

Table V. Transfer of Electrons from the Surroundings to the Valence Shell upon Core Ionization (dq/dN) and an Estimate of the Second Order Correction to the Relaxation Energy ($\Delta R(\text{corr})$)

molecule	dq/dN	$\Delta dq/dN$	$\Delta R(\text{corr})^a$ (eV)
F ₂	0.62	0.0	0.0
HF	0.26	-0.36	1.39
ClF	0.50	-0.12	0.46
Cl ₂	0.45	0.0	0.0
HCl	0.25	-0.20	0.34
C/F	0.34	-0.11	0.19
Br ₂	0.49	0.0	0.0
HBr	0.27	-0.22	0.23
I ₂	0.45	0.0	0.0
HI	0.23	-0.22	0.17

$$^a \Delta R(\text{corr}) = (2/3)\Delta[(dk/dN)(dq/dN)].$$

HF than for the other two species.

Turning to possible problems with the relaxation model, we note that the fluorine Auger energies are those for population of the $2s^{2-}$ hole state in fluorine. This state is not strictly a core state as required by the model. However, results obtained by Weightman, Thomas, and Jennison¹⁵ indicate that this double-hole state is well localized in F₂ and, therefore, that the model is applicable.

The large value of ΔR for (HF-F₂) suggests that there is a larger transfer of charge toward the ionized atom in F₂ than in HF. In this case, we must consider higher order corrections to the model. Thomas¹⁰ has derived a second-order correction to eq 3. A more correct ΔR value is given by

$$\Delta R = \Delta\alpha/2 + (2/3)\Delta[(dk/dN)(dq/dN)] \quad (7)$$

where k is the change in core-ionization energy per unit charge removed from the valence shell, N the number of core electrons in the atom to be ionized, and dq/dN the transfer of electrons from the surroundings to the valence shell upon core ionization. The derivative dk/dN is negative, and if more electrons are transferred toward the ionized atom for F₂ than for HF, $\Delta dq/dN$ is also negative and a positive correction term should be added to the negative value for $\Delta R(\text{exptl})$ in Table II. This will make $\Delta R(\text{exptl})$ closer to the theoretical value.

A quantitative analysis of eq 7 is prevented by the uncertainty of estimating dk/dN and dq/dN . However, if we use dk/dN

values derived from Slater orbitals and $\Delta dq/dN$ from the population analysis, an estimate of the correction terms in eq 7 may be obtained. Table V shows that relative to X₂ $\Delta dq/dN$ is negative for all molecules. However, the larger value for HF combined with a large fluorine value for dk/dN make the correction 4 to 8 times larger for this molecule than for the other HX molecules. The calculated corrections are probably overestimated in this analysis, but the results suggest that the second-order correction term is more important for HF than for the other molecules. A reduction of $\Delta R(\text{exptl})$ to the ab initio value for HF would lower $\Delta V(\text{exptl})$ and the fluorine charge by about 10%. The trend and correlation in Figures 1 and 2, however, will not be changed significantly. The corrections for Cl and higher elements are less important since both dk/dN and $\Delta dq/dN$ are smaller for these elements.

Conclusion

The charge distribution in hydrogen halides and chlorine fluoride has been determined experimentally from the relative electrostatic potential at the halogen atom by use of a point-charge model. The potentials are obtained from combined measurements of core-ionization energies and Auger kinetic energies. The derived atomic charges are consistent with chemical experience and are linearly related to the electronegativity of the atoms.

The experimental results are verified by ab initio calculations with the standard Hartree-Fock method. The excellent agreement between experimental and theoretical results supports the validity of the model and gives confidence that it can be applied to other molecules.

The largest deviations between theory and experiment are found for the (HF-F₂) shifts in initial-state potential and relaxation energy. This discrepancy is probably due to a second-order relaxation effect, which is related to large differences in electron transfer upon ionization.

