Selenium Sulfide Ring Molecules

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The recent progress in the characterization of the complicated binary system of sulfur and selenium is reviewed. Synthetic methods have been developed to prepare stoichiometrically pure selenium sulfides. Raman spectroscopy and high-performance liquid chromatography have turned out to be efficient tools to characterize these stoichiometric compounds. The use of ^{77}Se NMR spectroscopy has enabled a real breakthrough in the identification of molecular species in the complicated mixtures formed in sulfur-selenium melts. *Ab initio* MO investigations have helped to understand the facile interconversion reactions between various heterocyclic selenium sulfides.

Sulfur and selenium both exhibit extensive allotropy involving a series of analogous homocyclic and chain-like molecules.[1-3] This chemical and structural similarity has led to investigations on the preparation, structure and composition of the binary system of the elements. The existence of mixed sulfur-selenium phases has been known for over a hundred years, but it is only with the advent of modern analytical techniques that the nature of these phases has become better under-

stood (for two recent reviews, see Refs. 4 and 5).

The first reliable indication that there are binary compounds in molten mixtures of sulfur and selenium as well as in the vapour phase over the melt came from vapour pressure measurements, though at the time, the composition and the structure of the compounds were left undiscussed.[6-10] Fergusson *et al.*[11] showed by X-ray powder diffraction that all sulfur-selenium phases over the whole composition range were isomor-

Table 1. The preparation of selenium sulfide ring molecules.

Method	Ref.
Molten mixtures of sulfur and selenium	4, 5
Reactions of SeO_2: (a) with H_2S	4, 5
(b) with $R-CS-NH-CH_2-C_6H_5$	13
Reactions of H_2Se: (a) with SO_2	14
(b) with S_nCl_2	15, 16
Reactions of H_2S_n: (a) with Se_2Cl_2	17
(b) with selenium bromides	18
Reaction of S_nCl_2/Se_2Cl_2 mixtures with KI	19
Reaction of $[Ti(C_5H_5)_2S_5]$ with Se_2Cl_2	20, 21
Reaction of $[Ti(C_5H_5)_2Se_5]$: (a) with SCl_2	22
(b) with S_2Cl_2	
(c) with Se_2Cl_2	
Irradiation of Se_8 in CS_2 solution	23
Electrolytic reduction of H_2SO_4/H_2SeO_4 mixtures	24

phous with one of the allotropes of either S_8 or Se_8, and deduced the existence of selenium sulfides of general formula Se_nS_{8-n} on the basis of their absorption spectra. The pioneering Raman work by Ward[12] also indicated the existence of various Se_nS_{8-n} molecules both in the solid and molten state. However, his detailed conclusions have recently been revised.[4]

It is now well established that heterocyclic selenium sulfides with covalent Se—S bonds are formed in molten mixtures of sulfur and selenium and by a variety of other synthetic routes. The most important methods of preparation are summarized in Table 1. The characterization of the reaction products has, however, turned out to be rather problematic, because in most cases it is not possible to study pure stoichiometric compounds since different Se_mS_n species of a given ring size tend to crystallize together, forming solid solutions of complicated molecular composition. All crystal structures reported thus far have been disordered, with sulfur and selenium statistically distributed over the atomic sites. Whereas it has been possible to deduce that the overall conformation of the selenium sulfide heterocycles is similar to those of homocyclic sulfur and selenium molecules of the same ring size, X-ray crystallography cannot be used for the identification of individual molecular species.[4,5]

In recent years there has been considerable progress in the chemistry of selenium sulfides. Pure stoichiometric compounds have been prepared and they have been characterized by vibrational analysis and high-performance liquid chromatography. Raman spectroscopy and HPLC have been shown to be convenient methods for gaining information on the composition of the selenium sulfide mixtures. The use of ^{77}Se NMR spectroscopy has enabled the identification of individual molecular species in the mixed crystalline phases obtained from sulfur-selenium melts. Furthermore, theoretical investigations have provided insight into the facile interconversion between the various molecular species which has been observed to take place in solution and in the molten state.

Pure stoichiometric selenium sulfides

Syntheses of pure stoichiometric selenium sulfides from sulfur-selenium melts have been claimed.[25,26] However, recent Raman spectro-

scopic studies[27-31] have shown that these phases must be mixtures of several molecular species. Indeed, the fractional crystallization studies of Ailwood and Fielding[32] indicate the isolation of stoichiometric species from the melts by extraction and recrystallization to be rather improbable. Schmidt and Wilhelm[16] have reported the synthesis of Se_2S_6 and Se_3S_5 by the reaction of S_2Cl_2 with H_2Se, but aside from the chemical composition there is no supporting evidence for the stoichiometry of the products, since they have not been structurally or spectroscopically characterized.

The first reliable reported preparation of pure stoichiometric selenium sulfides involved the use of bis(cyclopentadienyl)titanium pentasulfide $[Ti(C_5H_5)_2S_5]$. In 1968, Schmidt et al.[33] reported that this compound reacts with dichlorodisulfane to form cycloheptasulfur:

$$[Ti(C_5H_5)_2S_5] + S_2Cl_2$$
$$\rightarrow S_7 + [Ti(C_5H_5)_2Cl_2] \quad (1)$$
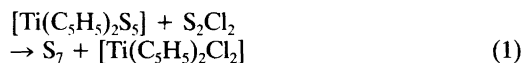
Varying the length of the sulfur chain in the chlorosulfane, several different homocyclic sulfur species have been synthesized.[1,2] The reaction of $[Ti(C_5H_5)_2S_5]$ with dichlorodiselane, Se_2Cl_2, was expected to be analogous and produce a seven-membered Se_2S_5 ring molecule in which the Se—Se bond of Se_2Cl_2 is retained:[20,21]

$$[Ti(C_5H_5)_2S_5] + Se_2Cl_2$$
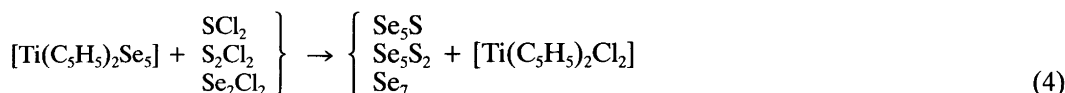$$\rightarrow Se_2S_5 + [Ti(C_5H_5)_2Cl_2] \quad (2)$$
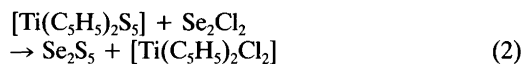
By following the reaction by reversed-phase HPLC using homocyclic sulfur species as reference materials (for HPLC studies of S_n species, see Ref. 1), it can, indeed, be observed that a seven-membered product is initially formed, but rapidly decomposes in the CS_2 solution at room temperature to give a six-membered and an eight-membered species:

$$2\ Se_2S_5 \rightarrow Se_3S_5 + SeS_5 \quad (3)$$

All three selenium sulfides could be isolated by crystallization, and their purity was controlled by HPLC. The chromatograms indicated that the six- and seven-membered products each contained only one component.[21] The chromatogram of the eight-membered product showed, in addition to one main product, traces of other eight-

membered species.[20] The identification and characterization of the molecular species is discussed below.

