Semiempirical Method MNDO for the Evaluation of the Effect of Different Substituents at the Imine-Carbon Position on the Acetaldemine-Vinylamine Tautomerization and Comparison to the Substitution at α-Position

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MNDO calculations have been employed to study the effect of some substituents of the acetaldemine-vinylamine tautomeric system at the imine-carbon position of CH₃CXNH, where X = H, F, CN, NH₂, NO₂, BH₂, CH₃ and CF₃. It is found that the substituents F, NH₂ and NO₂ encourage the formation of the enamine tautomer. The substituents CN, CH₃, CF₃ and BH₂ encourage the formation of the imine tautomer. Isodesmic reactions, free energy change (ΔG), charge distribution and energy gap (Eg) between HOMO and LUMO were used to prove these findings. Resonance stabilization was a major factor in the determination of the most stable tautomer. These results were compared with previous work on the substitution at the σ-carbon position.

Key words: Acetaldemine; Vinylamine; Tautomerism; Imine/enamine; Resonance; MNDO.

1. Introduction

In any compound that has at least one hydrogen atom attached to a carbon atom forming C=X, where X is O, N or S, the “H–C–C=X ↔ C=C–X–H” equilibrium is possible, that is tautomerism. The tautomerism is not possible without this α-hydrogen. In some systems the double bond may be replaced by an aromatic ring to give a ring-chain tautomeric system.

\[ \text{HO} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{H} \]

The study of tautomeric equilibria is challenging for chemists because of experimental difficulties, but presently, computational methods help to solve many problems [1]. Tautomerism is a very important phenomenon in biological systems. For example, theoretical studies of the imine/enamine equilibrium in penicillin have contributed to the understanding of the interaction of penicillin antibiotics with their target [2–3].

As to the effect of substituents on chemical reactions, all workers accept that steric and electronic factors determine this effect. Other factors are also important in individual cases [4]. The steric effect is determined by the size of the substituent. The presence of electron releasing or withdrawing substituents is known as the electronic effect. The electron release or withdrawal is a result of the combination of inductive, field and resonance effects. Since most of the atoms that substitute hydrogen are more electronegative than hydrogen, the inductive effect is a withdrawal of electrons from the carbon attached to the substituent, except with substituents like methyl or ethyl groups. The inductive effect operates through σ-bonds in molecules therefore it weakens rapidly with increasing distance from the substituent [5]. The field effect arises from the dipole moment of the molecule and operates through the environment of the molecule, and in the same direction as the inductive effect [6]. Most of the experimental and theoretical studies indicate that the field effect outweighs the inductive effect [7].

The resonance (delocalization of π-electrons) effect is a stabilizing effect. It leads to electron withdrawal from a negatively charged center or releases electrons to a positively charged center. Because the overall electronic effect is a combination of inductive, field and resonance effects, groups like NH2 and OCH3 are electron releasing (by resonance) in some cases, depending on the structure even though they are electron-
withdrawing when only field and inductive effects are considered. Theoretical investigation of acetaldimine and vinylamine was started in 1980 by Pross and co-workers [8]. It was found by many workers [9–13] that the imine form predominates enamine in the acetaldimine / vinylamine tautomeric system and is thermodynamically more stable than enamine, \( \text{H}_3\text{CCHNH} \rightleftharpoons \text{CH}_2\text{CHNH}_2 \).

2. Results and Discussion

2.1. Anti and Syn Conformers of the Substituted Acetaldimine

It was found that the anti conformer is more stable than the syn conformer in the case of the unsubstituted acetaldimine. This was discussed in terms of the repulsive and attractive forces between the positive and negative charges at the atoms in the conformers. The discussion also involved other theoretical work done at different levels of calculations [9].

