MINDO-Forces Study on the Keto-Enol Tautomerism of α-Substituted Acetaldehydes $XCH_2CH{=}O$ (X = H, F, OH, CN, NH_2, NO_2, CH_3, CF_3, OCH_3): Comparison with Acetyl Derivatives

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MINDO-Forces calculations with complete geometry optimization have been performed on α-substituted acetaldehydes $XCH_2CH{=}O$ and their enols (X = H, F, OH, CN, NH_2, NO_2, CH_3, CF_3, OCH_3). All substituents were found to decrease the stability of the acetaldehyde and mostly in the case of electron withdrawing capacity (e. g NO_2 and CF_3). This agrees with theoretical calculations, except in the case of F. The substituent effects on the stabilities in this study are compared with results obtained from our previous theoretical calculations on acetyl derivatives. Geometrical parameters, electron densities, and Gibbs free energies are reported.

Key words: α-Substituted Acetaldehyde; Keto – Enol Tautomerism; Acetyl Derivative.

1. Introduction

Recently [1], we have studied acetaldehyde and vinyl alcohol

$H_3C(CO)H \rightleftarrows H_2CCHOH$

and have shown that the calculated heat of formation of acetaldehyde ($\Delta H_f = -43.645$ kcal/mol) is less than that of vinyl alcohol ($\Delta H_f = -33.194$ kcal/mol), suggesting that ketone is more stable than its enol counterpart, i. e. ketone lies 10.451 kcal/mol below its enol counterpart, which agrees with other experimental and theoretical calculations [2, 3 – 8]. The stability of the ketone was also supported by thermodynamic calculations [1]. $\Delta G_r = 10.157$ kcal/mol was found, suggesting stabilization of ketone over its enol counterpart.

Also, it was found [1] that the effect of a substituent on the carbonyl carbon of the keto-enol tautomerism of acetaldehydes CH_3COX (X=H, OH, CH_3, NH_2, OH, F, CN, CF_3) depends on the electronic nature of the substituent. Substituents with electronic releasing capacity (e.g. F, OH, OCH_3) tend to stabilize the keto tautomers, while substituents with electron withdrawing capacity (e.g. NO_3, CF_3) tend to destabilize the keto tautomers. The results were confirmed by Gibbs free energy calculations, isodesmic reactions and orbital energies.

In the present paper we are interested in the substituent effects on the tautomerism of α-substituted acetaldehyde. We employ the MINDO-Forces method [9] to examine the substituent effects on the tautomerism of $XCH_2C(CO)H$, where X = H, F, OH, CN, NH_2, NO_2, CH_3, CF_3 and OCH_3.

2. Results and Discussion

2.1. Effect of Substituents

The semiemperical MINDO-Forces method [9] was used to calculate the optimized geometries of α-acetaldehydes and their enols. The results of the optimized geometrical parameters are given in Table 1. All substituents, in the case of acetaldehyde, cause a decrease in the bond angle C1C2H2 at which the substituent is attached, and an increase in the adjacent bond lengths (C1-C2 and C2-H2), except in the case of the substituent F, where the opposite holds [1, 9e – g]. Similarly, the effect of substituents on the geometrical parameters of vinyl alcohol holds.

2.2. Effect of F

The substituent F in compound **2** (Table 2) decreases the electron density on carbon C2 and increases it on the atoms C1 and H2, which suggests that F acts as electron releasing [1].

From the charge distribution of compound **2**, obtained from the electron density (Table 2), it fol-

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Table 1. Optimized geometrical parameters of α-substituted acetaldehydes and their enol counterparts.

