CNDO calculations of some thioamides—II

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Abstract. CNDO calculation is made for thioformamide, N-methylthioformamide (both in cis and trans forms) and N, N-dimethyl thioformamide. The charges, bond orders, dipole moments and ionization potentials of molecules are discussed and comparison made with corresponding amides. The barrier to internal rotation about C=N bond for thioformamide and N-chloroacetamide is reported along with changes in the charges on atoms and dipole moment of molecules with rotation. The trans form of N-methyl thioformamide is found to be more stable than cis isomer by 4-9 Kcal/mole.

Keywords. CNDO calculation; thioamide.

1. Introduction

In amide molecules, it is well known that no single valence bond structure is consistent with their properties. This is due to delocalization of carbonyl π-electrons and nitrogen lone pair electrons resulting in partial double bond character of C=N bond (Morris et al 1961; Cannon 1955, 1956; Venkata Ramiah and Venkata Chalapathi 1968, 1971; Srinivas Rao et al 1974, 1975). In amides oxygen 2p orbitals partake in π-conjugation. In thioamides sulfur atom takes the place of oxygen in amides. The functional group in thioamides is planar as in amides leading to similar type of π-conjugation. However, since the sulfur atom has a higher atomic number the valence orbitals involved are 3s and 3p. Though the 3d orbitals are not filled up, because it has almost the same energy as valence orbitals yet they are to be included in the basis set of thioamide molecules. In addition to this difference, the sulfur valence orbitals are more extended in space and thus affect the conjugation differently from oxygen 2p orbitals.

2. Method of calculation

CNDO calculation is made for thioformamide, N-methyl thioformamide (both in cis and trans configuration) and N, N-dimethyl thioformamide using programme QCP 142 CNINDO (Dobosh) on CDC 3600 computer. We have used the same C=S and C=N distances for all the thioamides considered. The bond lengths are 1.731 Å and 1.324 Å respectively. The N–C, N–H and C–H bond lengths adopted are 1.47 Å, 1 Å and 1.09 Å respectively. The bond angles around nitrogen and carbon of functional group are taken to be 120° and carbon of methyl group is taken to be sp3 hybridized. The structure of the considered molecules is presented in figure 1.
Figure 1. Structure of thioamides studied. θ-angle the dipole moment makes with C–N bond and ϕ is the angle of rotation of NH₂ group used in barrier of internal rotation.

Table 1. Charges and mobile bond orders of the molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Total charges (π + σ)*</th>
<th>Net π-charges*</th>
<th>Mobile bond orders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S  C  N  H₁</td>
<td>S  C  N</td>
<td>C=S</td>
</tr>
<tr>
<td>Thioformamide</td>
<td>-341</td>
<td>+165 -127 +20</td>
<td>-619 +304 +316</td>
</tr>
<tr>
<td>N-methyl thioformamide</td>
<td>-359</td>
<td>+160 -75 +16</td>
<td>-625 +286 +359</td>
</tr>
<tr>
<td>(Cis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-methyl thioformamide</td>
<td>-363</td>
<td>+156 -74 +11</td>
<td>-634 +289 +362</td>
</tr>
<tr>
<td>(Trans)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N, N-dimethyl-thioformamide</td>
<td>-385</td>
<td>+152 -19 +7</td>
<td>-644 +274 +406</td>
</tr>
</tbody>
</table>

* Charges are given in the units of 10⁻²⁹ of electronic charge.

### 3. Results and discussion

The total charges (π + σ), net π-charges and mobile bond orders calculated are presented in table 1. The nitrogen has a deficit in π-charge indicating delocalization of lone pair electrons to C=S bond. Further the value of delocalization of lone pair of thioformamide (+0.316 e) is more than in corresponding formamide (+0.18 e) Pople and Gordon 1967, whereas σ-charges on both these molecules are almost the same. This larger delocalization of nitrogen lone pair gives rise to higher double bond character to C–N bond in thioformamide 0.625 compared 0.42 (Pople and Gordon 1967) in formamide. Correspondingly C=S bond order decreases considerably compared to C=O bond order in amide. This is because of larger spatial requirement of sulfur valence electrons and consequent increase in the C=S bond length. The reduced overlap between sulfur 3p and carbon 2p diminishes the capacity of sulfur to form double bond which in turn enhances the double bond character of C–N bond. The assigned stretching vibrational frequencies (Usha Bai and Venkata Ramiah 1971) of C–N bond in thioformamide, N-methyl thioformamide (amide band III) and N, N-dimethyl thioformamide are 1325 cm⁻¹, 1297 cm⁻¹ and 1540 cm⁻¹ respectively. In the corresponding amides the assigned
frequencies are 1309 cm\(^{-1}\), 1248 cm\(^{-1}\) and 1502 cm\(^{-1}\) respectively. Thus the C–N stretching frequencies of thioamides are systematically higher than those of the corresponding amides and this could be due to higher double bond character of C–N bond.

