

## Solution Conformation and Pseudorotational Barriers of 1,3,7,9-Tetraselenacyclododecane and its 5,5,11,11-Tetramethyl Derivative

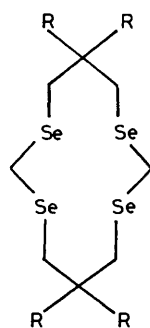
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1,3,7,9-Tetraselenacyclododecane and its 5,5,11,11-tetramethyl analogue are shown by dynamic n.m.r. studies to have a [3333] quadrangular conformation in which the selenium atoms occupy only side positions, and to possess pseudorotational barriers of 6.0 and 7.6 kcal mol<sup>-1</sup>, respectively.

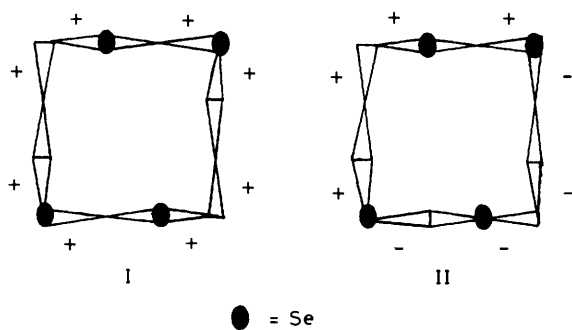
We have recently reported<sup>1</sup> that 1,3,7,9-tetraselenacyclododecane (**1**) exists, in the solid state, in two distinct quadrangular conformations in both of which selenium atoms occupy alternate corner and side positions. In contrast, we show herein that the preferred conformation in solution of (**1**) and its 5,5,11,11-tetramethyl analogue (**2**) is a [3333] quadrangle with the selenium atoms occupying only side positions. This work is the first recorded dynamic n.m.r. study of a selenium coronand.

Cyclododecane as well as its polyoxa, polythia, and polyselena derivatives exist in the solid state in quadrangular conformations.<sup>1-4</sup> The corners of these quadrangles are formed by two consecutive *gauche* torsion angles which may be either of the same sign (genuine corner)<sup>5</sup> or of opposite sign (pseudo corner).<sup>5</sup> Cyclododecane<sup>2</sup> and 1,4,7,10-tetrathia-cyclododecane<sup>3</sup> both exist in a conformation having four genuine corners (type I torsional sequence or quadrangular [3333]),<sup>5</sup> the latter having the S atoms in the corner positions. In contrast, in the molecular conformation of 1,4,7,10-tetraoxacyclododecane<sup>4</sup> there are alternating genuine and pseudo corners (type II torsional sequence or biangular [66]),<sup>5</sup> with the oxygen atoms occupying side positions. The structure



(1) R = H

(2) R = Me



of (**1**)<sup>1</sup> contains both type I and type II conformers in which, however, the selenium atoms occur in alternate corner and side positions; in the type II conformer the corner selenium atoms occupy the pseudo corners.

In contrast to the conformational preference of (**1**) in the solid state,<sup>1</sup> the oxygen congener of (**1**), namely 1,3,7,9-tetraoxacyclododecane, has been reported<sup>6</sup> to exist in solution in a type I conformation with the oxygen atoms occupying side positions. It was of interest, therefore, to probe the solution conformational behaviour of (**1**).

The <sup>1</sup>H n.m.r. spectrum of (**1**) in CFC1<sub>3</sub>/CD<sub>2</sub>Cl<sub>2</sub> (85:15) at 400 MHz shows temperature-dependent behaviour for only the Se-CH<sub>2</sub>-C resonance. This signal (δ 2.82) broadens at about 165 K and reaches the coalescence point at 133 K, the practical low-temperature limit of our instrument. The Se-CH<sub>2</sub>-Se (δ 3.56) and the C-CH<sub>2</sub>-C (δ 1.98) resonances remain unaffected. In addition, the <sup>77</sup>Se (δ 198) and <sup>13</sup>C n.m.r. spectra (down to 154 K) do not show any changes with temperature due to chemical exchange. The <sup>1</sup>H n.m.r. spectrum of the tetramethyl derivative (**2**) exhibits similar behaviour to that of (**1**), the Se-CH<sub>2</sub>-C signal (δ 3.01) broadening at about 185 K and splitting into two signals (δ 2.72 and 3.10) below 165 K, while the Se-CH<sub>2</sub>-Se (δ 3.64) and methyl (δ 1.19) signals remain unchanged (Figure 1). The splitting of the Se-CH<sub>2</sub>-C signal to give an AB system (<sup>1</sup>J<sub>AB</sub> 9.5 Hz) at 141 K shows that these geminal hydrogen atoms are diastereotopic. As is the case with (**1**), the <sup>77</sup>Se (δ 148) and <sup>13</sup>C n.m.r. spectra (down to 154 K) do not show any changes with temperature attributable to chemical exchange. The <sup>1</sup>H n.m.r. spectrum at 141 K is consistent only with a preferred conformation displaying three mutually perpendicular two-fold axes. The assignment presumes that the Se-CH<sub>2</sub>-Se and Me<sub>2</sub>C signals remain unsplit because the groups are stereochemically equivalent and not because the signals are accidentally isochronous.† We propose that (**1**) and (**2**) undergo site exchange as shown in Figure 2.<sup>6</sup> Similar conformational behaviour has been observed<sup>7</sup> for the oxygen congener, 1,3,7,9-tetraoxacyclododecane, and its 2,2,8,8-tetramethyl derivative.

