

Natural Abundance ^{13}C and ^{29}Si ENDOR Studies of Cyclopolysilane Radical Anions

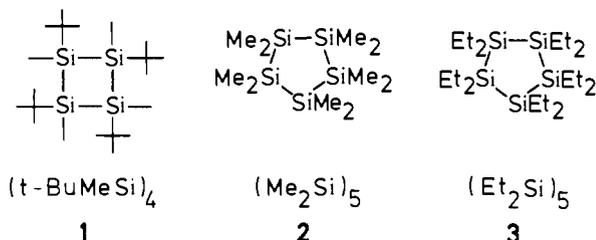
B. Kirste,^{1a} R. West,^{1b} and H. Kurreck*^{1a}

Contribution from the Institut für Organische Chemie der Freien Universität Berlin, 1000 Berlin 33, West Germany, and the University of Wisconsin, Madison, Wisconsin 53706. Received November 1, 1984

Abstract: ^{13}C and ^{29}Si ENDOR signals of the peralkylcyclosilane radical anions, $(t\text{-BuMeSi})_4^{\cdot-}$ and $(\text{Et}_2\text{Si})_5^{\cdot-}$, have been observed in natural abundance; this is the first ^{29}Si ENDOR study of silicon-centered radicals. The relaxation behavior of the ^{29}Si and ^{13}C nuclei have been investigated. The ENDOR results show only a small hyperfine anisotropy for ^{29}Si , consistent with Si-Si σ^* or 3d spin population but not with π -type delocalization. The relaxation behavior of ^{13}C nuclei and the temperature dependence of hyperfine couplings are interpreted in terms of internal molecular dynamics.

Nonproton ENDOR spectroscopy of radicals in solution has developed rapidly during recent years, and the conditions for obtaining an optimum ENDOR response are now well understood theoretically.² However, when dealing with isotopes occurring in low natural abundance (e.g., ^2H , ^{13}C , ^{15}N), isotopic enrichment has usually been necessary.³⁻⁵ Only a few observations of fluid solution ^{13}C ENDOR in natural abundance have been reported to date,⁶⁻⁹ and recently the first ^{29}Si ENDOR experiment succeeded.¹⁰ It was beneficial for these studies that the low-abundance nuclei exhibited fairly large *isotropic* hyperfine splittings but small *anisotropic* hyperfine components. Thus, saturation of the NMR transitions could be achieved with weak radio frequency fields, avoiding problems caused by high power levels.

The earlier ^{29}Si ENDOR study dealt with radicals containing several equivalent trialkylsilyl groups attached to a carbon π system. Here we report on the first successful ^{29}Si ENDOR study of silicon-centered radicals, namely peralkylcyclosilane radical anions. The cyclic polyanions are of special interest because of



their thermal and chemical stability and their unique bonding properties.^{11,12} In some respects these saturated compounds resemble aromatic hydrocarbons, and evidence of electron delo-

calization is found in their ultraviolet¹³ and photoelectron spectra¹⁴ as well as in the EPR spectra of their radical anions¹⁵⁻¹⁹ and cations.²⁰

The three radical anions investigated, $1^{\cdot-}$ - $3^{\cdot-}$, have previously been studied by EPR; in this paper we show that more detailed information about hyperfine coupling constants and their signs and temperature dependences becomes accessible from ^1H , ^{13}C , and ^{29}Si ENDOR and TRIPLE²¹ experiments. These data allow a better insight into the electronic structure and the dynamic behavior of the cyclosilane radical anions.

Experimental Section

The syntheses of *trans*-1,2,3,4-tetra-*tert*-butyltetramethylcyclohexasilane (**1**),¹⁶ dexamethylcyclopentasilane (**2**),²² and decaethylcyclopentasilane (**3**)²³ have been described previously. Sample cells for EPR/ENDOR investigations were degassed and sealed off on a high-vacuum line, and radical anions were generated by reduction with sodium/potassium alloy in dimethoxyethane (DME)/2-methyltetrahydrofuran (MTHF) at 200 K. The ENDOR and TRIPLE instrumentation basically consists of a Bruker ER 220D EPR spectrometer equipped with a Bruker cavity (ER 200ENB) and home-built NMR facilities described elsewhere.²⁴ ENDOR spectra were accumulated by using a Nicolet 1170 signal averager employing 1K data points; 32 or 64 scans were taken, 30 s per scan.

