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Gas-Phase Structure and Vibrational Spectra of Dimethoxydisulfane, $(\text{CH}_3\text{O})_2\text{S}_2$ ^{1,2}

Ralf Steudel* and Heinar Schmidt

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-10623 Berlin, Germany

Edgar Baumeister and Heinz Oberhammer

Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-72076 Tübingen, Germany

Tibor Koritsanszky†

*Institut für Kristallographie, Freie Universität Berlin, D-14195 Berlin, Germany**Received: December 2, 1994; In Final Form: March 14, 1995*[®]

The gas-phase structure of dimethoxydisulfane $(\text{CH}_3\text{O})_2\text{S}_2$ was determined by electron diffraction. The molecule is chainlike and of symmetry C_1 . Selected experimental geometrical parameters are $d(\text{SS})$ 196.0(3) pm, $d(\text{SO})$ 165.3(3) pm, $d(\text{CO})$ 143.2(3) pm, $\alpha(\text{OSS})$ 108.2(3)°, $\alpha(\text{COS})$ 114.5(4)°, $\tau(\text{SS})$ 91(4)°, $\tau(\text{SO}) \pm 7(3)$ °. Ab-initio MO calculations at the HF/6-311G** level resulted in three conformational isomers originating from rotation about the two SO bond axes. The most stable conformer among these is in keeping with the gas-phase structure. The two other rotamers are both of symmetry C_2 . Infrared and Raman spectra of gaseous, liquid, and crystalline dimethoxydisulfane and its fully deuterated derivative were recorded. The 30 fundamental modes were assigned using the vibrational wavenumbers calculated for the three rotamers by the ab-initio MO method.

Introduction

Dimethoxydisulfane is the methyl ester of dihydroxydisulfane HOSSOH, the chainlike isomer of thiosulfurous acid. This molecule has recently been detected in the gas phase by means of neutralization–reionization mass spectrometry, but the free acid is unstable and hence unknown in condensed phases.³ The geometries and energies of seven isomeric structures of $\text{H}_2\text{S}_2\text{O}_2$ were calculated at the HF/6-31G* level including electron correlation up to the fourth order of Moeller–Plesset perturbation theory. Among these, the chainlike isomer is one of the most stable.⁴ This isomer can as well be thought to be derived from tetrasulfane, H_2S_4 , by substituting the terminal sulfur atoms with oxygen. Analogously to the sulfanes, the organic esters form a homologous series of dialkoxypolysulfanes ROS_nOR which have been detected with up to 18 sulfur atoms in the chain by reversed-phase HPLC.⁵

The chalcogen–chalcogen bonds in such bivalent compounds are known to prefer gauche conformations with typical dihedral angles of 80–90°, which is usually attributed to lone-pair interactions.⁶ Two rotamers are possible for each chalcogen–chalcogen bond, representing segments of right-hand or left-hand helices. Thus, we may characterize a chalcogen–chalcogen bond by the sign of its dihedral angle (+ and –, respectively). The total number of conceivable rotamers grows with the chain length. Dimethoxysulfane $(\text{CH}_3\text{OSOCH}_3)$, **1**, the first member of the series, has three possible rotamers: two helical ones of symmetry C_2 (++) and (--) and one of symmetry C_s (+–). Electron diffraction⁷ and X-ray diffraction⁸ studies on **1** revealed that the molecule adopts the C_2 structure both in the gas phase and in the crystal. While electron diffraction is not able to distinguish between both enantiomers, the X-ray study shows their presence in the unit cell related by a center of inversion. Dimethoxydisulfane $(\text{CH}_3\text{OSSOCH}_3)$, **2**,

having a sulfur–sulfur bond in addition, can adopt three enantiomeric pairs of conformers: the sequences of signs +++, ++–, and –+– correspond to rotamers of symmetries C_2 (**2a**), C_1 (**2b**) and C_2 (**2c**), respectively (see Figure 1; the enantiomers are omitted). In the solid state, conformer **2a** was found by X-ray diffraction analysis, but the molecule deviates slightly from the ideal symmetry C_2 .⁹

We here report on the gas-phase structure of dimethoxydisulfane as determined by electron diffraction and by ab-initio MO calculations at the HF/6-311G** level. In addition, we investigated the vibrational spectra of dimethoxydisulfane and dimethoxydisulfane- d_6 in the gaseous, the liquid, and the solid state and compared the spectra with the calculated wavenumbers of the three rotamers. This study was aimed at examining whether the rotational isomerism has an influence on the vibrational spectra as it is known for dialkylidissulfanes RSSR, for which the C–S and S–S stretching frequencies are dependent on the rotational geometry of the adjacent C–S bond and on the dihedral angle of the S–S bond.¹⁰

Experimental Section

Dimethoxydisulfane was prepared from dichlorosulfane and methanol according to Thompson et al.¹¹ Repeated distillation was necessary to remove dimethyl sulfite, which is the main byproduct. The purity was monitored by infrared spectroscopy of the vapor as well as by ¹H NMR spectroscopy. Dimethoxydisulfane- d_6 was prepared in the same manner using methanol- d_4 (99.5 % D; Fluka).

The electron diffraction analysis was carried out with a Balzers gas diffractograph KD-G2¹² at two camera distances (25 and 50 cm from nozzle to plate) with an accelerating voltage of 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The temperature of the sample reservoir was kept at 20 °C and that of the inlet system and nozzle at room temperature. The camera pressure did not exceed 3×10^{-3} Pa during the experiment. The exposure times were 4–8

† On leave from the Central Research Institute of Chemistry of the Hungarian Academy of Science, H-1525, Budapest, Hungary.

