INTERNATIONAL ANATOLIA ACADEMIC ONLINE JOURNAL
e-ISSN 2148-3159 HEALTH SCIENCES RESEARCH ARTICLES

COMPUTATIONAL EXAMINATION OF DEGRADATION REACTIONS OF BUTRALIN

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Geliş Tarihi/Received	Kabul Tarihi/Accepted	Yayın Tarihi/Published
04-11-2020	17-11-2020	31-12-2020

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Cite this article as:
Kürümoğlu, Ş., Yalçın Gürkan, Y. (2020). Computational examination of degradation reactions of butralin. IAAOJ Health Sciences, 6(3), 337-346.

ABSTRACT
In this study, the possible reaction paths between the OH radical of the Butralin molecule, one of the pesticide molecules, were determined. Optimized geometries were drawn with Gauss View 5. Then, the lowest energy states were found by geometric optimization with Gaussian 09 programe. Geometric structure analysis was made and bond lengths and bond angles were calculated. The aim of this study is to determine the most likely reaction path of Butralin molecule and OH radical interaction among pesticide molecules in gase and water phase. The effect of solvent water, COSMO was used as the dissolving model and it has a stabilizing effect by reducing the energy in reactions. The lowest energy molecule has the most stable structure. Accordingly, the most stable fragment of the Butralin molecule is the F5 molecule. These results will guide experimental studies and determine the fragmentation mechanism.

Keywords: Butralin, hydroxyl radical, DFT, Gaussian09

BUTRALİN MOLEKÜLÜNÜN BOZUNMA REAKSİYONLARININ HESAPSAL İNCELENMESİ

ÖZET
Bu çalışmada pestisit moleküllerinden Butralin molekülünün OH radikali arasındaki meydana getireceği olası reaksiyon yolları belirlenmiştir. Optimize geometrileri Gauss View 5 ile çizilmiştir. Daha sonra, Gaussian 09 programı ile geometrik optimizasyon yapılarak en düşük enerjili halleri bulunmuştur. Geometrik yapı analizi yapılmış ve bağ uzunlukları ile bağ açıları hesaplanmıştır. Bu çalışmadaki amaç, gaz fazı ve sulu ortam içinde pestisit moleküllerinden Butralin molekülünün ve OH radikali etkileşiminin en muhtemel reaksiyon yolu belirlemektir. Çözücü suyun etkisi, çözme modeli olarak COSMO kullanılmış ve reaksiyonlarda enerjiyi azaltıp stabilize edici bir etkiye sahiptir. En düşük enerjili molekül en kararlı yapıya sahiptir. Buna göre Butralin molekülünün en kararlı fragmanı F5 molekülüdür. Bu sonuçlar deneysel çalışmalara yol gösterecek olup parçalanma mekanizmasını belirlemektedir.

Anahtar Kelimeler: Butralin, hidroksil radikali, kuantum mekaniksel yöntemler, Gaussian09

INTRODUCTION

Pesticides are contaminated to the water, soil and atmosphere during production or as a result of its use. Pesticides can evaporate from the soil into the air, as well as the particles in the atmosphere exposed to pesticides turn into rainwater, reach the soil, underground waters with pesticide plants, or leak or flow into groundwater. (1) Pesticides affect human health directly and indirectly. Occupational accidents that occur during the production and use of pesticides immediately show the negative effects of drugs on human health. (2)

In addition to chronic toxicity of pesticides by residue, it has been determined in recent years that some of them have mutagenic, teratogenic and carcinogenic effects in humans. Pesticide deposits on plants, on the other hand, sometimes pass to humans and animals through food, and can create sudden poisoning, and even hazards that affect the genetic structure and can cause cancer. (3)

Pesticides are non-specific chemical substances used to control creatures called pests. They accumulate in adipose tissue in humans. Pesticides cause environmental pollution by polluting water and soil. In addition, they leave an effect by entering into the body of living species that are not targeted for use. Especially easily soluble in water can easily penetrate water resources. Those that do not biochemically break down in the soil accumulate in the soil. Powder pesticides are well transported in wind and water, carrying pesticide pollution to remote areas. (4)

Butralin molecule, which belongs to the chemical group of Dinitroaniline, has many advantages such as easy to use as a herbicide, broad spectrum weed control, low toxicity, low residue. However, it contains a large amount of volatile organic solvents in the production, packaging and handling process. Therefore; It can cause great harm to humans, animals and the environment. (5-6)

The aim of this study is to computationally examine the degradation reactions in order to remove the Butraline molecule, the pesticide molecule that poses a great risk to human health, from water sources and to transform it into harmless molecules.

METHODS

Degradation reactions of molecules to be investigated will be examined by molecular modeling methods and theoretical approaches will be proposed for reaction pathways. For this purpose, possible reactions were calculated using Gaussian09 package program. DFT method was used in the theoratical study.

