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

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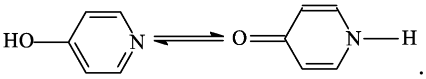
MNDO calculations have been employed to study the effect of some substituents of the acetaldemine-vinylamine tautomeric system at the imine-carbon position of CH_3CXNH, where X = H, F, CN, NH_2, NO_2, BH_2, CH_3 and CF_3. It is found that the substitutents F, NH_2 and NO_2 encourage the formation of the enamine tautomer. The substitutents CN, CH_3, CF_3 and BH_2 encourage the formation of the imine tautomer. Isodesmic reactions, free energy change (ΔG), charge distribution and energy gap (E_g) 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.



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 overweighs 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 NH_2 and OCH_3 are electron releasing (by resonance) in some cases, depending on the structure even though they are electron-

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withdrawing when only field and inductive effects are considered.

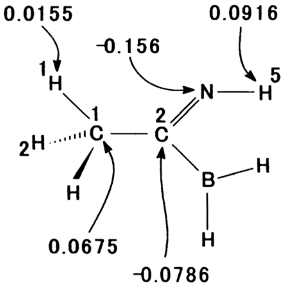
Theoretical investigation of acetaldemine and vinylamine was started in 1980 by Pross and co-workers [8]. It was found by may workers [9 – 13] that the imine form predominінates enamine in the acetaldemine / vinylamine tautomeric system and is thermodynamically more stable than enamine, $H_3CCHNH \leftrightarrows CH_2CHNH_2$.

2. Results and Discussion

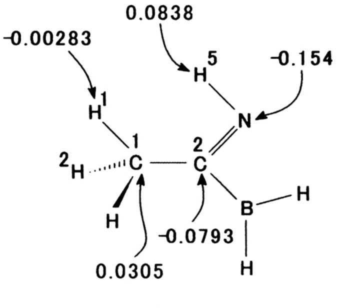
2.1. Anti and Syn Conformers of the Substituted Acetaldemine

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, NO_2 and CH_3 substituted acetaldemine 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 NO_2 substituents with lower energy for the more stable anti conformer. The other substituents, namely NH_2, BH_2, and CF_3, give more stable syn conformers with small energy differences between the two conformers (NH_2: 0.0782, BH_2: 0.387, CF_3: 0.320 kcal/mol). For example, the charges on the atoms of the syn and anti conformers of BH_2-substituted acetaldemine 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.



Anti



Syn

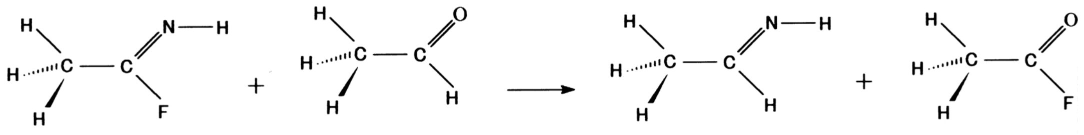
2.2. Unsubstituted Acetaldemine/vinylamine Parent Pair

It is found that acetaldemine 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, ΔH_f, of both tautomers and the free energy change, ΔG, for the tautomerization reaction, including the results of previous work, is shown in [9].

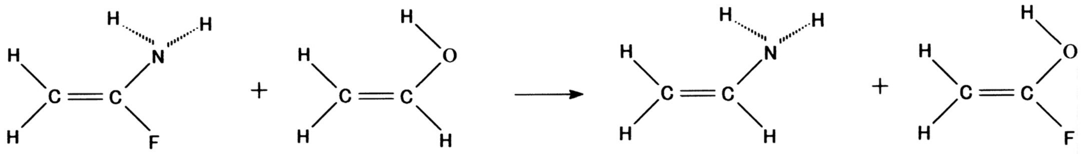
2.3. Effect of Substituents

It was found in a previous study on the effect of different substituents on the α-position of acetaldemine/vinylaime [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 BH_2, CN or NO. This was attributed to a resonance effect of these substituents with the C=C of the enamine.