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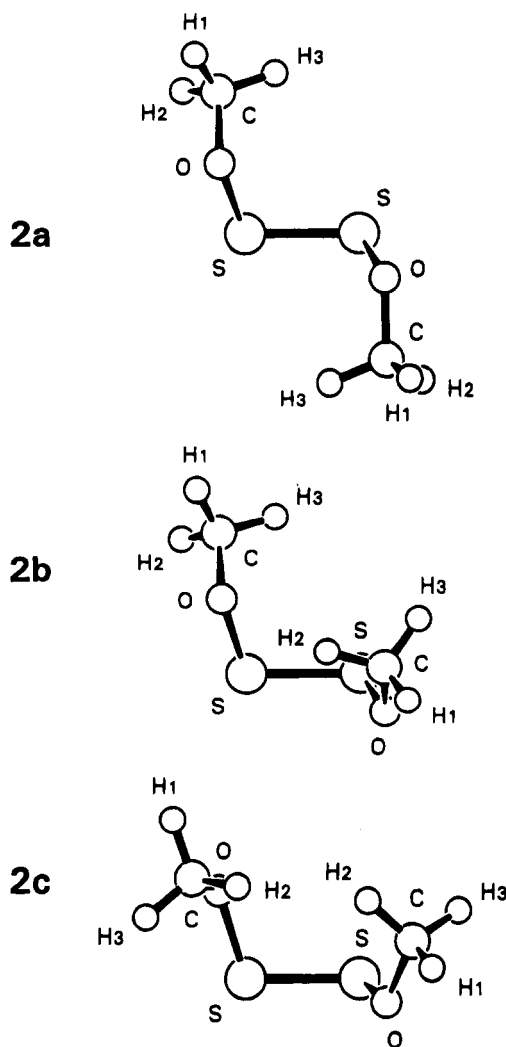


Figure 1. Calculated structures of the three conformers (**2a–2c**) of $(\text{CH}_3\text{O})_2\text{S}_2$.

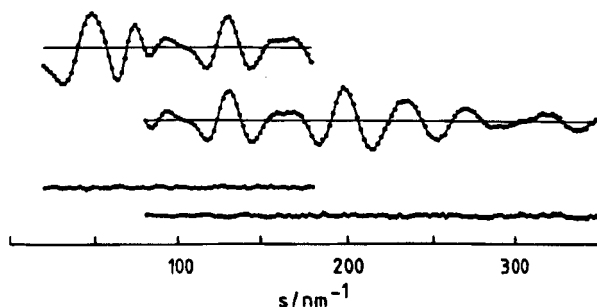


Figure 2. Experimental (\circ) and calculated (—) molecular scattering intensities and differences for $(\text{CH}_3\text{O})_2\text{S}_2$.

s for the longer camera distance and 18–27 s for the short distance. Two photographic plates for each camera distance were analyzed by the usual procedures.¹³ Averaged molecular scattering intensities in the s -ranges 20–180 and 80–350 nm^{-1} in steps of 2 nm^{-1} are presented in Figure 2.

Infrared spectra were recorded with a Perkin Elmer 580 B grating instrument (wavenumber accuracy better than 0.5 cm^{-1}). An evacuated 10 cm gas cuvette with KBr windows was filled with the sample to the saturation vapor pressure at 25 $^\circ\text{C}$ (1.6 kPa). Raman spectra were obtained with an ISA spectrometer (Jobin Yvon U 1000 double monochromator, cooled GaAs photomultiplier, and Mac 80A computer) equipped with a Spectra Physics krypton ion laser operating at 647.09 nm. The samples were sealed in ampules. Raman spectra of the liquid

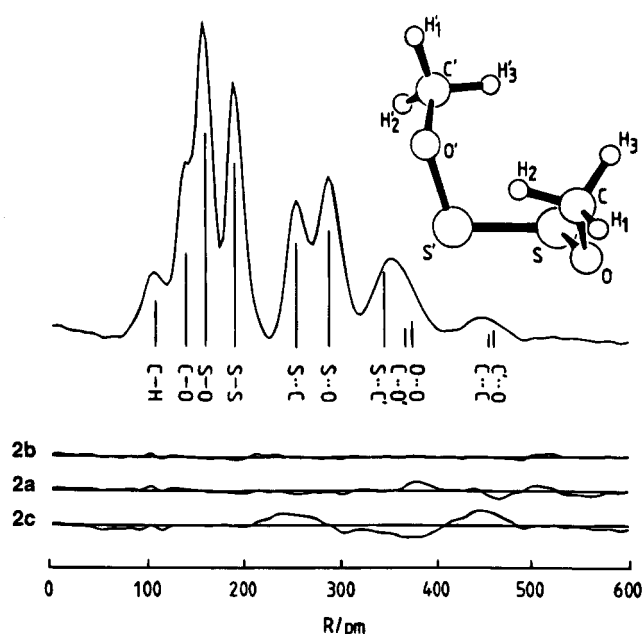


Figure 3. Experimental radial distribution function for $(\text{CH}_3\text{O})_2\text{S}_2$ and difference curves (below) for the conformers **2a**, **2b**, and **2c**. Interatomic distances for **2b** are indicated by vertical bars; the positions of $\text{O}\cdots\text{H}$ ($'$), $\text{C}\cdots\text{H}'$ and $\text{H}\cdots\text{H}'$ distances are not marked.

were recorded at 25 $^\circ\text{C}$. The spectra of the solid were obtained by cooling the sample to -100 or -130 $^\circ\text{C}$ with cold N_2 gas. Since the compound tends to remain liquid on cooling even well below its melting point and to solidify as a glasslike material, crystallization was achieved by shock-freezing the sample with liquid nitrogen and subsequent warmup with partial melting followed by annealing in the cold N_2 gas stream at the indicated temperatures.

