15N and 77Se Nuclear Magnetic Resonance Study of Selenium Diimides and Aminoselenanes

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Selenium diimides R(N(SeN)R) [R = 'Bu (1a), 'Oct (1b)], the eight-membered heterocycle 'BuN(SeSeSe),N'Bu (2) and the aminoselenanes of the type [R(Cl,Se),N],Se (4a,b) and [(Me,Se),N]Se (5) were studied by multinuclear NMR with emphasis on 15N NMR for detection of coupling constants J(77Se15N). The selenium diimides possess the largest values of J(77Se15N) observed so far (1a: 158.4 and 163.5 Hz, 1b: 158.6 and 162.8 Hz). Compound 1b was found to be much more stable than 1a, the heterocycle 2 being the major decomposition product of 1a. The selenium diimides (1a,b) react readily with hexachlorodisilane to give the bis[alkyl(trichlorosilyl)amino]selenanes 4a,b. The solid state 13C, 15N and 77Se CP/MAS NMR spectra of bis[bis(trimethylsilyl)amino]selenane (5) gave results in accord with the known crystal structure, and there is agreement with the solution state NMR data.

Introduction

The rich chemistry of sulfur-nitrogen compounds has attracted considerable interest in the corresponding field of selenium chemistry [1, 2]. Among other physical methods, 77Se NMR has proved particularly useful for the characterization of mixtures as well as of pure selenium compounds [3–6]. In the case of selenium-nitrogen compounds, 15N NMR should be similarly helpful, in particular if 15N–15N spin-spin coupling can be detected [J(77Se15N)]. However, so far only some chemical shifts δ15N of selenium-nitrogen compounds have been reported [7, 8, 9a] and, to the best of our knowledge, even fewer values J(77Se15N) have been measured in the cationic compound [Se3N2Cl]+[Cl–] [9a] (J(77Se15N) = 117.8 Hz), in 1,2,3-selenadiazole derivatives [9b] (range of values |J(77Se15N)|: 83.4–92.2 Hz) and in selenylamines of the type (CF3Se)3–NH8 [10] [n = 0 (78.4 Hz), 1 (74.7 Hz), 2 (60.1 Hz)].

In this paper we report on 15N and 77Se NMR of the selenium-nitrogen compounds 1 to 5. Such data were unknown for the selenium diimides 1a [2f] and 1b. We have also studied the dynamic behaviour of 1 for comparison with the corresponding sulfur diimides. The decomposition of 1a was reinvestigated by 77Se NMR; a major decomposition product was shown to be the eight-membered heterocycle 2 [11].

There is some 77Se NMR spectroscopic evidence that the five-membered ring 3, reported previously as a decomposition product of 1a [2f] or its trimer Se3(N'Bu), [11], is present in the mixture during decomposition. In analogy to the investigation of the reactivity of sulfur diimides towards disilanes [12], the reaction of 1a,b with SiCl4 was carried out to prepare the new dianimoselenanes 4a,b. For comparison, 15N, 29Si and 77Se NMR data of bis[bis(trimethylsilyl)amino]selenane (5) [13] were obtained both for the solid and liquid state.

Results and Discussion

Selenium diimides and their decomposition

The selenium diimides 1a,b were obtained following the described preparation of 1a [2f]. The
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\[
\text{SeCl}_4 + 6 \text{RNH}_2 \xrightarrow{\text{Et}_2\text{O}, -40^\circ \text{C}} \text{R(\text{NSeN})R} + 4 \text{RNH}_3\text{Cl} \quad (1)
\]

\[
2\text{SeOCl}_2 + 6 \text{RNH}_2 \xrightarrow{\text{Et}_2\text{O}, \sim -30^\circ \text{C}} \text{R(\text{NSeN})R} + 4 \text{RNH}_3\text{Cl} + \text{SeO}_2 \quad (2)
\]

The synthesis of \(1a\) according to Eqn. (2) can be improved by adding a catalytic amount of \(\text{AlCl}_3\).