The analogous reactions of bis(cyclopentadienyl)titanium pentaselenide with SCl_2, S_2Cl_2 or Se_2Cl_2 also resulted in the isolation of pure stoichiometric products, as judged from the analytical and HPLC data.[22] The S—S bond in S_2Cl_2 and the Se—Se bond in Se_2Cl_2 can also here be expected to survive the reaction without cleavage [eqn. (4)].

similar to those of the homocyclic sulfur[34-38] and selenium[39-42] species of corresponding ring size (see Fig. 1). This is exemplified in Table 2 by a comparison of the torsion angles in Se_5S_2 with the corresponding angles in S_7. The case of the seven-membered molecules is interesting, since the unique torsion angle of $0°$ leads to significant perturbations in the bond lengths throughout the molecule.

Raman spectroscopy has been shown to be a powerful tool for the study of homocyclic sulfur

$$[Ti(C_5H_5)_2Se_5] + \left.\begin{array}{c} SCl_2 \\ S_2Cl_2 \\ Se_2Cl_2 \end{array}\right\} \rightarrow \left\{\begin{array}{l} Se_5S \\ Se_5S_2 \\ Se_7 \end{array}\right. + [Ti(C_5H_5)_2Cl_2] \tag{4}$$

Surprisingly, the selenium-rich six- and seven-membered species Se_5S, Se_5S_2 and Se_7 turned out to be much more stable than the sulfur-rich species S_7, Se_2S_5 or SeS_5, and could be stored in the solid state at room temperature for days without appreciable decomposition. In CS_2 solution, however, also they decompose producing various heterocyclic selenium sulfides.

All the products from the reactions mentioned above were characterized by X-ray crystallography and Raman spectroscopy. As expected, all the crystal structures were disordered.[20-22] It was, however, shown that the overall conformations of the Se_nS_{6-n}, Se_nS_{7-n} and Se_nS_{8-n} rings are

molecules, S_n $(n = 6-20)$,[1] as well as of homocyclic selenium molecules, Se_n $(n = 6,8)$.[3] The spectra of the different species are very characteristic and reflect not only their molecular size and symmetry but also the bond distance pattern.[43,44] It is possible to detect discrete molecular entities even in mixtures of several homologues. It was therefore expected that the identification of the selenium sulfides formed in the reactions shown in eqns. (2)–(4) could also be based on an assignment of their low-temperature Raman spectra.

The fundamental vibrations of various six- and seven-membered,[45] as well as eight-membered selenium sulfides[30] have been calculated using the extended Urey-Bradley force field which has been shown suitable for several homocyclic sul-
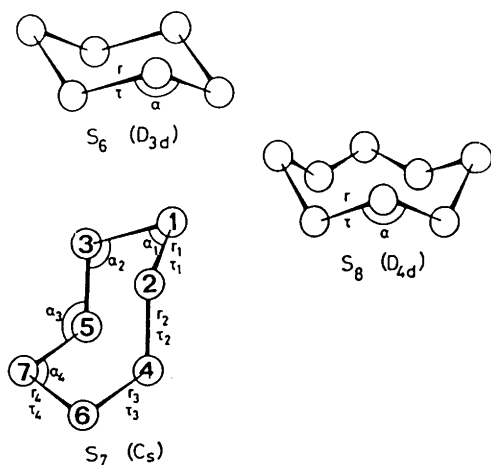

Fig. 1. The molecular structures of S_6, S_7 and S_8, indicating the numbering of the atoms in the seven-membered molecule.

Table 2. Comparison of torsion angles (°) in $1,2-Se_5S_2$ and $\gamma-S_7$.

Torsion angle[a]	$\gamma-S_7$[b]	$1,2-Se_5S_2$[c]
3−1−2−4	−77.73(7)	−80.1(4)
2−1−3−5	75.60(6)	78.0(4)
1−2−4−6	108.78(6)	109.4(3)
1−3−5−7	−106.78(6)	−109.0(3)
2−4−6−7	−82.48(6)	−81.3(2)
3−5−7−6	83.97(6)	85.3(2)
4−6−7−5	−0.43(7)	−1.5(2)

[a]For numbering of the atoms in the seven-membered ring molecule, see Fig. 1. [b]From Ref. 35. [c]From Ref. 22. The occupational factors for selenium (mol %) in the atomic sites are as follows: sites 1 and 2, 25 %; sites 3 and 4, 85 %; sites 5 and 7, 100 %; site 6, 90 %.
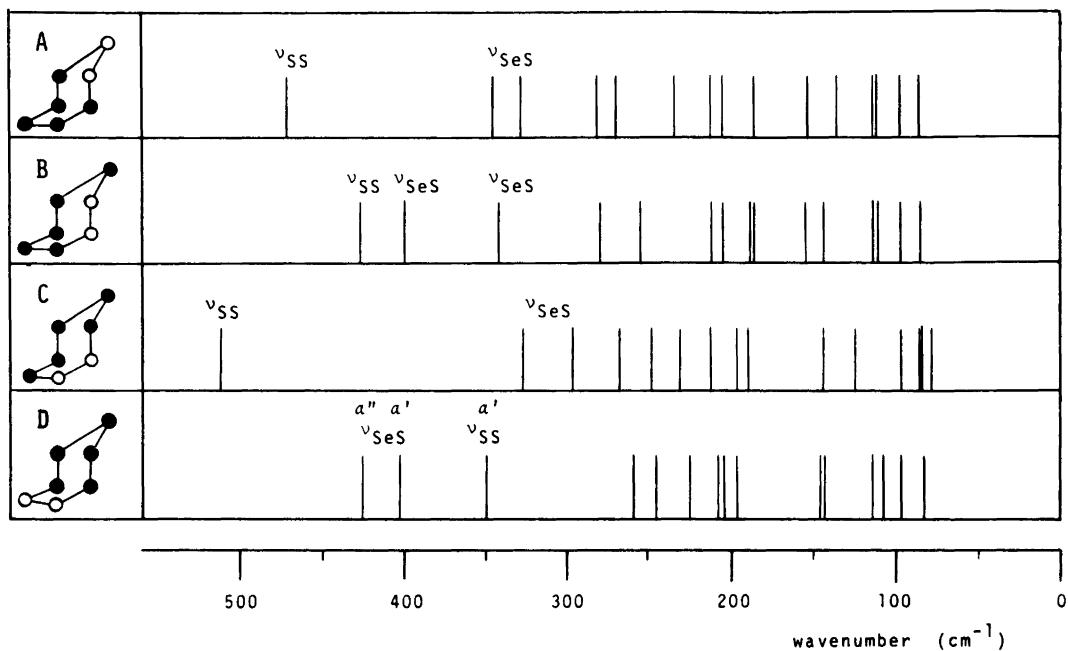
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Fig. 2. The fundamental vibrations of the various conformational isomers of 1,2−Se_5S_2 as calculated using the Urey-Bradley force field.[45]

fur[46-48] and selenium[49,50] molecules, as well as for heterocyclic S_7NH,[51] $S_4(NH)_4$,[52] S_8O[53] and S_4N_4.[54] The force constants and structural parameters for Se_nS_{6-n}, Se_nS_{7-n} and Se_nS_{8-n} were adapted from analogous sulfur and selenium molecules. The force field calculations indicated that in general, the stretching vibrations of the various selenium sulfides differ sufficiently to allow the identification of the species. Because of the bond length

