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# 2,11-DISELENA[3,3]METACYCLOPHANE - SYNTHESIS AND VARIABLE TEMPERATURE PMR SPECTRUM

Reginald H. Mitchell,
Department of Chemistry, University of Victoria,
Victoria, B. C. V8W 2Y2 Canada.

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Despite the considerable recent interest[1-3] in dithia[3,3]cyclophanes no diselena[3,3]cyclophane has thus far been reported. I now report the synthesis and variable temperature pmr spectrum of 2,11-diselena[3,3]metacyclophane **1**. Reaction of m-xylylene bromide with anhydrous sodium selenide (Alfa) in dry DMSO or hexamethylphosphoramide gave 5-10% yields of **1**, mp 121-122°. Use of aqueous or ethanolic solvents or attempted isolation of selenols gave heavy contamination with diselenides.[4,5] The structure of **1** was confirmed by analysis, mass ($M^+$ at m/e 368) and pmr spectroscopy (figure 1). At 20°C the methylene bridge pmr absorptions (3.78δ) are deshielded by 0.24 ppm, whereas the internal aromatic hydrogens (6.46δ) are shielded by 0.58 ppm from those of the cyclic trimer (mp 130-132°). This effect is more marked than in the case of 2,11-dithia [3,3]metacyclophane.[3] The room temperature spectrum is consistent with the molecule conformationally flipping between various syn and anti conformers.[1] Cooling to -110°C freezes out one particular anti conformer (such as that shown in the photograph) in which one of the internal protons is pushed directly into the opposite π cloud and is highly shielded to 4.50δ, the other internal proton being in a normal aromatic environment. The average position of these two protons would be ca. 5.7δ if a simple exchange process were occurring at room temperature. The observed average position indicates that other conformers have become more dominant. From the coalescence temperature of -95°C and $\Delta\nu$ = 226Hz an estimate[7] of the energy barrier to flipping, $\Delta G^{\pm}$ is 8.0 kcal/mole. This presumably reflects the slightly greater size of selenium compared with sulfur, since the corresponding thiacyclophane is still mobile at -110°C. We are currently investigating the chemistry of this compound and thank the University of Victoria and National Research Council for support of this work.

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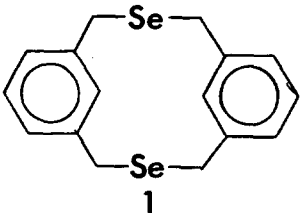
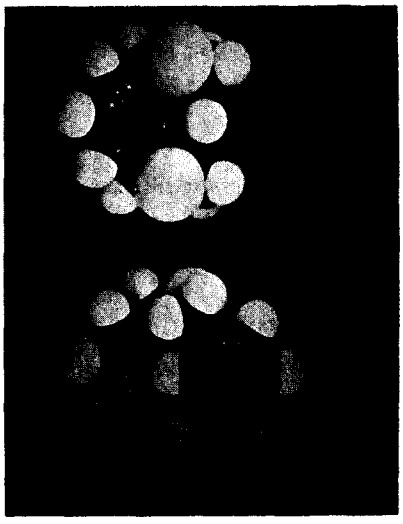



1



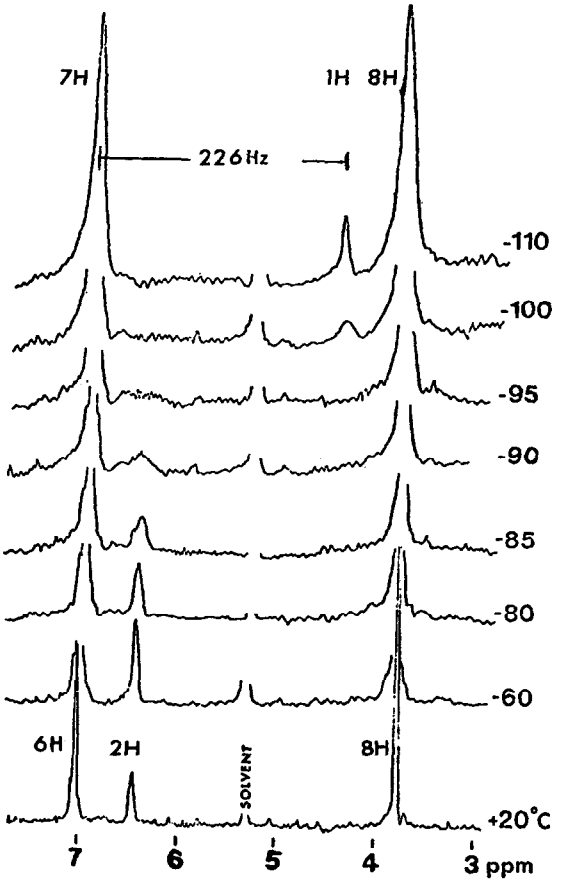



Figure 1 - Pmr spectrum of **1** in $CD_2Cl_2$-$CDCl_3$ (3:1) recorded on a Perkin-Elmer R32-90MHz spectrometer.