Angewandte
International Edition Chemie

Small-Ring Systems

DOI: 10.1002/anie.201108982

Cyclic SiS_2: A New Perspective on the Walsh Rules**

Leonie Anna Mück, Valerio Lattanzi, Sven Thorwirth, Michael C. McCarthy, and Jürgen Gauss*

The global minimum of sixteen-electron triatomics is predicted to be linear by the Walsh rules.[1] Indeed, for molecules containing first-row elements (for example CO_2, N_2O) this is a well-established principle.[2] Regarding heavier elements, though, the situation is often more complicated. First, the bonding changes dramatically when going from the first to second or higher rows in the periodic table; for example, classical π bonds are not readily formed when heavy elements are involved.[3] This substantial difference in bonding is vividly demonstrated, for example, by the curious case of HPSi, which was recently shown to possess a nonlinear bridged structure.[4] Second, potential energy surfaces can become very flat and complex, even for simple molecules, as shown by the plethora of exotic structures that Si_2H_2 provides.[5] Thus, it is not surprising that exceptions to the Walsh rules have been encountered in the case of heavy-element compounds. As an example we mention the fourteen-electron triatomic Si_2S, for which the instability of Si–Si π bonds leads to a singlet ring with C_{2v} symmetry as the global minimum.[6]

In line with the Walsh rules, quantum-chemical calculations predict that for the sixteen-electron triatomics EE'_2 ($E = C, Si, Ge$; $E' = O, S$), the linear form is the global minimum but that non-linear isomers exist as local minima (Table 1). These isomers appear to be cyclic; that is, stabilized by a bond between the two chalcogen atoms. The energy difference between linear and cyclic isomers decreases upon inclusion of heavier elements, suggesting that doubly substituted species, such as SiS_2 and GeS_2, possess cyclic forms that are sufficiently stable to make them plausible candidates for laboratory detection. However, there is presently no experimental evidence for any of the cyclic isomers shown in Table 1. With respect to SiS_2, Davy and Holiday predicted an energy difference of 18.2 kcal mol^{-1} between the linear and cyclic form based on quantum-chemical calculations at the CCSD/TZ2P level of theory.[7] Experimentally, however, only the linear isomer has been comprehensively characterized by Schnöckel and Köppe by means of Raman spectroscopy.[8]

Table 1: Energy difference between the cyclic and linear form of EE'_2 and the geometrical parameters for the cyclic species.[a]

	CO_2	CS_2	SiO_2	SiS_2	GeO_2	GeS_2
$\Delta E^{[b]}$	143.1	69.4	59.2	19.3	33.8	6.53
$\alpha(E'\text{-}E\text{-}E')^{[b]}$	72.6	75.7	57.7	61.5	53.4	59.0
$r(E'{-}E)^{[b]}$	1.3193	1.7330	1.6541	2.1188	1.7702	2.2038
$r(E'{-}E')^{[b]}$	1.5625	2.1265	1.5971	2.1681	1.5916	2.1712

[a] $E = C,Si,Ge$; $E' = O,S$. Energy difference ΔE [kcal mol^{-1}], angles α [°], bond lengths r [Å]. [b] CCSD(T)/cc-pVQZ level of theory.

In the following, we present the first observation and characterization of cyclic SiS_2 as the result of a joint theoretical and experimental effort. As SiS_2 has a substantial dipole moment ($\mu_b \approx 1.4$ D), the method of choice for its detection in the gas phase is rotational spectroscopy. To guide such measurements, highly accurate theoretical predictions are indispensable.[9] For SiS_2, searches were based on quantum-chemical calculations using state-of-the-art coupled-cluster techniques[10] and additivity schemes[11] (see Experimental and Theoretical Methods) to obtain a best estimate structure and the corresponding rotational constants A_e, B_e, and C_e. The resulting rotational constants were further augmented by computed vibrational corrections[12] so as to provide the spectroscopically relevant constants A_0, B_0, and C_0 ($B_0 = B_e + \Delta B_{vib}$ with ΔB_{vib} as the zero-point vibrational correction).