alternation in the seven-membered ring molecules, the stretching modes provide a particularly sensitive test not only for the molecular species and structural isomers, but also for the particular conformational isomer in the solid state. This is exemplified in Fig. 2 by the calculated fundamental vibrations of the four conformational isomers of Se_5S_2.
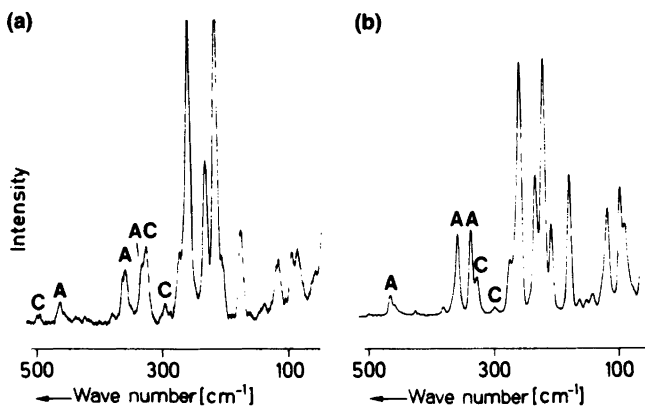
The comparison of the calculated wavenum-

Fig. 3. The Raman spectrum of 1,2−Se_5S_2: (a) The sample was crystallized from CS_2 at −50 °C. (b) The sample was warmed to −10 °C. Subsequent heating did not result in any further changes in the spectrum. Both spectra were recorded at −100 °C (Ref. 22).

bers with those observed in the Raman spectra of the three crystalline products from the reaction of [Ti(C$_5$H$_5$)$_2$S$_5$] with Se$_2$Cl$_2$ enabled complete assignments of the Raman spectra to be made on the basis of the structures SeS$_5$, 1,2-Se$_2$S$_5$ and 1,2,3-Se$_3$S$_5$.[20,45] Least-squares fitting of the calculated wavenumbers to those observed yielded values for the Urey-Bradley and the valence force constants which are reasonable by comparison with the corresponding force constants for S$_n$ (n = 6–8)[46,48] and for Se$_n$ (n = 6,8).[49,50]

It is interesting to note that the Se-Se bond in solid 1,2-Se$_2$S$_5$ is in the position adjacent to the bond having a torsion angle of 0°, and is thus the shortest possible Se-Se bond in the molecule (cf. S$_7$[35]).

The calculated vibrational wavenumbers for Se$_5$S and Se$_7$ are also in good agreement with those observed in the Raman spectra.[22,45] While the Raman spectrum of Se$_5$S$_2$ (see Fig. 3) can be assigned assuming a single chemical species, it cannot be interpreted in terms of a single conformation. Comparing the calculated wavenumbers

for the isomers A–D (see Fig. 2) with the observed Raman spectrum it was concluded that the Se$_5$S$_2$ crystals contained mainly isomers A and C, with only traces of isomers B and D present.[22] The freshly precipitated crystals at low temperature seem to contain roughly equal amounts of isomers A and C, but when the temperature is allowed to rise or the crystallization is carried out at higher temperatures, the proportion of A is increased, being ca. 80% at 20°C (see Fig. 3). The disorder in the structure determined by X-ray crystallography at 20°C supports the conclusions presented above (see Table 2).[22] The atomic positions 5 and 7 (for the numbering of atoms, see Fig. 1) are occupied only by selenium, ruling out the isomer D. Taking into account that there are two crystallographically different ways to place isomer A in the lattice, the observed disorder indicates that the abundance of isomer A is ca. 85% and that of C ca. 15%.

The reaction of chlorosulfanes with hydrogen selenide produces a simple mixture, the main components of which have been identified as S$_8$

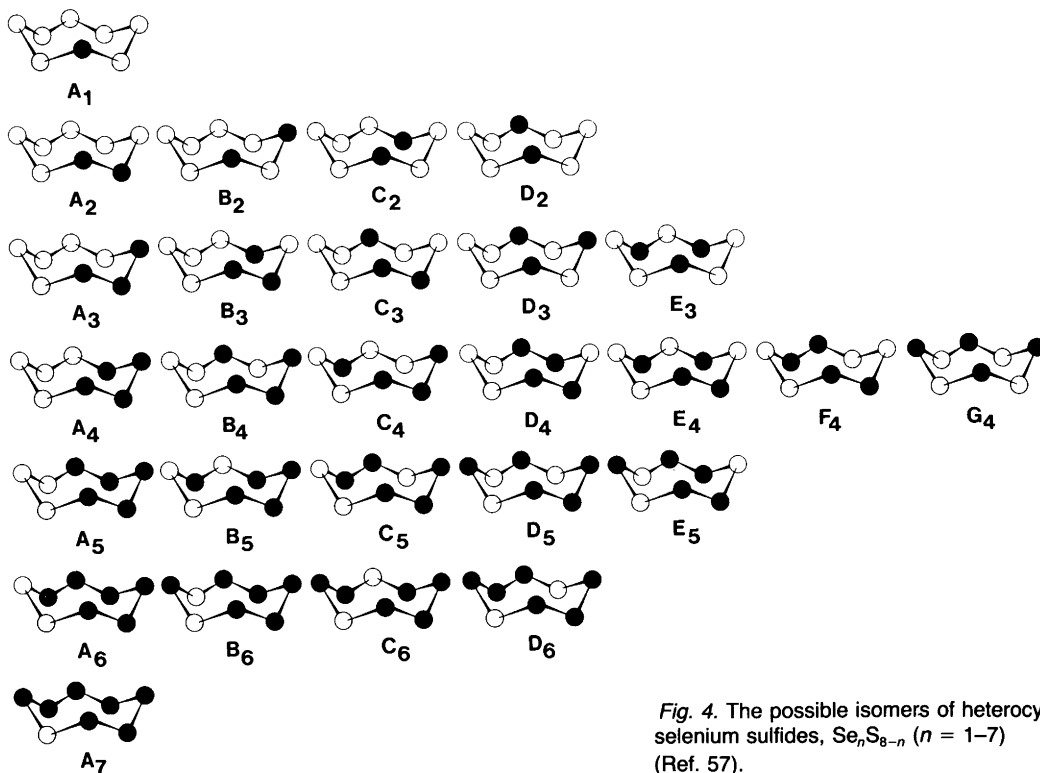Fig. 4. The possible isomers of heterocyclic selenium sulfides, Se$_n$S$_{8-n}$ (n = 1–7) (Ref. 57).

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and SeS_7 by vibrational analysis.[3,55] The force constants calculated for SeS_7 by use of the GVFF[55] are in general agreement with the corresponding force constants calculated for $1,2,3\text{-}Se_3S_5$ species using the MUBFF.[20]

The characterization of selenium sulfide mixtures

Most of the preparative procedures listed in Table 1 produce mixtures of various selenium sulfides. The eight-membered Se_nS_{8-n} ring molecules are the most abundant and most stable species found in these mixtures, though the HPLC investigations indicate that in CS_2 solutions they exist in equilibrium with small amounts of the six- and seven-membered species.[56] All the possible eight-membered selenium sulfides are shown in Fig. 4.

