Inorg. Chem. **2009**, *48*, 2269−2272

Inorganic Chemistry

Article

Characterization of *cis*- and *trans*-HSSOH via Rotational Spectroscopy and Quantum-Chemical Calculations

Monika Koerber,[†] Oliver Baum,[†] Thomas F. Giesen,[*,†] Stephan Schlemmer,[*,†] Josef Hahn,[‡] and Jürgen Gauss[*,§]

I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln, Germany, Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany, and Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Received October 29, 2008

Assisted by high-level quantum-chemical calculations, the *cis* and *trans* conformers of HSSOH have been unambiguously identified among the products of the flash-vacuum pyrolysis of *tert*-butylthiosulfinic acid S-*tert*-butylester by using rotational spectroscopy.

Introduction

Besides the simple XH_2 compounds the elements oxygen and sulfur also form chain-like hydrogen compounds of the formula H_2X_n with n greater than 1. Those are in particular well characterized for sulfur for which sulfanes up to $n = 35$ have been identified using ^{1}H NMR spectroscopy.[1] Gas-phase investigations with a subsequent characterization of the molecular structure, however, have only been reported for H_2S_2 and H_2S_3.[2−6] For the latter, both the *cis* and *trans* form were identified using rotational spectroscopy,[4,5] and the structures could be deduced from the obtained spectroscopic parameters.[6] Less is known about the corresponding compounds of oxygen. While H_2O_2 is well characterized, H_2O_3 has only recently been investigated in detail, and the structure of the *trans* form has been determined.[7] Turning to the mixed chain-like hydrogen compounds of oxygen and sulfur, even less is known. Oxadisulfane (HSOH) has been identified among the products of the matrix reaction of oxygen atoms with H_2S, as well as in a mass spectrometric study of a mixture of H_2S and N_2O.[8,9] However, a thorough gas-phase characterization including determination of the structure has only recently been accomplished using rotational spectroscopy.[10−13] Some indication for the existence of 1-oxatrisulfane (HSSOH) has also been given in the literature, but the assignment of the corresponding IR band in ref 14 should be considered tentative. A conclusive proof for the existence of HSSOH is presented in the following where we report, assisted by high-level quantum-chemical calculations, on the detection and characterization of both the *cis* and *trans* form of HSSOH in the gas phase using rotational spectroscopy.

Results and Discussion

According to our quantum-chemical calculations, the *cis* and *trans* form of HSSOH are stable species with the *trans* form favored by about 2 kJ/mol. The structural parameters

---

* To whom correspondence should be addressed. E-mail: giesen@ph1.uni-koeln.de (T.F.G.), schlemmer@ph1.uni-koeln.de (S.S.), gauss@uni-mainz.de (J.G.).

[†] I. Physikalisches Institut, Universität zu Köln.

[‡] Institut für Anorganische Chemie, Universität zu Köln.

[§] Universität Mainz.

(1) Hahn, J. *Z. Naturforsch.* **1985**, *B40*, 263.
(2) Winnewisser, G.; Winnewisser, M.; Gordy, W. *J. Chem. Phys.* **1968**, *49*, 3465.
(3) Behrend, J.; Mittler, P.; Winnewisser, G.; Yamada, K. M. T. *J. Mol. Spectrosc.* **1991**, *150*, 99.
(4) Mauer, D.; Winnewisser, G.; Yamada, K. M. T.; Hahn, J.; Reinartz, K. *Z. Naturforsch.* **1988**, *A43*, 617.
(5) Liedtke, M.; Saleck, A. H.; Yamada, K. M. T.; Winnewisser, G.; Cremer, D.; Kraka, E.; Dolgner, A.; Hahn, J.; Dobos, A. *J. Phys. Chem.* **1993**, *97*, 11204.
(6) Liedtke, M.; Yamada, K. M. T.; Winnewisser, G.; Hahn, J. *J. Mol. Struct.* **1997**, *413−414*, 265.
(7) Suma, K.; Sumiyoshi, Y.; Endo, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14998.
(8) Smardzewski, R. R.; Lin, M. C. *J. Chem. Phys.* **1977**, *66*, 3197.
(9) Iraqi, M.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *221*, 359.
(10) Winnewisser, G.; Lewen, F.; Thorwirth, S.; Behnke, M.; Hahn, J.; Gauss, J.; Herbst, E. *Chem.−Eur. J.* **2003**, *9*, 5501.
(11) Behnke, M.; Suhr, J.; Thorwirth, S.; Lewen, F.; Lichau, H.; Hahn, J.; Gauss, J.; Yamada, K. M. T.; Winnewisser, G. *J. Mol. Spectrosc.* **2003**, *221*, 121.
(12) Brünken., S.; Behnke, M.; Thorwirth, S.; Yamada, K. M. T.; Giesen, T.; Lewen, F.; Hahn, J.; Winnewisser, G. *J. Mol. Struct.* **2005**, *742*, 237.
(13) Baum, O.; Esser, S.; Gierse, N.; Brünken, S.; Lewen, F.; Hahn, J.; Gauss, J.; Schlemmer, S.; Giesen, T. F. *J. Mol. Struct.* **2006**, *795*, 256.
(14) Königshofen, A.; Behnke, M.; Hoverath, M.; Hahn, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1779.

