

Spin-1/2 Nucleus Scalar Coupled to Quadrupolar Nuclei: Analysis of ⁷⁷Se Spectra in 2,1,3-Benzoselenadiazole

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One-bond scalar spin–spin couplings of ⁷⁷Se (spin-1/2) to nitrogen are usually large and can be comparable with quadrupolar relaxation rates of ¹⁴N nuclei in nonviscous liquids (1). At room temperature, the ⁷⁷Se signal in a benzene solution of the title compound **1** is substantially broadened; its width-at-half-height is equal to 120 Hz while the width of the ¹⁴N signal is about 240 Hz. The characteristics of the relevant electric field gradient (EFG) tensors, calculated at a DFT level (2), are given in Fig. 1. The molecular geometry assumed in the calculations of the EFG's was optimized using TURBOMOLE program with the DFT option (3). We previously managed to determine the ⁷⁷Se–¹⁵N coupling constant of 105 ± 0.2 Hz (for 0.5 mol/liter solution of **1** in DMSO at 320 K) from the ⁷⁷Se satellites (natural abundance 7.58%) in the natural-abundance ¹⁵N spectrum (1b). From the broadening of the central ¹⁵N line and from the width of the ¹⁴N signal we could also assess the absolute magnitude of the ¹⁵N–¹⁴N coupling constant to be smaller than 7.5 Hz. In that experiment, accumulation of as many as 100,000 scans for 48 h was required. We therefore sought an alternative, possibly less time-consuming way of measuring the selenium–nitrogen coupling constants in related selenazo compounds. As has long been known, when only one quadrupolar nucleus is scalar coupled to a spin-1/2 nucleus, the lineshape of the broadened resonance signal of the latter can be described by an equation (4) which is formally identical to the lineshape equation for multisite chemical exchange. In **1**, two isochronous ¹⁴N nuclei are coupled to the selenium nucleus. It follows from our earlier theoretical considerations (5) that in such a case the analogy with multisite exchange generally breaks down, and the full apparatus of the Bloch–Wangsness–Redfield (BWR) relaxation theory (6, 7) should be used to describe the ⁷⁷Se signal. The difficulties in the direct measurement of the selenium–nitrogen coupling constant have prompted us to explore the indirect way, involving lineshape analysis of the more readily measurable ⁷⁷Se and ¹⁴N spectra.

Compound **1** was synthesized according to a published pro-

cedure (8). Proton-decoupled NMR spectra of ⁷⁷Se and ¹⁴N in **1** were measured using a Bruker Avance DRX 500 MHz spectrometer, equipped with a BVT3000 temperature unit and a broadband probe, in the temperature range 303–393 K. The samples containing ca. 0.2 and 0.3 mol/liter solutions of **1** in benzene-*d*₆ and toluene-*d*₈, respectively, were degassed and sealed under vacuum of about 0.1 Torr in NMR tubes (WILMAD, o.d. 5mm, i.d. 3.44 mm). The ⁷⁷Se spectra were recorded by applying a 20° pulse with repetition time between 117 and 225 ms, depending on the signal width. Up to 350,000 scans (11 h) were recorded. Possible distortions of the ⁷⁷Se lineshapes due to incomplete recovery of the ⁷⁷Se subsystem between the pulses seem negligible; no *T*₁-relaxation mechanisms that might cause a multiexponential recovery can be identified for the ⁷⁷Se nucleus in **1**.

The BWR equation describing the proton-decoupled spectra of **1** reads

$$\frac{d|\rho\rangle}{dt} = \left\{ -i[\mathbf{L}_Z(\nu_{0A}, \nu_{0X}) + \mathbf{L}_J(J_{AX}, J_{AA})] - \frac{1}{2\pi T_2^*} \mathbf{1} \right\} |\rho\rangle + \mathbf{R}(j_a, j_c) |\rho - \rho_0\rangle, \quad [1]$$

where \mathbf{L}_Z is the Zeeman superhamiltonian of ⁷⁷Se (A) and ¹⁴N (X), \mathbf{L}_J describes ⁷⁷Se– and ¹⁴N–¹⁴N *J*-couplings; the term $-(2\pi T_2^*)^{-1} \mathbf{1}$ represents field inhomogeneity broadening of the resonance lines, and \mathbf{R} is the BWR relaxation matrix describing quadrupolar relaxation in the X₂ subsystem in the extreme narrowing approximation. The spin superoperators entering \mathbf{R} (see, e.g., Ref. (9)) are normalized in such a way that in absence of the ⁷⁷Se–¹⁴N coupling the quadrupolar relaxation times *T*₁ = *T*₂ of the nitrogen nuclei would be equal to $(2\pi j_a)^{-1}$, where *j*_a is the spectral density (at frequency 0) of the quadrupolar autocorrelation function for each of the equivalent nitrogen nuclei. The quantity *j*_c entering Eq. [1] is the spectral density of the corresponding cross-correlation function. Because the electric field gradient tensors at the different ¹⁴N nuclei are symmetry-related, the ratio *j*_c/*j*_a = *r* directly measures the degree of correlation of the fluctuating quadrupolar