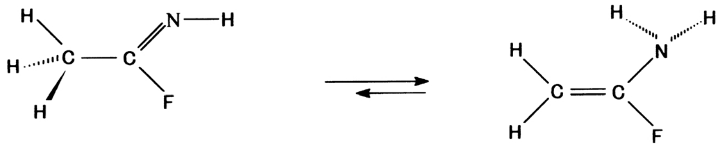
In this study, all substituents (F, CN, NH_2, NO_2, BH_2, CH_3 and CF_3) at the imine-carbon position have increased the length of the double bonds (C1, C2 and C2N) in substituted imines (Table 1A) and their corresponding enamines (Table 1B). The effect on the other bond lengths was negligible. All of 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 NO_2-substituted imine and enamine, where also this bond (C2N) stays unchanged in the



1 (1)



1a (2)



1 **1a** (3)

CF_3-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 BH_2 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 NO_2-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 NH_2, $+3.31$ for BH_2, -4.30 for CH_3 and $+5.91$ degrees for CF_3 (Table 1A). In the substituted enamine this change was -2.42 for CN, -2.01 for NH_2, $+3.96$ for NO_2, -5.43 for BH_2, -4.10 for CH_3 and -1.78 for CF_3 (Table 1B).

Effect of F and NH_2 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-substiuent 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.

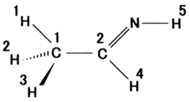
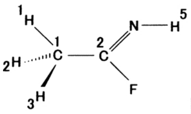
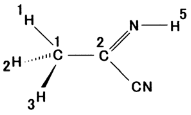
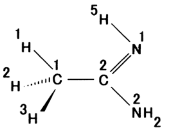
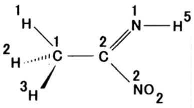
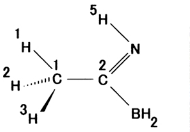
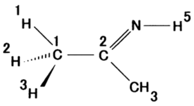
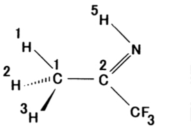
 **1**	H1C1, 1.108; C1C2, 1.505; C2N, 1.287; NH5, 1.006. H1C1C2, 113.48; C1C2N, 121.51; C2NH5, 113.72; H4C2C1, 114.36; H3C1C2, 109.70.
 **2**	H1C1, 1.107; C1C2, 1.521; C2N, 1.293; NH5, 1.004. H1C1C2, 111.31; C1C2N, 121.86; C2NH5, 116.66; FC2C1, 116.83; H3C1C2, 110.29.
 **3**	H1C1, 1.108; C1C2, 1.517; C2N, 1.291; NH5, 1.005. H1C1C2, 112.38; C1C2N, 119.22; C2NH5, 115.55; CC2C1, 116.74; H3C2C3, 110.11.
 **4**	H1C1, 1.109; C1C2, 1.516; C2N1, 1.298; N1H5, 1.004. H1C1C2, 111.69; C1C2N1, 127.87; C2N1H5, 114.53; N2C2C1, 115.87; H3C1C2, 111.08.
 **5**	H1C1, 1.110; C1C2, 1.513; C2N, 1.273; NH5, 1.003. H1C1C2, 110.39; C1C2N1, 122.42; C2N1H5, 121.15; H3C1C2, 111.05; N2C2C1, 116.51.
 **6**	H1C1, 1.110; C1C2, 1.517; C2N, 1.296; NH5, 1.008. H1C1C2, 113.207; C1C2N, 124.82; C2NH5, 115.27; H3C2C1, 110.44; C1C2B, 119.06.
 **7**	H1C1, 1.108; C1C2, 1.517; C2N, 1.292; NH5, 1.006. H1C1C2, 113.01; C1C2N, 117.21; C2NH5, 114.90; H3C1C2, 110.30; C1C2C, 117.09.
 **8**	H1C1, 1.110; C1C2, 1.511; C2N, 1.287; NH5, 1.005. H1C1C2, 111.57; C1C2N, 127.42; C2NH5, 115.93; H3C1C2, 110.91; C1C2C, 119.82.

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.

