

Silicon-Carbon Double Bond: Theory Takes a Round

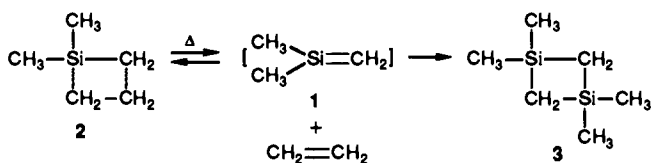
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Abstract: Six *b*-dipole rotational transitions have been observed between 8 and 9.2 GHz for the transient species 1,1-dimethylsilaethylene (DMSE) produced by thermal decomposition of 1,1-dimethylsilacyclobutane at ~ 1000 °C. The Si=C and C—C bond lengths determined from these observations are in excellent agreement with theoretical predictions [*Acc. Chem. Res.* **1982**, *15*, 283]. Analysis of the quartet fine structure from internal rotation gives a barrier $V_3 = 1004$ (17) cal/mol, a methyl top moment of inertia $I_a = 3.18$ (5) $\mu\text{Å}^2$, and a top axis to *b*-axis angle $\theta = 55.6$ (1)°. The fit of the line centers with a rigid-rotor model finds *A*, *B*, and *C* rotational constants to be 6037.93, 5896.78, and 3093.70 MHz, respectively. The heavy-atom effective structure determined from these parameters is $r_e(\text{Si}=\text{C}) = 1.692$ (3) Å, $r_e(\text{C}—\text{Si}) = 1.868$ (3) Å, and $\angle(\text{C}—\text{Si}—\text{C}) = 111.4$ (2)°. The methyl groups do not appear to be tilted appreciably; however, the observed $\angle(\text{C}—\text{Si}—\text{C})$ is 2.3° smaller than predicted. The furnaces and procedures developed for the formation and observation of DMSE are described. They are applicable to other transient and reactive species.

The title of this paper stems from a lively review a few years ago by Schaefer,¹ entitled "The Silicon-Carbon Double Bond: A Healthy Rivalry between Theory and Experiment". The concluding remarks distill the flavor of the rivalry, "...on three questions for which there appear (at present) to be striking conflicts between theory and experiment. Although we suspect that theory is correct in all three cases, these apparent discrepancies will... be ultimately adjudicated by new and definitive experiments."

The question we address here is the length of the Si=C double bond in 1,1-dimethylsilaethylene (DMSE, **1**) which is a short-lived intermediate produced by thermal decomposition of 1,1-dimethylsilacyclobutane (DMSCB, **2**).² In turn, the DMSE dimerizes very rapidly to the stable species 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB, **3**). The high reactivity of DMSE and of other small silaolefins has made their experimental study a difficult challenge.



Perhaps because of this limitation, the silaethylenes became a popular target in the mid 1970s for theoretical predictions of the Si=C double bond length. The predictions quickly ranged from 1.63 to 1.75 Å, converging on 1.692 Å at the time of Schaefer's review.¹ Just prior to that review, Mahaffy et al.³ ventured to determine the heavy-atom structure of DMSE by electron diffraction (ED) from the decomposition products of DMSCB. The ED study led to an approximate value of 1.83 (4) Å for the Si=C bond length, the main problem being the accurate separation of the electron scattering by DMSE from that by the other species in the beam from the pyrolysis.

The large discrepancy between the theoretical value of 1.692 Å for $r_e(\text{Si}=\text{C})$ and the ED value of 1.83 (4) Å encouraged further experimental work on the problem. Two X-ray crystallographic studies have since been reported of solid, highly substituted silaethylenes stable at room temperature.^{4,5} Also, we were challenged⁶ into trying for a microwave determination of the rotational

spectrum of DMSE as the traditional method of an accurate structure of a volatile, small, stable, polar molecule. A preliminary account has been given of the furnace and techniques used to produce and observe the microwave spectrum of transient species.⁷ The results obtained for DMSE are in excellent accord with the theoretically predicted structure. Details of the study and a much more complete analysis of the spectrum are given below.

