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

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The †Se NMR spectrum of 1,2-Se۵۵۵۵ exhibits one
singlet at 1077.3 ppm indicating pseudorotation in
solution; the same conclusion is reached from the
solution Raman spectrum of S۷۷۷۷ showing characteristic
line broadening compared to the solid state spectrum.

The homocyclic S۷۷۷۷ 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 S۷۷۷۷ 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 S۷۷۷۷ 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-Se۵۵۵۵ 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-Se۵۵۵۵ from titanocene pentasulfide and Se۵۵۵۵ and recorded the †Se NMR
spectrum in CS۲ solution (natural abundance of †Se,
Jeol FX900 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 [(CH۵۵۵۵۵۵)۵۵۵۵ 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-Se۵۵۵۵. After 12 h (ca. 120,000 scans) three additional peaks at 784.5,
653.4, and 559.9 ppm with an approximate intensity
time scale which can only be understood assuming
pseudorotation. It seems very unlikely that in solu-
tion the Se atoms just move to the equivalent posi-
tions 6 and 7 (see Fig. 1) but after crystallization are
conclude that pseudorotation of the entire ring takes
place thus averaging also the two different Se posi-
tions.

Our spectra show that in solution the Se atoms of 1,2-Se۵۵۵۵ are magnetically equivalent on the NMR
time scale which can only be understood assuming pseudorotation. It seems very unlikely that in solu-
tion the Se atoms just move to the equivalent posi-
tions 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 posi-
tions.

To further demonstrate the pseudorotation of seven-membered chalcogen rings at 20 °C we have recorded the Raman spectrum of S۷۷۷۷ dissolved in CS۲

Fig. 1. Molecular structure of the chalcogen rings S۷۷۷۷ [6a] and 1,2-Se۵۵۵۵ [6b] and most probably also of 1,2-Se۵۵۵۵۵۵ [5].

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Fig. 2. $^{77}$Se NMR spectra of freshly dissolved 1,2-Se$_2$S$_5$ 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$_3$S$_5$ (653.4 and 559.9 ppm) in addition (top). The two small satellites of the Se$_2$S$_5$ 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.

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Fig. 3. Raman spectra of crystalline S\textsubscript{7} at -100 °C (top, slit widths 1.9 cm\textsuperscript{-1}) and of S\textsubscript{7} dissolved in CS\textsubscript{2} at 20 °C (bottom, slit widths 3.19 cm\textsuperscript{-1}) recorded using 647.1 nm laser excitation (ISA Raman spectrometer with double monochromator [10]).