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# Barrier to Rotation in Thioformamide: Implications for Amide Resonance

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**Abstract:** We investigate the energetics of rotation about the C−N bond in thioformamide at the molecular and atomic levels using the HF/6-311++G**//HF/6-311++G** level of theory. The barrier to rotation is 19.9 kcal $\mathrm{mol}^{-1}$ and is dominated by the increase in the C−N distance and the consequent loss in attractive energies between carbon and nitrogen. The origin of the barrier to rotation is shown to be the same as that found in formamide. There is a large transfer of charge from nitrogen to carbon as the system moves away from planarity, but, unlike the essentially unchanged oxygen in formamide, sulfur also transfers charge to carbon upon rotation. It is the preference of the amide nitrogen for planarity, making it more electronegative and better able to stabilized itself by withdrawing charge from its bonded neighbors, that dictates the barrier to rotation about the C−N bond. The Fermi hole is used to quantitatively demonstrate that there is little delocalization of the $\pi$ charge density from nitrogen to sulfur. The larger barrier to rotation in thioamides and the negligible delocalization of $\pi$ charge from nitrogen to sulfur is inconsistent with the expectations of the resonance model but is consistent with a the view that (thio)amides behave as '(thio)formylamines'.

## Introduction

The hindered rotation about the C−N bond of amides, the peptide bond, provides proteins with the ability to form the secondary and tertiary structures fundamental to biological activity.[1] The most widely subscribed explanation for the hindered rotation in amides employs the resonance model.[2,3] Resonance predicts there is a significant contribution to the stabilization of planar amides from the delocalization of electronic charge from the amide nitrogen to the carbonyl oxygen, and the resulting partial double bond provides hindrance to C−N bond rotation.

Recent theoretical studies have questioned the need of the resonance model to explain the hindered rotation within amides.[4,5] These works demonstrated that the predicted effect upon the distribution of electronic charge in amides resulting from rotation of the C−N bond away from planarity was in conflict with the actual redistribution. The carbonyl oxygen was essentially unchanged during rotation, and the flow of charge was from amide nitrogen to carbonyl carbon. It is the preference of the amide nitrogen for planarity, making itself more effectively electronegative and better able to withdraw charge from its bonded neighbors and stabilize itself, that creates the barrier to rotation in amides. Considering formamide as a 'formyl-amine' correctly predicts the redistribution of electronic charge, the geometric and energetic consequences, and the changes in molecular reactivity as a function of rotation about the C−N bond.[6] This model and the underlying theoretical basis have been challenged,[7] but the critiques were shown to be not physically correct.[8,9]

That the large barriers to rotation in thioamides are larger than in corresponding amides has been known for some time.[10−14] In fact, the barrier to rotation in substituted thioformamides is large enough that the cis and trans isomers are separable by chromatography.[15,16] Wiberg and Rablen recently studied the barrier to rotation in thioformamide and found it to be 18.8 and 18.0 kcal $\mathrm{mol}^{-1}$, using MP2/6-31+G* and the G2 methodology, respectively.[17] While these large barriers were attributed to greater 'amide resonance' than in amides themselves,[17] the lesser electronegativity of sulfur in comparison to oxygen would lead one to expect that the barrier to rotation about the C−N bond would be smaller than that in the amide analogs.

We present an investigation of the origins of the barrier to rotation about the C−N bond in thioformamide using molecular and subsystem quantum mechanics.[18] The changes in atomic and molecular properties due to C−N bond rotation clearly show that the dominant change is the interaction between the C and N atoms, with much smaller changes in the interaction between C and S. These changes in properties mirror those found in the rotation of formamide, demonstrating that the origins of the

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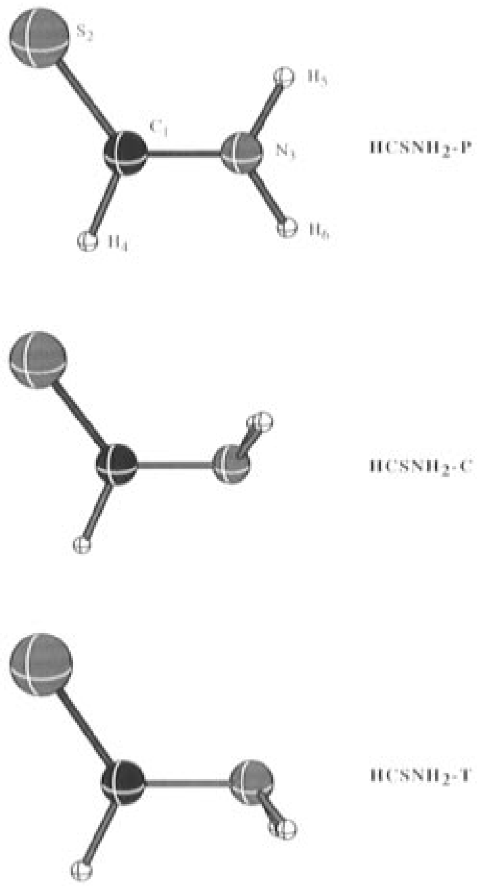

