JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 108, NUMBER 8 APRIL 16, 1986

^{77}Se NMR. Application of $J_{\text{Se-Se}}$ to the Analysis of Dialkyl Polyselenides

Hanne Eggert,* Ole Nielsen, and Lars Henriksen

Contribution from the Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark. *Received July 12, 1985*

Abstract: Elemental selenium is partially reduced via either disproportionation or reaction with sodium methanolate and hydrazine in dipolar aprotic media. These reductions both give polyselenide ions with a known average chain length, Se_n^{2-} ($3 \le n \le 7$). Alkylation of these anions proceeds with loss of selenium and formation of a mixture of dialkyl polyselenides, R–Se$_m$–R (**2**), with an average chain length $m \sim 2.25$–2.50. ^{77}Se chemical shifts and ^{1}H–^{77}Se and ^{77}Se–^{77}Se coupling constants were measured for various dialkyl polyselenide mixtures. By observation of the selenium satellites in the ^{77}Se NMR spectra the existence in the mixture of di-, tri-, tetra-, and pentaselenides was proved and the structure of the higher polyselenides established as linear chains. ^{77}Se–^{80}Se isotope effects on the ^{77}Se chemical shifts were measured and used for assignment of the homonuclear ^{77}Se coupling constants. The ^{77}Se chemical shifts of selenides show a large temperature variation. It is shown that such a large variation coupled with sample spinning can give rise to artificial signal splitting in proton noise decoupled NMR spectra.

While organic polysulfides (**1**, $m \le 6$) are well-documented substances,[1] little information on the corresponding selenium compounds (**2**) is available. A number of diaryl triselenides have

$$\underset{\mathbf{1}}{\text{R–S}_m\text{–R}} \qquad \underset{\mathbf{2}}{\text{R–Se}_m\text{–R}}$$

been isolated and shown to be stable substances,[2] and the structure of one member of this class has been determined by X-ray diffraction.[3] Only a few dialkyl triselenides appear in the literature. Diethyl and perfluorodiethyl triselenides have been mentioned briefly,[4,5] the ^{77}Se chemical shifts have been reported for triseleno-3,3′-dipropionic acid and -5,5′-dipentanoic acid,[6] 1,2,3-triselenolan was isolated and identified by mass spectroscopy,[7] and the structure of bis(di-*tert*-butylmethyl) triselenide was determined by X-ray crystallography.[8] No higher polyselenides have been characterized although their presence as impurities in crude preparations of dialkyl diselenides has been suspected.[9]

In order to obtain information on the occurrence, stability, and structure of dialkyl polyselenides, we have alkylated solutions of polyselenide ions with various alkyl halides or tosylates and subjected the resulting mixtures of **2** to ^{77}Se NMR analysis (^{77}Se: spin $^1/_2$, natural abundance 7.6%). This powerful analytical technique is particularly well suited for analysis of mixtures of selenium compounds for several reasons:[10] (1) The proton noise decoupled spectra are simple and contain only a few signals per compound. (2) The chemical shift range is large so that overlapping signals are usually avoided even for closely related species. (3) Auxiliary information on the connectivity of the observed signals is available by the measurement of the ^{77}Se–^{77}Se satellite spectrum, ^{77}Se–^{1}H couplings, and selenium chemical shift isotope effects.

Results and Discussion

Preparation and Alkylation of Polyselenide Anions. Polyselenide anions are in principle formed by the partial reduction of selenium. In the present study, we have employed two different methods to effect this reduction. In the first, we utilized the disproportionation of selenium into the selenite and polyselenide ion[9] which proceeds in a quantitative manner according to eq 1 in dipolar aprotic solvents.[11]

$$(2n + 1)\text{Se} + 6\text{OH}^- \rightarrow \text{SeO}_3^{2-} + 2\text{Se}_n^{2-} + 3\text{H}_2\text{O} \qquad (1)$$

In the second, the hydrazine reduction of selenium[12] was modified by the use of sodium methanolate (4 M in methanol) as the base in DMF or Me$_2$SO solution (eq 2). By the way of

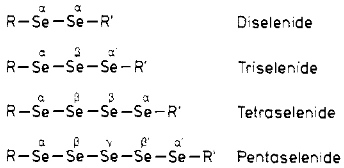
$$2n\text{Se} + 4\text{MeO}^- + \text{N}_2\text{H}_4 \rightarrow 2\text{Se}_n^{2-} + 4\text{MeOH} + \text{N}_2 \qquad (2)$$

this modification, the base was quantitatively consumed and a

---

[1] Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333.
[2] Reinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 4.
[3] Shibaeva, R. P.; Kaminskii, V. F.; Kostyuchenko, E. E.; Yagubskii, E. B. *J. Organomet. Chem.* **1984**, *260*, 293.
[4] Levi, G. R.; Baroni, A. *Atti Accad. Naz. Lincei Mem., Cl. Sci. Fis., Mat. Nat.; Rend.* **1929**, *9* (6), 1019.
[5] Desjardins, C. D.; Passmore, J. *J. Chem. Soc., Dalton Trans.* **1973**, 2314; *Can. J. Chem.* **1977**, *55*, 3136.
[6] Fredga, A.; Gronowitz, S.; Hörnfeldt, A.-B. *Chim. Scr.* **1975**, *8*, 15.
[7] Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1980**, *45*, 2632.
[8] McKinnon, B. J.; de Mayo, P.; Payne, N. C., Ruge, B. *Nouv. J. Chem.* **1978**, *2*, 91.
[9] Günther, W. H. H. In "Organic Selenium Compounds"; Klayman, D. L., Günther, W. H., Eds.; Wiley: New York, 1973; pp 51–52.
[10] Johannsen, I.; Eggert, H. *J. Am. Chem. Soc.* **1984**, *106*, 1240.
[11] Henriksen, L. In "Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium"; Berry, F. J., McWhinnie, W. R., Eds.; The University of Aston in Birmingham: Birmingham, AL, 1983; p 242.
[12] Syper, L.; Meochowski, J. *Synthesis* **1984**, 439.

