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Bond Strengthening by Deformation of Bond Angles

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Torsion potentials about the $X-\ddot{X}H$ bond in homosubstituted primary carbenes (X = C) and silylenes (X = Si) have been investigated at the multireference averaged coupled pair functional (MRACPF) level of theory. For the triplet species, the potentials are quite flat, but large barriers of torsion have been observed for the singlet states of all carbenes and silylenes whose carbon or silicon atom adjacent to the divalent atom formes small bond angles with two of its further substitutents; other geometry parameters, even the bond angle at the divalent atom, proved to be of little or no importance. The said kind of deformation encourages the formation of a weak dative π-like bond between the two X atoms, which by its 2-fold symmetry with respect to torsion about the bond axis is responsible for the observed two-minima torsion potential.

1. Introduction

Silylenes, compounds with a divalent Si atom ($\ddot{\mathrm{Si}}$), are the silicon analogues of carbenes and are thought to be key intermediates in the thermal decomposition of silanes in the gas phase. Contrasting its carbon analogue methylene (CH_2), silylene (SiH_2) features a singlet ground state, as do all homosubstituted silylenes investigated so far. Most of silylene chemistry involves the singlet state exclusively.

In our previous work on silicon hydride thermochemistry,[1] we found that internal rotation about Si−Si bonds was hampered by sizable barriers in some silylenes where the divalent Si atom was connected to a three-ring, e.g., cyclotrisilanylsilylene $Si_3H_4-\ddot{Si}-H$. Generally speaking, silicon hydride torsion potentials are very flat; for example, the torsional barrier in disilane (Si_2H_6) amounts to 4 kJ/mol. The silylenes in question, however, showed torsion barriers in the range of 30 kJ/mol. Further investigation revealed that anomalously high barriers were accompanied by a marked energetic stabilization of these singlet carbenes with respect to both the corresponding triplet state and the singlet states of other primary silylenes.

Although comparable observations have not been reported in the literature about silylenes, the effect is well-known in carbon chemistry: Cyclopropylmethylene, the carbon analogue of the former mentioned silicon compound, has been studied in detail[2,3] and the high barrier has been explained by interaction of an occupied a″ C−C bonding orbital with the formally empty carbene *p* orbital, assuming C_s symmetry. The experimental characterization of dicyclopropylmethylene as a ground-state singlet[4] is a striking evidence for the efficient stabilization of singlet carbenes by cyclopropyl substituents.

Substituent-induced shifts in the relative stabilities of singlet and triplet carbenes have been explained by two independent arguments: electronegativity and π donation.

Electropositive substituents, as Li in CHLi, form bonds with high s character to the carbon atom; consequently, the p character of the in-plane lone pair increases, its orbital energy approches that of the out-of-plane (π) orbital, and triplet occupation becomes increasingly favored. On the other side, electronegative substituents, as F in CHF, withdraw electrons inductively via bonds of high p character, which leads to an in-plane lone pair of higher s character and, thus, to a stabilized singlet state. The other model involves donation from the substituent's lone pairs into the unoccupied carbene π orbital and consequent stabilization of the singlet state as the main mechanism affecting the singlet triplet separation.

As most electronegative substituents tend to be good π donors, the predictions of both models largely overlap; Feller, however, showed that the singlet triplet splittings of $C(NH_2)_2$, $C(OH)_2$, and CF_2 can be better understood in terms of donation strenght than in terms of electronegativity.[5] As will become clear in this work, π donation is also able to explain the conformation-dependent stabilization of cyclopropylmethylene and related compounds in a natural way.

It is the purpose of this paper to present further data on three-ring substituted carbenes and silylenes and to offer some insight to the physical reason of their stabilization.

2. Computational Methods

The potential energy curves presented in this paper were obtained by constrained geometry optimization followed by single-point energy calculations at the pseudostationary point. Because most of the structures discussed in this work are not stationary points on the potential hypersurface, we report only electronic energies; no-zero point vibrational energies have been determained.

Geometry optimization for singlet states was performed at the MCSCF (multiconfiguration self-consistent field) level of theory where the active space consisted of the two frontier orbitals (CAS(2,2) wave function). Triplet states, on the other hand, could be treated with an ROHF (restricted open-shell Hartree−Fock) wave function. Single-point energies were calculated with the size-consistent ACPF method based on the same kind of reference function as was used in the geometry optimization process; carbon core orbitals were excluded from the list of active orbitals (frozen core approximation). In a few cases, CCSD[T] calculations (coupled cluster singles and doubles with triples perturbationally approximated) were performed and found to agree perfectly with the ACPF data.

