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

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The ^{77}Se NMR spectrum of 1,2-Se$_2$S$_5$ exhibits one singlet at 1077.3 ppm indicating pseudorotation in solution; the same conclusion is reached from the solution Raman spectrum of S$_7$ showing characteristic line broadening compared to the solid state spectrum.

The homocyclic S$_7$ 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 S$_7$ 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 S$_7$ 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-Se$_2$S$_5$ 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-Se$_2$S$_5$ from titanocene pentasulfide and Se$_2$Cl$_2$, and recorded the ^{77}Se NMR
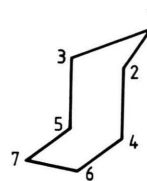
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Fig. 1. Molecular structure of the chalcogen rings S$_7$ [6a] and 1,2-Se$_5$S$_2$ [6b] and most probably also of 1,2-Se$_2$S$_5$ [5].

spectrum in CS$_2$ solution (natural abundance of ^{77}Se, Jeol FX 90 Q 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 [(CH$_3$)$_2$Se 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-Se$_2$S$_5$. 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 SeS$_5$ and 1,2,3-Se$_3$S$_5$ in addition to 1,2-Se$_2$S$_5$ as the only species [5]. The six-membered ring SeS$_5$ previously not observed by NMR and the eight-membered ring 1,2,3-Se$_3$S$_5$ result from disproportionation of 1,2-Se$_2$S$_5$ according to equation (1) [5].

$$2 \ 1,2\text{-Se}_2\text{S}_5 \rightarrow \text{SeS}_5 + 1,2,3\text{-Se}_3\text{S}_5 \tag{1}$$
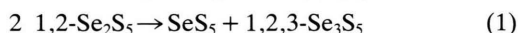
The ^{77}Se NMR spectrum of 1,2,3-Se$_3$S$_5$ is known [7] (signals at 654 and 561 ppm, intensity ratio 1:2); consequently we assign the peaks at 653.4 and 559.9 ppm to 1,2,3-Se$_3$S$_5$ and the remaining peak at 784.5 ppm to SeS$_5$. The intensity ratio fits equation (1).

The NMR signals of SeS$_5$ and 1,2-Se$_2$S$_5$ do not coincide with the signals of 14 eight-membered rings of type Se$_n$S$_{8-n}$ ($n = 1 \cdots 8$) 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$_n$S$_{8-n}$ molecules as in extracts of quenched melts of the two elements.

