Synthesis and Molecular Structure of Disulfane

Josef Hahn*, Petra Schmidt, and Klaus Reinartz
Institut für Anorganische Chemie der Universität zu Köln. Greinstraße 6, D-5000 Köln 41

Jörg Behrend, Gisbert Winnewisser*, and Koichi M. T. Yamada
Erstes Physikalisches Institut der Universität zu Köln, Zülpicher Straße 77, D-5000 Köln 41

Dedicated to Prof. Marianne Baudler on the occasion of her 70th birthday
Z. Naturforsch. 46b, 1338–1342 (1991); received April 4, 1991

Disulfane, Deuterodisulfane, Molecular Structure

The synthesis and structure of disulfane are presented. Pure disulfane, H₂S₂, has been obtained by the cracking distillation of raw sulfane mixtures in a rotary evaporator, thus substituting the classical cracking column for the rotating flask of the evaporator. Pure, gaseous dideuterodisulfane could be generated by the solvolysis of bis(methylidyphenylisilyl)disulfane, (MePh₂Si)₂S₂, with D₂O in the presence of trichloroacetic acid as stabilizing agent. Partially deuterated disulfane has been prepared by H,D exchange between pure H₂S₂ and DCl. For the first time the molecular structure of HSSH has been determined based solely on microwave spectroscopy with the following parameters: r(SS) = 2.0564 Å, r(SH) = 1.3421 Å, dihedral angle γ = 90.34 °, and γ(SSH) = 97.88 °.

Introduction

Besides the elements carbon, silicon, and phosphorus especially sulfur shows the ability of catenation. Despite of the high S–S bond energy, the sulfanes strongly tend to disproportionation reactions, thus withstanding detailed spectroscopic investigation. The present paper contributes new aspects to the synthesis and structure of disulfane.

Disulfane, H₂S₂, was first isolated in 1906 by Bloch and Höhn [1] who managed to distill this compound as a “light yellowish waterlike liquid” from raw sulfane mixtures generated by acid de- 

and H₂S₃ distill off from the cracking column, whereas the long chain sulfanes and sulfur flow to the bottom. Disulfane and trisulfane may be condensed into separate traps, but need further distil- 

ation in the past. Despite the fact that disulfane has now been known for fifty years, many of its chemi-

cal and spectroscopic properties need further in- 

vestigation. This may be a consequence of the fact, 

that disulfane is still believed to be a compound 

difficult to prepare. This paper describes the pro-

gress that was achieved in the synthetic as well as the spectroscopic field.

Reprint requests to Dr. J. Hahn or Prof. Dr. G. Winnewisser.
Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen 0932–0776/91/1000–1338/$ 01.00/0
Preparative Results

a) $H_2S_2$

The synthesis of disulfane could be simplified by substituting the classical cracking column by a slightly modified commercial rotary evaporator (see Fig. 1). The cracking process takes place in the rotating flask K1, which obviously brings about the same effect as the large surface of the cracking column. The new apparatus is smaller than the old one and much easier to clean after the cracking process. The shape of the condensor is identical to that used by Feher, Laue, and Winkhaus [4] for distillative purification of trisulfane. This condensor offers the possibility of separating higher sulfanes form the gaseous products. The separation of pure trisulfane at the bottom of this condensor needs further modification of the procedure and is presently under study. So far we succeeded in isolating pure $H_2S_2$ in the trap F1 whereas a mixture of $H_2S_3$ and higher homologues has been obtained in K2.

Fig. 1. Apparatus for cracking raw sulfanes and generation of pure disulfane; K1: rotating flask of the rotary evaporator; K2: flask for the separation of $H_2S_3$ and higher volatile sulfanes; F1: trap for the condensation of $H_2S_3$; F2: double trap for the condensation of $H_2S$.

b) $D_2S_2$

As reported earlier [5], deuterosulfanes, $D_2S_n$, of definite chain length $n$ can be obtained by the reaction of novel silylsulfanes, $(MePh_2Si)_2S_n$, with deuterotrifluoroacetic acid in benzene solution. However, this procedure is not suited to prepare pure gaseous $D_2S_2$ as needed for spectroscopic investigations, because its boiling point (70 °C) is very similar to that of benzene and trifluoroacetic acid. In order to overcome this difficulty the reaction was carried out without solvent using the less volatile trichloroacetic acid, which is generated in situ from its anhydride and $D_2O$. As a consequence of the low nucleophilicity of the acid and the high viscosity of the reaction mixture, the rate of $D_2S_2$ formation becomes too low. Fortunately it was found that the reaction rate can be increased significantly, if the cleavage of the anhydride is carried out with an excess of $D_2O$. Most surprisingly, decomposition of $D_2S_2$ does not occur, although this is normally caused even by traces of water. From a reaction mixture of $(MePh_2Si)_2S_2$, $(CCl_3CO)_2O$, and $D_2O$, in the molar ratio of ca. 1.0 : 3.5 : 4.48, $D_2S_2$ can be evaporated directly into the cell of the microwave spectrometer. Under the conditions chosen the solvolysis of the silylester is thus caused by $D_2O$ whereas trichloroacetic acid only acts as a stabilizer.

