grateful to Professor M. Ōki of our university for the permission to use DNMR3[34] and LSQM2 programs and for valuable discussions, Professor N. Inamoto of our university for the permission to use the spinning band distillation apparatus, Dr. H. Hirota of our university for the measurements of the high-resolution mass spectra, Professor S. Nishimura of Tokyo University of Agriculture and Technology for his guidance in the catalytic hydrogenation, and The Ministry of Education for the purchase of a Jeol-FX90Q spectrometer. We are also indebted to the referees for valuable suggestions.

Registry No. **7**, 78705-55-2; **8**, 78705-56-3; **9**, 80639-04-9; **10**, 72036-76-1; **11**, 72036-78-3; **14**, 62859-46-5; **15**, 88131-16-2; **16**, 88131-17-3; **17**, 92-51-3.

The Microwave Spectrum, Structure, and Electric Dipole Moment of 1,2,4-Trithiolane

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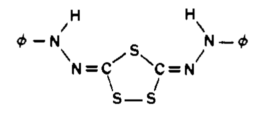
Abstract: The rotational spectra of eight isotopic species of 1,2,4-trithiolane (the sulfur analogue of ethylene ozonide) were assigned and a structure determined by least-squares fitting of the moments of inertia. The molecule has a disulfide-twist half-chair conformation with C_2 symmetry. The structural parameters for the ring atoms are the following: r(S–S) = 2.044 (2) Å, $r(\text{C–S}_s)$ = 1.829 (2) Å, $r(\text{C–S}_d)$ = 1.808 (2) Å, ∠C–S–S = 93.8 (1)°, ∠C–S–C = 99.4 (1)°, ∠S–C–S = 110.0 (1)°, τ(C–S–S–C) = 52.8 (3)°, τ(S–S–C–S) = 46.4 (4)°, and τ(C–S–C–S) = 20.2 (1.0)°. Vibrational satellites (v = 1–4) from an antisymmetric mode with a fundamental frequency of 82 ± 10 cm^{-1} were observed. A dipole moment of 0.465 (4) D was determined. No effects of fluxional behavior were observed since all the measurements were on vibrational states considerably below the estimated barrier to pseudorotation of 3–6 kcal mol^{-1}.

The structure and conformational properties of disulfides and cyclic disulfides have attracted interest because of the bearing they have on the structure of cystine residues in proteins. Scheraga and co-workers[1] have used vibrational and crystallographic data along with theoretical calculations to obtain insight on changes in properties when the dihedral angle, τ(CS–SC), is varied. Bock and co-workers have investigated the correlation between the photoelectron spectra and dihedral angle[2] and provided an especially extensive study of the fluxionality properties of 1,2-dithiolane[2c] ($\overline{\text{CH}_2\text{–CH}_2\text{–CH}_2\text{–S–S}}$) and its radical cation using photoelectron spectroscopy (PES), electron-spin resonance, and ab initio calculations. On the other hand, there has been little gas-phase structural data from microwave (MW) or electron-diffraction studies of cyclic disulfides.

As an outgrowth of our interest in ozonide structures, we undertook a MW study of 1,2,4-trithiolane, $\overline{\text{CH}_2\text{–S–S–CH}_2\text{–S}}$ (sometimes called trithio ozonide), which is the sulfur analogue of ethylene ozonide and the prototype species in the 1,2,4-trithiolane series. Until Morita and Kobayashi[3] provided a reliable synthesis and several bona fide properties in 1967, there was little previous discussion of it in the literature.[4] On the basis of its vibrational and PES spectra,[5] C_2 symmetry has been deduced and a CS–SC dihedral angle of about 50° was estimated. Molecular mechanics calculations[6] have also indicated a twisted conformer with a dihedral angle of about 46° while a flexible conformation and a low barrier to pseudorotation (≤6 kcal mol^{-1}) have been inferred from its proton NMR spectrum[7] which remains a singlet at temperatures down to −117 °C.

