MINDO-Forces Study on Substituted Nitromethane $\rightleftharpoons$ *aci*-Nitromethane Tautomerism

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Z. Naturforsch. **60a,** 47 – 53 (2005); received October 3, 2004

MINDO-Forces calculations with complete geometry optimization have been performed on nitromethane, *aci*-nitromethane and X-substituted nitromethane and *aci*-nitromethane (X = F, OH, NH_2, CH_3, CN, CF_3, NO_2, CHO). It is found that nitromethane is more stable than *aci*-nitromethane by 9.337 kcal/mol. This agrees with theoretical calculations. Thermodynamically, substituted *aci*-nitro tautomers are more stable than the corresponding nitromethane, except in case of the substituent F. Geometrical parameters, heats of formation, electron densities, Gibbs free energies and isodesmic reactions are reported.

Key words: Nitromethane; *aci*-Nitromethane; Tautomerism.

1. Introduction

Recently we have studied the keto-enol tautomerism in three-membered [1], four-membered [2] and five-membered rings [3], and have shown by thermodynamic calculations that the tautomerism is enhanced in going from three-membered to five-membered rings. Also, a study of the acetaldehyde-vinyl tautomerism [4] did show that ΔG is about 10.157 kcal/mol, suggesting an extra stabilization of acetaldehyde over vinyl alcohol.

We have now extended our work on nitro $\rightleftharpoons$ *aci*-nitro tautomerism. The *aci*-nitro compounds contain –N(=O)-OH [5]. They are thermodynamically unfavorable tautomers of nitroalkanes [5 – 7]. Still, nitronic acids play an important role as reactive intermediates in many redox, photochemical, and pyrolysis reaction [5 – 9], and in syntheses such as the Nef and Victor Meyer reactions [10].

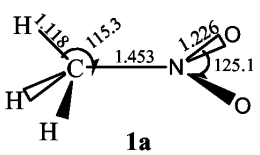
Lammertsma and Prasad [6a] have shown an energy difference between the nitromethane and *aci*-nitromethane tautomers amounting to 14.1 kcal/mol in favor of nitromethane. This energy difference is closely related to acetaldehyde and vinyl alcohol tautomers (10.451 kcal/mol) [4a], which may suggest that substitution of nitro compounds can lead to enhanced tautomerism as in the case of many keto derivatives [5]. Therefore this paper aims to give more theoretical insight to the effect of substituents such as F, OH, NH_2, CH_3, CN, CF_3, NO_2, and CHO on the nitromethane and *aci*-nitromethane tautomers using the MINDO-Forces method [11], whereby the molecular energy of the tautomers obtained from the semiempirical MINDO/3 MO method [12] was completely minimized by the Murtagh-Sargent technique [13]. The energy of the derivatives was calculated according to Pulay's method [14]. The program allows the variation of the β-parameter with a consistent geometrical change. A full description of the program and its applications is given in [11a].

2. Results and Discussion

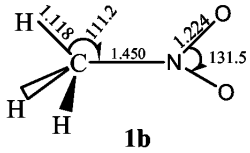
We discuss first the energies of nitromethane and *aci*-nitromethane, followed by the effect of substitutions.

2.1. Parent Nitromethane and aci-Nitromethane

Nitromethane, CH_3NO_2. The staggered (**1a**) and eclipsed (**1b**) conformations



1a

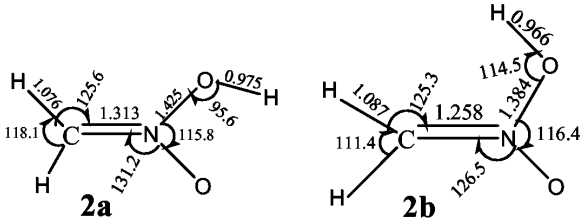


1b

of nitromethane were considered. The calculated heats

of formation of **1a** and **1b** are −10.479 kcal/mol and −10.475 kcal/mol, suggesting that the two orientations are very close in energy. The rotational barrier is 4 cal/mol, agreeing almost with the microwave study (6 cal/mol) [15] and with the theoretical calculations [16]. The microwave spectroscopy [17] supports **1b**, and the neutron diffraction data at 15 K [18] support **1a**.

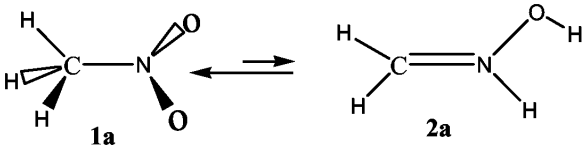
aci-Nitromethane, CH_2=NO_2H. The *cis* (**2a**) and *trans* (**2b**) conformations



of *aci*-nitromethane were considered. The forms **2a** and **2b** differ in the orientation of the OH relative to the NO unit.