Results

For the sake of clarity, compound **3** will be considered first. (Only ^1H ENDOR signals could be obtained from $2^{\cdot-}$ so far because of problems with radical concentrations and background signals.) The EPR spectrum¹⁷ of $3^{\cdot-}$ (Figure 1, top) shows a strong central peak (inhomogeneous line width 13 μT at 220 K) with no resolved ^1H hyperfine structure and a multitude of satellite lines due to molecules containing ^{13}C or ^{29}Si nuclei ($I = 1/2$). The satellites were previously assigned from their relative intensities and the natural abundances of ^{29}Si and ^{13}C , 4.7% and 1.1%,

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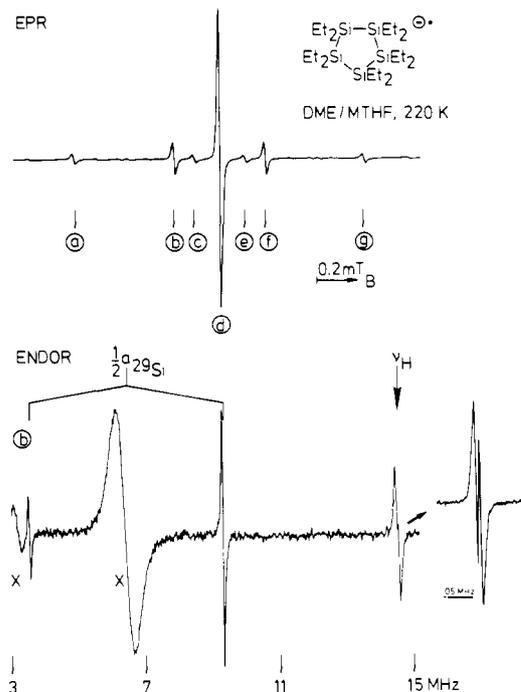


Figure 1. Top: EPR spectrum of 3^- . Bottom: ENDOR spectrum of 3^- obtained with field setting b exhibiting ^1H and natural-abundance ^{29}Si signals; Na/K, DME/MTHF, 190 K. The inset shows the ^1H ENDOR signals recorded under high-resolution conditions on an expanded scale. The broad lines marked X are "EPR type" lines which arise probably from a modulation of the static magnetic field or of the microwave field by the radio frequency field.²⁵

respectively; the assignments are $a_{\text{C-13}} = 39.5$ MHz (10 C; a,g), $a_{\text{C-13}} = 6.9$ MHz (10 C; c,e), and $a_{\text{Si-29}} = 12.39$ MHz (5 Si; b,f).¹⁷ On lowering the temperature, the EPR lines are broadened to a different extent; the pair of satellite lines c,e is no longer seen at 170 K.

In Figure 1 (bottom) the ENDOR spectrum of 3^- obtained with the field setting marked b is depicted. It shows a pair of overlapping ^1H ENDOR lines (cf. inset) around the free proton frequency ($\nu_{\text{H}} = 14.62$ MHz) and a pair of ^{29}Si ENDOR lines centered about $|a_{\text{Si-29}}/2| = 6.44$ MHz, separated by $2\nu_{\text{Si}} = 5.80$ MHz. Thus, the ENDOR experiment confirms the assignment of the EPR line pair (b,f) to molecules bearing one ^{29}Si . The optimum ^{29}Si ENDOR effect occurred at (190 ± 5) K, but signals were observed over the temperature range between 180 and 220 K. The ^{29}Si hyperfine coupling constant is significantly temperature dependent, $d|a|/dT = -16$ kHz/K. The appearance of the ENDOR spectra did not change on switching to the high-field setting (f), i.e., cross-relaxation effects are negligible (vide infra). The high-frequency ^{29}Si ENDOR line could be saturated with an applied radio frequency field of $B_{\text{rf}} = 0.85$ mT (in the rotating frame), and an unsaturated line width of (57 ± 5) kHz was measured. It is noteworthy that a weak ^{29}Si ENDOR signal could even be detected with the field set on the central EPR peak (d), undoubtedly arising from molecules containing two ^{29}Si nuclei (EPR intensity: 1.2%).