Compound \(1b\) is much more stable than \(1a\); there is hardly any decomposition in toluene solution after 3 days at ambient temperature, indicating the greater stabilizing effect of the tert-octyl group \([-\text{C(CH}_3)_2\text{C(CH}_3)_2\text{CH}_3]\) as compared to the tert-buty1 group \([-\text{C(CH}_3)_3]\). If the decomposition of \(1a\) in solution is monitored by \(^{77}\)Se NMR (see Fig. 1), the formation of many different species becomes obvious. The composition of these mixtures appears to depend strongly on temperature, solvent, time and also, possibly, on the presence of minor impurities introduced during the synthesis of \(1a\). Thus, the \(^{77}\)Se NMR spectra shown in Fig. 1 are not fully representative of the whole course of decomposition. However, they show the growing \(^{77}\)Se NMR signals of the major decomposition product \(2\) which can be isolated in the pure state and which has also been prepared by a different route and characterized by an X-ray analysis [11]. Another attempt to monitor the decomposition of \(1a\) (in toluene solution after 3 days at \(28^\circ \text{C}\) and 14 days at \(-78^\circ \text{C}\)) gave broadened \(^{77}\)Se NMR signals (\(\delta^{77}\text{Se}: 1155.8\) and \(878.0\)) in an approximate 2:1 ratio as required for an intermediate with the structure of \(3\) or its trimer.

The selenium diimides \(1a, b\) are sufficiently stable for full NMR spectroscopic characterization in solution (see Table I). At room temperature or below, the Z/E-configuration is rigid with respect to the NMR time scale, as shown by two sets of \(^1\)H, \(^{13}\)C, \(^{14}\)N and \(^{15}\)N NMR signals for NR(Z) and NR(E) groups. This behaviour corresponds to that of the sulfur diimides. However, the barrier to configurational isomerization \((Z/E \leftrightarrow E/Z)\) is considerably higher in the selenium diimides \(1a, b\). \(1a\): \(\Delta G^\# = 65.0 \pm 1\) kJ/mol; \(1b\): \(\Delta G^\# = 63.0 \pm 1\) kJ/mol) as compared to \(\text{Bu(NSN)Bu}\) (\(\Delta G^\# = 54.4\) kJ/mol [14]) and \(\text{Oct(NSN)Oct}\) (\(\Delta G^\# = 50.5 \pm 1\) kJ/mol). It is conceivable that this difference is mainly due to steric effects, considering that the longer Se=N bonds allow more space for the alkyl group in Z-position with respect to repulsive interactions with the lone pair of electrons located at the other nitrogen atom bearing the alkyl group in E-position. This is in agreement with the finding for sulfur diimides R(NSN)R that this barrier to rotation/inversion becomes higher with less bulky groups R [15]. Two-dimensional (2D) \(^{13}\)C/\(^1\)H heteronuclear shift correlations served for mutual assignment of \(^{13}\)C and \(^1\)H NMR signals.

Since \(^{15}\)N NMR spectra could be obtained by polarization transfer techniques (e.g., refocused INEPT [16], see Fig. 2), it was easy to use selective \(^1\)H decoupling in order to correlate \(^1\)H and \(^{15}\)N resonance signals. On the basis of the unambiguous assignment of the \(^{15}\)N NMR signals (\textit{vide infra}), all
Table I. $^1$H, $^{13}$C, $^{15}$N and $^{77}$Se NMR data of the selenium diimides R(NSeN)R $^1$a, $^1$b and of their sulfur analogues $^1$a(S), $^1$b(S).

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>$^1$H (Z)-R</th>
<th>$^1$H (E)-R</th>
<th>$^{13}$C (Z)-R</th>
<th>$^{13}$C (E)-R</th>
<th>$^{15}$N</th>
<th>$^{15}$N</th>
<th>$^{77}$Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$a</td>
<td>1.56</td>
<td>1.13</td>
<td>28.7</td>
<td>32.9</td>
<td>+1.5c</td>
<td>+106.4d</td>
<td>1653.8f</td>
</tr>
<tr>
<td>$^1$b</td>
<td>1.51</td>
<td>1.07</td>
<td>29.6</td>
<td>32.6</td>
<td>-105.9</td>
<td>-6.6</td>
<td>-</td>
</tr>
<tr>
<td>$^1$a(S)</td>
<td>1.66</td>
<td>1.18</td>
<td>29.2</td>
<td>34.2</td>
<td>+3.2b</td>
<td>+111.9j</td>
<td>1642.6i</td>
</tr>
<tr>
<td>$^1$b(S)</td>
<td>1.07</td>
<td>0.86</td>
<td>31.9</td>
<td>31.8</td>
<td>32.3</td>
<td>32.0</td>
<td>-</td>
</tr>
<tr>
<td>$^1$a</td>
<td>1.77</td>
<td>1.35</td>
<td>53.3</td>
<td>56.8</td>
<td>31.7</td>
<td>31.7</td>
<td></td>
</tr>
<tr>
<td>$^1$b</td>
<td>1.02</td>
<td>0.85</td>
<td>32.2</td>
<td>31.9</td>
<td>32.2</td>
<td>31.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. 30.4 MHz $^{15}$N NMR spectrum of the di-tert-butyl selenium diimide $^1$a in [D$_8$]toluene at $-10^\circ$C. $^{77}$Se satellites for $^{15}$N are marked by asterisks.