Experimental Section

Microwave spectroscopy has been used somewhat sparingly to characterize transient species with lifetimes the order of seconds or longer. Heated waveguide cells have been used for species present at thermal equilibrium in a static system at high enough concentrations. An example of this is the observation by Legon's group⁸ of gaseous $\text{NH}_3\text{—HCl}$ dimer in equilibrium with solid NH_4Cl at 200 °C. High-temperature flow systems have been employed to generate species by thermal decomposition. Chloroketene ($\text{ClHC}=\text{C}=\text{O}$) was produced by flow pyrolysis of monochloroacetyl chloride ($\text{CCH}_2\text{ClCOCl}$) in a 10-cm quartz tube at 700 °C.⁹ It was observed by passing the decomposition products through the 2-m conventional cell of the spectrometer. A flow-system approach, also used in the electron diffraction study,³ seemed applicable to DMSE. However, its high reactivity led us to seek a design minimizing transit time and reaction opportunity between furnace and detection.

Fortunately, the spectrometer available for the study lent itself to adaptation for the purpose. It is the Mark II, Balle-Flygare Fourier transform spectrometer¹⁰ with a pulsed supersonic nozzle as the sample source. The basic design and characteristics have been reported¹¹ as have a number of modifications to improve sensitivity, reliability, and ease of operation.¹² Ordinarily, the spectrometer is used to produce weakly bonded dimers and small clusters and determine their rotational spectra.

In the operation, a carrier gas such as Ar or "first run" neon (a 70/30 Ne/He mixture) at ~ 1 or 1.5 atm is seeded with 1 or 2% of cluster-forming species. The gas mixture is pulsed into an evacuated Fabry-Perot cavity by a supersonic nozzle (1-mm diameter). The valve operates at a frequency of 30 Hz, giving gas pulses 2 ms in length. As the gas expands, it cools to a rotational temperature of ~ 3 K and small clusters form. Each gas pulse is excited during the expansion by a train of 20 0.2- μs microwave pulses at the frequency to which the cavity is tuned. The free induction decays (FID's) after the microwave pulses are digitized, averaged, and accumulated.¹² Finally the Fourier transform of the accumulated FID gives the signal in the frequency domain from the expanding gas at frequencies within ± 0.5 MHz of the excitation frequency.

Placement of a furnace in the gas path *before* the pulsed valve inevitably lengthens the time between formation of pyrolysis products and

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(6) H.S.G. is indebted to Robb Gutowsky who called this problem to his attention.

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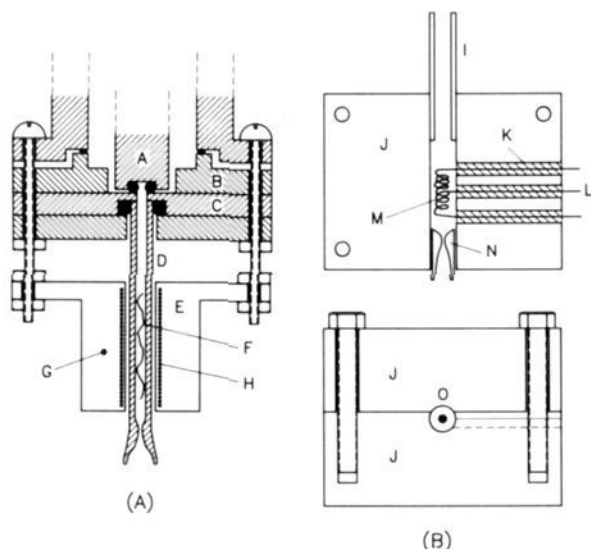


Figure 1. Heated nozzle extensions developed to generate DMSE by thermal decomposition of DMSCB at 1000 °C.

their observation in the Fabry-Perot cavity. Furthermore, it requires that the valve operate reliably at the high pyrolysis temperatures employed. Because of these considerations and after some experimentation, the strategy was adopted of making the furnace a down-stream extension of the pulsed valve. Two different versions of this approach were tried, with comparable results in the flash pyrolysis of DMSCB. Sketches of both are shown in Figure 1.

The first, in Figure 1A, is a cylindrical zone furnace (E) built by embedding a coil (H) (3.2-mm i.d.) of 18-gauge (0.127 mm) Pt wire in moldable alumina (Zircar Products Inc.). A thermocouple (G) was inserted close to the Pt coil but electrically insulated from it. A disk of alumina (1 1/4 in. diameter) was cemented to this structure for support and to serve as a platform for attachment of leads to the heating coil and thermocouple.

A 3-cm length of 1.7-mm-i.d. quartz tube (D) passes through the bore of the furnace and is held in place by an O-ring seal on the bottom of the pulsed valve (A, B, C) (General Valve No. 8-1-900). The exit end of this extension has a constriction (0.7-mm i.d.) followed by a Laval-type nozzle. The signal from DMSE was improved somewhat by placing an irregularly twisted piece of Nichrome wire (F) inside the hot area of the quartz tube. Presumably the wire spoils laminar flow of the gas in the tube and enhances heat transfer to the gas.