In the present work, the anti conformer is found to be more stable than the syn conformer for F, CN, NO2 and CH3 substituted acetaldimine at the imine-carbon position. The energy difference between the two conformers was found to be in the range of 0.730 kcal/mol for CN and 3.43 kcal/mol for the NO2 substituents with lower energy for the more stable anti conformer. The other substituents, namely NH2, BH2, and CF3, give more stable syn conformers with small energy differences between the two conformers (NH2: 0.0782, BH2: 0.387, CF3: 0.320 kcal/mol). For example, the charges on the atoms of the syn and anti conformers of BH2-substituted acetaldimine show that the forces of repulsion between H1 and C1 and between the H1 and H5 in the anti conformer are replaced by attractive forces in the syn conformer. This would be the reason for the extra stability of the syn conformer provided the same bonds are involved in both conformers, where the bond energies and atomization energies have no effect on the difference in stability between the two conformers. The other forces of attraction and repulsion in the two conformers are the equal.

2.2. Unsubstituted Acetaldimine/vinylamine Parent Pair

It is found that acetaldimine is energetically more stable than vinylamine with an energy difference of 5.224 kcal/mol. A detailed discussion in the light of heats of formation, \( \Delta H_f \), of both tautomers and the free energy change, \( \Delta G \), for the tautomerization reaction, including the results of previous work, is shown in [9].

2.3. Effect of Substituents

It was found in a previous study on the effect of different substituents on the \( \alpha \)-position of acetaldimine/vinylamine [17] that all of double bonds in substituted imine (C=C) and enamine (C=N) were lengthened, and that this was accompanied by a decrease in the bond order. The effect on the C=C bond of enamines was more significant when the substituents were BH2, CN or NO. This was attributed to a resonance effect of these substituents with the C=C of the enamine.

In this study, all substituents (F, CN, NH2, NO2, BH2, CH3 and CF3) at the imine-carbon position have increased the length of the double bonds (C1, C2 and C2N) in substituted imines (Table 1A) and their corresponding enamines (Table 1B). The effect on the other bond lengths was negligible. All of the C1, C2 and C2N bond lengths increased in both of the tautomeric structures below with the exception of the C2N bond length in the NO2-substituted imine and enamine, where also this bond (C2N) stays unchanged in the
CF₃-substituted imine. The substitution at the imine-carbon position allows resonance between the double bonds and the lone pairs of the substituents in both tautomers, while the substituent at the α-position allows resonance only in the substituted enamine. The consequences of resonance are: decrease in the electron density and bond lengthening [17]. This leads to the belief that the lengthening in the double bonds (C1C2 and C2N) in both structures is mainly due to resonance of these double bonds with the lone pairs of the substituents. The bond lengthening was accompanied with a decrease in the electron density (Tables 2A and 2B). The BH₂ substituent has no lone pairs but the B atom has an empty π orbital [13] which can accept the electron density from C=C in imine and C=N in enamine.

A look at the C1C2N bond angles in both tautomers (where the substituents were attached) shows that this bond angle is affected to different extents, depending on the substituent. There is a decrease or increase in this bond angle by less than 1.00 degree in the F- and NO₂-substituted imines and F-substituted enamines. The change in this bond angle (C1C2N) in the substituted imine was −2.29 for CN, +6.36 for NH₂, +3.31 for BH₂, −4.30 for CH₃ and +5.91 degrees for CF₃ (Table 1A). In the substituted enamine this change was −2.42 for CN, −2.01 for NH₂, +3.96 for NO₂, −5.43 for BH₂, −4.10 for CH₃ and −1.78 for CF₃ (Table 1B).

Effect of F and NH₂ Substituents

Positive energy changes for the isodesmic reaction mean that the species is stabilized by the substituent, and negative values mean destabilization [14–16]. The calculated energy changes (ΔH) for the isodesmic reactions of both F-substituted acetaldemin (1) and vinylamine (2) are negative, but (ΔH) of reaction (1) (−2.621 kcal/mol) is more negative than that of reaction (2) (−1.395 kcal/mol), which means that the F-substituent destabilizes imine 1 more than enamine 1a.
Table 1A. Optimized geometrical parameters (bond lengths in Å and bond angles in degrees) calculated by MNDO for the unsubstituted and imine-carbon substituted acetaldimines.

Table 1B. Optimized geometrical parameters (bond lengths in Å and bond angles in degrees) calculated by MNDO for the unsubstituted and carbon-2 substituted vinylamines.

