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High-Level Coupled-Cluster Methods for Electron Spin Resonance Spectra: On the Experimental Spectrum of the Silacyclobutane Radical Cation

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The silacyclobutane radical cation is a prototype intermediate in chemical reactions involving Si based organic molecules. In the interest of its full characterization, the experimentally determined isotropic hyperfine coupling constants of the hydrogens in silacyclobutane radical cation (c-SiC_3^+) have raised some interesting questions, leading to different interpretations of the spectrum. To help resolve this discrepancy, we report very high-level theoretical results with coupled-cluster theory using its analytical, response density matrix procedure, and recently proposed basis sets that are specific to ESR. The detailed studies of geometries, basis set effects, and electron correlation tend to support the B3LYP/6-31G**-based reassignment of the ESR spectrum of the c-SiC_3^+ radical cation by Fängström et al.

Introduction

Radicals, as open shell systems, can frequently be well characterized by electron spin resonance (ESR) spectroscopy. ESR spectroscopy provides valuable information about the distribution of unpaired electrons in a radical by measuring the interaction between the electron and the nuclear spin. The hyperfine coupling can be factored into an isotropic part (Fermi contact) and an anisotropic part. Electronic structure theory focuses on the Fermi contact term, which when conventionally evaluated as a Dirac delta function, is a local property. This makes accurate ab initio correlated calculations higly demanding. Important factors to be considered for an adequate description of the isotropic hyperfine coupling constants (iHFCC) include a basis that can describe the local delta function operator, the spin-polarization correction for restricted and unrestricted open-shell references, and the electron correlation correction.[1,2,3,4] The numerical result can be highly sensitive to all the above, and the silacyclobutane radical cation offers a “real-world” example.

The isotropic HFC constants of the alkane radical cations in halocarbon matrices have attracted the attention of many researchers in the past decade.[5−7] In particular, the ESR spectra of silacyclohexane (c-$SiC_5^{\bullet+}$) radical cation and its methyl derivatives have been investigated to determine how electronic and geometric structures change by substituting one or more carbons of the cyclohexane ring by silicon(s).[5] Removing one electron from 1-methylsilacyclohexane changes the geometrical structure from C_s to C_1 with one Si−C bond elongated. These studies were expanded to other alkylsilane radical cations with four- and five-membered rings as well as linear cations with carbon numbers of 3 and 4. Komaguchi et al. [6] have reported on the structure and ring puckering motion of the silacyclobutane radical cation c-$SiC_3^{\bullet+}$ in perfluorocyclohexane matrixes at low temperatures. The radical cation shows temperature-dependent ESR spectra between 4 and 170 K. The 4 K spectrum is complex, due to line width broadening from tunneling effects. Upon warming to 170 K the spectrum is reversibly changed into triplets of 26 and 14 G. By comparison to the spectra of selectively deuterated and methylated silacyclobutane radical cations, the 14 G splitting was attributed to the hydrogens at silicon. Assuming thermal averaging of two pairs of nonequivalent hydrogens and using a two-site jump model, signals of 43, 17, 11, and 9 G were assigned. The isotropic splittings of 43 and 9 G were attributed to the equatorial and axial hydrogens at C3 whereas the 17 and 11 G splittings were assigned to the equatorial and axial hydrogens at silicon. On the basis of the experimental HF splitting of c-$SiC_3^{\bullet+}$ at 4 K, it was concluded that the molecule has a structure with C_1 symmetry, as that observed for c-$SiC_5^{\bullet+}$. [The observed temperature-dependent ESR spectra were attributed to a ring puckering motion of the radical cation.]

Recently Fängström et al. reanalyzed the above-mentioned ESR experiments using ab initio methods and density functional theory.[7] The geometry optimization and energy calculations were carried out at the B3LYP/6-31G(d,p) and MP2-fc/6-31G(d,p) levels. The equilibrium structure was in agreement with the equivalent results of Komaguchi et al.[6] at both levels of theory, a ring structure of C_1 symmetry in which one of the Si−C bonds is elongated. Both levels of calculation gave similar results for the structure of the radical ground state, the main difference being in the puckering angle, which is found to be 146° at the MP2-fc level and 153° at the B3LYP level. The iHFCCs were calculated using the B3LYP functional with the 6-31G(d,p) and 6-311+G(2df,p) basis sets. Fängström et al. then performed ESR line-shape simulations to obtain revised experimental values. Except for the ring puckering motion, vibrational averaging corrections were not considered (static approximation). For the experimentally unresolved coupling constants calculated values were used. The revised values at 4 K were assigned to $H_{Si,e}$ (15 G), $H_{Si,a}$ (13 G), $H_{C3,e}$ (49 G), and $H_{C2,e}$ (10 G). These recent results differ by 10−20% from the original values by Komaguchi et al. and, in particular, assign the 10 G coupling constant to $H_{C2,e}$ instead of $H_{C3,a}$. Fängström et al. also reanalyzed the temperature dependence of the rate constants and suggest that a change of slope at higher temperatures might be caused by a combination of ring puckering and Si−C bond length alternation.