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The Intrinsic Reaction Coordinate and the Rotational Barrier in Silaethylene

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Abstract: The intrinsic reaction coordinate (IRC) is a minimum-energy pathway connecting reactants to products via the transition state. An improved algorithm for the determination of an IRC is presented. The method is illustrated for the rotation of the silicon-carbon double bond in silaethylene. This IRC shows all coordinates vary smoothly during the rotation from the planar to twisted structures, except for a slight pyramidalization at carbon. The rotational barrier is found to be about 37 kcal/mol, in good agreement with experimental estimates.

The most promising approach for the extension of chemical dynamics past triatomic systems appears to be a reaction path methodology.² Such an approach transforms the large number of nuclear coordinates needed to specify the geometry of a

polyatomic system to a unique coordinate, the distance along a reaction path connecting reactants to products via one or more transition states and possibly stable intermediates. The remaining coordinates are chosen to be orthogonal to the reaction coordinate

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and might, for example, be presumed to be harmonic in nature. A chemical reaction would thus be viewed as a system traveling through a $3N - 7$ dimensional "harmonic tube". By making certain simplifying approximations regarding the dynamics of these remaining degrees of freedom, reaction path Hamiltonians of varying sophistication can be formulated.² The curvature of the reaction path couples these orthogonal vibrational modes to motion along the reaction path, thus permitting energy exchange between these modes and the reactive channel.³⁻⁵ The advances due to the adoption of reaction path approaches have made polyatomic dynamical calculations feasible.²⁻⁸

A reaction path on a potential energy surface in mass-weighted coordinates was introduced in 1971.⁹ The intrinsic reaction coordinate (IRC) reaction path has been popularized by Fukui, whose developments of the idea have recently been reviewed by that author.^{10,11} This reaction path is a solution of the classical equations of motion, under the constraint that the velocity at any given point along the path is zero. This constraint produces an intrinsic or "minimum energy path", i.e., one that must traverse the saddle point(s) of a reaction. In a certain sense, this path is also the shortest path connecting reactants to products.¹² An entirely equivalent manner of viewing this path is as a "steepest descent path" from the transition state(s) in both the forward and reverse directions. Thus following the energy gradient downhill from a transition state produces a smooth reaction path.¹³ The improved gradient following method due to Ishida, Morokuma, and Komornicki¹⁴ appears to be the most computationally practical way of determining an IRC in mass weighted coordinates. An alternative approach, presented by Müller,¹⁵ generates the next point on the reaction path by minimizing the energy on a hypercircle of small radius about each point already known to be on the reaction path.

In the present paper we present our implementation of the method of Ishida et al.¹⁴ This method has already been applied in our laboratories to a number of chemical reactions.¹⁶⁻¹⁸ Beyond opening up the possibility of application to polyatomic reaction dynamics, the IRC's so generated have a number of other practical advantages. Tracing the IRC can identify the reactants and products connected by a particular transition state,¹⁹ in the not infrequent event that these are not self-evident from the structure of a transition or the nature of the imaginary normal mode. Furthermore, the identification of points on the reaction path, in addition to the reactants, transition state, and products, yields information about events in the entrance or exit channels. The type of information thus obtained may be geometric (when bonds break or form, when angles distort, etc.) or electronic (as monitored perhaps through localized orbitals²⁰). We intend to use the IRC

procedure described here in photochemical applications to study the evolution of initially vertically excited states. The energy gradient along the IRC can be analyzed in order to understand why a reaction takes a particular path.²¹

In the following we review the IRC algorithm of Ishida et al.¹⁴ and present our improvements in its automation. We then illustrate the method by considering the rotation barrier for the carbon-silicon double bond in silaethylene.

IRC Methodology

The algorithm of Ishida, Morokuma, and Komornicki¹⁴ for the determination of an IRC is sketched below. In order to account for the differing masses of atoms, mass-weighted Cartesian coordinates are adopted

$$Q_i = \sqrt{m_i} q_i$$

where q_i is any of the Cartesian coordinates of atom i whose mass is m_i . The mass-weighted gradient is then obtained from the gradient in Cartesian space by

$$G_i = g_i / \sqrt{m_i}$$

Given a set of nuclear coordinates \mathbf{q}_0 on the reaction path, one follows the direction of steepest descent, generating a finite step

$$\Delta Q = -A G_0 \quad \Delta q_i = \Delta Q_i / \sqrt{m_i} \quad \mathbf{q}_1 = \mathbf{q}_0 + \Delta \mathbf{q}$$

