

Published in final edited form as:

*Science*. 2006 May 5; 312(5774): 722–724.

## Cyclopropenylidenes: From Interstellar Space to an Isolated Derivative in the Laboratory

Vincent Lavallo<sup>1</sup>, Yves Canac<sup>1</sup>, Bruno Donnadiou<sup>1</sup>, Wolfgang W. Schoeller<sup>2</sup>, and Guy Bertrand<sup>1,\*</sup>

<sup>1</sup> University of California, Riverside–CNRS Joint Research Chemistry Laboratory (Unité Mixte Internationale 2957), Department of Chemistry, University of California, Riverside, CA 92521–0403, USA

<sup>2</sup> Fakultät für Chemie der Universität, Postfach 10 01 31, D-33615 Bielefeld, Germany

### Abstract

Like many of the molecular species that have been detected in the interstellar medium, the singlet carbene cyclopropenylidene (C<sub>3</sub>H<sub>2</sub>) has been presumed to be too unstable to isolate in the laboratory. However, by appending  $\pi$ -electron-donating amino groups to the triangular skeleton, we prepared a cyclopropenylidene derivative that is stable at room temperature. In contrast to previously isolated carbenes, this compound does not require a heteroatom adjacent to the electron-deficient carbon to confer stability. Despite the presence of amino groups, the geometric parameters of the cyclic skeleton, revealed by x-ray crystallography, are only slightly perturbed relative to those of the calculated structure of unsubstituted cyclopropenylidene. Stable cyclopropenylidene derivatives might thus serve as models for a better understanding of the formation of carbon-bearing molecules in the interstellar medium.

Carbenes are compounds with a neutral dicoordinate carbon atom, which features either two singly occupied nonbonding orbitals (a triplet state) or a lone pair and an accessible vacant orbital (a singlet state). With only six electrons in its valence shell, the carbene center defies the octet rule, and for a long time carbenes have been considered as prototypical reactive intermediates (1,2). During the past two decades, carbene chemistry has undergone a profound revolution. Persistent triplet carbenes have been observed (3), and singlet carbenes have been isolated (4–6) and even become powerful tools for synthetic chemists (7,8). However, it is generally believed that singlet carbenes can be isolated only if their electron deficiency is reduced by the presence of at least one  $\pi$ -donor heteroatom directly bonded to the carbene center (9).

Cyclopropenylidene (C<sub>3</sub>H<sub>2</sub>) **1a** is a cyclic singlet carbene (Fig. 1). Since its first radio astronomical detection in 1985 (10), it has been inferred to be the most abundant cyclic hydrocarbon observed in interstellar space (11). It is detectable in molecular clouds, circumstellar shells, and at least one external galaxy. Cyclopropenylidene **1a** and its linear isomers **2a** and **3a** have also been observed in several hydrocarbon-rich flames and may be involved in the chemistry of soot formation (12). Although carbenes are very reactive, they are not necessarily prone to self-rearrangement, which accounts for their stability in the near-vacuum of deep space and in the low-density medium of flame. However, cyclopropenylidene **1a** appears to be highly unstable in condensed phases. Reisenauer *et al.* were able to detect the molecule by infrared spectroscopy in a solid argon matrix, but it survives for only a few hours at 35 to 40 K and then polymerizes (13). The quest for cyclopropenylidenes in the laboratory has not been restricted to the parent compound **1a**. Because amino groups are known to stabilize

\*To whom correspondence should be addressed. E-mail: gbertran@mail.ucr.edu.

the corresponding cyclopropenium salts (**4**) (**14**), bis(dialkylamino)cyclopropenylienes such as **1c** have been among the most frequently targeted derivatives (15–17). The transient existence of **1c** has been postulated based on chemical trapping experiments, but it has been described as a highly unstable molecule, defying isolation or even observation in the free state (15–21).

Calculations predict that the rearrangement of **1a** into other C<sub>3</sub>H<sub>2</sub> isomers, propadienyliene **2a** and propynylidene **3a**, is quite unlikely, because the latter are higher in energy by 42 to 58 and 54 to 92 kJ/mol, respectively (12,22,23). Moreover, cyclopropenylienes (**1**) feature a large singlet-triplet energy gap: 191 kJ/mol for **1a** and 249 kJ/mol for the simplest amino-substituted derivative **1b** (24), which should prevent the dimerization (25–27) and subsequent polymerization. Although the gap value calculated for **1b** is smaller than for Arduengo's carbenes **A** (28) and **B** (29) (Fig. 2) [351 and 288 kJ/mol (30), respectively], it is comparable to that of the very stable Alder's carbene **C** (31) [242 kJ/mol (30)] and much larger than that of the first isolated carbene **D** (32) [113 kJ/mol (33)].