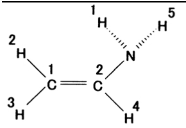
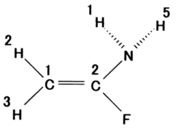
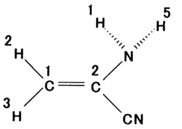
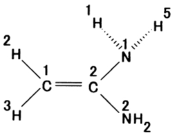
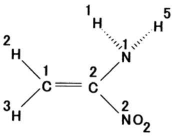
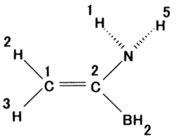
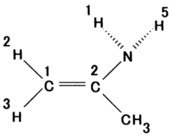
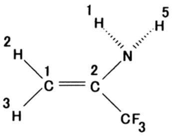
 **1a**	H2C1, 1.088; C1C2, 1.346; C2N; 1.421; NH5, 1.008; C1H3, 1.007. H2C1C2, 124.90; C1C2N, 125.31; C2NH5, 110.40; H4C2C1, 120.97; H3C1C2, 121.37.
 **2a**	H2C1, 1.086; C1C2, 1.359; C2N; 1.431; NH5, 1.007; C1H3, 1.087. H2C1C2, 122.80; C1C2N, 124.88; C2NH5, 110.97; H3C1C2, 122.66; FC2C1, 122.55.
 **3a**	H2C1, 1.088; C1C2, 1.355; C2N; 1.430; NH5, 1.008; C1H3, 1.088. H2C1C2, 123.94; C1C2N, 122.89; C2NH5, 111.36; H3C2C1, 122.44; ClC2C, 122.04.
 **4a**	H2C1, 1.087; C1C2, 1.356; C2N1; 1.430; N1H5, 1.008; C1H3, 1.088. H2C1C2, 123.99; C1C2N1, 123.30; C2N1H5, 110.87; H3C1C2, 123.26; C1C2N2, 123.33.
 **5a**	H2C1, 1.090; C1C2, 1.347; C2N; 1.417; NH5, 1.008; C1H3, 1.089. H2C1C2, 1122.23; C1C2N1, 129.27; C2N1H5, 111.03; H3C1C2, 124.10; C1C2N2, 120.22.
 **6a**	H2C1, 1.090; C1C2, 1.361; C2N; 1.433; NH5, 1.008; C1H3, 1.089. H2C1C2, 124.65; C1C2N, 119.88; C2NH5, 111.92; H3C1C2, 122.55; C1C2B, 121.14.
 **7a**	H2C1, 1.088; C1C2, 1.354; C2N; 1.430; NH5, 1.008; C1H3, 1.088. H2C1C2, 124.33; C1C2N, 121.21; C2NH5, 111.73; H3C1C2, 122.63; C1C2C, 122.84.
 **8a**	H2C1, 1.090; C1C2, 1.351; C2N; 1.426; NH5, 1.008; C1H3, 1.008. H2C1C2, 123.15; C1C2N, 123.53; C2NH5, 111.41; H3C1C2, 123.94; C1C2C, 123.15.

Table 2A. Calculated electron densities on the atoms of unsubstituted and substituted acetaldemines at the imine-carbon position.