Electron Diffraction Analysis. The three considered rotamers **2a**, **2b**, and **2c** can be distinguished by their non-bonding $\text{C}\cdots\text{C}'$ and $\text{C}\cdots\text{O}$ distances. The experimental radial distribution function (see Figure 3) exhibits a peak for the corresponding distances at 450–460 pm. Only the asymmetrical conformer **2b** has its $\text{C}\cdots\text{C}'$ and $\text{C}\cdots\text{O}$ distances in this range. The helical conformer **2a** can be excluded since its $\text{C}\cdots\text{C}'$ distance would be expected from calculations to be 565 pm. The short conformer **2c** can be ruled out for the same reason since the $\text{C}\cdots\text{C}'$ and $\text{C}\cdots\text{O}$ distances would be expected at about 400 pm. **2b** reproduces the experimental curve, while neither **2a** nor **2c** does as can be seen from the difference curves in Figure 3. For the structure refinement we allowed for the presence of rotamer **2b** only. The geometric parameters of both halves of the molecule were set equal. This constraint is justified by the ab-initio calculations (see Table 3) which predict very small differences between these parameters except for the COSS dihedral angles. The calculated difference, however, is smaller than the experimental uncertainty for this angle. The methyl groups were assumed to possess C_{3v} symmetry and to stagger the neighboring S–O bond. A tilt angle between the C_3 axis of the methyl group and the C–O bond was introduced using the angle which we obtained for dimethoxysulfane by least-squares refinement.⁷ Vibrational amplitudes were grouped for $\text{S}\cdots\text{H}'$, $\text{O}\cdots\text{H}'$, $\text{C}\cdots\text{H}'$, and $\text{H}\cdots\text{H}'$. Further constraints are evident from Table 1. With these assumptions nine geometrical parameters and 11 vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$: $\text{OSSO}/\text{COSS} = 0.76$, $\text{OSSO}/a_9 = -0.84$, $\text{OSSO}/a_7 = -0.75$, $\text{COSS}/a_9 = -0.85$, and $\text{SS}/a_{11} = 0.68$. The interatomic distances and vibrational amplitudes are listed in Table 1, and the geometrical parameters are given in Table 2.

TABLE 1: Interatomic Distances and Vibrational Amplitudes of (CH₃O)₂S₂^a

	distance (pm)	amplitude	
S—S	196.0(3)	5.9(2)	<i>a</i> ₁
S—O	165.0(3)	5.8(2)	<i>a</i> ₂
O—C	143.0(3)	5.1(2)	<i>a</i> ₃
C—H	111.3(9)	11.6(7)	<i>a</i> ₄
S···C	259	7.7(3)	<i>a</i> ₅
S···O	293	9.1(4)	<i>a</i> ₆
S···C'	346	} 17(2)	<i>a</i> ₇
O···O'	373		
O···C	364		
O···C'	459	} 23(4)	<i>a</i> ₈
C···C'	454		
S···H ₁	352	12(8)	<i>a</i> ₉
S···H ₂	282	24(5)	<i>a</i> ₁₀
S···H'	301–442	20 ^b	
O···H ₁	210	} 11(1.4)	<i>a</i> ₁₁
O···H ₂	215		
O···H'	288–540	20 ^b	
C···H'	394–558	21 ^b	
H···H	179	12 ^b	
H···H'	294–648	20 ^b	

^a For numbering of atoms see Figure 3. ^b Not refined.**TABLE 2: Geometrical Parameters of (CH₃O)₂S₂ by Electron Diffraction, X-ray Diffraction,⁹ and ab-Initio Calculation (Distances in Picometers, Bond and Dihedral Angles in Degrees)**

	gas phase ^a	crystal ^b	ab-initio ^c
S—S	196.0(3)	197.2(1)	202.0
S—O	165.3(3)	165.8(4)	163.5
O—C	143.2(3)	143.5(1)	141.3
C—H	111.5(9)	99.1(2)	108.3
O—S—S	108.2(3)	108.2(1)	105.3
C—O—S	114.5(4)	114.5(1)	117.2
O—C—H	110.6(10)	109.4(7)	109.3
O—S—S—O	91(4)	81.5(1)	86.7
C—O—S—S	±74(3)	75(3)	±82.8
tilt CH ₃	2.9 ^d		3.0 ^e

^a *r*_a distances and \angle_{α} angles. Error limits are 3 σ values. ^b Temperature 110 K; mean values are given. ^c HF/6-311G**¹⁵; mean values are given for conformer **2b**. ^d Angle between assumed C₃ axis and C—O bond; not refined. ^e $\frac{2}{3} [(O-C-H_{\text{gauche}}) - (O-C-H_{\text{trans}})]$.

Ab-Initio MO Calculations. Molecular orbital calculations were performed with the GAUSSIAN92¹⁴ program package at the Hartree–Fock level using 3-21G* and 6-311G** standard basis sets. The starting geometry was based on the X-ray structural data. For the methyl groups an idealized structure was taken. The optimization of this molecule led to a stationary point corresponding to a structure of symmetry C₂. In an additional optimization C₂ symmetry was imposed, leading to conformer **2a**. By changing the sign of one or both SO dihedral angles, starting geometries were obtained for the rotamers **2b** and **2c**. All conformers were preoptimized with the 3-21G* basis set. In all cases, the final cycle of the optimization resulted in changes in the maximum of force and displacement far below the threshold limits (0.000 45 and 0.0018 au, respectively) applied as convergence criteria. These conformers are depicted in Figure 1 in a view perpendicular to the S—S bond axes. Rotamer **2b** (++) is found to be most stable followed by **2a** (+++) and **2c** (-+-). The calculated structural parameters of **2a–2c** are listed in Table 3. The relative energies given in Table 3 include the zero-point vibrational energies scaled by 0.9135 according to a suggestion of Pople et al.¹⁵

Results and Discussion

Molecular Structure. In accordance with the calculations, the electron diffraction analysis shows conformer **2b** to be the