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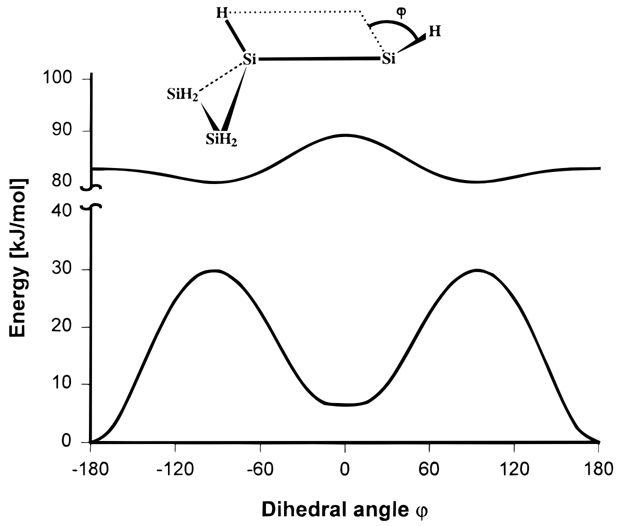

Figure 1. Torsion potential of cyclotrisilanyl-silylene. Lower curve: singlet state. Upper curve: triplet state.

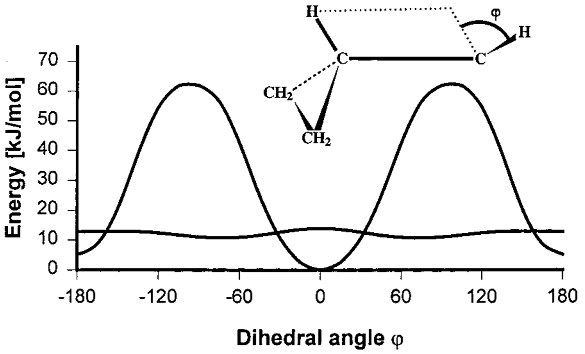

Figure 2. Torsion potential of cyclopropyl-methylene. Lower curve: singlet state. Upper curve: triplet state.

All geometries and potential energy curves for silicon compounds were obtained using a local pseudopotential described earlier.[6] Geometry optimization was carried out employing a *triple-ζ* basis with p and d type polarization functions located at the hydrogen and heavy atoms, respectively. The same basis was used for the determination of ACPF energies. For carbon compounds, we used the standard 6-311G* basis.[10]

For the very simplest systems, $XH_3-\ddot{X}H$, we were able to perform correlated calculations at the all-electron level with the augmented correlation-consistent triple-ζ (cc-avtz) basis set of Dunning.[7]

Both computer programs GAMESS[8] (for geometry optimization) and MOLPRO[9] (for single-point energies) have been adapted to our pseudopotential. Contour plots shown in this publication were prepared using MOLDEN[12] in conjunction with GAMESS.

3. Results and Discussion

The first systems investigated were the cyclic species $X_3H_5-\ddot{X}H$; to find out in which way the three ring is responsible for the effects observed, we then simplified the systems first to the open-chain species $(XH_3)_2XH-\ddot{X}H$. In a second step, we made our systems even smaller, arriving at the simplest homosubstituted carbene or silylene, $XH_3-\ddot{X}H$.

$X_3H_5-\ddot{X}H$. The first systems investigated are cyclotrisilanylsilylene and cyclopropylmethylene, whose torsion potentials are shown in Figures 1 and 2, respectively. The dihedral angle $H-X-\ddot{X}-H$, ϕ, is chosen as a reaction coordinate; geometries with $\phi = 0°$ and $\phi = 180°$ are called *synperiplanar* (eclipsed, cisoid) and *antiperiplanar* (staggered, transoid), respectively. In these two conformations, both molecules show C_s symmetry.

Rotational barriers in saturated silanes, like disilane, are of the order of 4 kJ/mol. In its triplet state, cyclotrisilanylsilylene (Figure 1) shows the flat torsion potential reminiscent of such saturated species. In contrast to Si_2H_6, where rotation about the Si−Si bond results in three equivalent minima corresponding to the staggered conformation, the cyclic compound shows only two equivalent gauche minima, where ϕ amounts to about $\pm 90°$. The two nonequivalent maxima at $\phi = 0$ and 180° correspond to the synperiplanar and antiperiplanar conformations and lie about 9 and 3 kJ/mol above the minima, respectively.

The singlet's torsional potential shows two equivalent maxima at $\phi \approx \pm 90°$ and two nonequivalent minima $\phi = 0$ and 180°, where the antiperiplanar conformer lies 30 kJ/mol and the synperiplanar conformer 27 kJ/mol below the two maxima.

One might ask whether the large barrier in the singlet state arises from a stabilization of the periplanar ($\phi = 0$ *or* 180°) or a destabilization of the gauche ($\phi \approx 90°$) conformers. Observing that the vertical singlet triplet splitting of 50 kJ/mol at $\phi = 90°$ is of the order of adiabatic singlet triplet splittings of other primary silylenes (50−55 kJ/mol),[1] whereas at $\phi = 0$ or 180° it is about 80 kJ/mol, we conclude that both periplanar conformers are extra stabilized by a mechanism not found in acyclic silylenes.