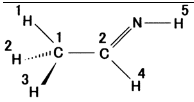
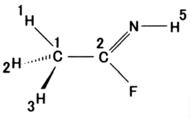
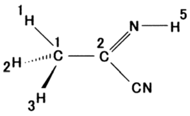
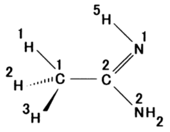
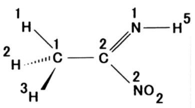
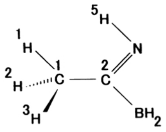
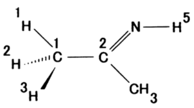
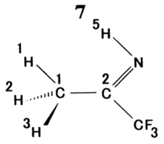
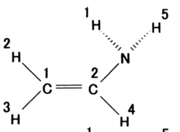
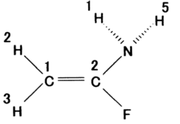
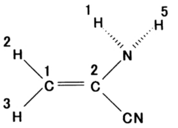
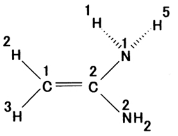
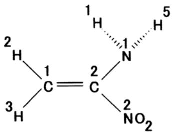
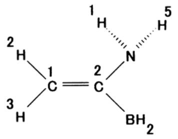
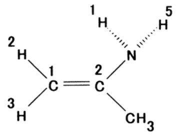
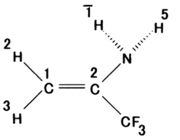
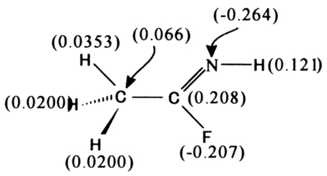
 **1**	H1(0.9784), C1(3.949), C2(3.975), N(5.227), H5(0.9066), H2(0.9966), H3(0.9966)
 **2**	H1(0.9647), C1(3.934), C2(3.792), N(5.263), H5(0.8791), F(7.207), H2(0.9799), H3(0.9799)
 **3**	H1(0.9703), C1(3.935), C2(3.891), N1(5.185), H5(0.8908), C3(4.110), N2(5.043), H2(0.9873), H3(0.9873)
 **4**	H1(0.9937), C1(3.958), C2(3.904), N1(5.284), H5(0.8987), N2(5.253), H2(0.9919), H3(0.9755), H4(0.8606), H6(0.8791)
 **5**	H1(0.9621), C1(3.929), C2(3.902), N1(5.185), H5(0.8346), N2(4.600), H2(0.9663), H3(0.9663), O1(6.342), O2(6.316)
 **6**	H1(1.003), C1(3.970), C2(4.079), N(5.154), H5(0.9162), B(3.790), H2(0.9902), H3(0.9902), H4(1.043), H6(1.064)
 **7**	H1(0.9786), C1(3.933), C2(4.018), N(5.216), H5(0.9094), C3(3.971), H2(0.9991), H3(0.9991), H4(0.9890), H6(0.9890), H7(0.9965)
 **8**	H1(0.9847), C1(3.964), C2(4.035), N(5.164), H5(0.8774), C3(3.363), H2(0.9697), H3(0.96971), F1(7.233), F2(7.220), F3(7.220)

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

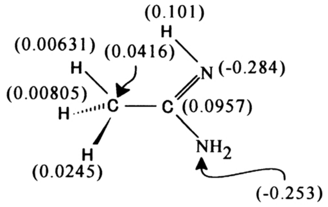
	H2(0.9541), C1(4.133), C2(4.006), N(5.240), H1(0.944) H5(0.8892), H3(0.8900), H4(0.9338)
 **2a**	H2(0.9373), C1(4.150), C2(3.804), N(5.255), H1(0.8678) H5(0.8717), H3(0.9320), F(7.182)
 **3a**	H2(0.9432), C1(4.059), C2(3.940), N1(5.225), H1(0.8799), H5(0.8829), H3(0.9420), C3(4.057), N2(5.070)
 **4a**	H2(0.9494), C1(4.175), C2(3.921), N1(5.241), H1(0.8788) H5(0.8831), H3(0.9499), N2(5.241), H4(0.8830), H6(0.8788)
 **5a**	H2(0.9312), C1(4.038), C2(3.986), N1(5.226), H1(0.8593) H5(0.8664), H3(0.9205), N2(4.524), O1(6.334), O2(6.315)
 **6a**	H2(0.9587), C1(4.009), C2(4.104), N(5.228), H1(0.8901) H5(0.9006), H3(0.9533), B(2.839), H4(1.058), H6(1.059)
	H2(0.9560), C1(4.109), C2(4.046), N(5.230), H1(0.8924) H5(0.9819), H3(0.9549), C3(3.925), H4(0.9974), H6(0.9924), H7(1.006)
 **8a**	H2(0.9399), C1(4.028), C2(4.091), N(5.220), H1(0.8750) H5(0.8785), H3(0.9303), C3(3.350), F1(7.231), F2(7.218), F3(7.237)

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

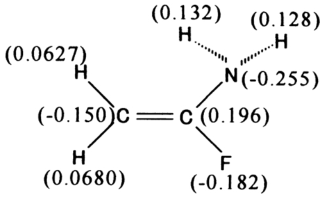
Inspection of the charges on the atoms of structures **1** and **1a** below supports this direction of the tautomerization reaction (3), where all forces in structure **1a** are attractive, while the forces on the left hand side of structure **1** are all repulsive. Besides the carbon-carbon repulsion force this makes structure **1a** (enamine) preferable.