The calculated heat of formation of **2a** (−1.142 kcal/mol) is smaller than that of **2b** (0.922 kcal/mol), suggesting that **2a** is preferred. This agrees with theoretical calculations [6a].

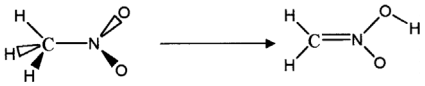
Tautomerism. The energy difference between nitromethane (**1a**) and *aci*-nitromethane (**2a**) (ΔE = 9.337 kcal/mol) agrees almost with that of the G1 level (14.1 kcal/mol) [6a] in favor of nitromethane.



This energy difference ΔE is sensitive to the method employed, as illustrated by the larger ΔE of 22.9 kcal/mol at MP2/6-31G* (ZPE uncorrected) and 19.1 kcal/mol at MP4/6-311++G**+ scaled ZPE [6a].

The stability of nitromethane is supported by thermodynamic calculations (Table 1), which show that the change in Gibbs free energy (ΔG_r) of nitromethane and *aci*-nitromethane is 6.332 kcal/mol. This suggests that nitromethane is more stable than *aci*-nitromethane. This ΔG_r will be taken as reference for comparison between X-substituted nitromethane and *aci*-nitromethane, in order to investigate the relative stability of substituted nitromethane ⇌ *aci*-nitromethane tautomerism.

Table 1. Gibbs free energies of substituted nitromethane ⇌ *aci*-nitromethane tautomerism.

X	 ΔG [kcal/mol]
H	6.332
F	0.020
OH	−1.984
NH_2	−12.546
CH_3	−6.348
CN	−8.901
CF_3	−12.183
NO_2	−19.614
CHO	−11.366

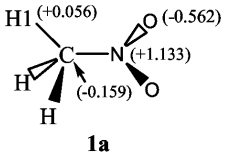
2.2. Effect of Substituents

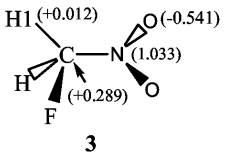
The semiempirical MINDO-Forces method [11] was used to calculate the optimized geometries of substituted nitromethane and *aci*-nitromethane. The results of the optimized geometrical parameters are given in Figure 1. All substituents cause changes in the geometrical parameters compared to the parent (without substitution), and mostly where the substituent is attached.

Effect of F

The substituent F in compound **3** (Fig. 1) decreases the electron density on the C atom and increases it on the atoms N and H1, which suggests that F acts as electron releasing [1–4].

From the charge distribution of compound **3** obtained from the electron density (Fig. 1) it follows that the NO_2 group is destabilized due to electrostatic repulsion between C and N (which both carry positive charges), compared to the parent **1a** [1–4, 19, 20]. This means that **3** will be destabilized and this facilitates the *aci*-nitro formation:





This is confirmed by calculation of the Gibbs energy (ΔG_r) for F substituted nitro ⇌ *aci*-nitro (Table 1),