More detailed structures are available for three substituted 1,2,4-trithiolanes containing exo-carbon double bonds.[8-10] Species



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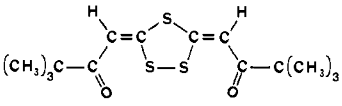

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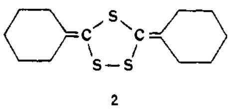

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1 and **2** are twisted about the disulfide linkage (τ(CS–SC) $\approx$ 42°) while a sulfide envelope conformer was found for **3** (τ(CS–SC) $\approx$ 0°). This paper reports the conformation and detailed structural parameters for the simplest member of this series, 1,2,4-trithiolane.

Experimental Section

Synthesis. The synthesis of 1,2,4-trithiolane (hereafter trithiolane) followed a scaled-down procedure reported by Morita and Kobayashi.[3] CH_2Cl_2 (25 mL) was added to 25 mL of aqueous $Na_2S_{2.5}$ ($\sim$1.25 M). After about 1 day, the nonaqueous layer was separated and the more volatile CH_2Cl_2 was removed by using a rotary evaporator. The crude trithiolane was purified by low-pressure distillation ($\sim$0.5 torr at 115 °C; 10% yield). The product was confirmed by mass spectroscopy and NMR.[3] Its vapor pressure at room temperature was less than 0.25 torr, and the material did not easily transfer on a vacuum line.

Deuterated Species. A sample of 3,5-dideuterio-1,2,4-trithiolane was prepared similarly by using 25 mL of 98% $CHDCl_2$. The latter was prepared by reducing $CDCl_3$ (99.6% D) with tributyltin hydride.[11,12] The chloroform and methylene chloride were separated by fractional distillation. A purity of 98% was determined by VPC. Mass spectroscopy indicated the deuterium content was 97%. A sample of trithiolane containing the normal, d_1, and *3,5-d_2* species was also synthesized by using 12 mL of CH_2Cl_2 and 13 mL of $CHDCl_2$. The synthesis of 1,2,4-trithiolane-*3,3-d_2* employed 1.5 mL of CH_2Cl_2 and 1.5 mL of CD_2Cl_2. The yield was low and only a few spectroscopic measurements could be performed before the sample was depleted.

Spectrometer. Spectra were recorded with a HP 8460A spectrometer between 18 and 40 GHz. Both Stark modulation and radio frequency–microwave double resonance (RFMWDR) were employed.[13] Weak transitions were measured by using a microcomputer system that permitted signal averaging. It was based on a Motorola M6800 microcomputer system (Southwest Technical Products Co.) with 40 kbytes of memory and home-built analog–digital interfaces.

Spectra. The spectrum was sparse and exhibited weak, sharp transitions. Approximately 50 μ_a-dipole R-branch transitions were assigned up to $J = 9 \rightarrow 10$ Hz. A selection of these transitions is listed in Table I. A centrifugal distortion fit of all the transitions gave agreement with a standard deviation of 0.02 MHz,[14] with a maximum correction of only 0.7 MHz for a $7_{7,0} \rightarrow 8_{7,1}$ transition.

The presence of intensity alternations (due to nuclear spin statistics in the ratio of 5/3) was evident in transitions arising from symmetric vs. antisymmetric levels. From this observation and the moments of inertia which indicate a nonplanar heavy-atom framework, it can be concluded that the molecule belongs to the C_2 rather than the C_{2v} point group.

The trithiolane sample prepared by using approximately equal amounts of CH_2Cl_2 and $CHDCl_2$ gave transitions of the normal species along with species monodueterated at both an equatorial and an axial site. The monodeuterated species possess C_1 symmetry and neither exhibited alternating nuclear spin statistics. Seventeen R-branch transitions were assigned for each species.

