

# Stabilization studies 4-aminoantipyrene by quantum calculations

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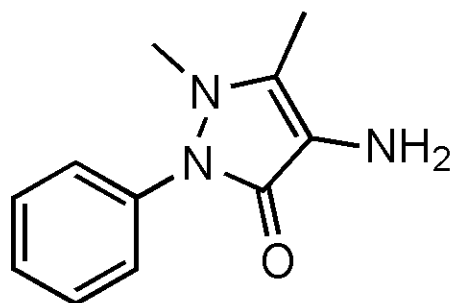
## Abstract;

In this study, Stabilization studies has been studied by using of AM1 and MNDO. The calculations methods used with complete geometry optimization have been performed on 4-aminoantipyrene. Thermodynamically with theoretical calculations. Geometrical parameters, heats of formation, electron densities and orbital energies (HOMO-LUMO) are also studied.

## Introduction

Tautomerism refers to the equilibrium between two different structures of the same compound. It is a phototropic rearrangement in which a hydrogen at the  $\alpha$ - position to a carbon-heteroatom double bond migrates to the heteroatom and forms a C-C double bond [1 – 4].

Processes involving proton transfer between interconversion tautomers are of fundamental importance in synthetic and mechanistic chemistry. This includes the keto-enol, imine-enamine, oxime-nitroso, hydrazoazo, and phenol-keto isomerization [5].



## Computational studies

### *AM1 and MNDO*

The molecular representation sketch of the reference compound was plotted using ChemBioOffice 2010 software. All the quantum chemical calculations were performed using the **AM1** and **MNDO** methodology, while the molecular atomic charges were calculated via the Mulliken Charges.

## Results and Discussion

### *Computational Studies*

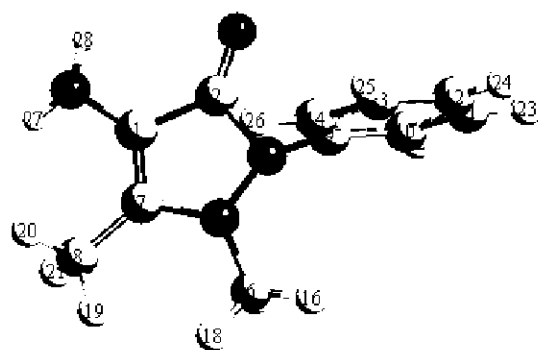
#### *Mulliken Charges*

An earlier study had shown that the atomic charges were affected by the presence of the substituent of the rings. With the aid of a reference model, 4-

aminoantipyrene with optimized geometries and 3D geometrical structures are given in Figure 1. The data showed that the highest atomic charge (Table 1) by using of AM1 and MNDO was  $[O_3 -0.304]$ ,  $[O_3 -0.3117]$  respectively, followed by the next charge value at  $[N_{15} -0.2775]$ ,  $[N_4 -0.2539]$ . These data clearly showed that these atoms are most reactive toward the addition substitution reactions. The determined bond angle and twist angle, stretch, bend, stretch-bend, torsion and the 3D geometrical structure indicated that this molecule is a non-planar molecule with the stereochemistry at C(1)-C(7): (E).

**Figure 1.** Optimized 3D geometrical structures for 4-aminoantipyrene

AM1



MNDO

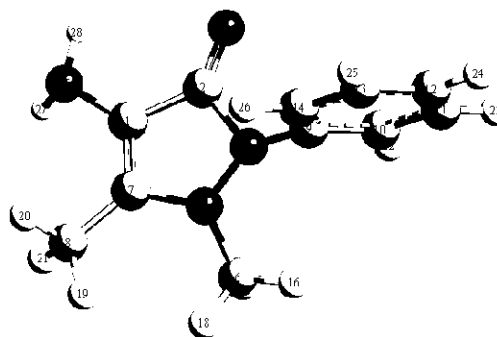


Table 1: Mulliken Charges for 4-aminoantipyrene using AM1 and MNDO methods

Atoms	AM1/ Charges	Atoms	AM1/ Charges	Atoms	MNDO/ Charges	Atoms	MNDO/ Charges
C(1)	-0.1160	N(15)	-0.2775	C(1)	-0.1103	N(15)	-0.1931
C(2)	0.3050	H(16)	0.1034	C(2)	0.3557	H(16)	0.0168
O(3)	-0.3040	H(17)	0.0736	O(3)	-0.3117	H(17)	-0.0070
N(4)	-0.1932	H(18)	0.0951	N(4)	-0.2539	H(18)	0.0075
N(5)	-0.0864	H(19)	0.0934	N(5)	-0.1718	H(19)	0.0092
C(6)	-0.1280	H(20)	0.1032	C(6)	0.1604	H(20)	0.0217
C(7)	-0.0810	H(21)	0.0852	C(7)	0.0090	H(21)	0.0047
C(8)	-0.1599	H(22)	0.1460	C(8)	0.0873	H(22)	0.0719
C(9)	0.0241	H(23)	0.1349	C(9)	0.0512	H(23)	0.0628
C(10)	-0.0979	H(24)	0.1329	C(10)	-0.0219	H(24)	0.0623
C(11)	-0.1336	H(25)	0.1349	C(11)	-0.0669	H(25)	0.0627
C(12)	-0.1220	H(26)	0.1466	C(12)	-0.0473	H(26)	0.0713
C(13)	-0.1303	H(27)	0.1750	C(13)	-0.0630	H(27)	0.1079
C(14)	-0.1181	H(28)	0.1945	C(14)	-0.0394	H(28)	0.1241