A very similar picture is found for the potential energy curves of cyclopropylmethylene, as shown in Figure 2. The triplet has two equivalent gauche ($\phi \approx \pm 75°$) minima, which lie only 3 and 2 kJ/mol below the synperiplanar and antiperiplanar maxima, respectively. Note that these barriers are significantly lower than the barriers between rotamers in hydrocarbons (e.g., 14 kJ/mol for ethane).

All homosubstituted acyclic carbenes investigated so far have triplet ground states; e.g., methylmethylene's adiabatic singlet triplet splitting is −28 kJ/mol at this level of theory, where the negative sign indicates a triplet ground state. Cyclopropylmethylene, however, has a singlet ground state; we note, though, that the triplet curve falls below the singlet curve for most dihedral angles ϕ. In the singlet state, the synperiplanar and antiperiplanar conformers are energetically favored, lying 62 and 57 kJ/mol below the gauche maxima. Vertical singlet triplet splittings for the synperiplanar minimum, the gauche maxima and the antiperiplanar minimum are 11, −51, and 6 kJ/mol, respectively. That the barrier arises from stabilization of the periplanar conformations is obvious from the change of ground-state multiplicity.

The high barrier of interconversion between the synperiplanar and the antiperiplanar conformers of cyclopropylmethylene has been noted before[2] and has been explained by interaction of the empty carbene p orbital (LUMO) with the cyclopropyl ring. The LUMO plotted in the paper of Shevlin et. al.[2] shows significant contributions of the ring carbon atoms, particularly the secondary ones. It remains unclear, though, whether this stabilization requires a chemical bond between the two secondary C atoms. If such a bond is not necessary, it remains open why acyclic carbenes cannot profit from this type of interaction.

On the other hand, Feller's explanation of the stability trends in heterosubstituted carbenes[5] can be applied to homosubstituted carbenes, provided that a doubly occupied C−C bonding orbital of appropriate symmetry takes the place of the lone pair as an electron donor. In C_s symmetry, cyclopropylmethylene does have an occupied C−C bonding orbital of a″ symmetry which may serve this purpose.

While Shevlin's paper suggests a type of hyperconjugative interaction between the divalent $\ddot{C}$ atom and the two secondary carbon atoms in the ring, Feller's explanation is based on interaction between adjacent atoms: It simply involves the formation of a dative π-like bond between the $\ddot{c}$ atom and its next neighbor.

$(XH_3)_2XH-\ddot{X}H$. To investigate the precise role of the three-ring for the singlet stability in $X_3H_5-\ddot{X}H$, we resorted to the open-chain analogues $X(XH_3)_2H-\ddot{X}H$, isopropylmethylene and 2-silyltrisilan-1,1-diyl. Only small rotational barriers, however, were found for these systems. For silicon, we found the lowest minimum for $\phi = 180°$ and two maxima for $\phi \approx \pm 105°$ (8 kJ/mol). The region about $\phi = 0°$ is very flat and lies about 6 kJ/mol above the minimum. The torsional potential of the triplet state ascends monotonically from the antiperiplanar ($\phi = 180°$) minimum to the synperiplanar ($\phi = 0°$) maximum, which lies 4 kJ/mol above the minimum.

For the carbon species in its triplet state, we find three nearly isoenergetic minima at $\phi = \pm 60$ and 180° separated by three maxima about 2 kJ/mol higher. In the singlet state, isopropylmethylene shows two rather flat regions at $\phi \approx \pm 60°$ and another at $\phi \approx 180°$. These three regions are separated by sharp maxima at $\phi = 0°$ (8 kJ/mol) and $\phi \approx \pm 120°$ (9 kJ/mol).

To sum up, the singlet states of $(XH_3)_2XH-\ddot{X}H$ have quite flat torsional potentials of approximate 3-fold symmetry; this is in sharp contrast to the high barriers and approximate 2-fold symmetry reported in the previous section for the cyclic compounds, $X_3H_5-\ddot{X}H$.

At first glance, it seems surprising that two molecules which have similar topology and even geometry differ that drastically in their torsion potentials. The main differences between the two species are the small bond angles and the additional X−X bond in the three-ring structures. To separate these two factors, we brought the acyclic systems nearer to the cyclic ones without introducing a new X−X bond: We restrained the XH_3-X-XH_3 bond angle, labeled α in the rest of this work, to smaller values.

Even for a moderately small bond angle, $\alpha = 90°$, we find the silicon species' torsion potential significantly changed: The antiperiplanar and synperiplanar conformations turn out minima, with the antiperiplanar favored by 5 kJ/mol. These two minima are separated by two equivalent barriers at $\phi \approx \pm 100°$, 15 kJ/mol above the antiperiplanar minimum. Thus, this torsion potential has the same properties as that of cyclotrisilanylsilylene.

The triplet's curve does not change significantly by the geometry restriction imposed. This demonstrates that the triplet's torsion profile is largely insensitive to the deformation, so we focused our further investigation to the singlet state exclusively; we will, however, occasionally resort to the triplet as a conformation-insensitive refererence.