Raman spectroscopy and HPLC have turned out to be useful in the characterization of selenium sulfide mixtures. With the discovery of pure stoichiometric compounds, many of the conclusions based on these investigations have been verified.

Force constant calculations for selected Se_nS_{8-n} species[30,55] have established that the Se-S stretching vibration in the region 400–320 cm^{-1} is very sensitive to the chemical environment in the molecule. In the case of an isolated selenium atom (the structural unit -S-Se-S-) the vibrational coupling causes a large splitting between the symmetric and asymmetric stretching vibrations (the Raman lines are expected in the regions 400–380 and 340–320 cm^{-1}). If there are two or more adjacent selenium atoms (the structural unit -S-Se_n-S-), the Se-S bonds are further separated and the vibrational coupling is much smaller. The symmetric and asymmetric stretching modes are then expected to occur near each other, at around 360 cm^{-1}. It has been concluded from an examination of the Raman spectra of the crystalline phases prepared from molten mixtures of sulfur and selenium (see Fig. 5) that while both types of structural units may be present in these mixtures, molecules containing adjacent selenium atoms seem to be more abundant.[3,30] This finds support from the fact that Raman lines are observed in the Se-Se stretching region of ca. 260 cm^{-1} even when the selenium content of the mixtures is very low.[27-30,58] In addition to selenium
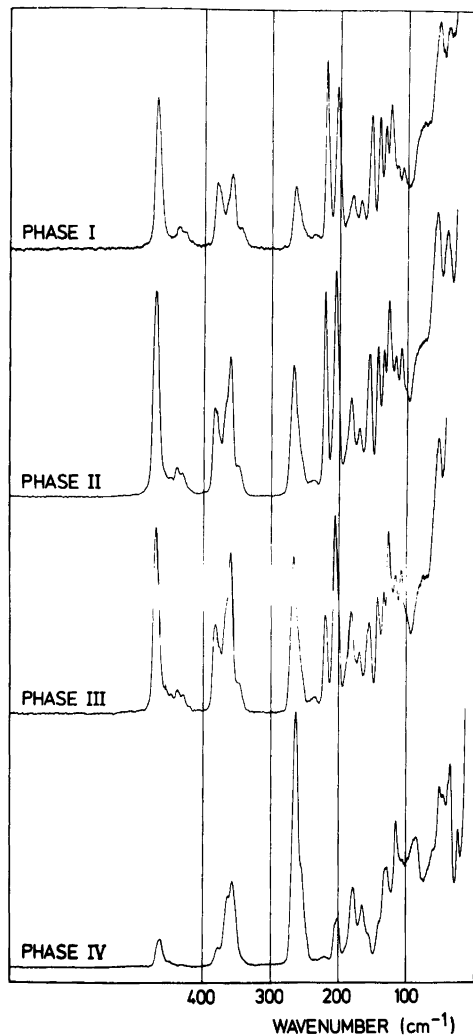

Fig. 5. The Raman spectra of four crystalline sulfur-selenium phases recorded at −100 °C. The phases were prepared from molten mixtures of sulfur and selenium with the following initial compositions (mol % Se): phase I, 12.5; phase II, 25.0; phase III, 37.5; phase IV, 50.0 (Ref. 30).

sulfides, cyclooctasulfur and -selenium were also detected in some samples.[30]

Steudel and Strauss[19] have investigated by HPLC a mixture of eight-membered selenium sulfide ring molecules which are formed in the reaction of dichlorosulfane and dichlorodiselane with potassium iodide in CS_2 solution. They in-

terpreted the eight peaks observed in the chromatogram in terms of the seven possible Se_nS_{8-n} ($n = 1$–8) molecules in which all selenium atoms are adjacent to each other (A_{1-7}; see Fig. 4), and Se_8. The interpretation is based on the relationship between the retention time and the number of selenium atoms in the molecule.[3,19] It was observed that S_8 was not formed in the reaction.

The use of ^{77}Se NMR spectroscopy has enabled a real breakthrough in the identification of discrete selenium sulfides in the complicated mixtures formed in sulfur-selenium melts.[57,59] The samples have been prepared by quenching melts with up to 50 mol % of selenium at liquid nitrogen temperature, crystallizing the resulting amorphous mass from carbon disulfide, and redissolv-
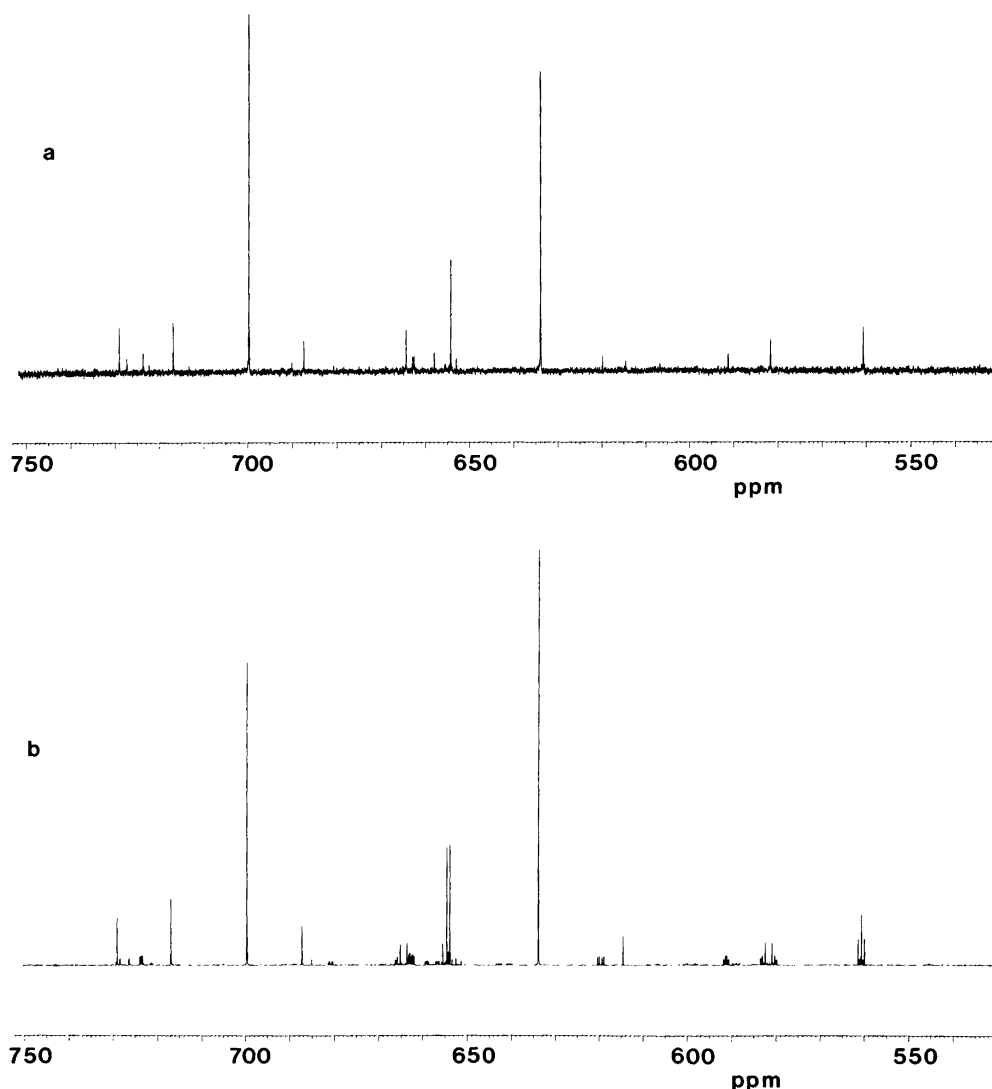

Fig. 6. The ^{77}Se NMR spectra of two samples prepared from molten mixtures of sulfur and selenium with an initial composition of 30 mol % of selenium: (a) A sample with natural abundance selenium. (b) A sample enriched with [77]Se (94 %). The samples were prepared by quenching the melts, crystallizing the amorphous mass from CS_2, and redissolving the recrystallized material in CS_2. The spectra were recorded on the solutions thus obtained (Ref. 57).

ing the orange-red crystals in CS_2. The ^{77}Se NMR spectra were recorded on solutions thus obtained.

