Evidence from ^{13}C and ^{29}Si Hyperfine Structure Calculations against the σ*-Configuration of Cyclopolysilane Radical Anions As Determined by ENDOR Spectroscopy

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The isotropic hyperfine splitting constants at the magnetic nuclei ^{13}C and ^{29}Si in the permethylcyclotetrasilane radical anion are well reproduced at the UMP2/VTZPD//UHF/VTZPD level of theory. The radical has a π-type $^2A_{2u}$ electronic configuration. This is in contrast to the σ-type configuration determined by ENDOR spectroscopy on the basis of the small ^{29}Si hyperfine anisotropy found in peralkylcyclopolysilane radical anions. The components of the hyperfine dipolar tensor $A'(^{29}\mathrm{Si})$ are computed to be small since the unpaired electron is mainly delocalized into the Si-3p$_\pi$ outer-valence atomic orbitals. The ^{29}Si hyperfine anisotropy is computed to be 99.5 MHz^2 at the UHF/VTZPD level, in agreement with the ENDOR prediction for peralkylcyclopolysilane anions (30−100 MHz^2).

Introduction

There is a current debate on the electronic configuration of silane radical anions. West and co-workers[1−3] found by means of ESR spectroscopy that in peralkylcyclopolysilane radical anions $[(\mathrm{RR'Si})_n]^{\bullet-}$, $n = 4-6$, the unpaired electron is completely delocalized over the ring and suggested that the singly occupied molecular orbital (SOMO) should be composed of the normally empty 4p$_\pi$ and 3d$_\pi$ silicon atomic orbitals (AOs) since the small values observed experimentally for the ^{29}Si hyperfine splitting (hfs) constant $a(^{29}\mathrm{Si})$ indicated no participation of the 3s silicon AOs in the SOMO. Later, on the basis of ENDOR experiments[4] predicting a small ^{29}Si hyperfine anisotropy for $[(\mathrm{RR'Si})_n]^{\bullet-}$, $n = 4$ and 5, they suggested[5] that the SOMO should be a linear combination of the antibonding Si−Si ($\sigma^*_{\mathrm{Si-Si}}$) and Si−C ($\sigma^*_{\mathrm{Si-C}}$) σ-type orbitals (σ* model). By contrast, Grev and Schaefer[6] on the basis of the nature of the lowest unoccupied molecular orbital (LUMO) found in ab initio calculations performed on unsubstituted cyclopolysilanes $(\mathrm{H_2Si})_n$, $n = 3-5$, proposed a π-configuration for the SOMO (π* model) in which the Si-3p$_\pi$ AOs are in phase with each other, i.e. π-bonding Si−Si ($\pi_{\mathrm{Si-Si}}$), and out of phase with respect to the AOs of the substituents R, i.e. π-antibonding Si−R ($\pi^*_{\mathrm{Si-R}}$). The π* model was supported by Tossell et al.[7] since they computed a small ^{29}Si hyperfine anisotropy for the cyclotrisilane radical anion $[(\mathrm{H_2Si})_3]^{\bullet-}$ in the π-type configuration using low-level ab initio calculations (CISD/3-21G* employing a modest subset of virtual orbitals in the configuration interaction (CI) expansion). This unexpected finding was attributed to a d-like appearance of the Si AOs in the SOMO. However, doubt was recently expressed about the validity of the π* model since linear polysilane anions were found to have a σ-type electronic configuration by analyzing their ET spectra.[8] Insight into this dispute can be gained comparing the experimental ^{29}Si and ^{13}C hfs constants of $[(\mathrm{Me_2Si})_4]^{\bullet-}$, the simplest cyclopolysilane radical anion studied by ESR spectroscopy, with those computed with reliable ab initio calculations.