We then decreased α further, down to 60°. At this stage, however, it became necessary to introduce further geometry constraints in order to prevent fragmentation during geometry optimization: To compensate for the repulsion between the two SiH_3 groups, we had to keep the $X-XH_3$ bond lengths fixed at 2.34 Å. For this system, the torsion barrier is 56 kJ/mol (larger than cyclotrisilanylsilylene), and the potential qualitatively reproduces all features of Figure 1. We recognize that the additional geometry constraints might well lead to an overestimization of the torsion barrier.

The results obtained for the singlet carbon species, isopropylmethylene, closely parallel those of its silicon analogue. At $\alpha = 60°$, two minima are observed in the torsion potential, the synperiplanar being the lower one. The barrier between the two minimum conformers amounts to about 89 kJ/mol, which is again larger than the barrier found for cycloproylmethylene.

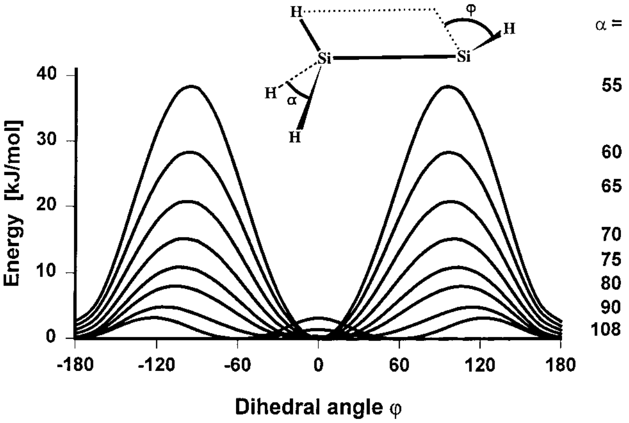

Figure 3. Torsion potential of singlet silylsilylene at fixed H−Si−H bond angles α. The curves have been shifted to a common energy origin.

$XH_3-\ddot{X}H$. Having seen that neither the form of the torsion potential nor the barrier height require a three-ring substituent, but that both depend on the small X−X−X bond angles only, we wanted to make clear whether the X−X bonds are essential for the effect observed. Thus, we simplified our systems further, replacing the XH_3 groups by H atoms.

In Figure 3, we present torsional potentials of singlet silylsilylene, $SiH_3-\ddot{Si}H$, for various α values. As soon as α falls below 90°, the maximum at $\phi = 0°$ (synperiplanar conformation) disappears and the remaining two maxima shift from $\phi = \pm 120°$ to $\phi \approx \pm 90°$; the barrier heights increase from 3 to 28 kJ/mol at $\alpha = 60°$. This is the same order of magnitude as for the cyclic species, cyclotrisilanylsilylene.

Very similar results are obtained for methylmethylene, $CH_3-\ddot{C}H$, where the barrier reaches 106 kJ/mol at $\alpha = 60°$. Apart from different energy scaling, the result for methylmethylene equals that of silylsilylene and does not justify a figure of its own; instead, numerical results for all molecules investigated in this paper are found in Table 1.

In both the C and Si species, further diminution of α *below* the 60° limit will further increase the stabilization of periplanar conformations and, thus, result in even higher torsional barriers. Such extremely acute bond angles are, however, unlikely to appear in any real-world systems.

At this point, it becomes clear that the stabilization of periplanar conformers in cyclic $X_3H_5-\ddot{X}H$ does not require any of the three X−X bonds in the three-ring but solely depends on the acute X−X−X (or H−X−H) bond angle, α. We now tackle the question in which way the small bond angle in vicinity to a divalent X atom can lead to a significant and conformation-dependent stabilization. Starting with the silicon compound, we will derive our arguments from analysis of energies, geometries, and the wave function.

The statement "periplanar conformations of $SiH_3-\ddot{Si}H$ are stabilized at low α" can be restated in an equivalent way: "the bond angle α in silylsilylene can be compressed more easily if the conformation is periplanar". The latter view allows us to compare different conformations and multiplicities of silylsilylene simultaneously.

The energetic cost of constraining α in triplet silylsilylene from its minimum value (≈108°) to 60° ranges from 140 to 145 kJ/mol, depending on ϕ. The small range of energies reflects the insensitivity of the triplet silylene with respect to conformation. In the singlet state, we find 113 kJ/mol for the synperi-