As potential difficulties in DFT based calculations might occur that could affect such an analysis, in this work, we reinvestigate the ESR spectrum of the silacyclobutane radical

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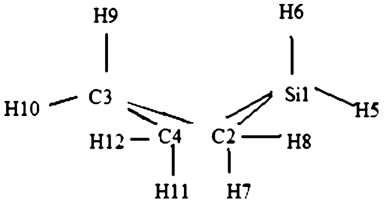

Figure 1. Structure and numbering of atoms of the silacyclobutane radical cation. The puckering angle is Si−C2−C4−C3.

cation at the coupled cluster level using a variety of specially constructed basis sets to attempt to offer a more definitive assignment. In separate work, we studied the influence of geometry, basis set, and correlation on the isotropic HFCCs of three small organic radicals, $CH_3^\bullet$, $C_2H_3^\bullet$, and $H_2CN^\bullet$. We found that each of these factors can have significant influence on the calculated iHFCCs of the hydrogen atoms (up to 10%) and that improved geometries, methods and basis sets lead to improved iHFCCs.[8] A recent study by Byrd et al.[9] concluded that bond lengths in radicals are most reliably calculated using U-B3LYP, CCSD and ROHF-CCSD(T) with 6-31G(d,p) or, better, cc-pVTZ basis sets. The quality of calculated bond angles was not discussed because of too little data. We found the 7° difference in the puckering angles calculated by Fängström et al. reason enough to optimize the geometry of c-SiC_3^+ at several levels of theory.

A second possible improvement is related to the basis set used in calculating the iHFCCs. The 6-31G(d,p) and 6-311+G-(2df,p) basis sets are not intended for the description of the electron density at the nucleus. Special basis sets have been developed for use with ROHF-CIS,[10] B3LYP[11] and correlated MO[12,13] methods. To obtain even higher quality results, we apply our recently proposed bases [8,12] with CCSD and CCSD(T) to the calculation of iHFCC's. Comparing the results at different levels of CC-theory also allows us to estimate the degree of convergence of our results in an attempt to be as definitive as possible for a molecule of the size of the silacyclobutane radical cation.

Computational Details

The geometry of the (puckered) ground-state structure of C_1 symmetry was optimized at different levels of theory and basis sets. At the MBPT(2) and CCSD(T) levels we used the cc-pVDZ basis of Dunning et al.[14,15] and the ACES II program system.[16] The RI-MP2[17,18] optimization was carried out using the VTZPP[19,20] basis (polarization functions as in cc-pVTZ) and the TURBOMOLE (version 5) program.[21] For the B3LYP optimization we employed the 6-31G(d,p)[22−25] as well as the cc-pVDZ and cc-pVTZ basis sets and the Q-Chem (version 2.0) program.[26] An unrestricted Hartree−Fock (UHF) reference and the frozen core (fc) approximation were used with all wave function methods. Spherical harmonic functions were used for all basis sets except 6-31G(d,p).

The hydrogen isotropic hyperfine coupling constants (iHFCCs) of silacyclobutane radical cation are calculated *analytically* with ACES II, using the coupled cluster (CC) "relaxed density matrix" approach and an unrestricted Hartree−Fock (UHF) reference. The calculations are performed using the CCSD and CCSD(T) methods with a variety of basis sets. Because the core orbitals at carbon and silicon have nearly no influence on the spin densities at the hydrogens, we applied the frozen core approximation. We employed the cc-pVDZ and aug-cc-pVDZ basis sets of Dunning et al.[14,15] together with hydrogen basis sets derived from them.[12] The cc-pVDZ-s5 basis set ([9s,1p]/(7s,1p)) was derived from the regular cc-pVDZ basis by adding 5 tight s-functions with the tight exponents obtained by multiplying the biggest s-exponent of the previous basis set by a constant (4 in this case). Helgaker et al.[27] showed that this type of expansion of the cc-basis sets in conjunction with uncontracted s-primitives leads to a smoothly convergent series of NMR coupling constants, largely due to good values for the Fermi contact term which depends on accurate description of the electron density at the nuclei. The cc-pVDZ-t5s-a5 basis set ([9s,1p]/(5s,1p)) is constructed differently. In them, the parent cc-basis is uncontracted, and five s-functions form an even tempered extension from the tightest regular s-function to 999999. The six tightest s-primitives are contracted into two groups. The aug-cc-pVDZ-t5s-a6 basis set is closely related. These basis sets were systematically tested in calculations on small organic radicals ($CH_3^\bullet$, $C_2H_3^\bullet$, and $H_2CN^\bullet$).[8] The iHFCCs of $H_2CN^\bullet$ are nearly exclusively dependent on the geometry. The EPR-2 basis set by Barone et al.[11] is of very similar accuracy for these three molecules.