10.1021/ic802076f CCC: $40.75

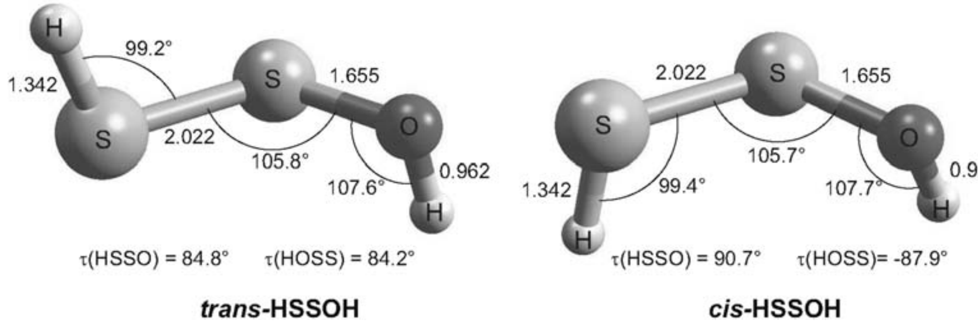


Figure 1. Structures of *cis*- and *trans*-HSSOH. Geometrical parameters (distances in Å, angles in degrees) from CCSD(T)/cc-pCVQZ calculations.

Table 1. Ground-State Rotational Parameters (in MHz) for *cis*- and *trans*-HSSOH

	cis-HSSOH		*trans*-HSSOH	
	experimental	calculated[a]	experimental	calculated[a]
A_0	21145.93422(66)	21120.1	21071.08204(75)	21045.7
B_0	4479.923012(205)	4470.9	4490.04249(34)	4481.7
C_0	3828.342693(207)	3821.0	3833.20651(35)	3826.3

[a] CCSD(T)/cc-pCVQZ calculations with vibrational corrections obtained at the MP2/cc-pVTZ level.

given in Figure 1 have been obtained in high-level coupled-cluster calculations at the CCSD(T) level[15] by employing a core-polarized quadruple-ζ (cc-pCVQZ) set from Dunning′s hierarchy of correlation-consistent basis sets.[16] These geometrical parameters can be used to make predictions for the rotational constants of both forms. The latter need to be corrected for vibrational corrections (obtained with second-order vibrational perturbation theory[17] and the required force fields computed using second-order Møller−Plesset (MP2) perturbation theory using the cc-pVTZ basis[16]) and the final values obtained in this way (A_0, B_0, and C_0) are given in Table 1. For calibration, the same calculations have been performed for H_2S_3, and these calculations provide a conservative error estimate for the predictions of the *A* constant of about 100 MHz and for the *B* and *C* constants of about 10 MHz.

The main problem in the experimental investigation of mixed hydrogen compounds of sulfur and oxygen is that there are no straightforward synthetic routes available. As shown for HSOH, pyrolytic reactions, that is, the thermal decomposition of di-*tert*-butyl sulfoxide (*t*Bu-S(O)-*t*Bu), offer a viable route to circumvent that problem. In the case of HSSOH, a similar strategy was already employed by Königshofen et al.[14] via the flash-vacuum pyrolysis (FVP) of *tert*-butylthio-sulfinic acid S-*tert*-butylester (*t*Bu-S(O)S-*t*Bu) (see Scheme 1). In the present work, we combine the FVP of *t*Bu-S(O)S-*t*Bu with a direct measurement of the rotational spectrum under flow conditions.

On the basis of the quantum-chemical predictions for the rotational constants (see Table 1), in the spectroscopic investigations a search for the rotational transitions of the *cis* isomer, that is, the isomer with the larger dipole moment, (*cis*: $\mu_a = 0.187$ D, $\mu_b = 0.538$ D, $\mu_c = 2.179$ D, *trans*: $\mu_a = 0.195$ D, $\mu_b = 0.539$ D, $\mu_c = 0.550$ D, CCSD(T)/cc-pCVQZ calculations) was carried out in the frequency range of 75 to 120 GHz. Figure 2 (lower part) shows rotational *b*- and *c*-type transitions of *cis*-HSSOH recorded applying frequency modulation.