**Figure 1.** Three thioformamide structures considered in this study.

rotational barriers are similar. Using the Fermi hole as a quantitative measure of electronic localization and delocalization,[18−20] we demonstrate that there is no significant delocalization of electronic charge between the N and S atoms in planar thioformamide nor between N and O in formamide. These results are then discussed in light of the expectations of the amide resonance model and the predictions made by the ‘formylamine’ model for the barrier to rotation in amides.

## Methodology

We have considered the planar ($HCSNH_2$-P), cis-pyramidal ($HCSNH_2$-C), and trans-pyramidal ($HCSNH_2$-T) structures of thioformamide, Figure 1. All the atomic and molecular properties were determined from the triple-$\zeta$, polarized, diffuse, and balanced HF/6-311++G** wave functions determined at conformations optimized using the same level of theory.[21] Each stationary point on the potential energy surface was characterized via the determination of analytical second derivatives. The planar thioformamide, with $C_s$ symmetry, was a minimum, while each of the $C_s$-constrained pyramidal structures had one imaginary frequency that corresponded to rotation of the $NH_2$ group. We used closed-shell, SCF procedures without the addition of electron correlation because they correctly and adequately reproduce the barrier of rotation,[17] with the added benefit that each of the energetic contributions to the molecular and atomic energies defined within the usual, fixed-nucleus Hamiltonian is clearly defined within this theoretical model. The molecular calculations were performed using the GAMESS program suite.[22] The HF/6-311++G** wave function was used to determine the properties of the charge distribution and the atomic properties, using the theory of atoms in molecules as implemented within the AIMPAC suite of programs.[23] The appropriate weighted density distribution was integrated over the atomic basin (the volume of real space which is associated with a given nucleus) giving the atomic contribution to a given molecular property.[18]

In order to address the amount of delocalization in a quantitative manner, we have investigated the Fermi hole[18,19] and its integrated average values over and between the atoms of interest. The wave function for a many-electron system must be antisymmetric with respect to the permutation of the space−spin coordinates for every pair of electrons to account for the indistinguishability of the electrons, as demanded by the Pauli principle. This antisymmetry constraint requires that no two electrons with the same spin occupy the same point in space. The result on the spatial distribution of charge of an electron is described by the “Fermi hole”. This is a distribution function for an electron of given spin, defined relative to a uncorrelated pair density, that determines the decrease in the probability of finding another electron with the same spin relative to the fixed position of the electron in question. The Fermi hole describes the way in which the charge of the reference electron is spread out in space, excluding the presence of an identical amount of same-spin density. In other words, as an electron moves through space, it carries with it a Fermi hole of ever changing shape, the density of the electron being spread out in the manner described by its Fermi hole. The extent of localization or delocalization of the density of the electron is determined by the corresponding localization of its Fermi hole. The integration of the Fermi hole density for every possible position of the reference electron within an atom is a measure to which the electrons are localized within that atom. Similarly, the integration of the Fermi hole density, whose reference electron is located within atom $\Omega$, over atom $\Omega'$ yields the extent to which the electronic charge in atom $\Omega$ is delocalized to atom $\Omega'$. This technique has been being applied to the study of localization and delocalization in a wide variety of systems, providing a quantitative basis for the concept of electron delocalization.[24−26] We apply this technique to the investigation of delocalization of total and $\pi$ density in thioformamide and formamide.

## Results

**Molecular and Atomic Properties.** The total molecular energy and the contributions to the potential energy for the $HCSNH_2$-P, $HCSNH_2$-C, and $HCSNH_2$-T conformations of thioformamide are listed in Table 1. The planar conformation is the lowest energy structure, with the cis and trans transition states 19.9 and 21.6 kcal mol$^{-1}$ less stable, respectively. Energetically, both barriers are dominated by a loss of attractive energies upon twisting, larger than the corresponding loss in repulsion, $|\Delta V_a| > |\Delta V_r|$. The energetic changes are consistent with bond lengthening processes in which the loss in attraction between the bonded fragments outstrips any decrease in repulsion as the atoms move away from one another. This pattern of energy change has also been observed in the barrier to rotation in ethane,[27] the barrier to inversion in ammonia,[27] and the barrier to rotation in formamide.[6] Given that both $HCSNH_2$-C and $HCSNH_2$-T rotamers display the same barrier energetics, the discussion shall be limited to conformations