Geometry Optimization

We optimized the geometry of the silacyclobutane radical cation at the B3LYP, MBPT(2)-fc and CCSD(T)-fc/cc-pVDZ levels. We also performed B3LYP/cc-pVTZ and RI-MP2-fc/TZVPP optimizations. For direct comparison with the results of Fängström et al., we include the B3LYP/6-31G(d,p) structure in our study.

Table 1 contains all bond lengths, some bond angles and the puckering angle (Si1−C2−C4−C3) of the optimized structures. The six levels of theory can be categorized as DFT and MO methods or as using DZ and TZ basis sets. The 6-31G(d,p) basis set is "in between" as the Cartesian d-functions at C and Si have the effect of a third s-function. Comparison shows that the RI-MP2-fc/TZVPP and B3LYP/cc-pVTZ bond lengths are shorter than those calculated using the cc-pVDZ basis set. The 6-31G(d,p) results are usually closer to the cc-pVTZ values. The most prominent exception to the DZ/TZ pattern is the C2−C3 distance, which is longer in the DFT calculations. This parallels the variation of the puckering angle, which are 153.4−155.3° in the B3LYP calculations but 146.9−148.5° at the MO-based levels of theory. The Si−C bonds exhibit the largest variation with the level of theory: up to 0.05 Å. The other bond lengths vary by less than 0.02 Å. The bond angles of the four-membered ring vary by 2−4°. The angles involving one hydrogen atom vary by less than 2.3° and the angles between two hydrogen atoms change by less than 0.7°. The bond angles (including the ones not given in Table 1) usually follow either the DZ/TZ or the DFT/MO pattern. There is no clear preference for one of the patterns.

The recent work of Byrd et al.[9] shows that the mean absolute errors of computed bond lengths decrease from CCSD(T)-fc/cc-pVDZ over MP2-fc/cc-pVDZ to MP2-fc/cc-pVTZ. We find that the bond lengths in c-SiC_3^+ become shorter in the same sequence. The study by Byrd et al. also points out that these methods can be troubled by problems with the Hartree−Fock reference function whereas CCSD-fc and B3LYP do not have that problem. However, the small cluster amplitudes T_1 and T_2 obtained from (CCSD(T)-fc/cc-pVDZ: max. $T_1 = 0.04$ and max. $T_2 = 0.02$) show that correlation is not very strong in c-SiC_3^+. Therefore we expect the basis set effect to be dominant and think that the RI-MP2-fc/TZVPP geometry is likely to be better than the MBPT(2)-fc and CCSD(T)-fc/cc-pVDZ geometries. Because the puckering angle is about 148° for all MO based methods, we suspect that the larger puckering angle in

TABLE 1: Equilibrium Geometry of the Silacyclobutane Radical Cation (Puckered Structure)[a]

method: basis set:	B3LYP cc-pVDZ	B3LYP 6-31G(d,p)	RI-MP2[b] cc-pVTZ	RI-MP2[b] VTZPP	MBPT(2)[a] cc-pVDZ	CCSD(T)[a] cc-pVDZ
			Bond Lengths/å			
R(C4−Si)	2.300	2.265	2.269	2.255	2.307	2.311
R(C2−Si)	1.870	1.855	1.851	1.841	1.864	1.876
R(C2−C3)	1.590	1.596	1.594	1.577	1.579	1.587
R(C3−C4)	1.499	1.502	1.495	1.497	1.507	1.514
R(Si−H5)	1.485	1.475	1.474	1.467	1.477	1.481
R(Si−H6)	1.485	1.474	1.473	1.467	1.477	1.481
R(C2−H7)	1.099	1.092	1.087	1.087	1.102	1.105
R(C2−H8)	1.100	1.092	1.087	1.086	1.101	1.104
R(C3−H9)	1.106	1.101	1.096	1.094	1.107	1.110
R(C3−H10)	1.098	1.091	1.086	1.086	1.100	1.103
R(C4−H11)	1.100	1.092	1.087	1.087	1.101	1.105
R(C4−H12)	1.097	1.089	1.085	1.083	1.099	1.102
			Bond Angles/deg			
∠C2SiC4	71.6	73.9	73.3	73.2	71.3	71.3
∠SiC2C3	95.5	92.6	93.3	92.0	94.1	94.4
∠C2C3C4	105.7	107.4	107.0	106.5	105.5	105.3
∠SiC4C3	82.1	80.5	80.9	79.4	80.0	80.7
γ	155.3	153.4	153.9	146.9	146.9	148.5

