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Generation of “Sumanenylidene”: A Ground-State Triplet Carbene on a Curved π-Conjugated Periphery

Yumi Yakiyama,[1] Yufeng Wang,[1] Sayaka Hatano,[2] Manabu Abe,[2] and Hidehiro Sakurai*[1]

Abstract: We have observed the generation of sumanenylidene (**2**), a divalent, neutral carbon species on the benzylic position of sumanene (**1**), We have also clarified experimentally and theoretically that the ground state of **2** was triplet and that its singlet-triplet energy gap (ΔE_{ST}) value was similar to that of fluorenylidene. The curved structure of **2** yields slightly better spin delocalization onto the two adjacent aromatic rings than planar systems do because of the unpaired spins on σ- and π-orbitals. The synthetic application of the carbene precursor, diazosumanene (**5**), with various thiocarbonyl compounds revealed its usefulness to prepare tetra-substituted alkene compounds (e.g. having a strong electron donor unit) directly conjugated with the **1** moiety.

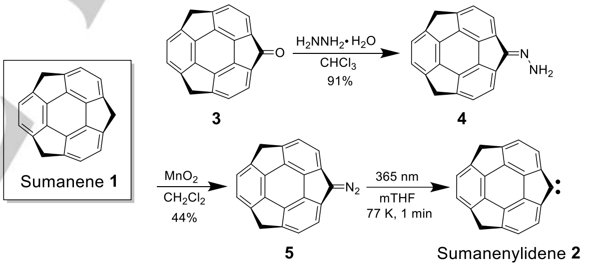
Introduction

Carbene is a divalent, neutral carbon species with two unshared valence electrons. It works as an effective reaction intermediate in organic synthesis. The structures and reactivity of carbenes have been investigated for more than 50 years.[1] Carbenes can take two possible spin states at the ground state, (i.e., singlet and triplet), and especially in the case of ground-state triplet carbenes, strong relationships exist between zero-field parameters obtained by electron spin resonance (ESR) and the geometry around the carbene center and the substituent effect.[2,3] In addition, carbene reactivity is influenced from its singlet-triplet energy gap (ΔE_{ST}).[4] Recent work has focused on much more complicated systems, such as polycarbenes, to show the unique properties of new type of carbenes.[5]

Buckybowls represented by corannulene and sumanene (**1**), the partial structure of C_{60}, have been studied in terms of both fundamental and material chemistry.[6] Their curved structures and bent π-orbitals give them unique properties that cannot be observed in the planar π-conjugated molecules, especially in spin chemistry.[7] This motivated us to generate the carbene moiety on the curved π molecule and to investigate the effects of the curved structure on the structural and electronic relationship. To achieve this challenging work, we focused on sumanene (**1**) (Scheme 1), which possesses the well-investigated fluorenylidene skeleton[2a,4b,8] as a partial structure. In this paper we show the preparation of sumanene-based carbene, sumanenylidene (**2**), having clarified its structural and electronic information by zero-field parameters obtained from ESR measurement, density functional theory (DFT) calculation, and reactivity against cyclohexane. In addition, the applicability of the carbene precursor, diazosumanene (**5**), for Barton–Kellogg reaction and the details of the resulting olefins were discussed.

Results and Discussion

Preparation of **5**, a precursor of **2**, was conducted from sumanenone (**3**)[9] through the conventional route, including hydrazination, followed by MnO_2 oxidation, as shown in Scheme 1. The successful preparation of **5** was confirmed by IR measurement. The clear N-N stretching mode was observed at 2045 cm^{-1}, which is almost the same value as that of diazofluorene (2042 cm^{-1}, see Supporting information).[10] The stability of **5** in the solution state was low when initiating decomposition within 1.5 hour, and it was stable under air in the solid state.



Scheme 1. Structure of sumanene **1** and the preparation of sumanenylidene (**2**) via diazosumanene (**5**).

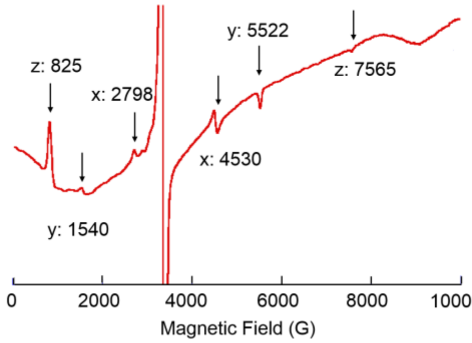


Figure 1. ESR spectrum of **2** in 77 K MTHF glassy matrix measured at 9.40 GHz.