Our spectra show that in solution the Se atoms of 1,2-Se$_2$S$_5$ 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 S$_7$ dissolved in CS$_2$
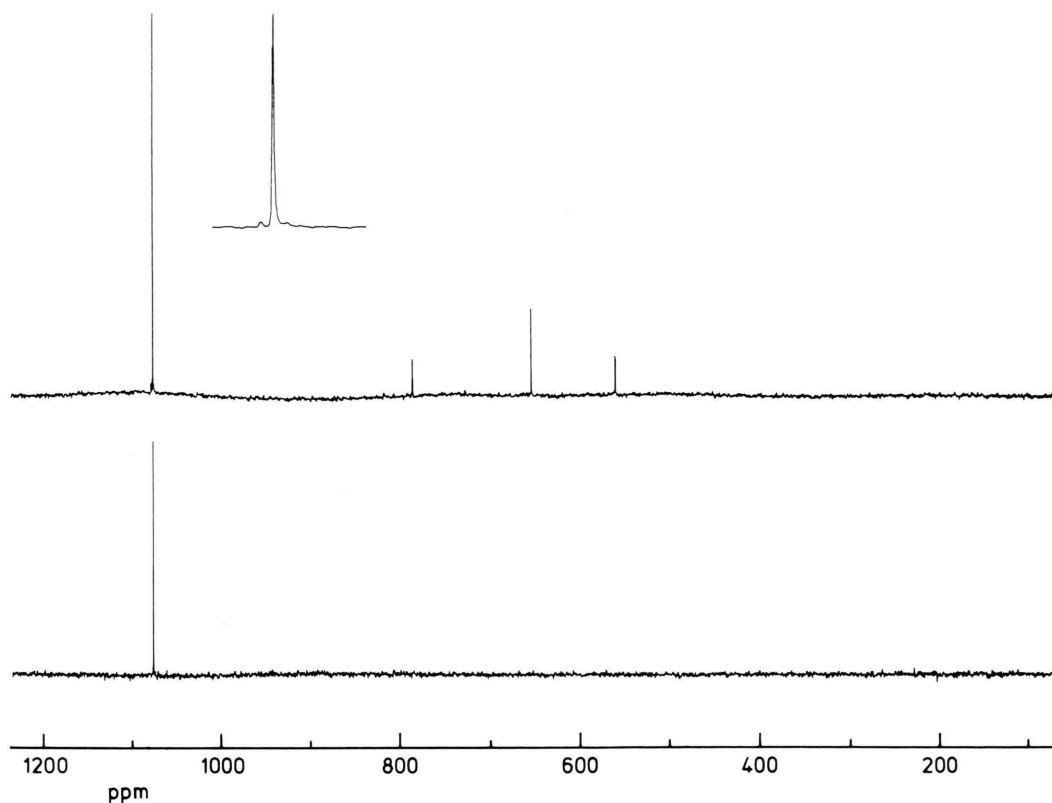
Fig. 2. ^{77}Se NMR spectra of freshly dissolved 1,2-Se_2S_5 in CS_2 (bottom) and of the same solution measured with data accumulation for 12 h and showing the decomposition products SeS_5 (784.5 ppm) and 1,2,3-Se_3S_5 (653.4 and 559.9 ppm) in addition (top). The two small satellites of the Se_2S_5 signal (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.
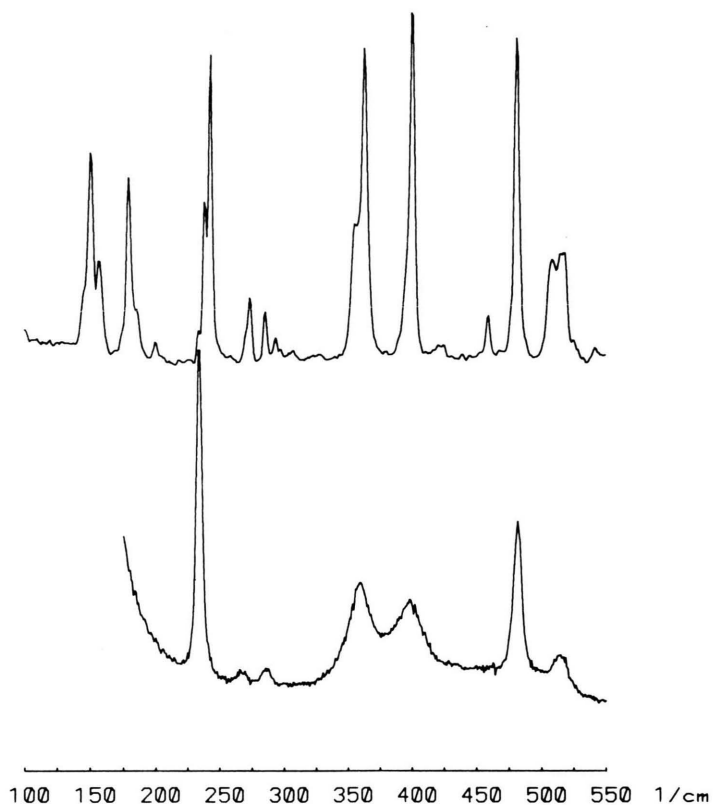
Fig. 3. Raman spectra of crystalline S_7 at $-100\,°C$ (top, slit widths $1.9\ cm^{-1}$) and of S_7 dissolved in CS_2 at $20\,°C$ (bottom, slit widths $3.19\ cm^{-1}$) recorded using $647.1\ nm$ laser excitation (ISA Raman spectrometer with double monochromator [10]).

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