

Article

Thermodynamic and Theoretical Studies of the Imide Derivatives

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Abstract: Based on DFT (density functional theory) using B3LYP/6-31G method, theoretical investigations applied to demonstrate the structural, electronic properties and stability of (N,N'-(1,4-phenylene)bis(1,8-naphthalimide)) is more stable than the compound (N-(4-amino phenyl)1,8-naphthalimide) by (-1.2762 eV or -29.4299 Kcal.mol⁻¹) depending on the values of HOMO, synthesis reaction of imide is spontaneous and endothermic at temperature 275°C according to the values of ΔrS , ΔrG and ΔrH .

Keywords: imide; DFT; HOMO; spontaneous; endothermic

1. Introduction

Cyclic imides are important family of organic compounds possess structural features which confer potential biological activity and pharmaceutical use [1,2]. Their molecules contain an imide ring with a general structure [-CO-N(R)-CO-], so that they are hydrophobic and neutral and can therefore cross biological membranes in vivo. A diversity of biological activities and pharmaceutical uses have been attributed to them, such as antibacterial, antifungal, anti-nociceptive, anticonvulsant and antitumor [3]. The preparation of imides has received considerable attention during recent year A number of methods such as acylation of amides with acyl chlorides, anhydrides and carboxylic esters or acids [4-6], amino carbonylation of aryl bromides [7], reaction of azalactones with oxygen and palladium [8] have been reported for the preparation of acyclic imides. However, most of these methods suffer from drawbacks such as long reaction times, low yields, high temperature and producing side-products. Organic reactions assisted by microwave irradiation have attracted considerable attention in recent years [9-13]. The main benefits of the microwave reactions are much improved reaction rates, higher yields and formation of cleaner products. A noteworthy advantage of modern scientific microwave apparatus is the ability to control reaction parameters such as temperature, pressure and reaction times accurately.

2. Results

Reaction p-Phenylene diamine with 1,8-Naphthalic anhydride produces imide, this reaction has been studied theoretically depending by density function theory, in the light of the active groups in the reactants there is the possibility of the production of two imides compounds are (Imide1 and Imide2). Showed the electronic properties of these products that compound (Imide2) is more stable than the compound (Imide1) by (-1.2762 eV or -29.4299 Kcal.mol⁻¹) depending on the values of high occupied molecular orbital (HOMO) in the table (1). Comparing the values gap energy for two compounds (Imide1 and Imide2) are: (2.8314 eV, 4.0104 eV) respectively, shows us that the compound (Imide2) is more stable because the greater the value of gap energy leads to increased stability [20,21].

Thermodynamic study of the reaction has been made through calculation of the change in enthalpy (ΔrH), the change in entropy (ΔrS) and the change in Gibbs energy (ΔrG) of the reaction at two temperature (room temperature 25°C=298°K and temperature 275°C=548°K), in figure (1) reaction

(1) and reaction (2) at room temperature $25^{\circ}\text{C}=298^{\circ}\text{K}$ are not spontaneous according to the values of Δ_rS (negative value) and Δ_rG (positive value) thermodynamically not favoured; instead the reverse is favoured, but from values of Δ_rH the reaction (1) endothermic (positive value) and reaction (2) exothermic (negative value). While figure (2) both reactions are spontaneous and endothermic according to the values of Δ_rS (positive value), Δ_rG (negative value) thermodynamically favoured and Δ_rH (positive value) [22,23]. In figure (3) the HOMO and LUMO electronic distributions for reactants (p-Phenylene diamine and 1,8-Naphthalic anhydride), showing the mechanism of reaction between reactants, in HOMO of p-Phenylene diamine as we note the concentration of electron density on the nitrogen atoms that is attack the carbon atoms in the carbonyl group in HOMO of 1,8-Naphthalic anhydride to produce imide in the last. We conclude that synthesis reaction of imide compounds needs to heat up to 275°C and the reaction (2) more stable than reaction (1) thermodynamically.

Table 1: Physical values of all molecules were calculated with B3LYP/6-31G.

Molecules	Enthalpy (H) Kcal.mol ⁻¹		Entropy (S) Cal.mol ⁻¹ .K ⁻¹		E _{HOMO} eV	E _{LUMO} eV	Gap energy (E _{LUMO} -E _{HOMO}) eV
	298 K	548 K	298 K	548 K			
water	14.670	16.226	45.142	50.126	-7.8807	1.4370	9.3177
p-Phenylene diamine	88.537	-----	80.177	-----	-4.1514	0.5440	4.6954
1,8-Naphthalic anhydride	101.367	-----	98.578	-----	-7.0094	-2.9535	4.0559
Compound (Imide 1)	175.306	197.958	130.524	185.507	-5.2366	-2.4052	2.8314
Compound (Imide 2)	261.180	296.622	177.613	262.922	-6.5128	-2.5024	4.0104

Figure (1). The reaction of synthesis new derivative imide and values of Δ_rH , Δ_rS and Δ_rG at room temperature $25^{\circ}\text{C}=298^{\circ}\text{K}$.