0002-7863/86/1508-1725$01.50/0



$\text{R}-\overset{\alpha}{\text{Se}}-\overset{\alpha}{\text{Se}}-\text{R}'$ Diselenide

$\text{R}-\overset{\alpha}{\text{Se}}-\overset{\beta}{\text{Se}}-\overset{\alpha'}{\text{Se}}-\text{R}'$ Triselenide

$\text{R}-\overset{\alpha}{\text{Se}}-\overset{\beta}{\text{Se}}-\overset{\beta}{\text{Se}}-\overset{\alpha}{\text{Se}}-\text{R}'$ Tetraselenide

$\text{R}-\overset{\alpha}{\text{Se}}-\overset{\beta}{\text{Se}}-\overset{\gamma}{\text{Se}}-\overset{\beta'}{\text{Se}}-\overset{\alpha'}{\text{Se}}-\text{R}'$ Pentaselenide

Figure 1. Structure and numbering of R–Se_m–R.

Table I. Dialkyl Polyselenides R–Se_m–R Prepared according to Equation 3 with $n = 4$

R	X	reaction time, h	m	composition,[a] % Se_2	Se_3	Se_4	Se_5
octyl	Br	<0.1	2.46	64	26	7	2[b]
pentyl	Br	<0.1	2.25	78	19	3	
2-ethylhexyl	Br	0.5	2.24	79	18	3	
cyclohexyl	Br	30	2.41	70	25	8	
1-propylbutyl	OTs	3	2.30	75	21	4	
1-methyl-4-ethylhexyl	OTs	3	2.24	80	16	4	
benzyl	Br	<0.1	2.37	75	17	6	2
2,4-Dichlorobenzyl	Cl	<0.1	2.37	74	17	7	2

[a] Total amount of dialkyl polyselenides isolated accounted for better than 90% of polyselenide anion initially present. [b] The hexaselenide (~0.5%) was also detected.

homogeneous solution of sodium polyselenide obtained within a few minutes at room temperature.

The quantitative nature of either reaction allows the preparation of a polyselenide solution with a predetermined average chain length, n. A study of the selenium consumption during the hydrazine reduction with sodium methanolate as the limiting reagent indicated that values of n up to 7 could be obtained. The reduction was also followed by volumetric determination of the nitrogen evolved. This study showed that the reduction for $n \geq 4$ proceeded within 2 min at room temperature. For $n < 4$, this was followed by a slower reduction to $n = 3$ which took ~25 min. No reduction beyond this value was observed.

The alkylations were in both cases performed in situ by adding the appropriate alkyl halide or tosylate. The compositions of the product mixtures R–Se_m–R (**2**) were determined by means of the ^{77}Se NMR spectra (see below). Since the Se^α signals (see Figure 1) of all homologues in a series have comparable line width, the relative peak heights can be taken as a direct measure of the mole fractions— if a sufficient signal noise ratio is reached; otherwise, the method systematically underestimates the small peaks. The composition of the product mixture of **2** for a common value of n was found to be independent of the mode of formation of the polyselenide anion reagent.

However, the alkylation is accompanied by selenium precipitation (eq 3), and the average chain length in **2**, m, has not been observed to exceed ca. 2.6.

$$\text{Se}_n^{2-} + 2\text{RX} \rightarrow \text{R–Se}_m\text{–R} + (n)-(m)\text{Se} \qquad (3)$$

Table I shows the composition of a series of dialkyl polyselenide mixtures prepared from an anion reagent with $n = 4$. These entries which cover a wide variety of alkyl group structures as well as a large range of reaction periods do not reveal any large, or systematic, variation in the polyselenide composition.

Table II presents the composition of a series of dioctyl polyselenide mixtures as a function of the calculated average chain length, n, of the anion reagent. A steady increase in the selenium content of the product is seen when n is increased from 2 to 3. For values of $n \leq 2.5$, this content depends on the mode of preparation. When octyl bromide is added ca. 2 min after the start of the hydrazine reduction, free base and hydrazine are present during the alkylation and the reduction of the alkylated products gives rise to monoselenides via alkylation of selenoate ion.[12] If 30 min is allowed for the reduction to reach the $n = 3$ stage, no monoselenide is observed and the same is true if the polyselenide ion reagent is prepared by the disproportionation route. A further increase of n beyond 3, however, results in less selenium incorporation in the product, and for $n > 4$, a constant value of $m = 2.46$ is observed. This value appears to be the equilibrium selenium content. Compounds containing Se–Se bonds generally undergo reversible Se-exchange reactions in the presence of an acid catalyst,[11] and in fact values of m close to 2.46 were found both when a dioctyl polyselenide with $m = 2.6$ was treated with trichloroacetic acid (TCA) and when a pure diselenide was equilibrated with selenium in the presence of TCA (eq 4). These results imply that a selenium content above 2.46 must be caused by kinetic control. The details of these reactions are under further investigation.

Table II. Composition of Dioctyl Polyselenide Mixtures $\text{C}_8\text{H}_{17}\text{–Se}_m\text{–C}_8\text{H}_{17}$ as a Function of the Average Polyselenide Chain Length, n

n	m	composition, % Se_1	Se_2	Se_3	Se_4	Se_5
2.0[a]	1.91	17	75	8		
2.0[b]	2.31	0	72	25	3	
2.5[a]	1.94	19	68	12	1	
2.5[b]	2.30	0	74	23	3	
2.75	2.46	0	65	26	8	1
3.0	2.62	0	55	32	10	3[c]
3.25	2.52	0	62	28	8	2[c]
4.0	2.49	0	64	26	7	2[c]
5.0	2.46	0	63	29	7	1
7.0	2.46	0	63	28	7	2

[a] Reduction for 2 min prior to the addition of octyl bromide. [b] Reduction for 25 min prior to the addition of octyl bromide. [c] Traces of hexaselenide detected.

$$\text{R–Se}_{2.6}\text{–R} \xrightarrow[-\text{Se}]{\text{H}^+} \text{R–Se}_{2.46}\text{–R} \xleftarrow[+\text{Se}]{\text{H}^+} \text{R–Se}_2\text{–R} \qquad (4)$$

^{77}Se–^{77}Se Coupling Constants. The analysis of the dialkyl polyselenide mixtures was performed by observation of selenium satellites in the proton-noise-decoupled ^{77}Se NMR spectra. These selenium satellites arise from molecules containing two ^{77}Se isotopes. If the two ^{77}Se nuclei are found on nonequivalent positions, they will couple and give rise to an AB satellite spectrum placed around the chemical shifts of the mother peaks. In order for this AB satellite spectrum to be resolved from the mother peaks, the coupling constant of the satellite spectrum must exceed the width of the mother peaks at the level of satellite peak heights. Due to ^{77}Se–^{77}Se coupling in the satellite spectrum, this height is only half the natural abundance for ^{77}Se (7.6%). Depending on the δ_{AB}/J ratio of the AB satellite spectrum, the intensity of the outer pairs of lines can be further decreased. In the present study, the line width in 3% height is normally 3–4 Hz, and satellite spectra with a coupling constant smaller than this are therefore not observable.