The second, more modular furnace is shown in Figure 1B. Two blocks of aluminum (J) (1 × 3/4 × 1/2 in.) were bolted together by the largest faces. A 1/8 in.-diameter hole (O) was drilled along the shorter axis of their boundary. The center of the hole is displaced about 1 mm from the boundary. Thus, when separated, one of the blocks has a shallow channel (about 120°) and the other a deep channel (about 240°). The block with the deeper channel then had three parallel grooves (K) (2 × 2 mm) milled from the channel to the side of the block. A Pt coil (M) (18-gauge wire) was mounted in the channel with the leads held in the outer two of the lateral grooves with alumina cement. A thermocouple (L) made from 50-μm Chromel and Alumel wires was cemented in the middle groove with the junction at the Pt coil.

A brass tube (I) was plugged into the upper end of the channel, and a small, machined aluminum Laval-type nozzle (N) was plugged into the outer end. The two aluminum blocks were then rebolted together. No gaskets were necessary because of the close-fitting parts. The extension of the brass tube (I) was then plugged into the bottom of the pulsed valve.

A range of operating parameters was tried with remarkably small changes in DMSE signal strength. For both of the pyrolysis schemes, the best signal was obtained with a 0.7-mm orifice and a Laval nozzle. In the modular source, Figure 1B, different sizes of heater coils were tested. The effect on the signal was not dramatic, but the best signal was found when using a very small coil (1-mm diameter, 2 mm long) immediately before the expansion nozzle.

The actual signal strengths obtained for DMSE were uncommonly weak for a covalently bonded species with a large dipole moment, estimated below to be ~1.9 D. Much stronger signals were found for other transient species prepared with the same pyrolysis nozzles. This, for example, was the case with chloroketene produced from monochloroacetyl chloride.⁹ It shows that the transient species is cooled adequately in its expansion with the carrier gas and that the extent of pyrolysis of

Table I. Rotational Constants (MHz) Predicted for the Theoretical and Electron Diffraction Structures of DMSE Compared with Those Observed

source	A	B	C	trans type
DZ+d SCF ¹	6026.11	5843.10	3078.58	<i>b</i> -dipole
electron diffraction ³	5843.10	5584.07	2958.92	<i>a</i> -dipole
microwave ^a	6037.93	5896.78	3093.70	<i>b</i> -dipole

^aRigid-rotor constants from fitting line centers in Table II.

the precursor is high in spite of the short exposure to the furnace. Therefore, the weak signal for DMSE must be due to its high rate of dimerization (a fast second-order process) in the short interval of perhaps 0.1 ms between pyrolysis and the jet expansion.

Results and Analysis

Transitions and Their Identification. The rotational spectrum of the DMSCB precursor apparently has not been reported. Therefore, the first step in our experiments was to identify a strong transition of DMSCB that could be used to monitor its thermal decomposition. An approximate spectrum was predicted from known structures of related molecules and guided the search to a series of three transitions, at 8889.2, 8896.1, and 8903.0 MHz. Each transition has several components extending over ~0.5 MHz, caused probably by internal rotation of the two nonequivalent methyl groups and perhaps perturbed further by the ring inversion. The strongest transition, at 8903 MHz, is most likely the $1_{01} \rightarrow 2_{12}$ *b*-dipole transition. It was used as the monitor.

The search for transitions of DMSE was straightforward. The 8903-MHz precursor transition was observed as the heater current was turned up. When operation of the furnace reduced the DMSCB transition to about one-tenth of its unheated intensity, the spectrometer was retuned to search for DMSE transitions. This corresponded to a furnace temperature of about 1000 °C, depending upon the configuration of the furnace and the operating pressure of the pulsed nozzle. Rotational spectra were predicted for the theoretically calculated structure¹ (T) and also for an "electron diffraction" structure³ (ED) differing only in having a longer Si=C double bond length of 1.815 Å instead of 1.692 Å. The rotational constants predicted for the two alternatives are given in Table I. It is seen that DMSE is an oblate, near-symmetric top with the Si=C bond an *a*-dipole axis for the ED structure and *b*-dipole for the T.

