# DYNAMIC $^{77}$Se NMR OF PHENYLSELENYL CYCLOHEXANE DERIVATIVES

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Abstract: For phenylselenyl cyclohexane (1) ring inversion barriers ($\Delta G^{\neq}_{278}$) of 11.7 ± 0.2 (eq-1 ⟶ ax-1) and 10.5 ± 0.2 kcal/mol (ax-1 ⟶ eq-1) and an A-value of 1.1 were determined. Extraordinarily large diamagnetic $\gamma$ effects of ca 30-40 ppm per $CH_2$ group were found.

Although $^{77}$Se has rather favourable NMR properties (I=1/2, 7.6% natural abundance and a receptivity of 2.98 relative to $^{13}$C) little is known about the structure dependence of $^{77}$Se chemical shifts [$\delta(^{77}$Se)] in aliphatic compounds[1]. In this communication we want to report on temperature-dependent $^{77}$Se NMR spectra of some phenylselenyl cyclohexane derivatives which were prepared by the treatment of diphenyldiselenide with sodium borohydride and subsequent addition of the corresponding bromides or methanesulphonates[2,3]:
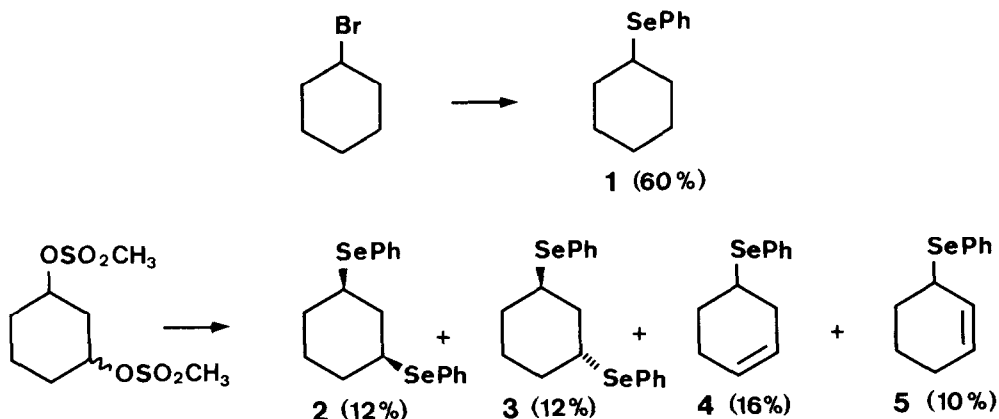


The $^{77}$Se NMR spectra shown in Fig.1 indicate conformational interconversions of 1 and 3. At low temperatures (223 K) the equatorially and axially substituted isomers of 1 (Fig.1a) give separate signals with an intensity ratio of 9.2 : 1. The energy barriers for the ring inversion can be determined using approximation equations for the evaluation of dynamic NMR spectra[4]. The rate constants were estimated for the temperature of maximum line broadening of the main signal (278 ± 5 K) with the equations $k_{eq \to ax} = 2\pi p_{ax} \Delta v$ and $k_{ax \to eq} = 2\pi p_{eq} \Delta v$; $p_{ax}$ and $p_{eq}$ are the popu-

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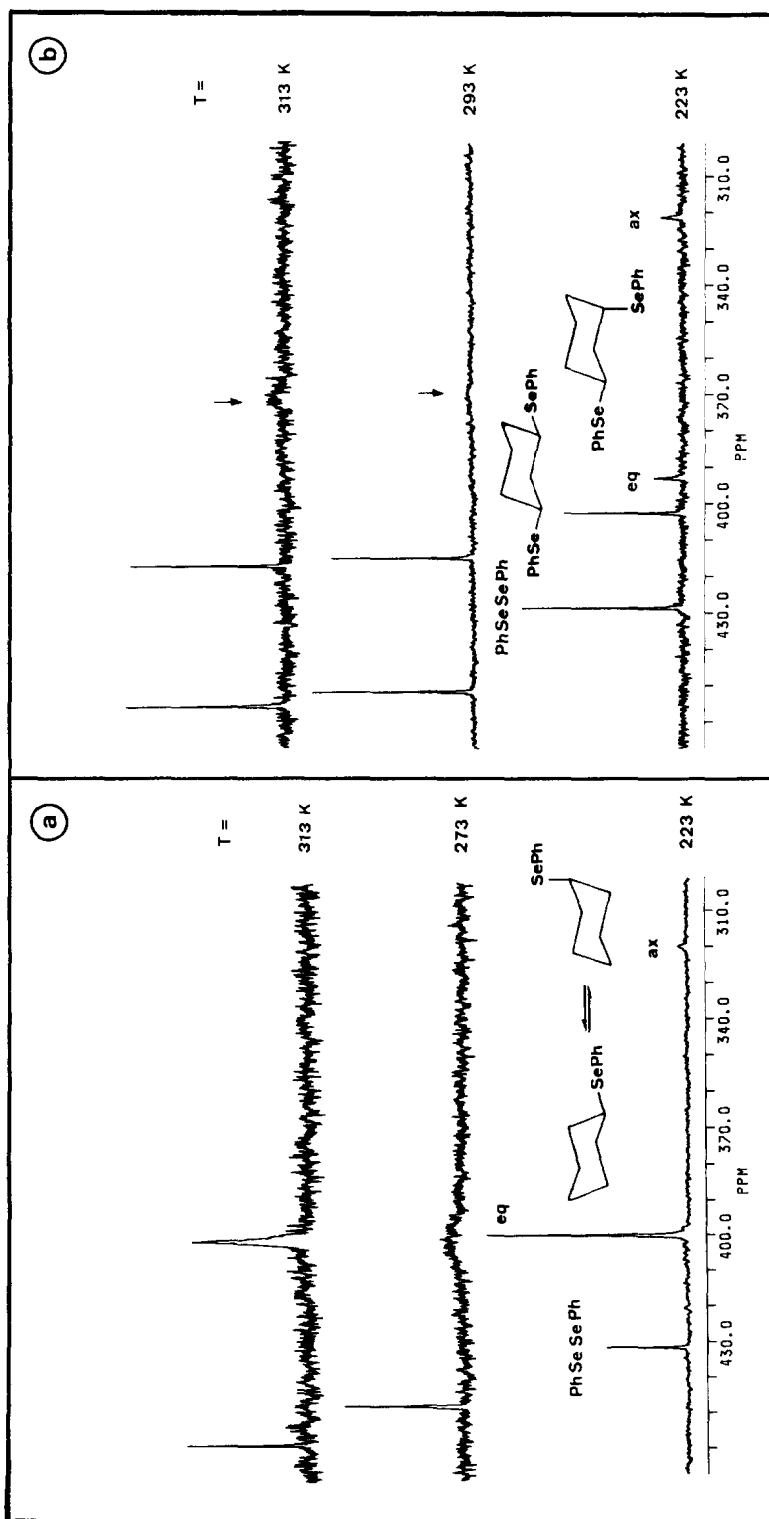
Fig. 1: Temperature-dependent $^{77}$Se NMR spectra of **1** (a) and a 1 : 1 – mixture of **2** and **3** (b), in $(CD_3)_2CO$