Computational Details

Ab initio unrestricted Hartee−Fock (UHF) calculations have been performed on cyclotetrasilane radical anions $[(\mathrm{R_2Si})_4]^{\bullet-}$ (R = H, Me) and on their neutral parents with the GAUSSIAN 94 system of programs[9] running on either RISC-6000 IBM or DEC AlphaStation 500 computers. Geometries and hfs constants have been determined employing the 6-311G** valence-triple-ζ basis set (VTZ)[10,11] supplemented with polarization functions (*P*), p-functions on hydrogens and five-component d-functions on heavy atoms.[12] Calculations have also been carried out augmenting the basis set with diffuse functions, s- and p-functions on heavy atoms and s-functions on hydrogens (6-311++G**). In order to investigate their influence on both the structural parameters and magnetic properties, the exponents, $\alpha(\lambda)$, of the diffuse functions (*D′*) have been varied proportionally to the difference between the exponents (α_{out}) of the outermost valence functions and those (α_{diff}) of the standard diffuse functions (*D*).[13]

$$\alpha(\lambda) = \alpha_{\mathrm{out}} + \lambda(\alpha_{\mathrm{diff}} - \alpha_{\mathrm{out}}) \qquad (1)$$

Vibrational frequency analysis has been performed at the stationary points to ensure true minimum geometries. The stability of the UHF wave functions has also been tested. There is no evidence of symmetry breaking in the radical anions due to HF-doublet instability.[14]

Hfs constants $a(\mathrm{X})$ at the magnetic nuclei X (X = ^{29}Si, ^{13}C) have been computed using correlated methods, namely, Møller−Plesset perturbation theory up to fourth order (UMP*n*, $n = 2-4$)[15] and quadratic configuration interaction with single and double substitutions (UQCISD)[16] for R = H, and UMP2 for R = Me. Core electrons have been held frozen since their inclusion was found to give a small contribution to ^{13}C hfs constants using an UHF reference determinant where spin-polarization effects are included explicitly,[17,18] and exploratory calculations have shown that core−electron correlation also has little effect on ^{29}Si hfs constants, the computed $a(^{29}\mathrm{Si})$ value in $[(\mathrm{H_2Si})_4]^{\bullet-}$ being 11.82 and 11.94 G at the UMP2(frozen-core)/VTZPD and UMP2(full)/VTZPD levels, respectively, using the VTZPD optimized geometry. No further compressed s-functions have been added to the 6-311G basis set to describe the spin-polarization of the core s-shells since this VTZ basis set is of full double-ζ quality in the s-space and of valence triple-ζ quality in the p-space[11,19] Only a single shell of d-functions with standard exponent has been included at heavy atoms since the use of two sets of d-functions obtained by multiplying and dividing the standard d-exponent by a factor of 2, as suggested by Chipman[20] to achieve stable results in spin-restricted

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multiconfiguration self-consistent-field (MCSCF) calculations, decreases only slightly the $a(^{29}Si)$ value (11.47 G). It should be remarked that reliable results were, however, obtained also in the spin-restricted MCSCF calculations using only one set of d-functions by optimizing the single d-exponent.

Evaluation of hfs constants directly from the generalized density matrix computed with the Z-vector method[21,22] is computationally too demanding for a system as large as $[(Me_2Si)_4]^{\bullet-}$ even at the UMP2 level; hence the $a(X)$ values have been calculated from the Fermi contact spin densities $Q_X(0)$,

$$a(X) = (8\pi/3)g_e\beta_e g_X\beta_X Q_X(0) \qquad (2)$$

determined by finite-field perturbation theory.[23,24] The Fermi contact spin density has been computed evaluating the energy shift, $\partial E(\mu)/\partial\mu$, induced by the application of a finite Fermi-contact field μ by a central difference approximation to the energy derivative.

$$Q_X(0) = \partial E(\mu)/\partial\mu \cong (E(\mu) - E(-\mu))/2\mu \qquad (3)$$

A value of $\mu = 0.0005$ au was proved to be sufficient to obtain numerical accuracy.[18,25] In fact, the value of $a(^{29}Si)$ in $[(H_2Si)_4]^{\bullet-}$ computed directly from the generalized density matrix (11.817 G) is reproduced up to the second decimal digit by the finite-field method (11.818 G) at the UMP2/VTZPD//UHF/VTZPD level. Relativistic effects at the Si atom have been neglected since they are estimated to give a very small contribution (about 1%)[26,27] to ^{29}Si hfs constants.

