A Molecular Orbital Study of Silylated Carbenes

Ryoji Noyori, Masashi Yamakawa, and Wataru Ando*

Department of Chemistry, Nagoya University, Chikusa, Nagoya 464

** Department of Chemistry, The University of Tsukuba, Niihari-gun, Ibaraki, 300-31*

(Received May 11, 1977)

The geometry and electronic properties of methylene, methylcarbene, carboxycarbene, phenylcarbene, trimethylsilylcarbene, silylcarbene, carboxysilylcarbene, and phenylsilylcarbene have been determined by MINDO/3 calculation. Introduction of a silyl group results in considerable decrease in ionization potential of carbenes. The electron affinity is increased to some extent by such substitution. The computation suggests a bent geometry for optimized triplet trimethylsilylcarbene structure, in conflict with a recent postulate that the ground-state molecule has an essentially linear structure.

Silylcarbenes generated by photolysis of the corresponding diazo compounds display intriguing behavior.[1-9] One is the relative reactivity of alkenes in the cyclopropanation of these carbenes. Ordinary carbenes are electrophilic and in most cases undergo cycloaddition preferentially to the more alkylated alkenes,[10] whereas the reactivity of ethoxycarbonyltrimethylsilylcarbene toward alkenes decreases with increasing methyl substitution on the double bond.[3] Another is the mode of reaction with dialkyl sulfides. Most carbenes react with sulfides in an electrophilic manner to produce sulfur ylides;[10] in contrast, reaction of silylcarbenes results in the formation of formal sulfur–carbon bond

$$RC(N_2)COOC_2H_5 \xrightarrow{h\nu} RCCOOC_2H_5 + N_2$$

R=H or $Si(CH_3)_3$

$$RCCOOC_2H_5 + \text{Olefin} \longrightarrow \text{cyclopropane-}COOC_2H_5$$

$$HCCOOC_2H_5 + R'_2S \longrightarrow R'_2\overset{+}{S}\text{-}\overset{-}{C}HCOOC_2H_5$$

$$(CH_3)_3SiCCOOC_2H_5 + R'_2S \longrightarrow R'S\text{-}C(Si(CH_3)_3)(COOC_2H_5)\text{-}R'$$

insertion products.[11] In addition, trimethylsilylcarbene has received attention as a precursor of a silaethylene.[6-9] These interesting features have prompted us

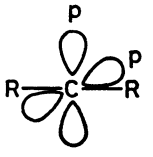
$$(CH_3)_3SiCHN_2 \xrightarrow{h\nu} (CH_3)_3SiCH + N_2$$

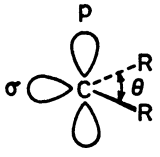
$$(CH_3)_3SiCH \longrightarrow (CH_3)_2Si{=}CHCH_3$$

to examine the electronic structures of the carbenes by semi-empirical SCF MO calculations.

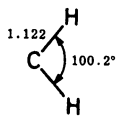
Results and Discussion

A linear carbene has two perpendicular 2p orbitals into which two valence electrons are to be placed. Degeneracy is removed on bending, giving a σ orbital (in the plane in which bending takes place) and leaving p orbital (perpendicular to the plane).[12] When a conjugative group is attached to the divalent carbon,

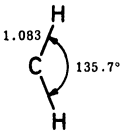




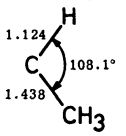
bending can occur in either in-plane or out-of-plane manner. The levels of these orbitals are affected in various ways by interaction with the adjacent carbene substituents. Thus total molecular energies vary as a function of bond angle, θ. We calculated the structures of four silylcarbenes and some related species according to the MINDO/3 method.[13] Contribution of silicon d orbitals was not explicitly considered. In order to perform the calculation, the program supplied by the Quantum Chemistry Program Exchange (QCPE) was modified for use with the FACOM 230-60 computer at Nagoya University. For carbenes **1**—**7**, the bond lengths, bond angles, and torsional angle were optimized. For large substituents such as phenyl or carboxyl, some fixed parameters were used. The molecular structures thus obtained are given in the molecular formulas; the details are summarized in Table 1. Geometries of the triplet states were determined by this method and the electronic structures by unrestricted Hartree-Fock type SCF calculations, not by the conventional *half-electron method.*[13] Electronic properties of the carbenes are given in Table 2. The ionization potential (IP) of the carbenes and the electron affinity (EA),