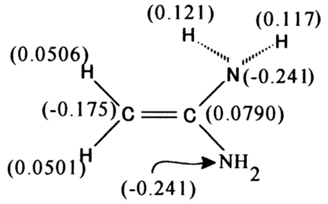
1



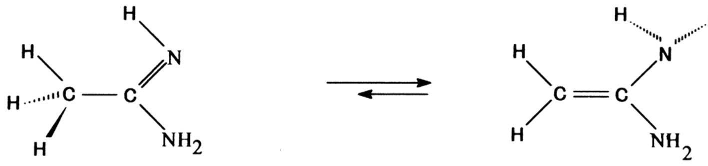
2



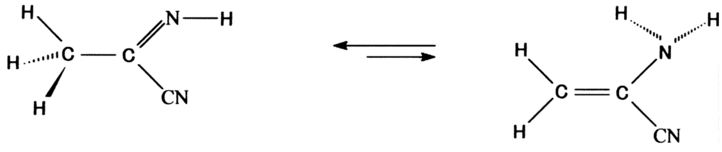
1a



2a



2 **2a** (4)



3 **3a** (5)

Previous work [9, 17] shows that the substitution of the fluorine atom at α-position makes imine slightly more stable than enamine, and therefore has an opposite effect to the substitution at the imine carbon position.

The calculated ΔH 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.

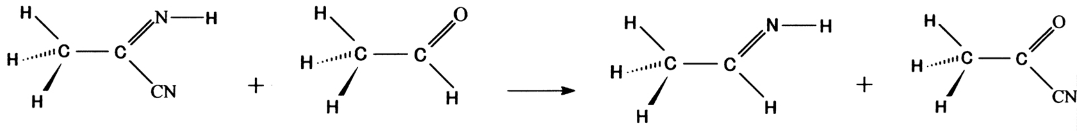
The charges of both tautomeric structures show that the enamine **2a** contains more attraction forces than imine **2**, which makes it more stable.

Previous work [17] shows that the NH_2 substituent has an opposite effect when the substitution is at the α-position.

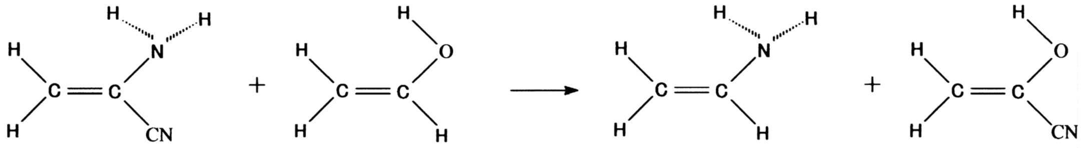
Effect of CN Substituent

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 (ΔS) 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, ΔG, 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 ΔH values of 2.571 and 2.145 kcal/mol, respectively. This means that the CN substituent stabilizes imine **3** more than enam-

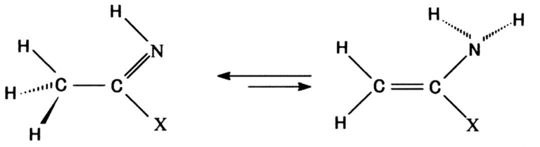


3 (6)



3a (7)

(a)



4 **4a** (8)

X	$10^3\Delta S$ kcal/mol	ΔH kcal/mol	ΔG kcal/mol
BH_2	−0.408	1.219	1.340
CH_3	−0.124	5.352	5.389
CF_3	0.353	4.473	4.368

(a) This structure is the anti conformer when X is CH_3.

Table 3. Energy changes (ΔH) of the isodesmic reactions of substituted imines and enamines at the imine-carbon position.

X	ΔH (kcal/mol) *(imine)	ΔH (kcal/mol) **(enamine)
BH_2	5.876	1.435
CH_3	0.613	−0.086
CF_3	0.417	0.295

ine **3a** because of the higher ΔH value of the isodesmic reaction. This also supports that the tautomerization reaction (5) is spontaeous in the reverse direction.