The ENDOR spectra of 3^- obtained with field settings a or g (Figure 2) show a pair of ^{13}C ENDOR lines centered about $|a_{\text{C-13}}/2| = 19.77$ MHz, separated by $2\nu_{\text{C}} = 7.34$ MHz (a). (The experimental value of ν_{C} exhibits a second-order shift of 40 kHz in agreement with expectation, $\delta\nu = a^2/4\nu_{\text{C}}$.) The relative signal intensities depend markedly upon the field setting, i.e., the low-frequency ^{13}C ENDOR line is more intense than the high-frequency line with the low-field setting (a) and vice versa for the high-field setting (g). This behavior is characteristic of cross-relaxation effects $W_{x1} > W_{x2}$ (see Discussion). The hyperfine coupling constants are collected in Table I.

The well-resolved EPR spectrum of 1^- at 290 K (DME) is depicted in Figure 3 (top).¹⁶ The two pairs of satellite subspectra

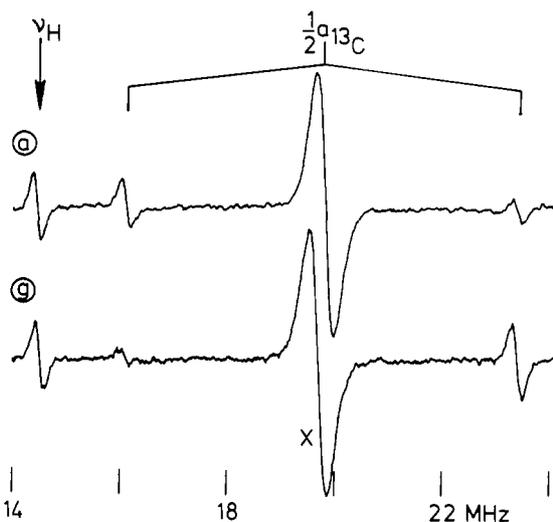


Figure 2. Natural-abundance ^{13}C ENDOR spectra of 3^- obtained with field settings a and g (cf. Figure 1), DME/MTHF, 220 K.

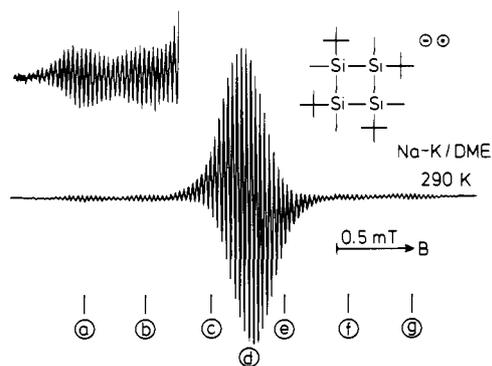


Figure 3. Top: EPR spectrum of 1^- . Bottom: ^1H and natural-abundance ^{29}Si ENDOR spectrum of 1^- obtained with field setting e.

Table I. g Values and Hyperfine Coupling Constants (MHz)^a

	1^-	2^-	3^-
g	2.0037	2.0032	2.0033
^{29}Si	+15.15	14.3 ^b	12.88
^{13}C	+59.07	44.9 ^{b,c}	39.46
	36.84		6.9 ^b
^1H	+1.45	1.52	0.08
	+0.86		

^aHFCs measured by ENDOR, accurate within ± 0.01 MHz. 1^- : 200 K, DME. 2^- , 3^- : 190 K, DME/MTHF. Signs given for 1^- are relative signs (from TRIPLE). ^bEPR data (1 G = 0.1 mT = 2.803 MHz). ^cFrom ref 18.

in the wings (a, b, f, g) were previously assigned to species with a ^{13}C nucleus in natural abundance, but the ^{29}Si satellite lines could not be observed.¹⁶ The resolution of the spectrum decreases on lowering the temperature. Since only broad unresolved peaks are observed below 230 K, the exact field positioning in the ENDOR

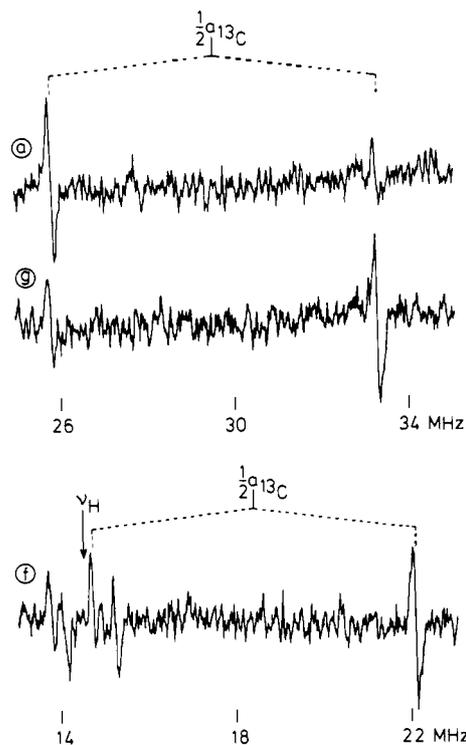


Figure 4. Natural-abundance ^{13}C ENDOR spectra of 1^- obtained with field settings a, g, and f (cf. Figure 3), DME, 200 K.