The spectra of the three possible 3,5-dideuterio-1,2,4-trithiolane species were measured in the sample prepared by using only $CHDCl_2$. The spectrum of the [3-$^2H_{eq}$,5-$^2H_{ax}$]-trithiolane did not show effects of nuclear spin statistics while the transitions of the 3-$^2H_{eq}$,5-$^2H_{eq}$ or 3-$^2H_{ax}$,5-$^2H_{ax}$ species exhibited the expected statistical weight ratio of 15/21. Between 9 and 13 transitions were measured for the three dideuterated species and rigid rotor spectral constants were calculated. The quality of the fits was comparable for all of the deuterated species (deviations $\leq$0.2 MHz).

A bootstrap procedure using the data from the normal and deuterated species along with several structural assumptions was employed to obtain good models[15] to help assign spectra of the $^{34}S_d$ and $^{34}S_s$ species[16] in natural abundance. Twenty-six transitions for the $^{34}S_d$ species were assigned and the absence of spin statistics was verified. Eight transitions of the $^{34}S_s$ species exhibiting the proper spin statistics were assigned. The spectral fits were better than ±0.1 MHz. The derived rotational constants indicated that the A constant for the normal and the $^{34}S_s$ species as well as the planar second moments $P_{bb} = \sum mb^2$ and $P_{cc} = \sum mc^2$ were identical within experimental error, as expected for isotopic substitution on the C_2 symmetry axis. Relative intensity measurements for this species and the $^{34}S_d$ species at both 21 and -20 °C gave values of 0.05 (1) and 0.08 (1), respectively, for the fractional population of the two species.

Table I. Assigned Microwave Transitions of 1,2,4-Trithiolane in the Ground Vibrational State (v = 0)

transition	frequency, MHz	obsd – calcd,[a] MHz
4(1,3) ← 3(1,2)	18 128.27	0.04
4(3,1) ← 3(3,0)	18 346.52	0.08
4(2,2) ← 3(2,1)	19 179.72	0.09
5(1,5) ← 4(1,4)	18 467.92	0.05
5(0,5) ← 4(0,4)	18 527.44	0.04
5(2,4) ← 4(2,3)	20 876.50	0.03
5(1,4) ← 4(1,3)	21 661.96	-0.01
5(3,3) ← 4(3,2)	22 215.25	0.03
5(4,2) ← 4(4,1)	22 440.62	0.02
5(4,1) ← 4(4,0)	22 596.33	-0.01
5(3,2) ← 4(3,1)	23 569.51	0.07
5(2,3) ← 4(2,2)	23 851.90	0.03
6(1,6) ← 5(1,5)	21 907.50	0.01
6(0,6) ← 5(0,5)	21 925.46	0.01
6(2,5) ← 5(2,4)	24 531.33	0.00
6(1,5) ← 5(1,4)	24 933.29	0.00
6(5,2) ← 5(5,1)	26 933.60	-0.09
6(5,1) ← 5(5,0)	26 972.94	-0.13
6(4,3) ← 5(4,2)	27 027.47	-0.04
6(4,2) ← 5(4,1)	27 623.22	-0.01
6(2,4) ← 5(2,3)	27 999.56	-0.06
6(3,3) ← 5(3,2)	28 795.85	-0.00
7(1,7) ← 6(1,6)	25 333.87	-0.03
7(0,7) ← 6(0,6)	25 338.88	-0.03
7(2,6) ← 6(2,5)	28 060.15	-0.07
7(1,6) ← 6(1,5)	28 220.63	-0.09
7(3,5) ← 6(3,4)	30 351.13	-0.11
7(6,2) ← 6(6,1)	31 393.70	-0.28
7(6,1) ← 6(6,0)	31 402.47	-0.37
7(4,4) ← 6(4,3)	31 511.48	-0.15
7(2,5) ← 6(2,4)	31 557.50	-0.21
7(5,3) ← 6(5,2)	31 608.98	-0.20
7(5,2) ← 6(5,1)	31 803.87	-0.22
7(4,3) ← 6(4,2)	32 988.19	-0.10
7(3,4) ← 6(3,3)	33 642.75	-0.15

[a] Calculated with the constants in Table II and a rigid rotor model.