The ^{29}Si hyperfine anisotropy defined as the trace of the square of the traceless hyperfine dipolar tensor (tr $A'^2(^{29}Si)$) has been determined evaluating the components A'_{ij} ($i,j = x,y,z$) as expectation values directly from the computed atomic spin density $\rho_{\mu\nu}$.

$$A'_{ij}(^{29}Si) = g_e\beta_e g_{Si}\beta_{Si}\sum_{\mu\nu}\rho_{\mu\nu}\langle\phi_\mu|(\mathbf{r}_{kSi}{}^2\delta_{ij} - 3\mathbf{r}_{kSi,i}\,\mathbf{r}_{kSi,j})/\mathbf{r}_{kSi}{}^5|\phi_\nu\rangle \qquad (4)$$

Results and Discussion

Reliable evaluation of the hfs constants for the permethylcyclotetrasilane radical anion is a hard and delicate task because the system is too large to be described by highly correlated wave functions employing quite flexible basis sets and the radical anion might be unstable in the gas phase since Grev and Schaefer[6] found that the vertical electron affinity (EA) of the unsubstituted cyclotetrasilane $(H_2Si)_4$ is negative even employing extended basis sets and estimating electron correlation with the CI method; that is, the energy of the nonoptimized radical anion was found to be higher than that of the neutral parent.

Recently, it was found[18,28] that the UQCISD method is capable of reproducing closely experimental hfs constants also using the moderate-sized Dunning full double-ζ basis set augmented with polarization functions (DZP)[29] when the UHF wave function is spin contaminated only by the quartet state. Calculation of hfs constants at the UQCISD level is prohibitive for a system as large as the permethylcyclotetrasilane radical anion even using the DZP basis set in conjunction with the finite-field approach. However, it was shown that reliable hfs constants can be obtained with the UMP2 method, which requires much less computational resources, employing the moderate-sized DZP[18,30] and VTZP[31] basis sets when the UHF reference wave function describes correctly the doublet state. In this case, the contributions to hfs values were found to derive essentially from the effects of amplitudes due to double substitutions in the UHF reference determinant that are little affected by truncation of the perturbative expansion at second order.

The VTZP basis set has been used throughout this work since it was developed to study anion species.[11] The basis set should be, however, augmented with diffuse functions to better describe the anion state. Unfortunately, preliminary calculations showed that also the permethylated cyclotetrasilane has a negative vertical EA in the gas phase at the UHF/VTZP level so that the addition of standard diffuse functions could provide unreliable information.[32] In fact, calculations performed on a kinetically unstable anion employing sufficiently diffuse functions tend to describe a system composed by the neutral molecule and a free electron. Cyclopolysilanes are known to form stable radical anions in solution; hence a reasonable estimate of the molecular properties of cyclopolysilane radical anions can be obtained constraining artificially the extra electron to be bound (boxing procedure)[33] by excluding diffuse functions from the basis set.[34] This approach worsens the description of the anion species, but it ensures that the extra electron experiences the molecular potential being confined in the valence-orbital space by the radial rigidity and the exponential decay of the basis functions. The instability of the permethylated cyclotetrasilane radical anions is, however, estimated to be small so that calculations performed including moderate or standard diffuse functions in the basis set could correctly describe this anion. This occurs when the positive energy of the lowest unoccupied molecular orbital in the neutral molecule is lower than that of diffuse orbitals of the same symmetry. In this case information on the reliability of the computed values for an observable can be obtained from stabilization graphs constructed varying the exponent of diffuse functions.[32,35]

Thus, we have first searched for a feasible and reliable approach to study the permethylcyclotetrasilane radical anion performing exploratory calculations on the unsubstituted cyclotetrasilane radical anion to determine the effect of diffuse functions and electron correlation on the molecular properties.