These calculations suggest that cyclopropenylienes might be isolable in the laboratory and have prompted us to challenge the discouraging experimental results described so far. Here we report the preparation and single-crystal x-ray diffraction study of bis(diisopropylamino) cyclopropenyliene **1c**. This compound is stable at room temperature even without stabilization of the carbene center by adjacent  $\pi$ -donor hetero-atoms, a necessary criterion for previously isolated carbenes.

Besides the photolysis and thermolysis of diazo derivatives, deprotonation of the conjugate acid of carbenes is by far the most popular method to generate singlet carbenes (4–9). A major advantage of deprotonation is its rapidity, even at low temperatures, so that carbenes that are only moderately stable can still be characterized. Moreover, for cyclopropenylienes, the conjugate acids, namely the cyclopropenium salts (**4**) (Fig. 1), are available in large quantities, thermally very stable, and easy to handle (14). The bis(diisopropylamino) derivative **4c** is even insensitive to water (34). In order to monitor the possible formation of the desired cyclopropenyliene **1c**, we calculated its <sup>13</sup>C nuclear magnetic resonance (NMR) spectrum (24). The carbene carbon and the two other ring carbons were predicted to give signals at 189 and 157 parts per million (ppm), respectively, distinct from the resonances of other compounds in the reaction mixture.

Dry diethyl ether was slowly added at –78°C to an equimolar mixture of cyclopropenium tetraphenylborate **4c** (X = BPh<sub>4</sub>) and potassium bis(trimethylsilyl)amide (35). After the mixture was stirred for half an hour at –78°C, the <sup>13</sup>C NMR signals at 99 and 133 ppm corresponding to the ring carbons of the starting cyclopropenium salt **4c** were absent, whereas new signals appeared at 185 and 159 ppm, in the range predicted for **1c**. These signals persisted when the solution was warmed to room temperature. After evaporation of diethyl ether under vacuum, dry hexane was added and the resulting suspension was stirred for 10 min. After filtration to remove potassium tetraphenylborate, the bright yellow solution was stored overnight at –20°C under an argon atmosphere, affording **1c** as yellow crystals in 20% yield.

In solution, dynamic <sup>1</sup>H and <sup>13</sup>C NMR behavior was observed for **1c**, corresponding to the exchange of isopropyl group environments. The CH resonances are broad at room temperature, but split to reveal two types of *i*-Pr groups at –30°C. The CH peaks coalesce at about –20°C and +10°C, in the <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra, respectively, corresponding to a free energy of activation for site exchange of about 53 kJ/mol. A major part of this exchange process must involve rotation about the N-C<sub>ring</sub> bonds, which suggests, as expected, a  $\pi$  donation from the amino groups to the electron-deficient ring. However, this donation is weaker

than in the starting material **4c**, for which the coalescence temperature in  $^1\text{H}$  NMR is about  $85^\circ\text{C}$ , which corresponds to a free energy of activation of about of 75 kJ/mol.

In the solid state, the ring and the amino groups of both the cyclopropenylidene **1c** and cationic precursor **4c** are nearly coplanar (Fig. 3), confirming the interaction of the nitrogen lone pairs with the  $\pi$  system of the ring. However, it is again apparent that this interaction is less intense for carbene **1c** than for the cationic precursor **4c**. Compared to **4c**, the CN bond distances (**1c**, 1.334; **4c**, 1.305 Å), as well as the bonds flanking the carbene center, are longer (**1c**, 1.404; **4c**, 1.359 Å), whereas the formally CC double bond is shorter (**1c**, 1.344; **4c**, 1.406 Å). The geometric parameters of the ring in the isolated cyclopropenylidene derivative **1c** are very close to those calculated for the parent compound **1a** (Fig. 4).