From the above it follows that AB satellite patterns will not be observed for the diselenides of this study due to equivalence of the two selenium nuclei. Dialkyl triselenides (see Figure 1) are expected to show one AB satellite spectrum around the two ^{77}Se chemical shifts corresponding to a one-bond ^{77}Se homonuclear coupling. In a dialkyl tetraselenide, the two nonequivalent ^{77}Se nuclei can either be connected to each other or be separated by a selenium atom. Thus, in the spectra of these compounds two mother peaks surrounded by two satellite AB spectra corresponding to a one- and two-bond ^{77}Se–^{77}Se coupling are expected.

Extending to a dialkyl pentaselenide, two nonequivalent ^{77}Se nuclei can be situated in four different ways as $\text{Se}^\alpha\text{Se}^\beta$, $\text{Se}^\alpha\text{Se}^\gamma$, $\text{Se}^\alpha\text{Se}^{\beta'}$, and $\text{Se}^\beta\text{Se}^\gamma$ (see Figure 1). Each combination will give rise to an AB satellite spectrum placed around the chemical shifts of the two ^{77}Se nuclei involved. It is seen that the α-selenium nuclei can be involved in three different couplings corresponding to a $^1J_{\text{Se–Se}}$, a $^2J_{\text{Se–Se}}$, and a $^3J_{\text{Se–Se}}$ coupling constant. The β-selenium nuclei can likewise take part in three AB spectra, but in this case, two $^2J_{\text{Se–Se}}$ and a $^3J_{\text{Se–Se}}$ coupling constants are involved. The γ-selenium nuclei can only take part in two AB satellite spectra corresponding to a $^1J_{\text{Se–Se}}$ and a $^2J_{\text{Se–Se}}$.

The ^{77}Se NMR spectra of the dialkyl polyselenide mixtures were all analyzed by using the above given account of the satellite patterns expected for each selenium homologue. Distinguishing

Table III. ^{77}Se–^{77}Se Coupling Constants (Hz) in Dialkyl Polyselenides R–Se$_m$–R

R	$m = 3$	$m = 4$		$m = 5$		
	$^1J_{Se-Se}$	$^1J_{Se-Se}$	$^2J_{Se-Se}$	$^1J_{Se^\alpha-Se^\beta}$	$^1J_{Se^\beta-Se^\gamma}$	$^2J_{Se^\alpha-Se^\gamma}$
octyl	4.4	19.5	115.1	22.7	29.3	114.0
2-ethylhexyl[a]	4.4	16.5	115.1	21.3	27.2	114.7
2,4-dichlorobenzyl	8.3	32.7	112.0			
1-methyl-4-ethylhexyl	11.7	44.0	114.7			
1-propylbutyl	13.7	47.3	116.7			
1,1-dimethylpropyl	26.9					

[a] Same value for both diastereomers.

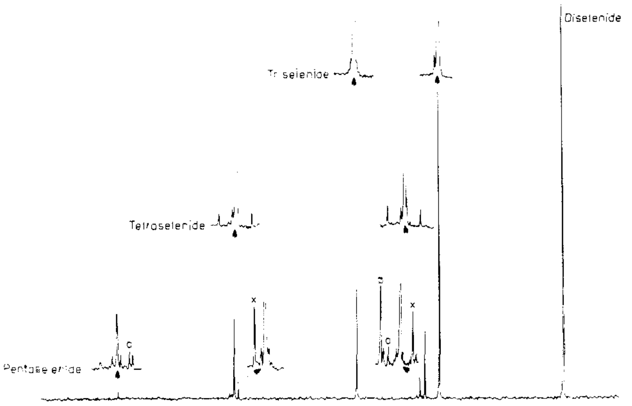


Figure 2. Proton noise decoupled ^{77}Se NMR spectrum of a dioctyl polyselenide mixture. Inserts (recorded with a reduced spectral width to increase resolution) show the selenium satellites. (x) Satellites from neighboring tetraselenide resonances. (O) Resonances from dioctyl hexa- and possibly heptaselenides.

between signals belonging to each homologue in a mixture was facilitated by the fact that all the dialkyl polyselenide mixtures investigated contained unequal amounts of the individual selenium homologues (see Table I). Furthermore, the dialkyl diselenides in the mixtures were in all cases identified by comparison with the spectrum of an authentic sample. This was also the case for the dibenzyl and bis(2,4-dichlorobenzyl) triselenides. The ^{77}Se NMR spectra of the dialkyl polyselenide mixtures contained mother peaks and associated satellite patterns in accordance with the presence of dialkyl tri-, tetra-, and pentaselenides in the mixtures. The structure of the higher polyselenides is herewith established as linear chains. The absolute values of the homonuclear ^{77}Se coupling constants measured are given in Table III. The ^{77}Se NMR spectrum of a dioctyl polyselenide mixture is shown in Figure 2. Expansions are given as inserts on the spectrum to show the selenium satellites.

For the tri- and tetraselenides, all the possible AB satellite spectra were resolved. In the case of pentaselenides, only three of the four possible satellite spectra were observed. In the spectra of the pentaselenides investigated, one satellite spectrum around the chemical shifts of Se$^\alpha$ and Se$^\beta$ was missing. Thus, the unresolved coupling must be either the one-bond Se$^\alpha$–Se$^\beta$ or the three-bond Se$^\alpha$–Se$^{\beta'}$ coupling. By observation of chemical shift isotope effects (see below), it can be concluded that the unresolved coupling constant corresponds to a three-bond ^{77}Se–^{77}Se coupling.

Very few studies have been reported on ^{77}Se–^{77}Se coupling constants. Besides the recent paper on the sterochemical dependence of $^3J_{Se-Se}$[10] and our forthcoming paper on $^2J_{Se-Se}$ and $^3J_{Se-Se}$ in alkenylic selenides,[13] only four other reports,[14-17] all on $^1J_{Se-Se}$ in diselenides, are available. The reported numerical values for $^1J_{Se-Se}$ range from 2 to 36 Hz.

