work. The method then not only reproduces the charge relationship but also supports the contention of π back-bonding in the halogens.

It can be argued that the same results would be obtained by assuming no FC or ClC π bonding and 0% s character in the halogen orbital involved in the σ bond. This would contradict the ESCA results presented above and electronegativity data presented in a separate paper.[23] Thus another assumption would be required to explain why F (or Cl) used different hybrids for different bonds. This of course is possible but unnecessary in light of Politzer's results.

Huheey also compared results he obtained for some of the molecules in Table III to Politzer's data.[28] He utilized an energy minimization method which allowed for three contributions, i.e., electronegativity energy, a Madelung potential energy using point charges, and a covalent energy term, His values also compared favorably with Politzer's. The present method does not require the use of all of the energy terms and thus requires much less input data. It also suggests that the ionic terms are not needed for the low polarity bonds. It does, however, indicate a possible direction to modify the present scheme to account more reasonably for high polarities such as in LiCCH.

Summary

A method is presented that allows the calculation of atomic charges in molecules to be done in a simple manner. Three relations are involved, viz., a definition of orbital electronegativity (eq 19), a bond electronegativity equalization scheme (eq 5), and a charge conservation principle (eq 6). It is shown that both empty and filled orbitals as well as variable bond orders are treated in a natural manner. This is done with the addition of b_i and $n_{A,i}{}^0$ terms in eq 19. Use of these relations leads to a series of simultaneous equations which are linear in orbital charge.

Results obtained from this method are compared to other theoretical (Mulliken population analysis, Politzer electron count method, and the PEOE method) and experimental ESCA data. It is shown that very good correlation is obtained. It is also shown that the method can provide a useful technique for analyzing bonding situations for type of bond and orbital used.

It should be noted that this scheme is designed to treat only inductive (through bond) effects. The treatment of properties which are sensitive to field effects (through space)[26,29] is thus outside of its scope.

Registry No. HLi, 7580-67-8; HCH_3, 74-82-8; HCH_2Me, 74-84-0; $HCHMe_2$, 74-98-6; $HCMe_3$, 75-28-5; $H_2C{=}CH_2$, 74-85-1; $HC\equiv CH$, 74-86-2; $MeNH_2$, 74-89-5; MeOH, 67-56-1; MeF, 593-55-3; MeCN, 75-05-8; HCN, 74-90-8; HCHO, 50-00-0; HAc, 75-07-0; HCO_2H, 64-18-6; HCO_2Me, 107-31-3; $HCONH_2$, 75-12-7; HCOF, 1493-02-3; HCF_3, 75-46-7; NH_3, 7664-41-7; H_2NNH_2, 302-01-2; $HNMe_2$, 124-40-3; H_2NCHO, 75-12-7; HNO_2, 7782-77-6; HNCO, 75-13-8; H_2O, 7732-18-5; HOAc, 64-19-7; HF, 7664-39-3; $HSiH_3$, 7803-62-5; H_2S, 7783-06-4; HSMe, 74-93-1; HCl, 7647-01-0; CH_2F_2, 75-10-5; CHF_3, 75-46-7; CF_4, 75-73-0; EtF, 353-36-6; MeAc, 67-64-1; $MeCF_3$, 420-46-2; MeOMe, 115-10-6; $LiC\equiv CH$, 1111-64-4; $FC\equiv CH$, 2713-09-9; $ClC\equiv CH$, 593-63-5; FCN, 1495-50-7; ClCN, 506-77-4; NCCN, 460-19-5; SCO, 463-58-1; OCO, 124-38-9; NNO, 10024-97-2.

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Theoretical Studies of Reactions of H_2SiNH and Its Isomer $HSiNH_2$

Thanh N. Truong and Mark S. Gordon*

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105. *Received August 5, 1985*

Abstract: The structure and reactivity of unsaturated singlet silicon-nitrogen compounds is theoretically investigated. Ab initio calculations demonstrate that the planar silylene $HSiNH_2$ is the global minimum on the $SiNH_3$ surface, with the planar doubly bound species H_2SiNH 18 kcal/mol higher in energy. The internal rotational barriers are computed to be 26.9 kcal/mol for $HSiNH_2$ and 37.9 kcal/mol for H_2SiNH. However, the barrier for the inversion of H_2SiNH is only 5.6 kcal/mol, so that inversion is favored over rotation for this species. The isomerization connecting H_2SiNH to $HSiNH_2$ has a barrier of 60 kcal/mol. The transition-state structures, as well as the exothermicities of the concerted hydrogenation processes of both compounds, are also examined.

