A THEORETICAL INVESTIGATION OF THE Si - Si DOUBLE BOND IN A SERIES OF SUBSTITUTED DISILENES

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Abstract: The nature of the Si-Si double bond in a number of substituted disilenes ($R_2Si=SiR_2$, $R=H$, CH_3 , *t*-butyl, mesityl) was investigated using the Fenske-Hall molecular orbital method. The results of the electronic structure calculations indicate that alkyl substituents serve to stabilize the Si-Si double bond electronically as well as sterically, while aryl substituents appear to destabilize the Si-Si bond. Calculations including d-orbital functions in the Si basis set show that the availability of d-orbitals on Si plays an important role in altering the compositions and lowering the energies of the virtual molecular orbitals. This result is in agreement with the experimentally observed spectroscopic transitions in the visible region and may also account for the relatively low rotational barriers that have been observed in the experimentally determined disilenes.

Introduction

Compounds containing multiple bonds between second-row elements (P, Si) are of considerable current interest¹ to both experimental and theoretical chemists. Molecules of this type have been proposed since 1877 although they have only recently been isolated and characterized. The first of these compounds to be unambiguously characterized was tetramesityldisilene, reported by West and coworkers in 1981.² Since then a number of disilenes, all stabilized by bulky substituents, have been synthesized and structurally characterized.³⁻¹⁰ While the disilenes are more reactive than their alkene counterparts, the general reactivity trends are similar. Disilenes structures can differ markedly from the structures of analogous alkenes. The Si-Si bond distances in disilenes show the same degrees of shortening (relative to the known Si-Si single bond lengths in silanes) as do C-C distances in alkenes relative to alkanes but disilenes are, in general, non planar, exhibiting both twisting and bending about the Si-Si axis.¹¹

Disilenes provide an interesting and challenging problem for the theoritician. The Si-Si bond lengths (determined by single-crystal X-ray studies) clearly indicate some degree of multiple bonding; however, the nonplanarity of disilenes and the low barrier to rotation about the Si-Si axis call into question the usual double bond assignment of one σ - and one π - bond. Furthermore the "Classical Double Bond Rule," as stated in many inorganic chemistry textbooks, implies that π -bonding using Si d-orbitals may be an important factor in the bonding of these compounds.¹²

Previous theoretical investigations of disilenes have concentrated on the geometry and stability of disilene, Si_2H_4 , in the singlet state, relative to its geometry and stability in the lowest lying triplet state.¹³⁻³² Michl and Raabe, in their 1985 review of silene chemistry, pointed out that the stability of singlet disilene relative to the triplet state has been underestimated in the early theoretical work^{1e} whereas Teramae²⁶ concluded that the ground-state electronic structure of disilene involves a significant contribution from the diradical (or triplet) state. Teramae also calculated longer Si-Si bond distances and larger deviations from planarity than those previously reported.²⁶ Few calculations have been done on substituted disilenes.^{17b, 19, 29, 32} Krogh-Jespersen investigated tetramethyldisilene, $Si_2(CH_3)_4$, and found that the ground state is a singlet with a *trans*-bent geometry.^{17b} The state corresponding to the planar geometry is 1.0 kcal/mole higher in energy. Inclusion of d-orbital functions in the silicon basis set reverses these states.

The goal of this study is to investigate the bonding in the known disilenes and to compare

their electronic structures with those of the corresponding alkenes in order to explain the experimentally observed similarities (reactivity patterns) and differences (electronic spectra and

rotational barriers). Calculations were performed on three known disilenes: tetra-(*t*-butyl)disilene, **3**, tetramesityldisilene, **4**, and *trans*-1,2-di-(*t*-butyl)-1,2-dimesityldisilene, **5**. Calculations were also performed on disilene, Si₂H₄, **1**, and tetramethyldisilene, **2**, in order to detect any trends upon substitution of bulkier substituents, as well as on tetraphenyldisilene, **6**, to determine the effect of an unsubstituted aryl group. For each disilene compound the calculations were done twice: with the minimal basis set and with an extended basis set that included d-orbital functions on Si.

METHODS

Molecular orbital calculations were carried out on a VAX 8600 computer system using the Fenske-Hall molecular orbital model.³³ This method is based on a nonparameterized, nonempirical approximate Hartree-Fock-Roothaan procedure. The results of each calculation (eigenvalues and eigenvectors) are completely determined by the geometry of the molecule and the nature and size of the basis set.

Basis Functions: Clementi's free atom double- ζ Hartree-Fock functions³⁴ were used for carbon and silicon. All but the valence shell p-functions were curve-fit to single- ζ form by use of the criterion of maximum overlap.³⁵ A value of 1.16 was used for the hydrogen atom 1s orbital exponent.³⁶ The exponent for the Si d-orbitals was set to 1.38.