The results presented in Table III for the one- and two-bond homonuclear ^{77}Se–^{77}Se coupling constants in dialkyl polyselenides show some interesting features: (1) The one-bond coupling constants measured are numerically much smaller than the coupling over two bonds. (2) $^1J_{Se-Se}$ coupling constants vary according to the selenide chain length; $^1J_{Se-Se}$ are about 4 times larger in tetraselenides than in the corresponding triselenides. $^2J_{Se-Se}$ do not show such a variation. (3) The magnitude of $^1J_{Se-Se}$ depends strongly on the size of the alkyl groups. Tri- and tetra-selenides show an increase in $^1J_{Se-Se}$ as the size of the alkyl groups decreases, while $^1J_{Se-Se}$ in diselenides[16] show the opposite steric effect. $^2J_{Se-Se}$ do not depend on the size of the alkyl groups.

In the paper on ^{77}Se–^{77}Se coupling constants in alkenylic selenides,[13] we have pointed out that lone-pair p-orbital overlap is likely to be involved in the transmission of the coupling. Examples of various cis and trans $^3J_{Se-Se}$, vinylic $^2J_{Se-Se}$, and homoallylic $^4J_{Se-Se}$ coupling constants were consistent with that proposal. The numerical much larger value of $^2J_{Se-Se}$ than $^1J_{Se-Se}$ found in the dialkyl polyselenides also supports the proposal: The lone-pair p orbitals of directly connected selenium atoms in the polyselenides of Table III are close to orthogonal, while selenium atoms separated with two bonds have the possibility of selenium lone-pair p-orbital overlap. Strong support for the involvement of selenium lone-pair p-orbital overlap in transmission of the coupling comes from the measurement of $^1J_{Se-Se}$ in cyclic five- and six-membered diselenides.[18] In these structures, the lone-pair p orbitals are forced to have a large overlap and the numerical value of $^1J_{Se-Se}$ shows a dramatic increase. Thus, values as high as 374 Hz have been measured for the one-bond Se–Se coupling constant, the largest Se–Se coupling constant so far observed.

Selenium Isotope Effects on ^{77}Se Chemical Shifts. The assignment of the measured homonuclear ^{77}Se coupling constants to specific couplings within each homologue as given in Table III was possible by observation of selenium isotope effects on the chemical shifts. Thus, the satellite spectra assigned to a one-bond ^{77}Se–^{77}Se coupling in Table III all have resonance frequencies which are shifted 0.7 Hz (±0.2) to low field from the corresponding mother peaks.

The AB satellite spectra in ^{77}Se NMR spectra arise as described above from species containing two nonequivalent ^{77}Se isotopes. The corresponding mother peaks consist of the overlapping resonances from species where the same two nuclei positions instead are occupied by ^{77}Se^{n}Se, n = 74, 76, 78, 80, and 82. The natural abundance of the selenium isotopes is as follows: ^{74}Se, 1.0%; ^{76}Se, 9.1%; ^{77}Se, 7.6%; ^{78}Se, 23.6%; ^{80}Se, 49.6%; and ^{82}Se, 8.8%. Thus, the isotopomer ^{77}Se^{80}Se will give rise to maximum intensity of the mother peaks, and the measured isotope effect of 0.7 Hz ± 0.2 (0.04 ppm) then corresponds to the isotopic substitution ^{77}Se $\rightarrow$ ^{80}Se. Within the applied resolution, the isotope shifts measured were all found to be of the same value. Previously selenium isotope effects on ^{77}Se chemical shifts in dimethyl diselenide have been reported.[19] A selenium isotope shift of 0.013 ppm per mass unit was measured. The shift goes to low field with decreasing mass. The isotope effect measured per mass unit for the dialkyl polyselenides is seen to compare closely to the one-bond isotope effect reported for dimethyl diselenide.

Assignment of some of the homonuclear ^{77}Se coupling constants measured follows directly from a chemical shift assignment (see below). The result hereof agrees with the assignment on the basis of isotope effects. Furthermore, the number of satellite spectra

---

(13) Johannsen, I.; Henriksen, L.; Eggert, H. *J. Org. Chem.*, in press.

(14) McFarlane, W. *J. Chem. Soc. A* **1969**, 670.

(15) Gragner, P.; Chapelle, S.; Paulmier, C. *Org. Magn. Reson.* **1980**, *14*, 240.

(16) Anderson, J. A.; Odom, J. D.; Zozulin, A. J. *Organometallics* **1984**, *3*, 1458.

(17) Gombler, W. *J. Magn. Reson.* **1983**, *53*, 69.

(18) Henriksen, L.; Nielsen, O.; Eggert, H., unpublished results.

(19) Jakobsen, H. J.; Hansen, R. S. *J. Magn. Reson.* **1978**, *30*, 397.

showing isotope effects equals the number of one-bond couplings possible in the systems studied. The assignment, as given in Table III, shows an internal consistent pattern of ${}^nJ_{Se-Se}$ in dialkyl polyselenides. Thus, it follows that AB satellite spectra showing isotope shifts as described above can be assigned to a one-bond ^{77}Se–^{77}Se coupling.

^{77}Se Chemical Shifts and ^{1}H–^{77}Se Coupling Constants. The assignment of chemical shifts within the individual homologues follows from consideration of the relative peak intensity together with measurements of ^{77}Se–^{1}H coupling constants. Thus, only ^{77}Se nuclei next to an alkyl group (Se$^\alpha$) show sizeable spin coupling to both the α and β protons of the alkyl group. The assignments of the observed splittings to ${}^2J$ and ${}^3J$ ^{77}Se–^{1}H couplings follow from the coupling pattern in the proton-coupled ^{77}Se NMR spectra and by intercomparison. Thus, generally, the Se$^\alpha$ nuclei show an extended ^{77}Se–^{1}H coupling pattern, while Se$^\beta$ and Se$^\gamma$ within a resolution of ±0.5 Hz give singlets in the proton-coupled spectra. In one case, dioctyl diselenide, a ^{77}Se–^{1}H coupling constant of 2 Hz corresponding to ${}^3J_{Se-Se-C\underline{H}}$ has been observed.