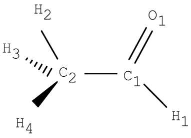
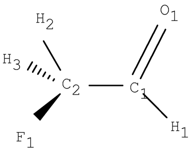
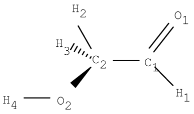
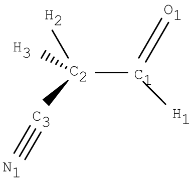
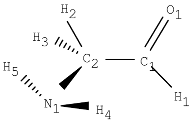
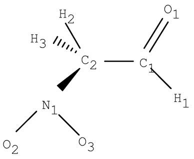
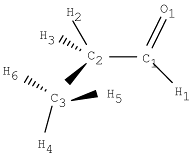
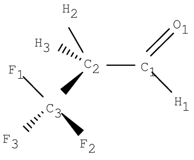
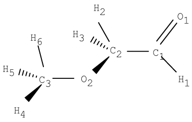
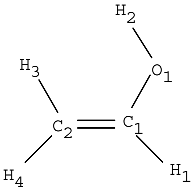
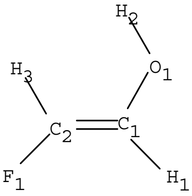
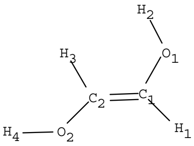
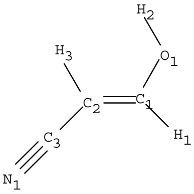
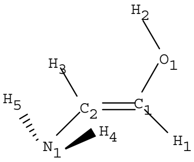
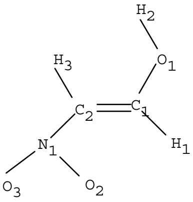
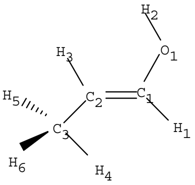
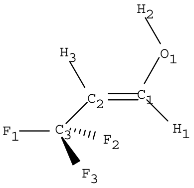
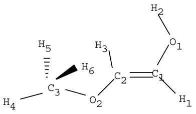
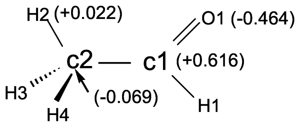
Molecule No. & Structure	Bond	Calculated Bond Length Å	Bond Angle	Calculated Angle Degree
1 	$O_1=C_1$	1.192	$<C_2C_1H_1$	111.5
	C_1-H_1	1.138	$<C_2C_1O_1$	127.3
	C_1-C_2	1.478	$<H_3C_2C_1$	111.6
	C_2-H_2	1.109	$<H_2C_2C_1$	114.4
2 	$O_1=C_1$	1.195	$<C_2C_1H_1$	112.3
	C_1-H_1	1.131	$<C_2C_1O_1$	125.4
	C_1-C_2	1.473	$<H_1C_1O_1$	122.2
	C_2-H_2	1.106	$<F_1C_2C_1$	99.0
	C_2-F_1	1.396	$<H_2C_2C_1$	118.9
3 	$O_1=C_1$	1.193	$<C_2C_1H_1$	114.8
	C_1-H_1	1.135	$<C_2C_1O_1$	124.1
	C_1-C_2	1.498	$<O_2C_2H_3$	113.0
	C_2-H_2	1.130	$<O_2C_2C_1$	109.4
	C_2-O_2	1.350	$<H_3C_2C_1$	111.5
	O_2-H_4	0.952	$<H_4O_2C_2$	110.4
4 	$O_1=C_1$	1.190	$<C_2C_1H_1$	115.1
	C_1-H_1	1.135	$<C_2C_1O_1$	122.9
	C_1-C_2	1.489	$<C_3C_2H_3$	110.8
	C_2-H_2	1.120	$<C_3C_2C_1$	112.7
	C_2-C_3	1.461	$<H_3C_2H_2$	104.1
	C_3-N_1	1.158	$<H_2C_2C_1$	109.6
5 	$O_1=C_1$	1.194	$<C_2C_1H_1$	113.1
	C_1-H_1	1.153	$<C_2C_1O_1$	124.9
	C_1-C_2	1.491	$<N_1C_2H_2$	115.2
	C_2-H_2	1.132	$<N_2C_2C_1$	112.4
	C_2-N_1	1.417	$<H_2C_2C_1$	109.3
	N_1-H_4	1.029	$<H_5N_1C_2$	111.8
6 	$O_1=C_2$	1.188	$<C_2C_1H_1$	115.3
	C_1-H_1	1.130	$<C_2C_1O_1$	122.7
	C_1-C_2	1.503	$<N_1C_2C_1$	114.0
	C_2-H_2	1.126	$<H_3C_2C_1$	108.5
	C_2-N_1	1.463	$<O_3N_1O_2$	132.0
	N_1-O_2	1.219	$<O_3N_1C_2$	113.1