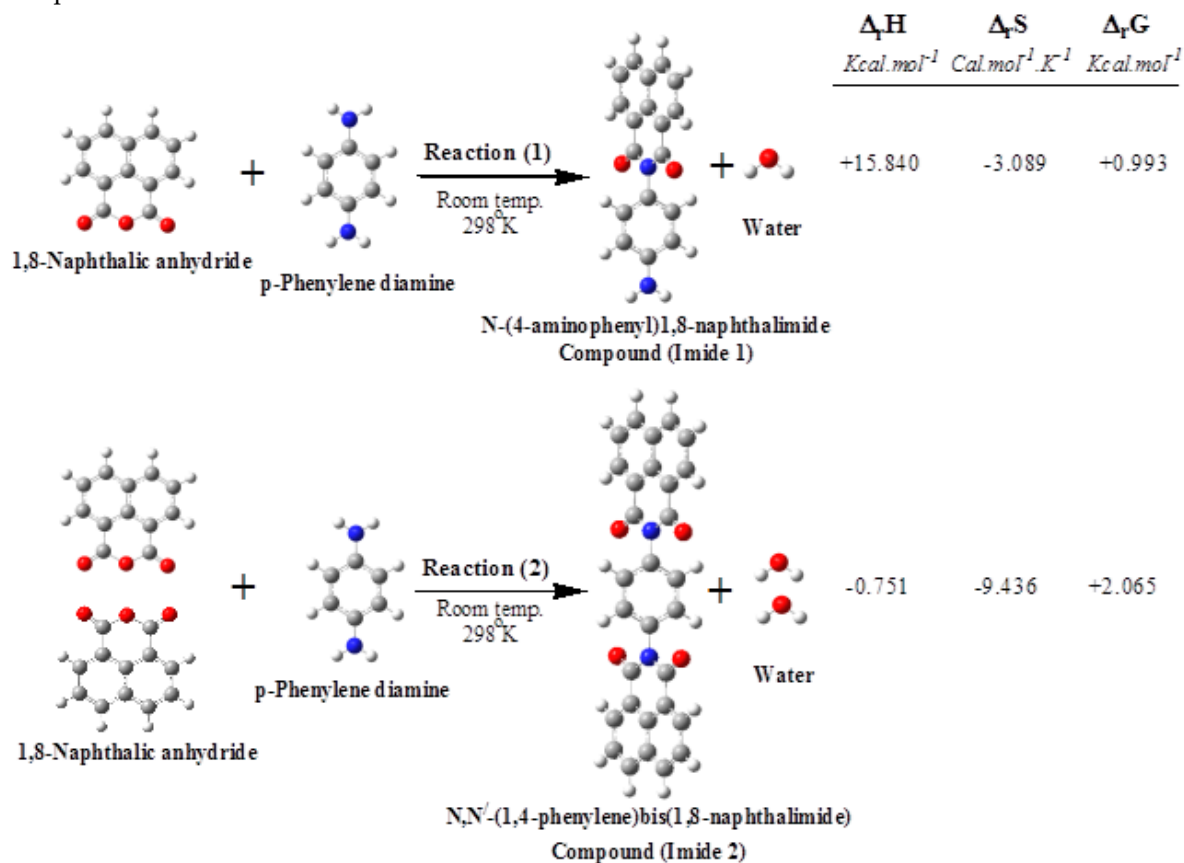


Figure (2). The reaction of synthesis new derivative imide and values of Δ_rH , Δ_rS and Δ_rG at temperature $275^\circ\text{C}=548^\circ\text{K}$.

