.4	19.5
ω_6	a ₁	111.0	1.0
ω_7	a ₂	534.0	0.0
ω_8	a ₂	300.8	0.0
ω_9	b ₁	535.4	85.2
ω_{10}	b ₁	291.7	3.1
ω_{11}	b ₂	3464.4	111.9
ω_{12}	b ₂	2099.1	4.1
ω_{13}	b ₂	711.7	4.7
ω_{14}	b ₂	663.6	19.1
ω_{15}	b ₂	270.5	3.9

^a Bond lengths (Å), bond angles (deg; (+/-) notions representing clockwise/counterclockwise directions from the first atoms), dipole moments (Debye), harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1. ^b From ref 55.

we will not recapitulate our results in detail. The structure of sulfide **9** exhibits C_{2v} symmetry in which the alkyne moieties display subtle in-plane deviations from linearity. The predicted infrared spectrum contains several characteristic vibrations of moderate intensity (Table 4). The in-plane scissoring vibration, which also represents the reaction coordinate for the cycloaromatization reaction, is predicted to be the lowest energy normal mode (ω_6 , 111 cm^{-1}). The computed dipole moment (0.75 D) for sulfide **9**, oriented with the negative end of the dipole at sulfur, is in excellent agreement with the experimental value (0.75 D) obtained from Stark splitting measurements.⁵⁵

Ethynylthiirene (10). The equilibrium structure of **10** (C_s symmetry) features nonequivalent C–S bonds of the thiirene ring (1.823, 1.892 Å; Table 5), as compared to the C–S bond of thiirene itself (1.856 Å) at the CCSD(T)/cc-pVTZ level.⁴² Although further studies of this issue are warranted, we infer that the unsymmetrical substitution pattern imparted by the ethynyl substituent provides a mechanism for distorting the symmetry and relieving the *anti*-aromatic character of the thiirene ring. The computed infrared spectrum of thiirene **10** reveals the absence of any moderately intense characteristic vibration that could serve as a basis for distinguishing **10** from other $\text{C}_4\text{H}_2\text{S}$ isomers. The relatively large dipole moment (2.07 D) makes thiirene **10** a plausible target

TABLE 5. Structural Properties of Ethynylthiirene (10)^a

Structures, Rotational Constants, and Dipole Moments			
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ
$r(\text{SC}_1)$	1.8446	1.8438	1.8227
$r(\text{C}_1\text{C}_2)$	1.3019	1.3106	1.2885
$r(\text{C}_2\text{C}_3)$	1.4073	1.4025	1.3809
$r(\text{C}_3\text{C}_4)$	1.2249	1.2331	1.2109
$r(\text{C}_1\text{H}_5)$	1.0872	1.0895	1.0696
$r(\text{C}_4\text{H}_6)$	1.0772	1.0788	1.0591
$\theta(\text{H}_5\text{C}_1\text{S})$	139.26	139.17	139.17
$\theta(\text{H}_5\text{C}_1\text{C}_2)$	149.04	148.11	148.72
$\theta(\text{C}_1\text{C}_2\text{C}_3)$	153.02	153.93	154.36
$\theta(\text{C}_2\text{C}_3\text{C}_4)$	-178.73	-178.40	-177.49
$\theta(\text{C}_3\text{C}_4\text{H}_6)$	+179.52	+179.22	+178.96
A_e	15156.3	15149.1	15365.5
B_e	2351.6	2324.0	2411.5
C_e	2035.7	2014.9	2084.4
μ	2.023	1.984	2.074

Harmonic Frequencies and Infrared Intensities
at the Level of CCSD(T)/cc-pVDZ

mode	symmetry	freq	intensity
ω_1	a'	3457.3	87.4
ω_2	a'	3299.5	12.7
ω_3	a'	2138.6	1.2
ω_4	a'	1777.9	11.1
ω_5	a'	970.8	11.4
ω_6	a'	869.6	13.6
ω_7	a'	676.2	29.1
ω_8	a'	611.9	30.9
ω_9	a'	500.5	1.3
ω_{10}	a'	327.2	1.6
ω_{11}	a'	157.0	0.7
ω_{12}	a''	651.1	33.9
ω_{13}	a''	578.1	23.6
ω_{14}	a''	437.7	8.0
ω_{15}	a''	198.0	8.0

^a Bond lengths (Å), bond angles (deg; (+/-) notions representing clockwise/counterclockwise directions from the first atoms), dipole moments (D), harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1.

for detection by rotational spectroscopy. The computed rotational constants will facilitate such an endeavor (Table 5).