TABLE 1: Barrier Heights (in kJ/mol), Maximum and Minimum Dihedral Angles φ, X−$\ddot{X}$ Bond Lengths, and φ-Dependent Bond Length Variation for All Singlet Carbenes and Silylenes Discussed in This Work

system	α	ΔE^a	$\varphi_{max}{}^b$	$\varphi_{min}{}^b$	$r_{X-\ddot{X}}{}^c$	$\Delta r_{X-\ddot{X}}{}^d$
$CH_3-\ddot{C}H$	55	130	90	0; 180	1.420	0.087 (6.1%)
	60	106	90	0; 180	1.433	0.071 (5.0%)
	65	85	90	0; 180	1.444	0.056 (3.8%)
	70	67	90	0; 180	1.454	0.043 (2.9%)
	75	51	90	0; 180	1.463	0.031 (2.1%)
	80	39	105	180; 0	1.471	0.023 (1.6%)
	90	21	105; 0	180; 15	1.482	0.014 (0.9%)
	≈108	6	0/120	60/180	1.495	0.008 (0.5%)
$C_3H_5-\ddot{C}H$	≈60	62	90	0; 180	1.435	0.050 (3.4%)
$CH(CH_3)_2-\ddot{C}H$	60	89	75	0; 180	1.360	0.070 (5.4%)
	≈108	8	120; 0	75; 180	1.493	0.011 (0.7%)
$SiH_3-\ddot{Si}H$	55	38	90	0; 180	2.332	0.057 (2.4%)
	60	28	90	0; 180	2.347	0.042 (1.8%)
	65	21	90	0; 180	2.359	0.030 (1.3%)
	70	15	105	0; 180	2.368	0.022 (0.9%)
	75	11	105	0; 180	2.375	0.016 (0.7%)
	80	8	105; 0	180; 15	2.381	0.011 (0.5%)
	90	5	120; 0	180; 30	2.387	0.008 (0.3%)
	≈108	3	0/120	60/180	2.393	0.007 (0.3%)
$Si_3H_5-\ddot{Si}H$	≈60	30	90	180; 0	2.344	0.048 (2.0%)
$SiH(SiH_3)_2-\ddot{Si}H$	60	56	90	180; 0	2.311	0.088 (3.7%)
	90	15	105	180; 0	2.374	0.026 (1.1%)
	≈108	8	105; 0	180; 30	2.395	0.018 (0.8%)

[a] Barrier height in kJ/mol. [b] Dihedral angles of maxima and minima of the torsion potential curve. Angles pertaining to symmetry equivalent structures are separated by a slash. [c] X−$\ddot{X}$ bond length at the minimum, in angstroms. [d] X−$\ddot{X}$ bond length variation during the torsion movement, both in angstroms and in percents of the minimum's bond length.

TABLE 2: Barrier Heights (in kJ/mol) and Maximum and Minimum Dihedral Angles φ for All Triplet Carbenes and Silylenes Discussed in This Work.

system	α	ΔE^a	$\varphi_{max}{}^b$	$\varphi_{min}{}^b$
$CH_3-\ddot{C}H$	55	9	180; 0	75
	60	7	180; 0	75
	65	5	180; 0	75
	70	4	0; 180	75
	75	3	0; 150	75; 180
	80	2	0; 135	60; 180
	90	2	135; 0	60; 180
	≈108	2	0/120	60/180
$C_3H_5-\ddot{C}H$	≈60	3	0; 180	75
$CH(CH_3)_2-\ddot{C}H$	60	9	180; 0	105
	≈108	2	0; 120	180; 60
$SiH_3-\ddot{Si}H$	55	8	0; 180	90
	60	6	0; 180	75
	65	4	0; 180	75
	70	2	0; 150	75; 180
	75	2	135; 0	60; 180
	80	2	135; 0	60; 180
	90	2	120; 0	180; 60
	≈108	1	0/120	60/180
$Si_3H_5-\ddot{Si}H$	≈60	9	0; 180	90
$SiH(SiH_3)_2-\ddot{Si}H$	60	17	0; 180	90
	90	4	0; 135	90; 180
	≈108	4	0	180

[a] Barrier height in kJ/mol. [b] Dihedral angles of maxima and minima of the torsion potential curve. Angles pertaining to symmetry equivalent structures are separated by a slash.

planar, 143 kJ/mol for the gauche, and 114 kJ/mol for the antiperiplanar conformation. Taking the triplet as a reference, we can detect a stabilization of the two periplanar conformations which is absent from the gauche conformation.

In contrast to saturated silanes with Si−Si bond lengths of about 2.34 Å, the Si−$\ddot{Si}$ bond in unconstrained silylsilylene is considerably longer (2.39 Å). Deformation of bond angle α does not influence this bond length at conformations near the barrier maximum ($\phi \approx \pm 90°$), but leads to a marked bond length contraction at both the synperiplanar and antiperiplanar conformations; for example, at $\alpha = 60°$ and $\phi = 0°$, the Si−$\ddot{Si}$ bond length has shrunk to 2.35 Å. Simultaneously, the Mulliken bond order increases from 0.92 at $\phi = 90°$ to 0.97 at $\phi = 0°$.

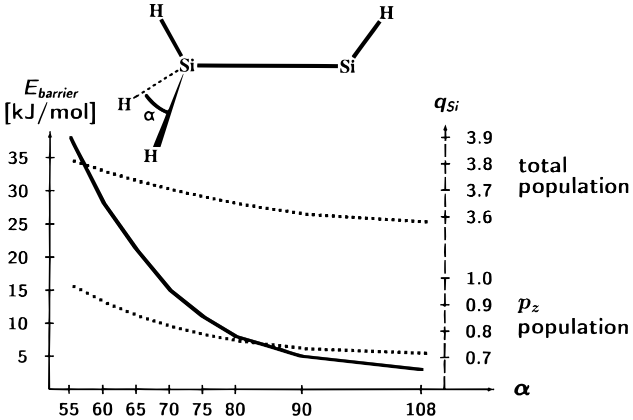

Figure 4. Energy barrier (full line) and electronic populations (dotted lines) at the Si atom in silylsilylene in dependence of the H−Si−H bond angle α.