The ^{77}Se isotope has a nuclear spin of 1/2, natural abundance of 7.58 % and a sensitivity of 2.98 relative to ^{13}C. This renders the acquisition of the spectra with modern FT spectrometers straightforward. The power of ^{77}Se NMR spectroscopy in the characterization of organic polyselenides,[60] and of some selenium-containing mono- and polycyclic cations[61-66] as well as of some Zintl-anions,[67] has also been demonstrated.

Fig. 6 shows two NMR spectra for samples of the same melt composition. The sample giving the spectrum shown in Fig. 6a was prepared using natural-abundance selenium. Due to the low abundance of the ^{77}Se isotope, the ^{77}Se-^{77}Se coupling is observed only as small satellites. The full coupling information is obtained when using selenium enriched with ^{77}Se (94 %; see Fig. 6b). The identification of the molecular species has been based on the combined information obtained from these two spectra, taking into account both the coupling data and the trends in the spectral parameters.[57,59] Details of the splitting patterns and the interpretation of the spectrum shown in Fig. 6b are given in Fig. 7.

The selenium sulfides identified on the basis of the NMR spectra are listed in Table 3. SeS_7 and $1,2-Se_2S_6$ are the main components in all samples produced with up to 50 mol % of selenium in the original melts. Two trends are apparent: Firstly,
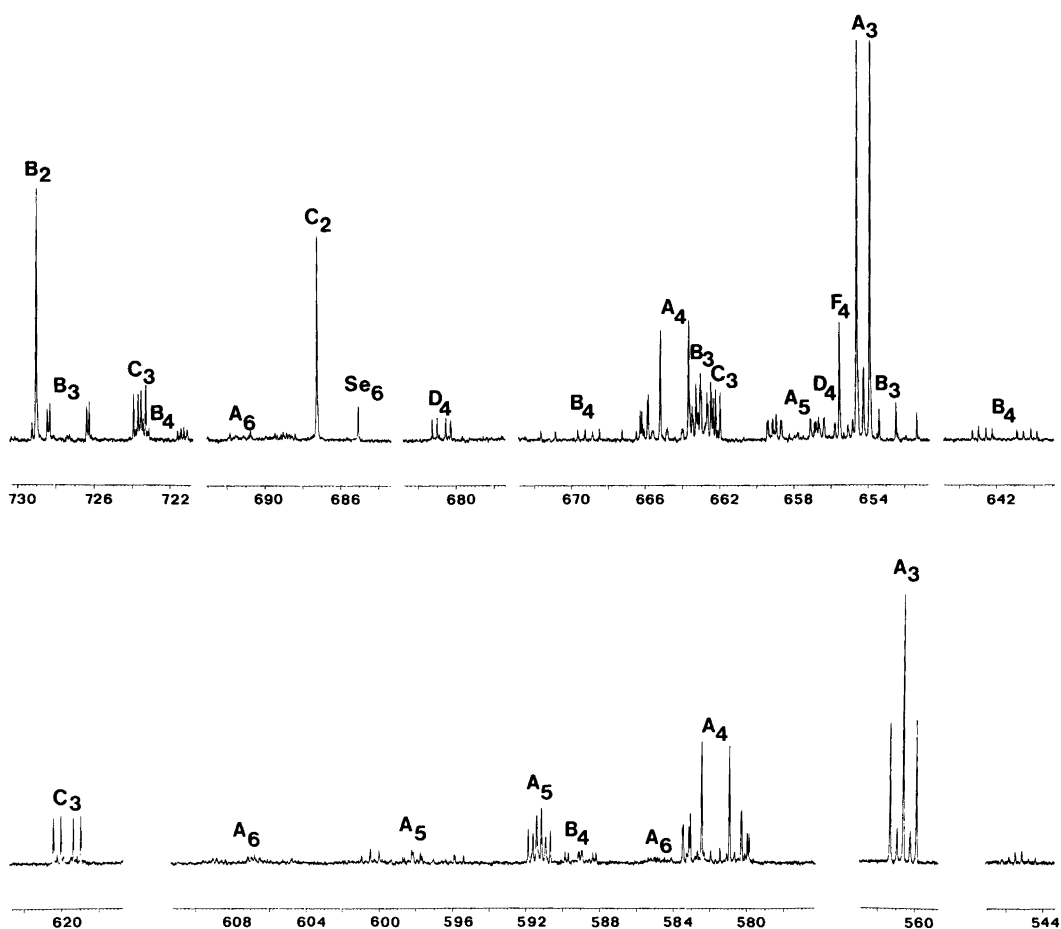

Fig. 7. Interpretation of the ^{77}Se NMR spectrum of the ^{77}Se-enriched sample (see Figs. 4 and 6b) (Ref. 57).

Table 3. Selenium sulfides identified by ^{77}Se NMR spectroscopy in CS_2 solutions of the crystalline phases obtained from sulfur-selenium melts.[57]

SeS$_7$ 1,2$-$Se$_2$S$_6$	1,3$-$Se$_2$S$_6$	1,4$-$Se$_2$S$_6$	1,5$-$Se$_2$S$_6$
1,2,3$-$Se$_3$S$_5$	1,2,4$-$Se$_3$S$_5$	1,2,5$-$Se$_3$S$_5$	
1,2,3,4$-$Se$_4$S$_4$	1,2,3,5$-$Se$_4$S$_4$	1,2,4,5$-$Se$_4$S$_4$	1,2,5,6$-$Se$_4$S$_4$
1,2,3$-$Se$_5$S$_3$			
1,2$-$Se$_6$S$_2$			
Se$_8$ (Se$_6$)			

the concentration of the molecular species in CS_2 decreases expectedly as the selenium content of the molecules increases. Secondly, for a given chemical composition, the isomer having all selenium atoms adjacent to each other is most abundant. This is in agreement with the Raman spectroscopic[30] and HPLC[19] studies. In addition to the components listed in Table 3, all mixtures contain substantial amounts of S_8 as indicated by the Raman spectra of analogous samples.[29,30]