Cyclopropenyldenemethanthione (11). Thioketene **11** bears a structural resemblance to the all-carbon analogue, 3-(didehydrovinylidene)cyclopropene (**5**),¹⁸ apart from the significant difference in the terminal C=S vs C=C: bond lengths (1.583 Å vs 1.269 Å; CCSD(T)/cc-pVTZ; Table 6). The C–C bonds constituting the ring of **11** are relatively localized (1.306 and 1.465 Å) with respect to those of carbene **5** (1.335 and 1.413 Å)¹⁸ and cyclopropenyldiene (1.325 and 1.422 Å)¹⁷ at the CCSD(T)/cc-pVTZ level. The computed infrared spectrum of **11** (Table 6) includes two intense vibrations for the cumulenyl stretch (ω_2 , 1965 cm^{-1} , 94 km/mol) and the ring stretch (ω_3 , 1603 cm^{-1} , 107 km/mol), as well as the absence of a strong acetylenic C–H stretch (ca. 3400 cm^{-1}). The calculated dipole moment of **11** (3.91 D) is the largest of any of the $\text{C}_4\text{H}_2\text{S}$ isomers included in this study. Although thioketene **11** is substantially less polar than carbene **5** (8.16 D),¹⁸ it is more polar than both thioketene (1.02 D)⁴⁷ and cyclopropenyldiene (3.43 D).⁵⁶ Carbene **5**

TABLE 6. Structural Properties of Cyclopropenyldenemethanthione (11)^a

Structures, Rotational Constants, and Dipole Moments			
parameter	CCSD/ cc-pVDZ	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ
$r(\text{SC}_1)$	1.5949	1.6010	1.5826
$r(\text{C}_1\text{C}_2)$	1.3043	1.3093	1.2879
$r(\text{C}_2\text{C}_3)$	1.4817	1.4888	1.4652
$r(\text{C}_3\text{H}_5)$	1.0883	1.0903	1.0705
$\theta(\text{C}_1\text{C}_2\text{C}_3)$	153.51	153.50	153.54
$\theta(\text{C}_2\text{C}_3\text{H}_5)$	145.61	145.65	145.25
A_e	32145.8	31867.3	32967.0
B_e	1846.5	1831.6	1885.5
C_e	1746.2	1732.1	1783.5
μ	3.765	3.636	3.910

Harmonic Frequencies and Infrared Intensities
at the Level of CCSD(T)/cc-pVDZ

mode	symmetry	freq	intensity
ω_1	a ₁	3316.0	4.3
ω_2	a ₁	1964.7	94.4
ω_3	a ₁	1603.4	106.8
ω_4	a ₁	1189.0	22.1
ω_5	a ₁	941.7	15.3
ω_6	a ₁	565.2	2.1
ω_7	a ₂	765.3	0.0
ω_8	b ₁	579.5	56.5
ω_9	b ₁	248.3	0.3
ω_{10}	b ₁	200.9	10.1
ω_{11}	b ₂	3271.1	8.9
ω_{12}	b ₂	1005.7	18.8
ω_{13}	b ₂	806.0	1.3
ω_{14}	b ₂	521.8	0.2
ω_{15}	b ₂	157.9	1.9

^a Bond lengths (Å), bond angles (degrees; (+/-) notions representing clockwise/counterclockwise directions from the first atoms), dipole moments (Debye), harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol), and rotational constants (MHz). Atom numbering is shown in Figure 1.

has been generated in an electrical discharge through diacetylene and characterized by microwave spectroscopy.⁵⁷

Other Isomers. A large number of $\text{C}_4\text{H}_2\text{S}$ isomers fall within an energy range of 40–50 kcal/mol above butatrienethione (**6**). The intent of this initial survey is not to provide a detailed structural analysis of each of these isomers. A few general comments are warranted, and interested readers may find further details in the Supporting Information. CCSD(T)/cc-pVDZ calculations are expected to provide a reliable picture of the higher energy isomers on the potential energy surface. 2,5-Didehydrothiophene (**12**) represents a difficult challenge for computation. Enormous effort has been expended in the pursuit of computational studies of the *m*-benzynes and *p*-benzynes diradicals,^{13,31} which pose similar problems. These studies establish that unrestricted coupled cluster methods, and certain density function methods (although not the widely used B3LYP functional—see below), provide satisfactory structures, energies, and vibrational frequencies. A detailed study of the isomeric didehydrothiophenes^{16,58–62} will be deferred to the future.