Here A is a positive scale factor, carrying the necessary conversion factors, and the minus sign corresponds to a downhill step. The parameter A determines how closely together the points on the IRC being traced will lie. We have found that a reasonable choice for A is given by taking the norm of the first of the preceding equations

$$A = |\Delta Q| / |G_0|$$

where the desired stride $|\Delta Q|$ is an input parameter. In practice, a stride of 0.15 Bohr-amu^{1/2} works well. A step size chosen in this way means the nuclear coordinates change about the same amount between each successive point on the IRC, while the energy will decrease by varying amounts between points depending on the steepness of the potential energy surface at any particular point. The original algorithm¹⁴ does not explicitly state how the step size A is to be chosen. Other workers⁷ have also chosen A so as to take steps of approximately constant length.

Because the step along the steepest descent direction at \mathbf{q}_0 is finite, the point \mathbf{q}_1 will not lie upon the reaction path. The gradient following procedure of Baskin et al.¹³ does not correct for this deviation. A new point \mathbf{q}_2 which does lie on the path is found by searching away from \mathbf{q}_1 for the minimum energy along the bisector \mathbf{d} of the unit vectors of the gradients at \mathbf{q}_0 and \mathbf{q}_1 , i.e.

$$\mathbf{d} = \mathbf{G}_0 / |\mathbf{G}_0| - \mathbf{G}_1 / |\mathbf{G}_1|$$

which is then normalized to a dimensionless unit vector \mathbf{D} . Usually we need only compute one energy, at a step δ along the vector \mathbf{D} , in addition to the energy at point \mathbf{q}_1 . (In practice, we normally take $\delta = 0.025$ bohr.) We get a third simultaneous equation, determining a parabolic fit to the energy along the line \mathbf{D} , by projecting the energy gradient at \mathbf{q}_1 onto this line. This saves at least one energy evaluation over the original algorithm.¹⁴ In the event that the distance from \mathbf{q}_1 to the minimum of this parabola exceeds 2δ we reject this fit in favor of an explicit, minimum-bracketing search. This occurs only when the IRC is rapidly curving and indicates that the stride being taken should probably be reduced.

The above procedure works only when \mathbf{G}_0 is nonvanishing and thus will not work for the initial step from the transition state. Following Ishida et al.¹⁴, we generate the full second derivative matrix at the saddle point. The unique mode with imaginary frequency then determines the initial direction away from the transition state. Since we know the value of the negative force

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constant k associated with this frequency, we take the harmonic step Δq that produces the desired energy lowering $k\Delta q^2/2$ (usually 0.5 mhartree). This choice prevents taking too large an energy step away from the saddle point when the imaginary frequency is large. The hypercircle minimization scheme of Müller¹⁵ would be perhaps more desirable for the first step, but it is not as easy to implement as this use of the imaginary normal mode. The full second derivative matrix needed for this initiating step is often generated anyway, in order to ensure that the stationary point is a true saddle point.

The above algorithm has been incorporated into GAMESS,²² one of the most widely used quantum chemistry program packages, and has been in routine use in our laboratories for about 1 year. All calculations described below were carried out with this program.

Generalization of the reaction path from Cartesian coordinates to internal coordinates has recently been discussed.²³

Silaethylene

As the simplest molecule containing the silicon-carbon double bond, silaethylene (H_2SiCH_2) has attracted a great deal of experimental and theoretical interest. Silaethylenes have long been implicated as reactive intermediates.²⁴ A substituted silaethylene was first isolated in 1976,²⁵ and the unsubstituted compound was unambiguously trapped in 1981.²⁶

A great deal of theoretical work has paralleled the experimental interest in this bond. In large part this work has been channeled into the study of the isomerization of silaethylene to methylsilylene (HSiCH_3) following the discovery by Gordon in 1978²⁷ that these isomers are nearly degenerate. Another major consideration has been the length of the silicon-carbon double bond. The hydrogen migration reaction and bond length prediction can apparently be treated by using standard methods at the Hartree-Fock level. Indeed, the earlier apparent disparities²⁸ between theory and experiment have now been resolved in favor of theory.²⁹