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The generation of **2** from **5** was confirmed by *in-situ* ESR measurement at 77 K (Figure 1). The degassed solution of **5** in 0.1 mM 2-methyltetrahydrofuran (MTHF) by Ar bubbling was sealed and was irradiated by a 365 nm LED lamp for 1 min (see Supporting Information). This afforded a total of six signals at 825, 1540, 2798, 4530, 5522, and 7565 G, which corresponded to the spin transitions along the x, y, and z axes, indicating that **2** was a ground-state triplet carbene, as observed in diphenylcarbene and fluorenylidene.[2] Notably, the signal positions were similar to reported ESR data on diphenylcarbene, which comprises part of the structure for **2**.[11] The spin distribution of **2** was also investigated both from the experimentally obtained the zero-field parameters and from calculations (Table 1 and Figure 2). The slightly smaller *D*/*hc* value of **2**, when compared with the other two, may suggest that the curved structure of **2** yields slightly better spin delocalization onto the two adjacent aromatic rings than planar diphenylcarbene and fluorenylidene do. This is because of better overlap of spin-existing σ- and π-orbitals at the carbene centre of **2** than those of planar molecules.

Table 1. Zero-field parameters and the structural information of diphenylcarbene, fluorenylidene and **2**, as obtained from ESR measurements and DFT calculations.

	Diphenylcarbene	Fluorenylidene	**2**
D/hc (cm^{-1})	0.4055[8b]	0.4078[2a]	0.39
E/hc (cm^{-1})	0.0194[8b]	0.0283[2a]	0.0253
E/D	0.0478[8b]	0.0693[2a]	0.065
Bond angle (°)	143.2[a]	112.1[a]	112.0[a]
ΔE_{ST} (kcal/mol)	7.22[b]	5.59[b]	5.80[b]

[a] Calculated at B3LYP/6-311+G(d,p) level of theory. [b] As density functionals do not include a Coulomb correlation term, nor do they treat nondynamic electron correlation accurately, they intrinsically misestimate the ΔE_{ST} values.[12] The ΔE_{ST} values have been adjusted by the 3.68 kcal/mol difference between the experimental (ΔE_{ST} = 9.05 kcal/mol)[13] and computed ΔE_{ST} for methylene (the correction is 3.68 kcal/mol at B3LYP/6-311+G(d,p)).

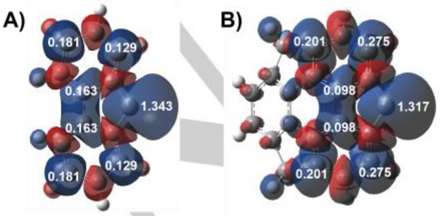


Figure 2. Spin density map of A) fluorenylidene and B) **2** calculated at UB3LYP/6-31G++(d,p) level of theory.

Indeed, the spin density, especially at the peripheral carbons on the fluorene skeleton in **2**, showed a higher value than that of fluorenylidene, also indicating better spin delocalization for **2**. Furthermore, the *E*/*hc* value, which is relates to the bond angle at the carbene center of **2**, was much larger than that of diphenylcarbene and was close to that of fluorenylidene. This tendency well reflected bond angle differences.

Next, the photo reaction of **5** by low-temperature matrix absorption spectroscopy was carried out (Figure 3). The 380 ± 10 nm pulse light irradiation immediately caused a decrease in the absorption band at 393 nm, which was attributable to the disappearance of **5**. Concurrently, the new absorption band generation at 410~440 nm was found to have a clear isosbestic point, indicating that only two species exist in the system, decreasing **5** and increasing **2**. These results also supported the effective generation of **2** from **5**.

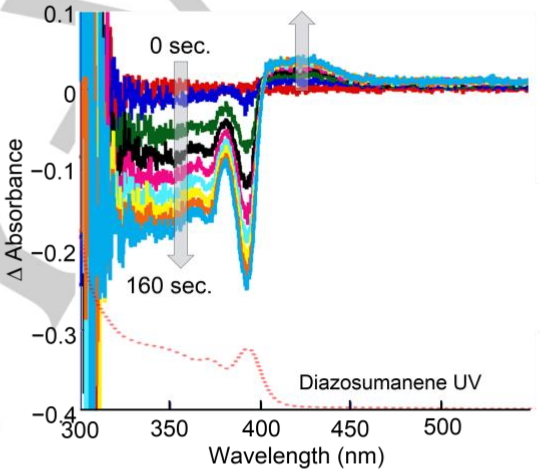
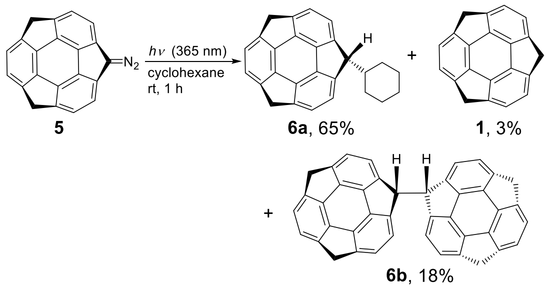