The interpretation of the NMR spectra of the selenium sulfide mixtures can be verified as follows: The coupling constants $^1J_{SeSe}$ and $^2J_{SeSe}$ are in good agreement with those obtained for organic polyselenides.[60] Also, the chemical shifts of the two NMR signals for 1,2,3-Se$_3$S$_5$,[59] which has been prepared by the reaction of $[Ti(C_5H_5)_2S_5]$ with Se_2Cl_2 and characterized by vibrational analysis,[20] are in agreement with the interpretation shown in Fig. 7. Furthermore, the spectral parameters show internally consistent trends which can be correlated with the molecular structures.[57]

The electronic structures and properties of the chalcogen-chalcogen bonds

Whereas a multitude of theoretical investigations on the electronic structures and properties of the S-S bonds in various chemical environments have been reported (for short summaries of recent work, see Refs. 68–72), the literature concerning Se-S and Se-Se bonds is rather sparse. Some semi-empirical calculations have been made on Se_8,[73,74] Se_6[75] and Se_nS_{8-n}[74] but owing to the computational limitations, the few existing *ab initio* studies have been mainly restricted to the hydrides HSe_mS_nH(with $m,n = 0–3$) as model compounds.[70,71,76] Comparative *ab initio* calculations

on CH_3SSCH_3 and $CH_3SeSeCH_3$ have also been reported.[77]

All the theoretical investigations reported so far have shown that the electronic structures of the S-S, Se-S and Se-Se bonds are remarkably similar (for an example on the comparison of the different $HSe_nS_{3-n}H$ species, see Fig. 8). This is also indicated by a comparison of the electronic absorption spectra of S_8 and Se_nS_{8-n}.[74] In the last case the author erroneously interprets the spectrum of the selenium sulfide phase assuming the molecular species to be 1,3,5,7-Se$_4$S$_4$ on the basis of an earlier Raman spectroscopic study by himself.[26] However, as pointed out by Eysel and Sunder,[28] the Raman spectrum in question shows the presence of S-S and Se-Se as well as Se-S bonds. Furthermore, the method of preparation from the equimolar melt results in the formation of a mixture of eight-membered selenium sulfide ring molecules, as discussed above. The recorded spectrum therefore indicates the similarities in the electronic structures of the various Se_nS_{8-n} species rather than the identity of any specified molecule.

The barriers to internal rotation around the three different chalcogen-chalcogen bonds are rather similar.[70] Also, the bond lengths vary in a similar fashion as a function of the torsion angle. The experimental support for these conclusions comes from a comparison of the crystal structures of 1,2-Se$_5$S$_2$[15] and S_7.[35] As discussed above (see Table 2), these molecules show similar conformations with identical alternations in the bond lengths. This has also been demonstrated by a normal coordinate treatment of 1,2-Se$_2$S$_5$.[45] This effect has been shown theoretically in the case of HSSSSH.[78] The cause of the observed alternation in the bond lengths of S_7 has been discussed by Steudel and Schuster.[47]
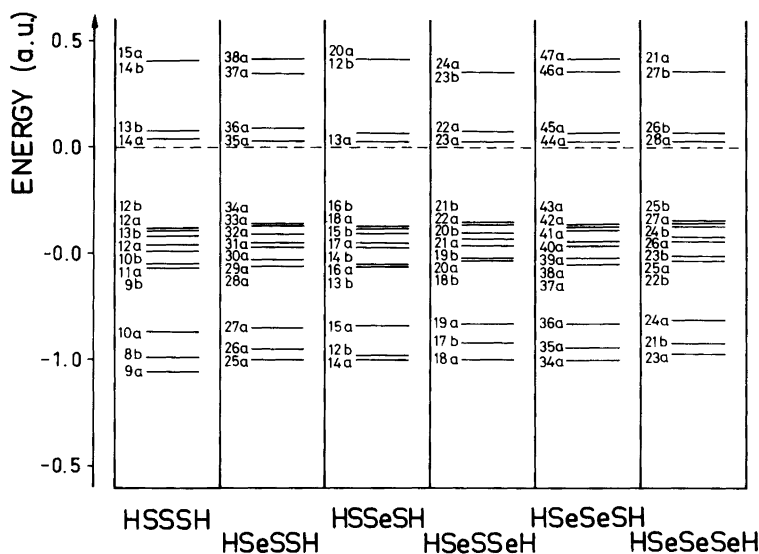
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Fig. 8. The electronic structures of various HX$_m$Y$_n$H molecules (X,Y = S, Se; *m,n* = 0–3) calculated using minimal basis sets of atomic orbitals (Ref. 70).
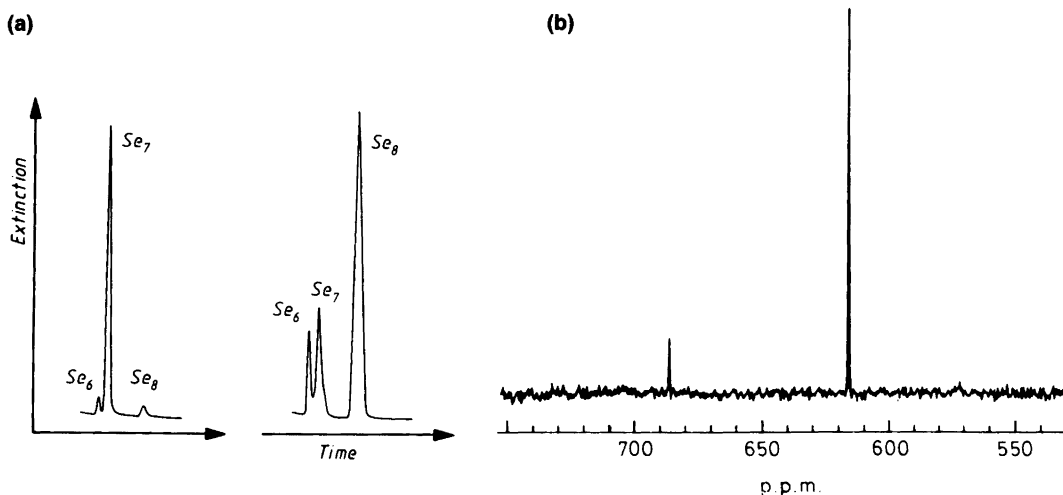

(a)

(b)

Fig. 9. Equilibrium establishment in CS$_2$ solutions of Se$_8$, Se$_7$ and Se$_6$. (a) The HPLC study shows how the equilibrium is attained upon dissolving solid Se$_7$ in CS$_2$. Se$_7$ is initially the main component in the solution, but its concentration rapidly decreases with the formation of Se$_8$ as the main component together with small amounts of Se$_6$ (Ref. 3). (b) The ^{77}Se NMR spectrum of the solution of [77]Se-enriched Se$_8$ in CS$_2$ shows two singlets which are interpreted as follows: The high-intensity signal is due to Se$_8$ and the low-intensity singlet to Se$_6$. Signals due to the four inequivalent nuclei of Se$_7$ are not observed, probably because of the complicated [77]Se–[77]Se coupling patterns which render the relative intensities of the multiplet components very low, so that they become lost in the background (Ref. 59).
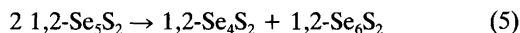
Interconversion reactions

It is well established that compounds containing cumulated S-S bonds undergo interconversion reactions. Typical examples are the decomposition of thermodynamically unstable sulfur molecules with the formation of stable S_8,[79] the decomposition of S_8 in the molten state or in organic solvents,[80,81] the polymerization and depolymerization of liquid sulfur,[79] the decomposition of organic polysulfanes, R_2S_n, on heating,[82,83] and the vulcanization of rubber.[84]