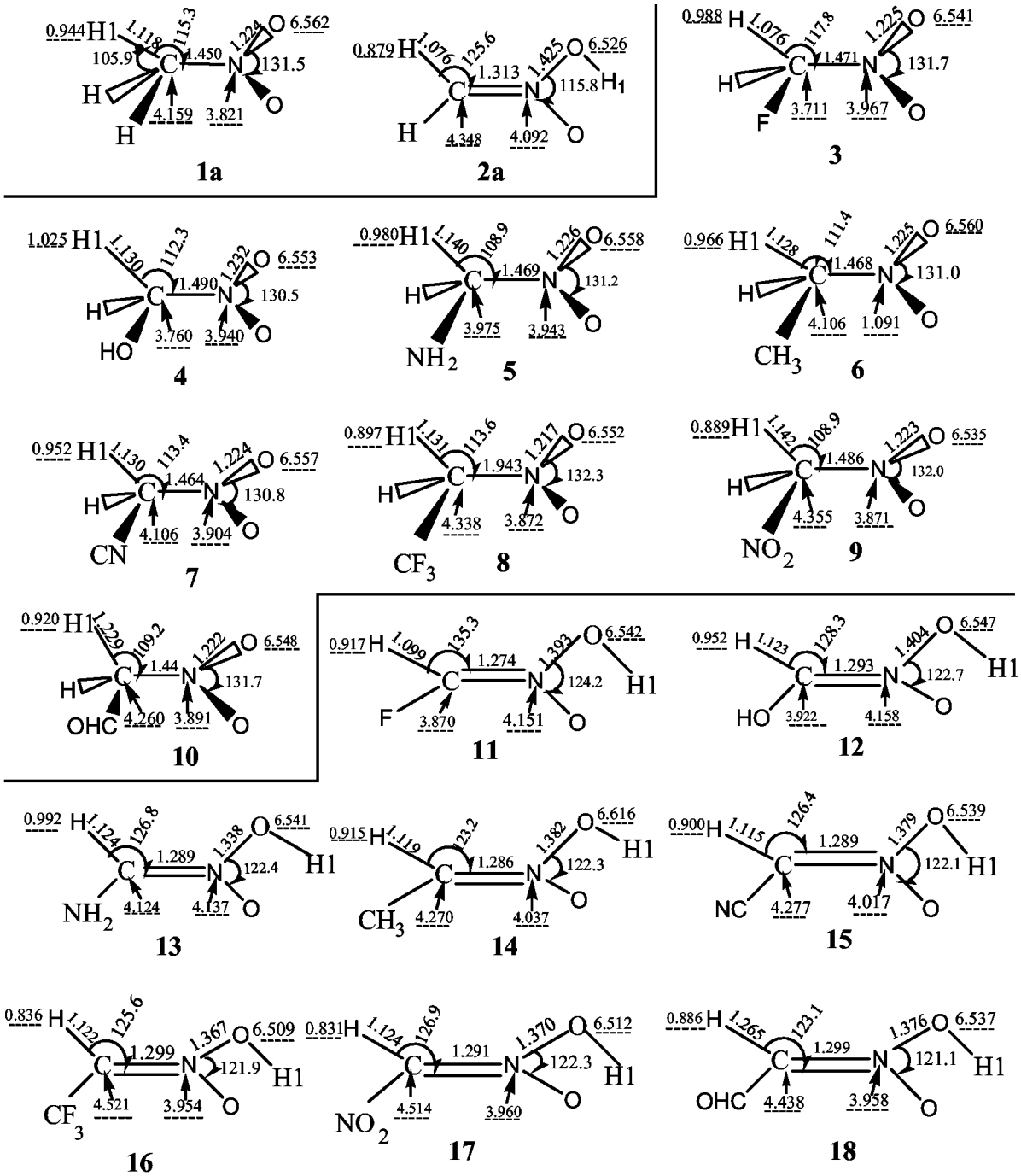
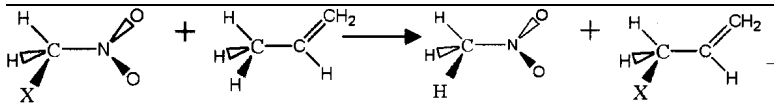
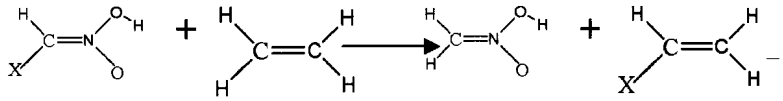


Fig. 1. Structures of substituted nitromethane and *aci*-nitromethane as obtained from MINDO-Forces calculations. Bond lengths are in Ångstroms and angles in degrees. Electron densities are underlined.

Table 2. Evaluation of substituent effects on substituted nitromethane ⇌ *aci*-nitromethane tautomerism via isodesmic reaction (ΔH_f in kcal/mol).

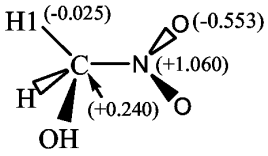
Isodesmic Reaction	X						
	OH	NH_2	CH_3	CN	CF_3	NO_2	CHO
	−6.683	3.297	3.991	8.486	0.962	1.005	1.913
	−1.448	11.113	12.074	16.259	12.914	13.089	14.501

which shows that ΔG_r ($\Delta G_r = 0.020$ kcal/mol) is less than that of the parent ($\Delta G_r = 6.332$ kcal/mol), suggesting a destabilization of **3**.

Effect of the OH group

The OH substituent in compound **4** also behaves as an electron releasing group, which decreases the electron density at C atom (the atom carrying the substituent) and increases it at the adjacent atoms N and H1 (Fig. 1) when compared with the parent **1a**.

From the charge distribution of compound **4** it follows that the NO_2 group will be destabilized due to electrostatic repulsion between C and N (which both carry positive charges) [1–4, 19, 20]. This means that **4** will be destabilized, and this facilitates the *aci*-nitro formation.