The rigid rotor rotational constants for all the assigned isotopic species are listed in Table II. The full set of observed transition frequencies of the normal and isotopic species is available as supplemental material.

Vibrational Satellites. The twisted form of trithiolane should have two low-frequency ring vibrational modes dependent on the barriers to pseudorotation and inversion.[17] One mode will be symmetric and the other antisymmetric with respect to the C_2 axis of the molecule. Microwave transitions were observed from four excited states associated with the antisymmetric state (v_{as} = 1 to 4). Transitions from excited states of the symmetric mode were not identified. The progression in the antisymmetric states was evident from their regular change in rotational constants and the behavior of the nuclear spin statistical weight factors. The transitions from states with V_{as} = 2, 4 had the same spin weights as the ground state while they reversed for v_{as} = 1, 3. The energy difference between the v = 0 and v_{as} = 1 states was estimated to be 82 ± 10 cm^{-1} from relative intensity measurements at room temperature. The rotational constants derived for the four excited vibrational states are listed in Table III. The transition frequencies are available as supplementary material. The regular progression in the vibrational satellite series as well as the modest centrifugal distortion corrections for the ground state denote the absence of unusually large amplitude vibrational effects for the states that were observed.

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(14) The constants obtained from the centrifugal distortion fit with use of Watson's representation I were (in MHz) A = 3819.353 (12), B = 2621.131 (2), C = 1710.615 (2) and (in kHz) Δ_J = 0.27 (1), Δ_{JK} = 0.33 (5), Δ_K = 0.35 (40), δ_J = 0.07 (1), δ_K = 0.40 (1). The fitting program was obtained from Prof. R. H. Schwendeman.

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Table II. Rotational Constants of Isotopically Substituted Species of 1,2,4-Trithiolane

species	*A*, MHz	*B*, MHz	*C*, MHz	κ^a	no. of transitions^c
normal	3819.367 (24)^b	2621.105 (3)	1710.601 (3)	−0.13646	59
$^2H_{eq}$	3679.820 (17)	2609.615 (3)	1677.389 (3)	−0.06891	17
$^2H_{ax}$	3701.014 (19)	2587.948 (3)	1698.298 (3)	−0.11156	18
$3\text{-}^2H_{eq},5\text{-}^2H_{ax}$	3567.507 (24)	2577.335 (4)	1665.346 (4)	−0.04110	12
$3\text{-}^2H_{eq},5\text{-}^2H_{eq}$	3544.577 (17)	2600.246 (3)	1645.066 (3)	+0.00571	9
$3\text{-}^2H_{ax},5\text{-}^2H_{ax}$	3587.536 (46)	2556.514 (7)	1685.510 (6)	−0.08413	13
$^{34}S_s$	3819.393 (81)	2545.556 (7)	1678.096 (4)	−0.18978	8
$^{34}S_d$	3763.125 (22)	2586.589 (3)	1686.475 (2)	−0.13311	26

^{a} κ is the asymmetry parameter: $(2A - B + C)/(B - C)$. ^{b} The uncertainty (in the last digits) represents one standard deviation of the fit. ^{c} The number of transitions assigned.

Table III. Rotational Constants (MHz) for the Ground State and the Excited Vibrational State Series Asymmetric to the C_2 Axis

ground state, *v*	*A*	*B*	*C*
0	3819.37 (2)^a	2621.11 (3)	1710.60 (3)
1^b	3816.53 (2)	2622.78 (3)	1709.21 (3)
2	3813.86 (2)	2623.85 (3)	1707.99 (3)
3	3811.58 (3)	2624.99 (4)	1706.78 (3)
4	3809.39 (9)	2626.01 (2)	1705.58 (3)

^{a} The uncertainty (in the last digits) represents one standard deviation of the fit. ^{b} $E_{v=1} - E_{v=0} = 82 \pm 10$ cm^{-1} from relative intensity measurements.