In this study, possible reaction pathways of the Butralin molecule were examined. For this purpose, butralin has been geometry optimization for its molecule and the most appropriate quantum mechanical method has been determined. Possible products were theoretically predicted and calcular examinations were carried out.

Molecular orbital calculations

Calculations of the most durable comforters of the butralin molecule were carried out using DFT/B3LYP/6-31G(d) methods. All molecular orbital calculations were used in Gaussview5 molecular representation program and Gaussian09W program.(7)

Solvent effect model

The energy of the fragmentation reactions of all organic compounds is affected by water molecules in the aqueous environment. In addition, geometry stretching in the solution is induced by H_2O. However, the results obtained in many studies are that the geometry changes of the soluble substance for both open and closed shell structures have a trivial effect. Therefore, in this study H_2 of His Butralin molecule to explain the solvent effect on + ·OH reaction energy; DFT/B3LYP/6-31G(d) method calculations were made and the COSMO (conductor-like screening solvation model) solvation model applied to the Gaussian package program was used. (8)

RESULTS

According to the conformer analysis carried out by molecular mechanical method, the lowest energy, most durable structure of the Butralin molecule is shown in figure 1.

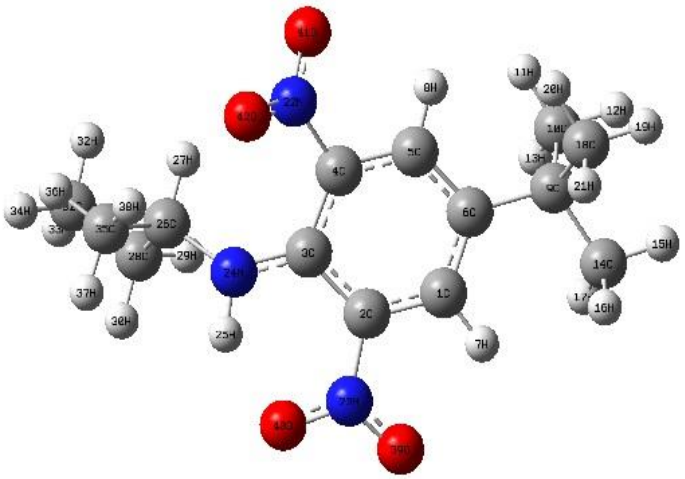


Figure 1. Optimum geometric structure of butralin molecule obtained by DFT method. (blue, nitrogen; white, hydrogen; red, oxygen; grey, carbon)

Butralin's most durable geometric structure is optimized with DFT/B3LYP/6-31G(d) methods. As a result of DFT calculations, Butralin's total energy in the gas phase is -634243.3262 kcal/mol, enthalpy -634242.7338 kcal/mol, gibbs free energy -634289.1933 kcal/mol. In addition, the total energy in the water phase, enthalpy and gibbs free energy respectively; -634250.1334 kcal/mol, -634249.541 kcal/mol, -634296.0539 kcal/mol. Optimized with DFT/B3LYP/6-31G(d) methods, butralin's geometric structure is shown in figure 1 and geometric parameters are shown in Table 1.

Table 1. Optimum geometric parameters of butralin

DFT		DFT	
Bond Lengths (A°)		Bond Angles (°)	
42O-22N	1.23	40O-23N-39O	122.03

22N-4C	1.47	25H-24N-26C	114.22
24N-25H	1.02	42O-22N-41O	124.24
24N-3C	1.35	4C-3C-2C	112.75
23N-2C	1.45	17H-14C-16H	108.25
40O-23N	1.25		
39O-23N	1.23		
1C-7H	1.08		
35C-26C	1.53		
10C-12H	1.10		
14C-16H	1.09		
4C-5C	1.39		