[a] The puckering angle (Γ, deg) is Si−C2−C4−C3. [b] Frozen core.

TABLE 2: Deviation of Calculated Isotropic Hyperfine Coupling Constants of Hydrogen Atoms from Reference Results[a]

		CH_3[b]		C_2H_3[c]			
method	basis set	G	%	G_{rms}	%$_{av.}$	G_{max}	%$_{max}$
UHF-CCSD-fc	cc-pVDZ:cc-pVDZ-t5s-a5[d]	−3.3	13.4	4.1	−12.9	−5.8	−25.8
UHF-CCSD-fc	EPR-2:cc-pVDZ-t5s-a5[d]	−2.9	11.7	4.1	−12.5	−5.8	−24.6
UHF-CCSD-fc	EPR-2[d]	−2.6	10.3	4.6	−14.1	−6.5	−27.0
UHF-CCSD(T)-fc	cc-pVDZ:cc-pVDZ-t5s-a5[d]	−2.8	11.1	3.6	−10.1	−5.4	−17.6
UHF-CCSD(T)-fc	EPR-2:cc-pVDZ-t5s-a5[d]	−2.3	9.3	3.5	−9.8	−5.3	−17.0
UHF-CCSD(T)-fc	EPR-2[d]	−2.0	8.0	4.0	−11.4	−6.0	−19.7
UHF-CCSD(T)-fc	6-31G(d,p)	−5.2	20.7	5.9	−18.5	−8.3	−34.6
UHF-CCSD(T)-fc	cc-pVTZ:cc-pVTZ-t5s-a5[d]	−0.9	3.6	3.1	−4.7	−5.3	−8.4
UHF-CCSD(T)-fc	6-311+G(2df,p)	0.6	−2.3	5.9	−11.3	−9.6	−15.0

[a] Experimental values corrected for solvent influence and large amplitude motions. [b] Geometry: CCSD-fc/cc-pVQZ. Max. $T_1 = -0.01$, max. $T_2 = -0.04$, projected $\langle S^2 \rangle = 0.751$. [c] Largest deviation from experiment: geometry: CCSD(T)-fc/cc-pVQZ (ref 29 recommended equilibrium structure). Max. $T_1 = 0.14$, max. $T_2 = 0.13$, projected $\langle S^2 \rangle = 0.780$. [d] Reference 8.

the B3LYP optimized structures might be an artifact, but lacking a large basis CCSD(T), we cannot be certain.

Isotropic Hyperfine Coupling Constants

As mentioned before, calculated iHFCCs can be dependent on the geometry, the correlation method, and the basis set used. Relevant results from test calculations on $CH_3^\bullet$ and $C_2H_3^\bullet$, a radical with nonequivalent hydrogen atoms, are shown in Table 2. On average, the EPR-2:cc-pVDZ-t5s-a5 basis set combination seems to perform best. The notation means cc-pVDZ-t5s-a5 at hydrogen and EPR-2 at all other atoms. For $CH_3^\bullet$, the results at the MBPT(2)-fc/cc-pVTZ geometry differ by less than 0.1 G and 0.1% from the values in Table 2. Because c-SiC_3^+ has T-amplitudes and projected $\langle S^2 \rangle$ (max. $T_1 = 0.04$, max. $T_2 = 0.02$, $\langle S^2 \rangle = 0.751$) comparable to those of CH_3, we expect the RI-MP2-fc/TZVPP geometry to be quite good. Table 2 also shows that the 6-31G(d,p) basis set, used in ref 7 to calculate the temperature-dependent iHFCCs, does not perform as well as the basis sets chosen for this work.

