

COMMUNICATIONS

A second rhomboidal isomer of SiC₃

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A second low-lying cyclic isomer of SiC₃ has been detected in a supersonic molecular beam by Fourier transform microwave spectroscopy. Calculated to lie about 5 kcal above the ground state rhomboid, the new isomer is also a planar rhomboid with a transannular bond, C_{2v} symmetry, and a singlet electronic ground state. The transannular bond, however, is between the Si and the opposite C, and the rotational spectrum as a result is that of an oblate, not a prolate, asymmetric rotor. Both rhomboidal isomers of SiC₃ are produced with comparable abundance under a wide range of experimental conditions, which suggests that cyclic isomers of longer silicon carbides may now be observable with the present techniques. Oblate SiC₃ is a plausible molecule for astronomical detection because it is calculated to be fairly polar, and because radio emission lines of the ground state rhomboid have already been detected in the circumstellar shell of the evolved carbon star IRC+ 10216. © 1999 American Institute of Physics. [S0021-9606(99)02840-8]

The recent laboratory^{1,2} and astronomical detection³ of the rhomboidal isomer **I** of SiC₃ shown in Fig. 1(a) suggests that small silicon-carbon rings closely related in structure and bonding to known or postulated carbon clusters are readily produced in supersonic molecular beams and in the interstellar gas. It would be surprising if other rings and chains of similar composition, perhaps significantly larger ones, were not produced in the laboratory and in space as well. Following laboratory detection of **I** (calculated to be the most stable isomer) and a linear triplet chain of SiC₃,⁴ the second ring isomer **II** in Fig. 1(b), calculated to lie only 5 kcal/mol (Ref. 5) above **I** has now been found. Like **I**, this isomer is a singlet planar rhomboid with C_{2v} symmetry, but with a carbon-silicon rather than a carbon-carbon transannular bond. Owing to the transannular bond and the two equivalent off-axis carbon nuclei, the rotational transitions of **II** are those of an oblate asymmetric top ($\kappa = 0.654$) where the values of K_a are restricted by nuclear spin statistics to even integers for the normal isotopic species (i.e., ²⁸SiC₃). The dipole moments of **I** and **II** are calculated by Alberts and co-workers⁵ to be 4.2 D and 2.2 D, respectively.

The rotational spectrum of oblate SiC₃ was detected by Fourier transform microwave (FTM) spectroscopy with the same supersonic molecular beam source recently used to detect **I** and five linear silicon-carbon chains,⁴ two with singlet electronic ground states (SiC₆ and SiC₈), and three with triplet ground states (SiC₃, SiC₅, and SiC₇). The spectrometer now operates from 5 to 43 GHz and is fully computer controlled so that automated scans covering wide frequency bands and requiring many hours of integration are readily conducted. The large mirrors (35 cm in diameter) of the Fabry-Perot cavity and first-stage amplifier can be cooled to the temperature of liquid nitrogen, reducing the system noise temperature to about 200 K and increasing thereby the sen-

sitivity of the spectrometer by nearly a factor of 4. By means of separate antennas tuned externally and independently for microwave drive and signal detection, optimal coupling of radiation into and out of the cavity of the spectrometer is now readily achieved over much of the centimeter-wave band. Efficiency of operation has also been improved by the addition of a gate valve that allows the axially oriented discharge nozzle to be removed and serviced without breaking vacuum, even with the system cold.

Measurements of the normal and six rare isotopic species of SiC₃, observed in natural abundance and with ¹³C enriched samples, provide conclusive evidence for our identification and yield the precise empirical structure in Fig. 1(b). Owing to the compact geometry of **II**, its rotational constants are fairly large, and only a small number of rotational transitions lie within the band of our spectrometer. As Fig. 2 indicates, for the normal, the ²⁹Si, and the ³⁰Si species, and that with a single ¹³C on the symmetry axis, four transitions are accessible in the frequency range of the FTM spectrometer: three in the $K_a = 0$ rotational ladder and one between the low-lying $K_a = 2$ and $K_a = 0$ ladders. These alone enable all three rotational constants to be determined to high accuracy. However, in addition, for the remaining three species with ¹³C substituted for either one or both equivalent carbon atoms or for all three carbon atoms, lines in the $K_a = \pm 1$ ladders are symmetry allowed, and up to four additional lines were measured, allowing an even better determination of the leading centrifugal distortion constants. The measured transitions and derived spectroscopic constants for the seven isotopic species of **II** are given in Tables I and II.

