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Computational examination of degradation reactions of Buprofezin

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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 Gaussian 09 package program. DFT method was used in the theoretical study. In this study, possible reaction paths in the reaction between pesticide substances and OH radical were determined. Fragmentation reaction requires energy; OH radicals are used to degrade pesticide substances. The lowest energy molecule has the most stable structure. According to *this*, when we list the pesticide substances and fragments from the most stable to the most unstable, they are F4, F2, F1, F3, Buprofezin. These results will guide experimental workers and determine the mechanism of fragmentation.

Keywords: Gaussian 09, DFT, Pesticide, Buprofezin.

INTRODUCTION

Due to the rapid increase in the world population and the decrease in natural resources as a result of population growth, various chemicals are used against pests such as insects, pathogenic organisms and weeds that will reduce yield, in order to increase agricultural production. Pesticides are among the most preferred chemicals. Many pesticides harm nature during production or use; they can mix with the atmosphere, soil and water resources.

Due to the increasing environmental pollution and climate crisis in the world, production activities have to be planned and implemented in a way that is sustainable and does not harm the environment. The methods used in agricultural production should be planned in a way that does not threaten human and environmental health [1]. If pesticides are used, it is of great importance to carry out qualitative and quantitative analyzes in soil and water resources. If the amount of pesticides does not exceed tolerance limits that will not adversely affect human health. and if it is above tolerance limits, it is of great importance to remove them from water and soil resources.

In addition to the residual chronic toxicity of pesticides, some of them have been found to have mutagenic, teratogenic and carcinogenic effects in humans in recent years. Pesticide deposits on plants, on the other hand, can sometimes pass to humans and animals through food, causing sudden poisoning, cancer, even dangers to genetic structure [2]. Behavior of pesticides in nature; degradation by soil microorganisms, chemical degradation (e.g. hydrolysis). adsorption and binding by organic and mineral soil. uptake by plant roots, evaporation, diluting effects of water flow processes [3]. Buprofezin is an insecticide with a thiadiazine structure. It acts by inhibiting chitin biosynthesis and subsequent cuticle deposition. It also has effects on the hormone levels of nymphs associated with moulting and on prostaglandin synthesis. It is not translocated in plants. It is for use on citrus fruit, tomato and lettuce [4]. The liver might be one of the major organs where Buprofezin accumulates and could represent the origin of an oxidative stress response following oral exposure to Buprofezin. During this process, Buprofezin at sublethal concentrations inhibited ATP production by promoting the conversion of energy metabolism from the aerobic TCA cycle and oxidative phosphorylation to anaerobic glycolysis [5].

The aim of this study is to computationally examine the degradation reactions of the pesticide molecule Buprofezin to remove it from water sources and convert it into harmless molecules.

METHODOLOGY

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 Gaussian 09 package program. DFT method was used in the theoretical study.

In this study, possible reaction pathways of the Buprofezin molecule were examined. For this purpose, Buprofezin was subjected to geometric optimization of its molecule and the most appropriate quantum mechanical method was determined. Possible products were theoretically predicted and calcular examinations were carried out.

Calculations of the most durable comforters of

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the Buprofezin molecule were carried out using DFT/B3LYP/6-31G(d) methods. All molecular orbital calculations were used in Gaussview5 molecular representation program and Gaussian 09W program [6].

The energy of the fragmentation reactions of all organic compounds is affected by water molecules in the aqueous environment. In addition, geometric 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 in order to explain the solvent effect of H_2O on Buprofezin molecule to explain the solvent effect on Buprofezin + ·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 [7].

RESULTS AND DISCUSSION

Fig. 1 shows the optimized geometric molecular structure of Buprofezin electronegative atoms attached to molecules; O. N. S are shown in color. The bond lengths, bond angles and Mulliken charges of molecules in Table 1 give preliminary information about the fragmentation sites of molecules.

When the Mulliken loads of the molecules in Table 1 are examined, the atoms with the highest electronegativity N_3. N_{20}. N_{21}. O_2 are written in bold in the table.

Electrochemical calculations in gaseous and aqueous phase were analyzed for each molecule. The ΔE energy. ΔH enthalpy and ΔG Gibbs free energy values in Table 7 are given separately for each molecule. When the Gibbs free energy values of ΔG were examined, it was seen that the ΔG value of each fragmentation was negative. Thus, we list the pesticide molecules from the most stable to the most unstable.

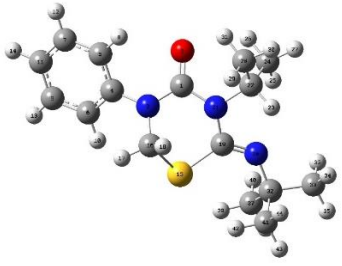


Figure 1. Optimized geometric structure of Buprofezin *via* DFT method. (grey. C; white . H; blue. N; red. O; yellow. S).

