Thermodynamic and Theoretical Studies of some N-substituted phthalimides Derivatives

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ABSTRACT

N,N′-(biphenyl)bisphthalimide and N-(4′-amino biphenyl) phthalimide were chosen in this study to compare the stability theoretically by density function theory (DFT) using B3LYP/6-31G method, the electronic properties of these imides indicate that compound (N,N′-(biphenyl)bisphthalimide) is more stable than the compound (N-(4′-aminobiphenyl) phthalimide) by (-0.8422 eV or -19.4215 Kcal.mol^{-1}) depending on the values of HOMO, synthesis reaction of imide is spontaneous and endothermic at temperature 150˚C according to the values of $\Delta_r S$, $\Delta_r G$ and $\Delta_r H$ thermodynamically.

INTRODUCTION

Imides are organic compounds for N-monoacyl derivatives of amide which may be open or cyclic chain. Cyclic imide constitute an important class of compounds possessing bis-amide linkage with common nitrogen. Imide very important molecules because their activity as antibacterial, antifungal, anti nociceptive, anticonvulsant and antitumor[1]. They have been useful building blocks in the synthesis of natural products[2] and other heterocycles as well[3]. Their ability to cross biological membranes *in-vivo*, due to their hydrophobicity is well established[4],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[5-7], amino carbonylation of aryl bromides[8] have been reported for the preparation of acyclic imides.

COMPUTATIONAL METHODS

Molecular geometries of the all molecules were fully optimized with the hybrid density functional theory (DFT) B3LYP method[9-11] using the 6–31G basis set[12,13] by means of the Gaussian 09, revision A.02[14] used for all geometry optimizitions, thermodynamic functions at conditions

(temperature=298˚K, 423˚K, and pressure= 1.0 Atm), high occupied molecular orbital (HOMO) , low unoccupied molecular orbital (LUMO) distribution, and some physical properties for all molecules.

RESULTS AND DISCUSSION

Reaction of biphenyl-4,4′- diamine with phthalic 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 (-0.8422 eV or -19.4215 $Kcal.mol^{-1}$) 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: (2.6090 eV, 3.3328 eV) respectively, shows us that the compound (Imide2) is more stable because the greater the value of gap energy leads to increased stability[15,16].

Thermodynamic study of the reaction has been made through calculation of the change in enthalpy (Δ_rH), the change in entropy (Δ_rS) and the change in Gibbs energy (Δ_rG) of the reaction at two temperature (room temperature 25˚C=298˚K and temperature 150˚C=423˚K), in Figure (1) reaction (1) and reaction (2) at room temperature 25˚C=298˚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)[17,18]. In Figure (3) the HOMO and LUMO electronic distributions for reactants (biphenyl-4,4′-diamine and phthalic anhydride), showing the mechanism of reaction between reactants, in HOMO of biphenyl-4,4′- 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 phthalic anhydride to produce imide in the last. We conclude that synthesis reaction of imide compounds needs to heat up to 150˚C and the reaction (2) more stable than reaction (1) thermodynamically.

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 150˚C=423˚K. The results showed that the reaction needs to heat up to

150˚C to be spontaneous and endothermic, compound (Imide2) is more stable than compound (Imide1) depending on the values of high occupied molecular orbital (HOMO).

Table1: Physical values of all molecules were calculated with B3LYP/6-31G.