The spectra of those isotopic species with nuclear spin also exhibit small spin-rotation hyperfine structure (hfs) which provides yet further confirmation of the identification. Similar structure was observed in the isotopic spectra of **I**,^{1,2}

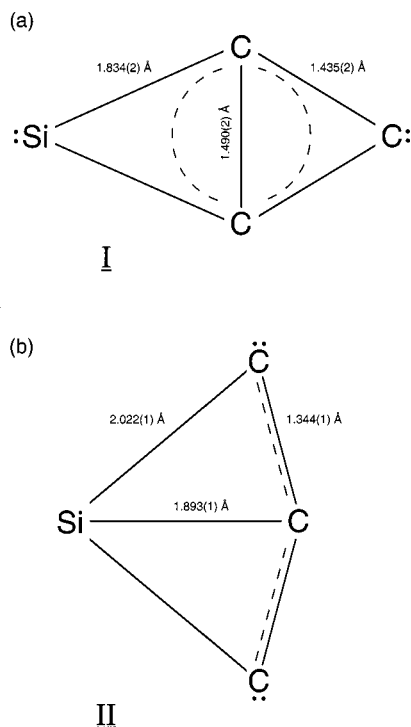


FIG. 1. Two rhomboidal isomers of SiC_3 : the previously discovered ground state **I** and the oblate ring **II** described here, calculated to lie at about 5 kcal higher in energy. Bond lengths of **I** are from Refs. 1 and 2, and those of **II** were adjusted by a least-squares fit to the lowest frequency transitions of seven isotopic species; each is fit to an accuracy of 0.1%, about the expected agreement when zero-point vibration motions are neglected. Statistical uncertainties in units of the last significant digit are given in parentheses. The dashed line represents the two π bonding electrons delocalized along the C_3 unit.

and again the three diagonal elements⁶ of the spin-rotation tensor have been determined to an accuracy of better than 15% for several of the singly substituted ^{13}C and ^{29}Si species and the doubly substituted off-axis ^{13}C species. For the fully ^{13}C substituted ring, fairly complex spin-rotation hfs agrees well with that calculated from the hyperfine constants of the singly substituted ^{13}C species. The hyperfine constants of the rare isotopic species of SiC_3 are summarized in the footnotes to Table II.

The structure of oblate SiC_3 has been obtained by adjusting the three bonds in Fig. 1(b) to reproduce the 33 measured transitions of the seven detected isotopic species, on the assumption of a planar geometry and C_{2v} symmetry. Planarity and rigidity of the ring are established by the small positive inertial defect, 0.075, which is comparable to that of **I** and other planar rings.² Our empirical structure and the theoretical one calculated at the CISD level of theory (see Table III) by Alberts *et al.*⁵ are in good agreement: the peripheral Si–C and C–C bonds differ by less than 0.005 Å in the two structures, and our transannular Si–C bond is only 0.013 Å longer than the one they calculate. The derived bond lengths suggest at least two interpretations of the valence structure of **II**: one with inverted tricoordinate silicon and carbon atoms because each atom is singly bonded with sp^2 hybridized orbitals to the three adjacent ligands on one side of a plane through that atom while maintaining planarity; the other with silicon tightly complexed to the central atom of linear C_3

