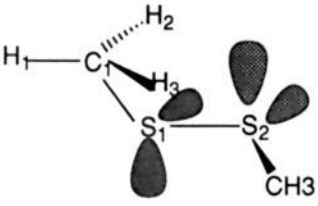
iations of the C–S–S–C dihedral angle associated with amino group charge density changes.

From the IGLO studies of ^{13}C shielding in hydrocarbons[19,21] it has been shown that the most important changes in the total shielding arise from paramagnetic contributions to the localized MO's. To study the origin of the angularly dependent substituent effects, the individual paramagnetic bond contributions (PBC) to the $(CH_3)_2S_2$ ^{13}C shielding from the four localized bonds (C1–S1, C1–H1, C1–H2, and C1–H3 in **1**) on carbon were fit in the least-squares sense to a truncated Fourier series. These PBC are plotted as a function of the dihedral angle ϕ in Figure 4. The paramagnetic bond contributions associated with the C1–S1 bond, which are plotted (open circles) in Figure 4, vary by somewhat more than 1 ppm over the whole range of dihedral angles. The average of the PBC from the C1–H2 and C1–H3 bonds (open squares in Figure 4) is used since this has a periodicity of 180°. These contributions vary by no more than 1 ppm over the whole range. The angularly dependent changes involving the C1–H1 bond (triangles in Figure 4) are most important. The conformational dependence of the C1 methyl shielding in **1** is almost entirely attributable to the paramagnetic bond contributions for the C1–H1 bond, which points away from a lone pair on S2.



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Radom et al. discussed the significance of the various V_i terms in eq 1 for the conformational dependence of the energies.[14] Although there is no obvious reason that the torsional features of the shielding should parallel the energies, in some cases they are similar. For example, the calculated isotropic ^{13}C shielding in ethane is very accurately described by the 3-fold term.[21] This term corresponds to interactions between the C–H bonds, which energetically favor staggered conformations. From eq 3 it can be seen that the ^{13}C isotropic shielding has contributions from the 2-fold term that are slightly larger than those from the 1-fold term. Radom et al.[14] analyzed the 1-fold term as arising from local dipole interactions at the two ends of the molecule. The 2-fold term, which is ascribed to interactions (back-donation) between lone pairs and bond pairs, is the dominant factor leading to the skew conformation of $(CH_3)_2S_2$. The back-donation of an S2 lone pairs to a bond pair on C1 might explain why paramagnetic bond contributions from the C1–H1 bond dominate the conformational features of the isotropic ^{13}C shielding in $(CH_3)_2S_2$.

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Registry No. dimethyl disulfide, 624-92-0.

Supplementary Material Available: Tables of optimized (HF/6-31G* with GAMESS) coordinates for dimethyl disulfide for eight values of the dihedral angle and optimized geometries at the MP2/6-31G** level using the Gaussian 88 codes for dihedral angles of 0°, 84.8°, and 180° (5 pages). Ordering information is given on any current masthead page.

Mechanistic, Structural, and Vibrational Aspects of the Dimerization of Silaethylene

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Abstract: The dimerization of silaethylene to form 1,3-disilacyclobutane (1,3-DSCB) and 1,2-disilacyclobutane (1,2-DSCB) is studied using ab initio quantum mechanical techniques. The dimerization reaction leading to 1,3-DSCB is predicted to proceed through a concerted 2S + 2S mechanism due to a relaxation of the Woodward–Hoffmann rules for this case. With use of a double-ζ basis set augmented with polarization functions on C and Si (DZ + d), at the single and double excitation coupled cluster (CCSD) level of theory, this reaction is predicted to be exothermic by 79.1 kcal/mol, and to have a barrier height of 5.2 kcal/mol. 1,2-DSCB is predicted to lie 19.8 kcal/mol higher in energy than 1,3-DSCB at the DZ + d self-consistent field (SCF) level of theory, and the dimerization reaction leading to 1,2-DSCB is predicted to proceed through a two-step mechanism involving a diradical intermediate.

Introduction

For more than 2 decades it has been known that silicon can and does form double bonds with carbon.[1] It was not until 1979, however, that the synthesis of the first of a family of relatively stable silenes, with the general formula $(Me_3Si)_2Si{=}C(OSiMe_3)R$, was reported by Brook et al.[2] Unlike previously known unstable silenes which dimerize in a head-to-tail fashion to produce 1,3-disilacyclobutanes (1,3-DSCBs),[3] most members of this family

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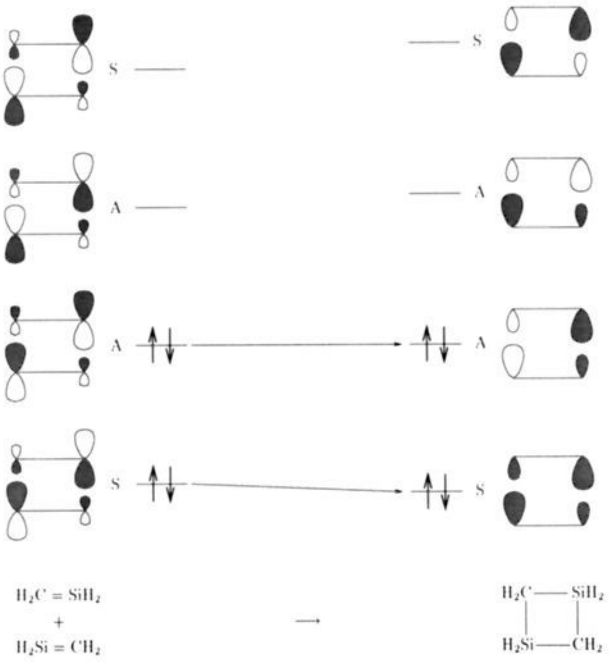

Figure 1. Correlation diagram for the head-to-tail dimerization reaction allowing for reduction in orbital symmetry. S and A designate a molecular orbital as symmetric or antisymmetric with respect to the C_2 axis perpendicular to the plane of the page.

of stable silenes dimerize head-to-head to form 1,2-disilacyclobutanes (1,2-DSCBs).[2,4-6] This head-to-head dimerization has also been observed as a competing reaction in the low pressure dimerization of $Me_2Si{=}C(Me)(SiMe_3)$,[7] and in the dimerization of $(Me_3Si)_2C{=}C{=}SiPh_2$.[8]

