Int. J. Electrochem. Sci., 7 **(2012)** 8468 - 8472

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Thermodynamic Studies on 4-Aminocoumarin tautomers

Ahmed A. Al-Amiery[1,2,*], *Huda Dhia Jaffar*[3], *Hasan R. Obayes*[1], *Ahmed Y. Musa*[4] , *Abdul Amir Hassan Kadhum*[2] *and Abu Bakar Mohamad*[2]

[1] Applied Chemistry Division, Applied Science Department, University of Technology (UOT), Baghdad, Iraq
[2] Department of Chemical & Process Engineering, Universiti Kebangsaan Malaysia (UKM), Selangor, 43000, Malaysia
[3] College of Education, Baghdad University, Baghdad, Iraq
[4] Department of Chemistry, Western University, 1151 Richmond Street, London, Ontario, Canada, N6A 3K7
[*]E-mail: dr.ahmed1975@gmail.com

Received: 16 June 2012 / *Accepted:* 8 August 2012 / *Published:* 1 September 2012

As there are no thermodynamic studies on the 4-aminocoumarin tautomerization molecule, this study was done for the first time in the world. 4-Aminocoumarin molecule stability was studied in the gaseous state and it has two isomers (imino form and amino form). The theoretical study and based on the results of density functions theory (DFT), imino possess higher stability state compared with amino. The thermodynamic values (the change in entropy ΔS and the change in enthalpy ΔH) of the isomerization form of amino to imino revealed that the conversion is spontaneous and endothermic.. The results showed that wavelength for greatest absorption (λ_{max}) of imino form is longer than amino and this is due to the formation of a new double bond which leads to the association distribution of the electronic density along the molecule in the imino form.

Keywords: 4-Aminocoumarin; entropy; enthalpy; HOMO; LUMO

1. INTRODUCTION

Coumarin and its derivatives represent one of the most active classes of compounds, possessing a wide spectrum of biological activity [1-4]. Optical applications of these compounds, such as laser dyes, nonlinear optical chromophores, fluorescent whiteners, fluorescent probes, polymer science, optical recording and solar energy collectors have been widely investigated [5-13]. Coumarins can be synthesized by the Perkin reaction, Pechmann reaction or by Knoevenagel condensation of salicylaldehydes with malonic acid or Meldrum's acid [14] with malonic esters and cyanoacetic esters.

Recently, the Wittig reaction in N,N-diethylaniline was also conveniently applied for the synthesis of coumarins [15].

The thermodynamical properties of the title compounds in have been calculated using DFT (B3LYP) method. This calculation is valuable for providing insight into molecular parameters, entropy and the enthalpy. The aim of this work is to explore the molecular dynamics and the structural parameters that govern the chemical structure, and to compare predictions made from theoretical observations.

2. RESULTS AND DISCUSSION

4-iminocoumarin and 4-aminocoumarin are two isomers as showed in Figure 1. The stability of these forms from the calculations of chemical quantum theory using the density functions theory (DFT) method indicated that the 4-iminocoumarin isomer is more stable than 4-aminocoumarin isomer (Table 1). This is evidenced by the value of the total energy calculated from each of them, that the energy of 4-iminocoumarin isomer is more than 4-aminocoumarin isomer by -0.032 a.u. or -19.951 Kcal.mol-1. Thermodynamic results showed that reaction (1) is spontaneous because of the positive value of the entropy change ($\Delta S = +0.063$ cal.mol^{-1}.K^{-1}) and therefore 4-iminocoumarin isomer is more stable than 4-aminocoumarin isomer. The negative value of enthalpy change ($\Delta H = -0.577$ Kcal.mol^{-1}) indicates that the reaction (1) is exothermic, while reaction (2) is not spontaneous and endothermic with values of ΔS and ΔH being -0.063 cal.mol^{-1}.K^{-1} and +0.577 Kcal.mol^{-1}, respectively. The stability of 4-iminocoumarin isomer is as shown in Figure (1).

In solid state physics, a band gap, also called an energy gap, is an energy range in a solid where no electron states can exist. The gap energy generally refers to the energy difference (in electron volts) between the Low Unoccupied Molecular Orbital (LUMO) and the HOMO in insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, which is able to move freely within the solid material. These molecules were calculated in gas phase media and hence the energy gap is based an approximation. The band gap energy values of these two isomers, namely, 4-iminocoumarin and 4-aminocoumarin are 5.126 eV and 4.567 eV, respectively; this indicates that thin molecule in gas phase is insulators for the electrical conductivity. Figure 2 shows the HOMO and the LUMO electronic distributions for both of the isomers. Other observations account for absorption maximum wavelength (λ_{max}) of both isomers of 4-iminocoumarin and 4-aminocoumarin to be 451.37 nm and 402.15 nm, respectively. The two isomers have no center of symmetry at all symmetry element hence they are classified as the identity, E. Such molecule belongs to the C_1 point group.