To explore the influence of the geometry, we calculated UHF-CCSD-fc/cc-pVDZ:cc-pVDZ-t5s-a5 iHFCCs at several geometries. Table 3 shows that the CCSD(T) and MBPT(2)/cc-pVDZ geometries give similar iHFCCs. The differences between iHFCCs computed at the MBPT(2)/cc-pVDZ and RI-MP2-fc/TZVPP optimized geometries are often larger than 20% of the TZVPP values. The iHFCCs computed at the B3LYP/cc-pVDZ and cc-pVTZ geometries vary by similar percentages. The larger iHFCCs at the B3LYP/cc-pVTZ geometry differ from those at the RI-MP2-fc/TZVPP geometry by less than 14%. Coupling constants calculated at the B3LYP/6-31G(d,p) geometry are closer to those at the B3LYP/cc-pVTZ geometry than those at the B3LYP/cc-pVDZ geometry, as might be expected for the geometry parameters. At the B3LYP/6-31G(d,p) geometry, the B3LYP/6-31G(d,p) iHFCCs differ by up to 36% from the CCSD/cc-pVDZ:cc-pVDZ-t5s-51 results. The B3LYP/6-31G(d,p) values differ by up to 30% from the B3LYP/6-31G(2df,p) coupling constants.

To see how a more complete treatment of electron correlation changes the computed iHFCCs, we performed CCSD(T)-fc/cc-pVDZ:cc-pVDZ-t5s-a5 calculations for the MBPT(2)-fc/cc-

TABLE 3: Isotropic Hyperfine Coupling Constants of Hydrogen Atoms in Gauss, Calculated at the UHF-CCSD-fc/cc-pVDZ:cc-pVDZ-t5s-a5 Level for Various Optimized Geometries

geometry	$H_{Si,e}$	$H_{Si,a}$	$H_{C2,e}$	$H_{C2,a}$	$H_{C3,e}$	$H_{C3,a}$	$H_{C4,e}$	$H_{C4,a}$
CCSD(T)-fc/cc-pVDZ	8.4	5.8	13.0	−1.6	42.2	−0.5	−11.3	−9.4
MBPT(2)-fc/cc-pVDZ	9.0	5.9	12.8	−1.8	45.4	−0.7	−11.7	−9.5
RI-MP2-fc/TZVPP	13.0	7.8	10.8	−1.9	50.9	−0.7	−12.3	−9.6
B3LYP/cc-pVDZ	7.5	6.7	9.8	−0.9	37.8	0.3	−10.7	−8.6
B3LYP/cc-pVTZ	11.3	8.7	11.2	−1.4	43.7	0.4	−11.4	−8.8
B3LYP/6-31G(d,p)	12.7	9.1	10.9	−1.5	45.1	0.4	−11.6	−8.7
B3LYP/6-31G(d,p)[a]	15.1	11.3	11.2	−1.4	50.1	0.2	−8.7	−5.6
B3LYP/6-31G(d,p)[b]	15.9	12.2	10.9	−1.4	49.5	0.4	−7.1	−4.3

[a] Reference 7: B3LYP/6-31G(d,p) iHFCCs. [b] Reference 7: B3LYP/6-311+G(2df,p) iHFCCs.

TABLE 4: Change in Isotropic Hyperfine Coupling Constants of Hydrogen Atoms Due to Correlation, Using the cc-pVDZ:cc-pVDZ-t5s-a5 Basis Set Combination

geometry	G	$H_{\mathrm{Si,e}}$	$H_{\mathrm{Si,a}}$	$H_{\mathrm{C2,e}}$	$H_{\mathrm{C2,a}}$	$H_{\mathrm{C3,e}}$	$H_{\mathrm{C3,a}}$	$H_{\mathrm{C4,e}}$	$H_{\mathrm{C4,a}}$
MBPT(2)-fc/cc-pVDZ	G^a	0.4	0.1	0.8	0.0	1.9	−0.2	0.9	0.9
RI-MP2-fc/TZVPP	G^a	0.5	0.2	0.6	0.0	2.1	−0.2	0.9	0.9
B3LYP/cc-pVTZ	G^a	0.4	0.2	0.7	0.0	1.8	−0.2	0.9	0.9
MBPT(2)-fc/cc-pVDZ	$\%^b$	4.1	2.1	5.8	0.9	4.0	22.2	−8.2	−10.6
RI-MP2-fc/TZVPP	$\%^b$	4.0	2.4	5.5	1.6	4.0	20.3	−7.5	−9.9
B3LYP/cc-pVTZ	$\%^b$	3.8	2.5	5.9	0.0	3.9	−83.3	−8.3	−11.1

[a] UHF-CCSD(T)-fc − UHF−CCSD-fc. [b] 100 × (CCSD(T)-fc − CCSD-fc)/CCSD(T)-fc.