I. Introduction

In recent years, there has been considerable interest in the study of reactive intermediates which possess multiple bonds to silicon. Silicon-silicon and silicon-carbon double bonds in particular have been well-studied both experimentally and theoretically.[1,2] However, relatively little attention has been paid to the silicon-nitrogen double bond.

The substituted silanimine, R_2SiNR, was observed in both gas-phase pyrolysis and photolysis by Sommer.[3,4] Wiberg has also reported some evidence for the formation of compounds containing silicon-nitrogen double bonds.[5] To our knowledge, no other experimental data for such species or its properties have been reported in the literature. While several calculations have been performed on the related triply (HSiN)[6,7] and singly (H_3SiNH_2)[8] bound species, no theoretical study of silanimine has appeared to date.

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In this work, several properties related to the molecular and electronic structures and reactivity of silanimine (I) and its isomer aminosilylene (II) in their closed shell singlet states will be presented. These include the internal rotation barriers of the two

$$\underset{\text{I}}{H_2Si{=}NH} \qquad \underset{\text{II}}{HSi{-}NH_2}$$

compounds, the isomerization transition state and related energetics, and the hydrogenation reactions of I and II.

II. Methods of Calculation

For the rotation of H_2SiNH, molecular structures and transition states are predicted at the multiconfiguration SCF (MCSCF) level. Internal rotation in this species will break the formal double bond, creating a diradical which requires a multiconfigurational description.

On the basis of the Full Optimized Reaction Space (FORS) method, the MCSCF wave functions only include those configurations arising from the active orbitals.[9] In this case, the active orbitals are σ, σ^*, π, and π^* for H_2SiNH. The active orbitals for the internal rotational transition state are chosen to be the σ, σ^*, and two unpaired and orthogonal p orbitals on the silicon and nitrogen. In all cases, the four electrons are distributed in all possible ways among the four active orbitals, while the other occupied orbitals are held fixed. This leads to 8 configurations in the MCSCF wave function for the rotation transition state of silanimine and 12 configurations for the planar structure. For all other reactions, the molecular geometries and transition states are computed at the single configuration SCF level.

The geometries of all species are optimized by using the 3-21G basis set,[10] augmented with d orbitals on both silicon and nitrogen, since previous studies have shown that d orbitals on nitrogen are important for the prediction of correct structures.[10,11] The exponents used are 0.395 for silicon[12] and 0.8 for nitrogen.[13] This basis set will be denoted as 3-21G* in this paper. To obtain more accurate energies and geometries, all structures other than the silanimine internal rotation transition state were reoptimized with use of the 6-31G** basis, which also includes p orbitals with an exponent of 1.1 for hydrogen.[10]

The silanimine rotational barrier is refined by computing MCSCF single points with the 6-31G* basis set.[10] This is then augmented by second-order CI (SOCI) calculations including all single and double excitations from each of the MCSCF configurations in which only the core orbitals, Si-H bonds, and N-H bonds are held doubly occupied. The SOCI calculation gives rise to 16500-17500 configurations, depending on the structure.

For the remaining reactions, electron correlation effects are incorporated by applying many-body perturbation theory.[14] Single point calculations were carried to fourth order, neglecting triple excitations, with the MC-311G** basis set at the 6-31G** geometries.[10] The former basis set refers to 6-311G**[15] for atoms in the first two rows of the periodic table. Since that basis does not exist for later rows, it is replaced with the extended basis developed by McLean and Chandler (MC),[16] augmented by the appropriate polarization functions. The single point calculations carried out in this manner are denoted as MP4(SDQ)[17]/MC-311G**//6-31G**.