c) $HSSD$

As the sulfanes clearly show acidic character, partially deuterated disulfane molecules undergo H,D exchange reactions even in the gas phase leading to an equilibrium between the components DSSD, HSSD, and HSSH [6]. On the other hand H,D exchange reactions provide a simple possibility to prepare partially deuterated sulfanes. Raw sulfane mixtures, for example, can partially be deuterated by shaking with a $D_2O$/$DCl$ mixture [7, 8]. If sulfanes of definite chain length are subjected to this procedure disproportionation reactions occur, which produce lower and higher homologues as well as elemental sulfur [8]. We now have been able to show that the chain length of $H_2S_2$ can completely be retained during the H,D exchange with DCl. The exchange was carried out by saturating $H_2S_2$ at $-78 °C$ with dry DCl gas, which was subsequently evaporated by warming up the sample to room temperature.
The degree of the exchange can be monitored NMR spectroscopically. After the sample had been saturated three times with DCl, ca. 50% exchange was observed. In accordance with the findings for HSD [9] the proton resonance of HSSD is shifted to high field by 0.016 ppm with respect to that of HSSH. A splitting of the signal by H,D coupling cannot be observed.

**Molecular Structure**

Although the first spectroscopic studies of the sulfanes were initiated in the 40's with the pioneering work of Fehér and Baudler [2, 3] who presented the first Raman spectra of individual sulfanes, it took more than 50 years before a reliable structure could be derived for the lowest polysulfane, HSSH. From the close resemblance of spectroscopic features observed for HSSH and its oxygen analog hydrogen peroxide, HOOH, Fehér and Baudler rightly concluded that the sulfanes must possess chain structures.

With two sulfur atoms involved, HSSH may be considered as the second member of a large sulfane family which can reach sulfur chain lengths up to 35. High resolution spectroscopy in the millimeter wave and infrared region has been performed within the last 20 years on the lower sulfanes only, i.e. for HSSH and HSSSH [10, 11]. Despite extensive investigations of the complex HSSH spectrum, the complete determination of the disulfane structure, based on microwave data only, had not been possible for more than 20 years until just very recently. The final clue in unravelling the structure was the completion of the difficult assignment of the rotational spectrum of the monodeuterated disulfane, HSSD. The rotational spectra of HSSH and DSSD have been assigned already 20 years ago, although many of the details have been revealed only within the last few years.

It is now well known that microwave and millimeterwave spectroscopy provides one of the most widely applicable and accurate methods for evaluation of molecular structures, by effectively determining from the measured rotational spectra the moments of inertia of the parent molecule as well as several selected isotopomers. The determination of the three moments of inertia of HSSD bridged the gap for the determination of the structure, solely by microwave spectroscopy.

The details of the structural determination [12] are rather complex and shall not be discussed here. It may suffice to mention two important spectral features which play a role in evaluating the structure and which are also of interest to the chemist:

1. For the symmetric species, HSSH and DSSD, due to the effects of nuclear statistical weights, all high resolution spectra exhibit a characteristic intensity alternation which serves as direct evidence of the molecules’ chain structure. Fig. 2 shows for DSSD an instructive illustration of the appearance of nuclear statistical weights on the relative intensities of the rotational lines. This 6:3 intensity alternation is caused by the nuclear statistics of the identical D nuclei which are exchanged by rotation of 180 degrees about the c-axis which happens to be perpendicular to the SS-bond and coincides with the C2 symmetry axis. Substitution of 34S for 32S in one position destroys the symmetry and the alternation of line intensities.

2. Since the disulfane molecule is not completely rigid, its nearly right-angle chain structure offers the possibility of internal torsional motion, i.e. the motion of the two SH-bonds relative to each other. This internal angular motion of the two SH groups leads to a torsional splitting which has been detected in the experimentally observed rotational and vibrational spectra [13]. The HSSH torsional problem has been solved and has led to the determination of two potential barriers: the cis-barrier height $V_{cis} = 2843 \pm 9$ cm$^{-1}$ (8.129 kcal/mol) and $V_{trans} = 2037 \pm 12$ cm$^{-1}$ (5.824 kcal/mol). For completeness it might be mentioned that the barriers of HOOH for motion over the cis- and trans-configurations are $V_{cis} = 2562 \pm 60$ cm$^{-1}$ (7.33 kcal/mol) and $V_{trans} = 387 \pm 20$ cm$^{-1}$ (1.106 kcal/mol), with the latter value considerably lower than for HSSH. HSSH is rather rigidly locked into an equilibrium geometry that is neither the cis- nor the trans-configuration but with a dihedral angle of 90.3(2)$^\circ$.