Chemical shift values and ^{77}Se–^{1}H coupling constants have previously been reported for some dialkyl diselenides.[16,20,21] These literature data are in accordance with the values of this study.

The ^{77}Se chemical shifts and J_{Se-H} coupling constants for the dialkyl di- and polyselenides are collected in Table IV. The chemical shift range for the various selenium nuclei covers more than 500 ppm and in all cases were signals corresponding to each selenium homologue in the polyselenide mixture resolved (see Figure 2). Beside the resonances given in Table IV, the dioctyl polyselenide mixture gave under certain reaction conditions (see Table II) rise to three minor signals of equal intensity close lying to the three signals of the dioctyl pentaselenide. The low intensity of these signals prohibited detection of ^{77}Se satellites. Based on the chemical shifts, the intensity ratio, and the ^{77}Se–^{1}H coupling constants, they are assigned to dioctyl hexaselenide.

Two of the dialkyl polyselenide mixtures investigated are with asymmetric alkyl groups, giving rise in the mixture to two diastereomers for each selenium homologue. With the asymmetric center at the α-carbon atom (R = 1-methyl-4-ethylhexyl), resolved signals for all the diastereomeric paris in the polyselenide mixture were obtained. When the asymmetric center is moved to the β-carbon atom (R = 2-ethylhexyl), only the triselenide gives resolved chemical shifts for diastereomeric pairs, within the applied instrumental resolution (±0.03 ppm).

The ^{77}Se NMR spectrum of the dicyclohexyl polyselenide mixture is temperature-dependent. A 55 °C, the spectrum shows five signals ($\Delta\nu_{1/2} \sim 3$ Hz) corresponding to a dicyclohexyl diselenide, triselenide, and tetraselenide. When the temperature was decreased, all peaks broadened, reached a maximum line width for the α-selenium signals about −20 °C. At −70 °C, the signals sharpened again. Besides five stronger signals, several additional weak lines now appeared in the spectrum. This temperature dependence is observed only for cyclohexyl as the alkyl group and is ascribed to ring inversion of the cyclohexyl ring. We have analyzed the low-temperature spectrum of the pure dicyclohexyl diselenide. The low-temperature spectrum revealed three weak lines beside one strong signal. The chemical shifts and relative intensities of the four lines are 407.8 (5), 370.0 (~1), 368.0 (100), and 290.4 ppm (5). Due to ring inversion, three conformers are possible for dicyclohexyl diselenide: a diequatorial, an equatorial axial, and a diaxial conformer. These will give rise to a total of four signals including two signals of equal intensity from the equatorial axial conformer. From the intensity ratios observed at −70 °C a value of 0.9 kcal/mol can be estimated by which the conformer of lowest energy is more stable than the axial equatorial conformer.

Temperature Dependence and Artificial Line Splitting of ^{77}Se NMR Signals. The ^{77}Se chemical shifts of the dialkyl polyselenides

Table IV. ^{77}Se Chemical Shifts (ppm) and ^{77}Se–^{1}H Coupling Constants (Hz) of Dialkyl Polyselenides R–Se$_m$–R

	$m = 2$			$m = 3$				$m = 4$				$m = 5$				
R	$\delta(^{77}Se^\alpha)$	$^2J_{Se-H}$	$^3J_{Se-H}$[c]	$\delta(^{77}Se^\alpha)$	$\delta(^{77}Se^\beta)$	$^2J_{Se^\alpha-H}$	$^3J_{Se^\alpha-H}$	$\delta(^{77}Se^\alpha)$	$\delta(^{77}Se^\beta)$	$^2J_{Se^\alpha-H}$	$^3J_{Se^\alpha-H}$	$\delta(^{77}Se^\alpha)$	$\delta(^{77}Se^\beta)$	$\delta(^{77}Se^\gamma)$	$^2J_{Se^\alpha-H}$	$^3J_{Se^\alpha-H}$
octyl	316.1	14.6	6.4	465.7	562.3	13.6	6.8	482.4	712.5	14.2	6.8	488.7	708.3	855.2	13.6	6.8
2-ethylhexyl[a]	294.7	12–13	6–7	432.5	601.9	*b*	*b*	450.3	730.7	*b*	*b*	457.1	728.9	854.7	*b*	*b*
				432.3	601.8											
benzyl	409.7	14.5		538.9	583.2	12.7		552.0	719.8	*d*	*d*					
2,4-dichlorobenzyl	408.4	16.0		542.9	584.9	14.7		556.5	723.8	15.1						
1-methyl-4-ethylhexyl[a]	381.9	*b*	*b*	581.4	484.0	*b*	*b*	585.2	681.0	*b*	*b*					
	381.7			581.2	483.6			585.1	680.5							
1-propylbutyl	342.0	17.6	8.8	532.3	475.8	19.5	8.3	545.6	670.4	22.0	8.8					
cyclohexyl	375.1	*b*	*b*	578.5	495.5	*b*	*b*	577.0	690.2	*b*	*b*					
1,1-dimethylpropyl	458.4	*b*	*b*	652.3	462.7	*b*	*b*	652.1	673.1	*b*	*b*					

[a] Mixture of two diastereomers. The resonance lines due to each component in the mixture could not be identified because the components were present in nearly equal amounts. [b] Unresolved multiplet. [c] Coupling to β-carbon hydrogens. For R = octyl, ${}^3J_{Se-H}$ = 2.0 Hz was resolved for coupling through a selenium atom. [d] Not measured.

---

(20) Rodger, C.; Sheppard, N.; McFarlane, C.; McFarlane, W. "NMR and The Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 12.

(21) Odom, J. D.; Dawson, W. H.; Ellis, P. D. *J. Am. Chem. Soc.* **1979**, *101*, 5815.