Figure 3. Low-temperature matrix absorption spectroscopy of the 0.1 mM MTHF solution of **5** with the irradiation of 380 ± 10nm at 77 K. The bottom dotted line shows the absorption spectrum of **5**.



Scheme 2. Reactivity confirmation of sumanenylidene **2** prepared by the 365 nm photo irradiation of **5** in cyclohexane.

As mentioned above, a carbene's reactivity is strongly affected by the energy relationship between the singlet and the triplet states. During a reaction with hydrocarbons, if the singlet carbene is predominant under the reaction condition, a C-H

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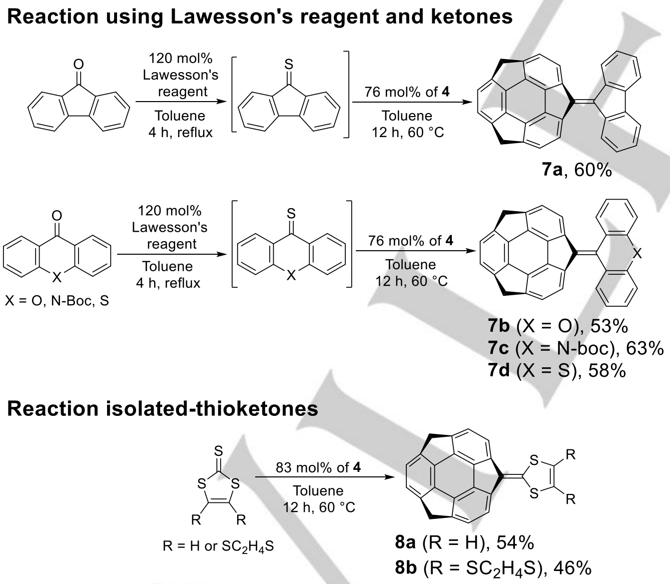
bond-inserted product (a hydrocarbon adduct) is obtained. Conversely, if the triplet carbene is more stable, the dimer product is observed in addition to C-H bond-inserted product. For example, diphenylcarbene gives the dimer as the main product,[14] while fluorenylidene mainly gives cyclohexane's C-H adduct instead of the dimer, despite the fact that both of the carbenes are ground-state triplets. The difference in reactivity strongly suggests independence from the spin state of the ground state and is well explained by each carbene's ΔE_{ST} values.[14a] Therefore, next we investigated the reactivity of **2** against cyclohexane. DFT calculations also supported the reactivity of **2** via its ΔE_{ST} value (Table 1).

The 12 mM cyclohexane solution of **2** was stirred at rt for 1 h under an irradiating 365-nm LED lamp, giving the cyclohexane adduct (**6a**) as the main product (65% yield) together with the **1** dimer (**6b**) (18% yield) and **1** (3% yield). It is known that the ΔE_{ST} value and the bond angle of the carbene center have a strong relationship.[15] If the bond angle of the carbene center is small, the ΔE_{ST} value tends to become small, which makes intercrossing from triplet to singlet easy. With **2**, the calculated bond angle at the triplet state and the ΔE_{ST} value were 112.0° and 5.80 kcal/mol, respectively, which were nearly the same as those of fluorenylidene (112.1° and 5.59 kcal/mol, respectively), and were significantly smaller than those of diphenylcarbene (143.2° and 7.22 kcal/mol, respectively). Thus, the reaction product of **2** with cyclohexane and these parameters clearly indicate that the reaction proceeded through the singlet state, even though **2** was a ground-state triplet species. This result also shows the high similarity of **2** to fluorenylidene.



Scheme 3. Barton-Kellogg reaction between diazosumanene (**5**) and thiocarbonyl species that were isolated or generated from corresponding ketones using Lawesson's reagent.

