Organometallics 1994, 13, 186-189

β-Silicon Effect on Singlet Carbene Stability

Hideaki Shimizu and Mark S. Gordon*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received July 19, 1993[⊗]

Calculations using double ζ plus polarization basis sets or effective core potentials and two configuration MCSCF wave functions augmented by multireference singles and doubles configuration interaction are used to investigate the effect of various substituents on the singlet-triplet splitting in methylene. Of particular interest is the conclusion that when CH_2SiH_3 or CH_2GeH_3 is a substituent, the cumulative effect of the polarizability of the C-Si and C-Ge bonds and the rotation of these bonds into the appropriate alignment required for effective electron donation into the carbene π orbital results in preferential stabilization of the corresponding singlet carbenes, a β-silicon (or germanium) effect analogous to that which is well-known in cation chemistry.

Introduction

Placing silyl groups in a position β to a positive center is well-known to stabilize that cation, a phenomenon referred to as the β-silicon effect.[1] This stabilizing effect makes E1 elimination easier, because the C-Si bond assumes the role of electron donor, due to σ-π orbital mixing, thereby stabilizing the intermediate carbenium ion in the elimination process. Theoretical studies[2,3] also predict the existence of stable cyclic structures in which the β-Si stabilizes the positive charge directly. This stabilizing effect raises the possibility that a β-silyl group may also stabilize a singlet carbene.[4,5]

The singlet-triplet energy gap in carbenes is very important, in view of the central role such species play in mechanistic organic chemistry and in view of the very different reactivities these species exhibit. It is therefore of interest to understand various ways in which one or the other spin state may be preferentially stabilized. In predicting the singlet-triplet splitting in carbenes, it is important to treat the two spin states in a balanced manner.[6,7] This can be tricky, since the singlet increasingly displays diradical character as the angle about the carbene carbon approaches linearity. As noted by Bauschlicher, Schaefer, and Bagus,[8] the simplest balanced treatment, assuming the use of an adequate basis set, is to describe the singlet using a two-configuration self-consistent field (TCSCF) wave function [or, equivalently, a single pair generalized valence bond (GVB) wave function], while using a restricted open shell (ROHF) wave function to describe the triplet. Such calculations, when augmented by a multireference (MR) configuration interaction (CI) calculation including all single and double excitations from the starting wave function,[8,9] provide singlet-triplet splittings which are in excellent agreement with both experiment and more elaborate calculations.[10]

Some substituent effects on the carbene singlet-triplet splitting are already well understood. Experimentally, it is known that the singlet is preferentially stabilized in the order $CH_2 < CHF < CF_2$.[11] While initial explanations for this observation were based purely on electronegativity arguments, Feller, Borden, and Davidson[12] clearly demonstrated, on the basis of calculations for CF_2, $C(OH)_2$, and $C(NH_2)_2$, that the key factor in stabilizing the singlet is π-electron donation from lone pairs on the substituent into the formally empty p_π orbital on the carbene carbon. Thus, the NH_2 group, with more polarizable lone pairs, is better able to stabilize the singlet than is OH or F.

In this paper, we examine the effect of substituents on the singlet-triplet splitting of CH_2, with particular emphasis on the effects of β-silyl groups, using a balanced MRCI approach based on MCSCF wave functions. The β-silicon effect is compared with that of other substituents, including methyl and ethyl groups and several that have been studied previously.

Computational Approach

Initial geometry optimizations were performed with the 3-21G(d) basis set,[13] using RHF and UHF wave functions for singlet and triplet states, respectively. Using those geometries as a starting point, the structures were reoptimized with TCSCF (singlets) or ROHF (triplets) wave functions, using the Huzinaga MINI(d,p) basis set.[14] For heavier substituents ($CHCH_2GeH_3$, $CHSiH_2SiH_3$), MINI(d,p) was replaced with the Stevens et al. effective core potential (ECP) together with a split valence plus

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) (a) Sommer, L. H.; Whitemore, F. C. *J. AM. Chem. Soc.* **1946**, *68*, 485. (b) Sommer, L. H.; Dorfman, E.; Goldberg, L. M.; Whitemore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 488. (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(2) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

(3) Nguyne, K. A.; Gordon, M. S.; Wang, G.-T.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798.

(4) Barton, T. J. *Int. Organosilicon Symp.* **1990**.

(5) Lambert, J. B. Private communication.

(6) Hay, P. J.; Hunt, W. J.; Goddard, W. A. *Chem. Phys. Lett.* **1972**, *53*, 4716.

(7) Meadows, J. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 4383.