Effect of Diffuse Functions on the Molecular Properties of $[(H_2Si)_4]^{\bullet-}$. Calculations have been performed on the unsubstituted cyclotetrasilane radical anion $[(H_2Si)_4]^{\bullet-}$ to study the effect of diffuse functions on the thermodynamic and kinetic stability of this class of radical anions as well as on the electron distribution in the SOMO. We have computed the adiabatic EA of the neutral cyclotetrasilane $(H_2Si)_4$ (a positive value indicates that the anion is thermodynamically stable) and the vertical ionization potential (IP) of the parent radical anion $[(H_2Si)_4]^{\bullet-}$ (a positive value when the anion is thermodynamically unstable indicates that the anion can be kinetically stable) varying the exponents of the diffuse functions as a function of the λ parameter (eq 1) at 0.1 intervals in the range 0.5−1.2.

The neutral cyclotetrasilane is computed to have a puckered structure (D_{2d} symmetry) at the UHF/VTZP level. Addition of the extra electron produces a planar anion species (D_{4h}) that has a π-type $^2A_{2u}$ electronic configuration. Table 1 shows that this radical anion is not only thermodynamically (negative adiabatic EA) but also kinetically unstable (negative vertical IP); that is, the optimized anion lies at higher energy also above the nonoptimized neutral parent. However, the adiabatic EA of the neutral molecule and the geometry and vertical IP of the anion species are little affected by augmenting the VTZP basis set with moderate ($\lambda = 0.5$) and standard diffuse functions at the UHF level. Inspection of the Mulliken population shows that the electron density in the diffuse functions in the SOMO is small. This is due to the fact that the lowest combination of the π-type diffuse orbitals lies higher in energy above the π^*

TABLE 1: Geometry,[a] Vertical IP (eV), and Si-p$_\pi$ Population in the SOMO (ρ) of $[(H_2Si)_4]^{\bullet-}$ along with Adiabatic EA (eV) of the Parent Neutral Molecule Computed at the UHF Level as a Function of the λ Parameter

	UHF/VTZP ($\lambda = 0.0$)	UHF/VTZPD′ ($\lambda = 0.5$)	UHF/VTZPD ($\lambda = 1.0$)
r(Si−Si)	2.3445	2.3441	2.3447 (2.3245, 2.3279)
r(Si−H)	1.5083	1.5084	1.5081 (1.5078, 1.5096)
∠H−Si−H	99.9	100.1	100.3 (100.2, 100.0)
vertical IP	−0.81	−0.78	−0.77
ρ(p$_\pi$ valence)	0.0406	0.0341	0.0387
ρ(p$_\pi$ outer-valence)	0.1195	0.1231	0.1017
ρ(p$_\pi$ diffuse)		0.0050	0.0241
adiabatic EA	−1.11	−1.07	−1.06

[a] Bond lengths in angstroms; bond angles in degrees. Values optimized at the UMP2 and UQCISD levels, respectively, are reported in parentheses.

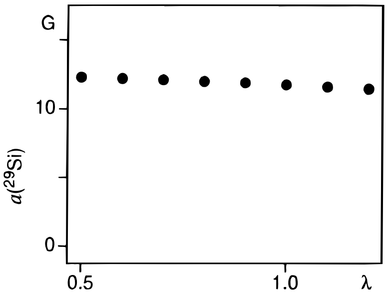

Figure 1. $a(^{29}Si)$ in $[(H_2Si)_4]^{\bullet-}$ computed at the UQCISD/VTZPD′//UHF/VTZPD level as a function of the λ parameter.