A modified version of GAMESS[18] was used to carry out the MCSCF and SOCI calculations, while the HF and MP4 calculations were performed with GAUSSIAN82.[19]

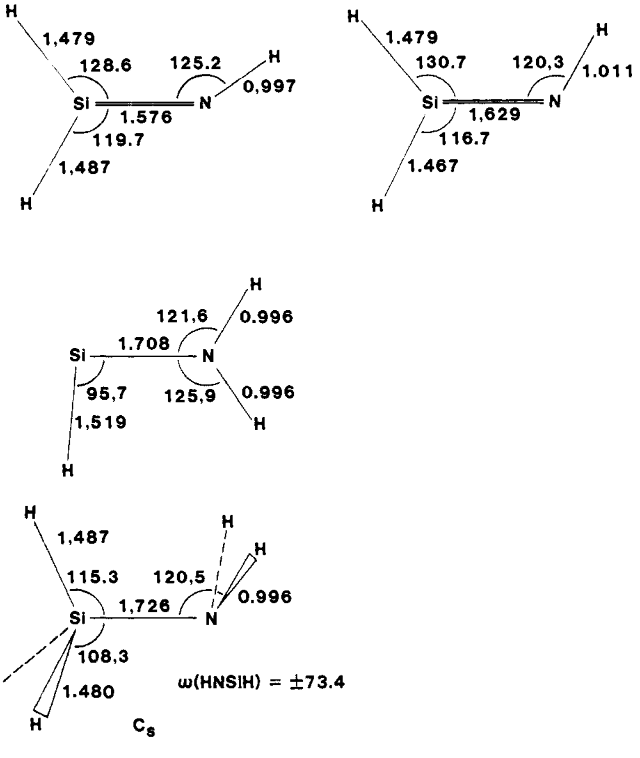

Figure 1. Structures of stable species. (Bond lengths in Å, angles in deg.)

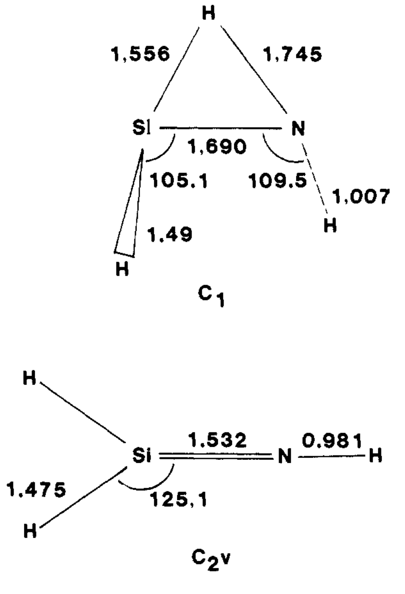

Figure 2. Structures of transition states. Top: 1,2-shift; HNSiH dihedral angle = 188.0°, HSiNH dihedral angle = 107.1°. Bottom: inversion. (Bond lengths in Å, angles in deg.)

III. Results and Discussion

A. Molecular Structures. The 6-31G** structures for the stable molecules considered in this paper are shown in Figure 1, along with the MCSCF planar structure for H_2SiNH. There is a noticeable increase in the Si-N bond length in the MCSCF structure compared to the HF structure due to the incorporation of antibonding character in the MCSCF wave functions. The Si-N single bond in $HSiNH_2$ is somewhat shorter than the normal Si-N

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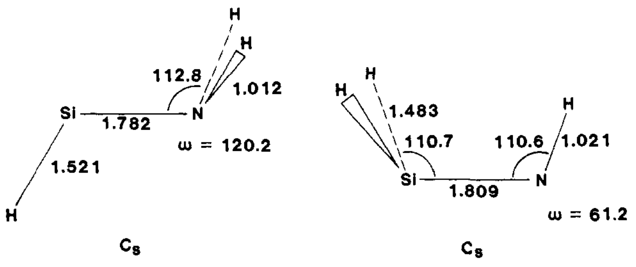

HF/6-31G** MCSCF/3-21G*

Figure 3. Rotation transition state structures of H_2SiNH and $HSiNH_2$. (HSiN angle = 99.3°.) (Bond lengths in Å, angles in deg.)