$^1$H and $^{13}$C resonances were assigned to the substituents in Z- and E-position, respectively. The $^{15}$N NMR signal at higher frequency belongs to the nitrogen atom bearing the substituent in E-position, following the assignment for sulfur diimides [17] which show the same pattern of $^{15}$N nuclear shielding. It is noticeable that both types of $^{15}$N nuclei in the selenium diimides are deshielded by $\approx$110 ppm with respect to those of the corresponding sulfur diimide. Since changes in the nuclear shielding of this type of $^{15}$N nuclei are dominated by the nature of the lone pair of electrons at the nitrogen atom and the energy of the LUMO (magnetically active, i.e. magnetic-dipole allowed $n\rightarrow\pi^*$ transition) [18], the LUMO in the selenium diimides is expected to be of lower energy as compared to the sulfur diimides. This argument has also been used to explain the $^{15}$N deshielding in phosphazoles with respect to azoles and in 1,2,3-selenadiazoles with respect to 1,2,3-thiadiazoles [19].

The $^{77}$Se values for $^1$a,b are at somewhat higher frequency as compared to those of other Se(IV) compounds [2c,e, 4a, 5a, 6c]. The linewidth of the $^{77}$Se resonance signal of $^1$ is mainly the result of partially relaxed scalar coupling $J(^{77}\text{Se}^{15}\text{N})$ [116.6 and 112.9 Hz, as calculated from the values $|J(^{77}\text{Se}^{15}\text{N})|$ (see Fig. 2)]. In the case of $^1$a, there is little overlap of the $^{14}$N NMR signals which allows to measure the linewidths of the two $^{14}$N resonances (415 and 600 Hz) and to calculate the relaxation times $T_2^1(^{14}\text{N})=0.77$ and 0.53 ms. Assuming that scalar relaxation of the second kind accounts for the broadening of the $^{77}$Se resonance signal, a linewidth of $\approx 70$ Hz can be evaluated, in reasonable agreement with the experimental value of $\approx 80$ Hz measured for $^1$a.
The isolated product 2 arising from decomposition of 1a was fully characterized by multinuclear NMR in solution (see Table II). Since neither 77Se NMR nor 1H and 13C NMR are conclusive with respect to the structure of the eight-membered ring, a 15N NMR spectrum of sufficient quality is necessary to observe the 77Se satellites according to 1J(77Se15N) and 2J(77Se15N) (see Fig. 3). This has been achieved by taking advantage of the long-range coupling 3J(15N1H) for the tert-butyl group (=2.5 Hz) in polarization transfer experiments. The observed pattern of the 77Se satellites does not fit to the structure of the five-membered ring 3, a potential candidate [2]. However, the structure of 2 is in accordance with the 15N NMR results since it requires one type of the coupling constant 1J(77Se15N) and also one type of 2J(77Se15N) with 77Se satellites in a 2:1 ratio.

Aminoselenanes 4a, b, 5

Hexachlorodisilane reacts with 1a, b in the same way as with sulfur diimides [12]. We propose that an adduct is formed initially, similar to the 1a-SnCl4 adduct (which however was prepared in

