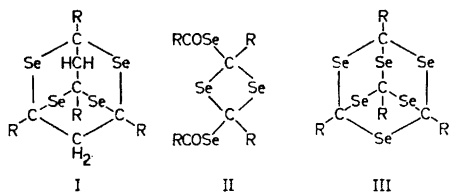


Synthesis of, and ^1H - ^{77}Se Coupling in, Polyselenaadamantanes

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As an extension of our work on polythia- and polyoxaadmantanes,^{1,2} the present paper reports their first known seleno analogues (I and III).^{*} These were obtained as colourless crystals essentially by the synthetic methods used for the corresponding sulphur compounds.¹ While the formation of the oxa and 2,4-dioxa analogues along with I was demonstrated by GLC-mass spectrometry, III was generally accompanied by the selenolester II (one isomer). Thioesters of the same type arise from chloro- and dichlorothioacetic acid under similar conditions.¹



The structures I–III were deduced from elemental analyses and spectra in the same way as their sulphur counterparts.¹ Further support was offered by the ^{77}Se satellites in the PMR spectra, see Table 1. An alternative structure of III with two 1,3-diselenetane rings may be rejected, as only one pair of ^{77}Se satellites was observed, and as $|J|$ was much larger than in II. By contrast, X-ray techniques are generally needed to rigorously exclude alternative structures of hexathiaadamantanes and related compounds.^{1,3} Alternative structures of I with four-membered rings are rendered unlikely by the large $|J|$ value 17.5 Hz.

In our opinion, ^{77}Se satellites deserve more general use than hitherto^{5,6} in

^{*} The abbreviations and symbols in Ref. 1 are used, and $\text{R}=\text{CH}_3$.

Table 1. PMR spectral data for I–III in CCl_4 . The ^1H - ^{77}Se coupling constant J and the number n of Se atoms contributing the ^{77}Se nucleus were obtained from the position and intensity, respectively, of each satellite pair relative to the central line, which was always a singlet.

Compound	Groups	Central line		^{77}Se satell.	
		δ in ppm	Area	$ J $ in Hz	n
I	R	1.96	3	17.5	2
	CH_2	2.00	1	3.8 ^a	4
II ^b	RCOSe	2.40	1	7.5	1
	RCSe_3	2.83	1	{ 5.0 8.4	{ 1 2
III	R	2.64	—	19.1	3

^a Being the AA' part of an AA'X spectrum with large $|J_{AA'}|$, only one pair of broad satellites is observed, yielding $\frac{1}{2}|J_{AX}+J_{A'X}|$.⁴

^b No more lines appeared in C_6H_6 or CHCl_3 .

elucidating the structure and conformation of selenium compounds. Most results should also be of indirect value to sulphur chemistry. Among the sulphur and selenium isotopes in nature, only ^{33}S and ^{77}Se have non-zero nuclear magnetic moments. The latter nucleus is by far the more useful in magnetic resonance, as it has spin quantum number $\frac{1}{2}$ and hence no electric quadrupole moment. ^{77}Se is also much more abundant (7.58 %) than ^{33}S .⁷ Yet, even in I–III, species with two or more ^{77}Se contribute negligibly to the PMR spectra. In I–III, ^1H - ^{77}Se spin-spin coupling can occur only through 3, 5, or 7 bonds (or through "space"). As seen from Table 1, only coupling through 3 bonds was observed, but this varies in magnitude within a considerable range according to molecular structure. What is now needed is that the relationships between J and various structural parameters be established. For that purpose, polyselenaadamantanes should be quite useful.

Of course, ^{77}Se chemical shifts and ^{77}Se - ^{77}Se coupling constants might also be informative,⁸ but we lack the requisite equipment.

Experimental. As hydrogen selenide is highly toxic, an efficient hood is vital. The yields may be far from optimal. Only a few characteristic bands from the IR spectra (in chloroform) are presented. The molecular weights calculated for I–III were confirmed by mass spectrometry.

1,3,5,7-Tetramethyl-2,4,6,8-tetraselenaadamantane (I). Hydrogen selenide was passed slowly for ca. 1 h over a freshly prepared and strongly stirred solution of 2.6 g of anhydrous zinc chloride and 2.0 g of 2,4-pentanedione in 8 ml of glacial acetic acid. After 24 h, 8 ml of conc. hydrochloric acid was added and the mixture extracted with 15 ml of chloroform. The extract was washed with water and analyzed by GLC, showing ca. 70 % I, 5 % oxa, and 25 % 2,4-dioxa analogue. The chloroform was evaporated and the residue recrystallized twice from 95 % ethanol, yielding 0.8 g of GLC-pure I, m.p. 167–168°. IR spectrum: 600m, 931s, 956m, 1030m, 1085s, 1141m/cm. (Found: C 26.4; H 3.6; Se 69.7. Calc. for $C_{10}H_{16}Se_4$: C 26.6; H 3.6; Se 69.9).

cis- or trans-2,4-Dimethyl-1,3-diselenetane-2,4-diselenol diacetate (II). 4.0 g of anhydrous aluminium chloride, dissolved in 7.85 g of acetyl chloride, was added slowly to ca. 10 g of liquid hydrogen selenide, with agitation and cooling in Dry Ice-methanol. After warming gradually to -20° for 3–5 days, the yellow semisolid mixture was suspended in 20 ml of methanol cooled in ice-water. The undissolved material (ca. 3 g) was collected, washed with methanol, air-dried and recrystallized twice from carbon tetrachloride, a small dark insoluble residue being discarded. The yield of PMR-pure II, m.p. 155–158° d., was ca. 1.3 g. IR spectrum: 581s, 636w, 944m, 1064s, 1109s, 1680s, 1705s/cm. The last two bands show the carbonyl groups. (Found: C 21.2; H 3.0; Se 68.8. Calc. for $C_8H_{12}O_2Se_4$: C 21.1; H 2.7; Se 69.3). II forms colourless crystals but faintly yellow solutions. It seems to be perfectly stable at 20° in the dark but is sensitive to various agents, particularly bases. It was not eluted in GLC.

Tetramethylhexaselenaadamantane (III). The mother liquor from the first recrystallization of II was passed through a 1.0×30 cm column of alumina. Whereas remaining II was retained or destroyed completely, III was eluted rapidly by carbon tetrachloride. This was evaporated and the residue recrystallized twice from butanone, yielding ca. 1.0 g of GLC- and PMR-pure III, m.p. 248–249° d. IR spectrum: 644s, 1010m, 1077s/cm. (Found: C 16.3; H 2.1; Se 81.1. Calc. for $C_8H_{12}Se_6$: C 16.5; H 2.1; Se 81.4).

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