(8) Bauschlicher, C. W.; Schaefer, H. F.; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

(9) Carter, E. A.; Goddard, W. A. *J. Chem. Phys.* **1988**, *88*, 1752.

(10) (a) Shin, S. K.; Goddard, W. A.; Beauchamp, J. L. *J. Chem. Phys.* **1990**, *93*, 4986. (b) Scuseria, G. S.; Durán, M.; Maclagan, R. G. A. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 3248. (c) Bauschlicher, C. W.; Langhoff, S. R.; Taylor, P. R. *J. Chem. Phys.* **1987**, *87*, 387. (d) Shaefer, H. F. *Science* **1986**, *231*, 1100. (e) Goddard, W. A. *Science* **1985**, *222*, 917.

(11) (a) Jensen, P.; Bunker, P. R.; *J. Chem. Phys.* **1988**, *89*, 1327. (b) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442. (c) Koda, S. *Chem. Phys. Lett.* **1978**, *55*, 353. Koda, S. *J. Chem. Phys.* **1986**, *66*, 383.

(12) Feller, D.; Borden, W. T.; Davidson, E. R. *Chem. Phys. Lett.* **1980**, *71*, 22.

(13) (a) Binklery, J.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(14) *Gaussian Basis Sets for Molucular Calculations*; Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H., Eds.; Elsevier: Amsterdam, 1984.

0276-7333/94/2313-0186$04.50/0

Table 1. Optimized Geometries for HCX and CX_2 Compounds[a]

	singlet			triplet		
	C–H/Å	C–X/Å	H–C–X/deg	C–H/Å	C–X/Å	H–C–X/deg
CH_2	1.109		101.4	1.082		126.1
	(1.11)		(102.4)	(1.077)		(134.0)
	[1.103]		[102.8]	[1.074]		[129.4]
$HCCH_3$	1.116	1.509	104.7	1.083	1.528	126.7
$HCNH_2$	1.107	1.342	104.0	1.089	1.434	122.9
HCOH	1.118	1.351	101.0	1.093	1.385	122.2
HCF	1.129	1.341	101.8	1.095	1.349	120.2
	(1.12)	(1.314)	(101.6)			
	[1.111]	[1.325]	[102.2]	[1.077]	[1.321]	[120.4]
$HCSiH_3$	1.103	1.950	109.0	1.080	1.858	144.8
	[1.123]	[1.951]	[106.1]	[1.073]	[1.867]	[140.4]
HCCl	1.111	1.727	102.3	1.092	1.702	124.0
	(1.12)	(1.689)	(103.4)			
	[1.101]	[1.762]	[102.0]	[1.075]	[1.735]	[123.3]
CF2		1.335	103.5		1.346	118.5
		(1.300)	(103.4)			
		[1.291]	[104.7]		[1.303]	[118.2]
$HCCH_2CH_3$	1.109	1.546	102.6	1.083	1.530	126.6
$HCSiH_2CH_3$	1.104	1.949	105.8	1.080	1.866	138.8
$HCCH_2SiH_3$	1.107	1.508	104.3	1.083	1.526	127.1
$HCCH_2GeH_3$[a]	1.115	1.471	105.9	1.094	1.503	128.7
$HCSiH_2SiH_3$[a]	1.114	1.911	106.6	1.092	1.861	139.9

[a] Experimental values ($^1A_1$ CH2: *Molecular Structure and Molecular Spectra III. ELectronic Spectra and Electronic Structure of Polyatomic Molecules*; Herzberg, G., Ed.; Van Nostrand: Princeton, NJ, 1966. $^3B_1$ CH2: Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724. CHF: Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *44*, 1541. CHCl: Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *45*, 525. CF2: (a) Matthews, C. W. *J. Chem. Phys.* **1967**, *5*, 1068. (b) Matthews, C. W. *Can. J. Phys.* **1967**, *45*, 2355) are given in parentheses and previously calculated values (CH_2, HCF, HCCl, and CF_2, ref 8; $HCSiH_3$, ref 9) are given in square brackets. [b] Geometries optimized at CASSCF/ECP(d,p).