A total of 214 assigned *Q*- as well as *R*-branch transitions of *cis*-HSSOH in the frequency range of 75−120 GHz have been analyzed using a least-squares fit to a Watson-type Hamiltonian in *S*-reduction employing Pickett′s program *spfit*.[18] The rotational parameters derived from the measurements are listed in Table 1 and show good agreement with the theoretical predictions. The search for the corresponding transitions of the *trans* isomer again exploited the quantum-chemical predictions of the relevant spectroscopic parameters which could be further improved by scaling. Figure 2 (upper part) shows a *b*- as well as a *c*-type rotational transition for this isomer again for the $^{r}Q_3$- branch, and in Table 1 we report the corresponding rotational constants obtained by fitting a total of 284 transitions. An unambiguous assignment of the spectra to the *cis* and *trans* isomer is possible based on the different ratios of the intensities for the *b*- and *c*-type transitions. While for the *cis* isomer the ratio of the corresponding dipole moment components, $|\mu_b/\mu_c|$, is 0.29(3) (theoretical value: 0.25), the same ratio for the *trans* isomer is 0.99(3) (theoretical value: 0.98). Analysis of the relative line intensities for the *trans* and *cis* isomers furthermore reveals, thereby employing the computed dipole components, that the *trans* isomer is more than two times more abundant among the pyrolysis products than the *cis* form. Assuming that this distribution is thermodynamically controlled, this indicates a higher stability for the *trans* isomer in agreement with quantum-chemical predictions.

Our assignment of the spectra to the *cis* and *trans* isomers of HSSOH is furthermore supported by the excellent agreement between experiment and theory for the corresponding differences in the rotational constants ($\Delta A_0 = A_0(cis) - A_0(trans)$, etc.). The experimental values are here 74.9, −10.1, and −4.9 MHz, while the theoretically predicted differences are 74.4, −10.8, and −5.3 MHz.

To get some insight into the mechanism of the pyrolysis of *t*Bu-S(O)S-*t*Bu, the temperature dependence of the product distribution has been investigated using rotational spectros-

---

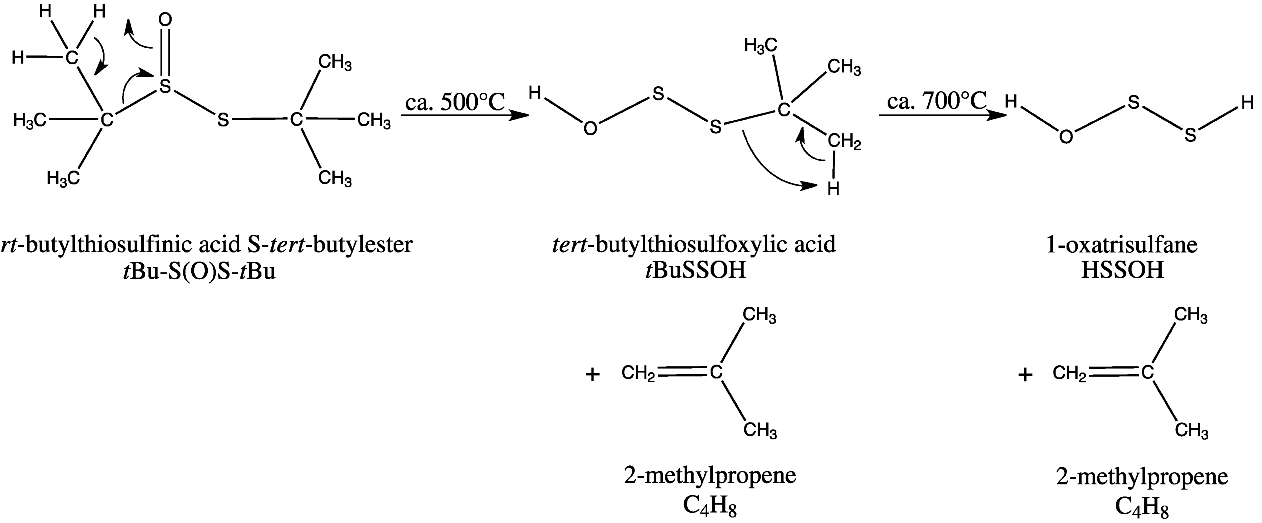
(15) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(16) (a) Dunning., T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (c) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572. (d) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(17) Stanton, J. F.; Gauss, J. *Int. Rev. Phys. Chem.* **2000**, *19*, 61.