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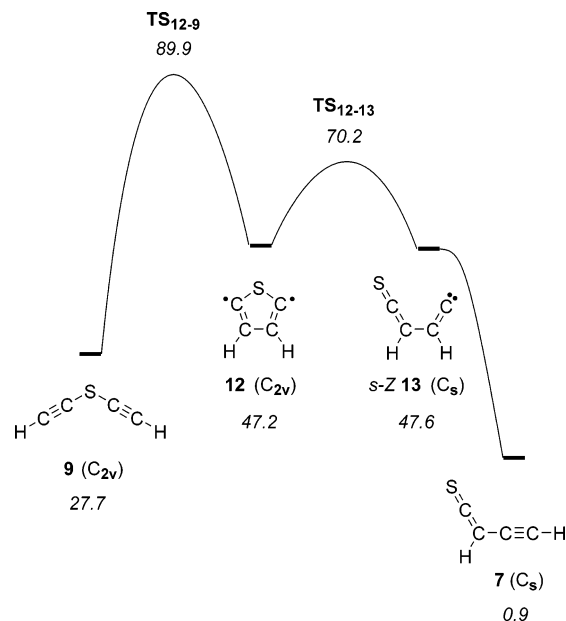
TABLE 7. Energies (kcal/mol) of Stationary Structures on the C₄H₂S Potential Energy Surface

	state	CCSD/cc-pVDZ			CCSD(T)/cc-pVDZ			CCSD(T)/cc-pVTZ		
		absolute ^a	ZPVE	relative	absolute ^a	ZPVE	relative	absolute ^a	ZPVE ^b	relative
6	¹ A ₁	0.00	25.03	0.00	0.00	24.51	0.00	0.00	24.51	0.00
7	¹ A'	-1.82	25.10	-1.76	0.89	24.55	0.94	1.64	24.55	1.68
8	¹ A ₁	9.86	23.46	8.28	13.41	22.84	11.74	10.81	22.84	9.14
9	¹ A'	23.82	24.00	22.78	27.70	23.40	26.60	25.29	23.40	24.19
10	¹ A ₁	30.12	24.46	29.55	32.81	23.80	32.11	30.44	23.80	29.74
11	¹ A'	27.46	25.10	27.53	30.28	24.50	30.27	30.60	24.50	30.59
12		42.94			47.19					
TS₁₂₋₉		85.91			89.94					
TS₁₂₋₁₃		69.00			70.17					
<i>s-Z-13</i>	¹ A'	43.94	23.72	42.63	47.61	23.06	46.16			
<i>s-E-13</i>	¹ A'	42.32	24.04	41.32	46.17	23.54	45.20	50.92	23.54	49.95
<i>s-Z-14</i>	³ A''	37.18	23.56	35.70	43.68	23.35	42.53			
<i>s-E-14</i>	³ A''	37.74	23.05	35.76	44.39	22.80	42.68			
<i>s-Z-15</i>	³ A''	48.90	24.16	48.03	55.26	23.89	54.63			
<i>s-E-15</i>	³ A''	51.12	23.95	50.03	57.77	23.64	56.91			
16	¹ A	39.24	25.56	39.77	40.18	25.07	40.74			
<i>s-Z-17</i>	³ A''	42.07	24.47	41.50	48.01	24.22	47.72			
<i>s-E-17</i>	³ A''	42.68	24.21	41.86	48.80	23.94	48.24			
18	¹ A'	44.88	24.68	44.53	46.15	24.19	45.83	48.64	24.19	48.32
19	¹ A'	49.65	25.06	49.67	48.77	24.71	48.97	52.91	24.71	53.11
20^c	¹ A ₁	44.83	26.01	45.80	44.48	25.55	45.52	48.04	25.55	49.09

^a Absolute energies (hartree) of **6**: -550.729333, -550.767103, and -551.052473, in the order of increasing level of theory. ^b Zero-point vibrational energies calculated at CCSD(T)/cc-pVDZ. ^c Bicyclic thione, which is not included in text. See the Supporting Information and ref 39 for the equilibrium structure.