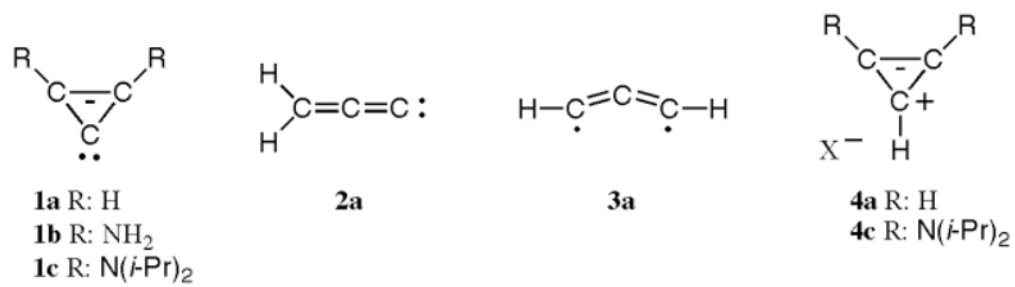
Although **1c** is sensitive to air, it is thermally very stable. Heating a toluene solution of **1c** at  $80^\circ\text{C}$  for 2 hours resulted in only  $\sim 10\%$  decomposition. Compound **1c** has a melting point of  $107^\circ$  to  $109^\circ\text{C}$ , and the NMR spectra of the melt indicate little if any decomposition.

Almost 50 years after the seminal discovery by Breslow (36) that cyclopropenium salts were stable at room temperature, cyclopropenylidene **1c** is a neutral analog of these classical  $2\pi$ -Huckel aromatic compounds. Stable cyclopropenylidenes might serve as models for a better understanding of the formation of carbon-bearing molecules in the interstellar medium. Moreover, the isolation of this molecule paves the way for the discovery of stable versions of other interstellar species previously thought to be unisolable under normal laboratory conditions.

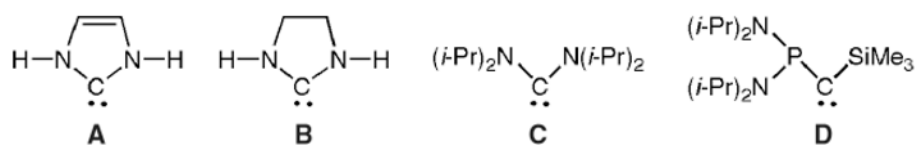
## References and Notes

1. Moss, RA.; Platz, MS.; Jones, M., Jr, editors. *Reactive Intermediate Chemistry*. Wiley; New York: 2004.
2. Brinker, UH., editor. *Advances in Carbene Chemistry*. JAI; Greenwich, CT: 2001.
3. Itoh T, Nakata Y, Hirai K, Tomioka H. *J Am Chem Soc* 2006;128:957. [PubMed: 16417387]
4. Hahn FE. *Angew Chem Int Ed Engl* 2006;45:1348. [PubMed: 16447297]
5. Alder RW, et al. *Angew Chem Int Ed Engl* 2004;43:5896. [PubMed: 15457494]
6. Bourissou D, Guerret O, Gabbai FP, Bertrand G. *Chem Rev* 2000;100:39. [PubMed: 11749234]
7. Peris E, Crabtree RH. *Coord Chem Rev* 2004;248:2239.
8. Scott NM, Nolan SP. *Eur J Inorg Chem* 2005;2005:1815.
9. Kirmse W. *Angew Chem Int Ed Engl* 2004;43:1767. [PubMed: 15054777]
10. Thaddeus P, Vrtilek JM, Gottlieb CA. *Astrophys J* 1985;299:L63.
11. Kaiser RI. *Chem Rev* 2002;102:1309. [PubMed: 11996539]
12. Taatjes CA, et al. *Phys Chem Chem Phys* 2005;7:806.
13. Reisenauer HP, Maier G, Riemann A, Hoffmann RW. *Angew Chem Int Ed Engl* 1984;23:641.
14. Komatsu K, Kitagawa K. *Chem Rev* 2003;103:1371. [PubMed: 12683786]
15. Yoshida Z. *Pure Appl Chem* 1982;54:1059.
16. Weiss R, Priesner C, Wolf H. *Angew Chem Int Ed Engl* 1978;17:446.
17. Weiss R, Hertel M, Wolf H. *Angew Chem Int Ed Engl* 1979;18:473.
18. Tamm M, Grzegorzewski A, Hahn FE. *J Organomet Chem* 1995;501:309.
19. Schumann H, et al. *Angew Chem Int Ed Engl* 1997;36:2232.
20. Cyclopropenylidene transition metal complexes have been known since 1968 (21), and main group adducts were recently reported (19).
21. Öfele K. *Angew Chem Int Ed Engl* 1968;7:950.
22. Patterson EV, Stanton JF, McMahon RJ. *J Am Chem Soc* 1997;119:5847.
23. Maier G, Preiss T, Reisenauer HP, Hess BA Jr, Schaad LJ. *J Am Chem Soc* 1994;116:2014.