The currently accepted rationale for the behavior of silenes is this: the "normal" silenes, in which the π bond is heavily polarized to the carbon, add in a concerted 2S + 2S fashion, while the "stable" silenes, in which the π bond polarization is lost, dimerize via a multistep diradical mechanism, reminiscent of ethylene. According to the Woodward–Hoffmann rules[9] for cycloaddition reactions, the 2S + 2S reaction is thermally forbidden, although it is believed that the polarization of the double bond leads to a relaxation of these rules.[3] Indeed, if one constructs a simple correlation diagram allowing for the reduction in orbital symmetry to the point group C_2 (Figure 1), then the 2S + 2S pathway becomes allowed for the head-to-tail dimerization. An analogous procedure for the head-to-head dimerization (Figure 2) predicts this reaction to be forbidden, consistent with the experimental evidence that the head-to-head dimerization is not concerted.[2,7,10] While the Woodward–Hoffmann rules do allow for another 2 + 2 cycloaddition reaction mechanism, namely, the 2S + 2A, this reaction would be too sterically hindered, even in the case of the parent silaethylene, to occur.[11]

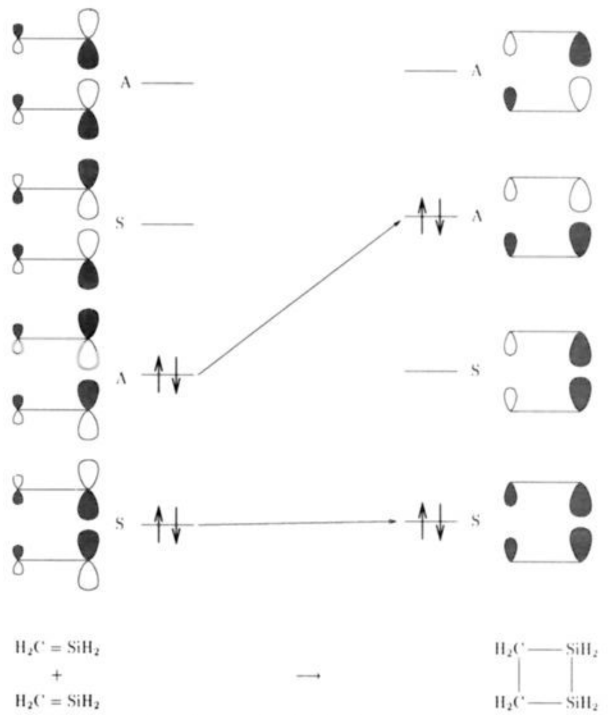

Figure 2. Correlation diagram for the head-to-head dimerization reaction allowing for reduction in orbital symmetry. S and A designate a molecular orbital as symmetric or antisymmetric with respect to the C_2 axis in the plane of the page.

Theoretical investigations of the dimerization of silenes have to date concentrated on the head-to-tail reaction. In 1977 Ahlrichs and Heinzmann[12] reported the results of an ab initio study of the head-to-tail reaction performed at the self-consistent field (SCF) level of theory. In their study, which employed a basis set of double-ζ quality, they predict the reaction to be exothermic by 76 kcal/mol. Because it was not possible at the time to fully optimize the structure of the transition state for the dimerization reaction, they provide only an upper bound of 14 kcal/mol to the barrier height. In 1983 Morokuma et al.[13] detailed the results of a study of the head-to-tail reaction performed at the 6-31G SCF level of theory. They predict a barrier height of 11.7 kcal/mol and a ΔE of −82.1 kcal/mol, in good agreement with Ahlrichs and Heinzmann's results. 6-31G** SCF single point energies determined at the 6-31G SCF geometries reduced the predicted barrier height to 2.7 kcal/mol and lowered ΔE to −89.8 kcal/mol. Single and double excitation configuration interaction (CISD) single point energies, including the Davidson correction for quadruple excitations (CISD + Q), determined using the 6-31G basis set, yield estimates of 12.3 kcal/mol for the classical barrier height and −69.1 kcal/mol for ΔE. In 1984 Apeloig and Karni[14] studied substituent effects on the stability of silenes, finding there to be little correlation between the stability of a silene and the heat of dimerization. They calculated dimerization energies for various monosubstituted silenes ranging from −70 to −84 kcal/mol. There are several studies of 1,3-DSCB itself,[15-18] the

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most thorough to date being one by Rempfer et al.[17] We are aware of no theoretical investigations of the head-to-head dimerization, although 1,2-DSCB has been studied by Kumar et al.,[18] who predict it to lie 19.9 kcal/mol above 1,3-DSCB at the 3-21G SCF level of theory.

In this paper we will present the results of a study of the head-to-tail dimerization performed at much higher levels of theory than were possible until quite recently. We have performed full geometry optimizations for silaethylene, 1,3-DSCB, and the transition state connecting them at the SCF, CISD, and single and double excitation coupled cluster (CCSD) levels of theory with a basis set of double-ζ quality on all atoms, augmented with polarization functions on carbon and silicon. With the same basis set we have fully optimized the geometry of 1,2-DSCB at the SCF level of theory. Because there are abundant experimental structural data with which to make comparison, we have also studied 1,3-DSCB at the SCF level of theory with basis sets of up to triple-ζ quality augmented with two sets of polarization functions on carbon and silicon, and present the first theoretical study of the infrared spectrum of 1,3-DSCB. Finally, we will discuss preliminary results for the theoretically more challenging head-to-head dimerization reaction.

Theoretical Approach

The basis set used here for carbon and hydrogen is Dunning's[19] double-ζ contraction of Huzinaga's[20] 9s5p primitive set for carbon, and 4s primitive set for hydrogen; that for silicon is the (11s7p/6s4p) basis of Dunning and Hay.[21] For hydrogen, the (4s/2s) set is scaled by a factor of 1.2; i.e., all primitive Gaussian orbital exponents are multiplied by $(1.2)^2 = 1.44$. The basis sets for silicon and carbon were each augmented with one set of six Cartesian d functions (x^2, y^2, z^2, xy, xz, and yz multiplied by $e^{-\alpha r^2}$), with $\alpha_d(\mathrm{C}) = 0.75$, and $\alpha_d(\mathrm{Si}) = 0.5$. This basis set, hereafter referred to as DZ + d, is technically designated Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), and H(4s/2s), and includes 96 contracted Gaussian basis functions. For the determination of the structure of 1,3-DSCB, which is known experimentally, two larger basis sets were used. The first is identical with the above DZ + d with two exceptions: (1) for the polarization functions on silicon and carbon, pure angular momentum d functions were used (i.e., the basis function derived from $d_{xx} + d_{yy} + d_{zz}$ which has overall s-type symmetry was removed from the basis set); (2) a set of 2p polarization functions ($\alpha_p = 0.75$) was added to each hydrogen. This basis set, referred to as DZ + P, thus includes 116 contracted Gaussian basis functions. The second basis consists of McLean and Chandler's[22] triple-ζ contraction of Huzinaga's 12s9p primitive set for silicon and Dunning's[23] triple-ζ contraction of Huzinaga's 10s6p primitive set for carbon and 5s primitive set for hydrogen, augmented with two sets of five d-like polarization functions on carbon and silicon ($\alpha_d(\mathrm{C}) = 1.5, 0.35$, $\alpha_d(\mathrm{Si}) = 1.0, 0.25$), and one set of 2p polarization functions ($\alpha_p = 0.75$) on hydrogen. This basis set (henceforth abbreviated as TZ2P) is technically designated Si(12s9p2d/6s5p2d), C(10s6p2d/5s3p2d), and H(5s1p/3s1p) and includes 158 contracted Gaussian basis functions.