7 	$O_1=C_1$	1.191	$<C_2C_1H_1$	111.8
	C_1-H_1	1.138	$<C_2C_1O_1$	126.9
	C_1-C_2	1.492	$<C_3C_2H_2$	109.3
	C_2-H_2	1.119	$<C_3C_2C_1$	115.9
	C_3-H_5	1.111	$<H_2C_2C_1$	110.3
8 	$O_1=C_1$	1.191	$<C_2C_1H_1$	112.7
	C_1-H_1	1.128	$<C_2C_1O_1$	123.3
	C_1-C_2	1.508	$<H_1C_1O_1$	123.9
	C_2-H_2	1.118	$<C_3C_2H_3$	109.2
	C_2-C_3	1.464	$<C_3C_2H_2$	107.8
	C_3-F_1	1.323	$<C_3C_2C_1$	113.5
			$<H_2C_2C_1$	111.6
			$<F_1C_3C_2$	112.4
				113.4
9 	$O_1=C_1$	1.196	$<C_2C_1H_1$	115.0
	C_1-H_1	1.134	$<C_2C_1O_1$	123.8
	C_1-C_2	1.493	$<O_2C_2H_2$	112.6
	C_2-H_2	1.131	$<O_2C_2C_1$	111.0
	C_2-O_2	1.356	$<H_3C_2H_2$	102.1
	C_3-H_4	1.118	$<H_2C_2C_1$	111.4
			$<H_6C_3H_4$	107.6
10 	O_1-C_1	1.321	$<H_2O_1C_1$	112.3
	O_1-H_2	0.953	$<C_2C_1H_1$	123.4
	C_1-H_1	1.117	$<C_2C_1O_1$	128.8
	$C_1=C_2$	1.328	$<H_1C_1O_1$	107.8
	C_2-H_3	1.097	$<H_3C_2C_1$	124.5
11 	O_1-C_1	1.328	$<H_2O_1C_1$	111.8
	O_1-H_2	0.953	$<C_2C_1H_1$	125.2
	C_1-H_1	1.110	$<H_1C_1O_1$	124.7
	$C_1=C_2$	1.235	$<F_1C_2H_3$	109.2
	C_2-H_3	1.095	$<F_1C_2C_1$	120.7
	C_2-F_1	1.374	$<H_3C_2C_1$	130.1
12 	O_1-C_1	1.332	$<H_2O_1C_1$	111.5
	O_1-H_2	0.953	$<C_2C_1H_1$	126.0
	C_1-H_1	1.110	$<C_2C_1O_1$	124.9
	$C_1=C_2$	1.342	$<O_2C_2H_3$	117.6
	C_2-H_3	1.116	$<O_2C_2C_1$	121.2
	C_2-O_2	1.331	$<H_3C_2C_1$	121.2
	O_2-H_4	0.951	$<H_4O_2C_2$	109.5
13 	O_1-C_1	1.314	$<H_2O_1C_1$	113.3
	O_1-H_2	0.953	$<C_2C_1H_1$	123.5
	C_1-H_1	1.117	$<C_2C_1O_1$	129.2
	$C_1=C_2$	1.343	$<H_1C_1O_1$	107.3
	C_2-H_3	1.108	$<C_3C_2H_3$	114.6
	C_2-C_3	1.436	$<C_3C_2C_1$	126.8
	C_3-N_1	1.160	$<H_3C_2C_1$	118.6
14 	O_1-C_1	1.323	$<H_2O_1C_1$	112.2
	O_1-H_2	0.953	$<C_2C_1H_1$	125.4
	C_1-H_1	1.116	$<C_2C_1O_1$	127.1
	$C_1=C_2$	1.340	$<N_1C_2C_1$	122.8
	C_2-H_3	1.121	$<H_3C_2C_1$	117.6
	C_2-N_1	1.393	$<H_5N_1H_4$	104.3
	N_1-H_4	1.033	$<H_4N_1C_2$	110.9
15 	O_1-C_1	1.301	$<H_2O_1C_1$	114.5
	O_1-H_2	0.954	$<C_2C_1H_1$	125.8
	C_1-H_1	1.117	$<C_2C_1O_1$	127.4
	$C_1=C_2$	1.359	$<N_1C_2H_3$	116.7
	C_2-H_3	1.114	$<N_1C_2C_1$	126.6
	C_2-N_1	1.409	$<O_3N_1O_2$	130.4
	N_1-O_2	1.229	$<O_2N_1C_2$	114.8