Ever since the first Raman spectra of the sulfanes became known, their chain structure has been established. Although high resolution spectra of HSSH immediately provided this assumption beyond any doubt [7], it turned out to be a surprisingly formidable task to derive a structure based entirely on microwave data. The complexity of the spectral assignment of the different isotopic species posed the main stumbling block. It took more
Fig. 2. Spectrum of the "Q_o"-branch of deuterated disulfane. The lines with high intensity at the lower frequency side arise from c-type transitions of the symmetric species D_2S_2 and show a 6:3 intensity alternation due to spin statistics. The isotopically substituted species DS^{34}SD is non-symmetric and exhibits a b-type spectrum which can be observed at the higher frequency side with lower intensity. It may be noticed that the displayed spectrum is spliced together from two recordings with different amplification causing an intensity difference between J = 2 and J = 3 of the b-type DS^{34}SD spectrum.

than 20 years of spectroscopic work to assemble a complete data set of moments of inertia from the appropriate rotational constants of HSSH, HS^{34}SH, DSSD, HSSD. The quoted structure is based on equilibrium moments of inertia which have been estimated by partially correcting the contributions from the torsional vibration. This motion is of large amplitude and is thus expected to introduce the highest uncertainties to the structural determination. The bond lengths and angles quoted in Fig. 3 may therefore be considered a "partially corrected equilibrium structure" of disulfane. This structure is in close accord with ab initio quantum chemical computations [14, 15].

We have extended our spectroscopic work to the higher sulfanes, HSSH and HSSSSH. From the assignment of the millimeterwave spectrum of HSSSH we were able to prove the existence of the cis-conformer only, although the trans-conformer should be present according to ab initio calculations. Determination of the structure of HSSSH and HSSSSH poses an equally promising as formidable task for future work.

Preparations

All experiments must be carried out under a dry atmosphere to prevent decomposition of the sulfanes. The inner surface of all glassware, which
comes into contact with sulfanes, must be absolutely dry and free of grease, furthermore the surface should be free of any scratches and must be acidified by boiling concentrated hydrochloric acid.

**Disulfane:** The crack distillation is carried out in a slightly modified rotary evaporator (Rotavapor, model E L-131, the spherical joint of the distribution head was substituted for a ground joint NS 24/38 to take up the multiple coil condenser). The latter is connected to a water jet pump via the trap F 1 and the double trap (see Fig. 1).

To perform the cracking process, the crude sulfane oil is placed into the flask K 1. After the apparatus has been evacuated to 16 Torr and the rotation of K 1 has been started (60 rpm), the double trap, the trap F 1, and the multiple coil condenser are cooled to −196 °C, −78 °C, and −10 °C, respectively. Then the oil bath is heated from room temperature to 80 °C within half an hour. As soon as the gas evolution recedes, the temperature is slowly increased to 100 °C within about a 6 h period. The sulfanes evaporating from K 1 are collected in K 2 (H 2 S 3 and higher homologues), in F 1 (H 2 S 2 ) and in the double trap (H 2 S). When starting with 140 ml of crude sulfane oil the following yields are obtained: H 2 S 2 ca. 30 ml (40 g); H 2 S 3 ca. 4.3 ml (6.4 g).

For storage purposes the disulfane must be condensed at 0 °C/13 Torr from F 1 into a flask cooled to −196 °C. The 1H NMR spectrum reveals a 0.5% contamination with H 2 S 3.

**Dideuterodisulfane:** A gently warmed mixture of 6.78 g (21.96 mmol) trichloroacetic acid anhydride and 0.55 g (27.46 mmol) D 2 O is added to 2.81 g (6.12 mmol) bis(methylidiphenylsilyl)disulfane, (MePh 2 Si) 2 S 2, contained in a Schlenk tube (ca. 2% excess of silylsulfane and anhydride in relation to their reaction with D 2 O). The mixture is held at ambient temperature for thirty minutes and is stored then at 8 °C overnight. During this time trichloroacetic acid separates by crystallization from the overlying faintly yellow-coloured liquid phase, which contains the D 2 S 2. The latter can be evaporated from this solution into the evacuated absorption cell of a microwave spectrometer. This process could be repeated several times without decomposition of D 2 S 2 over a period of one year. The sample was stored at −196 °C and was warmed up to room temperature shortly before another sample of D 2 S 2 was required.

**Partially deuterated disulfane:** 1 ml of disulfane is placed in a 50 ml tapered flask with a gas inlet tube and lateral stopcock. The H 2 S 2 is saturated with dry gaseous DCI at −78 °C. Then the mixture is allowed to warm to room temperature. Repeating this process of condensing and evaporating for three times leads to a 50% H,D exchange.