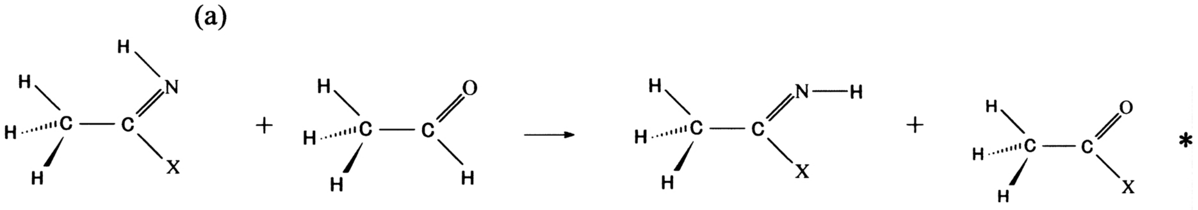
The effect of the CN substituent at the α-position was found to be the opposite [9, 17], where the tautomerization reaction was spontaneous in the forward direction.

Effect of CF_3, BH_2 and CH_3 Substituents

The energy difference (ΔH) 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 prefered for all these substituents. The entropy factor (ΔS) 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.

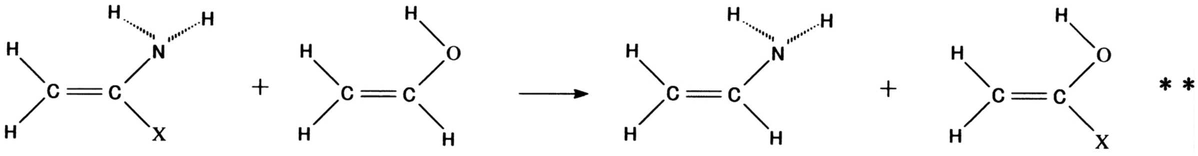
When X is CF_3 the entropy change is posititive, so it prefers the enamine **4a** formation, but it's magnitude at 298 K is not large enough to overcome the effect of the energy, which means that the resultant of both energy and entropy (ΔG) prefers imine **4** formation for this substituent, so, for 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 α-position, whereas an opposite effect was observed with the BH_2 substituent [9, 17].

The energy change (ΔH) for the isodesmic reactions for the substituted imines (*) and enamines (**) (X = BH_2 or CH_3, CF_3) are shown in Table 3. ΔH 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 ΔH. 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 α-position.

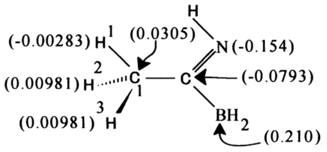


4

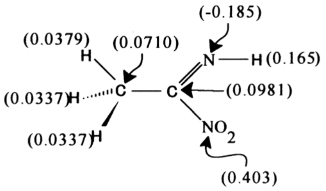
(a) This structure is the anti conformer when X is CH_3.



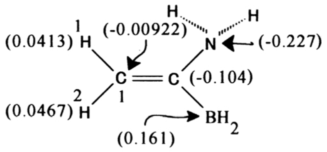
4a



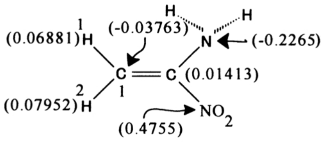
5



6



5a



6a

The CH_3-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).

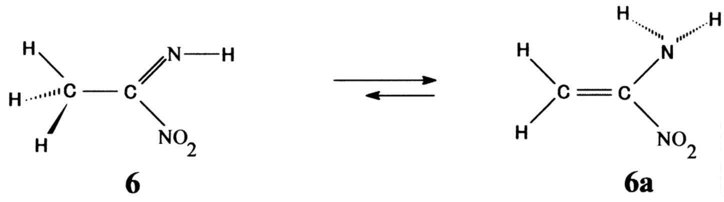
In the case of the CF_3 substituent, the imine **4** ($\Delta H = 0.417$ kcal/mol) is also more stabilized than the enamine **4a** ($\Delta H = 0.295$ kcal/mol). Therefore the tautomerization reaction (8) prefers the imine **4** side, also shown by the positive free energy change ($\Delta G = 4.368$ 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].