SCF energies were determined for the closed- and open-shell systems within the restricted Hartree–Fock SCF formalism. Singlet diradical species were described with two-configuration (TCSCF) wave functions. All structures were determined via analytic gradient techniques.[24] Transition states were located with use of eigenvector following methods.[25] All stationary points were characterized as minima, transition states, or higher-order stationary points via harmonic vibrational analyses of analytic second derivatives.[26] Zero-point vibrational energies (ZPVEs) were estimated by scaling the DZ + d SCF harmonic vibrational

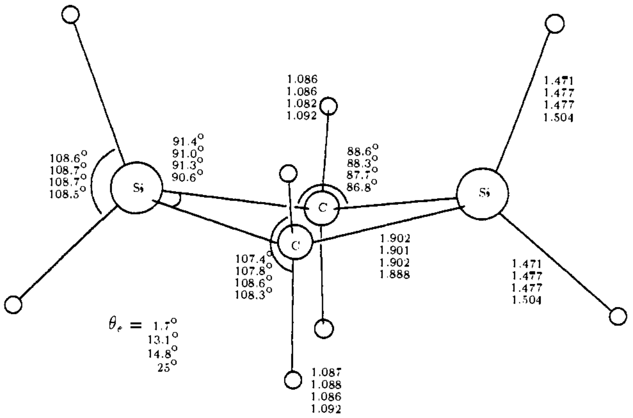

Figure 3. Equilibrium geometries for 1,3-disilacyclobutane predicted at the SCF level of theory. All bond distances are in angstroms; θ_e is the average of the Si–C–Si and C–Si–C out-of-plane angles. For each geometrical parameter the top value refers to the DZ + d SCF level of theory, the second value to the DZ + P SCF level of theory, the third to the TZ2P SCF level of theory, and the last to the experimental value given in ref 17.

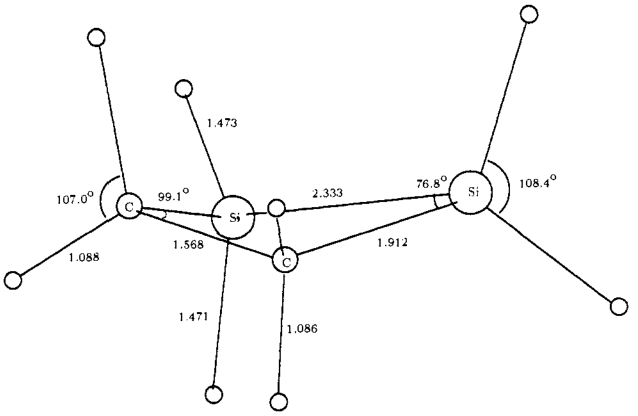

Figure 4. Equilibrium geometry for 1,2-disilacyclobutane predicted at the DZ + d SCF level of theory. All bond distances are in angstroms.

Table I. Summary of Total Energies (hartrees) and Relative Energies (kcal/mol) for 1,3-Disilacyclobutane and 1,2-Disilacyclobutane Predicted with the DZ + d Basis Set

	SCF	CISD	CISD + Q[a]	CCSD
	1,3-Disilacyclobutane			
D_{2h}	−658.236 75	−658.643 95	−658.700 02	−658.710 92
C_{2v}	−658.236 75	−658.644 23	−658.700 47	−658.711 46
barrier to planarity	0.00	0.18	0.28	0.34
	1,2-Disilacyclobutane			
C_{2v}	−658.204 27			
C_2	−658.206 61			
barrier to planarity	1.19			
ΔE (1,3→1,2)	18.9			
ΔH(1,3→1,2)	19.8			

[a] The CISD + Q energy is determined at the CISD optimized geometry.

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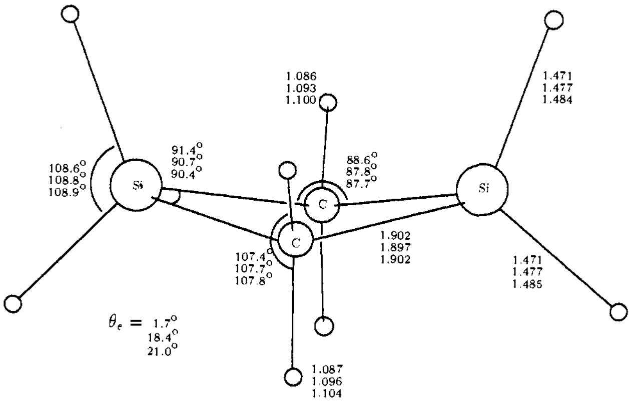


Figure 5. Higher level theoretical equilibrium geometries for 1,3-disilacyclobutane. All bond distances are in angstroms; θ_e is the average of the Si–C–Si and C–Si–C out-of-plane angles. For each geometrical parameter the top, middle, and bottom entries refer to DZ + d SCF, DZ + d CISD, and DZ + d CCSD levels of theory, respectively.

frequencies by a factor of 0.91.[27]

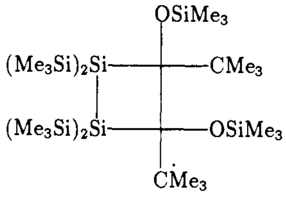
The head-to-tail dimerization reaction was also studied at the DZ + d single and double excitation configuration interaction (CISD)[28] and single and double excitation coupled cluster (CCSD)[29] levels of theory. Once again molecular structures were determined with use of analytic gradient methods.[30,31] In both the CISD and CCSD wave functions the 12 lowest energy molecular orbitals (corresponding to the core carbon 1s and silicon 1s, 2s, and 2p orbitals) were constrained to remain doubly occupied. Likewise, the six highest lying MOs were deleted from the correlation procedures. Thus, the largest correlated wave functions, those for the C_{2h} symmetry transition state, each included 80 197 configuration state functions.