Table IV. Principal Axis r_0 Coordinates in Å for Trithiolane^a

atom	a_0	b_0	c_0
S_s	−1.707 (1)^b	0.0	0.0
S_d	1.092 (1)	±0.979 (1)	±0.293 (1)
C	−0.524 (2)	±1.323 (3)	±0.441 (1)
H_{eq}	−0.881 (1)	±2.256 (1)	±0.010 (1)
H_{ax}	−0.428 (3)	±1.385 (1)	±1.526 (1)

^{a} Determined from least-squares fitting of isotopic data (Table II) and fixing C–H_{eq} at 1.088 Å.[16] ^{b} Uncertainties represent one standard deviation in the r_0 fit.

Dipole Moment. The Stark splittings were measured as a function of electric field for the following transitions: $7_{5,3} \rightarrow 8_{5,4}$ ($M = 1$), $7_{5,2} \rightarrow 8_{5,3}$ ($M = 1$), and $6_{4,2} \rightarrow 7_{4,3}$ ($M = 1, 2, 3$). The observed and calculated values of $\Delta\nu/E^2$ agreed to ±1% and yielded a dipole moment of $\mu_a = \mu_t = 0.465$ (4) D. The Stark effect data are available as supplementary material. Methanol was used to calibrate the spectrometer.[18]

Structure Determination. The microwave spectral data for trithiolane already presented have shown that the molecule belongs to the C_2 point group. Thirteen nonzero atomic coordinates (or 11 internal structural parameters) must be determined to completely define the structure. They can be evaluated from the moments of inertia of the normal species and the four single-substituted species (D_{ax}, D_{eq}, $^{34}S_s$, $^{34}S_d$).[19] With use of least-squares fitting methods, these data, along with the additional moments of inertia from the three dideuterated species, can be simultaneously fit to determine the so called r_0 coordinates and r_0 structure.[15]

It was found by this procedure that all of the r_0 coordinates could be determined with little ambiguity except for the *c* coordinate of H_{eq}. This coordinate is <0.1 Å, and both its magnitude and sign could be varied without altering the quality of the least-squares fit significantly ($\Delta I_{rms} \leq 0.006$ amu Å^2). Consequently, it was decided to set $d(C\text{–}H_{eq}) = 1.088$ Å as an additional constraint in the fitting process. This resulted in the r_0 coordinates listed in Table IV and the structural parameters in Table V. The r_s coordinates determined by using Kraitchman's equations[20] and the single-substitution data are within ±0.005 Å of the values in Table IV except for $c_{H_{eq}}$ where a value of |0.097| is obtained.

The structural parameters in Table V do not vary greatly with the calculation procedure except for parameters that involve H_{eq} (e.g., C–H_{eq} and $\angle H_{eq}\text{–C–}H_{ax}$). Apart from these latter parameters, the r_0 values in Table V are probably close to the so called r_z or average structure.[21] Uncertainty limits of ±0.01 Å and ±0.5° should be sufficient to encompass the r_z parameters. The parameters associated with H_{eq} are less well determined and an uncertainty of ±0.03 Å for $d(C\text{–}H_{eq})$ and ±3° for related angles is estimated. The structure is illustrated in Figures 1 and 2.[22]

Table V. Structural Parameters of 1,2,4-Trithiolane^a

bond lengths, Å		bond angle, deg		dihedral angle, deg	
S–S	2.044 (2)	C–S–S	93.8 (1)	C–S–S–C	52.8 (3)
C–S_s	1.829 (2)	C–S–C	99.4 (1)	S–S–C–S	46.4 (4)
C–S_d	1.808 (2)	S–C–S	110.0 (1)	C–S–C–S	20.2 (10)
C–H_{eq}	1.088^b	H–C–H	112.0 (2)		
C–H_{ax}	1.091 (1)	S_s–C–H_{eq}	108.2 (2)		
		S_d–C–H_{eq}	107.2 (2)		
		S_s–C–H_{ax}	109.8 (2)		
		S_d–C–H_{ax}	109.6 (2)		

^{a} Calculated from r_0 coordinates in Table IV. ^{b} Fixed at this value during the least-squares fitting analysis.