Table 2. Dihedral Angles (deg)

	singlet	triplet
$CHCH_2CH_3$	180.0	60.2
$CHSiH_2CH_3$	162.0	180.0
$CHCH_2SiH_3$	91.4	49.0
$CHCH_2GeH_3$[a]	91.6	55.5
$CHSiH_2SiH_3$[a]	89.0	43.6

[a] Geometries optimized at CASSCF/ECP(d,p).

polarization basis set.[15] Final energies were obtained using MRCI wave functions including single and double excitations from the reference wave functions, using the 6-31G(d,p)[16] or ECP basis sets. All calculations described in this paper were performed using the electronic structure program GAMESS.[17]

Results and Discussion

Geometries. The geometries predicted for the compounds considered here are summarized in Tables 1 and 2 and are compared with experimental and former theoretical geometries where the latter are available. The experimental geometry for singlet and triplet CH_2 are reasonably well reproduced, although the triplet angle is underestimated by several degrees. The predicted structures for singlet HCF, CF_2, and HCCl are also in good agreement with experiment. The largest deviation is an overestimation of the C–F and C–Cl bond lengths by about 0.03 Å. Our predicted geometries for the corresponding triplet states for these three molecules are in good agreement with previous theoretical results. In general, the angle about the carbene carbon is predicted to be 15–25° larger in each triplet state than in the corresponding singlet state, with an 18–22° difference being most common. An exception to this rule occurs for those cases in which a silicon atom is directly bonded to the carbene carbon. For the three such cases studied here, the singlet–triplet difference in bond angle increases to 33–35°.

Energetics. The predicted singlet–triplet energy gaps are summarized in Table 3 and compared with the results of earlier calculations and with available experimental data. For the compounds CH_2, CHF, and CF_2 the predicted splittings are in excellent agreement with experiment. The 6-31G(d,p) results are within 1 kcal/mol of the experimental splittings, while those predicted using the ECP method deteriorate only slightly. The splitting predicted here for silylcarbene is within 1 kcal/mol of that predicted by previous calculations,[9] while the splitting predicted here for HCCl is 4 kcal/mol smaller than that found previously.[9] Note that both methylcarbene and silylcarbene are predicted to have triplet ground states. The singlet–triplet gap is descreased by 4.5 kcal/mol when H is replaced by CH_3, whereas silyl substitution *increases* the singlet–triplet splitting by 9 kcal/mol, relative to the unsubstituted compound.

The effect of electronegative substituents is consistent with the previous discussion of Feller, Borden, and Davidson:[12] The relative stability of the singlet increases in the order HCF < HCOH < $HCNH_2$, with the singlet state lower in energy in all cases. Among all substituents examined here, NH_2 is most effective at stabilizing the singlet, while SiH_3 is the most effective at stabilizing the triplet state.

Now, let us compare the effect of extending the alkyl or silyl chain, relative to the singlet–triplet splitting in methyl- or silylcarbene. Replacing the methyl group by an ethyl group, for example, has only a small effect,

---

(15) Stevenc, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

(16) Ditchfield, H. R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. C–F: Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Si: Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. Cl: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(17) GAMESS (General Atomic and Molecular Electronic Structure System): (a) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L., Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52. (b) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S. Jensen, J. H.; Soseki, S.; Matsunaga, N.; Nguyne, K. A.; Su, S. Windus, T. L. *Comput. Chem.* **1993**, *14*, 1347.

Table 3. Singlet-Triplet Energy Gaps (kcal·mol^{-1}) of Substituted Carbenes

	this work[a]		previous study			
	6-31G(d,p)	ECP(d,p)	CASSCF[b]	MRCI[c]	MRCI[d]	experiment
CH_2	8.7	6.8	12.8		9.0	8.998 ± 0.014
$HCCH_3$	4.2	2.1				
$HCNH_2$	–32.9	–32.1				
HCOH	–25.7	–26.8				
HCF	–16.0	–16.5	–9.2	–13.2	–17.7	–14.8 ± 0.2
CF_2	–55.8	–55.0	–46.5		–57.5	–56.6
CHCl	–5.1	–6.0	–1.6	–5.4	–9.3	>–11.4 ± 0.3
$HCSiH_3$	17.8	16.7			18.4	
$HCCH_2CH_3$	3.4					
$HCCH_2SiH_3$	–1.2	–2.3				
$HCCH_2GeH_3$		–3.6				
$HCSiH_2CH_3$	18.1					
$HCSiH_2SiH_3$		14.7				

[a] Multireference CI with singles and doubles. [b] Reference 8. [c] Reference 10b. [d] Reference 9.

reducing the splitting by less than 1 kcal/mol. Replacing the silyl group by a disilyl group has a somewhat larger impact, reducing the predicted singlet–triplet gap by 2 kcal/mol. In both cases, the triplet remains the predicted ground state. Replacing the single silyl group with SiH_2CH_3 has almost no effect on the singlet–triplet splitting. In contrast, replacing a single methyl group with CH_2SiH_3 (the β-silicon effect) preferentially stabilizes the singlet by 5.5 kcal/mol (4.5 kcal/mol when ECP's are used). This is sufficient to reverse the order of the two states, with the predicted ground state now being the singlet. A similar (somewhat stronger) β-stabilizing effect is found for Ge. The ground state of H–C–CH_2GeH_3 is also predicted to be a singlet.