A search for SiS_2 was undertaken using the discharge products of H_2S and SiH_4 by means of Fourier transform microwave spectroscopy using experimental conditions that optimize lines of previously detected Si_2S[6] (see Experimental and Theoretical Methods). With these settings, a ±0.5% search in frequency was performed around the predicted fundamental rotational transition $J = 1_{1,1}–0_{0,0}$ at 11513 MHz ($A_0 + C_0$). A candidate line only 3 MHz higher in frequency than the prediction was found that possesses all the required characteristics of SiS_2: The line is discharge-dependent and requires the presence of both silane and hydrogen sulfide, indicating that the carrier is most likely composed of both sulfur and silicon. There was no detectable Zeeman effect in the presence of a strong permanent magnet mounted close to the spectrometer (as expected for a closed-shell molecule), and no additional fine or hyperfine structure was observed. In total, nine rotational b-type transitions were assigned to cyclic SiS_2. To confirm line assignments, all of the measured transitions were linked to one another using double-reso-

---

[*] L. A. Mück, Prof. Dr. J. Gauss
Institut für Physikalische Chemie, Universität Mainz
55099 Mainz (Germany)
E-mail: mueckl@uni-mainz.de
Dr. V. Lattanzi, Dr. M. C. McCarthy
Harvard-Smithsonian Centre for Astrophysics
60 Garden Street, Cambridge, MA 02138 (USA)
and
School of Engineering and Applied Sciences, Harvard University
Cambridge, MA 02138 (USA)
Dr. S. Thorwirth
I. Physikalisches Institut, Universität zu Köln
50937 Köln (Germany)

[**] J.G. and S.T. gratefully acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG) through grants GA370/5-1 and TH1301/3-1. L.A.M. is supported by a fellowship of the Graduate School of Excellence "MAINZ". The work in Cambridge is supported by NSF grant no. CHE-1058063.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108982.

nance techniques.[13] Overwhelming evidence that the lines arise from SiS_2 and from no other molecule is provided by detection of selected rotational transitions of the rare isotopic species $^{29}SiS_2$ and $^{28}Si^{34}S^{32}S$ [despite the low natural abundance of ^{29}Si (4.7%) and ^{34}S (4.2%)] at exactly the shifted frequencies expected from the calculated molecular structure. Sample rotational spectra of cyclic SiS_2 are shown in Figure 1.

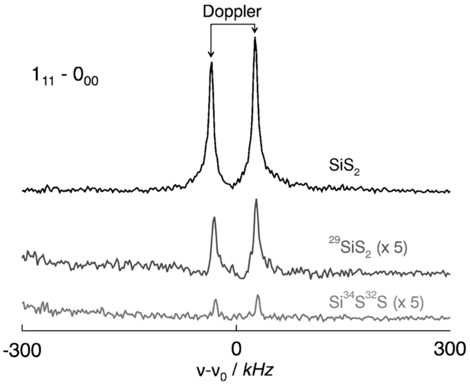

Figure 1. Fourier transform microwave spectra of the fundamental *b*-type rotational transition for the three isotopic species of SiS_2 discussed in the text. The instrumental lineshape results from the Doppler splitting of the Mach 2 supersonic molecular beam interacting with the two traveling waves that compose the standing wave of the confocal mode of the Fabry–Pérot cavity. Integration times were approximately 15 s for the normal species and 2 and 5 min for $Si^{34}S^{32}S$ and $^{29}SiS_2$, respectively.

Spectroscopic constants for all of the isotopic species were determined from a nonlinear least-squares analysis using a standard asymmetric-top Hamiltonian (see the Supporting Information for complete data sets). By a simultaneous fit of three rotational constants, *A*, *B*, and *C*, and four quartic centrifugal distortion constants, a root-mean-square (rms) accuracy of better than 1 kHz could be achieved for the parent isotopic species, which is well within the estimated experimental uncertainty of 3 kHz. For the rare isotopologues, only the three rotational constants were released in the fit and the centrifugal distortion parameters were kept fixed at their calculated values.

In Table 2 the experimentally determined rotational constants as well as their theoretical predictions for all isotopologues are given. The agreement between the theoretical predictions and the experimental values is very good, to about 0.25% and better.

As the rotational constants are inversely proportional to the moments of inertia about the three principal axes of the molecule, rotational spectroscopy is an ideal technique for the determination of the structural parameters. Determinations of bond lengths to an accuracy on the order of 0.010 Å[11a] by a least-squares minimization of the structural data with respect to the measured constants is normally possible. This accuracy can be improved to better than 0.001 Å if zero-point vibrational corrections are taken into account.[11b] The equilibrium geometry shown in Figure 2 was obtained in a least-squares fit with respect to the experimental moments of inertia after correcting for vibrational effects calculated quantum-chemically. The statistical uncertainties are much smaller than 0.0001 Å/0.01°, but the method is assumed to have intrinsic uncertainties of about 0.0005 Å.[9] The structure determined in this fashion closely agrees with the purely theoretical structure, which is assumed to have an accuracy of better than 0.001 Å.[14]