<table>
<thead>
<tr>
<th>Compound Nr.</th>
<th>δ(1H) (Me3Si)</th>
<th>δ(13C) (Me3Si)</th>
<th>δ(15N)</th>
<th>δ(29Si) (Cl3Si) (Me3Si)</th>
<th>δ(77Se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.23</td>
<td>30.7</td>
<td>64.8</td>
<td>-279.7[96.9, 9.7]</td>
<td>+1391.0, +1163.6</td>
</tr>
<tr>
<td>4a</td>
<td>1.39</td>
<td>31.8</td>
<td>63.7</td>
<td>-279.5[98.2] (29.2)</td>
<td>+1188.0</td>
</tr>
<tr>
<td>4a(S)f</td>
<td>1.40</td>
<td>30.8</td>
<td>63.6</td>
<td>-275.9[32.5]</td>
<td>-</td>
</tr>
<tr>
<td>4b CMe2</td>
<td>1.51</td>
<td>31.5</td>
<td>68.6</td>
<td>-306.5[93.6]</td>
<td>+1188.8</td>
</tr>
<tr>
<td>CH2</td>
<td>1.96</td>
<td>54.8</td>
<td></td>
<td>-333.6[74.2] [7.7]</td>
<td>+11.7</td>
</tr>
<tr>
<td>CMe3</td>
<td>0.91</td>
<td>31.6</td>
<td>31.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>4.3</td>
<td></td>
<td>-326.2[72.2]</td>
<td>+9.9</td>
</tr>
<tr>
<td>5(S)solid state</td>
<td>-2.74</td>
<td>5.1</td>
<td>6.2</td>
<td>-326.2+9.9</td>
<td>+113.0</td>
</tr>
<tr>
<td>5(S)</td>
<td>0.15</td>
<td>3.5</td>
<td></td>
<td>-325.0[8.6]</td>
<td>+10.6</td>
</tr>
<tr>
<td>5(S)solid state</td>
<td>n.m.</td>
<td>n.m.</td>
<td></td>
<td>n.m.</td>
<td>+7.8</td>
</tr>
</tbody>
</table>

Table II. 1H, 13C, 15N, 29Si and 77Se NMR data of the eight-membered heterocycle 1BuN(SeSeSe)2N'Bu (2) and of the aminoselenanes 4a, b, 5, and of their sulfur analogues 4a(S), 5(S) for comparison.

Fig. 3. 30.4 MHz 15N NMR spectrum of the eight-membered heterocycle 2 (10 mm o.d. tube; ca. 150 mg in 2 ml of CDC13; 25 ± 1 °C; refocused INEPT pulse sequence, based on 3J(15N1H); repetition time 8 s, acquisition time 2.5 s; 2700 scans; 8 h of spectrometer time). 77Se satellites for 1J(77Se15N) = 96.9 Hz and 2J(77Se15N) = 9.7 Hz are marked by asterisks.

In C6D6, CDC13 or [D6]toluene at 25 ± 1 °C, coupling constants are given in Hz in square brackets [1J(77Se15N) and 2J(77Se15N)]; in curved brackets (1J(29Si15N)); n.m. = not measured; b see Fig. 3; c see also Fig. 1; d see Fig. 4a; e 15N and 29Si NMR data from [12b]; f see Fig. 4b.
a different way [4b,c]) or to the corresponding sulfur diimide-SnCl₄ adduct [20] in which both nitrogen atoms are involved as donors. The short-lived adduct 1-Si₂Cl₆ apparently undergoes an intramolecular redox reaction leading quantitatively to the diaminoselenanes 4a,b [Eqn. (3)]. The compounds 4a,b are colourless solids which decompose slowly at room temperature in daylight to give red selenium and a number of unidentified products.

\[
\begin{align*}
R(NSeN)R + Cl_2Si-SiCl_3 & \rightarrow \text{R} \quad \text{N} \quad \text{N} \quad \text{R} \\
\text{Cl}_2\text{Si} & \quad \text{SiCl}_3 \\
\text{R} = ^{\text{Bu}} & \quad \text{d} \text{o}c \text{t} \\
\end{align*}
\]

(3)

The structures of 4a,b are apparent from the NMR data and from comparison with the data of the sulfur analogue of 4a [12a], given in Table II together with the data of compound 5.