H1C1, 1.108; C1C2, 1.505; C2N, 1.297; NHS, 1.006. H1C1C2, 113.48; C1C2N, 121.51; C2NH5, 113.72; H4C2C1, 114.36; H3C1C2, 109.70.

H1C1, 1.107; C1C2, 1.502; C2N, 1.293; NHS, 1.004. H1C1C2, 111.31; C1C2N, 121.86; C2NH5, 116.66; FC2C1, 116.83; H3C1C2, 110.29.

H1C1, 1.108; C1C2, 1.517; C2N, 1.291; NHS, 1.005. H1C1C2, 112.38; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.

H1C1, 1.108; C1C2, 1.512; C2N, 1.305; C1C2N, 119.09; C2NH5, 112.69; N2C2C1, 115.77; H3C1C2, 110.08.

H1C1, 1.108; C1C2, 1.513; C2N, 1.273; NHS, 1.003. H1C1C2, 110.39; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.

H1C1, 1.110; C1C2, 1.513; C2N, 1.273; NHS, 1.003. H1C1C2, 110.39; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.

H1C1, 1.110; C1C2, 1.513; C2N, 1.273; NHS, 1.003. H1C1C2, 110.39; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.

H1C1, 1.109; C1C2, 1.516; C2N1, 1.298; NHS, 1.004. H1C1C2, 111.69; C1C2N1, 127.87; C2NH5, 114.53; N2C2C1, 115.87; H3C1C2, 111.08.

H1C1, 1.108; C1C2, 1.512; C2N, 1.294; NHS, 1.005. H1C1C2, 112.38; C1C2N1, 129.27; C2NH5, 112.69; N2C2C1, 115.77; H3C1C2, 110.08.

H1C1, 1.110; C1C2, 1.513; C2N, 1.273; NHS, 1.003. H1C1C2, 110.39; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.

H1C1, 1.108; C1C2, 1.517; C2N, 1.296; NHS, 1.008. H1C1C2, 112.07; C1C2N, 124.82; C2NH5, 115.27; H3C2C1, 110.44; C1C2B, 119.06.

H1C1, 1.110; C1C2, 1.517; C2N, 1.296; NHS, 1.008. H1C1C2, 112.07; C1C2N, 124.82; C2NH5, 115.27; H3C2C1, 110.44; C1C2B, 119.06.

H1C1, 1.108; C1C2, 1.517; C2N, 1.292; NHS, 1.006. H1C1C2, 113.01; C1C2N, 117.21; C2NH5, 114.90; H3C2C1, 110.30; C1C2B, 117.09.

H1C1, 1.108; C1C2, 1.517; C2N, 1.292; NHS, 1.006. H1C1C2, 113.01; C1C2N, 117.21; C2NH5, 114.90; H3C2C1, 110.30; C1C2B, 117.09.

H1C1, 1.110; C1C2, 1.511; C2N, 1.287; NHS, 1.008. H1C1C2, 111.57; C1C2N, 127.42; C2NH5, 115.93; H3C2C1, 110.91; C1C2C, 119.82.

H1C1, 1.110; C1C2, 1.511; C2N, 1.287; NHS, 1.008. H1C1C2, 111.57; C1C2N, 127.42; C2NH5, 115.93; H3C2C1, 110.91; C1C2C, 119.82.
Table 2A. Calculated electron densities on the atoms of unsubstituted and substituted acetaldemines at the imine-carbon position.