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**Table 1.** Molecular Energetics of Planar, Cis Pyramidal, and Trans Pyramidal Thioformamide[a]

| | $HCSNH_2P$ | $HCSNH_2C$ | $\Delta_1{}^b$ | $HCSNH_2T$ | $\Delta_2$ | $\Delta_3$ |
|---|---|---|---|---|---|---|
| total $E$ | −491.6241 | −491.5911 | 0.0330 | −491.5881 | 0.0360 | 0.0030 |
| $V_{NE}$ | −1357.4709 | −1355.9674 | 1.5035 | −1355.7765 | 1.6944 | 0.1909 |
| $V_{EE}$ | 279.0472 | 278.2544 | −0.7928 | 278.2110 | −0.8362 | −0.0434 |
| $V_{NN}$ | 95.1757 | 94.5306 | −0.6451 | 94.3890 | −0.7867 | −0.1416 |
| $V$ | −983.2482 | −983.1822 | 0.0660 | −983.1762 | 0.0720 | 0.0060 |
| $\Delta E$ | | | 20.708 | | 22.590 | 1.883 |
| ZPE | 29.396 | 28.596 | −0.800 | 28.393 | −1.003 | −0.203 |
| $\Delta E$ | | | 19.908 | | 21.587 | 1.680 |

[a] The total and contributing energies are given in atomic units and have been corrected for the virial defect. The overall energy differences are in kcal mol$^{-1}$. [b] $\Delta_1 \equiv C - P$, $\Delta_2 \equiv T - P$, $\Delta_3 \equiv T - C$.

**Table 2.** Geometric Parameters within the Planar, Cis, and Trans Conformations of Thioforamide[a]

Bond Lengths

| | $H_4-C_1$ | $C_1-S_2$ | $C_1-N_3$ | $N_3-H_5$ | $N_3-H_6$ |
|---|---|---|---|---|---|
| $HCSNH_2P$ | 1.081 | 1.639 | 1.326 | 0.995 | 0.993 |
| $HCSNH_2C$ | 1.080 | 1.604 | 1.422 | 1.003 | 1.003 |
| $HCSNH_2T$ | 1.084 | 1.587 | 1.419 | 1.004 | 1.004 |

Bond Angles

| | $H_4-C_1-S_2$ | $S_2-C_1-N_3$ | $H_4-C_1-N_3$ | $C_1-N_3-H_5$ | $C_1-N_3-H_6$ | $H_5-N_3-H_6$ |
|---|---|---|---|---|---|---|
| $HCSNH_2P$ | 120.37 | 126.43 | 113.19 | 119.79 | 121.42 | 118.80 |
| $HCSNH_2C$ | 119.62 | 127.18 | 113.20 | 109.41 | 109.41 | 106.02 |
| $HCSNH_2T$ | 119.09 | 124.46 | 116.46 | 109.64 | 109.64 | 106.74 |

Torsion Angles

| | $H_4-C_1-N_3-H_5$ | $H_4-C_1-N_3-H_6$ | $S_2-C_1-N_3-H_5$ | $S_2-C_1-N_3-H_6$ |
|---|---|---|---|---|
| $HCSNH_2P$ | 0.00 | 180.00 | 0.00 | 180.00 |
| $HCSNH_2C$ | −122.13 | 122.13 | 57.87 | −57.87 |
| $HCSNH_2T$ | −58.43 | 58.43 | 121.57 | −121.57 |

[a] All bond lengths are given in Å and all bond and torsion angles in degrees. The atoms are labeled as in Figure 1.

$HCSNH_2$-P and $HCSNH_2$-C, but the properties of all three can be found in the tables.

The largest geometric change in bond length upon rotation of the amide bond (Table 2) is the lengthening of the C−N bond, by 0.10 Å. There is a smaller shortening of the C═S bond (0.04 Å) in the transition state, while the C−H and N−H bond lengths are essentially unchanged. There is relatively little change in the bond angles, with the exception of the C−N−H and H−N−H bond angles around nitrogen, which necessarily decrease as nitrogen pyramidalizes.

The properties of charge density at the bond critical points also reflect the change in interaction between C and N, Table 3.[28,18] The magnitude of charge at this critical point decreases by 10% as the associated interatomic distance lengthens. The Laplacian becomes nearly twice as negative since the valence shell of the carbon atom increases in size and magnitude. The ellipticity of charge at the critical point increases, showing a preference for the accumulation of electronic charge in the plane of the HSCN fragment. The bonded radius of the carbon atom (the distance from the nucleus to the bond critical point) increases, while that to nitrogen remains the same. The C−N bond lengthening contributes to the increase in size of the carbon atom, indicating a gain of charge from its bonded neighbors. The change in the C−S interaction is 1 order of magnitude less than that for C−N. The magnitude of charge at the bond critical point increases slightly, while the bonded radius of both carbon and sulfur decreases. The other interactions are relatively unchanged.