Similar interconversion reactions have been observed also for cyclooctaselenium. Upon dissolving Se_8 in CS_2, an equilibrium is rapidly established between Se_6, Se_7 and Se_8.[23,59] If pure Se_7 is

dissolved in CS_2, the same equilibrium position is eventually reached. This is demonstrated in Fig. 9. The decomposition of S_8 in CS_2 is much slower and requires heating under reflux.[2] In acetonitrile, however, the corresponding equilibrium is rapidly established.[85]

The decomposition of $1,2\text{-}Se_2S_5$ in CS_2 to produce Se_5S and $1,2,3\text{-}Se_3S_5$ [see eqn. (3)] is analogous to the interconversion reactions of homocyclic sulfur and selenium molecules discussed above, as is the decomposition of $1,2\text{-}Se_5S_2$:[22]

$$2\ 1,2\text{-}Se_5S_2 \rightarrow 1,2\text{-}Se_4S_2 + 1,2\text{-}Se_6S_2 \qquad (5)$$

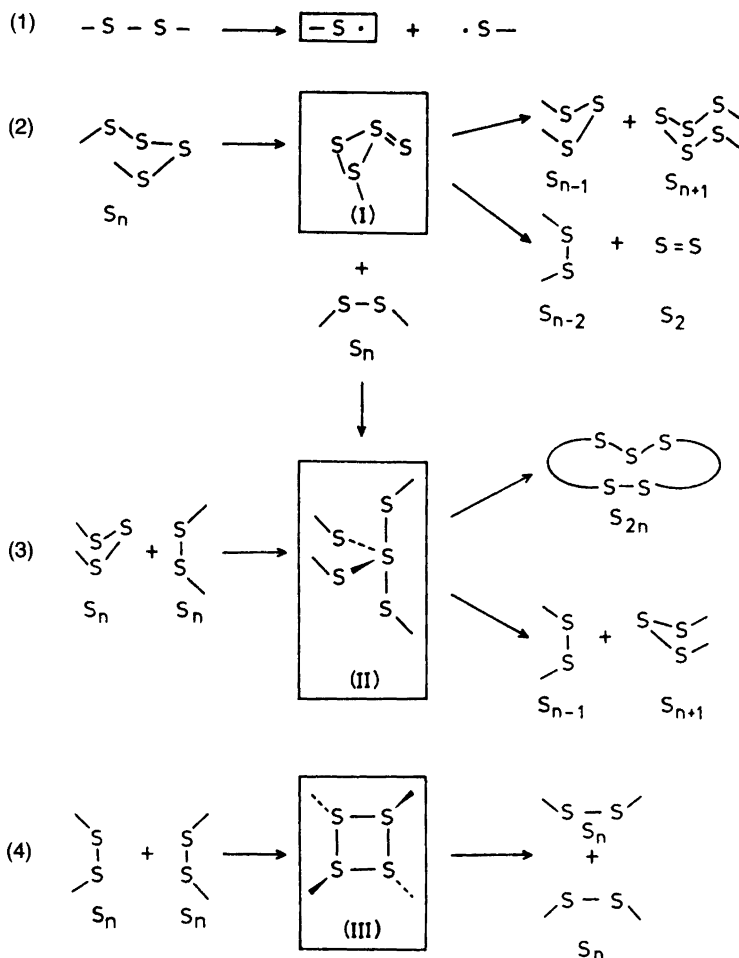The reaction products have been identified by vibrational analysis and by HPLC.

Fig. 10. The various suggested interconversion pathways for the compounds containing cumulated S-S bonds (adapted from Refs. 1 and 98).
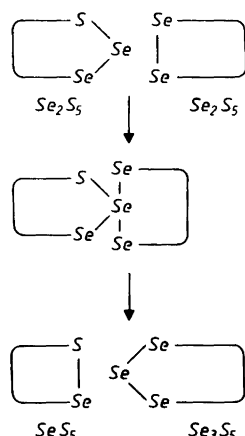
371

Fig. 11. The decomposition of 1,2—Se_2S_5 to SeS_5 and 1,2,3—Se_3S_5 involving a four-coordinated intermediate of type II (see Fig. 10) (Ref. 21).

The mechanism of such interconversion reactions is not clear. Several alternatives have been suggested for sulfur, as reviewed by Steudel[1] and shown in Fig. 10. It is also possible that there are several alternative mechanisms depending on the reaction conditions. For selenium, ionic intermediates have also been suggested.[86,87] While it is established that both sulfur and selenium can form such three-coordinated cationic species,[88–94] their existence in non-polar solvents is unlikely. In view of the similarities in the electronic structures of the S-S, Se-S and Se-Se bonds, it can be assumed that all interconversion reactions proceed in an analogous manner.

Though experimental data to support the existence of the different intermediates shown in Fig. 10 are extremely sparse, some information is available. Free radicals have not been detected in molten sulfur or organic solvents below the polymerization threshold at ca. 160 °C,[95–97] rendering pathway (1) in Fig. 10 unlikely under these conditions. Steudel [1] has therefore suggested that hypervalent intermediates of the types I and II could be involved in the interconversion. Several analogous species are known, demonstrating the existence of both types of coordination around sulfur (for some examples, see Refs. 98 and 99). Steudel and Strauss[21] have exemplified by use of the sulfurane-type intermediate (type II) how the decomposition of 1,2-Se_2S_5 to Se_5S and 1,2,3-Se_3S_5 might proceed (see Fig. 11).

Recently, the geometries and energies of for-

mation of the different types of interconversion intermediates shown in Fig. 10 were studied theoretically using model reactions of the four first members of the sulfane series H_2S_n (n = 1–4).[98] The calculated bond parameters of the sulfanes agree well with experimental information where available and accord well with the values expected for an unstrained S-S single bond (r = 206.6 pm, α = 106° and τ = 85°).[68,100] The calculated geometry of the radical HS· is also in agreement with the experimental data.[101]

The three types of hypervalent interconversion intermediates are exemplified by $(HS)_2SS$, $H_2S(SSH)_2$ and H_4S_4, and are shown in Fig. 12. The calculated structures of all these intermediates are reasonably consistent with those of analogous molecular species. The very long S-S bond in cyclic H_4S_4 (and the high energy of formation; see Table 4) renders this species a rather unlikely candidate for the interconversion intermediate.

The energies of formation of various model intermediates are listed in Table 4. The homolytic cleavage of the S-S bond of HSSH provides an estimate for the bond dissociation energy of the S-S single bond and is in agreement with the value observed experimentally.[102] With longer sulfur chains the energy needed to form two radicals is lowered, as also deduced from ESR and magnetic susceptibility measurements.[103]

Of the hypervalent species, the thiosulfoxide-type intermediate seems to be energetically rather favourable. Such species have often been proposed as suitable intermediates in the reactions of compounds containing S-S bond.[99,104] The energy of formation of sulfurane-type intermediates is comparable to the bond dissociation energy of the S-S bond. Considering that free radicals are not observed and that electronegative substituents stabilize the sulfurane-type coordination [compare with, for example, SF_4,[105,106] R_2SCl_2[107] and $(RO)_2S(OR)_2$[108]], it is conceivable that in the case of longer sulfur chains such intermediates are reasonable alternatives to the interconversion intermediates. It is also possible in the case of selenium that the four-coordinated species are formed more easily and, thus, that the interconversion of the selenium homocycles or selenium sulfide heterocycles proceeds via this route (see Fig. 11). Very recently, Steudel[109] has discussed the existence of hypervalent species in amorphous selenium.