B. Relative Energies. Nineteen minima on the C₄H₂S PES were structurally optimized in the series of coupled cluster calculations. Absolute and relative energies are given in Table 7. In terms of relative energies, the C₄H₂S isomers partition into three groups. The first group includes the low-energy isomers: cumulene (**6**), ethynylthioketene (**7**), and butadiynylthiol (**8**). The second group includes diethynyl sulfide (**9**), which is ca. 25 kcal/mol above **6**, and the three-membered cyclic isomers, ethynylthiirene (**10**) and cyclopropenylidenemethanthione (**11**), which lie ca. 30 kcal/mol above **6**. The third group includes C₄H₂S minima with relative energies between 40 and 50 kcal/mol above cumulene (**6**). We did not anticipate that diethynyl sulfide (**9**) would be so high in energy, inasmuch as it is the only isomer in the entire series that can be synthesized and isolated under ordinary laboratory conditions. The high relative energy of **9** makes for some interesting comparisons—for example, thiirene **10** is only 5 kcal/mol higher in energy than **9**. On the basis of earlier studies, we anticipated that the cycloaromatization reaction of **9** to afford 2,5-didehydrothiophene (**12**) would be endothermic by ca. 20 kcal/mol.¹⁴ Because our intuition concerning the relative energy of **9** was faulty, we did not anticipate that 2,5-didehydrothiophene (**12**) would be among the highest energy isomers in the study.

The relative energies (CCSD(T)/cc-pVTZ) for cumulene (**6**), ethynylthioketene (**7**), butadiynylthiol (**8**), and cyclopropenethioketene (**11**) exhibit reasonably good agreement with the MP2/6-31G* values reported by Teles et al.¹⁶ It is sobering to see the poor performance of DFT calculations in assessing the relative energies of these

SCHEME 2^a

^a CCSD(T)/cc-pVDZ energy (kcal/mol), relative to butatrienethione (**6**), in italics.

C₄H₂S isomers. Relative energies at the B3LYP/6-31G* level diverge from those at the CCSD(T)/cc-pVTZ level by as much as 15 kcal/mol for isomers **6**–**11**.⁴² As has been noted previously, the DFT calculations err in the differential stabilization of cumulene structures and destabilization of alkyne structures.^{18,24,25}

C. Rearrangement Pathways. The rearrangements of 2,5-didehydrothiophene (**12**) are of considerable interest (Scheme 2). Ring opening of singlet diradical **12** to diethynyl sulfide (**9**) is the microscopic reverse of the cycloaromatization reaction of **9** to **12**, which has been studied experimentally (in substituted systems)¹⁵ and computationally.¹⁴ We were struck by the fact that

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diethynyl sulfide (**9**) lies significantly higher in energy than several other C_4H_2S isomers, which led us to investigate whether alternative, low-energy rearrangement pathways might exist for the thiophene diradical (**12**). Our findings concerning the “retro-Bergman” ring-opening reaction of 2,5-didehydrothiophene (**12**) to diethynyl sulfide (**9**), $\Delta E = -19.5$ kcal/mol, $\Delta E^\ddagger = 42.7$ kcal/mol, are in reasonable agreement with those presented earlier.¹⁴ An alternative mode of ring opening, involving C–S bond cleavage in 2,5-didehydrothiophene (**12**) to afford the *s*-*Z*-thioetene vinylidene (**13**), occurs with a much lower barrier, $\Delta E^\ddagger = 23$ kcal/mol (Scheme 2). The *s*-*Z* and *s*-*E* vinylidenes (**13**) exist in a very flat region of the potential energy surface and the computational results depend critically on the theoretical methods employed. At our best level of theory, CCSD(T)/cc-pVTZ, *s*-*E*-vinylidene (*s*-*E*-**13**) is computed to be a true energy minimum on the singlet potential energy surface, while *s*-*Z*-vinylidene (*s*-*Z*-**13**) is computed to rearrange without barrier to ethynylthioetene (**7**). The existence of an alternate ring-opening pathway for thiophen-2,5-diyl (**12**) represents an important feature of the C_4H_2S potential energy surface. Specifically, thiophen-2,5-diyl (**12**) formed upon thermal cyclization of diethynyl sulfide (**9**) (activation barrier ca. 65 kcal/mol) will possess sufficient energy to undergo subsequent ring opening via C–S bond cleavage (activation barrier 20 kcal/mol). Unless diradical **12** is trapped efficiently, ring opening may ensue. This finding may be a factor in explaining the low yield of thiophene-derived trapping products obtained upon irradiation of substituted dialkynyl sulfides in solution.¹⁵