(18) Pickett, H. M. *J. Mol. Spectrosc.* **1991**, *148*, 371.

Scheme 1. Reaction Scheme for the Production of HSSOH via Flash-Vacuum Pyrolysis of *tert*-Butylthiosulfinic Acid S-*tert*-butylester



copy. Figure 3 shows the intensities of rotational lines (relative to the corresponding maximum) for both forms of HSSOH, 2-methylpropene, and S_2O as a function of the pyrolysis temperature. For each molecule, the relative intensities of six rotational lines have been averaged. Figure 3 points to two issues: the first is that, based on the temperature dependence of the formation of 2-methylpropene, which cannot be fitted to a single exponential, it is obvious that the pyrolysis takes place as a two-step reaction as has been already assumed in our reaction scheme. Both forms of HSSOH are only formed in the second step which starts at temperatures above 500 °C. Below 500 °C, the pyrolysis apparently stops after the elimination of the first 2-methylpropene and leads to *t*Bu-S(O)SH. The second issue is that the amount of HSSOH produced does not monotonically increase with temperature but rather has a maximum between 650 and 700 °C indicating that HSSOH is unstable at higher temperature and decomposes. To determine the lifetime of HSSOH, the decay of the HSSOH signal has been monitored (shown in Figure 4 for the *cis*-HSSOH $16_{4,13} \leftarrow 16_{3,13}$ transition). For this purpose the input and the output valve of the absorption cell were closed simultaneously. Figure 4 reveals an exponential decay with a 1/e lifetime of ≈ 7 s under the conditions of the experiment. This finding is comparable to the lifetime of about 5 s found for HSOH.[10] Therefore, these two molecules are similarly stable.

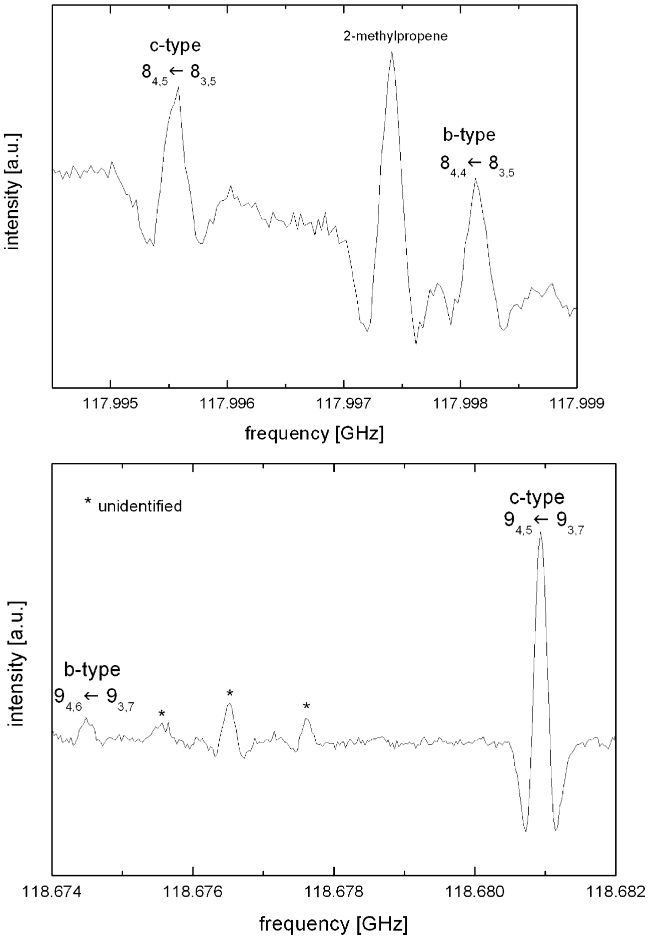


Figure 2. Rotational *b*- and *c*-type transitions belonging to the $^rQ_3$-branch of *cis*- (lower part) and *trans*-HSSOH (upper part), respectively. Unidentified lines are marked with an asterisk.

