Theoretical Studies of Reactions of Silanimine (H₂SiNH) and Its Isomer Aminosilylene (HSiNH₂)

Thanh N. Truong
Mark S. Gordon
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 CIC π bonding and 0% 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. 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. 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 3), 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 $n_{i0}$ 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) is thus outside of its scope.

Registry No. HLI, 7580-67-8; HCH, 74-82-8; HCHMe, 74-84-0; HCHMe 2, 74-98-6; HCHMe 3, 75-26-5; HCHMe 4, 75-85-1; HCHMe 5, 74-85-1; HC=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; HCOOH, 64-18-6; HCOOMe, 107-31-3; HCONH 2, 75-12-7; HCOF, 1493-02-3; HCF 3, 75-46-7; NH 3, 7664-17-7; HNNH 2, 302-01-2; HNMe 2, 124-40-3; H 2 NCOH, 75-12-7; HNO, 7782-77-6; HNCO, 7732-18-5; HCO, 64-19-7; HF, 7664-39-3; HSiOH, 7803-62-5; HSi, 7783-06-4; HSiMe, 74-93-1; HCl, 7647-01-0; CH 3 COF, 75-10-5; CHF, 75-46-7; CF 3, 75-73-0; EF, 353-36-6; MeAc, 67-64-1; MeCF 3, 420-46-2; MeOMe, 115-10-6; LiC==CH, 1111-64-4; FCN, 2713-09-9; CIF, 593-63-5; FCN, 506-19-5; NCCN, 460-19-3; SCO, 463-58-1; OCO, 124-38-9; NO, 11024-97-2.

Theoretical Studies of Reactions of H 2 SiNH and Its Isomer HSiNH 2

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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 2 surface, with the planar doubly bound species H 2 SiNH 18 kcal/mol higher in energy. The internal rotational barriers are computed to be 26.9 kcal/mol. However, the barrier for the inversion of HSiNH 2 is only 5.6 kcal/mol, so that inversion is favored over rotation for this species. The isomerization connecting H 2 SiNH 2 to HSiNH 1 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. However, relatively little attention has been paid to the silicon-nitrogen double bond.

The substituted silanimine, RSiNR, was observed in both gas-phase pyrolysis and photolysis by Sommer. Wiberg has also reported some evidence for the formation of compounds containing silicon-nitrogen double bonds. 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 (HSi) 2 N bound species, no theoretical study of silanimine has appeared to date.

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

II. Methods of Calculation

For the rotation of H2Si="NH, 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 (FORSS) method, the MCSCF wave functions only include those configurations arising from the active orbitals. In this case, the active orbitals are σ, σ*, π, and π* for H2Si="NH. 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, 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. The exponents used are 0.395 for silicon and 0.8 for nitrogen. This basis set will be denoted as 3-21G* in this paper. To obtain more accurate energies and geometries, all other reactions, the molecular geometries and transition states are computed at the single configuration SCF level.

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The silanimine rotational barrier is refined by computing MCSCF single points with the 6-31G* basis set, which also includes p orbitals with an exponent of 1.1 for hydrogen. The silanimine rotational barrier is refined by computing MCSCF single points with the 6-31G* basis set. This is then augmented by second-order CI (SOC) 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 SOC 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. Single point calculations were carried to fourth order, neglecting triple excitations, with the MC-311G** basis set at the 6-31G** geometries. The former basis set refers to 6-31G** 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), augmented by the appropriate polarization functions. The single point calculations carried out in this manner are denoted as MP4(SDQ)/MC-311G**/6-31G**.

A modified version of GAMESS was used to carry out the MCSCF and SOC calculations, while the HF and MP4 calculations were performed with GAUSSIAN82.

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 H2SiNH. 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 HSINH2 is somewhat shorter than the normal Si-N bond.
Theoretical Studies of Reactions of H,SiNH

Figure 3. Rotation transition state structures of H2SiNH and HSiNH2.

Figure 4. Transition state structures for H2SiNH and HSiNH2. (HSiN angle = 99.3°.) (Bond lengths in Å, angles in deg.)

single bond in saturated H2SiNH. 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 H2SiNH, HSiNH2, and H2SiNH, respectively, are 1247.82, 949.60, and 898.27 cm⁻¹. This indicates that the Si–N bond in HSiNH2 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 H2SiNH and HSiNH2 and for the inversion of H2SiNH 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, jumping from the Si–N bond length at the saddle point, the π bond is broken early as well. The inversion transition state has C2v symmetry and a very short Si–N bond length of 1.53 Å, compared to a normal double bond of 1.58 Å in H2SiNH.