The placement of the oxygen atoms across corners in oxygen coronands containing the 1,3-dioxa fragment<sup>8</sup> has been rationalized in terms of (i) minimization of 1,4 CH...HC contacts, and (ii) maximization of 1,4 CH...O attractive interactions.<sup>5,9</sup> The conformational preference in (**1**) and (**2**) can be similarly rationalized, although 1,4 CH...Se attractive interactions should be much less important. We note also that the preferred placement of the heteroatoms (X = O or Se) dictates *gauche, gauche* arrangements about X-C-X moieties and is consistent with expectations based on the anomeric effect.<sup>10,11</sup>

The barrier for conformational interconversion, ΔG<sup>‡</sup>, in (**2**) is ca. 7.6 kcal mol<sup>-1</sup> (T<sub>c</sub> 167 K)‡ and that in (**1**) is estimated to

† Similar behaviour is observed in CS<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> (85:15).

‡ k<sub>rot.</sub> = 2.221[(Δν)<sup>2</sup> + 6J<sub>AB</sub><sup>2</sup>]<sup>1/2</sup> at the coalescence temperature.

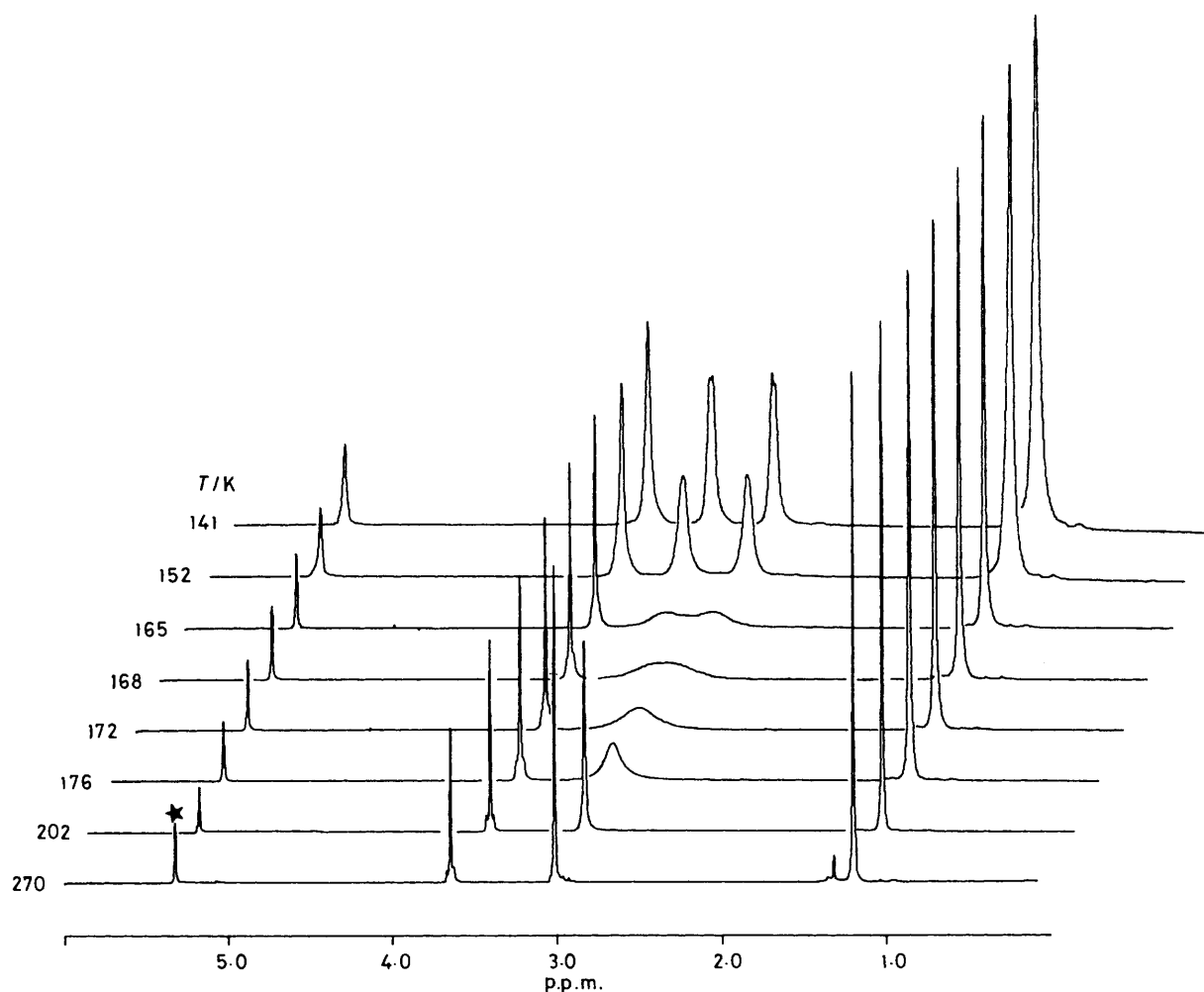


Figure 1. Variable temperature  $^1\text{H}$  n.m.r. (400 MHz) spectra of 5,5,11,11-tetramethyl-1,3,7,9-tetraselenacyclododecane (2) in  $\text{CFCl}_3/\text{CD}_2\text{Cl}_2$  (85:15); an asterisk indicates the residual solvent peak.