Geometry: The purpose of this study is to chart the effect of different substituents on the Si-Si interaction. This is done primarily by examining the total orbital overlap population and the π -orbital overlap population between the Si atoms. In order for any comparison to be valid the changes in overlap population must not be due to differences in Si-Si bond distances, therefore in all calculations the Si-Si bond distance was held constant at 2.143 Å so that comparisons of overlap populations would be valid. Other molecular geometries (C-Si bond lengths and C-Si-C bond angles) for **4** and **5** were taken from x-ray crystal structure data.^{2c, 8} The geometry (C-Si bond lengths and C-Si-C bond angles) of **3** was constructed from the data for **5**. The geometry (C-Si bond lengths and C-Si-C bond angles) of **2** was constructed using the same C-Si-C bond angle that was used for **3**. In addition, a Si-C bond length of 1.904 Å, a C-H bond length of 1.09 Å, and an H-C-H bond angle of 105° was used. The optimum planar geometry (Si-H bond lengths and H-Si-H bond angles) of **1** as determined by Krogh-Jespersen in 1985 was used.^{17b}

Fragment Orbital Analysis: All calculations except those for C₂H₄ and **1** were performed using the transformed basis approach.^{33d,37} A molecular orbital analysis was performed on each substituent, treated as a neutral radical (e.g., Me•, *t*-butyl•, and mes•). The resulting fragment molecular orbitals were used as a basis set for the calculations on the full molecule. This approach greatly simplifies the interpretation of the results for systems with large substituents.

RESULTS AND DISCUSSION

Minimal Basis Set. The results of the calculations on **1** and **2** indicate that the bonding in these molecules can best be described as being analogous to the bonding in the corresponding alkenes. There are no substantial differences between the C- and Si- multiply bonded species. The most important result, for the purposes of this study, is that the HOMO in each case is a pure Si $\pi\pi$ - $\pi\pi$ bonding molecular orbital and that the LUMO is the corresponding antibonding molecular orbital. The HOMO is stabilized by approximately 3 eV relative to the Si p-orbitals (approximately 2 eV in the case of the methyl substituted disilene) and there is no evidence to suggest that a diradical structure would be favored at this level of approximation.

Two competing effects are observed as the size of the alkyl substituent is increased from H (in **1**) to CH₃ (in **2**) to C(CH₃)₃ (in **3**). The first effect is that the energy of the HOMO (in all cases a Si-Si π -bonding orbital) increases relative to the energy of the Si atomic p-orbitals (Table I). The π bond is less stabilized (relative to the atomic p orbitals) in the bulkier **3** than in **1** or **2**. The second effect is that the total overlap population³⁸ between the Si atoms increases, implying that the alkyl groups are acting as electron donating groups (Table II). There is also significant interaction between the Si 3s orbitals and the lower energy *t*-butyl fragment orbitals, thus further stabilizing the molecule.

In tetramesityl disilene, **4**, the picture is slightly altered. The total overlap population between the Si atoms is substantially lower than that observed in **2** and **3**, indicating that the

phenyl rings are acting as electron-withdrawing groups. There are two important stabilizing effects, however, that are related to the molecular geometry. The solid-state geometry of **4** is such that two of the mesityl groups *cis* to each other are approximately in the same plane as the C₄Si₂ core, whereas the other two mesityl rings are approximately perpendicular to this plane (Figure

Molecule	Stabilization Energy ^b		HOMO-LUMO Gap		Observed Transitions	
	without d-orbitals	with d-orbitals	without d-orbitals	with d-orbitals	λ_{max} (nm)	ΔE_{obs} (eV)
1	3.06	3.15	9.18	4.36		
2	1.86	2.26	10.68	3.80	345 ^c	3.59
3	1.06	1.68	11.28	3.92	433 ^d	2.86
4	0.34	1.09	7.94	3.23	420 ^c	2.95
5	0.76	1.49	10.92	3.56	332 ^e	3.69

(a) All energies are in eV. (b) The stabilization energy is defined as the energy difference between the atomic Si p_y orbital and the π -bonding orbital in the disilene. (c) Reference 2a. (d) Reference 7. (e) Reference 8.

1a). While this is an adequate steric arrangement, one can imagine other less sterically hindered geometries.³⁹ The HOMO in **4** is a conjugated π system comprising both Si atoms and the π orbitals of the two mesityl rings that are approximately coplanar with the Si₂C₄ framework. This orbital is both Si-Si bonding and Si-ring bonding. The LUMO is Si-Si antibonding

and Si-ring bonding. The phenyl-Si-Si-phenyl conjugation apparently weakens the Si-Si bond, as evidenced by the decreased Si-Si overlap population, but provides some stabilization of the molecule due to delocalization.

The ortho-methyl groups on the mesityl rings that are oriented perpendicularly to the molecular plane contribute to the stability of the molecule. There is a substantial agostic interactions between all four of these methyl groups and the Si-Si bond (Figure 1) which provides some electron-donating alkyl functionality to offset the electron withdrawing aryl groups. This observation may help to explain why disilenes with 2,6-disubstituted aryl groups as substituents have been isolated but tetraphenyl disilene itself has not been isolated.