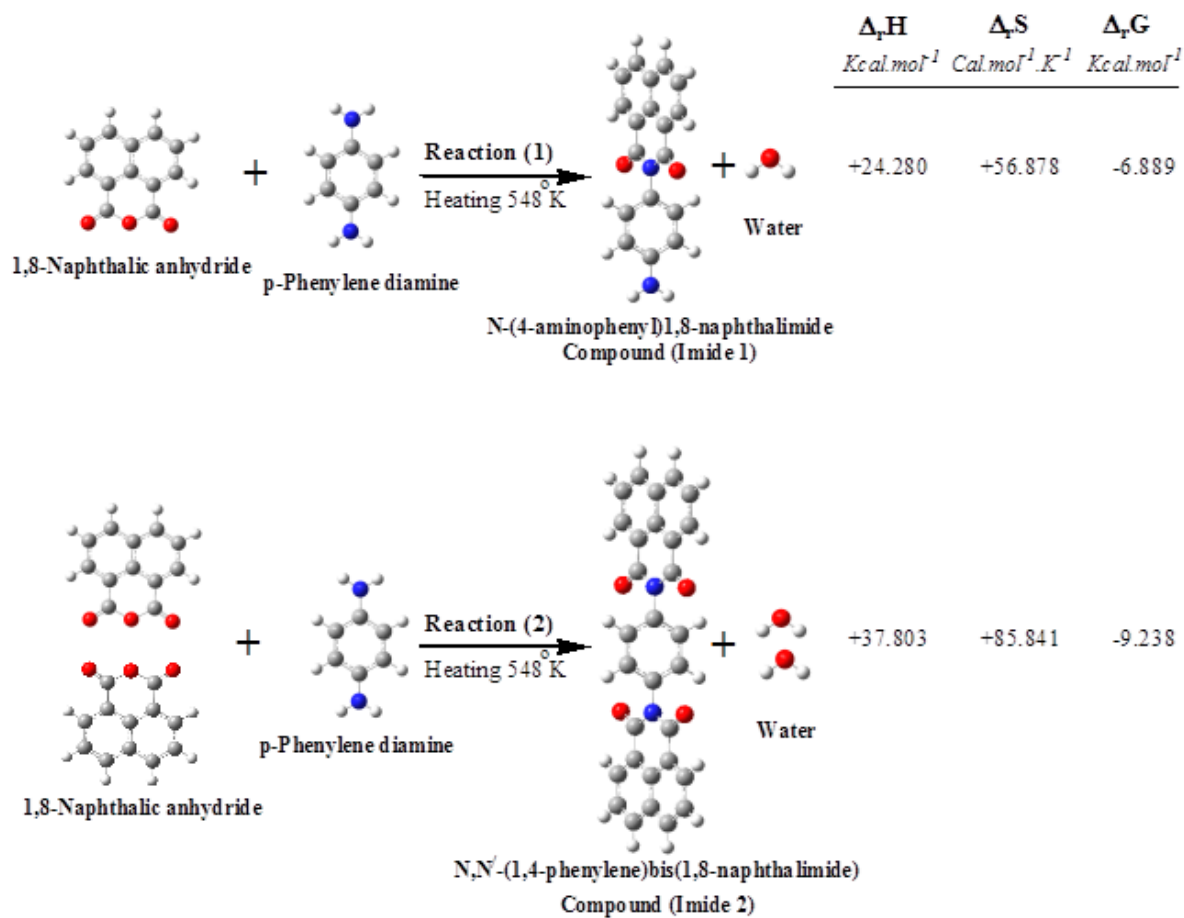
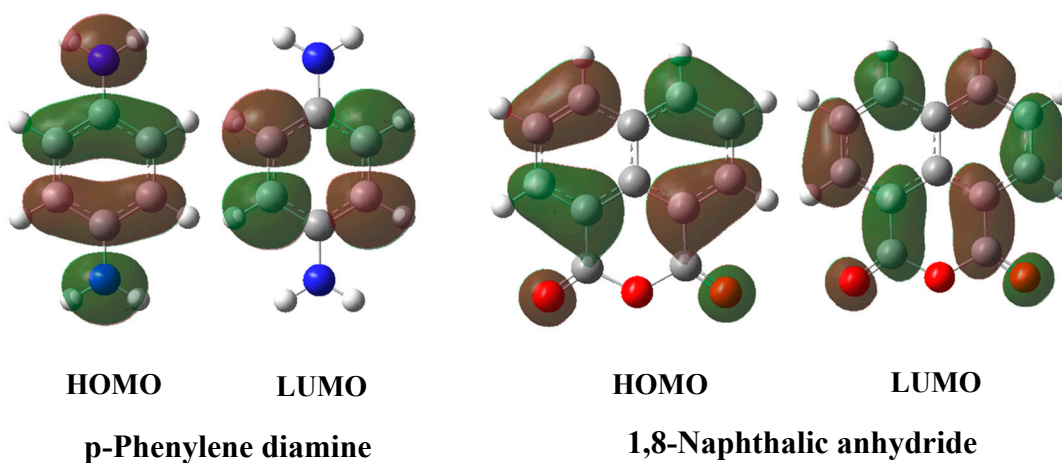


Figure (3). HOMO and LUMO of reactants (p-Phenylene diamine and 1,8-Naphthalic anhydride)



3. Materials and Methods

Computational Methods

Molecular geometries of the all molecules were fully optimized with the hybrid density functional theory (DFT) B3LYP method[14-16] using the 6-31G basis set[17,18] by means of the Gaussian 09, revision A.02[19] used for all geometry optimizations, thermodynamic functions at conditions (temperature=298°K, 548°K, and pressure= 1.0 Atm), high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) distribution, and some physical properties for all molecules.

4. Conclusions

The quantum chemistry calculations using the density function theory (DFT) method to thermodynamic study of production reaction of two imides compounds at room temperature 25°C=298°K and temperature 275°C=548°K. The results showed that the reaction needs to heat up to 275°C to be spontaneous and endothermic, compound (Imide2) is more stable than compound (Imide1) depending on the values of high occupied molecular orbital (HOMO).

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Author Contributions: H.R.O. conceived and designed the work; G.H. A. performed the calculations; M.S. analyzed the data; A.A.A. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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