Another rearrangement manifold of interest to us involves the formally antiaromatic thiirene **10**. Scheme 3 depicts the rearrangements linking thiirene **10** with other C_4H_2S isomers of similar or lower energy (**7**, **8**, and **9**). Thiirene, thioetene, and the thia-version of the Wolff rearrangement have been studied experimentally^{63,64} and computationally.^{65–70} Calculations predict a triplet electronic ground state for thioformyl carbene,^{65,66,68} but only one triplet thiocarbonyl carbene has been observed by ESR spectroscopy (and that assignment has been questioned).⁷¹ Our calculations for thiocarbonyl carbenes **14** and **15** indeed predict that each triplet carbene exists as a pair of *s*-*E*/*s*-*Z* conformational isomers. The singlet carbenes presumably partition between cyclization to afford thiirene **10**, [1,2]-shift to afford the thioetene **7** (Wolff rearrangement), or [1,2]-shift to afford alkynyl sulfides (**8** or **9**). Viable photochemical precursors to carbenes **14** and **15** are readily envisioned, and we hope to report experimental studies of these species in due course.

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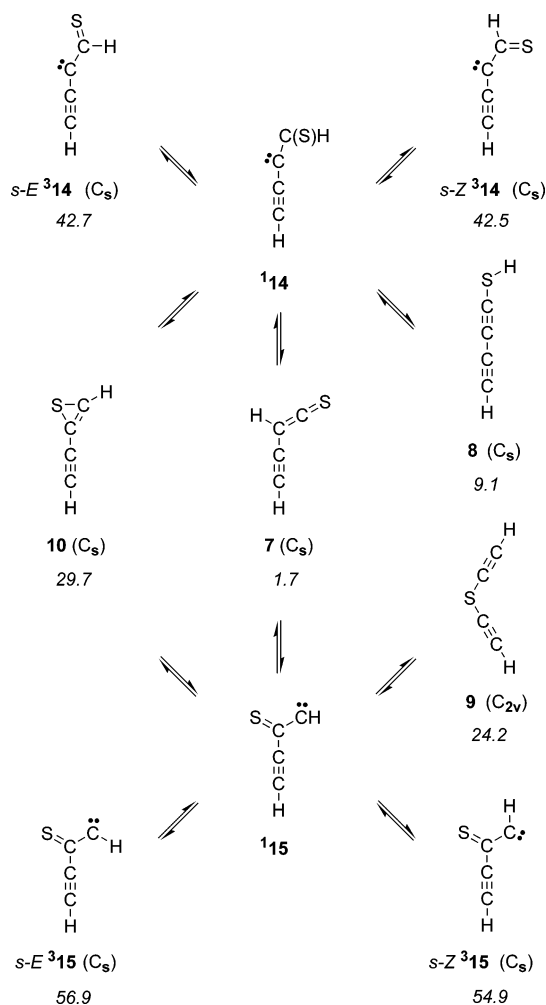
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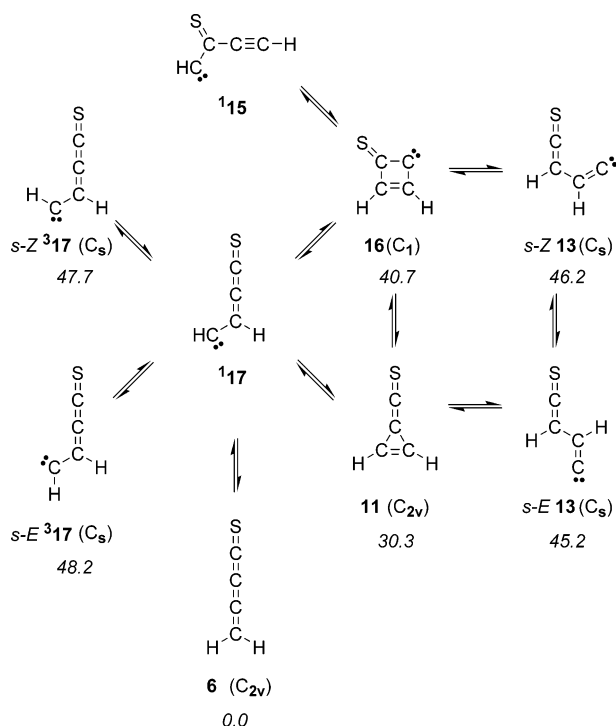
SCHEME 3^a

^a CCSD(T)/cc-pVDZ energy (kcal/mol, ZPVE corrected), relative to butatrienethione (**6**), in italics.