The relation between singlet stabilization and electron donation may be examined qualitatively by comparing the Mulliken population in the carbene π orbital with the calculated energy gap. This is shown in Figure 1, where it is clear that there is a qualitative correlation between the two quantities. So, the more effective a substituent is in donating electrons into the carbene π orbital, the more effective that substituent is in stabilizing the singlet state. This again emphasizes the point made by Feller et al.[12] that this π donation is a more important factor than electronegativity.[18] For comparison, the predicted singlet–triplet splittings are also plotted against the total Mulliken populations on the carbene carbon (Figure 2), where it is seen that this total population, and therefore substituent electronegativity, is not a good indicator of the stabilizing effect on the singlet state. This does not suggest that substituent electronegativity plays *no* role in stabilizing the singlet state of carbenes, since singlet CHF is much more stable than CHCl, for example.

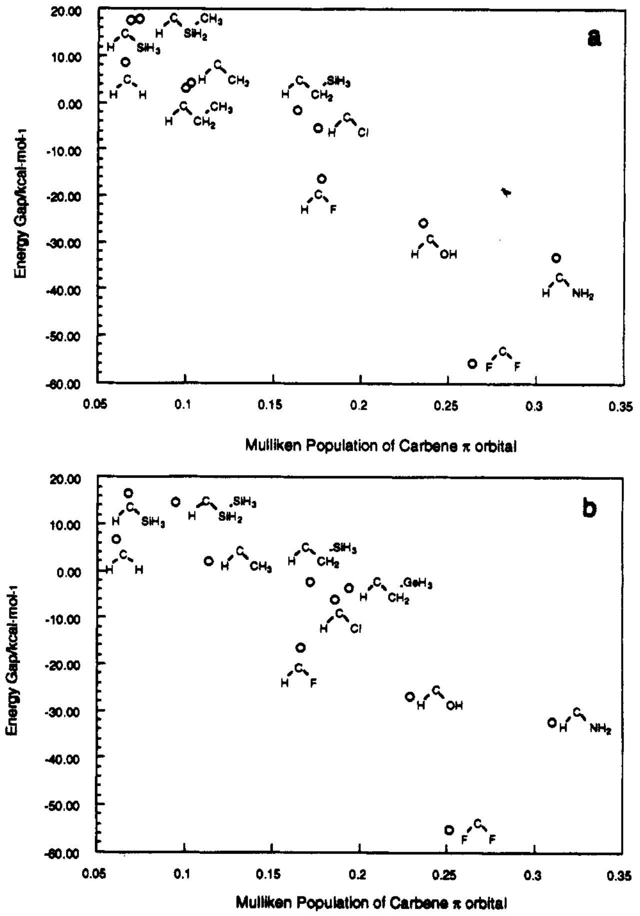

Figure 1. Singlet–triplet energy gaps and population of carbene π orbital: (a) MRCI/6-31G(d,p); (b) MRCI/ECP-(d,p).

One may also see from Figure 1 that replacing one of the hydrogens in CH_2 with either SiH_3 or SiH_2CH_3 has little effect on the population in the carbene π orbital. Methyl or ethyl substitution, on the other hand, results in an increase of about 0.035 electron in the carbene π orbital relative to the parent compound, and substitution of CH_2SiH_3 (the β-silicon effect) results in an increase in the population of the π orbital by about 0.1 electron. This latter effect is almost as large as the effect of Cl– or F– substitution, but still much smaller than the back-donation effect of either –OH or –NH_2 substitution. This π-donating ability must be related to both the greater polarizability of the C–Si electron density (relative to C–C) and to the ability of the C–Si bond to overlap effectively with the (formally empty) π orbital on the carbene carbon. The latter is aided by the geometry assumed by the β-silyl group. As shown in Table 2, the silyl group rotates by an angle of 91°, an almost perfect position to maximize this overlap. The β-silyl and β-germyl groups in the silylsilyl and methylgermyl substituted carbenes, respectively, also rotate by about 90°, while the methyl groups in ethylcarbene and silylmethylcarbene remain nearly coplanar. So, one would expect the β-silyl and β-germyl groups to be much more effective in π-donation, and therefore singlet stabilization, than the β-methyl groups. This is indeed found to be the case, except for H–C–SiH_2SiH_3. In Figure 3, both the singlet energy (relative to the optimized singlet geometry) and the Mulliken population in the π orbital

---

(18) Grev and co-workers [Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458] have discussed this back-donation effect with regard to the stabilization of singlet silylenes and germylenes.