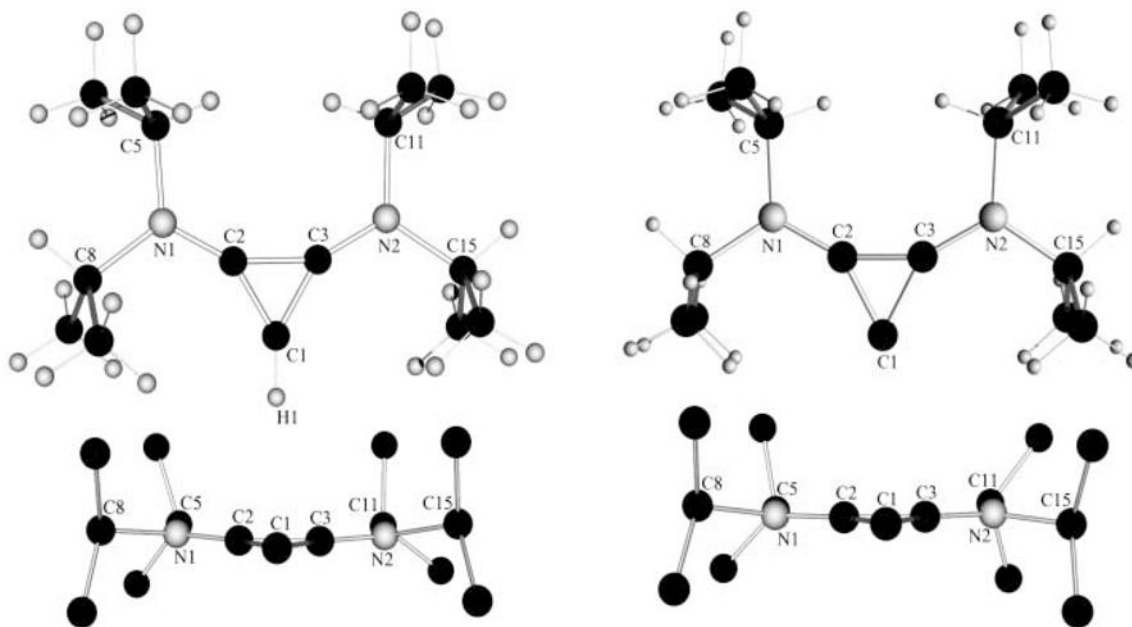
24. The singlet-triplet energy gap and the  $^{13}\text{C}$  NMR chemical shifts have been calculated at the RI-BP86/TZVP  $\beta$  ZPE correction level, and RI-BP86/TZVPP//RI-BP86/TZVP level, respectively, using Turbomole 5.7 (see [www.ipc.uni-karlsruhe.de/tch/tch1/turbomole/index.en.html](http://www.ipc.uni-karlsruhe.de/tch/tch1/turbomole/index.en.html) and references cited therein).
25. For discussions on carbene dimerization, see (5) and (26); cyclopropenyliene dimers, namely triafulvalenes, remain unknown (27).
26. Driess M, Grutzmacher H. *Angew Chem Int Ed Engl* 1996;35:828.
27. Halton B. *Eur J Org Chem* 2005;2005:3391.
28. Arduengo AJ III, Harlow RL, Kline M. *J Am Chem Soc* 1991;113:361.
29. Arduengo AJ III, Goerlich J, Marshall W. *J Am Chem Soc* 1995;117:11027.
30. Heinemann C, Thiel W. *Chem Phys Lett* 1994;217:11.
31. Alder RW, Allen PR, Murray M, Orpen AG. *Angew Chem Int Ed Engl* 1996;35:1121.
32. Igau A, Grützmacher H, Baceiredo A, Bertrand G. *J Am Chem Soc* 1988;110:6463.
33. Nyulaszi L, Szieberth D, Reffy J, Veszpremi T. *Theochemistry* 1998;453:91.
34. Weiss R, Priesner C. *Angew Chem Int Ed Engl* 1978;17:445.
35. Preparation methods and spectroscopic data for compounds **1c** and **4c** are available as supporting material on *Science Online*.
36. Breslow R. *J Am Chem Soc* 1957;79:5318.
37. We are grateful to NIH (grant R01 GM 68825) and RHODIA for financial support of this work. Metrical data for the solid-state structures of **1c** and **4c** are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC-602795 and CCDC-602794, respectively.