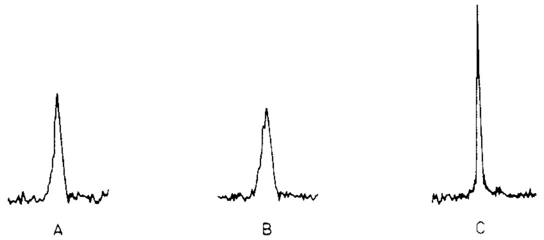


Figure 3. Line shape of the proton noise decoupled ^{77}Se and NMR signal of dibenzyl diselenide as a function of sample spinning rate. (A) 20 rev/s; (B) 24 rev/s; the signal splitting is 1.2 Hz. A and B are obtained with full decoupling power. (C) The decoupler power is reduced to ~10% relative to A and B. The small splitting observed (~0.5 Hz) is due to the selenium isotope shift on the shielding of a neighboring ^{77}Se nuclei.

display a pronounced temperature dependence of 0.1–0.3 ppm/deg (low-field shifts with increasing temperature). This extreme sensitivity to temperature creates problems for spectral resolution and the S/N ratio particularly when decoupling is required and often prevents observation of selenium satellites in ^{77}Se NMR spectra. At low magnetic field, the major source of thermal inconstancy is found to be thermal inhomogeneity of the sample due to finite thermal transfer rates of the decoupler heating. The line width of the signals indicates that a temperature difference of more than 1° develops within the sample solution when noise decoupling is applied. However, the temperature gradient in the sample does not cause simple line broadening of the signals. The spinning of the NMR tube influences the temperature distribution in the sample and the observed result is that the line shape is a function of the spinning rate, and occasionally lines are observed to split into two components. Figure 3 illustrates this effect for the ^{77}Se NMR signal of dibenzyl diselenide. This diselenide shows a chemical shift temperature variation of 0.12 ppm/deg (~2 Hz). The line width of the standard proton noise decoupled ^{77}Se signal shown is 2–3 Hz. When the decoupler power is carefully reduced to the minimum amount necessary (less than 10% of standard setting), the signal sharpens and the previously observed change in line shape and signal splitting dependent upon the rate of sample spinning disappears. The present results are obtained on a low-field instrument (^{77}Se: 17.10 MHz). By going to instruments with higher magnetic fields, the problem of thermal inhomogeneity coupled to sample spinning will certainly be more pronounced.

Recently,[17] the ^{77}Se NMR spectrum of the CH_3Se group of $CF_3SeSeCH_3$ has been reported to exhibit fine splitting. This splitting was attributed to the occurrence of two different conformers of the diselenide. However, the observed splitting may arise from thermal inhomogeneity of the sample solution coupled with sample spinning as discussed above. The chemical shifts of unsymmetrical diselenides often show very different temperature depencence,[22] and this explains the observation of signal splitting for only one of the two ^{77}Se signals.

Experimental Section

Sodium Polyselenide Solutions. A. By Disproportionation. A solvent (30 mL) consisting of Me_2SO (90%) and methanol (10%) was purged with nitrogen for 5 min. Sodium hydroxide (12 mmol) was introduced as a 50% (w/w) aqueous solution followed by the amount of powered grey selenium calculated (eq 1) to give the desired average chain length. The mixture was stirred at room temperature in a nitrogen atmosphere until the selenium was consumed and a dark solution with a precipitate of sodium selenite had formed (~10 min).

B. By Hydrazine Reduction. Dry DMF (20 mL) was purged with nitrogen for 5 min. Then sodium methanolate (8 mmol) was added as a 4 M solution in methanol immediately followed by 95% hydrazine (2.2 mmol) and the amount of powdered grey selenium calculated (eq 2) to give the desired average chain length. The mixture was stirred in an inert atmosphere until the nitrogen evolution had ceased (ca. 2 min for $n \geq 4$ but ca. 30 min for $n < 4$). The use of fairly dry reaction conditions is necessary in order to slow down the hydrolysis of DMF which consumes base through the formation of sodium formiate. This precaution is strictly necessary only in the reduction to triselenide ion; even in the presence of a few percent of water, the hydrolysis cannot compete with the rapid reduction of selenium to the $n = 4$ stage.

As exemplified below, DMF may be replaced with Me_2SO in this procedure in which case drying is unnecessary and hydrazine hydrate may be used. However, unless the anionic solution is alkylated rapidly, a slow redox process liberating dimethyl sulfide may be troublesome.

Dialkyl Polyselenides. To the sodium polyselenide solution prepared by method A or B was added 8.8 mmol (10% excess) of the appropriate alkyl halide or tosylate. (1-propylbutyl and 4-ethyl-1-methylhexyl tosylates were prepared from the corresponding alcohols immediately prior to their use since it was found that the corresponding commerical bromides on storage had isomerized to a mixture of all the possible secondary bromides.) The reaction mixture was left at room temperature under nitrogen in a stoppered flask until the solution turned orange usually with a precipitate of selenium. Water (50 mL) was added, and the product was extracted with petroleum ether (3 × 25 mL). The dried ($MgSO_4$) extract was evaporated in vacuo. The residue was dissolved in petroleum ether–methylene chloride (2:1) and filtered through silica gel (4 g), eluting with the same solvent until the entire orange polyselenide band had passed. After removal of solvent, the polyselenide mixture was heated to 50 °C at 0.2 torr in order to remove volatile contaminants, notably excess alkyl halide.

The percentages of the individual polyselenides were determined from the ^{77}Se NMR spectra and used for the calculation of the average chain length, m. In three instances, these results were compared with elemental analysis for carbon on dioctyl polyselenide mixtures and the following average chain lengths ($m_{^{77}Se}$, m_C) calculated: (1) 2.30, 2.22; (2) 2.22, 2.27; (3) 2.26, 2.23. Signals from the individual homologues in the two benzylic polyselenide mixtures were also detected in the ^{1}H NMR spectra where the $SeCH_2$ signals appeared as sharp separated singlets. In both cases, the two types of spectrum within the experimental error (±3%) predicted the same quantitative composition of the mixture.

Isolation of Bis(2,4-dichlorobenzyl) Diselenide and Bis(2,4-dichlorobenzyl) Triselenide. To a solution of sodium methanolate (4 mmol) and hydrazine hydrate (1.1 mmol) in Me_2SO (10 mL) was added selenium (8 mmol). The mixture was stirred for 5 min and then 2,4-dichlorobenzyl chloride (4 mmol) was added and the stirring continued for another 2 min. The crude dialkyl polyselenide mixture was isolated by the general procedure given above, however using methylene chloride for the extraction. Chromatography on silica gel with petroleum ether–5% methylene chloride as the eluent gave a pale-yellow fraction of pure diselenide followed by an intensely dark-yellow fraction of the triselenide contaminated with some diselenide. The higher polyselenides decomposed on the column, leaving a trail of red selenium. The residue from the first fraction was crystallized from hexane to give bis(2,4-dichlorobenzyl) diselenide as pale-yellow prisms: yield 0.82 mmol, 41%; mp 65–67 °C. Anal. Calcd for ($C_{14}H_{10}Cl_4Se_2$): C, 35.15%; H, 2.09%; Cl, 29.71%. Found: C, 35.12%; H, 2.12%; Cl, 29.68%.