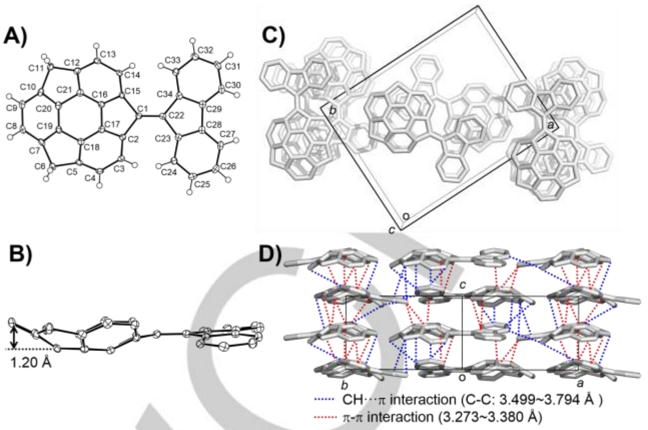


Figure 4. Crystal structure of **7a**. A) ORTEP drawing of **7a** with thermal ellipsoid at 50% probability. B) Bowl depth of the sumanene skeleton in **7a**. C) Packing structure viewed from the *c* axis. D) Intermolecular interactions both within and between the columns. Blue dotted lines: CH⋯π interaction; red dotted lines: π-π interaction. Hydrogen atoms in B)-D) are omitted for clarity.

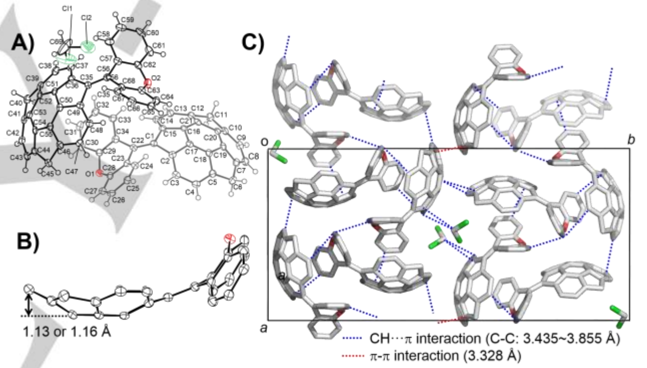


Figure 5. Crystal structure of **7b**. A) ORTEP drawing of **7b** with thermal ellipsoid at 50% probability. B) Bowl depth of the sumanene skeleton in **7b**. C) Packing structure viewed from the *c* axis with intermolecular interactions. Blue dotted lines: CH⋯π interaction; red dotted lines: π-π interaction. Grey, C; red, O; green, Cl. Hydrogen atoms in B) and C) are omitted for clarity.

Finally, the synthetic application of the carbene precursor, **5**, was investigated. The results of the Barton–Kellogg reaction of **5** with various thiocarbonyl species (either isolated or generated *in situ* from ketones with Lawesson's reagent) are shown in Scheme 3. Through the Barton–Kellogg reaction, the sterically crowded tetra-substituted alkenes (**7a**)-(**7d**) were prepared, which were directly conjugated to the **1** moiety in moderate yields. From the stable thiocarbonyl compounds, 1,3-dithiole-2-thione and 4,5- ethylenedithio-1,3-dithiole-2-thione, the corresponding adducts, (**8a**) and (**8b**), were also obtained in 54% and 46% yields, respectively. Within these products, **7a, 7b** and **8a** exhibited good crystallinity to afford single crystals of sufficient quality for X-ray analysis (Figures 4-6).

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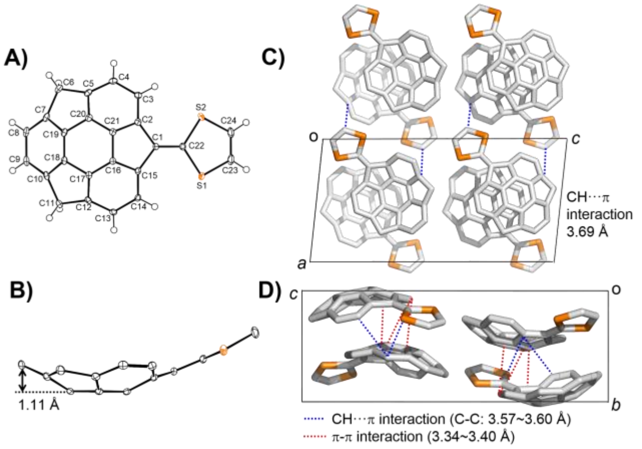

Figure 6. Crystal structure of **8a**. A) ORTEP drawing of **8a** with thermal ellipsoid at 50% probability. B) Bowl depth of the sumanene skeleton in **8a**. C) Packing structure viewed from the *b* axis with inter-columnar CH⋯π interaction. D) Intermolecular interactions both within the columns. Blue dotted lines: CH⋯π interaction; red dotted lines: π-π interaction. Grey, C; orange, S. Hydrogen atoms in B)-D) are omitted for clarity.