<table>
<thead>
<tr>
<th>Structure</th>
<th>H1</th>
<th>C1</th>
<th>C2</th>
<th>N</th>
<th>H5</th>
<th>H2</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9784</td>
<td>3.949</td>
<td>3.975</td>
<td>5.227</td>
<td>0.9066</td>
<td>0.9966</td>
<td>0.9966</td>
</tr>
<tr>
<td>2</td>
<td>0.9647</td>
<td>3.93</td>
<td>3.89</td>
<td>5.185</td>
<td>0.89</td>
<td>3.791</td>
<td>3.54</td>
</tr>
<tr>
<td>3</td>
<td>0.993</td>
<td>3.95</td>
<td>3.9</td>
<td>5.284</td>
<td>0.89</td>
<td>3.904</td>
<td>3.8</td>
</tr>
<tr>
<td>4</td>
<td>0.9621</td>
<td>3.92</td>
<td>3.92</td>
<td>5.185</td>
<td>0.89</td>
<td>3.904</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>1.003</td>
<td>3.97</td>
<td>3.97</td>
<td>5.227</td>
<td>0.9162</td>
<td>3.79</td>
<td>3.432</td>
</tr>
<tr>
<td>6</td>
<td>0.9786</td>
<td>3.93</td>
<td>3.91</td>
<td>5.216</td>
<td>0.9094</td>
<td>3.971</td>
<td>3.9890</td>
</tr>
<tr>
<td>7</td>
<td>0.9847</td>
<td>3.964</td>
<td>3.967</td>
<td>5.164</td>
<td>0.89</td>
<td>3.967</td>
<td>3.967</td>
</tr>
</tbody>
</table>

Table 2B. Calculated electron densities on the atoms of unsubstituted and substituted vinylamine at carbon-2 position.

<table>
<thead>
<tr>
<th>Structure</th>
<th>H2</th>
<th>C1</th>
<th>C2</th>
<th>N</th>
<th>F</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.9342</td>
<td>4.15</td>
<td>3.8</td>
<td>5.225</td>
<td>0.89</td>
<td>3.791</td>
<td>3.54</td>
<td>5.043</td>
</tr>
<tr>
<td>3</td>
<td>0.9937</td>
<td>3.95</td>
<td>3.95</td>
<td>5.263</td>
<td>0.89</td>
<td>3.904</td>
<td>3.8</td>
<td>5.253</td>
</tr>
<tr>
<td>4</td>
<td>0.9621</td>
<td>3.92</td>
<td>3.92</td>
<td>5.185</td>
<td>0.89</td>
<td>3.904</td>
<td>3.8</td>
<td>5.253</td>
</tr>
<tr>
<td>5</td>
<td>1.003</td>
<td>3.97</td>
<td>3.97</td>
<td>5.227</td>
<td>0.9162</td>
<td>3.79</td>
<td>3.432</td>
<td>0.9663</td>
</tr>
<tr>
<td>6</td>
<td>0.9786</td>
<td>3.93</td>
<td>3.91</td>
<td>5.216</td>
<td>0.9094</td>
<td>3.971</td>
<td>3.9890</td>
<td>0.9991</td>
</tr>
</tbody>
</table>

suggesting that the F-substituent encourages the enamine formation, and reaction (3) is spontaneous in the forward direction.

Inspection of the charges on the atoms of structures 1 and 1a below supports this direction of the tautomerization reaction (3), where all forces in structure 1a are attractive, while the forces on the left hand side of structure 1 are all repulsive. Besides the carbon-carbon repulsion force this makes structure 1a (enamine) preferable.
Previous work [9, 17] shows that the substitution of the fluorine atom at $\alpha$-position makes imine slightly more stable than enamine, and therefore has an opposite effect to the substitution at the imine carbon position.

The calculated $\Delta H$ for the isodesmic reaction of NH$_2$-substituted imine 2 ($-3.995$ kcal/mol) is more negative than that of the substituted enamine 2a ($-0.165$ kcal/mol), which makes it less stable, and the tautomerization process (4) prefers the enamine 2a formation.

The charges of both tautomeric structures show that the enamine 2a contains more attraction forces than imine 2, which makes it more stable.

Previous work [17] shows that the NH$_2$ substituent has an opposite effect when the substitution is at the $\alpha$-position.

**Effect of CN Substituent**

The calculated heat of formation of the CN-substituted imine 3 (41.24 kcal/mol) is less than that of the substituted enamine 3a (45.34 kcal/mol) with an energy difference of 4.101 kcal/mol, suggesting an extra stabilization of imine 3 over enamin 3a.