**Table 3.** Bond Critical Point Properties in Planar, Cis, and Trans Thioformamide[a]

| | $\rho(r)$ | $\nabla^2\rho(r)$ | $\epsilon$ | $r_a$ | $r_b$ |
|---|---|---|---|---|---|
| | | $HCSNH_2P$ | | | |
| $H_4-C_1$ | 0.300 | −1.157 | 0.003 | 0.711 | 1.332 |
| $C_1-S_2$ | 0.222 | 0.402 | 0.152 | 1.941 | 1.156 |
| $C_1-N_3$ | 0.339 | −0.652 | 0.056 | 0.840 | 1.665 |
| $N_3-H_5$ | 0.355 | −2.053 | 0.052 | 1.421 | 0.459 |
| $N_3-H_6$ | 0.358 | −2.012 | 0.056 | 1.409 | 0.467 |
| | | $HCSNH_2C$ | | | |
| $H_4-C_1$ | 0.302 | −1.163 | 0.008 | 0.705 | 1.336 |
| $C_1-S_2$ | 0.242 | 0.408 | 0.165 | 1.892 | 1.139 |
| $C_1-N_3$ | 0.304 | −1.078 | 0.132 | 1.040 | 1.649 |
| $N_3-H_5$ | 0.349 | −1.797 | 0.046 | 1.403 | 0.493 |
| $N_3-H_6$ | 0.349 | −1.797 | 0.046 | 1.403 | 0.493 |
| | | $HCSNH_2T$ | | | |
| $H_4-C_1$ | 0.297 | −1.125 | 0.006 | 0.719 | 1.329 |
| $C_1-S_2$ | 0.245 | 0.437 | 0.155 | 1.884 | 1.135 |
| $C_1-N_3$ | 0.304 | −1.076 | 0.126 | 1.020 | 1.662 |
| $N_3-H_5$ | 0.349 | −1.761 | 0.050 | 1.399 | 0.499 |
| $N_3-H_6$ | 0.349 | −1.761 | 0.050 | 1.399 | 0.499 |

[a] All values are in atomic units. The properties are determined at the (3,-1) critical point between the atoms: $\rho(r)$, the total charge density; $\nabla^2\rho(r)$, the Laplacian of the charge density; $\epsilon$, the ellipticity; $r_a$ and $r_b$, the bonded radii. The atom labels correspond to the diagram in Figure 1.

The largest changes in the atomic properties (Table 4) were found for the C and N atoms. The C atom gains 0.37 electron in population and is stabilized by 151.9 kcal mol$^{-1}$ in the transition state. This stabilization is due to gains in both intra-atom (from gain in population) and inter-atom (decrease in C═S interatomic distance) attractive energies. The attractive gains overcome the associated increase in atomic repulsive energies. The N atom, in contrast, loses 0.21 electron to its bonded neighbors and is destabilized by 157.5 kcal mol$^{-1}$, with the loss in attraction (both inter- and intra-atom) dominating the energetic destabilization. The S atom is destabilized (47.1 kcal mol$^{-1}$) as it gives up 0.25 electron to the rest of the molecule. The destabilization of S is also due to both inter- and intra-atom attraction as the N atom recedes from the C═S group (data not shown). The hydrogens bonded to nitrogen gain charge and are stabilized slightly, while the formyl hydrogen is essentially unchanged.

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**Table 4.** Atomic Properties of Planar, Cis, and Trans Thioformamide[a]