In the amides the reduction in the carbonyl bond order is accompanied by an increase in C–N bond order. Morris et al. (1961) and Vijaya Kumar and Murthy (1969) found linear relationship between C–N and C=O bond orders. The mobile bond orders of C–N and C=S also show a linear relationship (figure 2) showing that the delocalization of the nitrogen lone pair essentially determines

The greater double bond character of C–N bond in thioamides must also be reflected in higher barriers to internal rotation about C–N bond. We have calculated the barrier height in thioformamide and it turns out to be 29.4 Kcal/mole, which is higher than that observed in formamide. The experimental value is 27.9 ± 1.1 Kcal/mole in N, N-dimethyl thioformamide (Loewenstein 1964) compared to 20.6 to 21.6 Kcal/mole in N, N-dimethyl formamide (Rabinovitz and Pines 1969; Mannschreck et al 1967; Conti and Von Phillips born 1967).

In figure 3 we present a change in the energy of thioformamide molecule with angle of rotation \(\phi\) (defined in figure 1) about C–N bond. In figure 4 changes in net charges on sulfur, carbon and nitrogen and variation of dipole moment of molecule with rotation angle \(\phi\) are presented. The changes observed on sulfur and nitrogen are 0.161 e and 0.113 e respectively which are greater than that

![Figure 2](image2.png)

**Figure 2.** C=S vs C–N mobile bond orders.

![Figure 3](image3.png)

**Figure 3.** Energy of the thioformamide molecules as a function of \(\phi\). \(\phi = 0\) and \(\phi = 180\) represent planar structure of the molecule.
observed on carbon 0.015. This large variation of charge on sulfur and nitrogen must be due to decoupling of lone pair and C=S bond $\pi$-orbitals. Thus the barrier to internal rotation is due mostly to change in $\pi$-energy and the increased double bond character is consistent with increase in barrier in thioamides compared to amides.

In an earlier paper (Srinivas Rao et al) we have reported some properties of N-chloroacetamide. We present in this paper the calculated barrier to internal rotation for N-chloroacetamide. The barrier height of 16.7 Kcal/mole obtained is less than that of acetamide. The variation of the energy of molecule with angle of rotation $\phi$ is presented in figure 5. The variation of charges on atoms N, C, O and Cl and dipolemoment changes are presented in figure 6. Oxygen and nitrogen show larger variation than carbon and chlorine. Chlorine substitution in amide reduces the barrier.

In these thioamides the highest filled molecular orbitals exhibit similar behaviour as in amides. In the three molecules studied, the highest filled molecular orbitals are a $\pi$-orbital followed by non-bonding sulfur lone pair orbital. Both orbitals are almost degenerate similar to orbitals in formamide. With successive
Figure 6. Charges ‘q’ on atoms C, N, O, Cl and dipole moment of molecule of N-chloroacetamide as a function of angle $\phi$.

Table 2. The energies of two highest filled levels

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\pi$-level eV</th>
<th>Non-bonding lone pair level of sulfur eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thioformamide</td>
<td>10.62</td>
<td>10.72</td>
</tr>
<tr>
<td>N-methyli-thioformamide (Cis)</td>
<td>10.33</td>
<td>10.36</td>
</tr>
<tr>
<td>N-methyli-thioformamide (Trans)</td>
<td>10.30</td>
<td>10.60</td>
</tr>
<tr>
<td>N, N-dimethyl thioformamide</td>
<td>10.03</td>
<td>10.28</td>
</tr>
</tbody>
</table>

Methyl substitution at nitrogen both the orbitals more upwards, showing that the ionization potentials of thioamides decrease with such methyl substitution. The energies of two highest filled orbitals are presented in table 2.

The dipole moments of thioamides calculated by us are more than those in the corresponding amides in agreement with experimental observation. This shows that thioamide molecule is more polarizable essentially because of the fact that the C=S bond is more polar than C=O bond. The calculated dipole moments, direction of dipole moment and experimental dipole moments are given in table 3.
Table 3. The calculated and observed dipole moments

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dipole moment in debyes</th>
<th>θ Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thioformamide</td>
<td>4.298</td>
<td>35°34'</td>
</tr>
<tr>
<td>N-methyl thioformamide</td>
<td>4.553</td>
<td>31°41'</td>
</tr>
<tr>
<td>N-dimethyl thioformamide</td>
<td>4.972</td>
<td>31°42'</td>
</tr>
</tbody>
</table>

Infrared and NMR methods have shown that N-methylthioformamide also exists in cis and trans configurations as in the case of N-methylformamide. The trans form is more stable and experimentally this component is 88% of normal substance (Sandstrom and Uppstrom 1967; Suzuki 1962). The percentage of trans component is larger compared to that in the corresponding amide. Our calculations give trans form of the molecule to be stable by 4.9 Kcal/mole more than cis form, whereas the corresponding value for the amide is 1.25 Kcal/mole (Yan et al 1970). This larger stability of trans compared with cis form is due to larger spatial orbitals of sulfur and hence increasing steric repulsions.

The physical properties of thioamides show a gradual variation from amides. The differences in the physical properties can be attributed to (a) larger spatial requirement of sulfur orbitals reducing the capacity to form C=S double bond and (b) C=S bond being more polar than C=O bond.

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