Two other features of DMSE have significant effects upon the rotational spectrum, its dipole moment μ and the three-fold barrier V_3 to internal rotation of the two methyl groups. The dipole moment of course determines the intensity of the rotational transitions. Because of symmetry, the dipole moment in DMSE lies along the Si=C axis. In isobutylene, $\mu = 0.50$ D along the C=C axis,¹³ while for DMSE we estimate a larger value of 1.86 D. This comes from a bond moment approach using an ab initio calculated moment of 1.05 D for SiH₂=CH₂.² From this and the decomposition kinetics,² we predicted the DMSE transitions to be readily detectable.

The V_3 barrier is 2170 cal/mol in isobutylene,^{14,15} while that in propane is 3290 cal/mol.¹⁶ These data enabled us to scale the 1645 cal/mol barrier reported for dimethylsilane¹⁷ to predict a barrier of ~1100 cal/mol in DMSE. The hindered rotation of two equivalent methyl groups in a C_{2v} molecule splits the rotational transitions into three or four resolvable components¹⁸ with splittings depending upon V_3 , I_{ax} , and θ , where I_{ax} is the methyl group moment of inertia about the top's axis and θ is here the angle between the top axis and the *b*-axis (inertial frame). The 1100 cal/mol barrier predicted for DMSE is intermediate between those of isobutylene (2170 cal/mol)^{14,15} and of acetone (780 cal/mol).¹⁸ A comparison of the fine structure observed for them led us to expect DMSE

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transitions at low J to have four components with relative intensities of approximately 1/2/0.5/0.5 spread over 3–10 MHz.¹⁸

With these points in mind and for convenience in monitoring the DMSCB, the search for DMSE was made in the 8–10-GHz region where several low- J transitions were predicted for both the T and ED structures. Three transitions were found with the expected fine structure, centered at approximately 8228, 8416, and 9131 MHz. They disappear when the furnace is turned down. It proved possible to assign them on the basis of the spectrum predicted for the T rotational constants. The assignments were used to refine the rotational constants and obtain a more accurate prediction of additional transitions. By means of the latter, three more transitions were readily found, at 8004, 8831, and 9047 MHz. The six transitions are readily assigned as b -dipole (T structure), but attempts to assign them as a -dipole (ED structure) were unsuccessful.

Although the gases are heated to 1000 °C in the nozzle, the transitions are for the ground torsional state because of the extreme cooling the gases experience in the supersonic jet expansion. With nozzle and input gases at ambient temperature, the expanded gases have a rotational temperature of ~ 3 K.¹⁹

Internal Rotation and Rotational Constants. Analysis of the fine structure caused by the internal rotation is necessary to estimate the line centers more accurately and to find better values for the rotational constants. It also enables one to evaluate V_3 , I_a , and θ , the latter two providing relevant structural information. Numerous papers have dealt with the complexities of hindered rotation of two equivalent, interacting methyl groups. As an aid in applying them to DMSE we reexamined isobutylene, the carbon analogue, and our procedures here are very similar to those we utilized for it.¹⁵

For most transitions of DMSE, we found four components, as theoretically predicted for intermediate barrier cases.¹⁸ These are generally given symmetry labels A_1A_1 , EE, A_1E , and EA_1 with intensities of approximately 1/2/0.5/0.5 determined by the spin statistics of the protons. In our initial experiments,⁷ some of the outer components were missed. Also, a weak component reported at 8003.202 MHz is from something else, perhaps the ²⁹Si species. Assignment and fitting of the fine structure were accomplished in several stages by employing a computer program (KC3IAM). The program was developed by Kosten²⁰ from a variation²¹ on Woods' elegant analysis of a single top by the internal axis method.²²

A partial assignment of the initial data⁷ for the fine structure, based on intensities, gave approximate values for V_3 , I_a , and θ . These, with the approximate rotational constants, predicted the fine structure quite accurately. With that in hand, additional experiments enabled us to refine our measurements with the results given in Table II. The observed splittings were fitted to obtain the final values for V_3 , I_a , and θ as shown in Table II. In the fitting, the program calculates the fine structure components with respect to a rigid rotor line center. Comparison of the frequencies for calculated and observed components locates the actual, unperturbed line centers, also given in Table II. The line centers were fitted to a rigid-rotor model to obtain the experimental rotational constants given in Table I. The $3_{12} \rightarrow 3_{31}$ transition was not included in either fit. Its location at ~ 8227.5 MHz is a bit far from the line center predicted for it (8226.75 MHz) by the fit of the other five line centers, and its fine structure is off more than usual, a not uncommon occurrence. The poor fit of this transition may reflect sensitivity of the approximations in the theory to the near symmetric top character of DMSE.