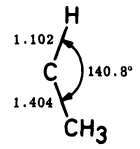
1S



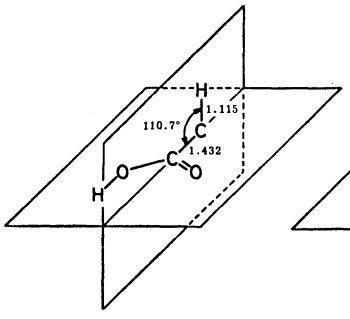
1T



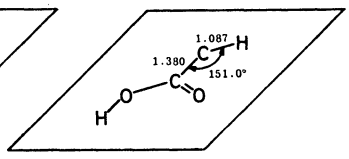
2S



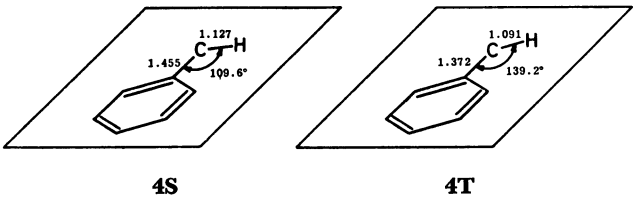
2T



3S



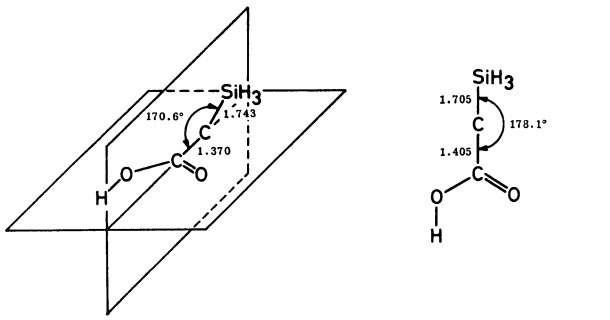
3T



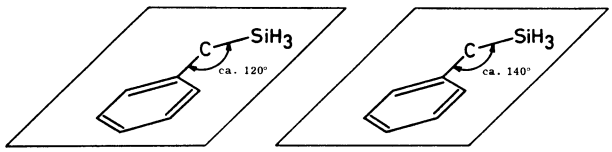
4S **4T**

5S **5T**

6S **6T**



7S **7T**



8S **8T**

as estimated as IP of the corresponding radical anions, provide the indication of nucleophilicity and electrophilicity, respectively. Electron density of the formally vacant p orbital ($d_{p\pi}$) and net atomic charge of the carbenic center might be related to the reactivity of these carbenes as well.[17]

Methylene (1). Calculations indicate that the triplet state (**1T**) is the ground state with minimum energy at an HCH bond angle of 135.7°, lying 11.8 kcal/mol below the lowest singlet state (**1S**) with bond angle of 100.2°. Calculated IP of **1S** is 9.94 eV. The result for this parent carbene species is in good agreement with experimental results.[18,19] The calculated EA value, 0.09 eV, is somewhat lower than the observed value, 0.21 eV.[18] The MINDO/3 calculation for **1** has been carried out,[13] but the IP of **1T** has not been reported.[20]

Methylcarbene (2). The 140.8° triplet (**2T**) was found to be the ground state. The 108.1° singlet (**2S**) lies 16.9 kcal/mol above **2T** and has IP of 8.86 eV. This value is 1.08 eV lower than that of **1S**. The EA value, 0.83 eV, is larger than that of simple methylene. Introduction of methyl group increases $d_{p\pi}$ by 0.12.[21]

Carboxycarbene (3). The carboxyl group was used as a model of the alkoxycarbonyl group. Both singlets and triplets with minimum energies have bent structures. The in-plane triplet is more stable than the singlet of out-of-plane bent structure. This is to be noted because alkoxycarbonylcarbenes formed from diazoacetates are known to behave usually as a singlet species.[22,23] The orbital stabilization of **3S** is attained as a result of both bending to acquire s character and π conjugation between the occupied σ orbital and carboxyl group. IP of **3S** is nearly identical with that of **1S**. As expected, this electron-withdrawing group increases the EA value, predicting the eminent electrophilic nature of carbene.

Phenylcarbene (4). In both **4S** and **4T**, all the atoms lie nearly on the same plane. In accord with experimental findings,[24] the ground state is a bent triplet (**4T**). The low IP (8.22 eV) and high EA (1.55 eV) for the singlet species (**4S**) characterize the electronic property. Its $d_{p\pi}$, 0.20 is rather high.[25]

Trimethylsilylcarbene (5). The ground state was indicated to be triplet, as has recently been demonstrated by experiments.[9] According to the present calculation, however, the ground state has a 147° bent structure (**5T**), which lies in marked contrast with the recent postulate that **5T** has a linear structure.[9] The lowest singlet state (**5S**) with bond angle of 115.6°, lying 32.9 kcal/mol above **5T**, has an IP of 8.25 eV. The IP is much lower than that of **1S** (9.94 eV) or **2S** (8.86 eV) but comparable with the one of the phenylated carbene **4S**. Electron density of the carbenic carbon, $d_{p\pi}$, is smaller than that in the case of **2S**. Thus the trimethylsilyl group, as compared with the methyl group, has been shown to decrease IP greatly but not to increase electron density of the divalent carbon. Lack of hyperconjugative stabilization of the vacant orbital may be the cause. On going from **2S** to **5S**, EA value increases by 0.93 eV.