A topic of great interest for any doubly bound system is the rotational barrier about that double bond. This rotational barrier is often identified with the strength of the π bond, assuming the σ bond is little changed by the rotation. We would expect the ground and excited potential energy surfaces of silaethylene to qualitatively resemble those of ethylene.³⁰ To wit: the ground singlet state should possess a barrier to rotation, while the singlet and triplet $\pi \rightarrow \pi^*$ vertical excited states should possess stable minima at the 90° rotated geometries. The rotated-triplet and the ground-singlet states should possess diradical character at the heavy atoms, while the excited singlet will display zwitterionic character at its rotated equilibrium geometry. A second zwitterionic state arising from the rotational stabilization of the doubly π excited molecule will lie just above the first.

However, silaethylene should differ from ethylene in two ways. The lowest rotated singlet and triplet states, which possess an unpaired electron at each heavy atom, will be pyramidalized at the silicon, as is the case for the silyl radical. The zwitterionic excited singlet, possessing a strong Si^+C^- polarity, should lie well below the zwitterionic state of opposite polarity. These two zwitterionic states are of great interest in the context of the "sudden

polarization" phenomenon³¹ which has been extensively studied for carbon alkenes,³² but they are not considered further here.

Some theoretical attention has been focused on the lowest rotated singlet and triplet states of silaethylene. The triplet is the more stable of these two diradical states, and it has received the lion's share of this attention.^{27,33-37} The more accurate results,³⁴⁻³⁷ i.e., those at the double- ζ Hartree-Fock (DZ HF) or better level, predict the excitation from the planar singlet to the rotated triplet to be about 28-38 kcal/mol, with the higher values predicted by the more extensive correlated calculations.^{35,37}

Although it represents the transition state for the barrier to rotation, the twisted singlet has received less attention than the triplet. The use of a closed-shell HF wave function for the rotated singlet leads to an erroneously large rotation barrier.^{33a} Ahlrichs and Heinzmann³⁴ have used spin-restricted singlet open-shell HF to treat the rotated species and two-configuration CI for the planar singlet. This treatment is the lowest level which is qualitatively correct and yields a rotational barrier of 45 kcal/mol. Thus the rotated singlet lies above the rotated triplet, as one would expect both from Hund's rule and comparison with ethylene. In a short communication, Hanamura et al.³⁸ also considered this rotated singlet, using a GVB-PP(6) wave function. They report a rotational barrier of 43 kcal/mol but give few other details. An early semiempirical study³⁹ predicts a π bond strength of 42 kcal/mol, based on hydrogenation energies rather than the rotational barrier. The *path* connecting the planar singlet to its rotational transition state has never been examined.

Walsh⁴⁰ has used experimental kinetic and thermodynamic data to estimate the π bond strength as 39 ± 5 kcal/mol in 1,1-dimethylsilaethylene (DMSE). An independent experiment⁴¹ gives a value of 38 kcal/mol for the π bond in DMSE. These experiments and the range of theoretical estimates (42-45 kcal/mol) quoted above for the π bond in silaethylene represent a significant fraction of the value in ethylene. For ethylene the rotational barrier is known to be 65 kcal/mol,⁴² while the π bond strength estimated from hydrogenation energies is 59 kcal/mol.⁴³

The rotation about a double bond involves the breaking of an electron pair, a process that necessitates a multiconfigurational (MCSCF) treatment. In the present case, the twisted singlet possesses a mirror plane of symmetry. This enables it to be treated at the open-shell HF level. However, the path leading from the closed-shell planar form to this open-shell transition state has no symmetry, and no HF treatment is capable of handling this transformation. We choose the full optimized reaction space (FORS) model for MCSCF calculations due to Ruedenberg⁴⁴ to describe this rotation. In the present case, the active orbitals correspond to the carbon-silicon σ , π , π^* , and σ^* orbitals of the planar molecule. The two π orbitals must be included to handle