Table 1 (continued).

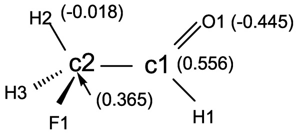
Molecule No. & Structure	Bond	Calculated Bond Length Å	Bond Angle	Calculated Angle Degree
16 	O_1-C_1	1.315	$<H_2O_1C_1$	113.2
	O_1-H_2	0.952	$<C_2C_1H_1$	123.5
	C_1-H_1	1.118	$<C_2C_1O_1$	129.2
	C_1=C_2	1.339	$<C_3C_2H_3$	114.4
	C_2-H_3	1.109	$<C_3C_2C_1$	127.4
	C_2-C_3	1.468	$<H_3C_2C_1$	118.3
	C_3-H_4	1.113	$<H_6C_3H_5$	106.1
17 	O_1-C_1	1.297	$<H_2O_1C_1$	113.8
	O_1-H_2	0.953	$<C_2C_1H_1$	123.9
	C_1-H_1	1.113	$<C_2C_1O_1$	126.1
	C_1=C_2	1.357	$<C_3C_2H_3$	115.0
	C_2-H_3	1.103	$<C_3C_2C_1$	125.3
	C_2-C_3	1.424	$<H_3C_2C_1$	119.8
	C_3-F_1	1.329	$<F_3C_3F_1$	111.2
18 	O_1-C_1		$<H_2O_1C_1$	
	O_1-H_2		$<C_2C_1H_1$	
	C_1-H_1	1.329 0.952	$<C_2C_1O_1$	112.5 126.5
	C_1=C_2	1.111 1.357	$<O_2C_2H_3$	124.5 119.0
	C_2-H_3	1.137 1.299	$<O_2C_2C_1$	123.8 117.2
	C_2-O_2	1.346 1.118	$<H_3C_2C_1$	117.8 107.9
	O_2-C_3		$<C_3O_2C_2$	
	C_3-H_4		$<H_4C_3O_2$	

lows that the carbonyl group will be destabilized due to electrostatic repulsion between C1 and C2 (which both carry positive charges), compared to the parent **1** [10, 11]. This means that the ketone **2** will be destabilized, and this facilitates enol formation.

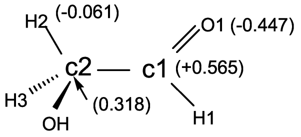
This is confirmed by calculation of the Gibbs energy (ΔG_r) for F substituted keto-enol (Table 3), which shows that ΔG_r ($\Delta G_r = 9.727$ kcal/mol) is less than that of the parent ($\Delta G_r = 10.157$ kcal/mol).



1



2



3

2.3. Effect of the OH Group

The OH substituent in compound **3** also behaves as an electron releasing group, which decreases the electron density at C2 (the atom carrying the substituent) and increases it at the adjacent atoms C1 and H2 (Table 2) when compared with the parent **1**.

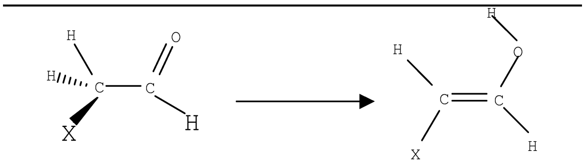
From the charge distribution of compound **3** it follows that the carbonyl group will be destabilized due to electrostatic repulsion between C1 and C2 (which both carry positive charges) [10–13]. This means that the ketone **3** will be destabilized, and this facilitates enol formation.

This is supported by thermodynamic calculation of ΔG_r (Table 3) for an OH substituted keto-enol system,

Table 2. Calculated electron densities of α-substituted acetaldehydes and their enol counterparts (see Table 1 for numbering).