Again the \[^{15}\text{N}\] NMR spectra of 4 (Fig. 4a) and 5 (Fig. 4b) are particularly instructive owing to the presence of \[^{29}\text{Si}\] and \[^{77}\text{Se}\] satellites due to \(^1J(\text{^{29}Si}\text{^{15}N})\) and \(^1J(\text{^{77}Se}\text{^{15}N})\). Since the crystal structure of 5 has been determined [13], solid state \[^{13}\text{C}\], \[^{15}\text{N}\], \[^{29}\text{Si}\] and \[^{77}\text{Se}\] CP/MAS (cross polarization/magic angle spinning) NMR spectra are of interest. These spectra are in complete agreement with the results from X-ray diffraction. As in the sulfur analogue of 5, there are two crystallographically different sites of \[^{13}\text{C}\] and \[^{29}\text{Si}\] nuclei and only one site of \[^{15}\text{N}\] and \[^{77}\text{Se}\] nuclei. The mean value of the isotropic \(^\delta\[^{29}\text{Si}\]\) in the solid state is very similar to \(^\delta\[^{29}\text{Si}\]\) in solution, whereas a difference of about 10 ppm is observed in the \(^\delta\[^{15}\text{N}\]\) values. This indicates that the conformation preferred on average in solution differs from the configuration adopted in the crystalline state. There is also a moderate difference in the \(^\delta\[^{77}\text{Se}\]\) values (16.6 ppm). The solid-state \[^{77}\text{Se}\] CP/MAS NMR spectrum (Fig. 5) shows a splitting due to non-averaged dipolar and quadrupolar \[^{77}\text{Se}\]–\[^{14}\text{N}\] interactions and to scalar \[^{77}\text{Se}\]–\[^{14}\text{N}\] coupling (\(^{14}\text{N}; I = 1\)).

\[
\text{Fig. 4. a) } 30.4 \text{ MHz } ^{15}\text{N} \text{ NMR spectrum of bis[(tert-butyl(trichlorosilyl)amino)selenane (4a)] (10 mm o.d. tube; } ca. 200 \text{ mg in } 2 \text{ ml of } C_6D_6; \text{ at } 25 \pm 1 \degree \text{C; refocused INEPT pulse sequence, based on } \frac{3}{15}\text{N}^1\text{H} = 2.5 \text{ Hz; repetition time } 8 \text{ s; acquisition time } 2.5 \text{ s; } 2300 \text{ scans; } 7 \text{ h of spectrometer time). }^{29}\text{Si} \text{ satellites for } \frac{1}{15}\text{N}^{29}\text{Si} = 29.2 \text{ Hz are marked by arrows and }^{77}\text{Se} \text{ satellites for } \frac{1}{15}\text{N}^{77}\text{Se} = 98.2 \text{ Hz by asterisks. b) } 30.4 \text{ MHz } ^{15}\text{N} \text{ NMR spectrum of bis[(trimethylsilyl)amino}selenane (5) (5 mm o.d. tube; } ca. 200 \text{ mg in } 0.5 \text{ ml of } C_6D_6; \text{ at } 25 \pm 1 \degree \text{C; refocused INEPT pulse sequence, based on } \frac{3}{15}\text{N}^{13}\text{C} = 1.3 \text{ Hz; repetition time } 8 \text{ s; acquisition time } 2.5 \text{ s; } 2000 \text{ scans; } 6 \text{ h of spectrometer time). }^{13}\text{C} \text{ satellites for } \frac{3}{15}\text{N}^{13}\text{C} = 1.8 \text{ Hz are marked by open cycles; }^{29}\text{Si} \text{ satellites for } \frac{1}{15}\text{N}^{29}\text{Si} = 7.7 \text{ Hz by arrows and }^{77}\text{Se} \text{ satellites for } \frac{1}{15}\text{N}^{77}\text{Se} = 74.2 \text{ Hz by asterisks.}
\]

This splitting pattern deviates strongly from a 1:2:3:2:1 pattern expected for scalar \[^{77}\text{Se}\]–\[^{14}\text{N}\] spin-spin coupling and slow transverse relaxation of the two \[^{14}\text{N}\] nuclei. However, the width of the splitting pattern (=200 Hz) is very close to the expected width (= 212 Hz) if \(^1J(\text{^{77}Se}\text{^{14}N})\) = 53 Hz, as calculated from \(^1J(\text{^{77}Se}\text{^{15}N})\). Attempts to simulate such a spectrum are of dubious value, considering that there are several experimentally almost unac-

cessible non-first-order contributions to solid state MAS NMR spectra of the X part of an \(^{2}\text{A}_{2}\text{X}\) spin system, in particular if quadrupolar nuclei are involved [21].
data, including coupling constants $J(^{77}\text{Se}^{15}\text{N})$, may be of considerable help in the structural assignment. With compound 5, another example has been given for linking liquid state NMR data with structural data from X-ray analysis via the solid state NMR data of crystalline material.