1,3- and 1,2-Disilacyclobutane

The equilibrium geometries predicted for 1,3-DSCB and 1,2-DSCB at the SCF level of theory are shown in Figures 3 and 4. Subsequent vibrational analyses proved these structures to be true minima at this level of theory. The DZ + d SCF, CISD, and CCSD equilibrium geometries predicted for 1,3-DSCB are shown in Figure 5. In Table I are summarized the absolute and relative energies of 1,3- and 1,2-DSCB.

At all levels of theory, agreement with the structures found in the electron diffraction work of Rempfer et al.[17] for 1,3-DSCB is good, with the exception of the ring puckering angle, θ_e, for which the experimental gas phase value is 25°. Rempfer et al., who also report some ab initio results for 1,3-DSCB, point out that this puckering angle is extremely sensitive to the level of theory employed. Thus, with a basis set of double-ζ quality, full geometry optimization yields a predicted ring structure which is planar, while when one set of polarization functions is added to silicon, the ring puckers slightly to 6°; with two sets of polarization functions on silicon and one on carbon, the angle increases to 15°. Our results, which were obtained with more balanced basis sets, are broadly consistent with those of Rempfer et al. in this regard. At the DZ + d SCF level of theory we find an average puckering angle (i.e., the average of the Si–C–Si and C–Si–C out-of-plane angles) of only 1.7°. By merely adding a single set of p functions to the hydrogen atoms (DZ + P), the puckering angle is increased to 13.1°. Adding two sets of polarization functions to the ring atoms (TZ2P) has only a slight further effect on the puckering angle, increasing it to 14.8°. Even more important than the basis set effect, however, is the effect of including electron correlation, considered for the first time in the present research. At the DZ + d CISD level of theory, the ring puckering angle is 18.4°, and at the CCSD level of theory, it is 21.0°, much closer to the experimental value[17] of 25 ± 2°. This sensitivity of the ring puckering angle to the level of theory employed is not surprising in light of the low barrier to planarity in the gas phase which at all levels of theory is predicted to be less than 0.4 kcal/mol, in good agreement with the experimental value of 81 cm^{-1} (0.23 kcal/mol).[32] Theory and experiment also agree that the C–Si–C angle is larger than the Si–C–Si angle. This finding has been discussed at length elsewhere[16,33] so we will not comment further on it here.

At the DZ + d SCF level of theory, 1,2-DSCB is predicted to lie 18.9 kcal/mol higher in energy than 1,3-DSCB, in good agreement with the value of 19.9 kcal/mol predicted by Kumar et al.[18] Inclusion of zero-point vibrational energy (ZPVE) yields an estimate of 19.8 kcal/mol for ΔH^{0K} for the reaction 1,3-DSCB → 1,2-DSCB. Unfortunately, for 1,2-DSCB there is no experimental structure with which to make comparison. The C–C ring bond is predicted at the DZ + d SCF level of theory to be 1.568 Å, somewhat long for a C–C single bond; however, this is consistent with Brook's finding[34] that the heavily substituted 1,2-DSCB (**1**) has a C–C bond length of 1.66 Å. The C–Si ring bond is also predicted to be a rather long C–Si single bond (1.912 Å versus 1.867 Å in methylsilane[35]). In the substituted **1** the experimental C–Si bond length is 2.00 Å, and in the 1,2-DSCB (**2**) it is 1.94 Å.[8] The Si–Si bond (2.333 Å), however, is predicted to be much closer to a normal Si–Si bond length (2.331 Å in disilane[36]). This too is consistent with the work of Brook et al. (2.37 Å)[34] and Ishikawa et al. (2.34 Å).[8]



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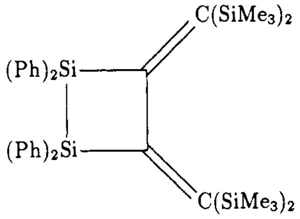

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The parent 1,2-DSCB is predicted to be more puckered than 1,3-DSCB, with a puckering angle of 30.7° (DZ + d SCF) and barrier to planarity of 1.2 kcal/mol. The substituted 1,2-DSCB (**2**) is puckered as well,[8] whereas the ring in **1** is known to be planar.[34] Given the low barrier to planarity in the gas phase (Table I), the planarity of **1** is not surprising.

This variability in degree of puckering is consistent with Irwin and Laane's detailed analysis[37] of the vibrational spectra of 1,3-DSCB in the vapor, liquid, and solid phases. They show that 1,3-DSCB is puckered in the vapor and liquid phases but planar in the solid state.

Vibrational Frequencies

Predicted harmonic vibrational frequencies and infrared intensities for 1,3-DSCB are given in Table II. Comparison is made with the experimental IR spectrum of Irwin and Laane,[37] and the numbering and description of the normal modes are theirs. Agreement between theory and experiment is good for some of the modes, but for many others, particularly those involving CH_2 and SiH_2 bending motions, agreement is very bad indeed. In particular, for ω_7, ω_8, ω_{11}, ω_{15}, ω_{16}, ω_{26}, and ω_{28} the frequencies

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Table II. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for the Equilibrium Structure of 1,3-Disilacyclobutane Predicted at the SCF Level of Theory with Three Different Basis Sets