lations of ax-1 and eq-1, repectively, and $\Delta v$ is the chemical shift difference at low temperature (6086 Hz $\cong$ 79.8 ppm)[5]. Thus, values of $\Delta G_{ea}^{\neq} = 11.7 \pm 0.2$ and $\Delta G_{ae}^{\neq} = 10.5 \pm 0.2$ kcal/mol were obtained which are a little higher than other ring inversion barriers in monosubstituted cyclohexanes[6]. The difference of 1.2 kcal/mol is the ground state free energy difference ($-\Delta G^o \equiv A$). The A-value can also be obtained directly from the peak area ratio at 223 K ($\Delta G^o = -RT \ln K$) giving 1.0. Since due to the extreme line broadening our calculations are based only on approximations we refrain from a discussion of this divergence in terms of temperature dependence and propose a "best" A-value of 1.1. It is somewhat larger than that of PhS (0.8)[7] and this is in accordance with the observation that in contrast to the halogens van der Waals radii apparently play an important role in the chalcogen group[7].

The populations of the two rotamers of 3 (Fig. 1b) are equal because they are mirror images. In contrast its cis-isomer 2 is conformationally rigid and hence its spectrum does not show any coalescence effect. This is a proof that the line broadening observed for 1 and 3 is indeed due to the ring inversion and not to restricted rotations in C-Se bonds[8]. A further confirmation is the fact that there are no coalescences for 4 and 5 as well at any temperature between 223 and 293K.

Table 1: $^{77}$Se chemical shifts of 1 – 5 at 293 and 223 K[a]

|  | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| 293 K | 398 ± 1 | 415.7 | 369 ± 1 | 392.3 | 400.8 |
| 223 K | 399.9<br>320.1 | 402.9 | 393.3<br>321.8 | 380.8 | 379.0 |

[a] In $(CD_3)_2CO$, relative to external neat $(CH_3)_2Se$ ($\delta = 0$)

The $^{77}$Se chemical shift differences for PhSe in axial and equatorial positions are remarkably large. Although a detailed interpretation of the structure dependence is mandatory and under investigation is this laboratory, it can already be stated that $^{77}$Se nuclei like many others (e.g. $^{13}C$, $^{15}N$ or $^{17}O$) experience diamagnetic $\gamma$ effects which, however, are extraordinarily large (here: 35 – 40 ppm per each $\gamma$-gauche $CH_2$). This is the reason why the line broadening of the $^{77}$Se resonances of 1 and 3 occurs at such unusually high temperatures; their $^{13}C$ signals do not show coalescence effects above 223 K.

Thus, $^{77}$Se is an excellent candidate for dynamic NMR investigations because chemical shift differences in various conformations may be extremely large.

NMR measurements: The $^{77}$Se NMR spectra were recorded at 76.27 MHz (Bruker AM-400) in 0.1 - 1 molar $(CD_3)_2CO$ solutions using ca 30° pulses and a repetition rate of 5 sec since the $^{77}$Se nuclei have rather long relaxation times $(T_1 \approx 10-15$ sec$)^9$. Moreover, NOE effects are insignificant for these compounds[9] so that the $^{77}$Se NMR spectra were obtained without $^1$H decoupling. In each instance some PhSeSePh was added as internal standard for line broadening determinations. As can be seen in Fig.1 $^{77}$Se chemical shifts are very sensitive to temperature changes[10]. All chemical shift values are referenced to the signal position of PhSeSePh in $CDCl_3$ solution ($\delta$ = 462.6) at 294 K corresponding to $\delta$ = 0 of neat $(CH_3)_2Se$; positive values indicating higher frequencies.

## References and Notes

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