Table 2: Rotational constants of $^{28}Si^{32}S^{32}S$, $^{29}Si^{32}S^{32}S$, and $^{28}Si^{34}S^{32}S$.[a]

	Experiment	Calculated[b]
$^{28}Si^{32}S^{32}S$		
A_0	7876.6558(29)	7870.4
B_0	6788.5884(13)	6804.5
C_0	3639.88541(73)	3643.1
$^{29}Si^{32}S^{32}S$		
A_0	7687.6208(22)	7681.4
B_0	6788.7144(18)	6804.5
C_0	3598.8984(12)	3602.2
$^{28}Si^{34}S^{32}S$	Experiment	Calculated[b]
A_0	7817.6872(20)	7811.7
B_0	6577.9718(18)	6593.3
C_0	3566.1760(13)	3569.4

[a] Values given in MHz. 1σ uncertainties (in parentheses) are given in units of the last significant digit. [b] For the level of theory, see Experimental and Theoretical Methods.

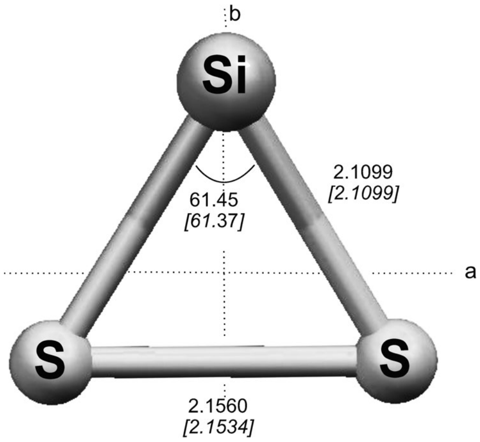

Figure 2. Semiexperimental equilibrium structure (bond lengths in Å, angles in °) of cyclic SiS_2 as obtained from the experimental rotational constants of SiS_2 and its isotopologues corrected for zero-point vibrational effects. Parameters obtained using coupled-cluster calculations (see Experimental and Theoretical Methods) are given in italics.

Two features play a key role in the stabilization of cyclic SiS_2. First, the tendency to form π bonds in the linear arrangement compared to CO_2 is diminished, primarily because hybridization between the s and p orbitals of the central atom E is not as pronounced.[3] The lack of hybridization allows for a smaller E′-E-E′ angle. Second, the strength of the single bond between the chalcogen atoms, the formation of which leads to the cyclic local minimum, is greater for sulfur than for oxygen.

This effect is also seen in the Walsh diagram of SiS_2, that is, in the plot of the orbital energies as a function of the E′-E-E′ angle (Figure 3). Upon bending, the π orbitals, which are

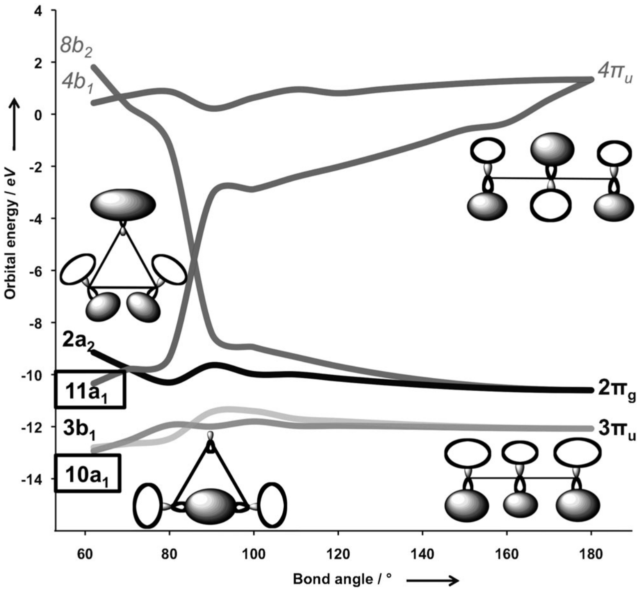

Figure 3. Angular dependence of orbital energies in SiS_2. Unoccupied orbitals are printed in italics. Important for the stabilization of cyclic SiS2 are the $10a_1$ and $11a_1$ orbitals; the qualitative sketch demonstrates bonding interactions between the sulfur atoms.

degenerate in the linear form, split. The transition from the linear to the cyclic form is accompanied by a change in orbital occupation, which occurs at an angle of approximately 90°. The Walsh diagram thus indicates a high transition barrier between the two isomers, which is essential for the kinetic stabilization of the cyclic form. The diagram shows only subtle deviations compared to CO_2. The first important difference is the extent to which the $11a_1$ orbital is lowered in energy upon decrease of the E′-E-E′ angle. Furthermore, the $10a_1$ orbital is destabilized with respect to the $3\pi_u$ orbital of the linear form in cyclic CO_2 while being stabilized in SiS_2. As the qualitative sketch shows, both the $11a_1$ and the $10a_1$ orbital include bonding interactions between the two sulfur atoms. Thus the major difference between CO_2 and SiS_2 is the degree of stabilization upon formation of the chalcogen–chalcogen bond. The S–S bond is only slightly longer (ca. 2.156 Å) than a usual S–S single bond (ca. 2.055 Å in case of H_2S_2[15]), which is a further indication for strong bonding interactions between the sulfur atoms.