TABLE 5: Change in Isotropic Hyperfine Coupling Constants of Hydrogen Atoms Due to Diffuse Functions[a] at the UHF-CCSD-fc/cc-pVDZ:cc-pVDZ-t5s-a5//RI-MP2-fc/VTZPP Level

different basis sets	$H_{\mathrm{Si,e}}$	$H_{\mathrm{Si,a}}$	$H_{\mathrm{C2,e}}$	$H_{\mathrm{C2,a}}$	$H_{\mathrm{C3,e}}$	$H_{\mathrm{C3,a}}$	$H_{\mathrm{C4,e}}$	$H_{\mathrm{C4,a}}$
Si, H_{Sie}, H_{Sia}	−0.11	−0.05	−0.05	0.00	−0.03	0.00	0.05	0.06
C2, H_{C2e}, H_{C2a}	0.05	0.03	−0.16	0.00	0.03	0.00	0.00	−0.06
C3, $H_{\mathrm{C2a,}}$ H_{C3a}	−0.10	−0.02	−0.05	0.00	0.00	−0.02	0.03	−0.08
C4, H_{C4e}, H_{C4a}	−0.02	−0.05	−0.10	−0.02	0.21	−0.03	−0.03	−0.08
all (extrapolated)	−0.18	−0.08	−0.35	−0.02	0.21	−0.05	0.05	−0.16

[a] aug-cc-pVDZ:aug-cc-pVDZ-t5s-a6 instead of cc-pVDZ:cc-pVDZ-t5s-a5 for selected atoms.

TABLE 6: Isotropic Hyperfine Coupling Constants of Hydrogen Atoms at the UHF-CCSD(T)-fc/X

geometry	Si, C	H	$H_{\mathrm{Si,e}}$	$H_{\mathrm{Si,a}}$	$H_{\mathrm{C2,e}}$	$H_{\mathrm{C2,a}}$	$H_{\mathrm{C3,e}}$	$H_{\mathrm{C3,a}}$	$H_{\mathrm{C4,e}}$	$H_{\mathrm{C4,a}}$
a	cc-pVDZ	cc-pVDZ-t5s-a5	13.6	7.9	11.4	−2.0	53.0	−0.9	−11.5	−8.7
a	EPR-2	EPR-2	13.7	8.4	10.8	−1.9	52.3	−0.9	−11.4	−8.6
a	EPR-2	cc-pVDZ-t5s-a5	13.9	8.5	11.0	−2.0	53.1	−0.9	−11.6	−8.7
b	cc-pVDZ	cc-pVDZ-t5s−a5	11.8	8.9	11.4	−1.4	45.4	0.2	−10.5	−7.9
b	EPR-2	EPR-2	12.0	9.3	10.8	−1.4	44.9	0.2	−10.4	−7.8
b	EPR-2	cc-pVDZ-t5s-a5	12.2	9.4	11.0	−1.5	45.6	0.2	−10.6	−7.9

[a] RI-MP2-fc/VTZPP. [b] B3LYP/cc-pVTZ.

pVDZ, RI-MP2-fc/TZVPP and B3LYP/cc-pVTZ geometries. Because correlation is small in this molecule, the perturbative treatment of connected triple excitations is appropriate. Table 4 shows that a better treatment of correlation tends to make the iHFCCs more positive (or less negative). The differences are usually smaller than 1 G, the only exception being (H_{C3e}), which has the largest iHFCC of the molecule. Expressed as percentages of the CCSD(T) values, the iHFCCs larger than 5 G change by ∼10% or less. The changes due to more complete treatment of correlation are not very dependent on the optimized geometries.