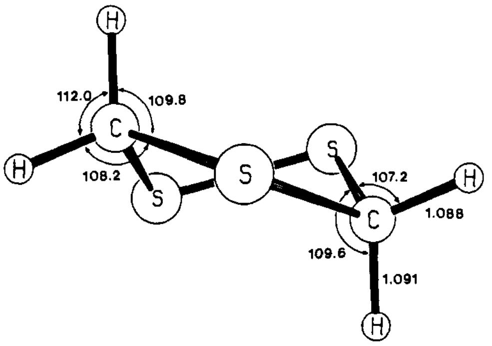

Figure 1. The structure of 1,2,4-trithiolane projected on the *bc* principal axes plane.

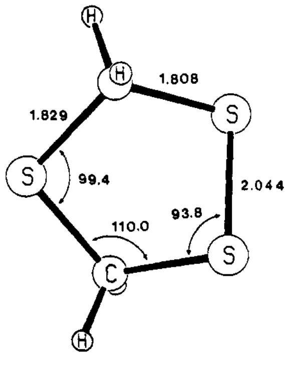

Figure 2. The structure of 1,2,4-trithiolane projected on the *ab* principal axes plane.

Structure and Discussion

One of the noteworthy findings has been the absence of vibrational perturbations from ring fluxionality. The ground and excited vibrational states which were observed are apparently well

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(19) The moments of inertia were determined from the rotational constants in Table II by using the relationship $B \cdot I_B = 505379.05$ MHz·amu·Å^2.

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(22) The figures were drawn by using the program ORTEP. C. K. Johnson, ORTEP. Oak Ridge National Laboratory Report No. ORNL-3794, 1965.

below the barriers to ring pseudorotation or inversion and so the MW spectrum "behaves" like a typical, fairly rigid species. It is difficult to draw any firm inferences about the barriers associated with the ring motion modes except to estimate a lower limit of about 500 cm^{-1} (1.5 kcal mol^{-1}) for the pseudorotation barrier based on the observed regularity in vibrational states up to $v_{as} = 4$. This can be compared with values of 3.1 kcal estimated for 1,2,4-trithiolane[6] and the upper limit of 6 kcal estimated for 3,5-dimethyl-1,2,4-trithiolane.[7] These estimated barrier limits, while consistent with a relatively rigid species as viewed by MW spectroscopy, are presumably still low enough to lead to the absence of any geminal H,H coupling (i.e., fluxional behavior) on the NMR time scale.[23]

There has been an interest in correlating the dihedral angle about disulfide bonds (τ(CS–SC)) with the S–S bond length[1b,24] and spectral features such as PES transitions[2,5] and S–S stretching frequencies.[1] In this respect, the PES results and τ(CS–SC) = 53° of trithiolane correlate reasonably well with related examples.[5a] However, the S–S bond length in trithiolane is projected to be about 2.06–2.08 Å on the basis of the suggestion that this bond lengthens when τ(CS–SC) decreases from the nominal 90° found in unstrained species.[1b,24] However, the observed S–S bond of 2.04 (1) Å is nearly identical with the results of 2.03–2.04 Å found in $(CH_3)_2S_2$ where τ(CS–SC) is about 85°.[25,26]

Other structural parameters in trithiolane viz d(C–S), ∠CSC, and the nearly tetrahedral ∠SCS are also close to values in unstrained compounds, for example, $(CH_3)_2S$ and $(CH_3)_2S_2$.[25,27] Only ∠CSS which is 9° smaller than in $(CH_3)_2S_2$ shows any marked perturbation upon incorporation into the ring. It is also noteworthy that the three ring dihedral angles are all several degrees larger than their counterparts in ethylene ozonide where τ(CO–OC) = 49.5°, τ(OO–CO) = 40.8°, and τ(CO–CO) = 16.2°.[28] It is apparent that trithiolane readily twists in the C_2 minimum energy conformation without inducing much strain in most structural parameters except for ∠CSS.

