Rhomboidal SiC₃

M. C. McCarthy, A. J. Apponi, and P. Thaddeus
Harvard–Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138
Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138

(Received 19 February 1999; accepted 31 March 1999)

During experiments to detect carbon chain molecules in the laboratory, an electrical discharge through a dilute mixture of silane and diacetylene was found to produce a molecule of unusual structure that is composed of only silicon and carbon. On spectroscopic analysis this molecule has been shown to have the elemental formula SiC₃, a closed-shell singlet electronic ground state, and a planar rhomboidal geometry that consists of atoms in the shape of a distorted four-membered ring with a transannular carbon–carbon bond. Rhomboidal SiC₃ is isovalent with rhombic C₄, a long predicted low-lying isomer of C₄ of similar structure which has so far eluded spectroscopic detection. Strong lines of SiC₃ can be observed under a wide range of experimental conditions, suggesting that this molecule is quite stable, and that kinetic and thermodynamic factors favor its formation. Radio emission lines of SiC₃ have now been detected in space in the molecular envelope of the carbon-rich star IRC+10216. © 1999 American Institute of Physics.

Studies of small carbon clusters are motivated by a desire to understand the chemistry of the interstellar medium, the formation of soot in combustion, and the role of small clusters in the formation of fullerenes. Organic molecules, many highly unsaturated and largely of carbon, constitute the great majority of the 123 molecules so far detected in space, but until now only four of these are cyclic in structure. One of the more conspicuous and unusual is the compact ring SiC₂, the carrier of the long known Merrill–Sanford bands in the blue-green spectrum of carbon-rich stars. There is much interest in larger silicon–carbon clusters because of their chemical and astronomical importance, and because they are closely related to pure carbon clusters, often possessing similar structure and chemical bonding, and a similarly rich architecture of linear and cyclic isomers.

Rhombic C₄ is a planar singlet ring that theory predicts is the simplest nonlinear isomer of an even-numbered pure carbon cluster. The small odd-numbered clusters C₃ to C₉ are expected to be cumulenic linear chains with singlet (1Σ⁺) electronic ground states and no low-lying isomers, but the even-numbered clusters C₄ to C₈, are expected to have two nearly isoenergetic low-lying isomers, a triplet (3Σ⁻) linear chain and a singlet (1A₁) ring. Many linear carbon clusters have recently been characterized in the gas phase by high-resolution infrared laser spectroscopy, but despite much effort, cyclic isomers have not been similarly detected. However, indirect evidence for rhombic C₄, and other nonlinear isomers of even-numbered carbon clusters up to C₈, has been obtained from Coulomb explosion experiments from reactivity and mobility studies of carbon cluster ions, and from infrared spectroscopy in argon matrices. SiC₃ is isovalent to C₄, and high-level ab initio calculations by Schaefer and co-workers indicate that SiC₃ possesses similar structure and bonding, with a rhomboidal ground state and a linear triplet isomer lying less than 5 kcal/mol higher in energy. For spectroscopic detection, SiC₃ has the advantage that replacing a carbon atom with silicon breaks the structural symmetry, producing a highly polar molecule with an intense radio spectrum. Indirect evidence for nonlinear isomers of SiC₃ and other small silicon–carbon clusters has recently been obtained from anion photoelectron spectroscopy.

In our Fourier transform microwave (FTM) experiment, silicon–carbon molecules are created by a small low-current cw discharge in the throat of a nozzle as a gas pulse of dilute silane (0.1%) and diacetylene (0.2%) in neon (99.7%) expands from a pulsed valve. Free expansion at the end of the nozzle forms a Mach 2 supersonic beam with a rotational temperature approaching 1 K. As the beam passes through a high-Q Fabry–Perot microwave cavity, a rotational transition is excited by a short pulse of resonant microwave radiation, and line radiation by the coherently rotating molecules is then detected by a sensitive liquid-nitrogen-cooled receiver. The same technique has recently been used to detect the microwave spectra of many new long carbon chain molecules, including linear SiC₆ and SiC₇. A description of the apparatus has been given elsewhere.

Isotopic substitution has established the identity of rhomboidal SiC₃ beyond reasonable doubt, and has provided a precise determination of the length of its individual bonds (Fig. 1). Besides the normal species, lines from five rare isotopic species have also been observed at precisely the expected isotopic shifts. Each line passes the usual chemical and magnetic tests: The carrier of each line is a silicon-containing molecule, none of the lines exhibit a detectable...
Zeeman effect, and each line is only produced in the presence of an electrical discharge. The intensities of lines from the rare isotopic species relative to those of the normal are close to those expected, and lines of the three $^{13}\text{C}$ isotopic species are enhanced when an isotopically enriched sample of $^{12}\text{CO}$ is used. As the energy level diagram in Fig. 2 indicates, for the normal, $^{29}\text{Si}$, $^{30}\text{Si}$, and the single $^{13}\text{C}$ species where $^{13}\text{C}$ is furthest from the Si in Fig. 1, the Bose statistics of the two equivalent off-axis $^{12}\text{C}$ nuclei restrict the observable transitions to those in the $K=0$ rotational ladder. For the remaining two species with $^{13}\text{C}$ substituted for one or both equivalent carbon atoms, lines in the $K=\pm 1$ symmetry allowed, and two additional lines were measured for each species. These additional lines enable all three rotational constants to be determined to high accuracy. Since only small changes in the zero-point vibrational energy are introduced by isotopic substitution, and $\text{SiC}_3$ is a fairly rigid planar molecule with a small inertial defect ($\Delta a=0.06$), the $A$ rotational constant for the four other isotopic species can be inferred with small uncertainty. The rotational constants for the normal species are tabulated in Table I.