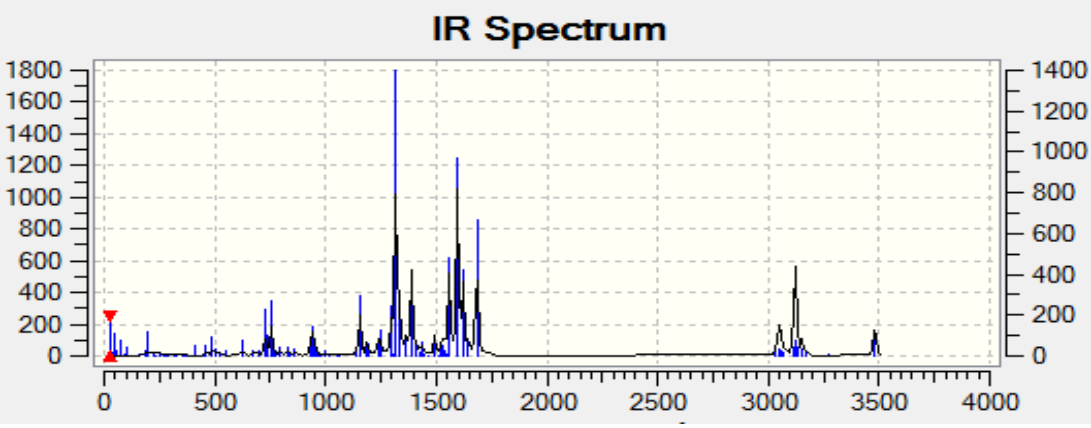


Figure 2. Calculated IR values of butralin

Possible reaction pathways of butralin were identified as N-C ligament fracture and C-C ligament fracture. Reaction centers are determined according to the mulliken load distribution of the molecule. According to the data in Table 2, the fragmentation reaction was caused by the electronegativeness of N. Butralin Mulliken loads obtained by DFT/B3LYP/6-31G(d) method determined as the most appropriate method are shown in Table 2.

Table 2. Mulliken loads of Butralin

Mulliken loads of Butralin		
1 C -0.242153	16 H 0.152078	31 C -0.453956
2 C 0.232179	17 H 0.152481	32 H 0.151128
3 C 0.367897	18 C-0.443194	33 H 0.154049
4 C 0.210936	19 H 0.147659	34 H 0.154894
5 C -0.202618	20 H 0.146877	35 C -0.450655
6 C 0.173062	21 H 0.151758	36 H 0.154337
7 H 0.191990	22 N 0.338186	37 H 0.143237
8 H 0.183968	23 N 0.376623	38 H 0.187897
9 C 0.012166	24 N -0.669393	39 O -0.400660
10 C -0.444634	25 H 0.378291	40 O -0.439295
11 H 0.149259	26 C 0.018513	41 O -0.380327
12 H 0.147576	27 H 0.158028	42 O -0.378127
13 H 0.150862	28 C -0.253443	
14 C -0.460710	29 H 0.142596	
15 H 0.149469	30 H 0.141169	

According to the values in Table 2, the nucleophylic centers of the molecule are N24. Possible reaction pathways for butralin are shown in Figure 3. Hydroxyl radical, a very active species, has a strong electrophilic character. It is therefore willing to attack the Butralin molecule and create reaction intermediates.