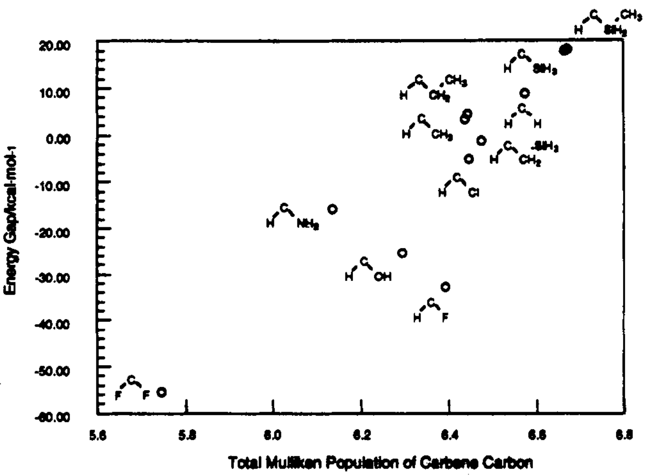

Figure 2. Singlet-triplet energy gaps and total population of carbene carbon.

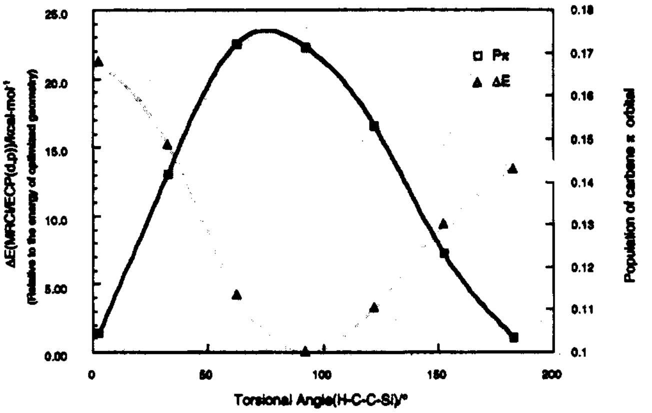

Figure 3. Energy and population change of singlet state with torsional angle for $CHCH_2SiH_3$.

are plotted as a function of the H–C–Si–Si torsional angle in $H–C–CH_2–SiH_3$. To obtain a simple qualitative picture, these calculations were performed using the TCSCF/SBK optimized singlet geometry, the angles and bond lengths then remaining fixed at those optimized values as the molecule is rotated. As suggested above, when the torsional angle is about 90°, the singlet–triplet splitting reaches its minimum value and the population in the carbene π orbital is a maximum. At the planar arrangements (0 or 180°), the reverse is true: there is little back-donation into the carbene π orbital and the singlet–triplet splitting is maximized.

A second geometric factor, the distance of the donating bond from the carbene carbon, must also be considered regarding the π back-donation. One qualitative measure of this is the distance *R* from the midpoint of the X–Y bond to the carbene carbon in $H–C–XH_2–YH_3$. The values of *R* are listed below for the five cases of interest. The two factors that determine *R* are the C–X distance and the C–X–Y angle. The combination of these two factors results in much smaller values of *R* for the three compounds that exhibit significant π donation and singlet stabilization (X, Y = C–Ge < C–Si < C–C) than in the other two (≪X,Y = Si–C, Si–Si). This helps to explain the relative small back-donation for $H–C–SiH_2SiH_3$, despite the favorable torsional angle for this species.

X	Y	*R* (Å)
C	C	1.998
C	Si	1.948
C	Ge	1.917
Si	C	2.472
Si	Si	2.478

Summary

The cumulative effect of the polarizability of the C–Si and C–Ge bonds and the rotation of these bonds into the appropriate alignment required for effective electron donation into the carbene π orbital results in preferential stabilization of the corresponding singlet carbenes relative to the lowest lying triplets, a β-silicon (or germanium) effect analogous to that which is well-known in cation chemistry.

Acknowledgment. This study was supported by Shin-Etsu Chemical Co., Ltd,, and by the National Science Foundation (CHE-8911911). The calculations were performed on IBM RS 6000/350 computers generously provided by Iowa State University. The authors are indebted to Professors Thomas Barton and Joseph Lambert for inspiring this work.

OM930490M