experiments was not crucial. An ENDOR spectrum taken with the central field setting (d) revealed two pairs of ^1H ENDOR lines. After the field was shifted to the wings of the central peak (position e), an additional pair of ^{29}Si ENDOR lines appeared, symmetrically spaced around $|a_{\text{Si-29}}/2| = 7.57$ MHz, separated by $2\nu_{\text{Si}} = 5.76$ MHz. This finding demonstrates that ENDOR may yield hyperfine coupling constants of magnetic nuclei present in natural abundance, even when the respective EPR satellites are concealed in the wings of the main spectrum.

The relative signs of the ^{29}Si and ^1H hyperfine couplings were determined by a general TRIPLE experiment. Pumping of one of the low-frequency proton NMR transitions resulted in a strong increase of the two high-frequency proton signal intensities and a significant decrease of the high-frequency ^{29}Si signal intensity. Thus, the two proton hyperfine couplings have the same sign. In the case of the ^{29}Si nucleus, the negative sign of the magnetogyric ratio has to be considered, resulting in a reversal of the rules employed for the interpretation of general TRIPLE spectra.^{21,24} Consequently, all three hyperfine couplings have the same sign, but the sign of the Si s spin density is opposite. The relaxation behavior of the ^{29}Si nuclei in 1^- is similar to those in 3^- (vide supra). Saturation of the high-frequency ^{29}Si ENDOR signal could almost be achieved with an applied radio frequency field of 0.7 mT: line width ≤ 65 kHz, absence of noticeable cross-relaxation effects (190–230 K). The optimum temperature for ^{29}Si ENDOR (200 ± 5 K) was only slightly higher than that for ^1H ENDOR (190 ± 5 K, referring to the outer pair of lines). Again, a significant temperature dependence of the ^{29}Si coupling was found, $d|a|/dT = -23$ kHz/K. The proton coupling constants are also temperature dependent, the larger coupling increasing (+1.8 kHz/K) and the smaller one decreasing (-1 kHz/K) with increasing temperature. Since this effect gives rise to an integral ratio of the two coupling constants around room temperature (1.57 MHz, 0.78 MHz),¹⁶ it accounts for the temperature dependence of the resolution of the EPR spectrum.

Figure 4 demonstrates that natural abundance ^{13}C ENDOR spectra of 1^- could be obtained without difficulty for two sets of carbon nuclei by selecting the appropriate field settings. The lines are centered about the respective value of $|a_{\text{C}}/2|$ and separated by $2\nu_{\text{C}}$; the measured values of ν_{C} exhibit second-order shifts of 90 and 30 kHz ($a_{\text{C}} = 59.1$ and 36.8 MHz, respectively). A

comparison of the two ^{13}C ENDOR spectra obtained with field settings a and g reveals pronounced cross-relaxation effects $W_{x1} > W_{x2}$. Since this effect also influences the ^1H ENDOR signal intensities, it can be used for a relative sign determination;²⁶⁻²⁹ the results showed that the larger ^{13}C coupling constant had the same sign as the proton coupling constants (see Table I). No significant cross-relaxation effects were observed for the ENDOR lines belonging to the smaller ^{13}C hyperfine splitting.