Effective Structure. The experimentally determined microwave rotational constants are compared in Table I with those calculated for the theoretical (T) and the electron diffraction (ED) structures. For the latter, we used the theoretical structure¹ except for r -(Si=C), where we employed 1.815 Å. This was reduced from the reported electron diffraction r_g (Si=C) value of 1.83 (4) Å

Table II. Rotational Properties of DMSE: Observed and Fitted Internal Rotation Splittings, Line Centers, and Internal Rotation Parameters^a

transition	obsd freq ^b (MHz)	splitting ^c (MHz)	Δ^d (kHz)
$0_{00} \rightarrow 1_{11}$	9133.565		
	31.892	1.673	6
	30.658	2.907	29
	29.760	3.805	16
	(9131.632)		0)
$2_{02} \rightarrow 2_{11}$	8417.467		
	5.662	1.805	-119
	3.286	4.181	212
	(8414.718)		293)
$2_{12} \rightarrow 2_{21}$	8838.492		
	33.588	4.904	-47
	29.922	8.570	-53
	27.380	11.112	-134
	(8832.8745)		198)
$3_{12} \rightarrow 3_{31}^e$	8228.486		
	7.761		
	6.010		
$3_{22} \rightarrow 3_{31}$	9054.588		
	47.671	6.917	63
	43.514	11.074	36
	37.845	16.743	33
	(9047.339)		-255)
$4_{22} \rightarrow 4_{31}$	8002.755		
	2.755	0	1
	2.586	0.169	31
	3.592	-0.837	-87
	(8002.487)		-238)

^a $V_3 = 1004$ (17) cal/mol, $I_a = 3.18$ (5) $\mu\text{Å}^2$, and $2\theta = 111.2$ (2)°. ^b Fine structure listed in order A_1A_1 , EE, A_1E , and EA_1 . Frequency and Δ in parentheses are for the approximate line center. ^c The splitting is with respect to the A_1A_1 component. ^d $\Delta = \text{obsd} - \text{calcd}$ frequency in fitting the splittings and the line centers. Rotational constants from fitting the line centers are given in Table I. ^e Not included in the fitting. See text.

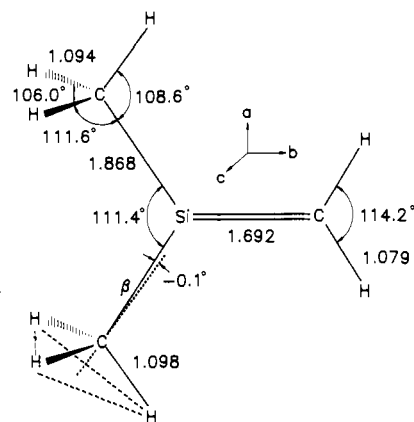


Figure 2. Effective (r_e) structure determined for the heavy atoms in DMSE. Positions of the methyl group hydrogens are taken from isobutylene and the ethylenic hydrogens from the theoretical predictions. The methyl group tilt is exaggerated for visibility.

to allow for possible high-temperature vibrational effects. It is seen that the experimental microwave rotational constants are much larger than the ED predictions, averaging 215 MHz greater. The microwave results are also larger than the T predictions but by a much smaller average of 27 MHz. In fact, the agreement is as good as the fit of the microwave rotational constants for isobutylene by its substitution structure, the latter predicting constants larger than observed.¹⁵ So it is clear that DMSE has a "short" Si=C double bond length and the question now is how short.

Although the C_{2v} symmetry of DMSE reduces its independent structural parameters to 10 (Figure 2), a complete structure determination is beyond our scope. Seven isotopic species were used^{13,23} for isobutylene. We could observe the ²⁹Si species of

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DMSE at natural abundance; however, the Si is very close to the center of mass and would give little or no additional, reliable information.¹⁵ Fortunately, the rotational constants of DMSE are determined largely by the structure of the heavy-atom skeleton, $C_2Si=C$, which has only three independent parameters, $r(C-Si)$, $r(Si=C)$ and $\angle(C-Si-C)$. Therefore, our overall strategy is to make the most of the data most readily obtained.