The residue from the second fraction on fractioned recrystallization from hexane yielded bis(2,4-dichlorobenzyl) triselenide as intensely yellow neeldes: yield 0.24 mmol, 12%; mp 105–107 °C. Anal. Calcd for $C_{14}H_{10}Cl_4Se_3$: C, 30.16%; H, 1.80%; Cl, 25.49%. Found: C, 30.24%; H, 1.81%; Cl, 25.33%.

^{77}Se NMR. The ^{77}Se NMR spectra were recorded at 17.10 MHz by using a JEOL FX90Q NMR instrument equipped with a broad-band probe. Chemical shifts and ^{77}Se–^{77}Se coupling constants were measured with complete proton decoupling. Chemical shifts and coupling constants were determined with a maximum of 0.49 Hz per data point. Chemical shifts are referenced to external dimethyl diselenide by frequency difference calculations. Depending on the actual solvent, solutions of $(CH_3)_2Se$ (1 M) in $CDCl_3$ or C_6D_6 were used (reference frequency 48701.5 and 48 767.8 Hz, respectively). All diselenides and dibenzyl and bis(2,4-dichlorobenzyl) triselenides were isolated as pure compounds. Data given for these selenides refer to $CDCl_3$ solutions (0.2–1 M) of pure compounds. Otherwise, room-temperature spectra were obtained from 40–60% solutions in $CDCl_3$ or C_6D_6 (R = octyl and benzyl, only) of the dialkyl polyselenide mixture. The probe temperature was held between 29 and 30 °C for all measurements except when otherwise stated. CH_2Cl_2 solutions were used for low-temperature spectra with $(CD_3)_2CO$ as the lock substance (external). In this case, chemical shifts are referenced to $(CH_3)_2Se$ in $(CD_3)_2CO$ (reference frequency 48 754.6 Hz).

Registry No. Se, 7782-49-2; $C_8H_{17}Br$, 111-83-1; $C_5H_{11}Br$, 110-53-2; $PhCH_2Br$, 100-39-0; $(2,4\text{-}Cl_2C_6H_3)CH_2Cl$, 94-99-5; $C_8H_{17}Se_2C_8H_{17}$, 52056-10-7; $PhCH_2Se_2CH_2Ph$, 1482-82-2; $[(2,4\text{-}Cl_2C_6H_3)CH_2]_2Se_2$, 57239-62-0; $(C_8H_{17})_2Se_3$, 100814-28-6; $(PhCH_2)_2Se_3$, 22015-44-7; $[(2,4\text{-}Cl_2C_6H_3)CH_2]_2Se_3$, 100814-31-1; $(C_8H_{17})_2Se_4$, 100814-37-7; $(PhCH_2)_2Se_4$, 22015-45-8; $[(2,4\text{-}Cl_2C_6H_3)CH_2]_2Se_4$, 100814-39-9; $(C_8H_{17})_2Se_5$, 100814-45-7; $(PhCH_2)_2Se_5$, 22015-46-9; $[(2,4\text{-}Cl_2C_6H_3)CH_2]_2Se_5$, 100814-47-9; 2-ethylhexyl bromide, 18908-66-2; cyclohexyl bromide, 108-85-0; 1-propylbutyl tosylate, 4883-86-7; 4-ethyl-1-

---

[22] Eggert, H.; Henriksen, L., unpublished results.

1730 J. Am. Chem. Soc. 1986, 108, 1730-1735

methylhexyl tosylate, 100814-22-0; bis(2-ethylhexyl) diselenide, 100814-23-1; bis(4-ethyl-1-methylhexyl) diselenide (isomer 1), 100814-24-2; bis(4-ethyl-1-methylhexyl) diselenide (isomer 2), 100814-25-3; bis(1-propylbutyl) diselenide, 100814-26-4; dicyclohexyl diselenide, 56592-97-3; bis(1,1-dimethylpropyl) diselenide, 100814-27-5; bis(2-ethylhexyl) triselenide (isomer 1), 100814-29-7; bis(2-ethylhexyl) triselenide (isomer 2), 100814-30-0; bis(4-ethyl-1-methylhexyl) triselenide (isomer 1), 100814-32-2; bis(4-ethyl-1-methylhexyl) triselenide (isomer 2), 100814-33-3; bis(1-propylbutyl) triselenide, 100814-34-4; dicyclohexyl triselenide, 100814-35-5; bis(1,1-dimethylpropyl) triselenide, 100814-36-6; bis(2-ethylhexyl) tetraselenide, 100814-38-8; bis(4-ethyl-1-methylhexyl) tetraselenide (isomer 1), 100814-40-2; bis(4-ethyl-1-methylhexyl) tetraselenide (isomer 2), 100814-41-3; bis(1-propylbutyl) tetraselenide, 100814-42-4; dicyclohexyl tetraselenide, 100814-43-5; bis(1,1-dimethylpropyl) tetraselenide, 100814-44-6; bis(2-ethylhexyl) pentaselenide, 100814-46-8; selenium-80, 14681-54-0.

High-Resolution ^{27}Al NMR of Aluminosilicates

E. Lippmaa,* A. Samoson, and M. Mägi

Contribution from the Institute of Chemical Physics and Biophysics of the Estonian Academy of Sciences, Tallinn 200001, USSR. *Received July 30, 1985*

Abstract: Recent advances in instrumentation and techniques have made a precise determination of isotropic chemical shifts of quadrupolar nuclei in solids practicable. Aluminum-27 chemical shifts in aluminosilicates closely parallel those of silicon-29 and display a similar dependence upon changes in both the first and second coordination spheres and the Al–O–Si bond angles.