Discussion

Assignment of Hyperfine Coupling Constants. An assignment of the proton couplings in 1^- has been given previously, based on simulations of the EPR spectrum ($a_{\text{Me}} = 1.57$ MHz, $a_{t\text{-Bu}} = 0.78$ MHz, 293 K).¹⁶ The fact that the *tert*-butyl ^1H ENDOR lines (36 protons) are smaller than the methyl signals (12 protons) at low temperatures (see Figure 3) is due not only to overlap effects³⁰ but also to a broadening of the *tert*-butyl signals. This effect might be ascribed to a hindered rotation of the bulky *tert*-butyl groups at low temperatures. The two measured ^{13}C splittings are due to the methyl carbons and the central carbons of the *tert*-butyl groups. The pronounced difference between these splittings (Table I) appears reasonable, considering the folded, butterfly conformation determined for 1 ,³¹ in which the *tert*-butyl groups occupy pseudoequatorial positions and the methyl groups pseudoaxial positions. The larger splitting is assigned to the methyl carbons, as discussed elsewhere.¹⁹

The observed proton splitting in 3^- (0.08 ± 0.01 MHz at 190 K, 0.10 MHz = $3.6 \mu\text{T}$ at 220 K) may be assigned to the methylene protons. This assignment is in accord with the observed EPR line width ($13 \mu\text{T}$ at 220 K). The striking difference from the methyl proton splitting in 2^- (1.52 MHz) suggests a pronounced conformational dependence of coupling constants in these systems. The larger ^{13}C splitting in 3^- can be assigned to the methylene carbon atoms in analogy to 2^- (Table I).

^{29}Si ENDOR, Relaxation Behavior. The ENDOR response depends in a complicated way on the various relaxation rates and the radiation-induced transition moments.³² The relaxation rates and consequently the optimum conditions for the ENDOR experiment are mainly determined by the g factor anisotropy, the hyperfine anisotropies ($\text{Tr } A^2$), the rotational correlation time τ_{R} , and the frequencies of Heisenberg and chemical exchange (assuming $S = 1/2$, $I = 1/2$). When different nuclei within the same molecule are compared, the relaxation behavior of each set of equivalent nuclei is governed by the respective hyperfine anisotropy $\text{Tr } A^2$. Conversely, the experimental parameters (optimum temperature, radio frequency field strengths B_{rf} , line widths) may be used to estimate the hyperfine anisotropy of the nucleus under study. The experimental finding that the optimum ENDOR conditions for ^{29}Si nuclei and protons are similar in the radicals investigated immediately rules out the possibility of a large ^{29}Si hyperfine anisotropy. A semiquantitative estimate can be inferred from the diagrams and equations for an optimum ENDOR effect given in ref 2:

(25) These lines have the width of EPR lines and appear at positions corresponding to the separation between the desaturated EPR component and further EPR peaks in frequency units. This effect may cause serious problems in ENDOR experiments on nuclei in low natural abundance, since only weak satellite lines contribute to the intensity of ENDOR signals, whereas all EPR peaks can give rise to background signals. Therefore, the shape of the EPR spectrum may be important for the success of the experiment. Very recently it could be shown that these drawbacks may be overcome by using extensively deuterated radicals for natural abundance ENDOR studies (ref 9).

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$$\tau_R^{\text{opt}} = 200(B/\text{Tr } A^2)^{0.44} \quad (1)$$

$$\frac{\nu_{\text{ENDOR}}}{\nu_{\text{H}}} B_n^{\text{opt}} \approx 100(B \cdot \text{Tr } A^2)^{1/2} \quad (2)$$

where τ_R is in ns, $\text{Tr } A^2$ in MHz^2 , and B_n in G; the parameter B characterizes the spin-rotational interaction, and ν_{ENDOR} is the ENDOR frequency, $\nu_{\text{ENDOR}} = |\nu_n \pm a/2|$. The rotational correlation time is given approximately by the Stokes-Einstein relation

$$\tau_R = V_{\text{eff}}\eta/kT \quad (3)$$

where V_{eff} is the effective molecular volume and η is the viscosity of the solvent. Assuming a molecular volume of about 740 \AA^3 for 3^- , the rotational correlation time is 0.74 ns at 190 K (DME/MTHF). Choosing (somewhat arbitrarily) $B \approx 1 \times 10^{-5}$ and a Heisenberg exchange parameter of $C = 1 \times 10^{-4}$ ($\omega_{\text{HE}} = C/\tau_R$), estimated values of $\text{Tr } A^2_{\text{Si}}$ fall into the range of 30–100 MHz^2 .