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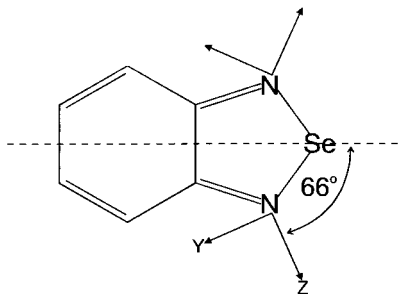


FIG. 1. Principal axes of the EFG tensors, calculated at a DFT level (2), for the nitrogen nuclei in 2,1,3-benzoselenadiazole, **1**. The principal values (MHz) are $V_{zz} = -3.68$, $V_{yy} = 2.40$, and $V_{xx} = 1.28$ ($\eta = -0.304$).

interactions at these nuclei. The spectra of both ^{77}Se and ^{14}N are insensitive to the signs of J_{AX} and J_{XX} , which can be seen from the transformation properties of Eq. [1] under the Liouville symmetry super-transformations described in Table 5 of Ref. (9).

We have written a computer program to iteratively analyze, using the Gauss–Newton scheme of the least-squares minimization, the spectra or, optionally, the FID functions of both the selenium and ^{14}N subsystems simultaneously. An essential part of the program is the RELAXAN routine mentioned previously (5). In the description of the ^{14}N signals of **1** the contributions of both the isotopomers of **1**, containing magnetically active and nonactive Se isotopes, were accounted for.

At ambient and elevated temperatures, the proton-decoupled ^{77}Se spectra of **1** can in principle be sensitive to each of the NMR parameters entering Eq. [1]. The proton-decoupled ^{14}N spectra, on the other hand, are sensitive only to J_{AX} and j_a in the whole temperature range where the extreme narrowing approximation is applicable (5). Convergence problems in the simultaneous iterative analysis of the ^{77}Se and ^{14}N spectra ought therefore to be much less severe than in the case of separate analyses. Actually, in the numerical computations described below no such problems have occurred despite the fact that at each temperature up to 12 lineshape parameters were varied simultaneously. Eight of them, amplitudes, baseline levels, dispersion admixtures, and positions of the resonances at the respective frequency axes, are of no interest in the present context but they are critical for the quality of the fits.

Numerical lineshape simulations of the sort reported earlier (5) reveal that the impact of J_{XX} , the coupling constants between the magnetically equivalent (in proton-decoupled spectra) ^{14}N nuclei, on the lineshape of ^{77}Se spectrum could be nonnegligible only in the limit of moderate quadrupolar relaxation rates where the fine structure due to the ^{77}Se – ^{14}N couplings starts to emerge. The dependence of the simulated spectra of ^{77}Se on the cross spectral density is more substantial. For the values of $|r|$ exceeding 0.8 it can even survive in the limit of fast quadrupolar relaxation (10, 11).

Keeping all this in mind, we performed iterative analyses of the pairs of spectra of **1** measured at four different temperatures. The unknown a priori value of J_{XX} was kept fixed. At each temperature, the calculations were repeated for three values, 0, 5, and 40 Hz, of J_{XX} . For both ^{77}Se and ^{14}N spectra, the magnitude of $1/\pi T_2^*$ was set to 0.2 Hz, which seemed reasonable since the linewidths in the ^1H spectra measured for the same sample using the same NMR probe never exceeded 1 Hz (the contribution to the ^{77}Se linewidth of the ^{77}Se T_2 -processes we assess to be negligible). For the runs with the assumed values 0 and 5 Hz of J_{XX} , the results delivered by the fitting algorithm at convergence were practically the same, regardless of whether the FID functions (including the data from both channels of the receiver) or the corresponding absorption spectra were taken as the input data. However, such an agreement could be achieved only when (i) in fitting the spectra, the line broadenings due to a limited acquisition time was accounted for by convoluting the theoretical lineshapes with the sinc functions, $\sin(2\pi\nu t_{\text{max}})/\nu t_{\text{max}}$, where t_{max} is the acquisition time, and (ii) in the analysis of the FIDs, the first four or eight points of the experimental FID functions were rejected (see caption to Fig. 3). Results of the lineshape analysis are collected in Table 1. The experimental ^{77}Se and ^{14}N spectra with the superimposed “best fit” theoretical spectra are displayed in Fig. 2, and for the experiment at 393 K, the corresponding ^{77}Se FID functions are shown in Fig. 3. In a related context, it was found advantageous to use in the lineshape analysis the FIDs instead of the spectra (12). This opinion is not supported by the results reported presently.

