The Barrier to Rotation about the Selenium–Selenium Bond in Diselenides. A Dynamic N.M.R. Study

J. E. Anderson[a] and L. Henriksen[b]

[a] Chemistry Department, University College, Gower Street, London WC1E 6BT, U.K.
[b] Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The barrier to rotation about the selenium–selenium bond in phenyl benzyl diselenide $PhSeSeCH_2Ph$ is determined to be 6.3 kcal mol⁻¹[†] as indicated by changes in the proton n.m.r. spectrum at low temperatures; this is *ca.* 1.4 kcal mol⁻¹ lower than the barrier in phenyl benzyl disulphide $PhSSCH_2Ph$.

There has been much recent interest in the barrier to rotation about the selenium–selenium bond in diselenides and whether it is higher than the corresponding barrier in disulphides.[1—3] Renugopalakrishnan[1] has satisfactorily calculated *ab initio* the known[‡] *trans*-rotational barrier in dimethyl disulphide. He found that the diselenide barrier is lower or higher than the disulphide barrier depending directly on the level of refinement of his MO calculations.

Gombler[2] has interpreted the ⁷⁷Se n.m.r. spectrum of methyl trifluoromethyl diselenide in terms of hindered rotation, implying a barrier as large as 17 kcal mol⁻¹, but ¹H and ¹⁹F n.m.r. spectra[6,7] do not support this interpretation. In the compound (1) the barrier is known[3] to be 12.5 kcal mol⁻¹, somewhat lower than in the corresponding disulphide (2), 16.2 kcal mol⁻¹, but this may reflect the properties of the tri-t-butylphenyl group, and is not necessarily a satisfactory model for a simple diselenide.

The barrier which one may hope to measure is that opposing the interconversion of two stable enantiomeric *gauche*-type conformations (3) and (4) in which the R–Se–Se–R dihedral angle[8] is near to ±80°, by way of an *anti*-transition state (5).[§]

A prochiral $-CX_2Y$ group should show separate signals for the groups X in the n.m.r. spectrum when interconversion is slow on the n.m.r. timescale. This particular strategy has been used by Fraser *et al.*[5] in a study of rotation in a series of disulphides $PhCH_2–S–S–R$.

Dibenzyl diselenide, (6) shows a singlet[¶] (δ 3.85) in its proton n.m.r. spectrum for the methylene protons, and a complex aromatic region. The singlet showed a broadening below −150 °C, but even at −164 °C, when the line width is *ca.* 90 Hz, separate signals for diastereotopic protons were not obtained. We next studied benzyl phenyl diselenide (7), since the rotational barrier in benzyl phenyl disulphide is 0.8 kcal/mol⁻¹ higher than that of dibenzyl disulphide.[5]

In its proton n.m.r. spectrum the benzyl phenyl diselenide (7)[9] shows a singlet[¶] (δ 4.25) for the methylene protons and a complex aromatic region. On lowering the temperature below *ca.* −125 °C, the singlet broadens compared with reference

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† 1 cal = 4.184 J.

‡ While the dimethyl disulphide rotational barrier has been estimated (ref. 4) at 9.5 kcal mol⁻¹ from the far i.r. spectrum, a more likely value is 7 kcal mol⁻¹ or slightly less, based on the dynamic n.m.r. results (ref. 5) for dibenzyl disulphide. The calculated values (ref. 1) are 6.27 or 8 kcal mol⁻¹ depending on the refinement of the MO calculations.

§ There seems to be general agreement that the rotational transition state with the two groups R and two sets of lone pair orbitals eclipsed '*syn*' will be of even higher energy than the *anti*.

$$R^1 \text{—Se}\!\!\!+\!\!\!\text{Se—}R^2 \qquad\qquad R^1\text{—S}\!\!\!+\!\!\!\text{S—}R^2$$

(1) $R^1 = R^2 = 2,4,6\text{ - Bu}^t_3C_6H_2$ (2) $R^1 = R^2 = 2,4,6\text{ - Bu}^t_3C_6H_2$
(6) $R^1 = R^2 = PhCH_2$
(7) $R^1 = Ph, \; R^2 = PhCH_2$

¶ The singlet has weak sidebands due to coupling of protons to 7.5% ⁷⁷Se [²J(¹H–⁷⁷Se) 14 Hz] but this was not observed in the very dilute $CHF_2Cl–CHFCl_2$ 1:4 solution used for the low-temperature n.m.r. measurements. Compound (7) is not isolable because of rapid chemical equilibration with the symmetric dibenzyl and biphenyl diselenides (ref. 6).

R
|
Se
R—Se

(3)

R
|
Se
Se—R

(4)

R
|
Se
|
Se
|
R

(5)
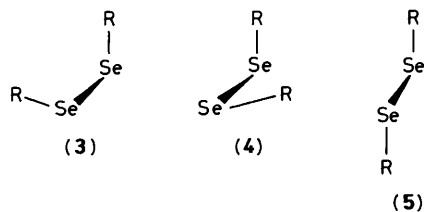
Table 1. Rotational barriers $\Delta G^{\ddagger}$, (kcal mol^{-1}) for dichalcogenides, R^1-X-X-R^2.

R^1, R^2	X = Se	X = S	$\Delta G^{\ddagger}_{Se}/\Delta G^{\ddagger}_{S}$
PhCH$_2$, Ph	6.3[a]	7.7[b]	0.82
PhCH$_2$	<5.6[a]	7.1[b]	<0.80
2,4,6-Bu$^t_3$C$_6$H$_2$	12.5[c]	16.2[c]	0.77

[a] This study. [b] Ref. 5. [c] Ref. 3.

solvent signals, and is split below $-142\ ^{\circ}$C into a broadened AB quartet (δ_{AB} ca. 29 Hz at 200 MHz, J_{AB} ca. 14 Hz). The changes suggest that the rate constant for interconversion (3) $\rightleftharpoons$ (4) is 100 s^{-1} at $-142\ ^{\circ}$C; therefore the free energy of activation for rotation is 6.3 kcal mol^{-1}.‖ An upper limit of 5.6 kcal mol^{-1} for the rotational barrier in the dibenzyl compound (6) can be estimated by the same method.

The barrier we have determined for (7) is 1.4 kcal mol^{-1} lower than that in the analogous disulphide PhCH$_2$SSPh,[5] and

‖ $k_{rotn.}$ = 2.221 $\sqrt{[(\delta v)^2 + 6J^2]}$ at the coalescence temperature.

the upper limit estimated for dibenzyl diselenide (6) is correspondingly less than for dibenzyl disulphide, see Table 1. These results and the data of reference 3 lead us to conclude that diselenide rotational barriers are generally about 20% lower than the corresponding disulphide ones. The increased central bond length in diselenides compared with disulphides seems to reduce p–p lone pair repulsions in an *anti* transition state.

References

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