The structures for the internal rotation transition states for H2SiNH and HSiNH2 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 C3 symmetry. It should be pointed out here that, for rotated silylamine, 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 silylamine and of amino-silylene are shown in Figure 4. The reverse directions of these reactions correspond to the 1,2- and 1,1-hydrogen elimination from H2SiNH2, respectively. These transition states are very similar to the elimination of H2 from disilane 20 and ethane. 21 Apparently, the nitrogen is better than phosphorus. Furthermore, nitrogen is better able to accommodate its nonplanar silylene isomer. 23 The elimination of H2 from disilane is planar. 20 The elimination of H2 from disilane is planar. 20

Table I. Total Energies of Molecules (Hartree)

<table>
<thead>
<tr>
<th>SCF/3-21G**</th>
<th>SCF/6-31G**</th>
<th>MP4/MC-31I G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SiNH</td>
<td>-1.122950</td>
<td>-1.131330</td>
</tr>
<tr>
<td>HSiNH</td>
<td>-343.34171</td>
<td>-345.05717</td>
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<tr>
<td>H2SiNH2</td>
<td>-344.573437</td>
<td>-346.294542</td>
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<tr>
<td>1,2-H shift TS</td>
<td>-343.240765</td>
<td>-344.953686</td>
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<tr>
<td>HSiNH inv. TS</td>
<td>-343.336465</td>
<td>-345.051280</td>
</tr>
<tr>
<td>H2SiNH rot. TS</td>
<td>-343.337711</td>
<td>-345.053570</td>
</tr>
<tr>
<td>1,2-H elim. TS</td>
<td>-344.399756</td>
<td>-346.129245</td>
</tr>
<tr>
<td>1,1-H elim. TS</td>
<td>-343.438762</td>
<td>-346.165707</td>
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*SCF/3-21G* including d orbitals on nitrogen. Single point MP4(SDQ)/MC-31G** at 6-31G** geometries.

Table II. Relative Energies (kcal/mol)

<table>
<thead>
<tr>
<th>SCF/3-21G**</th>
<th>SCF/6-31G**</th>
<th>MP4/MC-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSiNH</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H2SiNH</td>
<td>-23.7</td>
<td>-24.3</td>
</tr>
<tr>
<td>1,2-H shift TS</td>
<td>63.4</td>
<td>64.9</td>
</tr>
<tr>
<td>HSiNH inv. TS</td>
<td>3.3</td>
<td>3.7</td>
</tr>
<tr>
<td>HSiNH rot. TS</td>
<td>2.8</td>
<td>0.9</td>
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<tr>
<td>1,1-H elim. TS</td>
<td>84.5</td>
<td>80.8</td>
</tr>
<tr>
<td>1,2-H elim. TS</td>
<td>109.8</td>
<td>103.7</td>
</tr>
<tr>
<td>H2 + H2SiNH</td>
<td>68.2</td>
<td>66.5</td>
</tr>
<tr>
<td>H2 + HSiNH2</td>
<td>44.6</td>
<td>42.2</td>
</tr>
</tbody>
</table>

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

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 silylamine and of amino-silylene are shown in Figure 4. The reverse directions of these reactions correspond to the 1,2- and 1,1-hydrogen elimination from H2SiNH2, respectively. These transition states are very similar to the elimination of H2 from disilane and ethane. Apparently, the nitrogen is better than phosphorus. Furthermore, nitrogen is better able to accommodate its nonplanar silylene isomer. The elimination of H2 from disilane is planar. The elimination of H2 from disilane is planar.

References:
(22) Pope, J. A., private communication.
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* 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, H₂CNH. 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 including the nitrogen lone pair as an active orbital in the SOCI calculation.

The structure as well as the Si-N stretching frequency of HSIN₂ indicates that 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 table) 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 description above (four electrons occupying four active orbitals in all possible ways). Single point 6-31G* energies were then obtained with use of six orbitals (π, 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 0.008 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 H₂SiNH is therefore predicted to be approximately 37.9 kcal/mol. This π bond strength may also be estimated from the hydrogenation reaction of H₂SiNH. Combining the experimental Si–H,²⁷ N–H,²⁸ and H–H²⁹ 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 H₃ from silylamine H₂SiNH₂ 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 ethane²¹ and disilane,³² the 1,2-elimination has a large activation energy. Furthermore, the 1,1-elimination forms the most stable product, HSI:NH₂. 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, HSI:NH₂, is the global minimum on the potential energy surface of SiNH₂ with the planar doubly bound compound, H₂SiNH, 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 H₂SiNH 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 SOCl level of calculation.
(4) Although the structure and the Si–N stretching frequency of HSI:NH₂ 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 H₃ from H₂SiNH₂ 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 H₂SiNH 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 silaethylenel and disilene, 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.¹³

Acknowledgment. This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the National Science Foundation (CHE83-09948). The computer time provided by the North Dakota State University Computer Center is gratefully acknowledged. The authors have benefitted from several discussions with Dr. Michael W. Schmidt and Professor J. A. Pope.

Table III. Energetics for Internal Rotation of H₂SiNH

<table>
<thead>
<tr>
<th></th>
<th>H₂SiNH</th>
<th>H₂SiNH rot. TS</th>
<th>E₀ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSCF/3-21G*</td>
<td>-343.401 236a</td>
<td>-343.327 520a</td>
<td>46.3</td>
</tr>
<tr>
<td>MCSCF/6-31G*</td>
<td>-345.109 106a</td>
<td>-345.034 726a</td>
<td>46.7</td>
</tr>
<tr>
<td>SOCI/6-31G*</td>
<td>-345.180 614b</td>
<td>-345.120 245b</td>
<td>37.9</td>
</tr>
</tbody>
</table>

²⁴ electrons, 4 internal orbitals. ²⁵ electrons, 5 internal orbitals.