| | $C_1$ | $S_2$ | $N_3$ | $H_4$ | $H_5$ | $H_6$ | sum |
|---|---|---|---|---|---|---|---|
| | | | $HCSNH_2P$ | | | | |
| $N(\Omega)$ | 5.783 | 15.791 | 8.378 | 0.946 | 0.542 | 0.560 | 32.001 |
| $E(\Omega)$ | −37.610 | −397.365 | −55.165 | −0.608 | −0.432 | −0.444 | −491.624 |
| $V_{NEO}(\Omega)$ | −88.141 | −945.341 | −135.367 | −1.246 | −0.859 | −0.881 | |
| $V_A(\Omega)$ | −140.426 | −1004.598 | −193.112 | −9.094 | −5.207 | −5.043 | |
| $V_R(\Omega)$ | 65.204 | 209.866 | 82.781 | 7.878 | 4.343 | 4.155 | |
| | | | $HCSNH_2C$ | | | | |
| $N(\Omega)$ | 6.154 | 15.537 | 8.165 | 0.936 | 0.604 | 0.604 | 32.000 |
| $E(\Omega)$ | −37.852 | −397.290 | −54.914 | −0.606 | −0.465 | −0.465 | −491.591 |
| $V_{NEO}(\Omega)$ | −89.591 | −943.606 | −134.312 | −1.239 | −0.925 | −0.925 | |
| $V_A(\Omega)$ | −145.030 | −1002.453 | −188.070 | −8.964 | −5.728 | −5.728 | |
| $V_R(\Omega)$ | 69.325 | 207.872 | 78.242 | 7.752 | 4.799 | 4.799 | |
| | | | $HCSNH_2T$ | | | | |
| $N(\Omega)$ | 6.159 | 15.481 | 8.158 | 0.967 | 0.618 | 0.618 | 32.001 |
| $E(\Omega)$ | −37.849 | −397.268 | −54.913 | −0.616 | −0.471 | −0.471 | −491.588 |
| $V_{NEO}(\Omega)$ | −89.585 | −943.199 | −134.282 | −1.262 | −0.939 | −0.939 | |
| $V_A(\Omega)$ | −145.176 | −1001.630 | −188.418 | −9.269 | −5.646 | −5.646 | |
| $V_R(\Omega)$ | 69.478 | 207.094 | 78.591 | 8.036 | 4.705 | 4.705 | |

[a] All atomic properties are in atomic units. $N(\Omega)$ is the atomic population, $E(\Omega)$ is the atomic energy, $V_{NEO}(\Omega)$ is the intra-atomic attraction energy, $V_A(\Omega)$ is the total atomic attraction energy, and $V_R(\Omega)$ is the total atomic repulsion energy. The energetics have been corrected for the virial defect. For energies, 1 au = 627.51 kcal mol$^{-1}$.

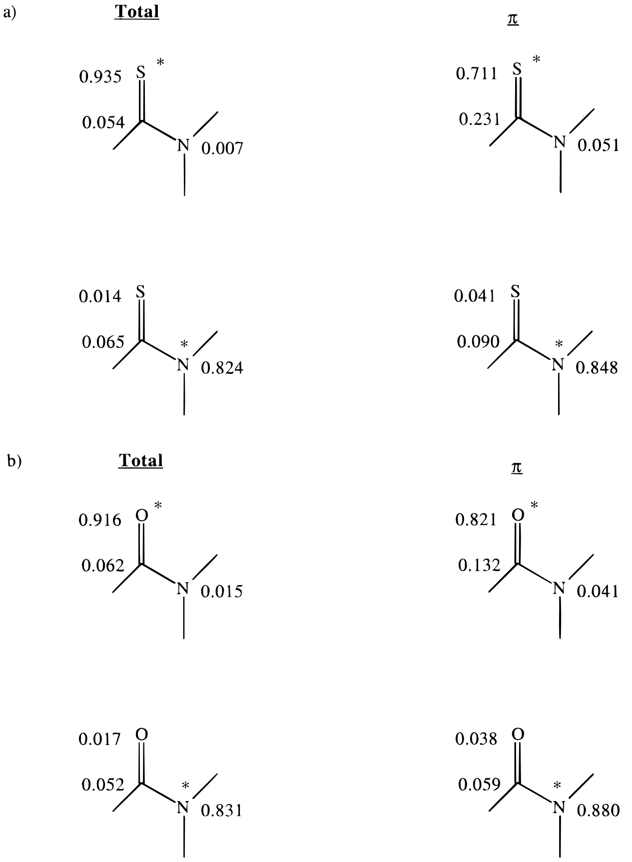

**Figure 2.** Integrated Fermi correlation, $F(\Omega,\Omega')$, for planar thioformamide (a) and formamide (b). The correlation using the total charge density is given at the left, and the correlation considering only the $\pi$ density is given at the right. The asterisk denotes the atom used as the origin of the correlation.