The charge distribution on the atoms of the substituted imine and enamine structures for these substituents show extra stability for imines. This is exemplified by the structures **5** and **5a** when the substituent is BH_2.

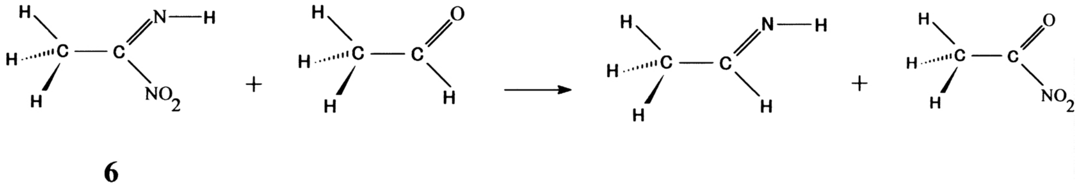
The carbon-carbon repulsion force at the center of structure **5a** is replaced by an attraction force in imine **5**, which is likely to make structure **5** more stable than enamine **5a**. At the same time the H2-C1 and H3-C1 repulsion forces in structure **5** are small because the charges on H1 and H2 are small (0.00981), which lowers their effect on the destabilizing imine **5**. Also the H1-C1 force in imine **5** is attractive.

Effect of NO_2 Substituent

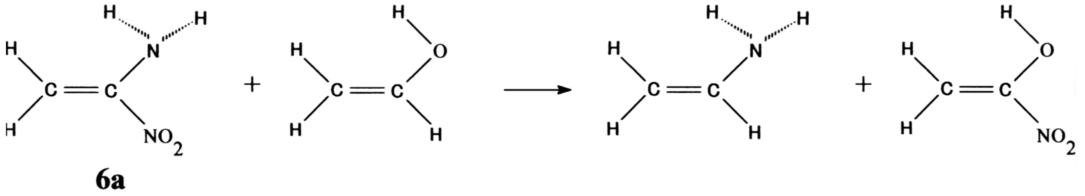
The structures **6** and **6a** below show the charge distribution on the atoms of the NO_2-substituted acetaldemine and vinylamine at the imine-carbon position. Close inspection of these charges shows that the positive charge on C1 (0.0710) of the imine **6** is re-



(9)



(10)



(11)

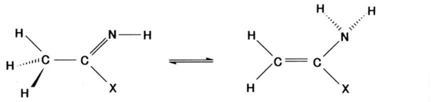
placed by a negative charge (−0.0376) on the same carbon of the enamine **6a**. This makes a number of repulsion forces in imine **6** to be replaced by attraction forces in enamine **6a**. This decrease in the number of repulsion forces and increase in attraction forces makes enamine **6a** more stable compared to imine **6**, which makes enamine **6a** preferable in the tautomerization reaction (9).

The isodesmic reactions for the NO_2-substituted imine (10) and enamine (11) give ΔH values of −1.702 and 2.554 kcal/mol respectively. The negative value means that the NO_2 substituent destabilizes the imine **6** and the positive value for enamine **6a** means that it is stabilized by the NO_2 substituent, so, these ΔH 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 NO_2 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, BH_2, CH_3 and CF_3” 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 NO_2 and NH_2 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

Table 4. Calculated orbital energies (HOMO and LUMO) of the substituted acetaldemine and the corresponding vinylamine at the imine-carbon position (eV), E = LUMO-HOMO.



	A **Imine (Acetylamine)**			**B** **Enamine (Vinylamine)**		
	LOMO	HUMO	E_g	LOMO	HUMO	E_g
H	−11.15	1.006	12.15	−9.171	1.216	10.39
F	−11.75	0.4936	12.24	−9.464	0.6209	10.085
CN	−12.03	−0.2091	11.82	−9.714	0.00824	9.722
NH2	−10.33	0.9918	10.33	−8.892	1.095	9.987
NO2	−11.58	−1.124	10.45	−10.57	−0.5482	10.02
BH2	−11.13	−0.2249	10.91	−9.379	−0.1269	9.506
CH3	−10.3	0.9918	11.33	−9.112	1.035	10.15
CF3	−12.16	−0.2706	10.89	−10.26	−0.1319	10.13

(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 α-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 α-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 α-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 α-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.

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