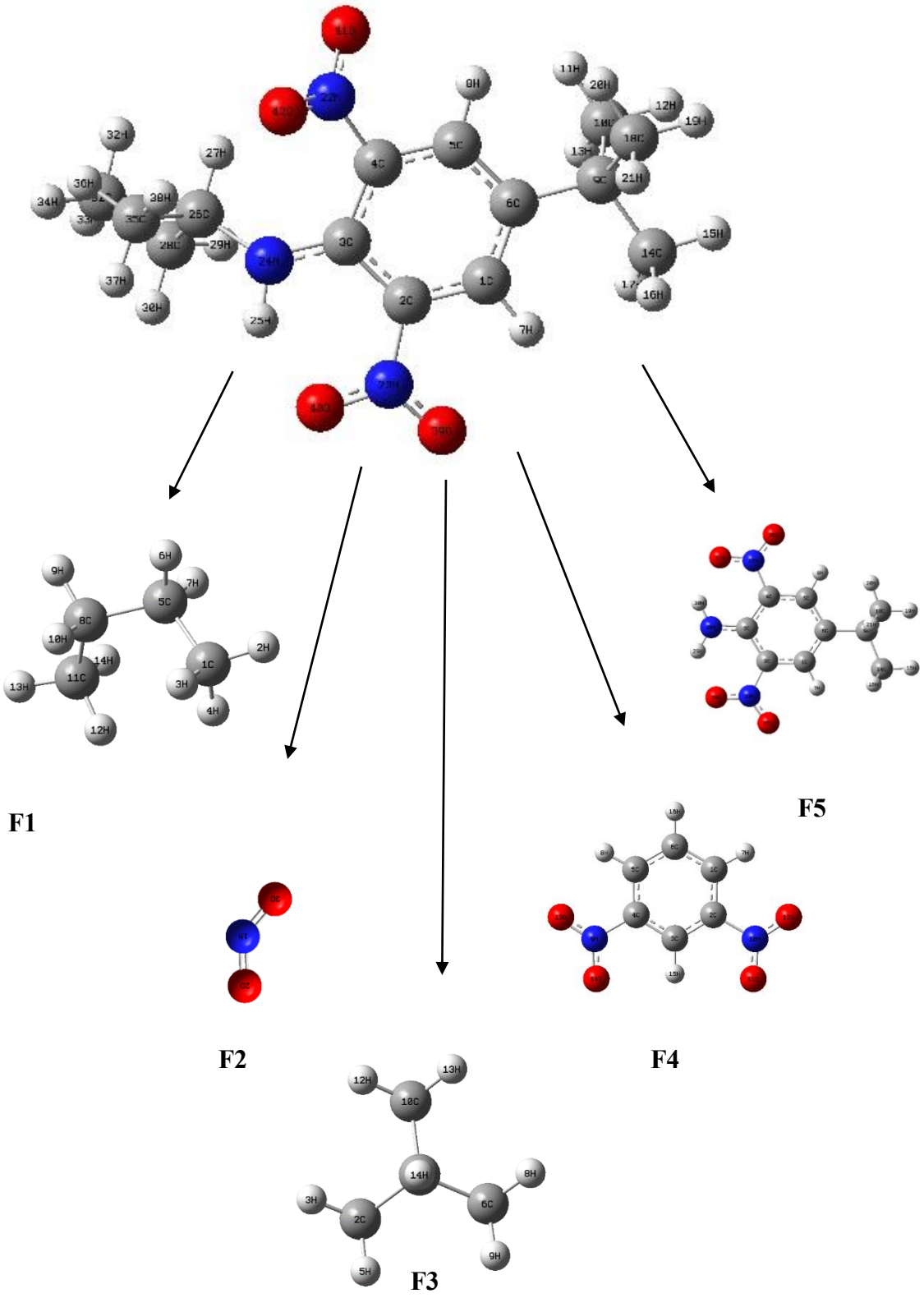
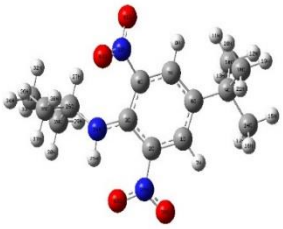
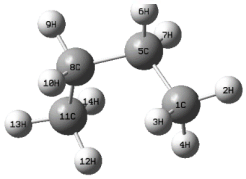
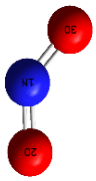
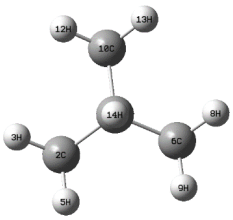
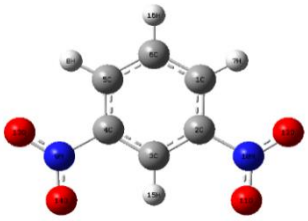
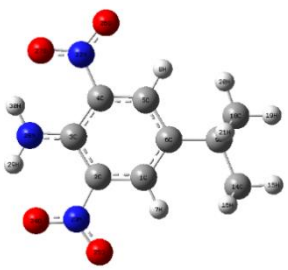


Figure 3. Possible reaction pathways of Butralin

Table 3. Energy- Enthalpy -Gibbs Free Energy of Compounds.

Compounds		Phase	ΔE Energy (kcal/mol)	ΔH Enthalpy (kcal/mol)	ΔG Gibbs Free Energy (kcal/mol)
Butralin		Gas	-634243.3262	-634242.7338	-634289.1933
		Water	*-634250.1334*	*-634249,541*	*-634296,0539*
F1		Gas	-99345.99182	-99345.39946	-99367.15708
		Water	*-99346.32566*	*-99345.73329*	*-99367.49468*
F2		Gas	-128677.2742	-128676.6812	-128693.7914
		Water	*-128678.0799*	*-128677.4875*	*-128694.5972*
F3		Gas	-99347.67292	-99347.08055	-99368.56772
		Water	*-99348.04817*	*-99347.4558*	*-99368.95489*
F4		Gas	-402315.4608	-402314.8684	-402343.9101
		Water	*-402322.0998*	*-402321.5074*	*-402350.627*
F5		Gas	-536504.651	-536504.0576	-536542.1654
		Water	*-537364.7731*	*-537364.1788*	*-537402.504*

CONCLUSIONS

Based on the data in Table 3, F5, one of the possible fragmentation paths of Butralin, has the lowest energy, that is, the most Butralin structure. This fragment occurs when the electronegative O atom breaks the ligament from the ring to which it is attached.In this study, possible reaction pathways were determined in the reaction between Butralin and OH radical. The fragmentation reaction needs energy. OH radicals are used to gradient pesticide substances in water. As seen in the resulting trailers, Butralin was reduced to F5 and became harmless to the environment. Our goal was to break down the pesticide substances that blend into the waters to the smallest substances that are harmless and remove the toxic effect from the waters. As the results show, this fragmentation was theoretically realized.

Acknowledgements

The authors greatly appreciate Tekirdag Namik Kemal University Research Foundation for financial support. Project number: NKUBAP.01.GA.20.260.

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