**Localization and Delocalization.** The integrated Fermi correlation, $F(\Omega,\Omega')$, both intra- ($\Omega = \Omega'$) and inter-($\Omega \neq \Omega'$) correlations, is given in Figure 2 for both thioformamide (a) and formamide (b). The atomic Fermi correlations for the total density and the $\pi$ density are listed as fractions of the total population, using both S and N as the origins for the correlations. For example, in Figure 2a, the first structure depicts the localization/delocalization within thioformamide using the total charge density and the sulfur atom as the origin of the reference electron. This yields the total density of S as 93.5% localized with the S atom, 5.4% delocalized to C, and 7.0% delocalized to N. Similarly, considering only the $\pi$ orbitals, the $\pi$ density of the S atom is 71.1% localized within its own volume, 23.1% delocalized to C, and 5.1% delocalized to N. This demonstrates that the electronic charge (both total and $\pi$) of S is primarily localized within the volume of S. There is appreciable delocalization of the $\pi$ density from S to C but little delocalization of either total or $\pi$ density to the N atom. A similar picture is seen for thioformamide using the basin of N as the origin of the reference electron. The total ($\pi$) density is 82.4% (84.8%) localized within the volume of N, 6.5% (9.0%) delocalized to C, and only 1.4% (4.1%) delocalized to S. This clearly shows that the primary interaction is between S or N and C. There is little delocalization from one end of the molecule to the other for either the total density or the $\pi$ density. The $\pi$ charge associated with the nitrogen and sulfur atoms is primarily localized within planar thioformamide.

This is also the result seen in formamide, Figure 2b. For planar formamide determined at the same level of theory, the total ($\pi$) density of the O atom is 91.6% (82.1%) localized, 6.2% (13.2%) delocalized to C, and 1.5% (4.1%) delocalized to N. Similarly, the total ($\pi$) density of the N atom is 83.1% (88.0%) localized, 5.6% (5.9%) delocalized to C, and 1.7% (3.8%) delocalized to O. There is little delocalization of charge from one end of the molecule of either the $\pi$ or total density. As with thioformamide, the total and $\pi$ density of planar formamide is largely localized.

Representative $\pi$ density Fermi holes of planar formamide and thioformamide are depicted in Figure 3. The qualitative result gleaned from the pictures in Figure 3 is that the $\pi$ electrons are largely localized in the both the planar formamide and thioformamide, whether the reference electron is placed in the N or O (S). The $\pi$ density is localized within the basin of the N, O, or S atom, and there is only a small fraction of the $\pi$ density delocalized from one end of the molecule to the other.

## Discussion

The resonance model rationalizes the large barrier to rotation about the C−N bond in amides as a significant contribution to the stability of the planar amide from a resonance structure in which electronic charge is transferred from the amide N to the carbonyl O via the $\pi$ system.[2,3] The driving force for this

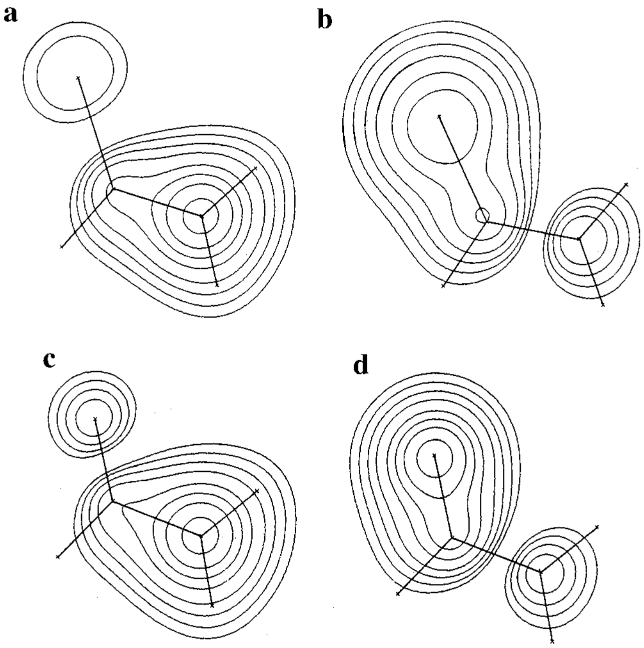

**Figure 3.** Contour diagrams which graphically display the extent of the Fermi holes for the $\pi$ density in thioformamide (a and b) and formamide (c and d). The reference electron is placed above S (b) and O (d). The reference electron was placed above the N atom (a and c).

mechanism is the greater electronegativity of O, pulling charge to itself. This predicts that the C$-$N bond length would shorten, having partial double-bond character and hindering rotation. When the amide C$-$N bond is rotated, this model predicts that the contribution from the delocalized structure will decrease, and consequently, charge should flow from the carbonyl group to the N atom. In thioformamide, the O atom is replaced by the less electronegative S atom. The S atom is more polarizable than O and could then better stabilize a negative charge, but this is not a sufficient driving force to pull charge from the much more electronegative N atom. This line of reasoning would then predict that there will be less charge pulled by S from N through the $\pi$ system of the molecule. As a result, the C$-$N bond should not shorten nor the C$=$S bond lengthen to the same extent as the analogous bonds in formamide. It would be difficult to predict the higher barrier to rotation observed in thioamides using the resonance model.