Next, we will consider what models for the electron spin distribution in 3^- are consistent with this result. The isotropic hyperfine coupling constants are proportional to spin populations of s orbitals. By using tabulated one-electron coupling constants,³³ an upper limit of 0.17 is obtained for the total s spin population; the spin population in carbon $2s$ orbitals is moderate (~ 0.12) and that in Si $3s$ orbitals ($a_0^{\text{Si}} = -3381 \text{ MHz}$) is particularly small (< 0.02). Thus, the bulk of the spin population must occupy p - or d -type Si orbitals (≥ 0.17 per Si atom). Furthermore, the small value for $\text{Tr } A^2_{\text{Si}}$ shows that these orbitals must be symmetrically distributed about the silicon nuclei. If, for example, the unpaired electron were in an MO constructed from Si $3p_z$ atomic orbitals, $\text{Tr } A^2_{\text{Si}}$ would be far higher, $\approx 1300 \text{ MHz}^2$ (as obtained from the tabulated value for the anisotropic hyperfine interaction, $\text{Tr } A^2_0 \approx 4.5 \times 10^4 \text{ MHz}^2$).²

According to a model presented elsewhere,¹⁸ the singly occupied molecular orbital (SOMO) may be represented as a linear combination of Si-C σ^* and symmetry adapted Si-Si σ^* hybrid orbitals involving silicon $3p_x$, $3p_y$, and $3p_z$ and carbon $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. If so, the Si $3p$ orbitals must be nearly equally occupied. Alternatively, the unpaired electron might occupy Si $3d$ orbitals. For hydrogen type $3d$ orbitals, a straightforward calculation yields $\text{Tr } A^2_{3d} = (1/49)\text{Tr } A^2_{3p}$ and hence the estimate $\text{Tr } A^2_{\text{Si}} \approx 25 \text{ MHz}^2$, in agreement with experiment.

¹³C ENDOR, Cross-Relaxation Effects. The most striking feature of some of the ¹³C ENDOR spectra obtained in this study (Figures 2 and 4) is the dependence of the signal amplitudes on the field setting, i.e., the $m_I(^{13}\text{C})$ EPR component being desaturated. Such an asymmetric intensity pattern is characteristic of cross-relaxation effects.^{24,34,35} Cross-relaxation effects are com-

monly found in ¹³C ENDOR spectra, and modulation of the anisotropic hyperfine interaction gives rise to dominant "flop-flop" processes, $W_{x2} = 6W_{x1}$. In this situation, the *high*-frequency ¹³C ENDOR line is more intense when saturating the low-field EPR component.^{4,35} However, in the present case the *low*-frequency ¹³C ENDOR line is more intense when saturating the low-field EPR component, indicating dominant "flip-flop" processes, $W_{x1} > W_{x2}$. These processes arise from the modulation of isotropic coupling constants,³²

$$W_{x1}^A = 2\pi^2(\overline{a^2(t)} - \bar{a}^2)\tau_1/(1 + \omega_e^2\tau_1^2) \quad (4)$$

where τ_1 is the characteristic correlation time. This case has rarely been observed.³⁶ A claim made for a dominant W_{x1} process in a Rb ENDOR experiment on an ion pair²⁶ had to be revised later on, and the effect was ascribed to the combined action of quadrupolar and dipolar relaxation.²⁷ Clearly, this possibility does not exist in the case of ¹³C ($I = 1/2$); the isotopic species under consideration does not contain ²⁹Si, the only magnetic nuclei being protons and one ¹³C nucleus. Consequently, a dynamic process giving rise to the modulation of the isotropic ¹³C hyperfine coupling must be responsible for the effect. (The anisotropic ¹³C hyperfine interaction is small in the systems under study which contain only saturated carbon atoms.) Although ion pairing might be responsible, we consider it more likely that the modulation is caused by internal motions. It should be noted that the substantial temperature dependence of the ¹H and ²⁹Si hyperfine coupling constants and the line-width effects observed in the EPR spectrum of 3^- give another hint of an appreciable amount of structural flexibility. The apparent D_{5h} symmetry of 3^- is probably due to rapid interconversions between conformations with puckered five-membered rings.

Conclusions

We find that natural-abundance ²⁹Si ENDOR investigations can be extended to silicon-centered radicals. Favorable conditions for ENDOR investigations of nuclei present in low natural abundance can be summarized as follows: small hyperfine anisotropies (and quadrupole interactions in the case of nuclei with $I \geq 1$), large isotropic hyperfine couplings, and the presence of several equivalent nuclei. The relaxation behavior of the ²⁹Si nuclei in the cyclosilanes allows the conclusion that the spin distribution around the silicon nuclei is nearly symmetrical. Besides a more detailed picture of the electronic structure of the cyclosilanes, evidence of internal motions in these systems has been obtained.

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