For isobutylene, the higher barrier leads to unresolvable splittings between the AE and EA fine structure components in low- J transitions. The other splittings are insufficient to obtain independent values for V_3 and I_a . In DMSE, the lower barrier leads to sizeable AE, EA splittings even at low J , for example, 0.9 MHz in the $0_{00} \rightarrow 1_{11}$ transition. Therefore, our fit of the splittings should give a reliable independent result for I_a . The value found is $3.18 (5) \mu\text{Å}^2$, which is the same as that obtained for isobutylene from its internal rotation splittings at higher J .³ The theoretical structure corresponds to a somewhat smaller I_a of $3.09 \mu\text{Å}^2$. It appears therefore that the methyl group structure in DMSE is closer to that of isobutylene than to the theoretical predictions, although the differences are not large.

The moment of inertia of the methyl group about its a -axis (I_a) is established by four parameters, the in-plane and out-of-plane $r(C-H)$'s and the in-plane/out-of-plane and out-of-plane/out-of-plane $\angle(H-C-H)$'s. In this representation, the angle θ between I_a and the overall inertial framework (b -axis) is an independent parameter. If I_a is at an angle to the $C-Si$ (or other $C-M$) bond, i.e., if $\theta \neq \frac{1}{2}\angle(C-Si-C)$, the methyl group is tilted by their difference β (Figure 2), at most 1 or 2° .²⁴ Alternatively, a methyl group and the orientation of its I_a axis can be described by the two $r(C-H)$'s and three angles, the in-plane and out-of-plane $\angle(H-C-Si)$'s and the out-of-plane/out-of-plane $\angle(H-C-H)$. The two structural representations are equivalent, each with five independent parameters. For ease of visualization, we use the first to describe the fitting procedures. However, the theoretical analysis used the latter representation, so for comparison we present our results also in that form but include the corresponding values for β .

In DMSE, if the isobutylene structure (without tilt) is accepted for the methyl groups and the theoretical structure is assumed for the ethylenic protons, the three heavy-atom parameters and the Me tilt remain. In principle, they are determinable by fitting the three observed rotational constants and the I_a to b -axis angle θ of $55.6 (1)^\circ$. However, the near planarity of DMSE reduces the independence of the observed quantities. Therefore, we explored the sensitivity of the fit to the four unknown parameters by holding one or two of them fixed in various ways. The validity of this procedure was tested on isobutylene for which a complete effective structure has been determined.¹⁵ The fitting of the rotational constants was performed with the versatile computer program STRFTQ written and generously provided by R. H. Schwendeman, incorporating the internal molecular coordinate system of Thompson.²⁵

The theoretically predicted structure¹ corresponds to a methyl group tilt of only -0.14° . By neglecting it, the value of $\theta = 55.6^\circ$ determined from the internal rotation fine structure becomes equal to $\frac{1}{2}\angle(C-Si-C) \equiv \gamma$. Imposing this as a condition on the fit, we obtain values of $1.870 (1)$ and $1.689 (1) \text{ Å}$ for $r_o(C-Si)$ and $r_o(Si=C)$. A check on the smallness of the tilt was made in a second fit where γ as well as the two r_o 's were adjusted but θ was held constant at the observed 55.6° . This led to $\gamma = 55.68^\circ$, giving the tilt ($\theta - \gamma$) to be -0.08° . Slightly different values, 1.868 and 1.692 Å , were found for the R_o 's. Zero tilt with an adjustable $\gamma = \theta$ gave the angles to be 55.74° and also had little effect on the r_o 's.

In all of the fits, the three rotational constants were fitted to a σ of $0.057 \mu\text{Å}^2$. In the last two fits, there were large σ 's for the determined parameters, indicating their insensitivity to the

Table III. Comparison of the Structure Theoretically Predicted for DMSE¹ with the Effective Structure Determined for It from the Rotational Spectrum

parameter ^a	theoret predictn	effective struct ^b
$r_o(C-Si)$	1.873	1.868 (3)
$r_o(Si=C)$	1.692	1.692 (3)
$r(C-H_o) \text{ Me}$	1.088	1.094 ^b
$r(C-H_i) \text{ Me}$	1.086	1.098 ^b
$r(C-H) \text{ ethylenic}$	1.079	1.079 ^c
$\angle(C-Si-C)$	113.7	111.4 (4)
$\angle(H-C-H) \text{ ethylenic}$	114.2	114.2 ^c
$\angle(H_o-C-Si) \text{ Me}$	111.5	111.6 ^b
$\angle(H_i-C-Si) \text{ Me}$	110.9	108.6 ^b
$\angle(H_o-C-H_o) \text{ Me}$	107.1	106.0 ^b
$\angle(I_a \text{ and } C-Si \text{ axes}) \text{ tilt, } \beta^d$	-0.14	-0.1