In order to further study the effect of aromatic ring substituents, calculations were done on tetraphenyl disilene in two geometries, one corresponding to the mesityl geometry (two rings approximately planar and two rings approximately perpendicular to the Si-Si bond), **6a**, and one corresponding to all rings rotated approximately 75° relative to the plane, **6b**. The total overlap population between the two Si atoms decreases substantially in both **6a** and **6b** relative to the total overlap population in **4** (Table II). This provides strong evidence in support of the stabilizing effect of alkyl substituents in the ortho-positions of the aromatic ring.

In the mixed substituted disilene, **5**, the mesityl groups are oriented perpendicularly to the Si-Si π bond in the solid state (Figure 1b) and do not contribute to any π delocalization. The effect of this is seen dramatically in the large increase in the Si-Si overlap population as compared with that of **4**. The HOMO in this system is a pure Si-Si π -bond, analogous to what was observed in the tetra-alkyl substituted systems, but there is still a strong interaction between the ortho-methyl groups on the two remaining mesityl rings and the Si atoms.

Expanded Basis Set. The composition and relative ordering of the occupied molecular orbitals are not substantially altered when d-orbitals are included in the Si basis set relative to what is observed in the minimal basis set calculations. A minor mixing of Si d-orbital character in the π -

Table II. Total Overlap Populations and π -Orbital Populations Between Silicon Atoms in Several Disilenes^a

Molecule	TOP ^b	π -OP ^c
1	1.315	0.499
2	1.396	0.535
3	1.438	0.559
4	1.368	0.505
5	1.456	0.588
6a	1.334	0.509
6b	1.340	0.496

(a) The Si-Si bond distance in each molecule is the same: 2.143Å, to allow for comparison of overlap populations. (b) See reference 38. (c) π -orbital population is the overlap population between the two silicon atoms in the π -bonding orbital only.

The decreased HOMO-LUMO gap correlates much better with the experimentally observed electronic transitions of the known disilenes that occur in the visible region of the spectrum (Table I).⁴⁴ Using the minimal basis set the HOMO-LUMO gap for the disilenes is of the same magnitude as that observed for alkenes. Alkenes generally exhibit $\pi - \pi^*$ transitions in the ultraviolet region of the spectrum.

Inclusion of the d-orbitals on Si also changes the composition of the LUMO from a Si $p_y - \text{Si } p_y$ π^* -antibonding orbital to a π -bonding orbital that is orthogonal to the HOMO and composed of a mixture of Si p_x and Si d_{xz} orbital character (Figure 2). The mixing of the d-orbital character with the p_x orbital allows the π -bond to be localized between the two silicon atoms and directed away from the substituents.

The lower rotation barrier of disilenes compared to that of alkenes may be attributed to both the smaller HOMO-LUMO gap and the altered character of the LUMO. We have not performed a population analysis in the excited state yet so these results cannot be compared with the results of the more accurate ab-initio methods for Si_2H_4 . However, it is possible that because of the smaller HOMO-LUMO gap a significant number of molecules may be in the first electronic excited state, $(\pi_y)^1 (\pi_x)^1$, rather than the

ground state, $(\pi_y)^2$, at room temperature. In the first excited state the π -bond in the molecule is essentially two half π -bonds with one of the half π -bonds having significantly higher energy. This will lead to an overall weaker π -bond than what would occur in the ground state, thereby lowering the rotation barrier.

Summary. Our calculations show that the bonding in disilenes is very sensitive to the substituents on the silicon atoms. Bulky substituents on the isolated disilenes serve not only to protect the Si-Si double bond sterically but also to stabilize the bond electronically. Alkyl groups are more stabilizing than aryl groups, providing greater electron donation into the double bond. Aryl substituents appear to be electron withdrawing, and therefore destabilizing. The enhanced reactivity of disilenes compared with that of alkenes may be attributed to the existence of low-lying unoccupied orbitals that have substantial Si d-orbital character. These virtual orbitals may also provide a low-energy pathway for rotation about the Si-Si axis.

bonding HOMOs occurs in several of the molecules studied. This mixing lowers the energies of the HOMOs slightly more than what is observed in the other occupied molecular orbitals.

The compositions and energies of the virtual (unoccupied) molecular orbitals are significantly altered when Si d-orbitals are included in the basis set.⁴¹ The substantial addition of Si d-orbital character in the LUMO significantly lowers its energy such that a large decrease in the HOMO-LUMO gap occurs in each molecule (Table I) along with a marked change in the nature of the LUMO. The effect of altering the character of frontier orbitals in main-group compounds by including d-orbital functions in the basis set of the main-group element is not unprecedented. Similar results have been obtained in molecules as diverse as SO_2 , H_2S ,⁴² CH_2Cl_2 , and CH_3I .⁴³

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