Spectroscopic Evidence for Pseudorotation of Seven-Membered Chalcogen Rings in Solution [1]

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Z. Naturforsch. **43b**, 245–247 (1988);
received October 7/October 12, 1987

⁷⁷Se NMR Spectra, Raman Spectra,
Elemental Sulfur, Selenium Sulfides

The ⁷⁷Se NMR spectrum of 1,2-Se₂S₅ exhibits one singlet at 1077.3 ppm indicating pseudorotation in solution; the same conclusion is reached from the solution Raman spectrum of S₇ showing characteristic line broadening compared to the solid state spectrum.

The homocyclic S₇ molecule is a constituent of gaseous and liquid elemental sulfur, of solidified liquid sulfur, of irradiated sulfur solutions, and of many chemically prepared sulfurs [2]. Evidence for pseudorotation of S₇ in the vapor phase at elevated temperatures has first been derived from the molar entropy calculated by statistical methods; the calculated and experimental values agree only when pseudorotation is postulated [3]. Later the height of the torsional barrier of SS bonds in sulfur rings has been estimated from the heat of formation of S₇ as ≤ 24 kJ/mol [4] which would result in pseudorotation at 20 °C. We now report direct evidence for pseudorotation of seven-membered chalcogen rings at room temperature by which process all ring atoms become equivalent within a certain time interval due to a simultaneous rotation (torsion) about several of the ring bonds.

The chair-like heterocycle 1,2-Se₂S₅ according to its Raman spectrum has two neighboring Se atoms in positions 4 and 6 of Fig. 1 resulting in non-equivalent selenium atoms [5]. We have now prepared chromatographically pure 1,2-Se₂S₅ from titanocene pentasulfide and Se₂Cl₂, and recorded the ⁷⁷Se NMR

Fig. 1. Molecular structure of the chalcogen rings S₇ [6a] and 1,2-Se₂S₅ [6b] and most probably also of 1,2-Se₂S₅ [5].

spectrum in CS₂ solution (natural abundance of ⁷⁷Se, Jeol FX90Q spectrometer, 17.03 MHz, 6 μs pulse width). After 2 h (ca. 20,000 scans) the spectrum showed only one peak at 1077.3 ppm [(CH₃)₂Se ext. standard]; see Fig. 2. No other signal was observed in the range 1235–65 ppm. We therefore assign the singlet at 1077.3 to 1,2-Se₂S₅. After 12 h (ca. 120,000 scans) three additional peaks at 784.5, 653.4, and 559.9 ppm with an approximate intensity ratio of 1:2:1 were observed (see Fig. 2). HPLC analysis of this solution showed the presence of SeS₅ and 1,2,3-Se₃S₅ in addition to 1,2-Se₂S₅ as the only species [5]. The six-membered ring SeS₅ previously not observed by NMR and the eight-membered ring 1,2,3-Se₃S₅ result from disproportionation of 1,2-Se₂S₅ according to equation (1) [5].

The ⁷⁷Se NMR spectrum of 1,2,3-Se₃S₅ is known [7] (signals at 654 and 561 ppm, intensity ratio 1:2); consequently we assign the peaks at 653.4 and 559.9 ppm to 1,2,3-Se₃S₅ and the remaining peak at 784.5 ppm to SeS₅. The intensity ratio fits equation (1).

The NMR signals of SeS₅ and 1,2-Se₂S₅ do not coincide with the signals of 14 eight-membered rings of type Se_nS_{8-n} (n = 1–8) which have been found in the region 560–729 ppm [7]. It should therefore be possible to detect six- and seven-membered selenium sulfide rings even in the presence of a large excess of Se_nS_{8-n} molecules as in extracts of quenched melts of the two elements.

Our spectra show that in solution the Se atoms of 1,2-Se₂S₅ are magnetically equivalent on the NMR time scale which can only be understood assuming pseudorotation. It seems very unlikely that in solution the Se atoms just move to the equivalent positions 6 and 7 (see Fig. 1) but after crystallization are found again only in positions 4 and 6. Therefore, we conclude that pseudorotation of the entire ring takes place thus averaging also the two different Se positions.