The influence of larger basis sets was difficult to determine. Due to hardware limitations, we could not calculate iHFCCs at the UHF-CCSD-fc/aug-cc-pVDZ:aug-cc-pVDZ-t5s-a6 level. Instead, we used the augmented basis sets for three atoms (e.g., Si and the two hydrogens attached to it) and the cc-pVDZ:cc-pVDZ-t5s-a5 basis set combination for the rest of the molecule. If the changes caused by the diffuse functions are reasonably additive, we can approximate the iHFCCs calculated with augmented basis sets at every atom by extrapolation. Table 5 shows that the individual as well as the extrapolated changes are quite small. This seems to indicate that enlarging the basis set has only little influence on the iHFCCs of *c*-SiC_3^+. To check this result, we used the EPR-2 basis sets, which are less flexible than cc-pVDZ:cc-VDZ-t5s-a5 for hydrogen but more flexible for the heavier atoms. Table 6 shows that the cc-pVDZ:cc-pVDZ-t5s-a5 and EPR-2 results are not very different. The iHFCCs change by ∼5% or less. The iHFCCs calculated with cc-pVDZ-t5s-a5 for hydrogens and EPR-2 for other atoms are very similar (differences of less than 0.2 G) to either the cc-pVDZ:cc-pVDZ-t5s-a5 or the EPR-2 results. This seems to indicate that flexibility of the heavy atom basis sets is important for the iHFCCs of some, but not all, hydrogen atoms. The differences between the cc-pVDZ:cc-pVDZ-t5s-a5 and EPR-2:cc-pVDZ-t5s-a5 values are a little larger than the extrapolated changes in Table 5 and often of the opposite sign. We conclude that using larger basis sets will change the calculated iHFCCs by a few percent, but we are unsure about the direction.

To check the quality of our results, we approximated the 170 K spectrum of *c*-$SiC_3^{+\bullet}$. At this temperature, individual molecules are rapidly moving between the enantiomeric minima. We employed the high-temperature limiting case of the two-site jump model, used by Komaguchi et al.;[6] i.e., we averaged the iHFCCs of pairs of hydrogens calculated at the equilibrium structure because the puckering motion transforms the axial hydrogen into an equatorial one. In contrast, the distinguished coordinate (DC) approach determines energies and properties along the reaction coordinate connecting the two enantiomers. Then vibrational wave functions are determined and the expectation values of the iHFCCs are calculated. This approach is superior to the jump model but needs more information to be applicable.

The left side of Table 7 shows the averaged iHFCCs corresponding to the puckering motion. The values computed at the RI-MP2-fc/TZVPP and B3LYP/cc-pVTZ geometries differ by ∼10% for the hydrogens at C3 and C4 and by about half that for the other hydrogens. The values at the RI-MP2 geometry are closer to both the experimental and the averaged values of Fängström et al. for the hydrogens at Si and C3. This means that our coupling constants are not as good as we think, the jump model is inadequate for this molecule, or the isomeric minima are connected by more than just the puckering motion. Considering the trends in the iHFCCs with respect to geometry, correlation and basis set, we believe that the error in our values is less than 25%. This means that inaccurate determination of the coupling constants is probably not the only reason for this discrepancy. We can compare the two-site jump model with results from the distinguished coordinate (DC) approach used by Fängström et. al. The average of their B3LYP/6-31G(d,p)//

TABLE 7: Averaged Isotropic Hyperfine Coupling Constants of Hydrogen Atoms Calculated at the ROHF-CCSD(T)-fc/DZ:cc-pVTZ-CBS2//X Level[a]

geometry	H_{Si}	H_{C2}	H_{C3}	H_{C4}	H_{Si}	$H_{C2,C4}$	H_{C3}
RI-MP2-fc/TZVPP	11.2	4.5	26.1	−10.1	11.2	−2.8	26.1
	(10.2)	(5.2)	(23.3)	(−9.6)	(10.2)	(−2.2)	(23.3)
B3LYP/cc-pVTZ	10.8	4.8	22.9	−9.3	10.8	−2.2	22.9
	(9.8)	(5.5)	(20.1)	(−8.8)	(9.8)	(−1.7)	(20.1)
MP2-fc/6-31G(d,p)[b]	12.0	5.3	26.8	−7.5	12.0	−1.1	26.8
					(11.0)	(−0.5)	(24.0)
DC[c]	11	6	24	−7			
exp[d]	14		26		14		26

[a] Values in parentheses are corrected by the difference between the averaged[b] and DC[c] values of Fängström et al. [b] Reference 7, B3LYP/6-31G(d,p)//MP2-fc/6-31G(d,p). [c] Reference 7, spectrum calculated for 170 K (puckering only) at $E_{Barr} = 349$ cm^{-1} from B3LYP/6-31G(d,p)//MP2-fc/6-31G(d,p) iHFCCs and MP2-fc/6-31G(d,p) energies. [d] Komaguchi et al. (170 K).[6]

MP2-fc/6-31G(d,p) iHFCCs differs by ~10% from their DC-results. The largest difference, 3 G, is seen at H_{C3}. This indicates that the error of the jump model is not the only reason either. The third reason, an additional pathway connecting the isomeric minima seems plausible: Fängström et al. found that the bond length alternation of the Si−C bonds also has a low barrier. Their reevaluation of the temperature dependent rate constant showed an increase in the activation energy at higher temperatures, which they attribute to increasing participation of the bond length alternation mode. This mode averages the iHFCCs of hydrogens at C2 and C4. The corresponding values are given on the right of Table 7. The agreement between the calculated and experimental coupling constants is much better than when only puckering is considered. The remaining deviations of 3−4 G may be due to not considering iHFCCs along the reaction path for bond length alternation or matrix effect. The magnitude is similar to the difference between the jump model and DC approach for the puckering motion.