The presented results clearly demonstrate that the predominant change upon pyramidalization of the nitrogen atom is the C$-$N interaction. As the $NH_2$ fragment rotates away from planarity, the nitrogen pyramidalizes and charge is transferred from N to its bonded neighbors, C and H. The interaction between C and S (similarly, C and O in formamide) is relatively unchanged, with only a small transfer of charge from S to C and small change in bond length. The energetics are dominated by the lengthening of the C$-$N bond and the resulting loss in intra- and inter-atomic stabilization of N.

Similarly, the barrier to inversion in amines is determined by the balance between the stabilization of N upon becoming planar and the destabilization of N's bonded neighbors.[27] Nitrogen energetically prefers being planar. A simple hybridization model would predict that the $sp^2$ hybridization of the planar conformation has more 's character' than the pyramidal $sp^3$ conformation. The consequences of the greater s character are that the atom is more electronegative and the majority of the electronic charge of the atom is brought closer to the nucleus, both processes stabilizing the N atom. The destabilization of the bonded neighbors arises from the withdrawal of charge to the more electronegative N and the increased repulsion due to the shortening of the N$-$X bond length. It is not the stabilization of the central N atom that determines the barrier to inversion but rather the sum of the destabilizations of its bonded neighbors.

To demonstrate this point, we list the changes in atomic properties of $NH_3$, $NH_2F$, and $NH_2SiH_3$ during inversion in Table 5. In the case of ammonia, N is stabilized by 18 kcal mol$^{-1}$ when made planar, but each of the hydrogen atoms is destabilized by 7 kcal mol$^{-1}$, yielding an overall destabilization of 3 kcal mol$^{-1}$ at the planar transition state. The same behavior is seen in $NH_2F$ and $NH_2SiH_3$. In both cases, the planar N withdrawals charge from all of its bonded neighbors and is stabilized by greater intra- and inter-atomic attraction. With the strongly electronegative substituent F, pyramidal N is less electronegative than F. But the planar N has a greater electronegativity and is able to reduce some of the stress exterted upon it by pulling charge from both H and F. As in $NH_3$, the barrier in $NH_2F$ is determined by the destabilization of the substituents bonded to N. With the electropositive substituent $SiH_3$, there is essentially no barrier to inversion as the stabilization gained by the planar N is not met with larger destabilization of its bonded neighbors.

One can view thioformamide as a 'thioformyl-amine' (and formamide as a 'formyl-amine') and correctly predict the molecular and atomic changes upon rotation about the C$-$N bond. The formyl or thioformyl group behaves merely as a substituent on an amine, and the barriers to rotations are special cases of a barrier to inversion of the corresponding amines. As shown by the changes in atomic and molecular energetics, atomic populations, and the integrated Fermi correlations, the barrier to rotation is determined by the interaction between C and N. This is readily understood in terms of the same hybridization argument used above for amines. As the planar $sp^2$ N pyramidalizes, its hybridization shifts toward $sp^3$, the result of which is that N becomes effectively less electronegative and surrenders electronic charge to its bonded neighbors. The distance between N and its neighbors increases as the strength of interaction is decreased. N is destabilized by both the loss of charge within its basin and the increase in distance to the neighboring nuclei. Conversely, all of the bonded neighbors are stabilized by the gain in population from the N. This is the case in amines and in both amides and thioamides. The driving force for the planarization of N is the stabilization of N through its increased electronegativity and subsequent withdrawal of charge from its bonded neighbors.

Considering the difference between amides and thioamides from this point of view yields a simple picture. As shown in Figure 4, the change in population and the energetic change can be grouped into contributions for the formyl and thioformyl groups. The softer thioformyl group donates more charge to the $NH_2$ group than does the more polarized formyl group in the planar conformation. Thus, rotating about the C$-$N bond, which leads to the rehybridization of the N and it pyramidalization, is more costly for the N atom and the $NH_2$ group in thioformamide. The atomic group, functional group, molecular energetics, and charge flow are consistent with those changes seen in the barrier to inversion in amines.[27] This substitution of S for O leads to an understandable change in the interactions between the formyl/thioformyl group and the rest of the molecule. This also rationalizes the increased out-of-plane bending potential for the $NH_2$ group in thioformamide.[17]