No comparable variation of bond length is found for the triplet state. Keeping in mind that both the stabilization and the bond length contraction affect only the singlet state, only periplanar conformations and only small α values, we are drawn to the conclusion that there is some causal connection between the two.

Apart from the Si−$\ddot{Si}$ bond length, no other geometry parameter changes significantly during the torsion movement. Of the most noteworthiness, the Si−$\ddot{Si}$−H bond angle, which is known to be often connected with the relative stabilities of singlet and triplet states in carbenes and silylenes, does not show a significant dependence of the dihedral angle ϕ, but remains nearly constant in the interval from 95° (synperiplanar) to 91° (antiperiplanar). We also note that the Si−$\ddot{Si}$−H bond angle is nearly independent of α. Last, recalculation of the torsion potential for several fixed values of the Si−$\ddot{Si}$−H bond angle in the interval 83−103° gave unaltered energy barriers.

Next, we observe that, by constraining α to low values, the 1a″ valence orbital, an H−Si−H binding MO of pseudo-π type, rises in energy and becomes the second-highest occupied orbital; at the same time, the amplitude at the tetravalent Si atom increases while the amplitudes at the H atoms decrease. The character of this orbital thus changes from a binding molecular orbital delocalized over the Si atom and two H atoms toward an p-AO of the Si atom.

There is also a good correlation between the Mulliken net charge on the tetravalent Si atom and the barrier height. Figure 4 visualizes, as a function of the H−Si−H bond angle α, the barrier height and for the periplanar conformers, the Si atom's total electron population and the population contributed by the $3p_z$ orbital (C_s symmetry with xy being the symmetry plane).

The total electron population on the Si atom increases from $\alpha \approx 108°$ to $\alpha = 60°$ by 0.19 electrons. All of this extra negative charge is hosted by the Si $3p_z$ atomic orbital, as can be seen in Figure 4. The respective populations of 3s, $3p_x$, and $3p_y$ type atomic orbitals do not depend much on α, and their contributions cancel each other. This simply reflects that, at small α values, the $3p_z$ atomic orbital gets higher weight in the occupied 1a″ valence MO. The increasing localization of the 1a″ valence orbital to the Si atom demonstrates the p orbital's small ability to support acute bond angles.

As occupation numbers for the $3p_x$, $3p_y$, and $3p_z$ atomic orbitals become increasingly different when α shrinks, we expect the electron distribution to become increasingly anisotropic. This conclusion is backed by an ab initio NMR study of Magyarfalvi and Pulay,[13] who reported unusually large ^{29}Si chemical shift anisotropies in three-ring silicon compounds. Acyclic compounds, such as silane and tetramethylsilane, have much smaller anisotropies, but if one Si bond angle is constrained to 60°, the authors found anisotropies comparable to those of genuine three-rings. Since tetramethylsilane and silane showed largely the same behavior, the authors concluded that "the anisotropy is mainly determained by the asymmetry of the bond angles on silicon and not by the bonding partner".

Population increase depends only weakly on ϕ: Diminishing α results in slightly more population shifted to the Si atom when the conformation is periplanar. For $\alpha = 60°$, the difference between synperiplanar ($\phi = 0°$) and gauche ($\phi = 90°$) amounts to 0.06 electrons. This comparatively small difference reflects the fact that the localization of the 1a″ valence MO at small α is slightly favored in periplanar conformations and hampered in the gauche conformation.

Although the 1a″ valence orbital is, at small α, less able to describe the Si−H bonds, it does meet both steric and energetic criteria to donate electrons into the formally empty $3p_z$ orbital (2a″) located at the divalent S̈i atom. As a prerequisite for efficient donation, there must be both (a) a large overlap between the two orbitals in question and (b) a high energy of the donor orbital (1a″). While condition (b) is fulfilled at any ϕ for small α, condition (a) requires a periplanar or near-periplanar conformation and is favored by localization of the 1a″ orbital at the tetravalent Si atom. The finding discussed in the previous paragraph corroborates the idea that energy gain through donation Si → S̈i increases the 1a″ orbital's tendency to localize at the tetravalent Si atom.

Consequently, we would expect the basis functions centered at the S̈i atom to contribute to the 1a″ molecular orbital more at $\phi = 0°$ and $\phi = 180°$ but less at $\phi = 90°$. We indeed find the population contribution of the S̈i atom to the 1a″ orbital to be 0.04 electrons at the synperiplanar but only 0.02 electrons at the gauche conformation: A weak dative bond of π-like axial symmetry has been formed between the two silicon atoms.