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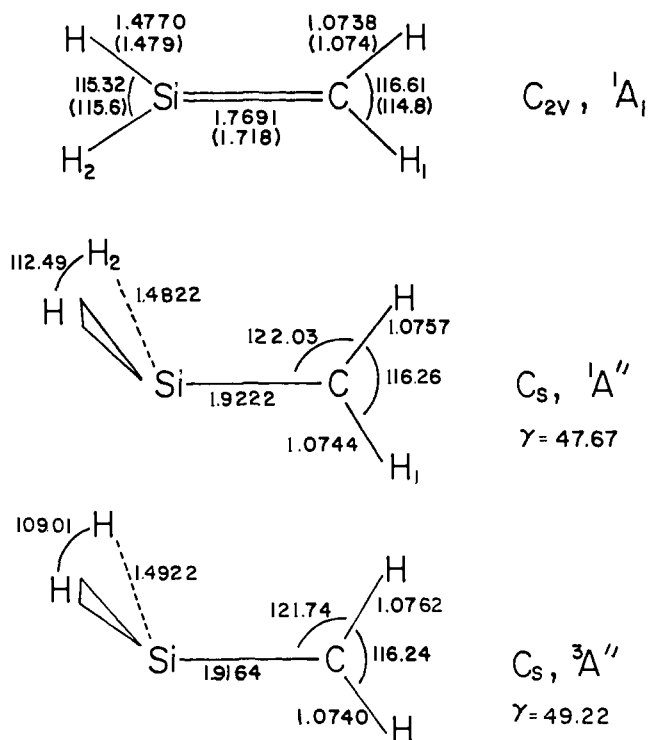


Figure 1. MCSCF/3-21G geometries for planar and singlet and triplet twisted silaethylene. Distances are in angstroms and angles in degrees. γ is the flap angle at silicon. The HF/3-21G geometry of silaethylene is given in parentheses.

the breakup of the π electron pair. The two σ orbitals are less crucial but are included since the σ bond elongates during the rotation, implying more left-right correlation in the twisted form. Distribution of the 4 reacting electrons within these active orbitals with all possible couplings leads to an MCSCF wave function containing 20 configurations. Most results presented below are taken from this MCSCF wave function. Equilibrium geometries, transition states, and the intrinsic reaction coordinate for the rotation of silaethylene were found by using the 3-21G basis.⁴⁵

The geometries of the stationary points located with the MCSCF wave function are presented in Figure 1. For the planar molecule, our silicon-carbon bond length (1.77 Å) is larger than the range of previously predicted DZ HF or higher level theoretical values (i.e., 1.69–1.72 Å).²⁸ Our value is larger since it is derived from a wave function without d polarization functions, and including only left-right but not angular and in-out correlating orbitals. Including these improvements in our wave functions would be expected to bring our value closer to the theoretical range given above. Figure 1 also includes the HF 3-21G structure of silaethylene, for which the Si-C bond length is indeed near the previously reported range. The full second derivative matrix for silaethylene was computed with the MCSCF wave function, by finite differencing of analytic first derivatives. This Hessian matrix for silaethylene is positive definite, confirming that this molecule is indeed planar.

Twisting about the silicon-carbon bond should lengthen it to a value more typical of a single bond. The structures of our (90°) twisted singlet and triplet state are also shown in Figure 1. As expected for two states with the same spatial orbital occupancies, these two have very similar structures. Keep in mind, however, that the singlet and triplet are rotational maxima and minima, respectively. Our Si-C bond length of 1.92 Å for these molecules is larger than the previously reported range of 1.85–1.88 Å, from DZ HF or better calculations.^{34,35,37} Again the discrepancy is due to our inclusion of the left-right correlating configurations. Note,