Molecules	Enthalpy (H) Kcal.mol^{-1} 298 K	Enthalpy (H) Kcal.mol^{-1} 423 K	Entropy (S) Cal.mol^{-1}.K^{-1} 298 K	Entropy (S) Cal.mol^{-1}.K^{-1} 423 K	E_{HOMO} eV	E_{LUMO} eV	Gap energy (E_{LUMO}–E_{HOMO}) eV
water	14.670	14.915	45.142	48.123	-7.8807	1.4370	9.3177
benzidine	143.572	------	105.363	------	-4.5013	0.2598	4.7611
phthalic anhydride	69.743	------	86.883	------	-8.0738	-2.9951	5.0787
Imide 1	198.009	209.071	141.537	172.934	-5.0493	-2.4403	2.6090
Imide 2	252.420	267.179	176.419	217.271	-5.8912	-2.5584	3.3328

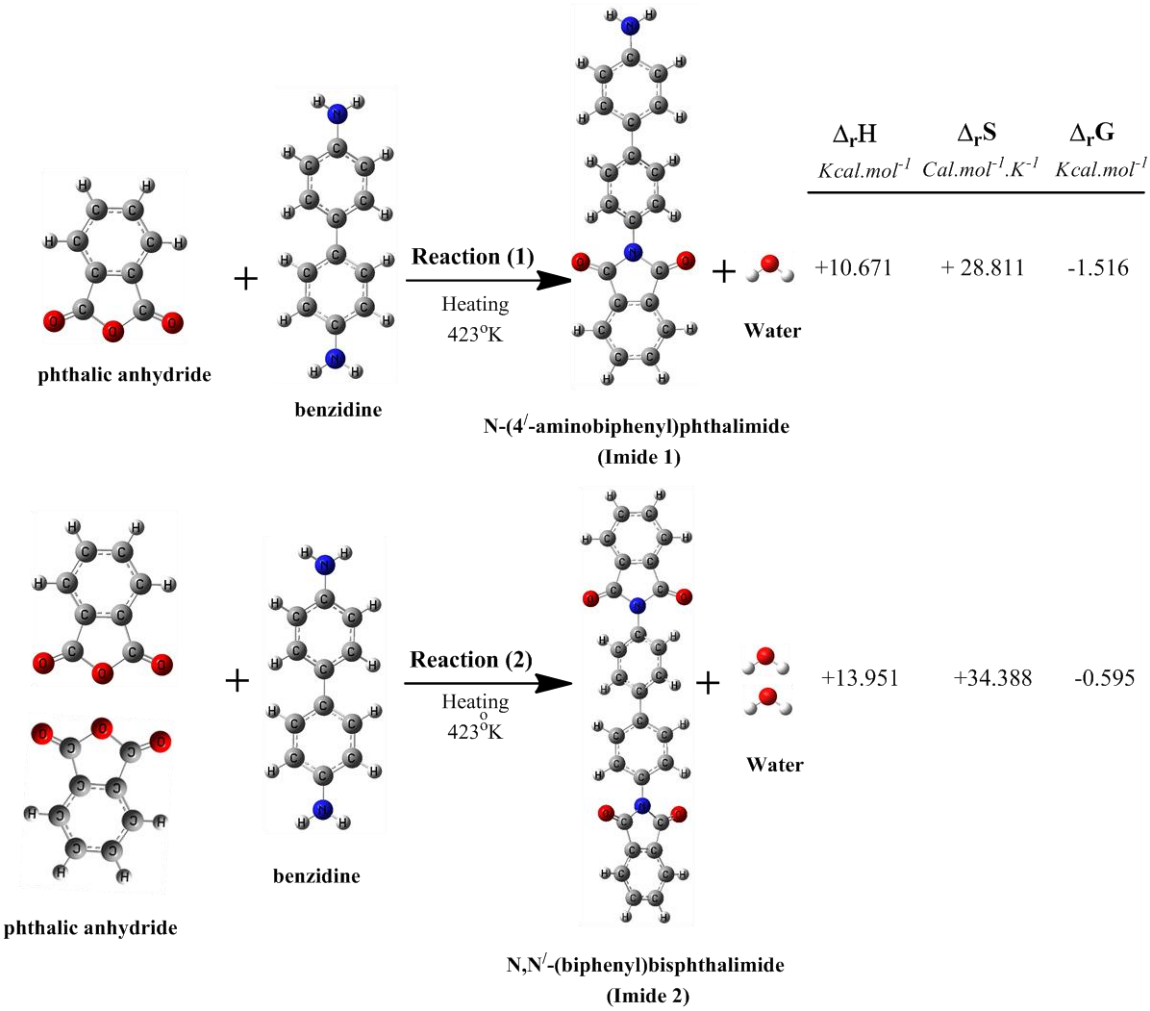

Figure (1). The reaction of synthesis new derivative imide and values of Δ_rH, Δ_rS and Δ_rG at room temperature 25˚C=298˚K.