It is not surprising that the S–S single bond is a pivotal feature in stabilizing cyclic SiS_2. The S–S single bond is among the most stable homonuclear single bonds in the periodic table, which is one reason for unusual structures found in the sulfur allotropes, including a large variety of S_n rings.[15,16] SiS_2 is an example of a class of sulfur compounds where this variety might even be extended by substitution of one sulfur atom with other second-row elements.[17] Apart from SiS_n, interesting examples include PS_n, H_2SiS_n, and HPS_n. The PS_n species are isoelectronic with the cations S_n^+, which have been detected by means of mass spectrometry up to $n=56$.[18] Along the same lines, SiS_n corresponds to the doubly charged cations S_n^{2+}, which to our knowledge are yet unknown experimentally. Compared to the homoatomic cations S_n^+ and S_n^{2+} the substituted species are often polar and thus are readily amenable to detection by rotational spectroscopy. Generally, the relationship between electronic and geometric structure in charged sulfur clusters might be studied in a more comprehensive manner by means of the substituted species ES_n (E = second-row element).

Apart from its theoretical interest, cyclic SiS_2 is also a plausible astronomical molecule, especially in light of the high abundance with which diatomic SiS is found in astronomical sources, such as the prototypical late-type star IRC + 10216.[19] From spectroscopic constants derived from the present work, the centimeter-wave spectrum of SiS_2 can now be predicted with sufficient accuracy so that astronomical searches can be undertaken with confidence with large radio telescopes, such as the Effelsberg 100 m or the Green Bank Telescope.

In conclusion, the first characterization of cyclic SiS_2 exemplifies the growing importance of theory in chemistry. Quantum-chemical calculations were not only essential for guiding the experiments: theoretical predictions on the stability of the compound preceded and motivated the experimental search. Furthermore, this study of SiS_2 provides a new perspective on the ubiquitous Walsh rules as it demonstrates the experimental accessibility of non-linear minima for sixteen-electron triatomics with heavy atoms.

Experimental and Theoretical Methods

Fourier transform microwave spectroscopy: All the measurements presented herein were performed using the spectrometer described in Ref. [20]. Cyclic SiS_2 was formed in the throat of a nozzle by applying a low-current dc discharge to a short gas pulse created by a fast mechanical valve. The gas phase molecular beam was formed by a mixture of silane (SiH_4) and hydrogen sulfide (H_2S) heavily diluted (0.1 %) in neon. To yield the strongest lines, the discharge potential was 1.2 kV and the flow rate (at standard temperature and pressure) was about 25 $cm^3 min^{-1}$ at the 6 Hz pulse rate of the nozzle with a stagnation pressure behind the valve of 2.5 kTorr.

Quantum-chemical calculations were performed using the CFOUR suite of programs.[21] The best-estimate structure for SiS_2 was obtained at a level denoted as fc-CCSD(T)/cc-pV∞Z + ΔT/cc-pVTZ + ΔQ/cc-pVDZ+Δcore/cc-pCV5Z[11] with the frozen-core CCSD(T) contribution extrapolated to the basis-set limit (indicated by cc-pV∞Z) and augmented by corrections for a full CC singles, doubles, triples (CCSDT) treatment (using the cc-pVTZ basis), for the effect of quadruple excitations at the CC singles, doubles, triples, quadruples (CCSDTQ) level (using the cc-pVDZ basis), and for core-valence correlation effects treated at the CCSD(T)/cc-pCV5Z level. Vibrational corrections for the rotational constants were obtained at the CCSD(T)/cc-pCVTZ level of theory using second-order vibrational perturbation theory.[9]

Received: December 20, 2011
Published online: February 28, 2012

Keywords: quantum-chemical calculations · rotational spectroscopy · silicon · sulfur · Walsh rules

---

[1] A. D. Walsh, *J. Chem. Soc.* **1953**, 2266–2288.
[2] W. Kutzelnigg in *Einführung in die Theoretische Chemie*, *Vol. 2*, Wiley-VCH, Weinheim, **1996**, pp. 10–20.
[3] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262–286; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272–295.