To further demonstrate the pseudorotation of seven-membered chalcogen rings at 20 °C we have recorded the Raman spectrum of S₇ dissolved in CS₂

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Fig. 2. ^{77}Se NMR spectra of freshly dissolved 1,2- Se_2S_5 in CS_2 (bottom) and of the same solution measured with data accumulation for 12 h and showing the decomposition products SeS_5 (784.5 ppm) and 1,2,3- Se_3S_5 (653.4 and 559.9 ppm) in addition (top). The two small satellites of the Se_2S_5 signal (see inset) have been identified as spinning side bands.

and compared it to the published solid state spectrum [3] (see Fig. 3). Pseudorotation is known to influence the half-widths of certain stretching modes dramatically due to coupling with low lying torsional modes and in particular due to the splitting of vibrational energy levels of the double minimum potential resulting in a number of allowed transitions of very similar energy (see the analyses for cyclopentane [8] and cycloheptane [9] and their derivatives). In solution the expected closely neighboring lines are not resolved and broad Raman signals will result. The spectra in Fig. 3 show that the half-width of the two SS stretching modes of S_7 near 360 and 400 cm^{-1} increases from 8 and 4 cm^{-1} , respectively, in solid S_7

to 24 and 31 cm^{-1} , respectively, for the CS_2 solution. On the other hand, the half-width of the totally symmetrical bending mode at 239 cm^{-1} although split into two lines in the solid state does not differ significantly in the two spectra indicating that neither temperature nor collisional (relaxation time) effects are responsible for the broad Raman lines in the solution spectrum. Pseudorotation therefore provides the best if not the only explanation.

Financial support by the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie is gratefully acknowledged.

Fig. 3. Raman spectra of crystalline S_7 at $-100\text{ }^{\circ}\text{C}$ (top, slit widths 1.9 cm^{-1}) and of S_7 dissolved in CS_2 at $20\text{ }^{\circ}\text{C}$ (bottom, slit widths 3.19 cm^{-1}) recorded using 647.1 nm laser excitation (ISA Raman spectrometer with double monochromator [10]).

- [1] Sulfur Compounds, Part 113; for Part 112 see R. Steudel, Th. Göbel, and G. Holdt, *Z. Naturforsch.* **43b**, 203 (1988).
- [2] R. Steudel, Elemental Sulfur and Related Homocyclic Compounds and Ions, in A. Müller and B. Krebs (eds): *Sulfur – The Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*, p. 3–37, Elsevier, Amsterdam (1984); *Top. Curr. Chem.* **102**, 149 (1982).
- [3] R. Steudel and F. Schuster, *J. Mol. Struct.* **44**, 149 (1978).
- [4] R. Steudel, *Z. Naturforsch.* **38b**, 543 (1983).
- [5] R. Steudel and E.-M. Strauss, *Angew. Chem.* **96**, 356 (1984); *Angew. Chem., Int. Ed. Engl.* **23**, 362 (1984).
- [6] a) R. Steudel, J. Steidel, J. Pickardt, F. Schuster, and R. Reinhardt, *Z. Naturforsch.* **35b**, 1378 (1980);
b) R. Steudel, M. Papavassiliou, E.-M. Strauss, and R. Laitinen, *Angew. Chem.* **98**, 81 (1986); *Angew. Chem., Int. Ed. Engl.* **25**, 99 (1986).
- [7] R. Laitinen and T. Pakkanen, *Inorg. Chem.* **26**, 2598 (1987); *J. Chem. Soc. Chem. Commun.* **1986**, 1381.
- [8] C. Rafilipomanana, D. Cavagnat, R. Cavagnat, J. C. Lassegues, and C. Biran, *J. Mol. Struct.* **127**, 283 (1985); C. Rafilipomanana, D. Cavagnat, and J. C. Lassegues, *J. Mol. Struct.* **129**, 215 (1985); T. Shimanouchi, *J. Chem. Phys.* **47**, 5018 (1967).
- [9] D. F. Bocian and H. L. Strauss, *J. Am. Chem. Soc.* **99**, 2866, 2876 (1977); D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss, *J. Am. Chem. Soc.* **97**, 687 (1975).
- [10] For details of the Raman equipment see R. Steudel and B. Holz, *Z. Naturforsch.* **42b**, 691 (1987).