There is considerable current interest in applying high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopic techniques to the study of a number of inorganic solids, such as minerals,[1] heterogeneous catalysts, and glasses. In particular, zeolites[2,3] have been attractive objects for these studies, yielding a large share of the spectra–structure relationships established for ^{29}Si chemical shifts in solids. It has been found that a change in the silicon coordination number with oxygen from four to six leads to an about 80-ppm diamagnetic shift,[4] species with different degrees of condensation of the SiO_4 tetrahedra span a 40-ppm-shift range,[1] each substitution of silicon by aluminum in the second coordination sphere causes an analytically useful 5-ppm paramagnetic shift,[2] and the mean Si–O–T bond angle dependence is close to –0.6 ppm per degree.[5,6] Effects of a similar nature could be expected in high-resolution ^{27}Al NMR spectra as well, but their study has been hampered by the relatively small chemical shift range in aluminosilicates, poor spectral resolution, and the unavoidable second-order quadrupolar line shifts, which are very significant even at the largest commercially available magnetic field strengths (11.7 T). High-resolution NMR spectroscopy of solid samples, spun rapidly under the magic angle (54.73°) to the strong polarizing magnetic field, often dubbed magic angle spinning nuclear magnetic resonance (MAS NMR), has proved to be the method of choice for a practically complete averaging of solid-state line broadenings of spin $I = {}^1/_2$ nuclei due to chemical shift anisotropy of the powder particles. In contrast to the $I = {}^1/_2$ nuclei, magic angle spinning can only diminish and modify the second-order quadrupolar line-broadening in the NMR spectra of nonintegral spin ($I = {}^3/_2, {}^5/_2, {}^7/_2, {}^9/_2$) quadrupolar nuclei,[7-9] but it is not possible to average it to zero. The variable angle sample spinning (VASS) technique[10,11] can provide sharper lines of quadrupolar nuclei in some samples but is of limited use because it does not average other line-broadening interactions.

The first ^{27}Al $I = {}^5/_2$, 100% abundance MAS NMR measurements[7,9,12-14] immediately indicated the value of this method for the study of inorganic solids. First systematic studies[13,15] were used to establish all the main features of ^{27}Al MAS NMR spectra, useful in probing the coordination, quantity, and location of aluminum atoms in aluminosilicates. However, most of the ^{27}Al chemical shift data published correspond to the line centers of gravity and are either uncorrected or only the stationary sample or MAS NMR line widths have been used for data refinement, yielding field-dependent chemical shifts. These apparent shifts are too low (diamagnetic) if uncorrected and too high (paramagnetic) if overcorrected by using the line width dependent correction terms and assuming a purely quadrupolar yet symmetric (Gaussian) line shape.[16] These difficulties, pertinent to all quadrupolar nuclei, have blurred the structurally significant fine structure in ^{27}Al chemical shift charts, thus limiting the usefulness of ^{27}Al MAS NMR to little more than coordination number determination. In fact, no variation of ^{27}Al chemical shifts with the average T–O–T bond angle in various zeolites could be found by Nagy et al.[15]

Not only are the line positions and line shapes affected by quadrupolar interaction with the electric field gradient (EFG) at the nucleus but the same is true of line intensities. The registered ^{27}Al MAS NMR line intensities are quantitatively correct only if the radio-frequency excitation pulse is sufficiently short. For a <5% error in the central transition centerband signal intensity, the effective spin flip angle must satisfy the condition[17]

$$(I + {}^1/_2)\omega_{\rm rf}t_1 \le \pi/6 \qquad (1)$$

Obviously, modern high-field, high-power NMR equipment, able to handle large radio-frequency pulses, is necessary for quantitatively exact MAS NMR measurements. Many of the above mentioned limitations in ^{27}Al chemical shift measurements have likewise been overcome through development of new MAS NMR techniques. The major objectives of this study were re-

---

(1) Lippmaa, E.; Mägi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A.-R. *J. Am. Chem. Soc.* **1980**, *102*, 4889.

(2) Lippmaa, E.; Mägi, M.; Samoson, A.; Tarmak, M.; Engelhardt, G. *J. Am. Chem. Soc.* **1981**, *103*, 4992.

(3) Klinowski, J. *Progr. NMR Spectrosc.* **1984**, *16*, 237.

(4) Lippmaa, E. T.; Samoson, A. V.; Brei, V. V.; Gorlov, Yu. I. *Dokl. AN SSSR* **1981**, *259*, 403.

(5) Thomas, J. M.; Klinowski, J.; Ramdas, S.; Hunter, B. K.; Tennakoon, D. T. B. *Chem. Phys. Lett.* **1983**, *102*, 158.

(6) Smith J. V.; Blackwell C. S. *Nature (London)* **1983**, *303*, 223.

(7) Müller, D.; Gessner, W.; Behrens, H.-J.; Scheler, G. *Chem. Phys. Lett.* **1981**, *79*, 59.

(8) Kundla, E.; Samoson, A.; Lippmaa, E. *Chem. Phys. Lett.* **1981**, *83*, 229.

(9) Freude, D.; Behrens, H.-J. *Cryst. Res. Technol.* **1981**, *16*, 36.

(10) Oldfield, E.; Schramm, S.; Meadows, M. D.; Smith, K. A.; Kinsey, R. A.; Ackerman, J. *J. Am. Chem. Soc.* **1982**, *104*, 919.

(11) Ganapathy, S.; Schramm, S.; Oldfield, E. *J. Chem. Phys.* **1982**, *77*, 4360.

(12) Mastikhin, V. M.; Krivoruchko, O. P.; Zolotovskii, B. P.; Bayanov, R. A. *React. Kinet. Catal. Lett.* **1981**, *18*, 117.

(13) Fyfe, C. A.; Gobbi, C. G.; Hartman, J. S.; Klinowski, J.; Thomas, J. M. *J. Phys. Chem.* **1982**, *86*, 1247.

(14) Meadows, M. D.; Smith, K. A.; Kinsey, R. A.; Rothgeb, T. M.; Skarjune, R. P.; Oldfield, E. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1351.

(15) Nagy, J. B.; Gabelica, Z.; Debras, G.; Derouane, E. G.; Gilson, J.-P.; Jacobs, P. A. *Zeolites* **1984**, *4*, 133.

(16) Freude, D.; Haase, J.; Pfeifer, H.; Prager, D.; Scheler, G. *Chem. Phys. Lett.* **1985**, *114*, 143.

(17) Samoson, A.; Lippmaa, E. *Phys. Rev. B* **1983**, *28*, 6567.

0002-7863/86/1508-1730$01.50/0