TABLE 2: Theoretical $a(^{29}Si)$ (gauss) for $[(H_2Si)_4]^{\bullet-}$ Computed at the UHF/VTZPD Geometry with Different Correlated Methods as a Function of the λ Parameter

λ	UMP2	UMP3	UMP4(DQ)	UMP4(SDQ)	UQCISD
0.0 (VTZP)	13.08	12.46	12.56	12.68	12.87
0.5	12.50	11.94	12.03	12.21	12.33
1.0 (VTZPD)	11.82	11.37	11.45	11.64	11.80

MO. Figure 1 shows that the value of the ^{29}Si hfs constant computed at the UQCISD level decreases only slightly and almost linearly with increasing value of λ. Thus, in this particular case the use of standard diffuse functions provides a reliable value of the hfs constant even if the anion is kinetically unstable.

Effect of Electron Correlation on $a(^{29}Si)$ of $[(H_2Si)_4]^{\bullet-}$. To verify whether the hfs constants of cyclopolysilane radical anions can be reliably computed estimating electron correlation at the UMP2 level, the ^{29}Si hfs constant in $[(H_2Si)_4]^{\bullet-}$ computed at the UMP2 level has been compared with that obtained at higher order in perturbation theory (UMPn, $n = 3$, 4) to assess the convergence of the doubles amplitudes as well as with that computed employing the more reliable UQCISD approach. Note that only two calculations carried out at the UQCISD level are necessary to evaluate $a(^{29}Si)$ with the finite-field method for all correlated methods investigated here.

Interestingly, Table 2 shows that the $a(^{29}Si)$ value does not change significantly on going from the UMP2 up to UQCISD approach, in line with the small spin contamination due to the quartet ($\langle S^2 \rangle = 0.7560$ (UHF) and 0.7500 after quartet annihilation). The contribution to the hfs constant due to doubles amplitudes converges rapidly in perturbation theory (compare UMP3 and UMP4(DQ) results), and the small overestimation in the $a(^{29}Si)$ value due to the incomplete description of the effects of doubles amplitudes in second-order perturbation theory (compare UMP2 and UMP3 results) is counterbalanced by the neglect of the contribution from singles amplitudes.

TABLE 3: Theoretical hfs Constants (gauss) for $[(Me_2Si)_4]^{\bullet-}$ Computed at the UMP2/VTZPD//UHF/VTZPD Level

	UMP2/VTZPD	experiment[a]
$a(^{29}Si)$	6.42	4.70,[b] 3.80[c]
$a(^{13}C)$	20.86	20.97

[a] From ref 36. [b] For R = Et, $a(^{13}C) = 18.4$. [c] For R = i-Pr, $a(^{13}C) = 16.49$.

It is often necessary to use highly correlated methods such as the UQCISD approach not only to compute reliable hfs constants but also to obtain reliable radical geometries when spin contamination is large. It should be of interest to explore the sensitivity of $a(^{29}Si)$ to geometry changes due to electron correlation even if in the present case spin contamination is small. The geometry of this radical anion has been reoptimized with the VTZPD basis set employing the UMP2 and UQCISD methods. The $a(^{29}Si)$ value computed at the UMP2/VTZPD level is not sensitive to the variations in the structural parameters due to the inclusion of electron correlation, being computed to be 11.82, 11.75, and 11.80 G at the UHF, UMP2, and UQCISD optimized geometries, respectively. The small variations found in the structural parameters on improving electron correlation (see Table 1) suggest that inclusion of higher excitations (triples) in the UQCISD approach should not be important in determining the radical geometry.

Hence, calculations at the UMP2/VTZPD//UHF/VTZPD level of theory should provide reliable estimate of the hfs constants for the permethylated cyclotetrasilane radical anion.