Silylcarbene (6). The optimized geometry and electronic properties are quite similar to those of the trimethyl derivative **5**.

Carboxysilylcarbene (7). For the sake of economy of calculation, silyl group was used as a model of the trimethylsilyl group. The carbene has also triplet ground state (**7T**). Unlike carboxy- or silylcarbene, the triplet state with minimum energy is of linear structure. The lowest singlet state (**7S**) of 170.6° bent structure, lying 23.5 kcal/mol above the ground state **7T**, is stabilized to a considerable extent through conjugation of the σ orbital (99.9% p-character) containing paired electrons with the adjacent carboxyl group. Notably, silyl group introduced into the carbene **3S** decreases the IP value by 1.11 eV, suggesting endowment of nucleophilicity. On the other hand, no change in electrophilicity can be expected, as seen from the comparable EA value. The $d_{p\pi}$ and net atomic charge of the carbene center were found to increase to some extent.

Phenylsilylcarbene (8). The structure could not be optimized because of the large framework. The ground

Table 1. Calculated molecular geometries of carbenes **2**—**7**

Carbene	Calcd bond length (Å), bond angles, and torsional angles
$CHCH_3$, **2S**	C-C; 1.438, CH_2-H; 1.112—1.113, C(carbene)-H; 1.124, ∠H-C-CH_3; 108.1°, ∠CH-CH_2-H; 112.5—114.0°, τ(H-C-CH_2-H); 60°[a]
2T	C-C; 1.404, CH_2-H; 1.106—1.123, C(carbene)-H; 1.102, ∠H-C-CH_3; 140.8°, ∠CH-CH_2-H; 112.1—113.4°, τ(H-C-CH_2-H); 60°[a]
CHCOOH, **3S**	C-C; 1.432, C=O; 1.230, C-O; 1.350, O-H; 0.955,[b] C-H; 1.115, ∠H-C-C; 110.7°, τ(H-C-C=O); 90.2°
3T	C-C; 1.380, C=O; 1.236, C-O; 1.355, O-H; 0.955,[b] C-H; 1.087, ∠H-C-C; 151.0°, τ(H-C-C=O); 0.0°
CHC_6H_5, **4S**	C(carbene)-C; 1.455, C(carbene)-H; 1.127, ∠H-C(carbene)-C; 109.6°, τ(H-C(carbene)-C=C); 5.8°[c]
4T	C(carbene)-C; 1.372, C(carbene)-H; 1.091, ∠H-C(carbene)-C; 139.2°, τ(H-C(carbene)-C=O); 5.8°[c]
$CHSi(CH_3)_3$, **5S**	C(carbene)-Si; 1.840, Si-CH_3; 1.885—1.888, CH_2-H; 1.114—1.115, ∠C(carbene)-Si-CH_3; 108.9—110.5°; ∠Si-CH_2-H; 115.0—115.5°,[a,d] C(carbene)-H; 1.117, ∠H-C(carbene)-Si; 115.6°, τ(H-C(carbene)-Si-CH_3); 60.1°
5T	C(carbene)-Si; 1.762, Si-CH_3; 1.889—1.895, CH_2-H; 1.116—1.117, ∠C(carbene)-Si-CH_3; 108.9—110.5°; ∠Si-CH_2-H; 115.0—115.6°,[a,d] C(carbene)-H; 1.099, ∠H-C(carbene)-Si; 147.0°, τ(∠H-C(carbene)-Si-CH_3); 60.1°
$CHSiH_3$, **6S**	C-Si; 1.786, Si-H; 1.480—1.481, ∠C-Si-H; 111.7—113.5°,[a] C-H; 1.116, ∠H-C-Si; 116.6°, τ(H-C-Si-H); 60.2°
6T	C-Si; 1.716, Si-H; 1.481—1.483, ∠C-Si-H; 110.1—110.5°,[a] C-H; 1.093, ∠H-C-Si; 145.5°, τ(H-C-Si-H); 60.0°
$C(SiH_3)COOH$, **7S**	C-C; 1.370, C=O; 1.245, C-O; 1.354, O-H; 0.954,[b] C-Si; 1.743, Si-H; 1.472—1.479, ∠C-Si-H; 108.3—112.8°,[a] ∠C-C-Si; 170.6°, τ(Si-C-C=O); 90.0°, τ(C-C-Si-H); 30.0°
7T	C-C; 1.405, C=O; 1.239, C-O; 1.342, O-H; 0.957,[b] C-Si; 1.705, Si-H; 1.487, ∠C-Si-H; 112.0—112.7°,[a] ∠C-C-Si; 178.1°, τ(Si-C-C=O); 0.0°, τ(C-C-Si-H); 60.0°