Figure (2). The reaction of synthesis new derivative imide and values of $\Delta_r H$, $\Delta_r S$ and $\Delta_r G$ at temperature 150˚C=423˚K.

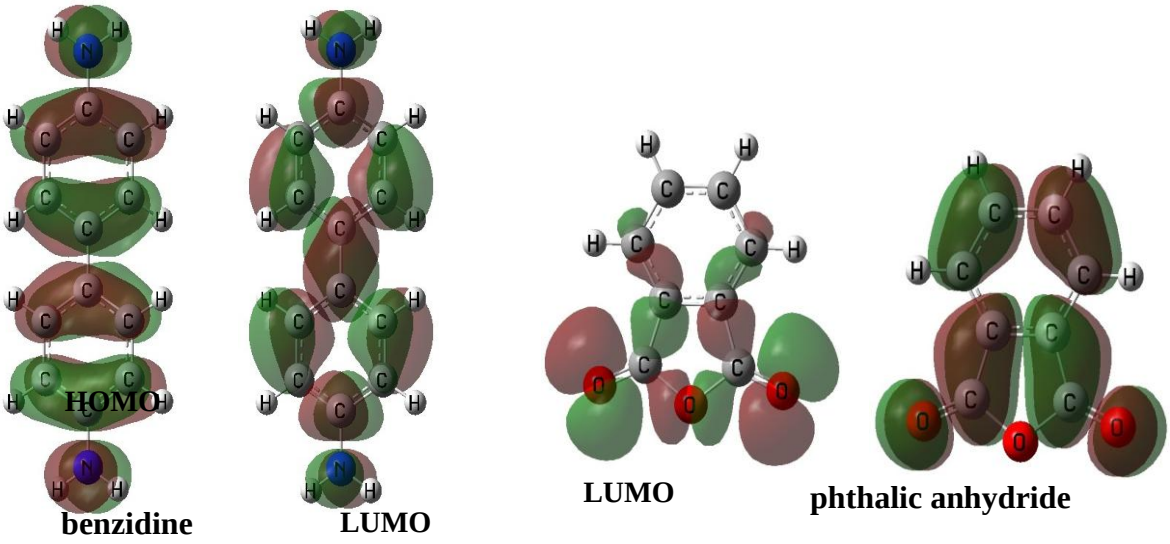

Figure (3). HOMO and LUMO of reactants (benzidine and phthalic anhydride.

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دراسة نظرية و ثرموديناميكية لبعض مشتقات N- معوض فثالئيمايد.

الخلاصة

N,N$^{/}$-(باي فنيل) ثنائي الفثالئيمايد و N-(4-امينوفنيل) فثالئيمايد تم اختيارها في هذا البحث للدراسة النظرية , بأستخدام نظرية دالة الكثافة الالكترونية (DFT) بأستخدام طريقة B3LYP/6-31G , اوضحت الدراسة بأن المركب N,N$^{/}$-(باي فنيل) ثنائي الفثالئيمايد اكثر استقرار من المركب N- (4-امينوفنيل) فثالئيمايد بالاعتماد على قيمة الHOMO (-0.8422 ev or -19.4215 Kcal.mol^{-1}) ,تفاعل تحضير الايمايد تلقائي و ماص للحرارة عند درجة حرارة 150 مئوية طبقا للقيم الثرموديناميكية Δ_rG ,Δ_rS و Δ_rH .