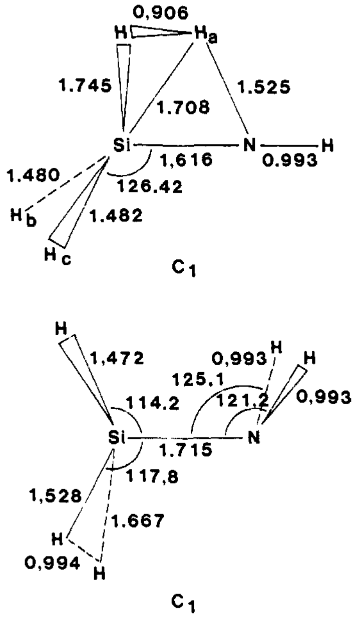

Figure 4. Transition state structures for H_2 + H_2SiNH and H_2 + $HSiNH_2$ at the HF/6-31G** level. For the top structure, HNSi angle = 135.4°, the H_bSiN angle = 125.4°, the $HNSiH_a$ dihedral angle = 203.1°, the $SiNH_aH$ dihedral angle = 7.4°, the H_bSiNH_a dihedral angle = −101.7°, and the H_cSiNH_a dihedral angle = 94.9°. (Bond lengths in Å, angles in deg.)

single bond in saturated H_3SiNH_2. This may be explained by the interaction between the nitrogen lone pair and the empty p orbital on silicon. Furthermore, the HF/3-21G* Si–N vibrational stretching frequencies for H_2SiNH, $HSiNH_2$, and H_3SiNH_2 respectively are 1247.82, 949.60, and 898.27 cm^{-1}. This indicates that the Si–N bond in $HSiNH_2$ is much closer to a single bond than a double bond but supports the notion that there is some lone pair–empty p orbital interaction.

The transition states for the isomerization connecting H_2SiNH and $HSiNH_2$ and for the inversion of H_2SiNH are shown in Figure 2. The short bond length of 1.56 Å between silicon and the migrating hydrogen and the almost single Si–N bond length indicate that the isomerization transition state occurs at an early stage with respect to the position of the migrating hydrogen. Apparently, judging from the Si–N bond length at the saddle point, the π bond is broken early as well. The inversion transition state has C_{2v} symmetry and a very short Si–N bond length of 1.53 Å, compared to a normal double bond of 1.58 Å in H_2SiNH.

The structures for the internal rotation transition states for H_2SiNH and $HSiNH_2$ are shown in Figure 3. The force constant matrix for each structure has one imaginary frequency corresponding to the internal rotational mode. Note that the Si–N bond length was increased substantially in both transition structures to a value considerably larger than that in silylamine (see Figure 1); thus, the double bond character in each case has been effectively removed. Both structures have C_s symmetry. It should be pointed out here that, for rotated silanimine, the structure with the imino hydrogen rotated by 180° also has a Hessian matrix with just one negative eigenvalue. At the current level of theory, the two structures only differ by 0.2 kcal/mol. The transition states for the hydrogenation of silanimine and of aminosilylene are shown in Figure 4. The reverse directions of these reactions correspond to the 1,2- and 1,1-hydrogen elimination from H_3SiNH_2, respectively. These transition states are very similar to the elimination of H_2 from disilane[20] and ethane.[21] It is particularly interesting for the hydrogenation of H_2SiNH that the hydrogen molecule initially attacks the silicon side to yield a saddle point resembling a complex between SiH_4 and NH. Only in the later stages of the reaction does one of the hydrogens move toward the nitrogen to form a new N–H bond.

Table I. Total Energies of Molecules (Hartree)

	SCF/3-21G*[a]	SCF/6-31G**	MP4/MC-311G**[b]
H_2	−1.122950	−1.131330	−1.167675
H_2SiNH	−343.341717	−345.057176	−345.402398
$HSiNH_2$	−343.379460	−345.095907	−345.430942
H_3SiNH_2	−344.573437	−346.294542	−346.660252
1,2-H shift TS	−343.240765	−344.953686	−345.313162
H_2SiNH inv. TS	−343.336465	−345.051280	−345.393530
$HSiNH_2$ rot. TS	−343.337171	−345.055750	−345.388107
1,2-H_2 elim. TS	−344.399756	−346.129245	−346.517251
1,1-H_2 elim. TS	−344.438762	−346.165707	−346.553110

[a] SCF/3-21G* including d orbitals on nitrogen. [b] Single point MP4(SDQ)/MC-311G** at 6-31G** geometries.