Table I. Reaction Path for Rotation in Silaethylene

point	energy ^a	R(SiC) ^b	Si flap ^c	C flap ^c	torsion ^c H ₁ CSiH ₂
planar	-327.356 55 (0.0)	1.769	0.0	0.0	0.0
28	-327.355 46 (0.7)	1.789	17.2	7.3	15.4
24	-327.354 60 (1.2)	1.792	23.0	9.4	24.1
20	-327.351 72 (3.0)	1.806	29.5	10.5	37.4
15	-327.341 02 (9.7)	1.848	38.2	11.4	60.0
12	-327.331 27 (15.9)	1.872	41.7	10.5	72.8
9	-327.320 16 (22.8)	1.891	44.3	8.7	84.8
5	-327.305 91 (31.8)	1.914	46.7	5.3	99.8
3	-327.300 80 (35.0)	1.920	47.3	3.3	106.7
1	-327.298 09 (36.7)	1.922	47.7	1.3	113.1
saddle	-327.297 59 (37.0)	1.922	47.7	0.0	117.0

^a In hartrees, with relative energies in kcal/mol in parentheses. ^b In angstroms. ^c In degrees.

however, that the magnitude of the bond length increase after rotation is consistent with the earlier calculations. For reference, the single bond length in methylsilane is found to be 1.867 Å by microwave spectroscopy.⁴⁶ The bond in twisted silaethylene thus seems to be a typical single bond, as expected. For the flap angle at silicon previous theoretical values for the triplet lie in the range 45–52°.^{34,35,37} Our structure for the triplet agrees well with these, and we find the singlet has nearly the same flap angle as does the triplet.

To begin tracing the intrinsic reaction coordinate from the twisted singlet back to its planar form, we obtained the full second derivative matrix for the MCSCF wave function. Normal coordinate analysis using this Hessian matrix yielded a twisting mode (a'') with an imaginary frequency of 949i cm⁻¹. This is the only imaginary mode present for this true transition state.

The total energies and coordinates at selected points along the rotational IRC are given in Table I. The flap angle at silicon decreases nearly uniformly as the molecule goes to planarity. The most important coordinate is the silicon-carbon bond length, which smoothly decreases as the molecule becomes planar. Note that the flap angle at carbon goes to 11°, although it is zero for both the planar and rotated forms. This slight pyramidalization is suggestive of carbanionic character, and the carbon atom is indeed negative in this molecule. The Mulliken charge⁴⁷ on carbon is -0.79 at the transition state and -0.84 for the planar form. This may be compared to the silicon charge of +0.71 at both end points. The remaining coordinates vary smoothly between their values at either end point of the IRC. Determination of the IRC was halted after 28 points were found. At this stage the energy is just 0.7 kcal/mol above the planar end point, but the molecule is still rather twisted. The small energy penalty for this twisting shows why bulky substituents can produce twisted silaethylenes.⁴⁸ Full geometric details for this IRC are available from the authors.

The energy of the triplet is -327.29916. With the energies for the two singlet stationary points shown in Table I, the MCSCF/3-21G classical barrier to rotation on the S_0 surface is 37.0 kcal/mol. The MCSCF/3-21G harmonic zero-point energy of silaethylene is 26.0 kcal/mol, and for the twisted singlet it is 24.4 kcal/mol. Thus inclusion of vibrational effects lowers the rotational barrier slightly, to 35.4 kcal/mol. The $S_0 - T_1$ separation is 36.0 kcal/mol.

Because the basis set used for the above calculations is small, and the treatment of electron correlation is limited to only a few configurations, the computed classical rotational barrier of 37.0 kcal/mol might seem to be in fortuitously good agreement with the experimental estimates of 39 ± 5⁴⁰ or 38 kcal/mol⁴¹ for the π bond in DMSE. We have performed larger, single-point calculations at the two singlet stationary points with the 6-31G* basis set,⁴⁹ containing both a larger sp basis and heavy-atom polari-

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zation. This basis gives a nearly unchanged MCSCF barrier of 36.8 kcal/mol. A second-order CI wave function, containing all double excitations from this MCSCF wave function, but keeping the bonds to hydrogen doubly occupied, gives a barrier of 36.9 kcal/mol. Unless correlation in the CH and SiH bonds has an effect, this barrier is remarkably insensitive to both the basis set and correlation effects beyond those included in the simple MCSCF wave function.

Summary

We have presented three improvements for the original IRC determination method.¹⁴ These improvements are (1) basing the step size taken on the norm of the gradient at the current IRC point, (2) using a gradient which must be calculated in any case to reduce the linear search time, and (3) taking a harmonically chosen step size away from the saddle point.