^aDistances are in angstroms and angles in degrees. H_i and H_o are in-plane and out-of-plane Me H's. ^bAssumed to fit experimental I_a ; see text. ^cParameters for the ethylenic H's are assumed to be as theoretically predicted. ^dThe negative tilt indicates that the in-plane H's are rotated away from the double bond (Figure 2).

fit. However, in the first fit, the σ 's for the r_o 's are less than 0.001 Å . This fact and the internal consistency of the results support their accuracy. The effective structural parameters we find for the heavy atoms are $r_o(C-Si) = 1.868 (3) \text{ Å}$, $r_o(Si=C) = 1.692 (3) \text{ Å}$, and $\angle(C-Si-C) = 111.4 (2)^\circ$. Also there appears to be a small methyl group tilt of about -0.1° . The assumed and derived structural parameters are summarized and compared with the theoretical predictions in Table III. The uncertainties of the derived parameters are estimated.

Discussion

It is clearly unambiguous that the species studied is 1,1-dimethylsilaethylene. It is produced by thermal decomposition of DMSCB. The internal rotation fine structure is characteristic of a species with two equivalent methyl groups. The barrier of 1004 cal/mol found for internal rotation is well within the ball park estimated for DMSE. The planar moment $P_c = 3.03 \mu\text{Å}^2$ is characteristic of a species planar except for two methyl groups with C_{2v} symmetry as in Figure 2. The near symmetric top rotational constants are consistent with a heavy-atom $C_2Si=C$ structure. Moreover, the observed rotational constants can be fitted quite accurately by modest adjustments in the theoretically predicted structure.

This is shown by the comparison in Table I of the experimental rotational constants with those calculated for the theoretical structure, with all of the latter somewhat small. The main difference is in B for which the experimental value is 43.8 MHz larger than predicted. The value of B is determined primarily by the distance from the methyl groups to the b -axis (C_2). To increase B in the fitting, the distance was decreased by reducing $\angle(C-Si-C)$ from 113.7 to $111.4 (2)^\circ$, a relatively large change, and also by shortening $r_o(C-Si)$ from 1.873 to 1.868 Å . The decrease in $r_o(C-Si)$ also puts the methyl group closer to the a -axis, which increases A by the needed 11.8 MHz . Finally, because of the near planarity of DMSE, these increases in A and B also increase C by the 15.1 MHz needed.

In comparing the experimental (r_o) and theoretical equilibrium (r_e) structures, allowance should be made for the effects of zero-point vibrational averaging, which makes $r_o > r_e$. This implies that even though the predicted and experimental values for $r(Si=C)$ are both 1.692 Å , the experimental value is actually a bit smaller than that predicted. Similarly the experimental value for $r(C-Si)$ is smaller than the theoretical by more than the apparent difference of 0.005 Å in Table III. A more appreciable difference between theory and experiment is found for the $\angle(C-Si-C)$, where the experimental value of 111.4° is 2.3° smaller than the predicted 113.7° . This seems a bit small in view of the experimental value of 115.6° reported for $\angle(C-C-C)$ in isobutylene.¹⁵ In any event, the r_o values found for the $C-Si$ and $Si=C$ bonds in DMSE are in excellent agreement with the theoretical predictions. Theory has definitely taken this round in

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the stimulating rivalry between theory and experiment.

It is also of interest to compare our result with X-ray crystallographic studies of solid silaethylenes stable at room temperature. The initial X-ray study, by Brook and co-workers,⁴ was of the highly substituted sila enol ether, $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)(1\text{-adamantyl})$. It gave a "long" $\text{Si}=\text{C}$ distance of 1.764 (3) Å. However, the bulky 1-adamantyl substituent noticeably twists the double bond, by 14.6°, and thereby lengthens it.¹ More recently an X-ray structure has been determined by Müller's group⁵ for $\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)(\text{SiMe-}t\text{-Bu}_2)$ in which the substituents are less bulky and less polar, giving a twist about the $\text{Si}=\text{C}$ bond of only 1.6°. In it, the $\text{Si}=\text{C}$ bond length of 1.702 (5) Å is substantially shorter. However, it is still definitely longer than the value of 1.692 (3) Å found for DMSE in the gas phase.