In methylmethylene ($CH_3{-}\ddot{C}H$), we find the same effects as in silylsilylene, but even more pronounced. In planar conformations, the C−C̈ bond length is contracted from its normal value 1.50 Å at obtuse α to 1.43 Å at $\alpha = 60°$, and again we find a correlation of bond length and Mulliken bond order: At $\alpha = 60°$, we find bond orders of 1.19 and 0.95 for synperiplanar and gauche conformations, respectively.

As noted for silylsilylene, there is negligible coupling between the torsion and C−C̈−H angle deformation. Largely independent of both α and ϕ, the C−C̈−H bond angle varies between 105 and 108° at our level of theory. As before, freezing this degree of freedom has no effect on the torsion potential.

A closer look at Mulliken populations of methylmethylene in its synperiplanar conformation reveals an important difference to the silicon compound. As depicted in Figure 5, the barrier height still goes parallel to the $2p_z$ orbital population, but the total C population increases significantly slower with the deformation than the $2p_z$ population: Reducing the bond angle from relaxed geometry ($\alpha \approx 108°$) to 60° increases the C atom's electron population in the $2p_z$ orbital by 0.13 electrons, but the gain in total population amounts to only 0.06 electrons, the latter being checked by the p_x and p_y orbitals' *decrease* of about 0.03 electrons each. Because of the simultaneous gain in p_z and loss in the p_x and p_y directions, we expect a large anisotropy of the electron density for methylmethylene at acute α angles.

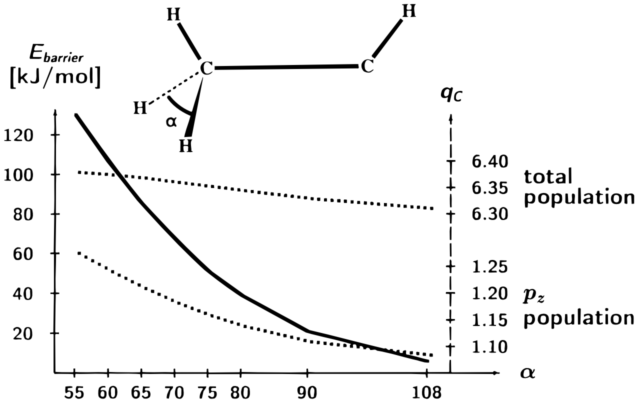

Figure 5. Energy barrier (full line) and electronic populations (dotted lines) at the C atom in methylmethylene in dependence of the H−C−H bond angle α.

Interaction between the 1a″ and the carbene $2p_z$ orbitals in methylmethylene has been studied before by Khodabandeh and Carter[11] by similar methods. For the minimum geometry, they found no significant participation of the $2p_z$ orbital in the 1a″ molecular orbital, but these authors did not consider the effect of strained bond angles.

For triplet methylmethylene, the energy needed to compress α from 108° to 60° varies from 150 to 155 kJ/mol, depending on ϕ. In singlet methylmethylene, the compression energy is much more sensitive to conformation, ranging from 89 kJ/mol ($\phi = 0°$) to 200 kJ/mol ($\phi = 90°$). Taking the triplet as a reference, we notice that there is evidence for both a stabilization of the periplanar and a destabilization of the gauche conformer of methylmethylene at small bond angle α. The effects of stabilization and destabilization cancel each other at $\phi = 60°$; at this dihedral angle, the energetic cost to constrain α to 60° is 154 kJ/mol. In this respect, methylmethylene does not resemble silylsilylene, where the singlet paralleled the triplet at $\phi = 90°$.

Because of the smaller problem size, we were able to perform calculations with a larger basis set for both silylsilylene and methylmethylene. Frozen core MRACPF calculations using Dunning's correlation consistent basis sets gave, however, results very similar to those reported in the previous paragraphs: In the case of silicon, going from a *triple*-ζ pseudopotential basis to a 6s5p3d2f all-electron basis set brought no qualitative change, but only reduced the barrier from 38 to 34 kJ/mol at $\alpha = 55°$; at relaxed α, the barrier is affected by a mere 0.2 kJ/mol. For the carbon compound, the improvement of the carbon 5s4p3d2f basis over the 4s3p1d basis was even smaller and did not exceed 2.5 kJ/mol in the torsional barrier. In all cases, the singlet state profits more than the triplet state from basis set augmentation: For methylmethylene, the singlet triplet splitting (defined as $E_{tr}-E_{sg}$) increases by about 13 kJ/mol, independent of α. For silylsilylene, the correction ranges from 1 kJ/mol at $\alpha = 55°$ to 6 kJ/mol at $\alpha = 108°$.