In the crystal structure, all the molecules showed different structural features. The bowl depths at the peripheral aromatic carbon were 1.20 Å for **7a**, 1.13 and 1.16 Å for **7b** (in two crystallographically independent units), and 1.11 Å for **8a,** while the depth of pristine **1** is 1.11 Å. When the packing structures of the three were compared, **7a** and **8a** provided columnar structures. Unlike already reported functionalized symmetrical sumanene derivatives, which form the well-stacked columnar structure for sumanene skeletons,[16] **7a** formed the head-tail stack type, in which sumanene and fluorene skeletons stacked alternatively. With its smaller group, **8a** provided slipped-stacked columns for sumanene skeletons. Within **7b**, no columnar stacking structure was found, which may be due to the presence of the non-planar xanthene skeleton and CH_2Cl_2 as a crystalline solvent. The main intermolecular interactions in all the packing structures were CH-π and π-π stacking interactions. The distances were 3.50~3.79 Å and 3.27~3.38 Å respectively in **7a**, 3.44~3.86 Å and 3.33 Å respectively in **6b** and 3.57~3.60 Å and 3.34~3.40 Å respectively in **8a**.

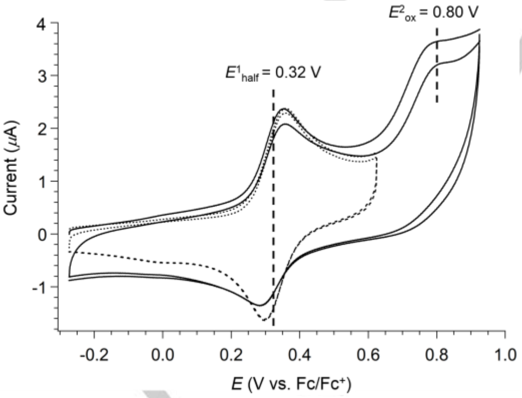

Figure 7. Cyclic voltammogram of **8a**. Ag/$AgNO_3$ reference electrode, measured at a glassy-carbon working electrode in a CH_2Cl_2 solution (1 × 10^{-4} M) containing [*n*-Bu_4N][ClO_4] (1 × 10^{-4} M) as a supporting electrolyte with Pt wire as a counter electrode. Scan Rate = 50 mV/s.

Since the 1,3-dithiol skeleton is the partial structure of tetrathiafulvalelne (TTF), **8a** was expected to be a strong donor molecule, having a curved-π structure. Figure 7 shows the cyclic voltammogram measured in CH_2Cl_2. One reversible redox wave and an irreversible oxidation peak were observed at 0.32 V and 0.80 V (vs. Fc/Fc^+), respectively. The reversible redox wave is attributable to the redox reaction at the one ring structure of the TTF moiety (0.30 V vs. Fc/Fc^+).[17] As expected, **8a** has high a potential to be a non-planar electron donor molecule.

Conclusions

For the first time we have generated a curved π-system-based carbene **2**. And we have clarified experimentally and theoretically that the ground state of **2** was triplet carbene and its ΔE_{ST} value resembled to that of fluorenylidene, which strongly affected its reactivity to mainly give C-H inserted product in the reaction with cyclohexane. We also demonstrated the synthetic utility of the precursor **5** with Barton-Kellogg reaction to afford various tetra-substituted alkenes. We hope that the research will trigger the new carbene chemistry at the curved π-system and now plan to expand the system into the multiple carbene systems.

Experimental Section

Low temperature ESR measurement: Diazosumanene **5** (0.8 mg, 2.8 mmol) in 3 mmϕ quartz ESR tube was dissolved in 2-mehtyltetrahydrofurane (3.0 mL) at 27 °C. The mixture was degassed by Ar bubbling for 30 min. The degassed solution was sealed and cooled to 77 K in an optical transmission ESR cavity and irradiated 365 nm light with ARK TECH Awill LED light source for 1 min. ESR spectrum was measured on a Bruker X-band E-500 spectrometer (9.400840 GHz).

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Keywords: Buckybowls • Carbenes • Curved-π systems • Diazo compounds • Olefination

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