Comp.#	C_1	C_2	C_3	H_1	H_2	H_3	H_4	H_5	H_6	N	O_1	O_2	O_3	F_1	F_2	F_3
1	3.384	4.069		1.139	0.978	0.983	0.983				6.464					
2	3.444	3.635		1.090	1.018	1.037					6.445			7.331		
3	3.435	3.682		1.107	1.061	1.078	0.743				6.447	6.447				
4	3.397	4.033	3.910	1.123	0.977	0.986				5.111	6.463					
5	3.416	3.914		1.128	1.045	1.018	0.931	0.933		5.157	6.458					
6	3.382	4.252		1.085	0.924	0.929				3.885	6.434	6.541	6.569			
7	3.395	4.037	3.916	1.139	0.994	1.002	1.023	1.017	1.015		6.463					
8	3.346	4.234	2.662	1.082	0.929	0.936					6.453			7.432	7.442	7.484
9	3.437	3.690	3.580	1.107	1.056	1.073	1.039	1.081	1.083		6.448	6.405				
10	3.632	4.193		1.062	0.748	0.959	0.963				6.442					
11	3.796	3.778		0.962	0.756	1.005					6.408			7.294		
12	3.811	3.874		0.975	0.762	1.045	0.752				6.412	6.410				
13	3.602	4.218	3.853	1.015	0.747	0.971				5.171	6.424					
14	3.683	4.088		1.010	0.753	1.033	0.951	0.951		5.108	6.424					
15	3.473	4.469		0.988	0.732	0.905				3.824	6.405	6.617	6.587			
16	3.627	4.219	3.848	1.019	0.751	0.983	1.047	1.039	1.039		6.428					
17	3.487	4.453	2.623	0.987	0.730	0.908					6.408			7.451	7.476	7.476
18	3.802	3.843	3.578	0.975	0.759	1.040	1.048	1.089	1.089		6.416	6.361				

Table 3. Gibbs free energies of keto-enol tautomerism of α-substituted acetaldehydes and their enol counterparts.



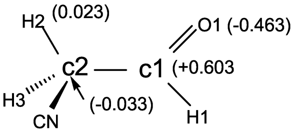
X	ΔG (kcal/mol)	X	ΔG (kcal/mol)
H	10.157 [1]	F	9.727
OH	1.762	CN	−1.460
NO_2	−12.880	NH_2	0.947
CH_3	0.602	CF_3	−5.392
OCH_3	2.225		

which shows that ΔG_r ($\Delta G_r = 1.762$ kcal/mol) is less than that of the parent ($\Delta G_r = 10.157$ kcal/mol).

The stabilization effect of the OH group on both the ketone **3** and its enol counterpart **12** (Table 4), is often confirmed by using isodesmic reactions [12–16]. A negative value indicates less stability, and a positive value more stability. It can be seen that the ΔH_r values of the isodesmic reactions are negative for both **3** ($\Delta H_r = -3.501$ kcal/mol) and **12** ($\Delta H_r = -4.167$ kcal/mol). From these values, the compounds **3** and **12** are destabilized by OH, but **3** is more stabilized than **12**. This agrees with the present thermodynamic calculation, which predict a small shift in equilibrium to the ketone side. This also, agrees with ab initio calculations [2], in which the OH substituent was found to lower the energy barrier of ketonization.

2.4. Effect of CN Group

The CN substituent in compound **4** decreases slightly the electron density on carbon C2, increases it on the adjacent carbon C1 and almost does no change it on H2 (Table 2). When compared with the parent **1**, it behaves as weakly electron releasing when attached to a system with low electron density. But, when substituted on carbonyl carbon (system with high electron density) [1], it behaves as weakly electron with drawing. In other words, the CN group behaves according to the electron demand [12, 17–22], i. e. it shows amphielectronic behavior.



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From the charge distribution of compound **4** follows that H2 carries positive charge (acidic), and hence facilitates enol formation (enol **13**). This is an expected result due to the stabilization of the enol **13** by delocalization of the C=C electrons [2]. I.e the $\pi*$ orbital of the CN substituent accepting the π electron density from the C=C double bond, the “pull and push” effect becomes operative, leading to a further stabilization of the enol **13**, as mentioned in previous work [2].

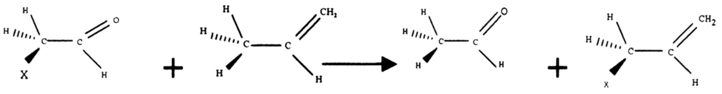
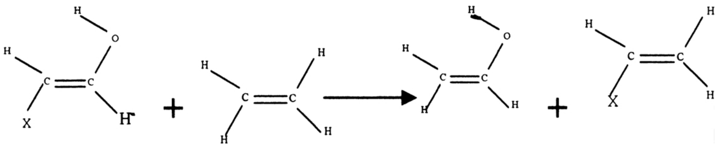
This result is confirmed by thermodynamic calculations of ΔG_r (Table 3), which gave $\Delta G_r = -1.460$ kcal/mol, suggesting a shift to the enol side.