TABLE 3: Calculated Structural Parameters^a and Relative Energies^b of Three Rotamers of (CH₃O)₂S₂

	2a C ₂	2b C ₁	2c C ₂
symmetry			
S—S	201.8	202.0	201.5
S—O	163.3	163.2, 163.9	163.9
O—C	141.2	141.3, 141.2	141.1
C—H ₁	108.1	108.1	108.1
C—H ₂	108.5	108.4	108.4
C—H ₃	108.5	108.5	108.5
O—S—S	106.0	105.3, 105.4	106.8
C—O—S	117.4	117.2, 117.2	117.0
O—C—H ₁	106.3	106.2, 106.4	106.2
O—C—H ₂	110.8	110.7, 110.8	111.3
O—C—H ₃	110.9	110.7, 110.8	111.1
O—S—S—O	82.3	86.7	90.8
C—O—S—S	82.5	-81.4, 84.2	-103.5
ΔE (kJ·mol ⁻¹) ^b	4.2	0	11.4

^a Distances in picometers, bond and dihedral angles in degrees. ^b HF/6-311G** energies, corrected for zpe (scaled by 0.9135).¹⁵

main constituent of the gas phase. Although this analysis gives no hint that there is a second conformer present, we cannot exclude a small concentration (less than 10%) of such a rotamer in the gas phase on account of methodological uncertainties. On the basis of the calculated relative energies of the three conformers, **2a** may occur in addition to **2b** in gaseous and in liquid dimethoxydisulfane, while **2c** is regarded as being of no significance. In fact, **2a** is found in the solid state, but the molecule clearly deviates from the perfect symmetry C₂ due to the molecular packing in the crystal.⁹ Rotamer **2b** has no symmetry, and the calculations show both S—O—CH₃ moieties to be different (Table 3). Nevertheless, the electron diffraction yields averaged data for both halves of the molecule. This has to be taken into account comparing the structures in Table 2.

The following discussion will be restricted to selected structural parameters. The most interesting structural features of molecule **2** are the S—S and S—O bond parameters, which have been discussed in detail in our preceding work on the crystal structure of **2**.⁹ The S—S bond is shorter than in most organic disulfanes, as is expected for a disulfane with two electron-withdrawing methoxy groups.⁹ The S—O bonds are longer by 2.5 pm than in the monosulfane **1**.⁷ Obviously, the substitution of one methoxy group by sulfur has no decisive effect on the S—O bond length, although this corresponds to a lowering of the oxidation number of sulfur from +II in **1** to +I in **2**. Unexpected results were obtained for the S—O dihedral angles. While the dihedral angle at the S—S bond is larger than in the crystalline compound by 10° but still within the usual range of 80–90°,⁹ the S—O dihedral angles are surprisingly small (±74(3)°). Thus, the latter confirm the values found in the crystal structure,⁹ but they are smaller than those calculated as well as those found in the monosulfane **1** (84(3)°).⁷ This is surprising because rotamer **2b** is sterically more demanding than **2a**. Presumably the S—S dihedral angle in **2b** is enlarged to compensate for the repulsion of the methoxy groups. The shortest nonbonding O···H distance between both methoxy groups is calculated to be 292 pm, which is clearly longer than the sum of the van der Waals radii (270 pm).¹⁶ Thus, hydrogen bonding can be excluded as the attracting force. In any case, a simple repulsive interaction of the lone pairs of oxygen and sulfur alone cannot explain the small S—O dihedral angles. The calculated dihedral angles depend on the computational method: ab-initio calculations on bivalent sulfur–oxygen compounds seem to overestimate this angle systematically at the HF/6-311G** level, while the HF/3-21G* method predicts SO dihedral angles of -75.5° and 81.3°, in better agreement

TABLE 4: Calculated Harmonic Wavenumbers (cm^{-1}) for the Three Rotamers of $(\text{CH}_3\text{O})_2\text{S}_2$ and Relative Infrared (IR) and Raman (Ra) Intensities

2a			2b			2c			assignment ^a
IR	Ra		IR	Ra		IR	Ra		
2932 (A)	1	41	2932 (A)	12	61	2931 (A)	17	41	$\nu(\text{CH}_3)$
2931 (B)	4	64	2931 (A)	12	54	2930 (B)	19	45	
2894 (B)	16	16	2899 (A)	16	18	2899 (A)	7	30	
2894 (A)	3	22	2896 (A)	17	23	2893 (B)	31	7	
2833 (A)	1	100	2835 (A)	18	100	2839 (A)	25	100	
2833 (B)	22	19	2834 (A)	20	8	2835 (B)	11	0.1	$\delta(\text{CH}_3)$
1449 (A)	2	0.6	1451 (A)	5	5	1453 (A)	3	5	
1449 (B)	3	9	1449 (A)	4	4	1447 (B)	3	5	
1439 (A)	≈ 0	12	1441 (A)	7	5	1439 (A)	1	5	
1439 (B)	5	0.2	1439 (A)	3	8	1436 (B)	4	3	
1426 (A)	0.4	3	1427 (A)	2	2	1429 (A)	2	3	$\rho(\text{CH}_3)$
1426 (B)	2	0.4	1426 (A)	2	2	1425 (B)	4	0.3	
1167 (A)	0.8	1	1169 (A)	0.9	1	1166 (A)	0.1	1	
1166 (B)	0.3	0.6	1166 (A)	1	1	1163 (B)	2	0.3	
1142 (B)	1	0.2	1146 (A)	1	1	1143 (A)	≈ 0	1	
1142 (A)	0.2	2	1142 (A)	2	1	1141 (B)	3	0.7	$\nu(\text{C}-\text{O})$
1043 (A)	0.8	3	1040 (A)	71	0.8	1049 (A)	100	2	
1031 (B)	100	1	1030 (A)	100	3	1028 (B)	51	1	
712 (A)	13	12	709 (A)	19	11	701 (A)	9	8	
692 (B)	20	7	691 (A)	39	8	689 (B)	43	7	
487 (A)	0.2	7	489 (A)	0.2	8	500 (A)	0.1	5	$\nu(\text{S}-\text{O})$
396 (A)	0.2	0.4	392 (A)	3	0.5	360 (A)	≈ 0	1	
362 (B)	3	0.4	372 (A)	0.9	0.4	350 (B)	3	0.2	
333 (B)	2	0.5	308 (A)	7	0.8	302 (B)	6	1	
231 (A)	0.1	1	259 (A)	1	2	262 (A)	2	2	
159 (A)	0.1	0.7	166 (A)	0.3	0.4	139 (A)	0.2	0.4	$\delta(\text{COS})$
157 (B)	0.2	0.3	161 (A)	0.6	0.4	137 (B)	0.6	0.3	
111 (A)	≈ 0	0.2	104 (A)	1	0.4	114 (A)	≈ 0	0.6	
73 (B)	2	0.1	89 (A)	2	0.4	60 (A)	0.6	0.1	
64 (A)	0.7	0.6	71 (A)	0.7	0.8	57 (B)	2	0.2	