4

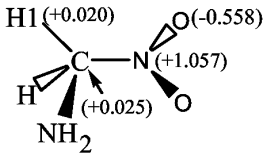
This is supported by a thermodynamic calculation of ΔG_r (Table 1) for OH substituted nitro ⇌ *aci*-nitro which shows that ΔG_r ($\Delta G_r = -1.984$ kcal/mol) is smaller than that of the parent ($\Delta G_r = 6.332$ kcal/mol).

The stabilization effect of the OH group on both **4** and its *aci*-nitro **12** (Table 2), is often confirmed by using isodesmic reactions [1–4, 21, 22]. 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 **4** ($\Delta H_r = -3.683$ kcal/mol) and **12** ($\Delta H_r = -1.448$ kcal/mol). From these values, compounds **4** and **12** are destabilized by OH, but **12** (more positive) is more stabilized than **4**. This agrees with the present thermodynamic calculation, which predicts a small shift in equilibrium to the *aci*-nitro side.

Effect of the NH_2 group

The substituent NH_2 behaves as an electron releasing group in compound **5** (Fig. 1); this is reflected by a decrease in the electron density at the C atom and an increase at the adjacent atoms N and H1, when compared with the parent **1a**.

From the charge distributions of **5** it follows that the NO_2 group will be destabilized due to electrostatic repulsion between C and N (which both carry positive charges) [1–4, 19, 20]. This means that **5** will be destabilized, and this facilitates the *aci*-nitro formation.



5

This is confirmed by a thermodynamic calculation (Table 1) of ΔG_r, which shows that ΔG_r ($\Delta G_r = -12.546$ kcal/mol) is less than that of the parent **1a** ($\Delta G_r = 6.332$ kcal/mol).

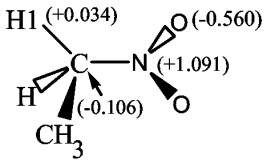
This result is supported by isodesmic reactions (Table 2): ΔH_r of **5** and **13** are positive ($\Delta H_r = 3.297$ kcal/mol for **5**, while $\Delta H_r = 11.113$ kcal/mol for **13**). From these values follows that the NH_2 group stabilizes both compounds, but **13** more. This explains the shift in equilibrium to the *aci*-nitro side.

Effect of the CH_3 group

The substituent CH_3 behaves as a weak electron releasing group in **6** (Fig. 1), when compared with the parent **1a**.

From the charge distributions of **6** follows that the electrostatic attraction between the atoms C and N is

less than in the parent **1a**, suggesting a destabilization of **6** compared to the parent **1a**.



6

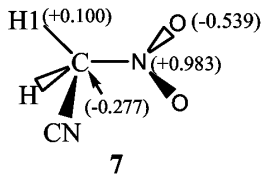
This is supported by calculation of the Gibbs energy ΔG_r (Table 1), which shows that ΔG_r ($\Delta G_r = -6.348$ kcal/mol) is less than that of the parent ($\Delta G_r = 6.332$ kcal/mol), suggesting a destabilization of **6**.

This result is confirmed by the isodesmic reactions (Table 2): ΔH_r of **6** and **14** is positive ($\Delta H_r = 3.991$ kcal/mol for **6**, while $\Delta H_r = 12.074$ kcal/mol for **14**). From these values follows that the CH_3 group stabilizes **6** and **14**, but **14** more, which explains the shift in equilibrium to the *aci*-nitro side.

Effect of the CN group

The CN substituent in compound **7** (Fig. 1) decreases slightly the electron density at the carbon atom, increases it at the adjacent nitrogen atom and almost does not change it at H1 (Fig. 1), when compared with the parent **1a**, *i. e.* behaves as weakly electron releasing when attached to a system with low electron density. But when substituted on a carbonyl carbon (system with high electron density) [4a], it behaves as weakly electron withdrawing. In other words, the CN group behaves according to electron demand [3, 23–28], *i. e.* it shows amphielectronic behavior.

The charge distribution of compound **7** shows that H1 carries more positive charge (acidic) than the parent **1a** (+0.056), and hence facilitates the *aci*-nitro **15** formation (Figure 1). This is an expected result due to the stabilization of the *aci*-nitro **15** by delocalization of the C=C electrons [29], *i. e.* the Π^* orbital of the CN substituent accepts the Π electron density from the C=C double bond, the "pull and push" effect becomes operative, leading to a further stabilization of the *aci*-nitro **15**, as mentioned in [29].