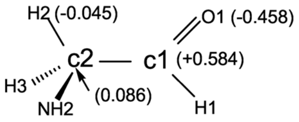
This is supported by the stabilization effect of the CN group on both the ketone and its enol counterpart (Table 4), using the isodesmic reaction. It can be seen that $\Delta H_r = -0.249$ kcal/mol for ketone **4**, while $\Delta H_r = 4.323$ kcal/mol for enol **13**. This indicates that CN stabilizes enol **13**, and the equilibrium shift to the enol side.

2.5. Effect of the NH_2 Group

The substituent NH_2 behaves as an electron releasing group in compound **5** (Table 2); this is reflected by

Table 4. Evaluation of substituent effects on keto-enol tautomerism of α-substituted acetaldehydes and their enol counterparts via isodesmic reactions (ΔH_f in kcal/mol).

Isodesmic Reaction	OH	CN	NO_2	NH_2	CH_3	CF_3	OCH_3
	−3.501	−0.249	−1.401	1.260	0.222	1.890	−0.880
	−4.167	4.323	7.306	0.781	0.122	7.470	−4.374



5

a decrease in the electron density at C2 and an increase at the adjacent atoms C1 and H2, when compared with the parent **1**.

From the charge distribution of **5** it follows that the carbonyl group will be destabilized due to electrostatic repulsion between C1 and C2, which both carry positive charges [10, 11]. This means that the ketone **5** will be destabilized and this facilitates enol formation.

This is confirmed by the thermodynamic calculation (Table 3), which shows that $\Delta G_{\mathrm{r}} = 0.947$ kcal/mol, while that of the parent **1** is $\Delta G_{\mathrm{r}} = 10.157$ kcal/mol).

This result is supported by isodesmic reactions (Table 4). It can be seen that the ΔH_{r} of **5** and **14** are positive ($\Delta H_{\mathrm{r}} = 1.260$ kcal/mol for **5** and $\Delta H_{\mathrm{r}} = 0.781$ kcal/mol for **14**). From these values follows that the NH_2 group stabilizes both compounds, but **5** then **14**. This explains a slight shift to the ketone side.

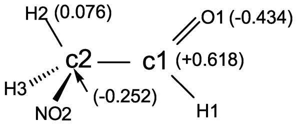
2.6. Effect of the NO_2 Group

The substituent NO_2 behaves as a strong electron withdrawing group in compound **6** (Table 2); this is reflected by an increase in the electron density at C2 and a decrease at the adjacent atoms C1 and H2, when compared with the parent **1**.

The charge distribution of compound **6** shows that H2 carries more positive charge (+0.076) than the parent **1** (+0.022), and facilitates the enol formation.

This result is confirmed by thermodynamic calculations (Table 3) of $\Delta G_{\mathrm{r}} = -12.880$ kcal/mol), which indicates that the reaction is spontaneous and the equilibrium shifts to the enol side.

This is supported by the isodesmic reactions (Table 4). It can be seen that the $\Delta H_{\mathrm{r}} = -1.401$ kcal/mol for ketone **6**, while $\Delta H_{\mathrm{r}} = 7.306$ kcal/mol for enol **15**.This indicates that NO_2 stabilizes enol **15**, and the equilibrium shifts to the enol side.



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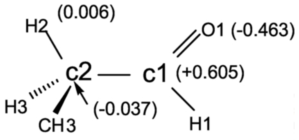


7

2.7. Effect of the CH_3 Group

The substituent CH_3 behaves as a weak electron releasing group in **7** (Table 2), when compared with the parent **1**.

From the charge distributions **7** it follows that the electronic attraction between C1 and C2 is less than that of the parent **1**, suggesting a destabilization of **7** compared to the parent **1**.

This is supported by calculation of Gibbs energy ΔG_{r} (Table 3), which shows that $\Delta G_{\mathrm{r}} = 0.602$ kcal/mol). This is less than that of the parent ($\Delta G_{\mathrm{r}} = 10.157$ kcal/mol), suggesting a destabilization of ketone **7**. The reaction is slightly nonspontaneous.

This result is confirmed by the isodesmic reactions (Table 4). ΔH_{r} of **7** and **16** is positive ($\Delta H_{\mathrm{r}} = 0.222$ kcal/mol for **7**, while $\Delta H_{\mathrm{r}} = 0.122$ kcal/mol for **16**). From these values follows that the CH_3 group stabilizes **7** and **16**, but **7** more, which explains the slight shift in the equilibrium to ketone side.