		DZ + d		DZ + P		TZ2P		experiment[a]		
		freq	int	freq	int	freq	int	freq	int	description
A_1	ω_{18}	3277	15	3268	10	3249	9	2965	m	CH_2 asym str (ip)
	ω_1	3224	0.06	3207	3	3185	4	2931	R	CH_2 sym str (ip)
	ω_2	2378	0.1	2332	16	2314	17	2156	R	SiH_2 sym str (ip)
	ω_{19}	2368	375	2323	297	2304	318	2157	vvs	SiH_2 asym str (ip)
	ω_3	1553	0.04	1529	2	1530	2	1373	R	CH_2 def (ip)
	ω_4	1063	0.08	1060	4	1054	5	(965)		SiH_2 def (ip)
	ω_{20}	885	147	877	137	869	122	965	s	CH_2 rock (ip)
	ω_5	795	0.1	797	7	783	12	745	m	ring breathing
	ω_{21}	505	24	523	17	524	16	438	mw	SiH_2 rock (ip)
	ω_6	453	0.2	428	0.05	424	5	380	mw	ring def
	ω_{22}	6	2	61	2	68	2	56		ring puckering
A_2	ω_7	1137	0	1104	0	1071	0	1260	R	CH_2 wag (op)
	ω_{16}	1038	0	1022	0	1008	0	(1120)	R	CH_2 twist (op)
	ω_8	847	0	840	0	829	0	865	R	SiH_2 wag (op)
	ω_9	675	0	672	0	655	0	620	R	ring mode
	ω_{17}	644	0	633	0	620	0	555	R	SiH_2 twist (op)
B_1	ω_{27}	2368	370	2323	297	2304	353	2147	vvs	SiH_2 sym str (op)
	ω_{10}	2366	0.03	2320	32	2301	19	(2156)	R	SiH_2 asym str (op)
	ω_{28}	1145	235	1118	250	1088	284	1258	vw	CH_2 wag (ip)
	ω_{11}	1081	0.05	1066	1	1053	2	1129	vw	CH_2 twist (ip)
	ω_{29}	1038	266	1035	221	1025	166	928	m	SiH_2 def (op)
	ω_{30}	693	46	689	44	674	52	644	m	SiH_2 rock (ip)
	ω_{12}	448	0.001	453	4	449	0.09	442	mw	SiH_2 rock (ip)
B_2	ω_{13}	3278	0.06	3269	3	3250	5	2995	w	CH_2 asym str (op)
	ω_{23}	3224	19	3206	12	3184	10	2930	w	CH_2 sym str (op)
	ω_{24}	1544	26	1519	27	1516	19	1363	mw	CH_2 def (op)
	ω_{25}	1004	520	1000	487	991	442	905	s	SiH_2 wag (ip)
	ω_{14}	850	0.02	842	1	830	1	(620)	R	SiH_2 twist (ip)
	ω_{26}	698	4	696	3	688	3	780	ms	ring mode
	ω_{15}	526	0.001	506	0.1	488	0.7	(965)		CH_2 rock (op)

[a] From ref 37; ip, in-phase; op, out-of-phase; s, strong; m, medium; w, weak; v, very; R, from Raman data. Frequencies in parentheses were assigned to other vibrations which were responsible for the intensities.

predicted at the SCF level are uniformly *below* the experimental fundamentals; DZ + P SCF theory usually yields predicted vibrational frequencies which are larger than the experimentally observed fundamentals.[38] Also note that, as the quality of the basis set is increased, the predicted vibrational frequencies decrease. Clearly, for the aforementioned "problem" frequencies, SCF theory and experiment are diverging; thus the present results raise the possibility of a reassignment of the 1,3-DSCB vibrational frequencies.

Before exploring the possibility of reassigning the vibrational frequencies of 1,3-DSCB, we thought it prudent to compare the IR spectrum of silacyclobutane predicted at the DZ + P SCF level of theory with the experimental spectrum of Laane.[39] (The DZ + P SCF level of theory was chosen for this purpose as it is the lowest level of theory at which 1,3-DSCB is predicted to be significantly puckered.) This comparison is presented in Table III. As can be seen, agreement between experiment and theory in this case is quite good, the experimentally observed fundamentals lying (on average) 9.3% below the DZ + P SCF harmonic frequencies. (In the calculation of this average, five frequencies were not used: an A′ mode at 168 cm^{-1} corresponding to the ring puckering mode, and four A″ modes which were described either as "very weak" or were not observed in the vapor phase.) From this average difference of 9.3%, we obtain a scale factor of 0.91 for our DZ + P SCF vibrational frequencies for 1,3-DSCB.

Given the good agreement between theory and experiment in the case of silacyclobutane, we feel confident in proposing a reassignment of the 1,3-DSCB vibrational frequencies. These reassignments, together with a comparison with the scaled DZ + P SCF vibrational frequencies, are summarized in Table IV. The reassignment of two of the fundamentals requires some comment, as in the proposed reassignment scheme they are assigned to vibrational modes of symmetry different from those in

Table III. Comparison between DZ + P SCF Harmonic Vibrational Frequencies and Observed Fundamental Frequencies for the Silacyclobutane Molecule, SiC_3H_8

	DZ + P SCF		experiment[a]		
	freq (cm^{-1})	int (km/mol)	freq	int	% diff
A′	3276	56	2992	vs	−8.7
	3248	26	2953	vs	−9.1
	3210	23	2935	m	−8.6
	3199	46	2873	m	−10.2
	2322	161	2145	vvs	−7.6
	2314	172	2145	vvs	−7.3
	1622	0.6	1458	vvw	−10.1
	1577	5	1422	m	−9.8
	1323	2	1191	mw	−10.0
	1288	28	1127	s	−12.5
	1062	161	962	vvs	−9.4
	996	42	906	ms	−9.0
	955	9	877	s	−8.2
	898	7	817	R	−9.0
	731	15	673	m	−7.9
	589	27	532	m	−9.7
	455	9	409	mw	−10.1
	163	0.3	158		−3.1[b]
A″	3271	22	2935	m	−10.3
	3205	40	2888	m	−9.9
	1565	8	1401	m	−10.5
	1414	3	1343	vw	−5.0[b]
	1352	2	1255	sol	−7.2[b]
	1207	2	1211	vw	−0.03[b]
	1060	0.1	1140	est	+7.5[b]
	1026	35	927	s	−9.6
	902	176	814	vs	−9.8
	813	14	736	m	−9.5
	702	4	653	sol	−7.0
	557	0.2	514	w	−7.7

[a] From ref 39: s, strong; m, medium; w, weak; v, very; R, from Raman data; sol, from solid spectra; est, estimated from solid spectra. [b] Value not used in calculation of average difference; see text.

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(38) See for example: Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.