^a Approximate description.

with experiment. Using the experimentally determined dihedral angles of dimethyl peroxide (119°)¹⁷ and dimethyldisulfane (85°)¹⁸ for comparison would lead us to expect an intermediate value. The S–O dihedral angle of methanesulfenic acid ($\text{CH}_3\text{S}-\text{OH}$) was found by microwave spectroscopy to be 94° .¹⁹ Unfortunately, experimental data are not available for the related methanesulfenic acid methyl ester $\text{CH}_3\text{O}-\text{SCH}_3$.

Vibrational Spectra. Each of the considered rotamers **2a**–**2c** has 30 fundamental vibrations, which all are expected to be infrared and Raman active. In the case of the C_2 conformers, 16 modes belong to the symmetry species A and 14 to the species B. Rotamer **2b** has no symmetry; hence all modes are of the symmetry species A (Table 4). The fundamental vibrations can be further subdivided into 11 stretching modes (ν), 14 deformation modes (10 δ and 4 ρ), and five torsional modes (τ).

The harmonic wavenumbers of the fundamental vibrations of **2a**–**2c** were calculated (HF/6-311G**) and scaled by 0.8929.¹⁵ They are listed in Table 4 together with their relative infrared and Raman intensities. The assignment given in Table 4 is based on the calculated displacement parameters. The designations indicate the predominant motion of a vibration since most of the fundamentals are coupled. This approach is satisfactory for all fundamentals except for $\tau(\text{CO})$, which seems to mix with other modes, especially with $\delta(\text{OSS})$, so that it could not be assigned unambiguously.

The infrared spectra of gaseous **2** are shown in Figure 4, the Raman spectra of liquid **2** are presented in Figure 5 and of the crystalline compound in Figure 6. In Tables 5 and 6 the observed wavenumbers of dimethoxydisulfane and of the deuterated compound are given.

Vibrations of the Methyl Groups. For the methyl groups 16 vibrational modes are expected (6 ν , 6 δ , and 4 ρ). The

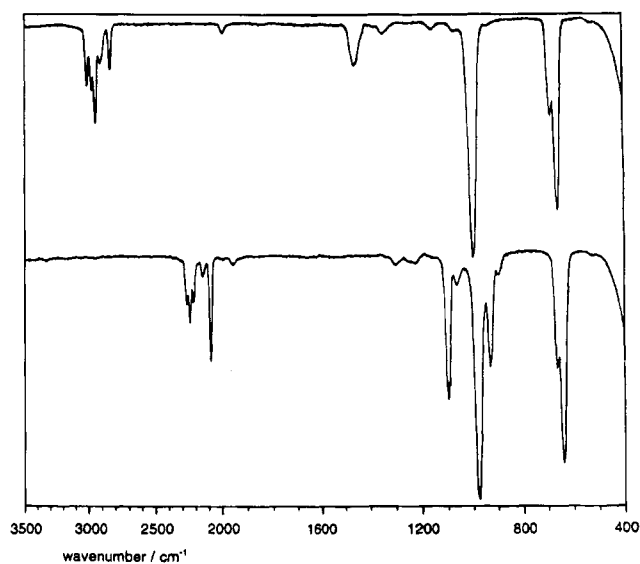


Figure 4. Infrared spectra of gaseous $(\text{CH}_3\text{O})_2\text{S}_2$ (top) and $(\text{CD}_3\text{O})_2\text{S}_2$ (bottom) at 25°C ; vapor pressure 1.6 kPa; ordinate, transmittance.

observed signals in the region $3200\text{--}1000\text{ cm}^{-1}$ are in accordance with those found for dimethoxydisulfane, **1**; for a detailed discussion the reader is referred to the corresponding publication.⁷ The remainder of the fundamentals to be considered are stretching and deformation modes of the COSSOC skeleton.