The dipole moments of 4-aminocoumarin and 4-iminocoumarin were also calculated and listed in Table **1**. The dipole moment for 4-aminocoumarin and 4-iminocoumarin were oriented outwards.

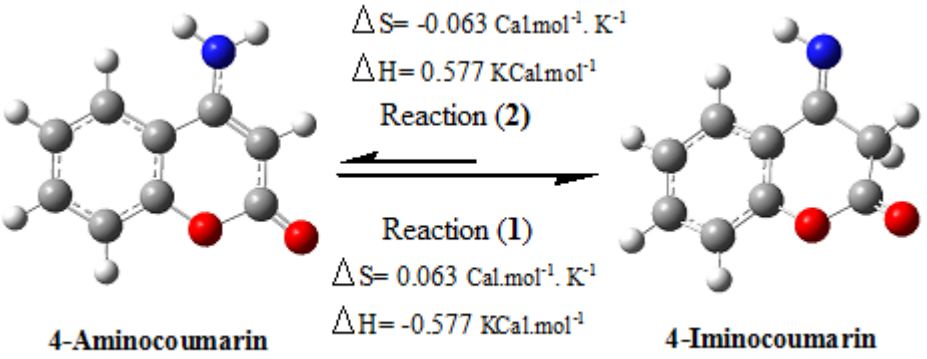
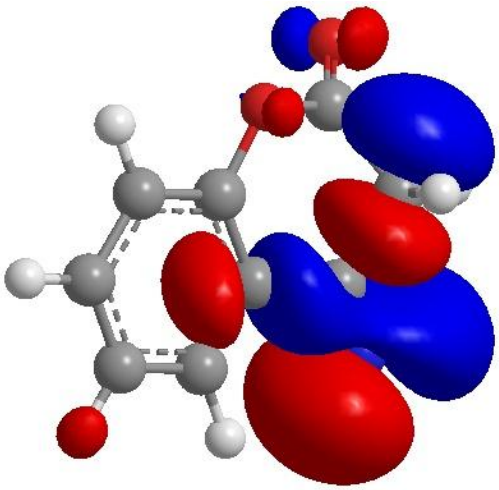


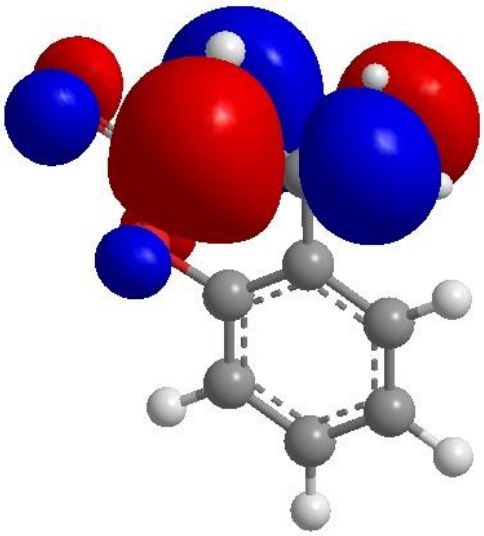
Figure 1. The optimized structure for two isomers (4-aminocoumarin and 4-iminocoumarin) and values of ΔS, ΔH.

Table 1. Calculated physical parameters for 4-aminocoumarin and 4-iminocoumarin.

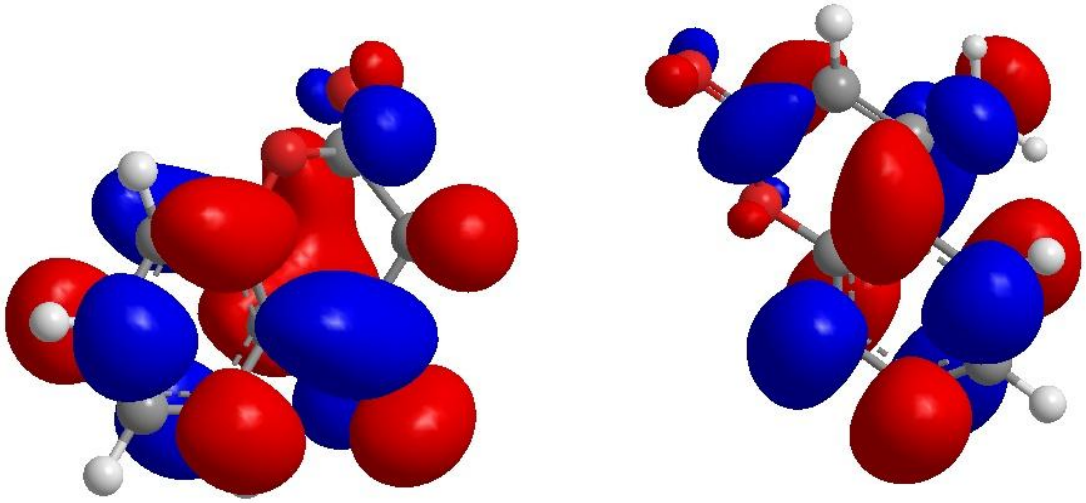
Parameter	4-aminocoumarin	4-iminocoumarin
Total energy / a.u.	-552.201	-552.232
Entropy (S) / cal.mol^{-1}.K^{-1}	93.324	93.387
Enthalpy (H) / Kcal.mol^{-1}	97.037	96.460
EHOMO / eV	-6.104	-7.001
ELUMO / eV	-1.536	-1.87
Gap energy (E_{LUMO} - E_{HOMO})/ eV	4.5679	5.1268
λ_{max} (E_{LUMO} - E_{HOMO})/ nm	402.15	451.37
Point group	C1	C1
Dipole moment / Debye	7.469	5.233