**Experimental**

All manipulations of samples were carried out in an atmosphere of dry Ar or N$_2$, observing all precautions to exclude oxygen or moisture. The compounds 1a, 1b [26] and 4 [12] were prepared following literature methods for the synthesis of the same or analogous compounds.

Compound 2 was isolated from the mixture of decomposition products of 1a. ‘Bu(NSeN)’Bu (1a) was kept as a yellow solid at 28 °C for several days. During the whole time the quality (solid) and the colour (yellow) of the sample remained unchanged. After 7 days NMR spectra of the mixture were recorded. They indicated the preferred formation of BuN = N’Bu and compound 2. Afterwards 2 was purified by washing with ether and drying in high vacuo.

**Bis[alkyl(trichlorosilyl)amino]selenanes 4a,b**

A solution of 271 mg (1 mmole) of hexachlorodisilane in 50 ml of hexane was cooled to -78 °C and 220 mg (1 mmole) of 1a or 333 mg (1 mmole) of 1b, respectively, dissolved in 10 ml of hexane, were added dropwise to the stirred solution. A white precipitate was formed. The reaction mixture was allowed to reach room temperature, and the solvent was removed in vacuo whereby 410 mg 4a (84%) remained as a colourless, air- and moisture-sensitive powder, m.p. 120 °C. In daylight slow decomposition took place with separation of red selenium. In the case of 4b, faster decomposition was observed.

NMR spectra were recorded using Jeol FX 90 Q and Bruker AC 300 instruments, equipped with multinuclear units and control units for measurements at variable temperature (see also Tables I–I I and Figures 1–5). The delays for the INEPT 15N NMR spectra (Bruker AC 300) were optimized for a small number of scans before the spectra were recorded over 6 to 10 h in order to observe 29Si and/or 77Se satellite signals. 29Si NMR spectra were also obtained by using INEPT experiments; this gave very well resolved 29Si NMR spectra, allowing in the case of 5 to measure the small coupling constant $J(^{77}\text{Se}^{29}\text{Si}) = 2.7$ Hz. 77Se NMR spectra were recorded using Jeol FX 90 Q and Bruker AC 300 instruments, equipped with multinuclear units and control units for measurements at variable temperature (see also Tables I–I I and Figures 1–5). The delays for the INEPT 15N NMR spectra (Bruker AC 300) were optimized for a small number of scans before the spectra were recorded over 6 to 10 h in order to observe 29Si and/or 77Se satellite signals. 29Si NMR spectra were also obtained by using INEPT experiments; this gave very well resolved 29Si NMR spectra, allowing in the case of 5 to measure the small coupling constant $J(^{77}\text{Se}^{29}\text{Si}) = 2.7$ Hz. 77Se NMR
spectra were directly measured with $^1$H decoupling. In the case of 5, it was also possible to apply the INEPT sequence, based on a long-range coupling constant $^3J(^{77}\text{Se}^\text{H})$. Solid state $^{13}$C, $^{15}$N, $^{31}$Si and $^{77}$Se CP/MAS NMR spectra were measured using a Bruker MSL 300 instrument. Compound 5 was packed in an air-tight Kel-F insert [25], fitting exactly into the commercial ZrO$_2$ rotors of the double bearing multinuclear probehead. Chemical shifts are given with respect to Me$_4$Si ($^1$H: C$_6$D$_5$: 2.03, C$_6$D$_6$: 7.15, CDCl$_3$: 7.24; $^{15}$N: C$_6$D$_5$: 7.0; C$_6$D$_6$: 7.24; $^{31}$C: C$_6$D$_5$: 20.4, C$_6$D$_6$: 128.0, CDCl$_3$: 77.0; $^{77}$Se: $\varepsilon(^{77}\text{Se}) = 19.867184 \text{ MHz}$), neat MeNO$_2$ ($^{15}$N: $\varepsilon(^{15}\text{N}) = 10.136767 \text{ MHz}$), Me$_2$Se ($^{77}$Se: $\varepsilon(^{77}\text{Se}) = 19.071523 \text{ MHz}$).

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