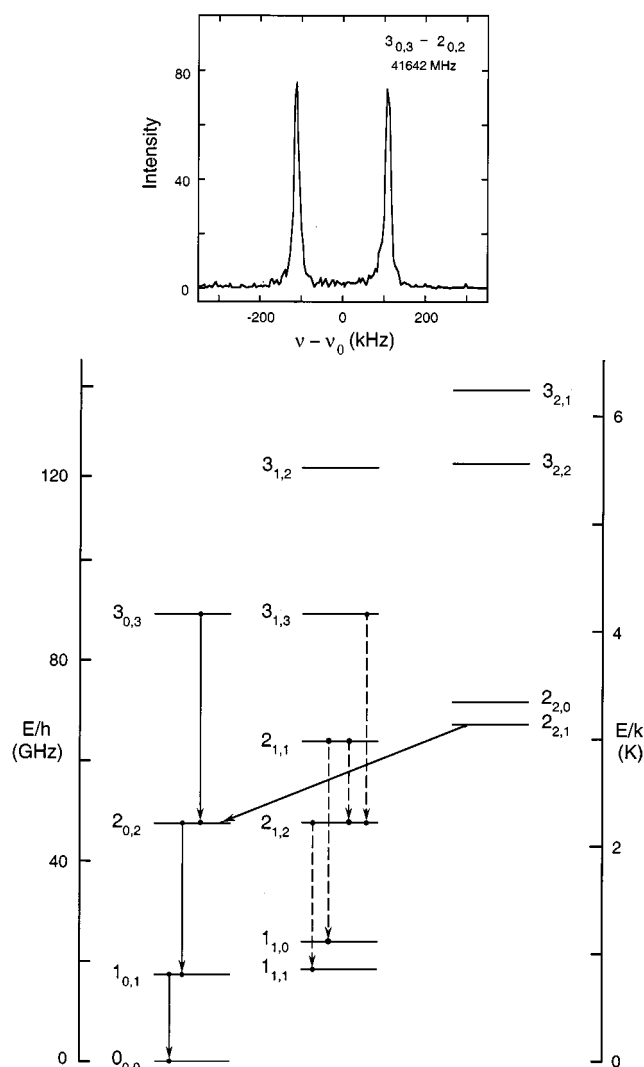


FIG. 2. Energy level diagram of the oblate isomer of SiC_3 , showing lines measured in the normal and in the rare isotopic species. Solid arrows indicate rotational transitions measured in the $K_a=0$ ladder for all seven isotopic species; dashed arrows indicate additional transitions measured in the $K_a=\pm 1$ ladder for the three ^{13}C isotopic species where either one or both equivalent carbon atoms or all three carbon atoms are replaced with ^{13}C . Each line passes the required chemical and magnetic tests: the carrier of each has been shown to contain silicon, none exhibit a detectable Zeeman effect, and each 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}C isotopic species are enhanced when an isotopically enriched sample of ^{13}CO is used. Inset: spectrum of the $3_{0,3}\rightarrow 2_{0,2}$ rotational transition of SiC_3 at 41 642 MHz, observed with an integration time of 5 min. The double-peaked lineshape 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 cavity.

because the peripheral Si–C bond is long (2.022 Å), the C–C bond is short (1.344 Å), and the CCC angle is bent less than 30° from linearity.

As the insert in Fig. 2 shows, high concentrations of the present rhomboidal isomer of SiC_3 have been achieved in our molecular beam. 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 **II** is calculated to be about 1.5×10^{11} molecules/gas pulse, which is about two times less

TABLE I. Microwave transitions of oblate SiC₃ isotopic species.

$J'_{K'_a, K'_c} \rightarrow J_{K_a, K_c}$	SiCC	²⁹ SiCCC	³⁰ SiCCC	SiCC ¹³ C on-axis	Si ¹³ CCC off-axis	Si ¹³ C ¹³ CC off-axis	Si ¹³ C ¹³ C ¹³ C
1 _{0,1} → 0 _{0,0}	17 281.329	17 006.660 ^a	16 749.672	16 994.854 ^a	16 997.449 ^a	16 825.066	16 561.557 ^a
2 _{0,2} → 1 _{0,1}	30 123.863	29 877.904	29 634.740	29 866.285	29 342.950 ^a	28 484.700	28 295.408
3 _{0,3} → 2 _{0,2}	41 641.985	41 256.310	40 893.618	41 239.017	40 638.582	39 656.246	39 288.112
2 _{2,1} → 2 _{0,2}	19 772.882				18 821.481 ^a		
2 _{1,1} → 2 _{1,2}					16 206.799 ^a		
2 _{1,2} → 1 _{1,1}					28 592.391 ^a	28 150.045 ^a	27 777.784 ^a
2 _{1,1} → 1 _{1,0}					39 396.849 ^a	39 149.623 ^a	38 467.881 ^a
3 _{1,3} → 2 _{1,2}					40 554.003	39 640.611	39 248.584

Note: Estimated measurement uncertainty: 2–5 kHz.

^aCentroid of hyperfine split line.

than **I**, but comparable to that of linear triplet SiC₃. Because all three isomers do not differ greatly in stability, it is not surprising that their abundances are comparable. Now that the three lowest energy structures have been identified and characterized, it may be possible to detect other isomers of SiC₃. The next lowest isomer according to theory is a triplet rhomboid similar in structure to **I**, but about 20 kcal/mol higher in energy. Detection of such highly energetic isomers may be possible, because carbon chains or ring-chains lying up to 1 eV above ground have recently been found in our molecular beam by the present technique.⁷

Even larger silicon–carbon rings are good candidates for laboratory detection since lines of carbon chains as long as HC₁₇N have been detected with the present spectrometer. As the theoretical calculations on SiC₃ demonstrate, larger silicon–carbon clusters probably possess a number of low-lying isomers, many of which could probably be found at the present level of detection sensitivity if *ab initio* calculations were available. Such calculations are an extremely useful guide to laboratory searches for new silicon rings because many may have unusual structures and rotational spectra that cannot be accurately predicted from standard Si–C and C–C bonds. Recent high-level calculations⁸ on

SiC₆, for example, might serve as a guide for laboratory searches for a singlet ring isomer with C_{2v} symmetry that is calculated to lie only 5 kcal/mol above the linear chain.