A relatively simple split valence MCSCF wave function was used to trace the IRC for the rotation of the prototypical silicon-carbon double bond. The IRC for the rotation of silaethylene shows that for the most part the coordinates vary smoothly during the rotation from the planar to twisted form. For example, the SiC bond length increases smoothly by about 0.15 Å as this bond loses its multiple character. However, the carbon atom is slightly

pyramidalized during the rotation although it is planar at the rotational transition state. As expected for a radical silicon center, the silicon atom is greatly pyramidalized during the rotation. The rotation barrier on the S_0 surface is about 37 kcal/mol. Thus the SiC π bond strength as estimated by the rotational barrier is intermediate to that found for the CC bond (65 kcal/mol⁴²) and the recently calculated SiSi π bond strength (22 kcal/mol⁵⁰). The SiC rotational barrier is very insensitive to calculational improvements such as heavy-atom polarization or extended correlation treatments. The calculated rotational barrier agrees very well with the experimental estimates of the π bond strength. Triplet silaethylene has a geometry very similar to the rotated singlet and lies about 1 kcal/mol below it.

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Theoretical Study on the Dimerization of Silanone and the Properties of the Polymeric Products $(H_2SiO)_n$ ($n = 2, 3,$ and 4). Comparison with Dimers $(H_2SiS)_2$ and $(H_2CO)_2$

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Abstract: In an attempt to extend knowledge of the reactivity of silicon-oxygen doubly bonded compounds (silanones), the potential energy surface of the dimerization of $H_2Si=O$ was investigated by means of ab initio molecular orbital calculations. The dimerization is found to proceed with no barrier to yield the cyclic product $(H_2SiO)_2$ by forming stepwise two new bonds. The structure, vibrational frequencies, and dimerization energy for the dimeric product $(H_2SiO)_2$ are compared with those for the similar cyclic dimers $(H_2SiS)_2$ and $(H_2CO)_2$ at the same level of theory. All these dimers have a planar four-membered ring with D_{2h} symmetry. The unusually short Si-Si distance in $(H_2SiO)_2$ is explained in terms of the greater affinity of silicon for oxygen. Also discussed are the structures and stability of the cyclic trimer $(H_2SiO)_3$ and tetramer $(H_2SiO)_4$.

There has currently been considerable interest in the possible existence of silicon-oxygen doubly bonded compounds, silanones.^{1,2} Experimental evidence for the transient existence has accumulated in the last few years.³ Since, however, most of the evidence is rather indirect, we have recently undertaken the theoretical studies of the thermodynamic and kinetic stability of the parent compound, $H_2Si=O$.^{2,4} In an attempt to extend knowledge of the reactivity, we report here the first ab initio calculations of the reaction of two $H_2Si=O$ molecules to form the dimeric product cyclodisiloxane $(H_2SiO)_2$.

There has been active work on polymeric cyclodisiloxanes $(R_2SiO)_n$, because of the practical importance. However, the lowest member ($n = 2$) of the series is almost unknown, and its chemistry is only recently starting to develop.⁵ In view of the situation we tried to explore the structure, vibrational frequencies,

and dimerization energy for the cyclic dimer $(H_2SiO)_2$ from a theoretical point of view. To characterize the properties of $(H_2SiO)_2$, we compared these results with those calculated for the similar cyclic dimers $(H_2SiS)_2$ and $(H_2CO)_2$ at the same level of theory. Also examined were the properties of the cyclic trimer $(H_2SiO)_3$ and tetramer $(H_2SiO)_4$.

Computational Details

All calculations were carried out for closed-shell singlets. Geometries were fully optimized at the Hartree-Fock (HF) level with the split-valence 3-21G⁶ and polarized 6-31G*⁷ basis sets by using the analytical energy gradient technique. The harmonic vibrational frequencies obtained at the HF/3-21G level were used to compute zero-point vibrational energies. The effects of electron correlation were calculated by means of second-order Møller-Plesset perturbation (MP2) theory,⁸ with

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