[4] V. Lattanzi, S. Thorwirth, D. T. Halfen, L. A. Mück, L. M. Ziurys, P. Thaddeus, J. Gauss, M. C. McCarthy, *Angew. Chem.* **2010**, *122*, 5795 – 5798; *Angew. Chem. Int. Ed.* **2010**, *49*, 5661 – 5664.

[5] M. Lein, A. Krapp, G. Frenking, *J. Am. Chem. Soc.* **2005**, *127*, 6290 – 6299.

[6] a) R. D. Davy, H. F. Schaefer III, *Chem. Phys. Lett.* **1995**, *255*, 171 – 178; b) M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, S. Thorwirth, J. Gauss, *J. Chem. Phys.* **2011**, *134*, 034306.

[7] a) R. D. Davy, S. Holiday, *Chem. Phys. Lett.* **1995**, *232*, 313 – 318; b) S. Wang, J. Feng, K. Yu, M. Cui, A. Ren, C. Sun, P. Liu, Z. Gao, F. Kong, *J. Mol. Struct. THEOCHEM* **2000**, *499*, 241 – 255.

[8] a) H. Schnöckel, R. Köppe, *J. Am. Chem. Soc.* **1989**, *111*, 4583 – 4586; b) M. Friesen, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1097 – 1100.

[9] C. Puzzarini, J. F. Stanton, J. Gauss, *Int. Rev. Phys. Chem.* **2000**, *29*, 273 – 367.

[10] I. Shavitt, R. J. Bartlett, *Many-Body Methods in Chemistry and Physics*: *MBPT and Coupled-Cluster Theory*, Cambridge University Press, Cambridge, **2009**.

[11] a) M. Heckert, M. Kállay, D. P. Tew, W. Klopper, J. Gauss, *J. Chem. Phys.* **2006**, *125*, 044108; b) C. Puzzarini, M. Heckert, J. Gauss, *J. Chem. Phys.* **2008**, *128*, 194108.

[12] I. M. Mills in K. N. Rao, C. W. Mathews, *Molecular Spectroscopy: Modern Research*, Academic Press, New York, **1972**.

[13] V. Lattanzi, P. Thaddeus, M. C. McCarthy, S. Thorwirth, *J. Chem. Phys.* **2010**, *133*, 194305.

[14] a) S. Thorwirth, L. A. Mück, J. Gauss, F. Tamassia, V. Lattanzi, M. C. McCarthy, *J. Phys. Chem. Lett.* **2011**, *2*, 1228 – 1231; b) S. Thorwirth, J. Gauss, M. C. McCarthy, F. Shindo, P. Thaddeus, *Chem. Commun.* **2008**, 5292 – 5294.

[15] a) R. Steudel, *Angew. Chem.* **1975**, *87*, 683 – 692; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 655 – 720; b) B. Meyer, *Chem. Rev.* **1976**, *76*, 367 – 388; c) J. Behrend, P. Mittler, G. Winnewisser, K. M. T. Yamada, *J. Mol. Spectrosc.* **1991**, *150*, 99 – 119.

[16] a) K. Isobe, Y. Ozawa, A. V. Demiguel, T. W. Zhao, K. M. Zhao, T. Nishioka, T. Ogura, T. Kitagawa, *Angew. Chem.* **1994**, *106*, 1934 – 1936; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1882 – 1883; b) S. Thorwirth, M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, H. Gupta, J. F. Stanton, *J. Chem. Phys.* **2005**, *123*, 054326; c) G. Ganteför, S. Hunsicker, R. O. Jones, *Chem. Phys. Lett.* **1995**, *236*, 43 – 39.

[17] Z. Mielke, G. D. Brabson, L. Andrews, *J. Phys. Chem.* **1991**, *95*, 75 – 79.

[18] a) T. P. Martin, *J. Chem. Phys.* **1984**, *81*, 4426 – 4432; b) A. K. Hearley, B. F. G. Johnson, J. S. McIndoe, D. G. Tuck, *Inorg. Chim. Acta* **2002**, *334*, 105 – 112.

[19] R. Mauersberger, U. Ott, C. Henkel, J. Cernicharo, R. Gallino, *Astron. Astrophys.* **2004**, *426*, 219 – 227.

[20] M. C. McCarthy, W. Chen, M. J. Travers, P. Thaddeus, *Astrophys. J. Suppl. Ser.* **2000**, *129*, 611 – 623.

[21] Additional Information can be found at http://www.cfour.de.