**Fig. 1.** Cyclopropenylenes **1a** to **1c**, propadienyldiene **2a**, propynylidene **3a**, and cyclopropenium salts **4a** and **4c**.

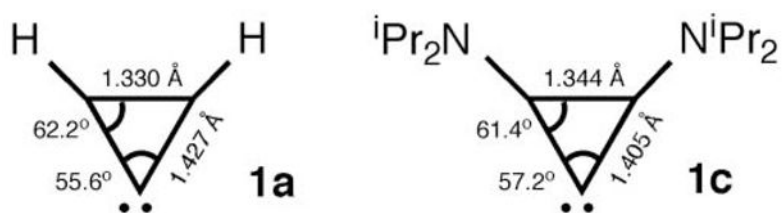


**Fig. 2.**  
Representative singlet carbenes.



**Fig. 3.**

Molecular (ORTEP) views of cyclopropenium tetraphenylborate **4c** (left) and cyclopropenylidene **1c** (right) in the solid state (for clarity, tetraphenylborate anion and H atoms are omitted in the left and bottom images, respectively). **4c**: C1-C2,  $1.360 \pm 3$  Å; C1-C3,  $1.358 \pm 3$  Å; C2-C3,  $1.406 \pm 3$  Å; C2-N1,  $1.305 \pm 3$  Å; C3-N2,  $1.308 \pm 3$  Å; C2-C1-C3,  $62.31^\circ \pm 17^\circ$ ; C1-C2-C3,  $58.79^\circ \pm 16^\circ$ ; C1-C3-C2,  $58.90^\circ \pm 16^\circ$ ; C1-C2-N1,  $148.9^\circ \pm 2^\circ$ ; C3-C2-N1,  $152.2^\circ \pm 2^\circ$ ; C1-C3-N2,  $149.5^\circ \pm 2^\circ$ ; C2-C3-N2,  $151.5^\circ \pm 2^\circ$ ; C2-N1-C8,  $118.2^\circ \pm 2^\circ$ ; C8-N1-C5,  $119.9^\circ \pm 2^\circ$ ; C2-N1-C5,  $121.8^\circ \pm 2^\circ$ ; C3-N2-C11,  $119.6^\circ \pm 2^\circ$ ; C3-N2-C15,  $117.9^\circ \pm 2^\circ$ ; C11-N2-C15,  $121.4^\circ \pm 2^\circ$ . **1c**: C1-C2,  $1.404 \pm 3$  Å; C1-C3,  $1.405 \pm 3$  Å; C2-C3,  $1.344 \pm 3$  Å; C2-N1,  $1.332 \pm 3$  Å; C3-N2,  $1.336 \pm 3$  Å; C2-C1-C3,  $57.19^\circ \pm 16^\circ$ ; C1-C2-C3,  $61.45^\circ \pm 18^\circ$ ; C1-C3-C2,  $61.36^\circ \pm 17^\circ$ ; C1-C2-N1,  $146.7^\circ \pm 2^\circ$ ; C3-C2-N1,  $151.8^\circ \pm 2^\circ$ ; C1-C3-N2,  $146.2^\circ \pm 2^\circ$ ; C2-C3-N2,  $152.4^\circ \pm 2^\circ$ ; C2-N1-C8,  $119.91^\circ \pm 19^\circ$ ; C8-N1-C5,  $119.0^\circ \pm 2^\circ$ ; C2-N1-C5,  $120.66^\circ \pm 19^\circ$ ; C3-N2-C11,  $120.9^\circ \pm 2^\circ$ ; C3-N2-C15,  $119.10^\circ \pm 19^\circ$ ; C11-N2-C15,  $119.94^\circ \pm 19^\circ$ .



**Fig. 4.** Geometric parameters for the cyclic skeleton of the parent compound **1a** (calculated) and derivative **1c** (observed)