Figure 6 shows MOLDEN plots of the 1a″ valence orbitals of both methylmethylene (top row: a and b) and silylsilylene (bottom row: c and d). The left-hand side pictures (a and c) belong to the synperiplanar minima ($\phi = 0°$ and $\alpha \approx 108°$); in the right-hand side series (b and d), the effect of restraining the bond angle α to 60° is shown. To facilitate horizontal comparison in these plots, all other geometry parameters except angle α have been set equal to those of the unrestrained system. By this procedure, we intend to show that the bonding

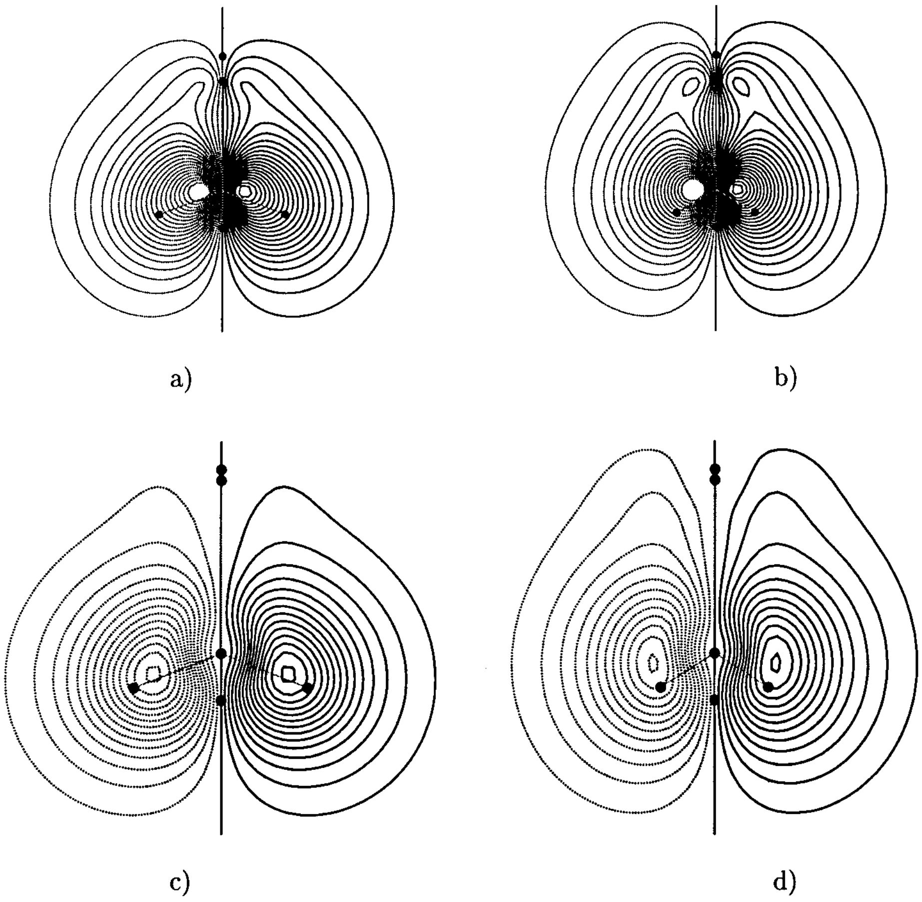

Figure 6. Contour plots of the 1a″ valence orbital of XH_3−XH species. The plot plane is perpendicular to the symmetry plane, containing both the X−X bond and the LUMO p orbital. (a) Methylmethylene, CH_3−CH, at its minimum geometry. (b) Same species, but H−C−H bond angle α set to 60° and all other geometry parameters as in (a). (c) Silylsilylene, SiH_3−SiH, at its minimum geometry. (d) Same species, but H−Si−H bond angle α set to 60° and all other geometry parameters as in (c).

interaction shown in these plots is not a consequence of, but the reason for the shorter $\ddot{X}$−X bond length.

In the carbon species (Figure 6b), the C−C bonding character of the 1a″ orbital can be seen both by its deformation toward the $\ddot{C}$ atom and by the appearance of a new orbital maximum in close vicinity of the divalent carbon atom. The silicon species, however, shows only a deformation toward the $\ddot{S}$i atom but no second orbital maximum (Figure 6d), reflecting the weaker π-bond which results in a significantly smaller barrier height.

The presence of a p-like orbital featuring partial "lone pair" character adjacent to the divalent atom puts the systems discussed here in line with heterosubstituted carbenes, which are long known to owe their stabilized singlet states partly to electronegativity effects, but even more to back-donation from the substituent to the divalent $\ddot{C}$ atom.[5]

4. Conclusions

In accordance with the results of other groups, we find a significant conformation-dependent stabilization of singlet carbenes and silylenes by three-membered ring substituents. We attribute this stabilization to a weak dative bond between the divalent atom and its next neighbor. The effect is more pronounced in carbenes than in silylenes and may even induce a change in ground-state multiplicity from singlet to triplet in the former.

We have demonstrated that neither the carbon or silicon ring nor the X−X bonds are essential for the described effects; the only important parameter is the bond angle on the atom neighboring the divalent center. Thus, similar phenomena may be expected in rigid bi- and polycyclic systems containing small rings, near the presence of crystal defects in solid carbon or silicon and in other instances where bond angles are far from their normal values.

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