The small angle found for $\angle(\text{C}-\text{Si}-\text{C})$ merits discussion. It comes largely from fitting the internal rotation fine structure, which gives $2\theta = 111.2(2)^\circ$, and from the "large" experimental value for the B rotational constant. In principle, a larger $\angle(\text{C}-\text{Si}-\text{C})$ could be obtained by forcing a large negative methyl group tilt on the fit, decreasing $r_0(\text{Si}=\text{C})$ and increasing $r_0(\text{C}-\text{Si})$. However, both the theoretical structure and the fitting of the DMSE rotational constants give a tilt of only about -0.1° .

The magnitude of the tilt is a measure of the extent to which the inherent C_{3v} symmetry of a methyl group is perturbed in

compounds where it is attached to a less symmetric group.^{21,26} In isobutylene, methyl group tilt of $0.8(2)^\circ$ was found.¹⁵ In DMSE, the methyl groups are farther apart and have only half as large a barrier to internal rotation, so one would expect smaller tilt in it. Indeed this is the case for propane and its silicon analogue. In propane, there apparently is tilt of the methyl groups by 0.8° toward the CH_2 group,²⁷ while in $(\text{CH}_3)_2\text{SiH}_2$ the value of 2θ is the same (111°) as $\angle(\text{C}-\text{Si}-\text{C})$ from the inertial analysis.¹⁷ Such arguments lead us to prefer the effective structure presented in Table III.

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Electronic Structures of Trifluoro-, Tricyano-, and Trinitromethane and Their Conjugate Bases

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Abstract: The electronic structures of CHF_3 , $\text{CH}(\text{CN})_3$, and $\text{CH}(\text{NO}_2)_3$ and their conjugate bases are studied at the HF/6-31G* and HF/6-31++G** levels of theory. Topological features of the electron densities in the systems under study are interpreted within the framework of Bader's theory of atoms in molecules. The observed changes in geometry, the electron densities at the critical points, and the GAPT charges reveal the presence of Y-aromaticity in the $\text{C}(\text{CN})_3^-$ and $\text{C}(\text{NO}_2)_3^-$ anions. Unusual weak bonds between the oxygen atoms belonging to different nitro groups in the $\text{C}(\text{NO}_2)_3^-$ anion are found. Absolute gas-phase acidities (proton affinities of the conjugate bases) are computed. There is no correlation between the acidities and any of the following molecular indices: the length and the stretching force constant of the C-H bond, the topological parameters of the C-H bond point, the Bader and GAPT atomic charges of the hydrogen atoms in the neutral molecules or of the carbon atoms in either neutral molecules or the corresponding anions. The GAPT charges appear to provide a better description of the electron density redistribution upon deprotonation than the Bader ones.

Introduction

Although methane is itself an extremely weak acid, some of its substituted derivatives have acidity comparable to that of inorganic acids. In particular, tricyanomethane (cyanoform) and trinitromethane (nitroform) form salts that are stable in water.¹ The extraordinary stability of the tricyanomethanide (cyanoformide) and trinitromethanide (nitroformide) anions is due to resonance effects. In contrast, the increased acidity of trifluoromethane (fluoroform) arises from the electron-withdrawing character of the fluorine substituent.

The modern quantum-mechanical calculations fare reasonably well in predicting both the gas-phase and in-solvent acidities. Accurate calculations of the absolute gas-phase acidities have become feasible after introduction by Chandrasekhar et al.² of

Gaussian basis sets augmented by diffuse functions. Subsequently, proton affinities of several systems were studied, including, for example, the $\text{CH}_{n-1}\text{X}_{4-n}^-$ ($n = 1-4$, $\text{X} = \text{F}, \text{CN}, \text{NO}_2$)³ and the XH_3^- ($\text{X} = \text{C}, \text{N}, \text{O}, \text{F}, \text{Si}, \text{P}, \text{S}$, and Cl)⁴ series of anions. Monte Carlo simulations utilizing ab initio generated information about molecular structures and potentials were used to calculate the acidities of several organic acids in water.⁵

Despite the important role they play in organic chemistry, relatively little is known about the electronic structures of cyanoform and nitroform and their conjugate bases. In fact, even the gas-phase geometries of $\text{CH}(\text{CN})_3$ ⁶ and $\text{CH}(\text{NO}_2)_3$ ⁷ are known

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