Summary and Conclusions

The ground-state geometry of the silacyclobutane radical cation was calculated using B3LYP, MP2 and CCSD(T) with double and triple-ζ valence basis sets. The C−H and Si−H bonds were 1−1.5 pm shorter with the cc-pVTZ basis set. The C−Si bonds were shorter by 2−5 pm. Independent of the basis set, the puckering angle was ~7° smaller with B3LYP than with MP2 or CCSD(T). Other differences of B3LYP/cc-pVTZ with respect to RI-MP2-fc/cc-pVTZ include 1−2 pm longer Si−C4, Si−C2 and C2−C3 bonds. As might be expected from a radical with only single bonds, correlation is small so that perturbation theory works well. Therefore we expect RI-MP2-fc/TZVPP to give the best geometry among the methods used. The B3LYP/6-31G(d) geometry is closer to the B3LYP/cc-pVTZ than to the B3LYP/cc-pVDZ geometry.

Isotropic hyperfine coupling constants (iHFCCs) larger than 5 G calculated at the valence triple-ζ geometries are up to 31% different from the coupling constants calculated at the corresponding valence double-ζ geometries. The iHFCCs (>5 G) calculated at the MP2 and B3LYP double or triple-ζ valence geometries differ by up to 15%. These changes are caused by changes in bond length by less than 2% for the DZ/TZ comparison and changes related to differences in the puckering angle of ~5%, showing that accurate geometries are important in the determination of iHFCCs. More complete treatment of correlation (CCSD(T) instead of CCSD) changed the iHFCCs by up to 10%, usually making them more positive. This effect was nearly independent of the geometries used. The effect of larger valence basis sets was difficult to determine. The two approaches used in this study show that the effect of the partially uncontracted s-functions at non-hydrogen atoms is up to 6% whereaas diffuse functions at all atoms change the iHFCCs by less than 3%,[8] suggests that the effect of aug-cc-pVTZ based basis sets might be 2−3 times as large as that going to aug-cc-pVDZ based basis sets. For the silacyclobutane radical cation the influence of the geometry optimization level seems to be about twice as large as the influence of connected triple excitations in the calculation of the iHFCCs. Approaching the complete basis set limit when calculating the iHFCCs is expected to have a slightly larger effect than including connected triple excitations.

We checked our results by comparing them with the 170 K spectrum of Komaguchi et al.[6] To this end, we averaged the iHFCCs calculated at equilibrium structures and corrected for the effects of integrating over the puckering motion using the results of Fängström et al. The values obtained from the RI-MP2-fc/TZVPP geometry are nearly 3 G lower than those of Komaguchi et al. and less than 1 G lower than those of Fängström et al. The iHFCCs obtained from the B3LYP/cc-pVTZ geometry are lower, especially for the hydrogens at C3. This suggests that the MP2 structure is better than the B3LYP structure, a conclusion also reached by Fängström et al., but for different reasons. However, the averaged iHFCCs of the hydrogens at C4 and Si are of the same magnitude. This would cause a quintet splitting of the 11G signal whereas, experimentally, a triplet is observed. The problem applies to a lesser degree to the iHFCCs calculated by Fängström et al. It would disappear if the Si−C bond length alternation suggested by them is sufficiently fast at 170 K. This mode interchanges the hydrogens at C2 and C4, averaging their iHFCCs. The resulting values are smaller than 3 G, small enough to be experimentally invisible.

The 4 K spectrum of the silacyclobutane radical cation is subject to strong line width broadening caused by tunneling effects. Therefore we cannot easily compare it with the experimental spectrum of Komaguchi et al. We find that the iHFCCs calculated at UHF-CCSD(T)-fc/EPR-2:cc-pVDZ-t5s-a5//RI-MP2-fc/TZVPP differ by less than 3 G from the B3LYP/6-31G(d,p)//MP2-fc/6-31G(d,p) values of Fängström et al. Considering the trends in iHFCCs due to geometry, basis set and correlation treatment, we think that the error of our best values is probably smaller than 25%. We feel that this confirms the reassignment of the spectrum of the silacyclobutane radical cation by Fängström et al.

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