Stretching Modes of the COSSOC Chain. Five vibrations are discussed in this section, two C–O and S–O stretching modes each and one S–S vibration. According to the calculations, the two $\nu(\text{S}-\text{O})$ are expected to interact weakly with each other, leading to one *in phase* (i.p.) and one *out of phase* (o.o.p.) vibration. A description as $\nu_s(\text{S}-\text{O})$ and $\nu_{as}(\text{S}-\text{O})$, for the

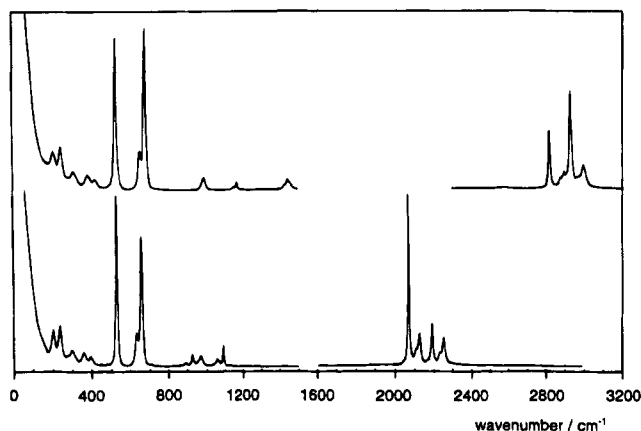


Figure 5. Raman spectra of liquid $(\text{CH}_3\text{O})_2\text{S}_2$ (top) and $(\text{CD}_3\text{O})_2\text{S}_2$ (bottom) at 25 °C; spectral slit width 2 cm^{-1} ; ordinate, intensity.

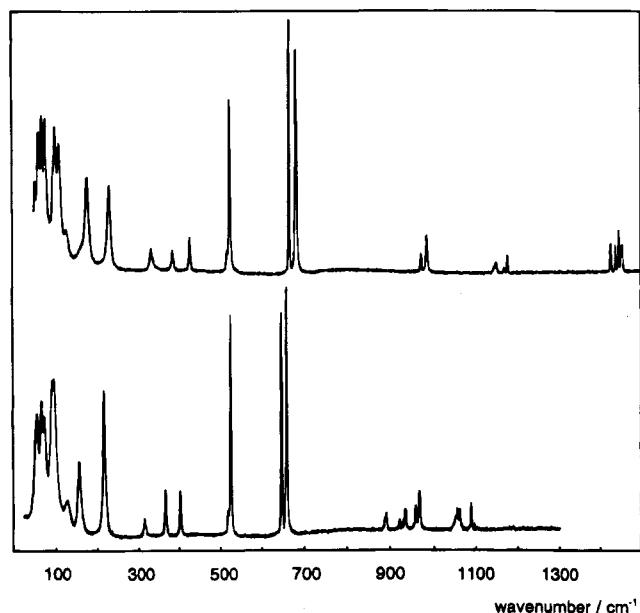


Figure 6. Raman spectra of crystalline $(\text{CH}_3\text{O})_2\text{S}_2$ (top) and $(\text{CD}_3\text{O})_2\text{S}_2$ (bottom) at -130 and -100 °C, respectively; spectral slit width 2 cm^{-1} ; ordinate, intensity.

former and the latter respectively, applies only to the rotamers of symmetry C_2 and has no meaning for **2b**, which has no symmetry. The same holds for the C—O stretching modes, which give rise to a very strong absorption at 1000 cm^{-1} in the infrared spectrum. Apparently, the difference between both wavenumbers is smaller than the half-width of the signal (35 cm^{-1}). In the Raman spectra these modes occur as two weak lines at 989 and 971 cm^{-1} . On deuteration the infrared absorption shifts to 978 cm^{-1} due to the increased mass of the methyl groups. This behavior is analogous to that of **17**¹. The S—O *in phase* and *out of phase* stretching vibrations occur as medium and strong absorptions at 688 and 662 cm^{-1} , respectively, while their intensities are reversed (very strong and medium) in the Raman spectra. Upon deuteration, like in the monosulfane, both wavenumbers are lowered by 22–24 cm^{-1} . A mixing with the methyl rocking modes may be assumed, as in the case of **1**. The S—O stretching modes of disulfane **2** are observed at lower wavenumbers than those of the monosulfane **1** (731 cm^{-1}),⁷ those of dimethyl sulfite (694, 738 cm^{-1}),²⁰ and those of other compounds with sulfur—oxygen single bond(s).

The S—S stretching mode of **2** is assigned to the strong Raman line at 530 cm^{-1} , which is unaffected by the deuteration and which exhibits the ³⁴S satellite in the low-temperature

TABLE 5: Observed Vibrational Data of $(\text{CH}_3\text{O})_2\text{S}_2$, Wavenumbers in cm^{-1}

infrared gaseous 25 °C	Raman		assignment
	liquid ^b 25 °C	crystalline -120 °C	
3002 m	2998 m,br	2999 m	$\nu(\text{CH}_3)$
		2972 m	$\nu(\text{CH}_3)$
2964 m	2969 w	2962 m	$\nu(\text{CH}_3)$
2940 s	2930 w	2929 s	$\nu(\text{CH}_3)^*$
		2922 s	$\nu(\text{CH}_3)^*$
2900 w	2894 m	2890 w	$2 \times 1455 = 2910$
	2877 w	2874 vw	$2 \times 1446 = 2892$
		2869 w	$2 \times 1438 = 2876$
2822 w	2819 s	2816 s	$2 \delta(\text{CH}_3)^*$
	2575 vw	2579 vw	
1989 vw			$2 \times 1000 = 2000$
1453 w	1455 w	1455 w	$\delta(\text{CH}_3)$
	1444 w	1446 w	
		1438 w	
		1426 w	
1377 vw			$2 \times 688 = 1376$
1345 vw			$662 + 688 = 1350$
		1175 w	$\rho(\text{CH}_3)$
1160 vw	1165 w	1168 vw	$\rho(\text{CH}_3)$
	1150 vw	1148 w	$\rho(\text{CH}_3)$
1078 vw			
1000 vs	989 w	985 w	$\nu(\text{CO})$ i.p.
940 vw	971 w	971 w	$\nu(\text{CO})$ o.o.p.
688 m	684 vs	684 vs	$\nu(\text{SO})$ i.p.
662 s	656 m	667 vs	$\nu(\text{SO})$ o.o.p.
527 vw	530 vs	525 s	$\nu(\text{SS})$
		518 vw	$\nu(^{34}\text{SS})$
	423 w	428 w	$\delta(\text{COS})$
	385 w	385 w	$\delta(\text{COS})$
	311 w	332 w	$101 + 232 = 333$
	248 m		$\delta(\text{OSS})$
	209 m	232 m	$\delta(\text{OSS})$
		178 m	$\tau(\text{CO})^a$
	129 sh	128 w	$\tau(\text{SO})^a$
		111 s	$\tau(\text{SO})^a$
		101 s	$\tau(\text{SS})$
		78 s	lattice
		69 s	
		62 s	
		53 m	