![FIG. 1. Experimental structure of rhomboidal $\text{SiC}_3$, a nearly symmetric prolate ($\kappa=-0.945$) top with $C_2v$ symmetry. As discussed in the text, bond lengths were adjusted by a least-squares fit to the lowest frequency transitions of six isotopic species; each is fit to an accuracy of 1%, about the expected agreement when zero-point vibration motions are neglected. Statistical uncertainties in units of the last significant digit are given in parentheses. Adopting the notation for rhombic $C_4$ (Ref. 2), the dashed circle represents the two $\pi$ bonding electrons delocalized over the bicyclic ring.](image1)

![FIG. 2. Energy level diagram of $\text{SiC}_3$ showing lines measured in the normal and in the rare isotopic species. Owing to the $C_3$ symmetry axis, $\text{SiC}_3$ has only $a$-type rotational transitions, and is sufficiently close to the symmetric top limit ($\kappa=-1$) that $K_a$ is a nearly good quantum number, and can accordingly be shortened to $K$. Solid arrows indicate rotational transitions measured in the $K=0$ ladder for all six isotopic species; dashed arrows indicate additional transitions measured in the $K=\pm 1$ ladder for the two $^{13}\text{C}$ isotopic species where one or both equivalent carbon atoms is replaced with $^{12}\text{C}$. Insert: spectrum of the $^{0}_{11}-^{0}_{00}$ rotational transition of $\text{SiC}_3$ at 11 670 MHz, observed with a single gas pulse and an integration time of 0.2 ms. The double-peaked line shape is the result of the Doppler shift of the Mach 2 molecular beam relative to the two traveling waves that compose the confocal mode of the Fabry–Perot.](image2)

![TABLE I. Rotational constants of rhomboidal $\text{SiC}_3$ (in MHz). [Uncertainties (1$\sigma$) are in units of the last significant digit.]](table1)
trations of rhomboidal SiC₃ have been achieved in our molecular beam to yield lines with a signal to noise exceeding 25 in a single 0.2 ms gas pulse. By comparison of line intensities in the beam with those of stable molecules with known fractional abundances [e.g., 1% carbonyl sulfide (OCS) in Ne], the abundance of rhomboidal SiC₃ is calculated to be $3 \times 10^{11}$ molecules per gas pulse—about twice that of the linear triplet isomer of SiC₃, which we have now also detected with the present spectrometer. The correlation of abundance with relative isomeric energies is not surprising, since both isomers have comparable stabilities, and similar trends in isomeric distribution versus stability have been observed for other carbon chains such as C₅H₂.¹⁴ Although entropic arguments favor the formation of linear over cyclic structures at high temperature because of the higher density of states that result from the low bending frequencies, though entropic arguments favor the formation of linear over the rhomboid relative to that of the chain by nearly an order of magnitude, suggesting that the formation of rhomboidal SiC₃ involves kinetic processes with activation or isomerization barriers.

Rhomboidal SiC₃ is a plausible molecule for astronomical detection, because SiC, SiC₂, and SiC₄ have all been detected in at least one astronomical source.¹⁵,¹⁶ The dipole moment of SiC₃ [calculated to be 4.2 D] is intermediate between that of SiC₂ [measured to be 2.39 D¹⁷] and SiC₄ [calculated to be 6.3 D¹⁶]. In a search with the NRAO 12 m telescope on Kitt Peak, seven lines have been found at the expected frequencies in IRC+10216—a sufficient number to be confident on detection and firmly established rhomboidal SiC₃ as the fifth and largest cyclic molecule so far identified in space. A more complete account of these observations will appear elsewhere.¹⁸

By analogy with SiC₂, rhomboidal SiC₃ may also possess strong electronic spectra in the visible or ultraviolet. At the densities at which it is produced in our molecular beam, such spectra may be detectable by standard laser techniques such as laser-induced fluorescence or cavity ring down spectroscopy.¹⁹ Because both the ground state rhomboid and linear triplet SiC₃ can be produced with such high abundance in the gas phase by the technique here, other isomers are also probably detectable. One of the most interesting candidates is a second low-lying oblate rhomboid close in energy to the linear triplet already detected. The lowest rotational transition of this ring are expected to lie near 18 and 30 GHz, both within range of FTM spectrometers like ours. Still larger silicon–carbon clusters analogous to cyclic C₆ and C₈ may be detectable as well.

Fourier transform microwave spectroscopy of molecular beams may prove to be a useful technique to detect and characterize the spectra and structure of pure carbon clusters, even though by symmetry these are generally nonpolar. The combination of high spectral resolution and good sensitivity may enable two types of experiment to be conducted with a spectrometer such as ours: detection of van der Waals complexes of carbon clusters and rare gas atoms, and ¹³C isotopic species of carbon clusters. The Ar–C₄ complex, for example, has many accessible rotational transitions in the microwave band, and lines should be readily detectable even if the complex is present at an abundance of 1% or less of the C₄ isomer. Since the line strength in FTM spectroscopy is proportional to the magnitude of the permanent electric dipole moment $\mu$ rather than $\mu^2$, in principle the rotational spectra of molecules with very small dipole moments can be observed, possibly for example, the ¹³C species of rhombic C₄. Theoretical calculations on complexes such as Ar–C₂ (Ref. 22) will serve as a starting point for laboratory searches.

We thank C. A. Gottlieb, W. Klemperer, J. F. Stanton, and H. F. Schaefer III for helpful discussions.

---


3 D. Zajfman et al., Science 258, 1129 (1992), and references therein.
6 M. T. Bowers, P. R. Kemper, G. von Helden, and P. A. M. van Koppen, Science 260, 1446 (1993), and references therein.