1,2,4-Trithiolane does differ somewhat from the other three trithiolanes noted in the introduction. The CS–SC dihedral angle in **1** and **2** is 41–42° and in **3** it is ~0°. In the latter, the sulfide envelope conformer is probably stabilized by S···O interactions. Also, the S–S bond distances are lengthened to 2.07 Å in **1** and **2** and to 2.10 Å in **3** while the C–S bonds are shortened by ~0.04–0.06 Å from the more typical values of 1.80–1.82 Å for a nominal C–S single bond.[25-27] Of course, the C–S bond distances in these compounds are probably affected by the adjacent double bonds to carbon (exo) which can interact with the trithiolane ring.

There have been two calculations on trithiolane with use of molecular mechanics[6] and the CNDO method.[5a] The MM study calculated the relative energies of several conformers ($C_2 < C_1 < C_s < C_{2v}$) and estimated τ(CS–SC) = 45.9° for the disulfide twist or C_2 half-chair conformer. The lowest C_1 conformer, an S_d envelope, was estimated to be 0.3 kcal higher than the C_2 form. This would give it an intensity similar to the $v = 1$ and $v = 2$ vibrational satellites of the C_2 form if it had the same dipole moment. No evidence for it was found in the microwave regions that were covered. Nevertheless, the possibility of another low-lying conformer populated at room temperature cannot be definitively eliminated since a small decrease (~0.2 D) in the spectrally active dipole components would drastically reduce transition intensities and modulation properties.

The CNDO calculation was primarily directed at assigning the PE ionization energies and estimating the dihedral angle (~50°) from the splitting of the two lowest transitions.[5a] Some other geometric parameters were also estimated and the ring-bond distances and angles were within ±0.02 Å and ±3.5° of the MW values. This study proposed a qualitative model which sheds light on the twisting of the ring. It suggests that an important interaction will involve the overlap of π orbitals on S_s, S_d with the CH_2 groups. The calculation was not sophisticated enough to provide a quantitative analysis of this proposal nor much insight on structural details such as the shrinkage in ∠CCS and the small difference between the C–S_s and C–S_d distances.

The same interactions but involving π orbitals on the oxygen atoms and the CH_2 groups were also recognized as important factors stabilizing the twisted conformation in ethylene ozonide[30] and other oxolanes.[31] Thus, while the oxolane and thiolane families have comparable conformational properties originating from similar interactions, details of behavior may still differ. For example, the dihedral angle about the S–S bond in 1,2-dithiolane[2c] and substituted dithiolanes[1b] decrease to ca. 30° upon replacement of S_d by $-CH_2-$ while in 1,2-dioxolane the O–O dihedral angle of 50 ± 2°[32] remains nearly identical with that of ethylene ozonide.[28] This contrast also brings to mind the remarkable diversity exhibited in S–S dihedral angles which can vary from 0° to 90° as various factors influence the conformational energetics.[1]

Acknowledgment. Our interest in trithiolane was stimulated by Prof. Hans Bock who brought it to our attention.[29] Mr. Philip Bloem developed much of the softward needed for computer control of the spectrometer and signal averaging. This study was supported by Grants CHE8005471 and 8303615 from the National Science Foundation, Washington, DC.

Registry No. 1,2,4-Trithiolane, 289-16-7; 3-deuterio-1,2,4-trithiolane, 88440-70-4; *cis*-3,5-dideuterio-1,2,4-trithiolane, 88440-71-5; *trans*-3,5-dideuterio-1,2,4-trithiolane, 88440-72-6; [4-^{34}S]1,2,4-trithiolane, 88440-73-7; [1-^{34}S]1,2,4-trithiolane, 88440-74-8.

Supplementary Material Available: Tables listing the transition frequencies of the eight isotopic species (Tables S1–S8), the four excited vibrational states (Tables S9–S12), and the second-order Stark-effect coefficients (Table S13) (7 pages). Ordering information is given on any current masthead page.

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