As can be seen from the data in Table 1, the results for J_{AX} and j_a are essentially independent of the assumed value of J_{XX} . The estimated values of J_{AX} do not differ much from the value of 75.5 Hz calculated from the ^{77}Se – ^{15}N coupling constant measured directly (1b). The least accurate is presumably the estimate of J_{AX} extracted from the spectra at 303 K. The results obtained from the spectra at higher temperatures, where out-

TABLE 1
Results of Lineshape Analysis for the ^{77}Se and ^{14}N Spectra of **1^a**

$T(\text{K})$	$J_{AX}(\text{Hz})$	$j_a(\text{Hz})$	$j_c(\text{Hz})$	$r = j_c/j_a$
303 ^b	78.0 ± 0.3	124.5 ± 0.5	37.4 ± 22.0	0.30 ± 0.18
	(78.3 ± 0.3)	(125.2 ± 0.4)	(67.2 ± 7.0)	(0.54 ± 0.06)
343 ^b	76.7 ± 0.3	73.4 ± 0.3	11.0 ± 8.6	0.15 ± 0.12
	(77.2 ± 0.3)	(73.2 ± 0.3)	(39.2 ± 2.4)	(0.54 ± 0.03)
383 ^b	76.6 ± 0.2	50.6 ± 0.2	1.0 ± 40.4	0.0 ± 0.8
	(76.9 ± 0.2)	(50.6 ± 0.2)	(25.2 ± 1.4)	(0.50 ± 0.03)
393 ^c	76.3 ± 0.2	53.4 ± 0.3	5.14 ± 11.1	0.10 ± 0.21
	(76.7 ± 0.2)	(53.6 ± 0.2)	(27.8 ± 0.9)	(0.52 ± 0.02)

^a Numbers without and within parentheses were obtained under assumption of $|J_{XX}| \leq 5$ Hz and $|J_{XX}| = 40$ Hz, respectively; standard errors are given.

^b Benzene solution.

^c Toluene solution.

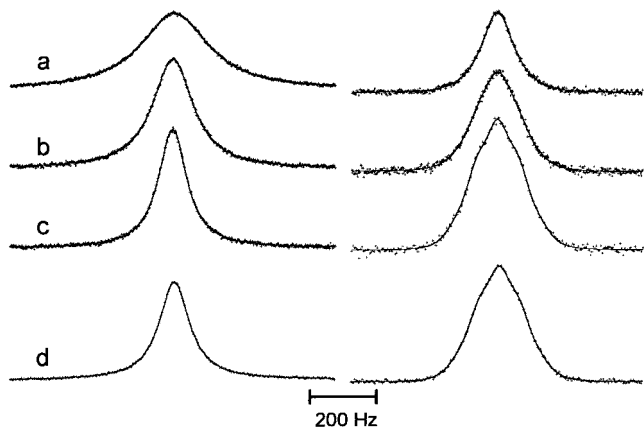


FIG. 2. Experimental $^{14}\text{N}\{^1\text{H}\}$ (left side) and $^{77}\text{Se}\{^1\text{H}\}$ (right side) spectra, measured at 303 (a), 343 (b), and 373 K (c) for a benzene solution of **1** and at 383 K for a toluene solution of **1** (d). The solid curves depict the superimposed "best fit" theoretical spectra.

lines of the fine structure start to emerge, are consistent. As the most realistic estimate for the $^{77}\text{Se}\text{-}^{14}\text{N}$ coupling constant we take the value of 76.5 ± 0.2 Hz; the discrepancy of 1 Hz relative to the value calculated from $J(^{77}\text{Se}\text{-}^{15}\text{N})$ may be due to a primary $^{14}\text{N}/^{15}\text{N}$ isotope effect. This estimate will remain practically unchanged even when the results obtained under the (presumably unrealistic) assumption of $|J_{\text{xx}}| = 40$ Hz are included. The way of determining unresolved coupling constants described here, which seems to be both efficient and accurate, can easily be extended to systems containing more than two quadrupolar nuclei.