Table II. Relative Energies (kcal/mol)

	SCF/3-21G*[a]	SCF/6-31G**	MP4/MC-311G**[b]
H_2SiNH	0.0	0.0	0.0
$HSiNH_2$	−23.7	−24.3	−17.9
1,2-H shift TS	63.4	64.9	56.0
H_2SiNH inv. TS	3.3	3.7	5.6
$HSiNH_2$ rot. TS	2.8	0.9	9.0
H_3SiNH_2	0.0	0.0	0.0
1,1-H_2 elim. TS	84.5	80.8	67.2
1,2-H_2 elim. TS	109.0	103.7	89.7
H_2 + H_2SiNH	68.2	66.5	56.6
H_2 + $HSiNH_2$	44.6	42.2	38.7

[a] SCF/3-21G* including d orbitals on nitrogen. [b] Single point MP4(SDQ)/MC-311G** at 6-31G** geometries.

B. Energetics. The HF and MP4 total energies for all species are summarized in Table I and their relative energies are shown in Table II. The global minimum on the ground state potential surface of $SiNH_3$ is planar $HSiNH_2$, whereas the normal planar doubly bound isomer H_2SiNH is 18 kcal/mol higher in energy. This is consistent with previous calculations on this surface.[22] In contrast, in the similar molecule $SiPH_3$, the planar doubly bound structure H_2SiPH is found to be 13 kcal/mol more stable than its nonplanar silylene isomer.[23] Apparently, the nitrogen is better able to accomplish π-like back-donation into the empty silicon p orbital, thereby stabilizing the silylene structure, than is phosphorus. Furthermore, nitrogen is better able to accommodate roughly sp^2 hybridization (i.e., ~120° angles) than is phosphorus, the latter preferring angles closer to 90°. Finally, inversion barriers are generally smaller at nitrogen than at phosphorus centers. Because of this, nitrogen is more likely than phosphorus to assume a planar structure.

The 1,2-hydrogen shift from silanimine to the corresponding silylene is found to have a 56-kcal/mol barrier. This large barrier is the same order of magnitude as that for its analogue H_2SiPH molecule.[23]

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Table III. Energetics for Internal Rotation of H_2SiNH

	H_2SiNH	H_2SiNH rot. TS	E_b (kcal/mol)
MCSCF/3-21G*	−343.401 236[a]	−343.327 520[a]	46.3
MCSCF/6-31G*	−345.109 106[a]	−345.034 726[a]	46.7
SOCI/6-31G*	−345.180 614[b]	−345.120 245[b]	37.9

[a] 4 electrons, 4 internal orbitals. [b] 6 electrons, 5 internal orbitals.

It is interesting to compare the barriers for inversion and internal rotation in silanimine. The inversion barrier is predicted to be just 5.6 kcal/mol at the MP4 level (Table II; note that a FORS-MCSCF/3-21G*//FORS-MCSCF/3-21G* calculation at the inversion transition state suggests very little configurational mixing). The calculated barrier is consistent with the previously reported small inversion barrier for the analogous compound formaldimine, H_2CNH.[24] For the internal rotation, the total energies computed with MCSCF and SOCI are listed in Table III. At this level of computation, the rotation barrier is calculated to be 37.9 kcal/mol (Table III). Thus, the inversion of silanimine is a more likely process than the rotation. Note that the MCSCF/6-31G* rotation barrier is 46.67 kcal/mol, much larger than the SOCI result. In part, this reflects the importance of ncluding the nitrogen lone pair as an active orbital in the SOCI calculation.