^a Tentative assignment. ^b Our values are in accordance with those measured by Goehring.²⁶ ^c *, Fermi resonance.

spectrum (see Figure 6). In contrast, no ³⁴S satellite could be detected for $\nu(\text{S—O})$. In accordance with the short S—S bond of **2** the S—S stretching wavenumber is considerably higher than would be expected for an unstrained organic disulfane (505–510 cm^{-1}).¹⁰

The wavenumbers of $\nu(\text{C—O})$ and $\nu(\text{S—O})$ are overestimated by the ab-initio MO calculations (Table 4), while that of $\nu(\text{S—S})$ is calculated too low by about 40 cm^{-1} . Comparing the three rotamers with each other, the corresponding wavenumbers differ by less than 10 cm^{-1} . This is less than the half-width of the peak in the gas-phase and liquid-phase spectra. Thus, $\nu(\text{C—O})$ and $\nu(\text{S—O})$ cannot be used to test for the presence of different rotamers in the liquid and the gas phase. The signals of the crystalline compound are much sharper (half-width: 2 and 4 cm^{-1} for $\nu(\text{S—O})$ and 3.5 cm^{-1} for $\nu(\text{S—S})$) but there is no additional splitting, indicating the presence of a second rotamer. The Raman spectrum of the glasslike solid (not shown) resembles the liquid-phase spectrum; even the peak width is the same as in the room temperature spectra: 11 cm^{-1} for $\nu(\text{S—O})$ and 14 cm^{-1} for $\nu(\text{S—S})$.

Bending Modes of the COSSOC Skeleton. These vibrations comprise two COS and OSS bending modes each and five torsional modes of the skeleton (CO, SO, and SS). The

TABLE 6: Observed Vibrational Data of (CD₃O)₂S₂, Wavenumbers in cm⁻¹

infrared gaseous 25 °C	Raman		assignment
	liquid 25 °C	crystalline -120 °C	
2252 w	2252 m		$\nu(\text{CD}_3)$
2230 w	2232 w		$\nu(\text{CD}_3)$
2200 w	2190 m		2 $\delta(\text{CD}_3)^*^c$
2135 w	2125 m		
2100 sh	2108 sh		
2074 m	2068 vs		$\nu(\text{CD}_3)^*$
1952 vw			$2 \times 978 = 1956$
1195 vw			$663 + 529 = 1192$
1118 vw			
1096 m	1090 w	1087 w	$\delta(\text{CD}_3)$
1063 vw		1060 w	$\delta(\text{CD}_3)$
	1055 w	1053 w	$\delta(\text{CD}_3)$
978 vs	971 w	966 w	$\nu(\text{CO})$
		957 w	$\varrho(\text{CD}_3)$
930 m	926 w	933 vw	$\varrho(\text{CD}_3)$
896 vw	889 w	891 w	$\varrho(\text{CD}_3)$
705 vw	705 vw		
663 m	660 s	660 vs	$\nu(\text{SO})$ i.p.
649 s	634 m	646 vs	$\nu(\text{SO})$ o.o.p.
	529 vs	525 vs	$\nu(\text{SS})$
		518 vw	$\nu(^{34}\text{SS})$
	396 w	402 w	$\delta(\text{COS})$
	359 w	365 w	$\delta(\text{COS})$
		326 sh	
	300 w	314 w	$95 + 216 = 311$
	281 sh		
	237 m		$\delta(\text{OSS})$
	203 m	216 s	$\delta(\text{OSS})$
		156 m	$\tau(\text{CO})^a$
		126 w	$\tau(\text{SO})^d$
		95 s,br	$\tau(\text{SS})/\tau(\text{SO})^b$
		73 s	} lattice
		66 s	
		56 s	
		33 m	

^a Tentative assignment. ^b Not resolved. ^c *, Fermi resonance.

assignment is difficult and suffers mainly from the uncertainty due to vibrational coupling which is expected to be stronger and more common for these vibrations. For the same reason, the usefulness of reference material for comparison is limited. Therefore, we borrow the assignment based on the HF calculations (see Table 4) and compare the observed wavenumbers to those of related molecules. Obviously, most of the frequencies in the region below 500 cm⁻¹ are underestimated by the calculations.

The wavenumbers of the COS deformation modes may be estimated from the CCS deformation modes of diethylsulfane²¹ and diethyldisulfane,^{10c} which have been assigned at 345 and 380 cm⁻¹ for the former and to 311–364 cm⁻¹ for the latter. The monosulfane **1** has its vibrations $\delta(\text{COS})$ at 432 and 423 cm⁻¹.⁷ Thus, the Raman lines at 423 and 385 cm⁻¹ in the spectrum of **2** are assigned to $\delta(\text{COS})$. The calculations leave ambiguity concerning the OSS deformations and the CO torsions, which seem to be mixed. The assignment given in Table 4 is somewhat arbitrary and mainly due to the expected degeneracy of $\tau(\text{CO})$, specifying this mode to the lower frequency. For dimethyldisulfane²² the CSS deformations have been assigned to 272 and 240 cm⁻¹ and for diethyldisulfane^{10c} to 178 and 202 cm⁻¹. In the case of dichlorodisulfane the SSCI deformation modes are observed at 244 and 210 cm⁻¹.²³ Thus, we can ascribe the Raman lines at 248 and 209 cm⁻¹ to $\delta(\text{OSS})$. The torsion around the C–O bond is presumed for a series of dialkyl ethers at 242 and 198 cm⁻¹ (on the basis of data for dimethyl ether).²⁴ In dimethyl sulfate these modes are thought to be situated at 253 cm⁻¹.²⁵ Although this supports