**Table 5.** Atomic Properties during Inversion of Ammonia, Fluoroamine, and Silylamine[a]

| | N | H | | sum |
|---|---|---|---|---|
| | | $NH_3$ | | |
| $N(\Omega)$ | 8.1193 (+0.1822) | 0.6269 (−0.0607) | | |
| $E(\Omega)$ | −54.7721 (−0.0821) | −0.4745 (+0.0327) | | −56.1955 (+0.0087) |
| $V_{NEO}(\Omega)$ | −133.9132 (−0.7459) | −0.9491 (+0.0630) | | |
| $V_A(\Omega)$ | −146.2411 (−1.1507) | −3.2884 (+0.2910) | | −156.1063 (−0.2779) |
| $V_R(\Omega)$ | 36.6092 (+0.9852) | 2.3383 (−0.2301) | | 43.7152 (+0.2955) |
| | | $NH_2F$ | | |
| | | | F | |
| $N(\Omega)$ | 7.3584 (+0.1978) | 0.5940 (−0.0872) | 9.4536 (−0.0185) | |
| $E(\Omega)$ | −54.3940 (−0.0883) | −0.4702 (+0.0451) | −99.6285 (+0.0064) | −154.9629 (+0.0249) |
| $V_{NEO}(\Omega)$ | −130.5968 (−0.8327) | −0.9255 (+0.1032) | −242.0097 (+0.0957) | |
| $V_A(\Omega)$ | −161.8874 (−2.0963) | −4.3807 (+0.6596) | −272.4139 (−0.1033) | −443.0626 (−0.8231) |
| $V_R(\Omega)$ | 53.0833 (+1.9185) | 3.4387 (−0.5691) | 73.1414 (+0.1159) | 133.1368 (+0.8729) |
| | | $NH_2SiH_3$ | | |
| | | | $SiH_3$ | |
| $N(\Omega)$ | 8.6545 (+0.0262) | 0.5838 (−0.0148) | 16.1798 (−0.0063) | |
| $E(\Omega)$ | −54.9492 (−0.0148) | −0.4507 (+0.0073) | −290.4437 (+0.0040) | −346.2945 (+0.0005) |
| $V_{NEO}(\Omega)$ | −135.6341 (−0.1218) | −0.9007 (+0.0155) | −677.1275 (+0.0663) | |
| $V_A(\Omega)$ | −187.2360 (−0.3993) | −4.8992 (+0.1224) | −756.6118 (+0.0351) | −953.6265 (−0.1647) |
| $V_R(\Omega)$ | 77.3263 (+0.3693) | 3.9968 (−0.1075) | 175.7107 (−0.0263) | 261.0364 (+0.1728) |

[a] All atomic properties are in atomic units. The values in parentheses are the changes in atomic properties upon reaching the planar transition state. $N(\Omega)$ is the atomic population, $E(\Omega)$ is the atomic energy, $V_{NEO}(\Omega)$ is the intra-atomic attraction energy, $V_A(\Omega)$ is the total atomic attraction energy, and $V_R(\Omega)$ is the total atomic repulsion energy. The energetics have been corrected for the virial defect. For energies, 1 au = 627.51 kcal $mol^{-1}$.

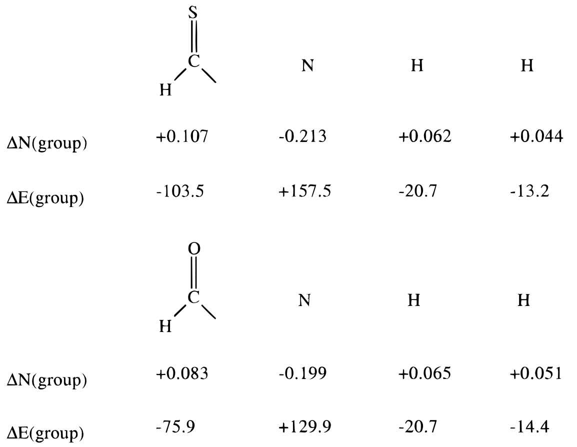

**Figure 4.** Atomic and functional group population and energy differences for thioformamide and formamide. The population differences are in e, and the energy differences are in kcal $mol^{-1}$.

## Conclusion

The barrier to rotation in thioformamide is larger than that of formamide, although the origin of the barrier is the same in both: the loss in attraction due to the lengthening of the C−N bond. The energetics, at the molecular and atomic levels, are the same for amines and thioamides. The barrier is the result of lost attractive energies between the C and N atoms as the latter pyramidalizes. The flow of charge is from N to C as the N atom pyramidalizes. The integrated Fermi correlation shows that there is little delocalization of either total or $\pi$ charge from the N to the S (O) atom in thioformamide (formamide) in the planar conformation. The primary difference between the two molecules is the greater donation of charge from the thioformyl group to the $NH_2$ group in the sulfur analog. This makes the pyramidalization of N more costly and increases the barrier to rotation about the C−N bond. This is the same process as seen in the inversion of amines, and the differences between amides and thioamides directly parallel the changes in amine inversion barriers with changes in its bonded substituents. The physical properties of (thio)amides can be readily understood using a model which treats the molecules as ‘(thio)formyl-amines’.

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