7

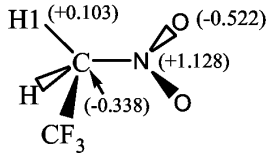
This result is confirmed by thermodynamic calculation of ΔG_r (Table 1), which shows a negative value ($\Delta G_r = -8.901$ kcal/mol), suggesting a shift to the *aci*-nitro side.

This is supported by the stabilization effect of the CN group on both **7** and **15** (Table 2). It can be seen that $\Delta H_r = 8.486$ kcal/mol for **7**, while $\Delta H_r = 16.259$ kcal/mol for **15**. This indicates that the CN group stabilizes **15**, and the equilibrium shifts to the *aci*-nitro side.

Effect of the CF_3 group

The substituent CF_3 behaves as a strong electron withdrawing group in **8** (Fig. 1); this is reflected by an increase in the electron density at the C atom and a decrease at the adjacent atoms N and H1, when compared with the parent **1a**.

The charge distribution of **8** shows that H1 carries more positive charge (+0.103) than the parent **1a** (+0.056), and hence facilitates the *aci*-nitro formation.



8

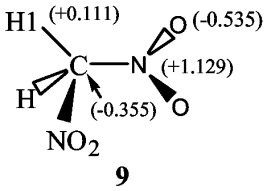
This is supported by thermodynamic calculation (Table 1), which shows that ΔG_r is negative ($\Delta G_r = -12.183$ kcal/mol). This indicates that the reaction is spontaneous and shifts to the *aci*-nitro side.

This is also confirmed by the isodesmic reactions (Table 2). It can be seen that ΔH_r of **8** and **16** is positive ($\Delta H_r = 0.962$ kcal/mol for **8**, $\Delta H_r = 12.914$ kcal/mol for **16**). From these values follows that the CF_3 group stabilizes **8** and **16**, but **16** more, which explains the shift in equilibrium to the *aci*-nitro side. This suggests that CF_3 destabilizes **8**.

Effect of the NO_2 group

The substituent NO_2 behaves as a strong electron withdrawing group in compound **9** (Fig. 1); this is reflected by an increase in the electron density at the C atom and a decrease at the adjacent atoms N and H1, when compared with the parent **1a**.

The charge distribution of compound **9** shows that H1 carries more positive charge (+0.111) than the parent **1a** (+0.056), and hence facilitates the *aci*-nitro formation.



9

This result is confirmed by thermodynamic calculation (Table 1) of ΔG_r ($\Delta G_r = -19.614$ kcal/mol). This indicates that the reaction is spontaneous and the equilibrium shifts to the *aci*-nitro side.

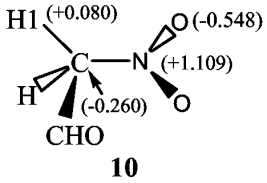
This result is also supported by isodesmic reactions (Table 2). It can be seen that $\Delta H_r = 1.005$ kcal/mol for **9**, while $\Delta H_r = 13.089$ kcal/mol for **17**. This indicates that the NO_2 group stabilizes **17**, and the equilibrium shifts to the *aci*-nitro side.

Effect of the CHO group

The substituent CHO behaves as strong electron withdrawing group in **10** (Fig. 1); this is reflected by an increase in the electron density at the C atom and a decrease at the adjacent atoms N and H1, when compared with the parent **1a**.

The charge distribution of **10** shows that H1 carries more positive charge (+0.080) than the parent **1a** (+0.056), and hence facilitates the *aci*-nitro formation.

This is supported by thermodynamic calculation (Table 1), which shows that ΔG_r ($\Delta G_r = -11.366$ kcal/mol) is less than that of the parent **1a** ($\Delta G_r = 6.332$ kcal/mol), suggesting a destabilization of **10** by the CHO group compared to the parent **1a**.



10

This result is also confirmed by the isodesmic reactions (Table 2): ΔH_r of **10** and **18** is positive ($\Delta H_r = 1.913$ kcal/mol for **10**, $\Delta H_r = 14.501$ kcal/mol for textbf18). From these values follows that the CHO group stabilizes both **10** and **18**, but **18** more. This explains the shift in equilibrium to the *aci*-nitro side.

All substituents have ΔG_r less than that of the parent **1a** (Table 1), suggesting a destabilization of the nitromethane by the substituents, in a similar way to that found in the case of α-substituted acetaldehydes [4a]. Thermodynamically, *aci*-nitro tautomers are more stable than nitro tautomers, except in the case of F as substituent (Table 1).

3. Conclusion

It can be concluded that nitromethane is more stable than *aci*-nitromethane. All substituents are found to decrease the stability of nitromethane. These results were confirmed by Gibbs free energy calculations and isodesmic reactions.

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