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Table IV. Proposed Reassignments for the Experimental IR Spectrum of 1,3-Disilacyclobutane, Compared with Scaled (scale factor 0.9074) DZ + P SCF Frequencies (cm^{-1}) and IR Intensities (km/mol)

		experiment[a]		scaled SCF		
		freq	int	freq	int	description
A_1	ν_{18}	2965	m	2965	10	CH_2 asym str (ip)
	ν_1	2930	w	2910	3	CH_2 sym str (ip)
	ν_{19}	2157	vvs	2108	297	SiH_2 asym str (ip)
	ν_2	2155	s	2116	16	SiH_2 sym str (ip)
	ν_3	1373	R	1387	2	CH_2 def (ip)
	ν_4	(965)		962	4	SiH_2 def (ip)
	ν_{20}	780	ms	796	137	CH_2 rock (ip)
	ν_5	745	m	723	7	ring breathing
	ν_{21}	438	mw	475	17	SiH_2 rock (ip)
	ν_6	380	mw	388	0.05	ring def
	ν_{22}	56		55	2	ring puckering
A_2	ν_7	N.O.[b]		1002	0	CH_2 wag (op)
	ν_{16}	N.O.		927	0	CH_2 twist (op)
	ν_8	N.O.		762	0	SiH_2 wag (op)
	ν_9	620	R	610	0	ring mode
	ν_{17}	555	R	574	0	SiH_2 twist (op)
B_1	ν_{10}	(2155)		2105	32	SiH_2 asym str (op)
	ν_{27}	2147	vvs	2108	297	SiH_2 sym str (op)
	ν_{28}	965	s	1015	250	CH_2 wag (ip)
	ν_{11}	N.O.		967	1	CH_2 twist (ip)
	ν_{29}	928	m	939	221	SiH_2 def (op)
	ν_{30}	644	m	625	44	ring mode
	ν_{12}	442	mw	411	4	SiH_2 rock (op)
B_2	ν_{13}	2995	w	2966	3	CH_2 asym str (op)
	ν_{23}	2930	w	2909	12	CH_2 sym str (op)
	ν_{24}	1363	mw	1378	27	CH_2 def (op)
	ν_{25}	905	s	907	487	SiH_2 wag (ip)
	ν_{14}	N.O.		764	1	SiH_2 twist (ip)
	ν_{26}	(620)	R	632	3	ring mode
	ν_{15}	N.O.		459	0.1	CH_2 rock (op)

[a] From ref 37; ip, in-phase; op, out-of-phase; s, strong; m, medium; w, weak; v, very; R, from Raman data. Frequencies in parentheses were assigned to other vibrations which were responsible for the intensities. [b] N.O., true fundamental not observed in proposed reassignment.

the original scheme. The strong feature at 965 cm^{-1}, assigned by Irwin and Laane to ν_{20} (A_1 CH_2 rock (in phase)), has been reassigned to ν_{28} (B_1 CH_2 wag (in phase)) as this mode matches up best with a strong theoretical feature predicted to lie at 1015 cm^{-1}. Likewise, the feature at 780 cm^{-1}, assigned by Irwin and Laane to ν_{26} (B_2 ring mode), has been reassigned to ν_{20} (A_1 CH_2 rock (in phase)). For 1,3-DSCB, modes of B_2 symmetry should be "A" type bands (i.e., they should have strong P and R branches with a sharp, intense Q branch), modes of B_1 symmetry should be "B" type bands (no Q branch, strong P and R branches), and modes of A_1 symmetry should be "C" type bands (similar to A bands, except the Q branch may not be much stronger than the P and R branches).[40] Without a detailed analysis of the observed spectrum, we cannot know whether the two reassigned modes mentioned above are of the correct type.

Head-to-Tail Dimerization Reaction

The transition state for the head-to-tail dimerization reaction was located in a straightforward manner by distorting the D_{2h} 1,3-DSCB structure into C_{2h} symmetry, and then maximizing the energy with respect to the reaction coordinate while minimizing the energy with respect to all other internal coordinates. Geometries predicted for the transition state for the formation of 1,3-DSCB at the DZ + d SCF, CISD, and CCSD levels of theory are summarized in Figure 6. This structure is a true transition state; i.e., it has only one imaginary vibrational frequency at the DZ + d SCF level of theory.

The structure of the transition state is much as one would expect from Hammond's postulate, i.e., the reaction is highly exothermic; hence the transition state should resemble the reactants more closely than the products. The Si–C bond lengths are only slightly longer in the transition state than in the reactant silaethylene molecule (1.707 Å vs 1.694 Å (DZ + d SCF), 1.712 Å vs 1.708 Å (DZ + d CISD), 1.735 Å vs 1.717 Å (DZ + d CCSD)). There are two interesting structural features to point out in the transition state. The first is that it is indeed planar, thus confirming the belief that the head-to-tail dimerization reaction proceeds through a concerted 2S + 2S mechanism. The second point of interest is the difference in the Si⋯Si and Si⋯C distances. At the DZ + d SCF level of theory these distances are nearly equal (3.003 Å and 3.004 Å, respectively), but with the inclusion of electron correlation, the Si⋯Si distance becomes much *shorter* than the Si⋯C distance. At the DZ + d CISD level of theory, the former is 0.107 Å shorter than the latter, and at the DZ + d CCSD level the difference is 0.322 Å. This is certainly counter to what one would expect at first glance, and the explanation for this effect cannot be trivial. However, considering the large distances involved, and the low barrier height (see below), it is not unreasonable to expect the transition state structure to be strongly influenced by some subtle combination of weak forces.

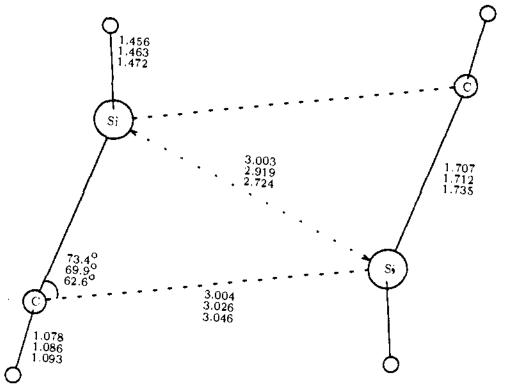

Figure 6. C_{2h} transition state geometries for the head-to-head dimerization reaction of silaethylene. All bond distances are in angstroms. For each geometrical parameter the top, middle, and bottom entries refer to DZ + d SCF, DZ + d CISD, and DZ + d CCSD levels of theory, respectively.

Table V. Summary of Total Energies (hartrees) and Relative Energies (kcal/mol) for the Reaction Leading to 1,3-Disilacyclobutane Predicted with the DZ + d Basis Set

	SCF	CISD	CISD + Q[a]	CCSD
H_2SiCH_2 + H_2SiCH_2	−658.09487	−658.50135	−658.56281	−658.57897
1,3-DSCB	−658.23675	−658.64423	−658.70047	−658.71146
transition state	−658.08897	−658.49816	−658.55849	−658.57295
ΔE for dimerization	89.0	89.7	86.4	83.1
ΔH for dimerization	85.0	85.7	82.4	79.1
$\Delta E^{\ddagger}$	3.7	2.0	2.7	3.8
$\Delta H^{\ddagger}$	5.1	3.4	4.1	5.2

[a] The CISD + Q energy is determined at the CISD geometry.