an argument for a likely mixture of $\tau(\text{CO})$ and $\delta(\text{OSS})$, we assign the Raman line at 178 cm⁻¹ to $\tau(\text{CO})$, taking into account the shift of the wavenumbers upon deuteration. The effect of substituting CH₃ by CD₃ is expected to be more pronounced for $\delta(\text{COS})$ and $\tau(\text{CO})$ than for $\delta(\text{OSS})$, $\tau(\text{SO})$, and $\tau(\text{SS})$. In fact, the wavenumbers of $\delta(\text{COS})$ are lowered by 27 and 26 cm⁻¹, those of $\delta(\text{OSS})$ by 11 and 6 cm⁻¹, and those of $\tau(\text{CO})$ by 20 cm⁻¹. On deuteration the frequency shift of the remaining torsional modes is low (2–6 cm⁻¹), as expected. Torsional modes of sulfur–sulfur bonds have been assigned to 116 cm⁻¹ in dimethyldisulfane²² and diethyl disulfane¹⁰ and to 108 cm⁻¹ in dichlorodisulfane.²³ Accordingly, this vibration is ascribed to the strong Raman line at 101 cm⁻¹ of crystalline **2**. The remaining fundamentals to be assigned are the SO torsional modes, which are attributed to the Raman lines at 128 and 111 cm⁻¹. In the spectrum of the deuterated compound the latter vibration is not resolved from $\tau(\text{SS})$. In the case of **1** the SO torsional modes have been tentatively assigned to the lowest observed Raman line of the liquid sample (98 cm⁻¹).⁷ On the basis of these results, we may complete the assignment for the monosulfane **1**: the CO torsional modes which we left unassigned may be ascribed to the signal at 168 cm⁻¹, and the 126 cm⁻¹ band can be attributed to the second (nondegenerate) SO torsion.

A weak Raman line of the disulfane **2** near 320 cm⁻¹ is explained by a combination of $\delta(\text{OSS})$ and $\tau(\text{SS})$. An analogous combination was observed for both diethyl- and ethylmethyl-disulfane.^{10c} Raman lines below 100 cm⁻¹ in the spectrum of **2** are ascribed to lattice modes.

One intention of this study was to search for different rotamers in the vapor and in the liquid by means of vibrational spectroscopy. However, the calculated wavenumbers of the rotamers **2a–2c** do not differ sufficiently in most cases. Especially the differences for characteristic modes such as $\nu(\text{S–O})$, $\nu(\text{C–O})$, or $\nu(\text{S–S})$ do not allow for an unambiguous identification of rotamers (see above). There are differences in the case of the low-frequency deformation modes between the calculated wavenumbers of the rotamers and also between liquid-phase and solid-state Raman spectra. If the latter differences are not due to the change from the liquid to the solid state, we may attribute this finding to the presence of different rotamers, but a clear distinction is not possible either. Unfortunately, the use of KBr windows for the infrared spectra prevented us from detecting the corresponding infrared absorptions of the gaseous compound. Thus, we interpret the spectra of the vapor as arising from **2b** and those of the crystals as belonging to **2a**, while ambiguity is left for the liquid phase, where both conformers may be present.

Comparing S–O and C–S stretching frequencies in methoxy-sulfanes and ethylsulfanes with respect to the influence of rotational isomerism, we may summarize that there is no correlation for $\nu(\text{S–O})$, unlike for $\nu(\text{C–S})$. In contrast to the CS bond, rotation about the SO bond is hindered, leading to gauche conformations. The three calculated conformers differ mainly in the sign of their SO dihedral angles, while the values of the angles are similar. Therefore, $\nu(\text{S–O})$ is roughly the same for these conformers. This does not mean that $\nu(\text{S–O})$ may not shift in the case of other alkoxy groups or if the SO dihedral angle is changing (e.g. by fixing it in a cyclic structure).

Conclusion

Dimethoxydisulfane occurs as two different rotational isomers in the gas phase and in the solid state. The molecule is chainlike and asymmetrical in the gas phase, while it adopts a slightly distorted C₂ conformation in the crystal. This result is supported

by ab-initio MO calculations which show the former conformer to be more stable than the latter by ca. 4 kJ·mol⁻¹. A third conformer of symmetry *C*₂ was found by the calculations to be less favorable due to sterical interaction of the methyl groups. Both experimentally determined conformers have similar geometrical parameters which are in good agreement with the HF calculations. The small S–O dihedral angles of the crystalline compound are confirmed by the gas-phase structure. Considering the molecular structures of dimethoxysulfane and dimethoxydisulfane, both compounds are suitable models for the structures of the free acids H₂SO₂ and H₂S₂O₂.

The vibrational spectra of dimethoxydisulfane and its perdeuterated derivative have been assigned to the 30 fundamental vibrations by comparison with the calculated spectra. Neither S–O nor C–O nor S–S stretching vibrations are suitable for identifying individual rotamers in a mixture because their frequencies are too similar. There is no indication for a dependence of the S–O stretching frequency on the rotational geometry of the S–O bond, most probably because this isomerism is restricted to gauche conformations, the S–O stretching frequencies of which are very similar. Therefore, it was impossible to identify a small concentration of a second conformer in the gas phase *via* infrared spectroscopy. For the same reason it cannot be excluded that both conformers **2a** and **2b** are present in the liquid.

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