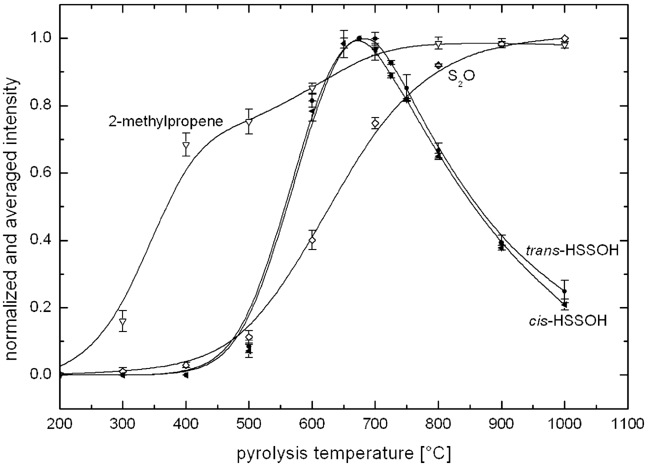


Figure 3. Temperature dependence of *t*Bu-S(O)S-*t*Bu pyrolysis product formation determined by rotational spectroscopy. For each molecule the intensities of six rotational lines have been recorded for different pyrolysis temperatures, normalized relative to the corresponding maximum and averaged.

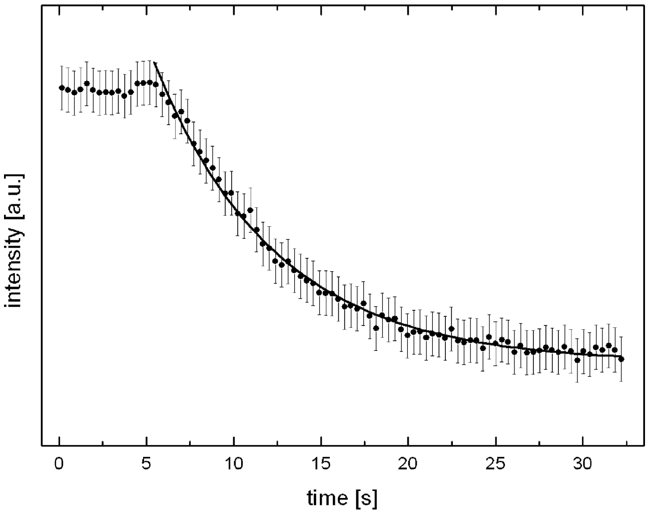


Figure 4. Experimental decay of the HSSOH signal (*cis*-HSSOH $16_{4,13} \leftarrow 16_{3,13}$ transition) after closing the input and the output valve of the absorption cell.

Conclusions

With HSSOH the first mixed chain-like oxygen−sulfur hydrogen compound in the series from HOOOH to HSSSH has been unequivocally detected and characterized using rotational spectroscopy. The determination of the geometrical structure of both forms, however, requires the investigation of other isotopic species of HSSOH. The detection of other mixed hydrogen compounds of oxygen and sulfur remains another challenge. Possible targets are here not only HSOSH, an energetically higher-lying isomer of HSSOH,[19] as well as HSOOH and HOSOH, but also compounds with branched structures. The main difficulty will be in particular to identify suitable techniques for the production of sufficiently large amounts of the compound of interest, while high-level quantum-chemical calculations can significantly facilitate the gas-phase characterization using rotational spectroscopy.

Experimental Section

HSSOH was produced *in situ* during the spectroscopic measurements by FVP of *t*Bu-S(O)S-*t*Bu as described in ref 14. A total gas pressure of 15 μbar was kept in the 4 m absorption cell providing a constant gas flow from the precursor sample. The pumping speed on the absorption cell was chosen to be about 2000 cm^3/s.

The rotational spectra have been measured in a range of 75 to 120 GHz employing an all solid-state spectrometer which uses the tripled output frequency of a synthesizer as radiation source and a Schottky diode as detector. To increase the sensitivity, the synthesizer signal was frequency modulated, and the output signal was detected in a second-derivative mode.

Quantum-Chemical Calculations

All reported quantum-chemical computations have been carried out with the CFOUR program package.[20]

Acknowledgment. This work has been supported in Köln by the European Commission (Contract No. MRTN-CT-2004-512202, “Quantitative Spectroscopy for Atmospheric and Astrophysical Research” (QUASAAR)) and in Mainz by the Deutsche Forschungsgemeinschaft, as well as the Fonds der Chemischen Industrie.

IC802076F

---

(19) Steudel, R.; Drozdova, Y.; Hertwig, R. H.; Koch, W. *J. Phys. Chem.* **1995**, *99*, 5319.

(20) A quantum chemical program package written by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D.; Metzroth, T.; O’Neill, D. P.; Price, D. R.; Prochnow, E.; Ruud, K.; Schiffmann, F.; Stopkowicz, S.; Tajti, A.; Varner, M. E.; Vázquez, J.; Wang, F.; Watts, J. D. and the integral packages MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P. R.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V.; van Wüllen, C. For the current version, see http://www.cfour.de.