In Table V are listed the absolute and relative energies of 1,3-DSCB, the separated limit for two silaethylene molecules, and the transition state connecting them. The dimerization energy ΔE is large (>80 kcal/mol) at all levels of theory, in agreement with the work of Ahlrichs and Heinzmann[12] and Morokuma et al.,[13] although we find no great fluctuation in ΔE with the addition of electron correlation as the latter authors do. Inclusion of a zero-point vibrational energy correction determined at the DZ + d SCF level of theory yields a prediction of 79.1 kcal/mol for the 0 K enthalpy of dimerization at the DZ + d CCSD level of theory.

The predicted classical barrier height for the head-to-tail dimerization reaction is very small (3.8 kcal/mol at the DZ + d CCSD level of theory). As with the dimerization energy, the predicted barrier height is not extremely sensitive to the level of theory employed. This too is in contrast with the work of Mo-

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(40) Herzberg, G. *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold; New York, 1945; p 483.

Table VI. Absolute Energies (hartrees), Relative Energies (kcal/mol), and Selected Geometrical Parameters[a] for Several Carbon–Carbon Bond-Broken Diradicals

	point group	electronic state	abs energy	rel energy	no. of imaginary frequencies	r_e(Si–Si)	r_e(C–Si)	θ_e(Si–Si–C)	τ_e(C–Si–Si–C)
1,2-Disilacyclobutane									
	C_2	^1A	−658.206 61	0.0	0	2.333	1.912	76.8	17.8
3	C_{2v}	$^3B_2$	−658.145 62	38.3	1	2.372	1.858	112.9	0.0
4	C_{2v}	$^1A_1$	−658.144 74	38.8	2	2.372	1.859	113.9	0.0
5	C_2	^1A	−658.144 78	38.8	1	2.335	1.866	110.8	36.8
6	C_2	^3B	−658.147 54	37.1	0	2.356	1.859	111.6	58.9
7	C_2	^1A	−658.147 95	36.8	0	2.366	1.855	112.8	70.1
8	C_{2h}	^3B_u	−658.147 12	37.3	0	2.355	1.860	112.0	180.0
9	C_{2h}	^1A_g	−658.149 45	35.9	0	2.369	1.851	111.0	180.0

[a] All bond lengths are given in angstroms.

Table VII. Absolute Energies (hartrees), Relative Energies (kcal/mol), and Selected Geometrical Parameters[a] for Several Silicon–Silicon Bond-Broken Diradicals

	point group	electronic state	abs energy	rel energy	no. of imaginary frequencies	r_e(C–C)	r_e(C–Si)	θ_e(C–C–Si)	τ_e(Si–C–C–Si)
1,2-Disilacyclobutane									
	C_2	^1A	−658.206 61	0.0	0	1.568	1.912	99.1	26.3
10	C_{2v}	$^3B_2$	−658.137 94	43.1	1	1.570	1.896	121.7	0.0
11	C_{2v}	$^1A_1$	−658.138 94	42.5	1	1.560	1.903	119.6	0.0
12	C_2	^3B	−658.145 76	38.2	0	1.548	1.896	117.0	69.4
13	C_2	^1B	−658.145 40	38.2	0	1.548	1.896	117.2	66.0
14	C_{2h}	^3B_u	−658.148 51	36.5	0	1.552	1.894	113.2	180.0
15	C_{2h}	^1A_g	−658.150 97	34.9	0	1.558	1.893	111.8	180.0
16	C_{2v}	$^3B_2$	−658.131 53	47.1	3	1.568	1.907	124.0	0.0

[a] All bond lengths are given in angstroms.

rokuma et al.,[13] who predict barrier heights in the range 2.7–12.3 kcal/mol. (It should be noted that Morokuma et al. did not optimize the geometries of the reactants or transition state at each level of theory. Also note that our DZ + d SCF results do compare well with their 6-31G** SCF results.) The low barrier height is, however, consistent with the experimental finding that the head-to-tail dimerization reaction occurs quite readily.[3] Inclusion of the ZPVE correction determined at the DZ + d SCF level of theory yields a final estimate of 5.2 kcal/mol (DZ + d CCSD) for the 0 K enthalpy of activation for the head-to-tail dimerization reaction.

Head-to-Head Dimerization Reaction

As alluded to above, the potential energy surface for the head-to-head reaction is far more complex than that for the head-to-tail reaction. In Table VI and Table VII are summarized the results obtained at the DZ + d SCF level of theory for several of the more interesting points on this surface. Our approach to this reaction was analogous to that described above for the head-to-tail reaction. Many attempts were made to locate closed-shell SCF stationary points corresponding to breaking the C–C and Si–Si bonds, but no such stationary points were found. Thus we decided to explore the head-to-head potential energy surface using open-shell (i.e., TCSCF for the singlet diradicals) wave functions.

The first stationary point located on the head-to-head triplet potential energy surface was a C_{2v} $^3B_2$ (**3**) carbon–carbon (by which we mean that the C–C distance is long, i.e., not a chemical bond) diradical which had only one imaginary vibrational frequency. The analogous open-shell $^1A_1$ structure (**4**) (all open-shell singlet structures discussed were described with TCSCF wave functions, and are thus described as ^1A states) had two imaginary frequencies. When these C_{2v} structures were allowed to relax into C_2 symmetry, each led to a gauche minimum (**6** and **7**). Then using eigenvector following techniques,[25] we found a ^1A stationary point of C_2 symmetry (**5**) which had only one imaginary frequency. Two other minima, a C_{2h} ^3B_u (**8**) structure and a C_{2h} ^1A_g (**9**) structure, were found on the carbon–carbon diradical surface. In a similar manner we have found triplet and singlet C_2 and C_{2h} minima on the silicon–silicon diradical (i.e., long Si–Si distance) surface (**12–15**). C_{2v} $^3B_2$ and $^1A_1$ (**10** and **11**) structures were found, each having one imaginary frequency. In both of these C_{2v} structures, the SiH_2 groups are pyramidalized, with the hydrogens pointing toward each other. The C_{2v} triplet having both SiH_2 groups rotated 180° (**16**) had three imaginary vibrational frequencies; the analogous C_{2v} singlet collapses into a poor description of the planar 1,2-DSCB.