The calculated entropy change ($\Delta S$) for the tautomerization reaction (5) is found to be slightly negative ($-0.119 \cdot 10^{-3}$ kcal/mol). This means that both energy and entropy favor the formation of imine 3. The calculated free energy, $\Delta G$, at 298 K was positive (4.137 kcal/mol), suggesting a spontaneous tautomerization reaction (5) in the reverse direction.

The isodesmic reactions of the substitution of imine (6) and enamine (7) show $\Delta H$ values of 2.571 and 2.145 kcal/mol, respectively. This means that the CN substituent stabilizes imine 3 more than enam-
ine 3a because of the higher $\Delta H$ value of the isodesmic reaction. This also supports that the tautomerization reaction (5) is spontaneous in the reverse direction.

The effect of the CN substituent at the $\alpha$-position was found to be the opposite [9, 17], where the tautomerization reaction was spontaneous in the forward direction.

**Effect of CF$_3$, BH$_2$ and CH$_3$ Substituents**

The energy difference ($\Delta H$) between the structures 4 and 4a, when X is BH$_2$, CH$_3$ or CF$_3$, is positive, which means that by the energy the imine 4 is preferred for all these substituents. The entropy factor ($\Delta S$) is negative when X is BH$_2$ or CH$_3$, this means that the entropy factor in these two substituents also prefers the imine 4 formation.

When X is CF$_3$ the entropy change is positive, so it prefers the enamine 4a formation, but its magnitude at 298 K is not large enough to overcome the effect of the energy, which means that the resultant of both energy and entropy ($\Delta G$) prefers imine 4 formation for this substituent, so, for all of these three substituents the free energy is positive and the imine 4 formation is preferred in the tautomerization reaction (8) below. In a previous work the same effect was observed in the case of CH$_3$ [8, 9] and CF$_3$ [9] substituents at $\alpha$-position, whereas an opposite effect was observed with the BH$_2$ substituent [9, 17].

The energy change ($\Delta H$) for the isodesmic reactions for the substituted imines (*) and enamines (**) (X = BH$_2$ or CH$_3$, CF$_3$) are shown in Table 3. $\Delta H$ for the BH$_2$ substituent is positive for substituted imine 4 (5.876 kcal/mol) and enamine 4a (1.435 kcal/mol), but it is more positive for the substituted imine 4. This means that the BH$_2$ substituent stabilizes both imine 4 and enamine 4a, but the former is stabilized more because it has a higher $\Delta H$. This encourages the tautomerization reaction (8) to be towards imine 4. This direction is also supported by the positive free energy change ($\Delta G = 1.340$ kcal/mol). Previous work [9, 17] shows that BH$_2$ has an opposite effect when this substituent was at the $\alpha$-position.

<table>
<thead>
<tr>
<th>X</th>
<th>$10^3 \Delta S$</th>
<th>$\Delta H$ (kcal/mol)</th>
<th>$\Delta G$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_2$</td>
<td>0.408</td>
<td>1.219</td>
<td>1.340</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>0.124</td>
<td>5.352</td>
<td>5.389</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>0.353</td>
<td>4.473</td>
<td>4.368</td>
</tr>
</tbody>
</table>

(a) This structure is the anti conformer when X is CH$_3$.
The CH₃-substituted imine 4 is found to be stabilized ($\Delta H = 0.613$), but the enamine 4a is slightly destabilized because it has a small negative energy change ($\Delta H = -0.086$). The result of this is the preference of the tautomerization reaction (8) towards the imine 4 direction, which is also shown by the positive free energy change ($\Delta G = 5.389$ kcal/mol).

In the case of the CF₃ substituent, the imine 4 ($\Delta H = 0.417$ kcal/mol) is also more stabilized than the enamine 4a ($\Delta H = 0.295$ kcal/mol). Therefore the tautomerization reaction (8) prefers the imine 4 side, also shown by the positive free energy change ($\Delta G = 4.368$ kcal/mol) for reaction (8). An opposite effect was observed when the substituent was at the α-position [9], even though some workers obtained the same effect as obtained in this work for this substituent at the α-position [17].