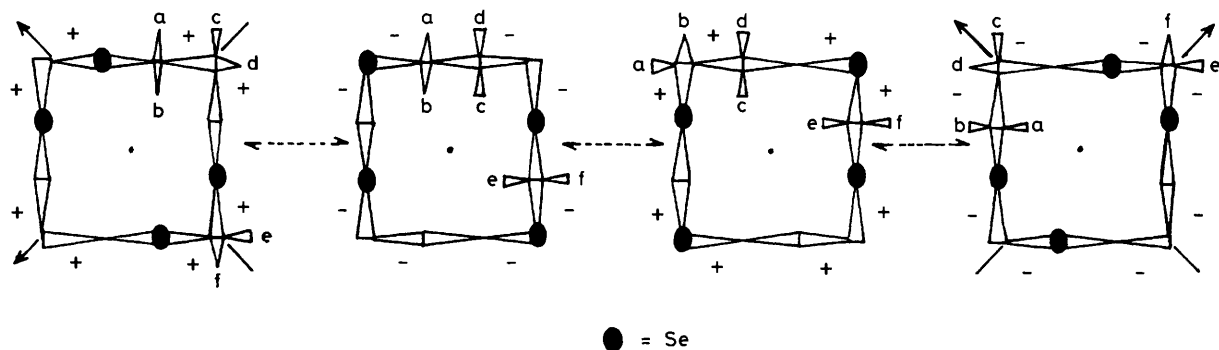


Figure 2. Conformational interconversion pathway for (1) and (2); (1)  $a = b = c = d = e = f = \text{H}$ ; (2)  $a = b = e = f = \text{H}$ ,  $c = d = \text{Me}$ .

be *ca.*  $6.0 \text{ kcal mol}^{-1}$  ( $T_c$  133 K), if we assume that  $\Delta v$  and  $^1J_{AB}$  for the exchanging protons are the same in (1) and (2). The conformational barriers for (1) and (2) are of similar magnitude to those in cyclododecane ( $7.3 \text{ kcal mol}^{-1}$ )<sup>12</sup> and

cyclododecanone ( $7.3 \text{ kcal mol}^{-1}$ )<sup>13</sup> and those for the two processes in 1,4,7,10-tetraoxacyclododecane ( $5.5$  and  $6.8 \text{ kcal mol}^{-1}$ )<sup>14</sup> but are much lower than that in the oxygen congener ( $11 \text{ kcal mol}^{-1}$ ).<sup>7</sup> The latter difference is attributable

to the relative ground-state stabilization of the oxygen congener, although some contribution from the alleviation of *syn*-eclipsing interactions in the transition state for pseudorotation in (1) and (2), due to the longer C–Se bonds, cannot be ruled out.

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