The structure as well as the Si–N stretching frequency of $HSiNH_2$ indicate it is closer to a singly bound molecule than a doubly bound one. However, the internal rotation barrier in this molecule is predicted to be a substantial 26.9 kcal/mol at the MP4(SDQ)/MC-311G**//6-31G** level (see Table II). Note that the addition of MP4 to the Hartree–Fock result raises the barrier by approximately 1 kcal/mol. The effect of triple excitations in MP4 (not shown in the tables) is to increase the barrier by an additional 0.6 kcal/mol.

Because of the large barrier for internal in aminosilylene and the indication of some double bond character due to lone pair interactions, this rotation was further investigated at the MCSCF level. Geometries were obtained with use of the 3-21G* basis within the FORS prescription desribed above (four electrons occupying four active orbitals in all possible ways). Single point 6-31G* energies were then obtained with use of six orbitals (σ, σ^*, Si and nitrogen lone pairs, silicon and nitrogen empty p orbitals) and the corresponding six electrons. At this level of computation, the internal rotation barrier is predicted to be 26.8 kcal/mol. This is virtually identical with the MP4/MC-311G** result. Furthermore, despite the large barrier, the largest natural orbital occupation number for a formally empty orbital (in a single configuration sense) is 0.088 in the silicon p orbital in the rotated structure. This is to be contrasted to occupation numbers of nearly unity in the diradical rotated silanimine. Thus, despite the large barrier, apparently induced by lone pair interactions, the internal rotation in aminosilylene is well-represented by a single configuration description.

Internal rotation barriers are often used to estimate the π bond strengths of doubly bound species.[25] The π bond strength of H_2SiNH is therefore predicted to be approximately 37.9 kcal/mol. This π bond strength may also be estimated from the hydrogenation reaction[26] of H_2SiNH. Combining the experimental Si–H,[27] N–H,[28] and H–H[29] bond energies with the calculated energy difference for the hydrogenation of silanimine gives an estimate for the π bond strength of silanimine as 32 kcal/mol. The difference between the two estimates of the π bond strength is similar to that found for other double bonds.[30]

The energetics for the 1,1- and 1,2-eliminations for H_2 from silylamine H_3SiNH_2 are given in Tables I and II. The activation energies of both processes are changed dramatically when correlated is included. For HF/6-31G** the barriers for the 1,1- and 1,2-eliminations are 80.8 and 103.7 kcal/mol, respectively. These are reduced to 67.2 and 89.7 kcal/mol at MP4. As for the dissociations of ethane[21] and disilane,[20] the 1,2-elimination has a large activation energy. Furthermore, the 1,1-elimination forms the most stable product, $HSiNH_2$. Therefore, it is not only kinetically but also thermodynamically more favorable than the 1,2-elimination.

IV. Conclusions

The major conclusions that can be drawn from this work are the following:

(1) The aminosilylene, $HSiNH_2$, is the global minimum on the potential energy surface of $SiNH_3$, with the planar doubly bound compound, H_2SiNH, 18 kcal/mol higher in energy.

(2) The 1,2-hydrogen shift from silanimine to aminosilylene is predicted to have a 60 kcal/mol activation energy.

(3) The barrier for the inversion of H_2SiNH is only 5.6 kcal/mol. The inversion is therefore favored over the internal rotation which has a barrier of 37.9 kcal/mol at the SOCI level of calculation.

(4) Although the structure and the Si–N stretching frequency of $HSiNH_2$ indicate that it is much closer to a single bond than a double bond, it has a large barrier to internal rotation at all computational levels. The most accurate value for this barrier is 26.9 kcal/mol obtained from MP4.

(5) The 1,1-elimination of H_2 from H_3SiNH_2 to give aminosilylene is both thermodynamically and kinetically favored over the 1,2-elimination. The barrier for the 1,1-elimination is 67.2 kcal/mol, whereas the activation energy for the 1,2-elimination is 89.7 kcal/mol.

(6) The π bond strength of H_2SiNH is predicted from the rotation barrier to be 37.9 kcal/mol. This may be compared with recent estimates of 37 and 22 kcal/mol for the π bond energies in silaethylene[31] and disilene,[32] respectively. A systematic analysis of double bonds between atoms in groups IV–VI, as well as comparisons with the related rotated triplet states, will be presented in a forthcoming paper.[33]

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