Isotropic hfs Constants of $[(Me_2Si)_4]^{\bullet-}$. Table 3 shows that the value of the $a(^{13}C)$ constant computed for $[(Me_2Si)_4]^{\bullet-}$ at the UMP2/VTZPD level is in excellent agreement with the experimental one, spin contamination remaining small also in the permethylated radical anion ($\langle S^2 \rangle = 0.7549$ (UHF) and 0.7500 after quartet annihilation). Unfortunately, the experimental value for $a(^{29}Si)$ is not available for $[(Me_2Si)_4]^{\bullet-}$; however, the computed UMP2/VTZPD value is only slightly greater than the value measured for R = Et and i-Pr. Interestingly, the trend in $a(^{29}Si)$ (Me(theory) > Et(exp) > i-Pr(exp)) parallels that displayed by the experimental $a(^{13}C)$ values along this series. The small decrease in $a(^{29}Si)$ and $a(^{13}C)$ upon successive methylation of the α-methyl substituent can be ascribed to delocalization of the unpaired electron into the β-methyl groups so that also the computed value of $a(^{29}Si)$ for $[(Me_2Si)_4]^{\bullet-}$ should be highly reliable. This confirms further that UMP2 calculations employing relatively small basis sets are capable of closely reproducing experimental hfs constants at heavy atoms when the UHF wave function describes correctly the doublet state.

^{29}Si Hyperfine Anisotropy of $[(Me_2Si)_4]^{\bullet-}$. To establish firmly that the permethylcyclotetrasilane radical anions have a π-type electronic configuration, it is important to compare the theoretical value of the ^{29}Si hyperfine anisotropy tr $A'^2(^{29}Si)$ with that estimated by ENDOR experiments[4] utilizing the equations derived from relaxation theory for determining the optimum ENDOR effect.[37] The components A'_{ij} of the hyperfine dipolar tensor have been computed as expectation values from the UHF atomic spin densities (eq 4) since electron correlation effects are not expected to sizably affect their values. Indeed, Table 4 shows that electron correlation estimated at the UMP2 level decreases the ^{29}Si hyperfine anisotropy less than 2% in exploratory calculations carried out using the less extensive valence double-ζ 6-31G (VDZ) and 6-31G** (VDZP) basis sets.[38] Interestingly, the addition of polarization d-functions slightly increases the ^{29}Si hyperfine anisotropy, so that the low anisotropy found for cyclopolysilane radical anions cannot be

TABLE 4: Hyperfine Anisotropy tr $A'^2(^{29}Si)$ in MHz^2 of $[(Me_2Si)_4]^{\bullet-}$ Computed at the UHF Level[a] with Different Basis Sets Using the UHF/VTZPD Geometry along with the Atomic Si Populations (ρ) in the SOMO

	VDZ	VDZP	VTZP	VTZPD
$A'^{2(^{29}Si)}$	146.3 (143.6)	154.3 (153.5)	137.8	99.5[b]
ρ(p_π inner-valence)			0.0013	0.0020
ρ(p_π valence)	0.0291	0.0263	0.0543	0.0303
ρ(p_π outer-valence)	0.1844	0.1692	0.1702	0.2066
ρ(p_π diffuse)				0.0492
ρ(d_π)		0.0268	0.0253	0.0170

[a] The computed UMP2 values for valence double-ζ basis sets are reported in parentheses. [b] The individual dipolar components in MHz are $A_{xx} = 5.58$, $A_{yy} = 2.35$, $A_{zz} = -7.93$; the x and y ($\equiv C_2$) axes are located in the σ_h plane.

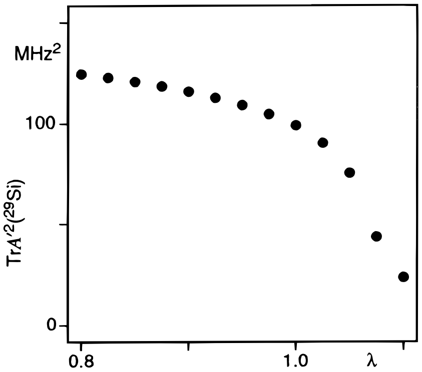

Figure 2. ^{29}Si hyperfine anisotropy in $[(Me_2Si)_4]^{\bullet-}$ computed at the UMP2/VTZPD′//UHF/VTZPD level as a function of the λ parameter.