Effect of NO₂ Substituent

The structures 6 and 6a below show the charge distribution on the atoms of the NO₂-substituted acetaldemine and vinylamine at the imine-carbon position. Close inspection of these charges shows that the positive charge on C1 (0.0710) of the imine 6 is re-
placed by a negative charge (−0.0376) on the same carbon of the enamine 6a. This makes a number of repulsion forces in imine 6 to be replaced by attraction forces in enamine 6a. This decrease in the number of repulsion forces and increase in attraction forces makes enamine 6a more stable compared to imine 6, which makes enamine 6a preferable in the tautomerization reaction (9).

The isodesmic reactions for the NO2-substituted imine (10) and enamine (11) give $\Delta H$ values of $-1.702$ and $2.554$ kcal/mol respectively. The negative value means that the NO2 substituent destabilizes the imine and the positive value for enamine means that it is stabilized by the NO2 substituent, so, these $\Delta H$ values for the isodesmic reactions also lead to the result that enamine 6a is more stable than the imine 6, which supports the results obtained by the charge distribution. The NO2 substituent at the α-position has the same effect as at the imine-carbon position [9].

**Orbital Energies (LOMO and HUMO)**

Introduction of the substituents at the imine-carbon position affects the orbital energies (HOMO and LUMO) of the substituted imine and enamine relative to those of their parent (Table 4). As discussed above, the “CN, BH2, CH3 and CF3” substituents encourage the reverse direction of the tautomerization reaction, which indicates extra stability of the imine over enamine. It is found that, for these substituents, the energy gap $E_g$ between the HOMO and LUMO is larger in the case of substituted imines A compared to the corresponding enamines B (Table 4). This agrees with the findings of this work, because a larger energy gap means that the compound is more stable [18–22]. The NO2 and NH2 substituents were found to encourage the enamine formation, but in both of these two cases the $E_g$ of the enamine is slightly larger than that of the imine, which suggests that some other factors

![Diagram](image)

Table 4. Calculated orbital energies (HOMO and LUMO) of the substituted acetaldimine and the corresponding vinylamine at the imine-carbon position (eV), $E = \text{LUMO} - \text{HOMO}$.

<table>
<thead>
<tr>
<th></th>
<th>Imine (Acetaldimine)</th>
<th>Enamine (Vinylamine)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LOMO</td>
<td>HUMO</td>
</tr>
<tr>
<td>H</td>
<td>−11.15</td>
<td>1.006</td>
</tr>
<tr>
<td>F</td>
<td>−11.75</td>
<td>0.4936</td>
</tr>
<tr>
<td>CN</td>
<td>−12.03</td>
<td>0.2091</td>
</tr>
<tr>
<td>NH2</td>
<td>−10.33</td>
<td>0.9918</td>
</tr>
<tr>
<td>NO2</td>
<td>−11.58</td>
<td>1.124</td>
</tr>
<tr>
<td>BH2</td>
<td>−11.13</td>
<td>−0.2249</td>
</tr>
<tr>
<td>CH3</td>
<td>−10.3</td>
<td>0.9918</td>
</tr>
<tr>
<td>CF3</td>
<td>−12.16</td>
<td>−0.2706</td>
</tr>
</tbody>
</table>
(like the resonance effect) are more important than $E_g$ in the stabilization of the enamine.

3. Conclusion

From the results obtained in this work it is found that F and NH$_2$ substituents at the imine-carbon position stabilize the enamine more than the imine. The substitution at the $\alpha$-position has an opposite effect in the case of fluorine. The CN substituent at the imine-carbon position makes the imine more stable than the enamine, this substituent at the $\alpha$-carbon position has an opposite effect. The BH$_2$, CH$_3$, and CF$_3$ substituents stabilize the imine more than the enamine. Substitution at the $\alpha$-position has the same effect in the case of CH$_3$ and CF$_3$ substituents, but an opposite effect in the case of BH$_2$ substituent.

The substitution of NO$_2$ at the imine-carbon position and the $\alpha$-position has the same effect. It stabilizes of the enamine more than the imine.

The main factor for the preference of the imine or enamine tautomer would be the resonance of the substituent with C=N in imine or C=C in enamine tautomers.