**AM1** and **MNDO** calculations have been performed for 4-aminoantipyrene. The optimized molecular structure of the most stable form is shown in Figure 1. The calculated energies are presented in Table 2. Molecular orbital calculations could provide a detailed description of the orbitals including the spatial characteristics, nodal patterns and individual atom contributions. The contour plots of the frontier orbitals for the ground state of 4-aminoantipyrene are shown

in Figure together with the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). It is interesting to observe that both orbitals are substantially distributed over the conjugation plane. In addition, it can also be seen from Figures 2 that the HOMO orbitals are located on the substituted molecule while LUMO orbitals resemble those obtained for the unsubstituted molecule and therefore the substitution has contributed an influence on the electron donation ability while imposing only a small impact on electron acceptance ability. The orbital energy levels of HOMO and LUMO of 4-aminoantipyrine are listed in Table 3. An electronic system with a larger HOMO-LUMO gap should be less reactive compare to the one having a smaller gap. In the present study, the HOMO-LUMO gap values of 4-aminoantipyrine by using AM1 and MNDO methods are at -6.49 and -7.029 eV respectively. The lower value in the HOMO and LUMO energy gap would explain the eventual charge transfer interaction taking place within the molecules.

Table 2. Total energy and Heat of Formation

Method	Total Energy Kcal/Mol	Heat of Formation Kcal/Mol
AM1	-58247.9174	35.3462
MNDO	-51113.2145	29.9441

Figure 2. Highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 4-aminoantipyrine

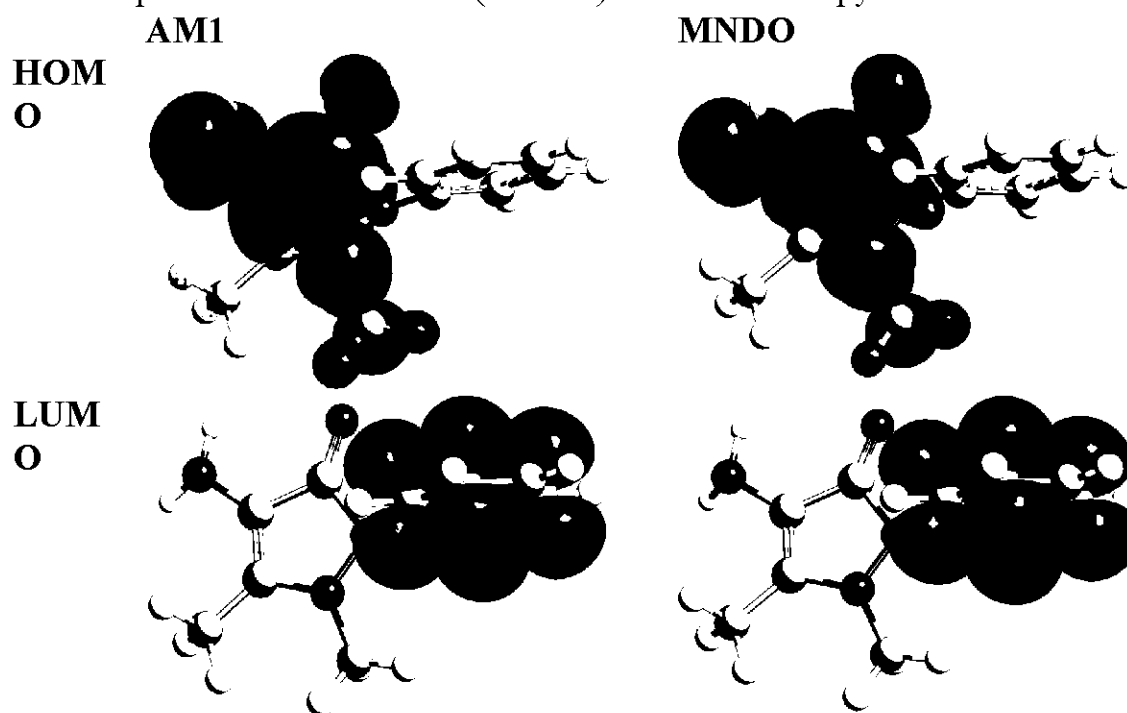


Table 3: Table 2. HOMO and LUMO energies (eV) of 4-aminoantipyrine

Method	HOMO	LUMO	$\Delta E$
AM1	-7.998	-1.058	6.49-
MNDO	-8.414	-1.385	-7.029

**References:**

- [1] C. C. Wu and M. H. Lien, J. Phys. Chem. A **100**, 594 (1996).  
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[4] M. T. Rogers and J. L. Burdett, Can. J. Chem. **43**, 1516 (1965).  
[5] C. C. Su, C. K. Lin, C. C. Wu, and M. H. Lien, J. Phys. Chem. A **103**, 3289 (1999).

## دراسات أستقرارية 4-aminoantipyrine في أستخدام حسابات الكمات (Quantum)

م. حمدان عبود عداي خضير

الخلاصة :

في هذه الدراسة بحثت دراسات الاستقرارية بأستخدام (AMI و MNDO). طرق الحسابات المستخدمة بأفضل العلوم الهندسية الكاملة التي انجزت على (-4-aminoantipyrine) وبصورة ديناميكية حرارية وبحسابات نظرية بمقاييس هندسية مجسمة ، حرارات تكوين ، ودرست ايضاً طاقات الاوربتال (HOMO-LUMO)