A third rearrangement manifold involves some higher energy isomers that may be considered to be derived from cyclopropene thioetene **11** (Scheme 4). From a mechanistic point of view, the relatively long C_2 – C_3 single bond (1.465 Å) in the equilibrium structure of **11** hints at the involvement of other structural isomers that lie moderately close in energy. Indeed, variation of the $\sigma(C_2$ – $C_3)$ distance of **11** allows three structural isomers to be engaged within 20 kcal/mol above **11** (Scheme 4). Singlet cyclobutenylidenethione (**16**) lies 10.5 kcal/mol above **11** and undergoes ring-contraction to the cyclic thioetene **11** with an activation energy of 16.6 kcal/mol. Cyclobutenylidenethione (**16**) exists as a puckered ring (C_1 symmetry), which interconverts with its enantiomer via a planar transition state.⁴² This behavior parallels the conformational properties of the unsubstituted cyclobutenylidene.^{72,73} The deviation from planarity in carbene **16** enables the filled π -orbital of the alkene to interact with the vacant orbital at the divalent carbon, and this stabilization places the singlet state of **16** substantially below the triplet in energy (ca. 13 kcal/mol).⁴² Lying 15

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SCHEME 4^a

^a CCSD(T)/cc-pVDZ energy (kcal/mol, ZPVE corrected), relative to butatrienethione (**6**), in italics.

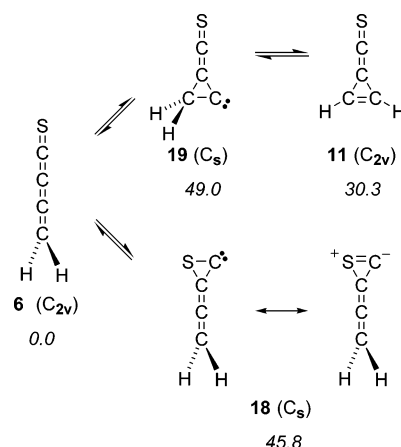
kcal/mol above **11**, the aforementioned *s-E*-vinylidene (*s-E*-**13**) inserts into the $\sigma(\text{C}-\text{H})$ bond to form **11** with an activation energy of ca. 22 kcal/mol. Last, rupture of the relatively long C₂–C₃ single bond in **11** affords singlet carbene **17**. This vinyl carbene derivative is computed to display a triplet electronic ground state, which will exist as a pair of planar conformational isomers.

Finally, Scheme 5 depicts isomerizations derived from out-of-plane deformations in the heavy-atom backbone of butatrienethione (**6**). By analogy with the known photochemical automerization of H₂C=C=C:⁷⁴ the cyclic isomers **18** and **19** may be accessible via deformation along the heavy-atom framework in electronic excited states of butatrienethione (**6**).

Summary

Six C₄H₂S isomers lie within 30 kcal/mol above butatrienethione (**6**), the apparent global minimum on the

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SCHEME 5^a

^a CCSD(T)/cc-pVDZ energy (kcal/mol, ZPVE corrected), relative to butatrienethione (**6**), in italics.

potential energy surface (Table 7). The equilibrium structural data for these isomers will facilitate their experimental detection and characterization. The surprisingly high relative energy of diethynyl sulfide (**9**), coupled with the very high barrier for thermal cycloaromatization of **9** to thiophene-2,5-diyl (**12**) and the modest barrier for C–S bond cleavage in thiophene-2,5-diyl (**12**), provide an important perspective concerning the thermal rearrangements of dialkynyl sulfides.

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Supporting Information Available: Cartesian coordinates, computed harmonic vibrational frequencies, and IR intensities, as well as relative energies of isomers computed using density functional methods (B3LYP/6-31G*). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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