Although the geometrical structure of oblate SiC₃ is now known precisely, additional laboratory data on centrifugal distortion is required to accurately predict the millimeter-wave lines that might best be detected in space. Because **II** is so compact, in the molecule-rich circumstellar shell of the evolved carbon star IRC+10216 [where **I**,³ two closely related silicon–carbon chains, SiC (Ref. 9) and SiC₄,¹⁰ and one ring, SiC₂,¹¹ have been found], the strongest lines of **II** are expected near 150 GHz—well above the frequency of the present measurements. Millimeter-wave spectroscopy of **II**, however, may be possible with the same absorption spectrometer used to study the higher rotational transitions and centrifugal distortion of **I**. With good centrifugal distortion constants, the spectrum could be calculated to high accuracy (i.e., to within a few parts in 10⁷ up to 300 GHz) over the entire range of interest to radio astronomers, and searches at exact frequencies with large radio telescopes might then succeed.

TABLE II. Spectroscopic constants of oblate SiC₃ isotopic species.

Constant ^a	SiCCC	²⁹ SiCCC	³⁰ SiCCC	SiCC ¹³ C on-axis	Si ¹³ CCC off-axis	Si ¹³ C ¹³ CC off-axis	Si ¹³ C ¹³ C ¹³ C
<i>A</i>	12 474.336(1)	12 474.422(7)	12 474.496(7)	12 473.448(7)	12 041.241(1)	11 513.278(4)	11 512.482(4)
<i>B</i>	11 345.140(2)	11 129.953(2)	10 929.390(2)	11 120.744(2)	11 199.958(2)	11 162.583(2)	10 953.461(2)
<i>C</i>	5936.239(1)	5876.756(1)	5820.332(1)	5874.159(1)	5797.5323(7)	5662.537(1)	5608.154(1)
$\Delta_J \times 10^3$	12.36(6)	12.4 ^e	12.4 ^e	12.4 ^e	10.2(1)	11.70(8)	11.51(8)
$\Delta_{JK} \times 10^3$	8.55 ^b	8.55 ^b	8.55 ^b	8.55 ^b	8.55 ^b	8.55 ^b	8.55 ^b
$\delta_J \times 10^3$	4.66 ^c	4.66 ^c	4.66 ^c	4.66 ^c	4.66(8)	4.66 ^c	4.66 ^c
$\delta_K \times 10^3$	11.9 ^c	11.9 ^c	11.9 ^c	11.9 ^c	11.9(3)	26.6(5)	27.0(5)
Inertial defect (amu Å ²):							
Δ	0.075	0.076	0.077	0.073	0.0774(1)	0.080	0.078
Kappa: ^d							
κ	0.654	0.592	0.536	0.590	0.731	0.880	0.811

^aRotational and centrifugal distortion constants (in MHz) derived in *I'* representation. Hyperfine tensor elements (in kHz) are $N_{aa} = 19(2)$, $N_{bb} = 23(2)$, and $N_{cc} = 8(1)$ for the off-axis ¹³C species; $N_{bb} + N_{cc} = -13(2)$ for the ²⁹Si species; $N_{bb} + N_{cc} = 8(2)$ for the on-axis ¹³C species; and $N_{bb} = 25(2)$ and $N_{cc} = 8(2)$ assuming $N_{aa} = 18$ for doubly substituted off-axis ¹³C species. Uncertainties (1 σ) for all constants are in units of the last significant digit.

^bConstrained to value of **I**, see Ref. 2.

^cConstrained to value of the off-axis ¹³C isotopic species.

^dRay's asymmetry parameter.

^eConstrained to value of the normal isotopic species.

TABLE III. Oblate SiC₃ structure.

Bond lengths (Å)	Experimental r_0^a	Theoretical CISD ^b
$r(\text{Si}-\text{C}_1)$ peripheral	2.022(1)	2.018
$r(\text{C}_1-\text{C}_2)$	1.344(1)	1.344
$r(\text{Si}-\text{C}_2)$ transannular	1.893(1)	1.880

^aStructure that best reproduces the observed rotational transitions of the seven isotopic species. Uncertainties in the last significant digit are given in parentheses.

^bFrom Ref. 5.

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