a) CH_3, $Si(CH_3)_3$, and SiH_3 groups are assumed to have approximately C_{3v} symmetry. b) Planar structure for COOH group was assumed; ∠C-C=O; 120°, ∠C-C-O; 120°, ∠C-O-H; 110°. c) Phenyl ring was treated as regular hexagon; C-C; 1.397 A, C-H; 1.084 A, bond angle; 120°. d) Angles of 60, 180, 300° are used for the torsional angle, τ(C(carbene)-Si-CH_2-H).

Table 2. Electronic properties of certain carbenes obtained by MINDO/3 method

Carbene	Occupation	θ, deg	IP, eV[a]	EA, eV[b]	$d_{p\pi}$[c,d]	Net atomic charge[d]	ΔH_f,[e] kcal/mol
CH_2, **1S**	σ^2	100.2	9.94	0.09	0.0	+0.19	100.2
1T	σp	135.7	9.92	−1.18[f]	1.0	−0.14	88.4
$CHCH_3$, **2S**	σ^2	108.1	8.86	0.83	0.12	+0.06	75.6
2T	σp	140.8	9.09	−0.39[f]	—	−0.15	58.7
CHCOOH, **3S**	σ^2	110.7	9.89	2.20	0.11	+0.04	−8.5
3T	σp	151.0	10.77	1.17	—	−0.13	−24.8
CHC_6H_5, **4S**	σ^2	109.6	8.22	1.55	0.20	0.0	118.9
4T	σp	139.2	8.08	0.69	—	−0.14	98.5
$CHSi(CH_3)_3$, **5S**	σ^2	115.6	8.25	1.76	0.05	−0.04	30.6
5T	σp	147.0	9.26	0.41	—	−0.21	−2.3
$CHSiH_3$, **6S**	σ^2	116.6	8.28	1.29	0.06	0.0	83.2
6T	σp	145.5	9.26	−0.09[f]	—	−0.15	50.8
$C(SiH_3)COOH$, **7S**	σ^2	170.6	8.78	2.58	0.21	−0.12	−38.2
7T	pp′	178.1	9.72	1.87	—	−0.18	−61.7

a) Ionization potential. b) Electron affinity. c) Electron density of carbene p orbital. d) In units of electron charge. e) Heat of formation. f) The negative value may be due to the underestimation of the core resonance integrals in this method.

state was estimated to be *ca.* 140° bent triplet (**8T**), the lowest singlet (**8S**) prefering an in-plane bent (*ca.* 120°) geometry.

Thus MINDO/3 method shows that introduction of silyl groups into the carbene center results in considerable decrease in IP's, thereby increasing nucleophilic character. The same perturbation, however, is observed with other substituents, particularly phenyl and methyl groups. Electrophilicity, as judged from the EA's, is affected by silyl substitution, the effect being highly dependent on the nature of other substituents on divalent carbon. Silyl moieties increase

electron density, $d_{p\pi}$, of the carbenic carbon, but the degree of the effect is less than methyl or phenyl substituent. Thus when the electronic properties of the silylcarbenes are compared with those of the related nonsilylated carbenes of the same singlet electronic configuration, we cannot anticipate any peculiar behavior of the former species. In order to interpret the unique reactivity of silylcarbenes, the bulkiness of silyl group[3] and efficiency of the S-T intersystem crossing should be taken into account. The silyl groups may exert strong influence on the nature of the transition state or intermediate of carbene *reactions* rather than the properties of the divalent species itself.

The MINDO/3 procedure is the most sophisticated semi-empirical SCF MO method at present and the accuracy of the calculations has been demonstrated by excellent agreement with experimental observations for a large number of ground state molecules. This is also the case for organosilicon compounds.[16] Nevertheless, the calculated bent geometry of **5** is inconsistent with the recent postulate that ground-state trimethylsilylcarbene has a linear geometry.[9] If the conclusion based on ESR study is correct,[26] one of the major causes of this controversy might be the influence of possible $d\pi$-$p\pi$ interaction, although such orbital effect is usually considered to be negligible.[27-29] If this were the case, it might present a rare example of d-orbital participation.

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