12 (a)

12 (b)

12 (c)

Fig. 12. The optimum geometries and the charge distribution of the hypervalent intermediates: (a) $(HS)_2SS$; (b) $H_2S(SSH)_2$; (c) H_4S_4. The geometries have been optimized utilizing the 4–31G* basis sets and the net atomic charges have been estimated by single-point energy calculations involving the optimized geometries and the 6-31G* basis sets, and making correction for electron correlation using second-order Møller-Plesset perturbation theory.[98,110] Blue colour indicates the negative charge and red the positive charge. The figures have been generated using the Chem-X program package.[111]
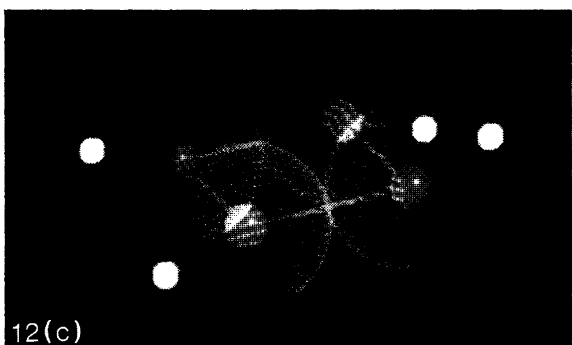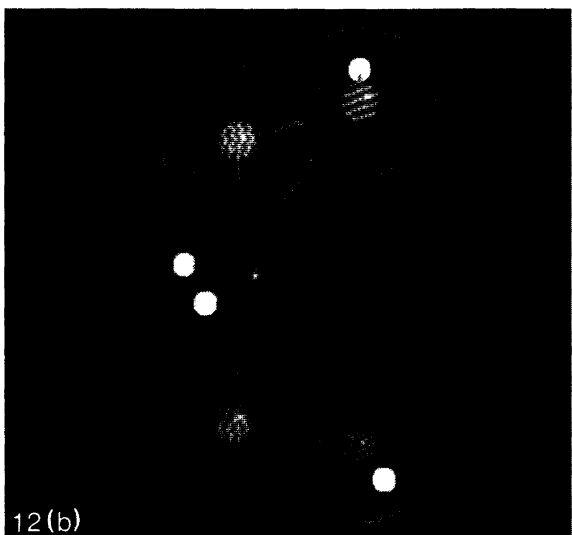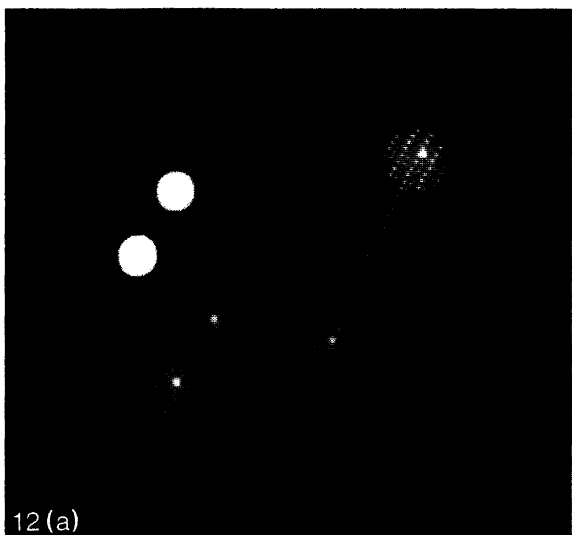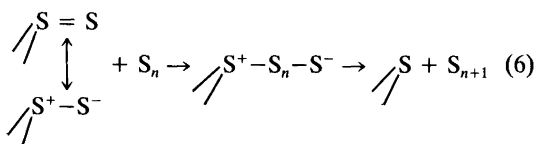
Table 4. Energy change (kJ mol^{-1}) during the formation of the selected hypervalent sulfur species. The values are based on single-point energy calculations using the 6-31G* basis set and 4-31G* optimized geometries. Electron correlation is taken into account utilizing second and third order Møller-Plesset perturbation theory (MP2 and MP3, respectively).[98]

Reaction	MP2	MP3	Exptl.
HSSH → 2 HS˙	229.3	218.8	276.1[a]
HSSSH → HS˙ + HSS˙	190.4	178.2	
HSSSSH → 2 HSS˙	153.1	138.9	148.1[b]
HSSH → H$_2$SS	137.2	141.0	
HSSSSH → (HS)$_2$SS	123.4	132.2	
HSH + H$_2$SS → H$_2$S(SH)$_2$	72.4	82.4	
HSH + (HS)$_2$SS → H$_2$S(SSH)$_2$	66.1	73.2	
HSH + HSSH → H$_2$S(SH)$_2$	209.6	223.4	
HSH + HSSSSH → H$_2$S(SSH)$_2$	189.5	205.4	
2 HSSH → H$_4$S$_4$	347.7	348.9	

[a]From Ref. 102. [b]From Ref. 103.

The charge distribution within the hypervalent intermediates is shown in Fig. 12. The considerable negative charge (ca. -0.4 e) on the terminal sulfur atom of the thiosulfoxide-type intermediate would render the species a strong nucleophile, as discussed by Laitinen *et al.*[98] [see eqn. (6)]. Bond scission in the attacked molecule, S_n, results in net sulfur atom transfer.

$$\begin{array}{c} \diagup S = S \\ \uparrow \\ \downarrow \\ \diagup S^+ - S^- \end{array} + S_n \rightarrow \diagup S^+ - S_n - S^- \rightarrow \diagup S + S_{n+1} \quad (6)$$

In the case of the sulfurane-type intermediate, the ease of pseudorotation at the four-coordinated sulfur can also lead to net sulfur or selenium atom transfer (see Figs. 10 and 11).

The charge distribution within the intermediates also prompts speculation on solvent effects.[98] The polar thiosulfoxide intermediate can be expected to be stabilized in polar solvents, and the non-polar sulfurane intermediates in non-polar solvents. It is quite possible that the actual interconversion pathway depends on the solvent used.

Outlook

The question of the composition of the sulfur-selenium binary system and of the structure of the heterocyclic selenium sulfides is over 100 years old. At least some answers have recently been emerging as a result of the development of synthetic techniques as well as of progress in modern analytical methods. It is now established that the different selenium sulfides undergo interconversion reactions in solution and in the molten state. Indeed, the main emphasis is presently shifting from purely structural investigations towards understanding the mechanism of these interconversion reactions. Theoretical comparisons of the S-S, Se-S and Se-Se bonds have indicated that the three bonds are relatively similar, and their cleavage and formation can therefore be expected to proceed in a similar fashion. Mechanistic studies of the reactions between the different selenium sulfides may well also provide information on the properties of compounds containing cumulated homonuclear S-S or Se-Se bonds which are of considerable importance in many technological and biological systems.

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