HOMO orbitals of 4-iminocoumarin



HOMO orbitals of 4-aminocoumarin



LUMO orbitals of 4-iminocoumarin LUMO orbitals of 4-aminocoumarin

Figure 2. HOMO, LUMO orbitals of 4-aminocoumarin and 4-iminocoumarin**.**

3. EXPERIMENTAL SECTION

Gaussian 03, Revision C.01 was used for the calculation of ground-state geometry was optimized to a local minimum without any symmetry restrictions using basis set 6-31G. The becke three-parameter hybrid (B3) exchange functional in combination with the Lee-Yang-Parr (LYP) correction functional (B3LYP) was used for all geometry optimizations, thermodynamic functions at conditions (temperature= 298.150 Kelvin, and pressure= 1.0 atm), High Occupied Molecular Orbital (HOMO) and Low Unoccupied Molecular Orbital (LUMO) distribution, and some physical properties for molecules [16-20].

4. CONCLUSIONS

The quantum chemistry calculations using the Density Function Theory (DFT) method to study stability of 4–iminocoumarin isomers in gaseous state have been carried out. The results showed that the isomer imino is more stable than isomer amino as was indicated via calculations of the total energy, energy of High Occupied Molecular Orbital (HOMO), the distribution of electron density, change in entropy and the change in enthalpy. The density function theory is capable of distinguishing between the more stable isomers. The stereochemistry was estimated and it was found that 4–iminocoumarin is not planar.

ACKNOWLEDGMENTS
This work was supported by University of Technology, Baghdad, Iraq and Universiti Kebangsaan Malaysia under the DIP-2012-02 grant.

References

1. A. El-Agrody, M. Abd El-Latif, N. El-Hady, A. Fakery1, A. Bedair, *Molecules* 6 (2001) 519.
2. D. Rositca, G. Nikolova, R. Vayssilov, R. Bojilova, *Molecules* 7 (2002) 420.
3. R. Flašík, H. Stankovicová, A. Gáplovský, J. Donovalová, *Molecules* 14 (2009) 4838.
4. K. Sergiy, I. Bylov, K. Sytnik, V. Chernykh, Y. Bilokin, *Molecules* 5 (2000) 1146.
5. S. Lin, P. Kuo, D. Yang, *Molecules* 12 (2007) 1316.
6. P. Verdía, F. Santamarta, E. Tojo, *Molecules* 16 (2011) 4379.
7. S. Mukhatar, R. Mujeebur, W. Ansari, G. Lemiere, A. De Groot, R. Dommisse, *Molecules* 4 (1999) 232.
8. C. Milan, M. Maja, B. Tomislav, D. Nela, R. Valentina, *Molecules* 14 (2009) 2501.
9. A. Al-Amiery, A. Kadhum, A. Mohamad, *Molecules* 17 (2012) 5713.
10. A. Kadhum, A. Mohamad, A. Al-Amiery, *Molecules* 16 (2011) 6969.
11. A. Al-Amiery, R. Al-Bayati, K. Saour, M. Radi, *Res. Chem. Intermediat.* 38 (2011) 559.
12. A. Kadhum, A. Al-Amiery, A. Musa and A. Mohamad, *Int. J. Mol. Sci.* 12 (2011) 5747.
13. A. Al-Amiery, A. Musa, A. Kadhum, and A. Mohamad, *Molecules,* 16 (2011) 6833.
14. G. Jones, Organic Reactions; John Wiley & Sons: New York, 15 (1967) 204.
15. N. Tuyen, S. Van, K. Norbert, *Tetrahedron Letters*, 44 (2003) 4199.
16. A. Al-Amiery, A. Kadhum, A. Mohamad, *Bioinorg. Chem. Appl.* 2012 (2012) 1.
17. A. Al-Amiery, *Res. Chem. Intermediat.* 38 (2012) 745.
18. S. Junaedi, A. Kadhum, A. Al-Amiery, A. Mohamad, M. Takriff, *Int. J. Electrochem. Sci.* 7 (2012) 3543.
19. A. Al-Amiery, Y. Al-Majedy, H. Ibrahim, A. Al-Tamimi, *Org. Med. Chem. Lett.* 2 (2012) 2.
20. A. Al-Amiery, Y. Al-Majedy, H. Abdulreazak,, H. Abood, *Bioinorg. Chem. Appl.* 2011 (2011) 1.