ascribed to the participation of Si d-orbitals in the SOMO as previously suggested.[7] In passing from the valence double-ζ to triple-ζ basis set there is a small decrease in the ^{29}Si hyperfine anisotropy. In fact, the Si-d_π population in the SOMO does not change appreciably, while the increase in odd-electron density in the valence Si-3p_π AOs is counterbalanced by the decrease in its dipolar contribution since the Si-3p_π valence orbital in the VTZ basis set is more diffuse than the corresponding one in the VDZ basis set. Addition of diffuse functions to the VTZ basis set decreases significantly the ^{29}Si hyperfine anisotropy; however, in this case their population in the SOMO is much smaller than that of the Si-3p_π outer-valence AOs, indicating that this value should be reliable enough. Indeed, Figure 2 shows that the ^{29}Si hyperfine anisotropy computed as a function of λ at 0.025 intervals in the range 0.8-1.1 decreases slightly up to $\lambda = 1.025$ and from here drops down rapidly because the extra electron tends to be mainly delocalized into the diffuse functions of the methyl groups.

The ^{29}Si hyperfine anisotropy computed at the UHF/VTZPD level (99.5 MHz^2) is in the range determined by ENDOR spectroscopy for this class of radical anions (30−100 MHz^2) but is much less than that estimated for an electron delocalized into pure Si-3p_π atomic orbitals ($\approx$1300 MHz^2).[4] To understand why the ^{29}Si hyperfine anisotropy is computed to be unexpectedly small in a π-type configuration, we have examined the Si atomic populations in the SOMO and estimated the contributions to hyperfine anisotropy arising from the single basis functions.

Table 4 shows that the unpaired electron is delocalized into the Si-3p_π outer-valence AOs rather than in the Si-3p_π valence AOs. The values of the components of the $A'(^{29}Si)$ dipolar tensor depend on the value of $\langle 1/r^3 \rangle$ so that the contribution to hyperfine anisotropy due to the mainly occupied Si AO in the SOMO, i.e. Si-3p_π outer-valence AO, could be small since this orbital is much more diffuse than the Si-3p_π valence AO. We have computed the values of the ^{29}Si hyperfine anisotropy due to electron occupation of the single basis functions. The computed value for the ^{29}Si-3p_π valence orbital (3.84×10^4 MHz^2) is slightly less than the experimental one for the free atom (4.50×10^4 MHz^2).[37] Interestingly, the values for the ^{29}Si-3p_π outer-valence and ^{29}Si-3d_π orbitals are computed to be much smaller than that for the ^{29}Si-3p_π valence orbital, the ratio being 0.0196 and 0.0094, respectively. A rough estimate of the contribution to the ^{29}Si hyperfine anisotropy from the single basis functions in $[(Me_2Si)_4]^{\bullet-}$ can be obtained by scaling down the computed values by the square of the Si atomic populations in the SOMO reported in Table 4. The contribution from the Si-3d_π AO is estimated to be negligible, while that deriving from the mainly occupied Si-3p_π outer-valence AO is estimated to be small, being slightly less than that deriving from the scarcely populated Si-3p_π valence AO at the UHF/VTZPD level. This is the reason that in the π-type configuration the ^{29}Si hyperfine anisotropy is unexpectedly low.

Conclusion

The present calculations show that the extra electron in the ground state of cyclotetrasilane radical anions occupies a π^* MO. The experimentally observed ^{13}C and ^{29}Si hyperfine structures are well reproduced. It has been shown that the unexpectedly low value of the ^{29}Si hyperfine anisotropy is due to the large delocalization of the unpaired electron into the Si-3p_π outer-valence atomic orbitals that have been computed to give a small contribution to the hyperfine anisotropy. Hence, the π^* model for cyclopolysilane radical anions is capable of explaining not only the low values of the isotropic ^{29}Si hfs constant observed experimentally with ESR spectroscopy but also the low values of the ^{29}Si hyperfine anisotropy estimated by ENDOR spectroscopy. Thus, reliable ab initio calculations at odds with the ENDOR suggestion indicate firmly that the unpaired electron in cyclopolysilanes is delocalized into a π^* MO.

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