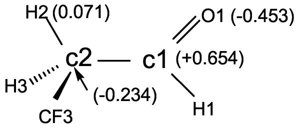
2.8. Effect of the CF_3 Group

The substituent CF_3 behaves as a strong electron withdrawing group in **8** (Table 2); this is reflected by an increase in the electron density at C2 and a decrease at the adjacent atoms C1 and H2, when compared with the parent **1**.

The charge distribution of **8** shows that H2 carries more positive charge (+0.071) than the parent **1** (+0.022), and hence facilitates enol formation.

This is supported by thermodynamic calculations (Table 3), which shows that ΔG_{r} is negative ($\Delta G_{\mathrm{r}} = -5.392$ kcal/mol). This indicates that the reaction is spontaneous and shifts to the enol side.

This is also confirmed by the isodesmic reactions (Table 4). It can be seen that ΔH_{r} of **8** and **17** is positive



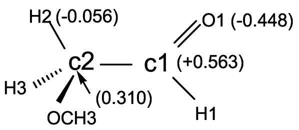
8

($\Delta H_r = 1.890$ kcal/mol for **8**, $\Delta H_r = 7.470$ kcal/mol for **17**). From these values follows that the CF_3 group stabilizes **8** and **17**, but **17** more, which explain the shift in equilibrium to the enol side. This suggest that CF_3 destabilizes the ketone.

2.9. Effect of the OCH_3 Group

The substituent OCH_3 behaves as strong electron releasing group in **9** (Table 2); this is reflected by a decrease in the electron density at C2 and an increase at the adjacent atoms C1 and H2, when compared with the parent **1**.

From the charge distributions of compound **9** it follows that the carbonyl group will be destabilized due to electrostatic repulsion between C1 and C2 (which both carry positive charges) [10, 11]. This means that the ketone **9** will be destabilized, and this facilitates enol formation.



9

This is supported by thermodynamic calculations (Table 3) which show that $\Delta G_r = 2.225$ kcal/mol, which is less than that of the parent **1** ($\Delta G_r = 10.157$ kcal/mol), suggesting a destabilization of **9** by the OCH_3 group compared to the parent **1**. The reaction is still non-spontaneous.

This result is also confirmed by the isodesmic reactions (Table 4). ΔH_r of **9** and **18** are negative ($\Delta H_r = -0.880$ kcal/mol for **9**, $\Delta H_r = -4.374$ kcal/mol **18**). From these values follows that OCH_3 destabilizes both **9** and **18** but **18** more, which explains the shift to the ketone side.

ΔG_r of all substituents is less than that of the parent **1** (Table 3), suggesting a destabilization of the ketone, and mostly by the electron withdrawing capacity (e. g. NO_2, CF_3).

Table 5. Comparison of the calculated Gibbs free energies (ΔG) in kcal/mol of α-substituted acetaldehydes and their enol counterparts with that of acetaldehydes derivatives.

	α-Substituted acetaldehydes	Acetaldehyde Derivatives [1]
H	10.157	10.157
F	9.727	24.056
OH	1.762	17.497
CN	−1.460	0.895
NO_2	−12.880	3.709
NH_2	0.947	5.974
CH_3	0.602	4.423
CF_3	−5.392	2.957
OC_3	2.225	17.493

The comparison between the calculated ΔG_r of α-substituted acetaldehydes and that of acetyl derivatives (Table 5) shows that π donating substituents (X=F, OH, OCH_3) increase the stability of the keto form in the case of the acetyl derivatives, where the substituents donate the π electron density directly to the adjacent carbonyl $\pi*$ orbital. This readily stabilizes the keto form and leads to a significant increase in their stability relative to the enol form, which agrees with theoretical calculations [2]. Also, the calculated ΔG_r of α-substituted acetaldehydes are poorly correlated with the corresponding acetyl derivatives (Table 5), which agrees with the theoretical calculations [2].

3. Conclusion

All substituents, in the case of α-substituted acetaldehydes, are found to decrease the stability of acetaldehyde, and mostly in the case of electron withdrawing capacity (e.g. NO_2, CF_3) compared to the parent **1**. The substituent CN group shows amphielectronic behavior. The calculated Gibbs free energies of α-substituted acetaldehydes are poorly correlated with corresponding acetyl derivatives. These results were confirmed by Gibbs free energy calculations and isodesmic reactions.

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