The values of j_c estimated under the assumption $|J_{\text{xx}}| \leq 5$ Hz point to a low degree of quadrupolar cross-correlation in the systems considered (benzene and toluene solutions of **1**) in the whole temperature range. These values come with large standard errors, which is not surprising in the case of the spectra at 303 and 343 K, because this could be anticipated from the already mentioned spectral simulations. However, the large standard error of j_c at 383 K is in striking contrast to expectations. We first blamed for this the relatively low signal-to-noise ratio in the ^{77}Se spectrum at 383 K. The high-temperature experiment was therefore repeated for a toluene solution of **1** in which a significant improvement of the quality of the spectrum was achieved. This, however, did not reduce the magnitude of the standard error of j_c at a satisfactory level. Then we found that for small values of $|r|$ the lineshape functions calculated for j_c and $-j_c$ are practically nondifferentiable. Accordingly, for the values of $|r|$ approaching 0 the two nearly equivalent minima at the sum-of-squares hypersurface, those at j_c and $-j_c$, may merge into a single, broad minimum. It is the curvature of the latter that, together with the magnitude of the rms error, determines the magnitude of the standard error involved. Therefore the results obtained for j_c can only be interpreted semiquantitatively. Nevertheless, the conclusion

that in the high temperature limit the quadrupolar cross-correlations are very low for the benzene and toluene solutions of **1** seems fully justified. It is interesting to note that for the calculated EFG tensors (see Fig. 1) and under the assumption of isotropic reorientation of the molecules of **1** the theoretical value of r calculated according to the prescription in Ref. (13) amounts to $+0.16$. As far as we know, this is the first attempt to determine quadrupolar cross-correlations in isotropic fluids.

The values of r obtained under the assumption of $J_{\text{xx}} = 40$ Hz differ significantly from zero (note their small standard errors). This is a clear confirmation of the prediction from numerical simulations (5) that in AX_2 systems the estimates of J_{xx} and r will show substantial statistical correlation. In the present case, the estimates made under the assumption $|J_{\text{xx}}| > 5$ Hz can be rejected on the basis of the results for a DMSO solution of **1** mentioned earlier. However, the observed statistical correlation between the estimates of J_{xx} and r provides indirect proof of the spectroscopic relevance of J -couplings between magnetically equivalent quadrupolar nuclei. Studies on related systems in which $|r|$ is close to unity might provide more direct evidence of the latter property. Such studies are under way.

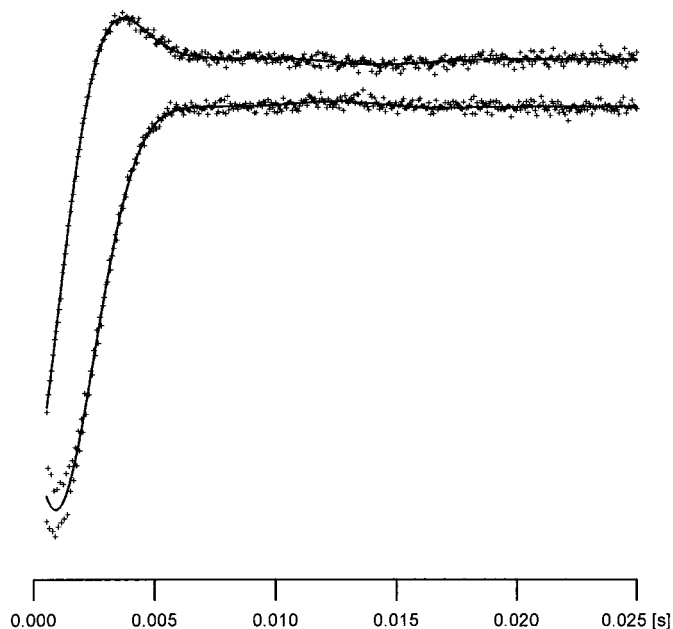


FIG. 3. Experimental (crosses) and theoretical "best fit" (solid lines) FID functions of the $^{77}\text{Se}\{^1\text{H}\}$ resonance in toluene solution of **1** at 393 K. The displayed components of the experimental FID were obtained from the raw data, registered in a digital mode, using CONVDTA program provided by the Bruker company. The first 4 points of the preprocessed data were rejected. The remaining 12 initial points from one of the receiver channels (lower plot) are still distorted, which is probably due to an incomplete removal, by the CONVDTA program, of the digital filter characteristics contained in the raw data. Retention of these 12 points in the input data for the least-squares calculations does not significantly affect the results.

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