The triplet diradical surface is rather easily interpreted in analogy to butane. Thus, in both the carbon–carbon and silicon–silicon bond-broken regions of the potential energy hypersurface, there is one C_{2h} minimum and two equivalent C_2 gauche minima, connected by a C_{2v} transition state. The barrier between the gauche carbon–carbon minima is 1.2 kcal/mol, and that between the gauche silicon–silicon minima is 4.9 kcal/mol, although there is probably a C_2 transition state which is lower in energy. Presumably the barrier between the gauche minima and the C_{2h} minimum will be lower for both diradicals than the corresponding gauche–gauche barriers. The larger barrier on the silicon–silicon surface can be rationalized by arguments based on steric effects; the C–C bond in the silicon–silicon diradical is ~1.6 Å, whereas the Si–Si bond in the carbon–carbon diradical is ~2.4 Å. Certainly the more crowded transition state would be expected to lie higher in energy.

The carbon–carbon bond-broken singlet surface is more complex than the analogous triplet surface. Here, we once again have three minima, but instead of the C_{2v} structure being a transition state, it is a higher order stationary point. The transition state on this surface (the C_2 ^1A structure) does not link the two gauche minima; instead it appears to be the transition state for breaking the C–C bond. The imaginary vibrational mode corresponds to stretching the C–C bond, and the structure of the transition state is intermediate between 1,2-DSCB and the C_2 minimum. The silicon–silicon singlet potential energy surface is similar to the silicon–silicon triplet surface, except, as stated above, no C_{2v} structure with the SiH_2 groups pointing away from each other was found. Also, despite many attempts, no transition state was found for breaking the Si–Si bond in 1,2-DSCB.

It is remarkable to note how flat the diradical surface is, with the lowest-lying diradical identified thus far (C_{2h} singlet silicon–silicon diradical) lying only 3.3 kcal/mol lower in energy than the highest-lying minimum (C_2 singlet silicon–silicon bond-broken diradical). Given the difference in bond energies for normal C–C single bonds (~88 kcal/mol)[41] and Si–Si single bonds (~74 kcal/mol),[42] one might expect the silicon–silicon diradicals to be lower lying than the carbon–carbon diradicals by ~14 kcal/mol. There are several factors which could explain why the carbon–carbon and silicon–silicon diradicals lie so close to each other. First there are steric effects. As noted above, the gauche silicon–silicon diradicals are more crowded than the gauche carbon–carbon diradicals. The magnitude of the steric effect can be seen by comparing the relative energies of the gauche and trans singlet minima. The trans silicon–silicon bond-broken diradical lies 1.0 kcal/mol lower in energy than the trans carbon–carbon diradical, but the gauche carbon–carbon diradical is 2.3 kcal/mol lower lying than the gauche silicon–silicon diradical. Second, there is the stabilization of the carbon radicals by the β silicons. This β silicon effect has been shown to stabilize carbon radicals by approximately 3 kcal/mol;[43] thus in the case one would expect the carbon–carbon diradical to be stabilized by ~6 kcal/mol relative to the silicon–silicon diradical. Finally, steric effects in 1,2-DSCB would be expected to destabilize the C–C bond relative to the Si–Si bond, and this destabilization is manifested in the unusually long C–C bond in 1,2-DSCB.

Based on our DZ + d SCF results, one would predict the head-to-head dimerization reaction to pass through a multistep mechanism involving first formation of a carbon–carbon bond-broken diradical intermediate, followed by ring closure. This prediction is consistent with what is known experimentally about the head-to-head surface.[2,7,10] Unfortunately, we have been unable to find a transition state linking the carbon–carbon diradical with two separated silaethylene molecules. Such a transition state, presumably, would require a multiconfiguration SCF treatment to be adequately described.

Concluding Remarks

The results we have presented lend credence to what has been long hypothesized, that the head-to-tail dimerization of silaethylene is a concerted 2S + 2S reaction despite this reaction normally being forbidden, and that the head-to-head dimerization reaction is a multistep process involving a diradical intermediate. These findings are consistent with the simple arguments presented in the Introduction concerning relaxation of orbital symmetry. Our results, however, cast little light on the question of why the head-to-head reaction is favored over the head-to-tail in some instances. Certainly this is fertile ground for further theoretical and experimental investigation.

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Registry No. 1,3-DSCB, 287-55-8; 1,2-DSCB, 14151-37-2; silaethylene, 51067-84-6.

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Effect of Bond Multiplicity upon Hydrogen Bonding and Proton Transfers. Double Bonded Atoms

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Abstract: Ab initio methods are used to study the interactions between $H_2C{=}CH_2$ and $H_2C{=}NH$ and their deprotonated anions. $(H_2CCH\text{-}H\cdots CHCH_2)^-$ is the most weakly bound with a complexation energy of 5.6 kcal/mol at the correlated MP2 level as compared to the stronger interaction of 10.3 for $(HNCH\text{-}H\cdots CHNH)^-$ where the peripheral C atom has been replaced by N. The strongest interaction of 15.4 kcal/mol is observed in $(H_2CN\text{-}H\cdots NCH_2)^-$ where N atoms participate directly in the H-bond. $(H_2CCH\text{-}H\cdots CHCH_2)^-$ contains the longest intermolecular separation while the N···N distance in the latter complex is the shortest. This separation between subunits undergoes a contraction between 0.5 and 0.9 Å as the proton reaches the transfer midpoint. The highest proton transfer barrier of 13 kcal/mol is observed for $(H_2CCH\text{-}H\cdots CHCH_2)^-$. In contrast, the small barrier in $(H_2CN\text{-}H\cdots NCH_2)^-$ is eliminated altogether when zero-point vibrations are considered. Transfer rates are computed using modified RRKM theory. These results are placed within the broader context of other complexes in which the atoms participating in the H-bond are single- and triple-bonded within their respective subunits so as to arrive at systematic conclusions regarding the effects of such multiple bonding upon the energetics of H-bond formation and proton transfer.

Introduction

The distinction in proton transfer properties between "normal" (N or O) acids on one hand, and C-acids, on the other, has been well documented in the literature over the years.[1-4] Differences that have been noted include much slower transfers between C atoms and Brønsted plots that remain linear over long stretches of p*K*. Among the explanations that have been offered are changes in hybridization (and slow ensuing geometry adjustments) that accompany proton transfers between C atoms, the poorer ability of C-acids to form H-bonds, and the necessity of solvent molecules to reorganize themselves in the transition state.

In an effort to identify unambiguously the underlying reason for these differences, ab initio calculations were recently carried out on a set of small molecules whose hybridization is well defined and whose small sizes preclude significant changes in internal geometry.[5] Moreover, the systems were studied in the absence of any solvent molecules and their complicating effects. The molecules studied there were HCCH and HCN, each of which contain a triple bond and at least nominal sp hybridization. The calculations revealed that a strong C-acid like HCN does indeed

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