When the Mulliken loads of the Buprofezin molecule in Table 1 are analysed. the electronegative atoms are N_3. O_2. N_{20}. N_{21}, respectively. As it can be seen in Figure 1. O_2 and N_{20} form a double bond with C_1 and C_{19} atoms. Since these bonds are stable, the bonds are not expected to break. N_{21}. O_2 atoms are the second and third electronegative atoms.

Buprofezin's most durable geometric structure is optimized with DFT/B3LYP/6-31G(d) methods. As a result of DFT calculations, Buprofezin's total energy in the gaseous phase is -791189 kcal mol^{-1}, enthalpy -791189 kcal mol^{-1}, Gibbs free energy -791234 kcal mol^{-1}. In addition, the total energy in the aqueous phase, enthalpy and Gibbs free energy are -791196 kcal mol^{-1}, -791195 kcal mol^{-1}, -791241 kcal mol^{-1}, respectively. Optimized with DFT/B3LYP/6-31G(d) methods, Buprofezin's geometric structure is shown in Figure 1 and geometric parameters are shown in Table 2.

Bond lengths of N_3-C_4 and N_{21}-C_{22} in Table 2 are 1.43 Å; 1.50 Å, respectively, and the bond angle of C_{19}-N_{20}-C_{32} is 128.98^0, while the bond angle of O_2-C_1-N_3 is the second widest bond angle with 122.62^0. Based on this information, it is expected that the methyl groups of C_4 and C_{22} atoms will break. So it is understood that this is the first stage of degradation mechanism. N_3 is the most electronegative atom. Looking at the area surrounded by this atom in Table 2, N_3-C_4 with a bond length of 1.43 Å although the N_3 atom is the most electronegative atom. Since there are bonds longer than this bond length, it is predicted that if there is a bond break here, it will happen after the other bonds. Even the fact that the bond angles N_3-C_4-C_5 and S_{15}-C_{19}-N_{21} in Table 2 are the widest ones, 120.79; 115.02, respectively, this will not change the situation. Buprofezin's fragments geometric structure and geometric parameters are shown in Tables 3-6.

The ΔE, ΔH and ΔG values in Table 7 are given separately for each molecule. Looking at the data in Table 7, fragment 4 (F4) of Buprofezin has the lowest energy. In other words, it has the most stable structure. This fragment is formed by bond breaking from the ring to which the electronegative N atom is attached.

In this study, possible reaction paths in the reaction between Buprofezin and OH radical were determined. The degradation reaction requires energy. OH radicals are used to degrade pesticide substances in water. As seen in the fragments obtained, Buprofezin was reduced to F4 and became harmless to the environment. Our aim was to break down the pesticides that are mixed with water down to the smallest harmless substances and remove their toxic effect from water. As can be seen from the results, this fragmentation took place theoretically.

Table 1. Energy values of Buprofezin in gaseous and aqueous phases. and their Mulliken loads at gaseous phase.

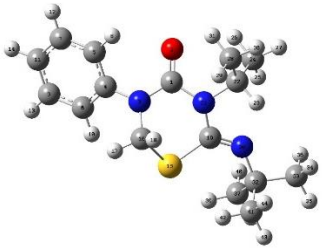
Buprofezin ($C_{16}H_{23}N_3OS$)	Gaseous Phase (kcal × mol^{-1})	Aqueous Phase (kcal × mol^{-1})	Mulliken Loads
	ΔE= -791189	-791196	**O_2 -0.508933**
	ΔH= -791189	-791195	**N_3 -0.525537**
	ΔG= -791234	-791241	C_6 -0.020480
			C_7 -0.010742
			C_9 -0.007077
			N_{20} -0.445599
			N_{21} -0.521956
			C_{28} -0.002347
			C_{33} -0.005052
			C_{37} -0.000872
			C_{41} -0.001032

Table 2. Bond lengths and bond angles of atoms of Buprofezin molecule.

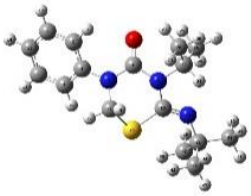
Buprofezin ($C_{16}H_{23}N_3OS$)	Bond Length	(Å)	Bond Angle	(º)
	C_1-O_2	1.22	O_2-C_1-N_3	**122.62**
	N_3-C_4	**1.43**	N_3-C_4-C_5	120.79
	N_3-C_{16}	1.44	N_3-C_{16}-S_{15}	110.96
	S_{15}-C_{19}	1.82	S_{15}-C_{19}-N_{21}	115.02
	C_{16}-S_{15}	1.83	C_{16}-S_{15}-C_{19}	95.23
	C_{19}-N_{20}	1.26	C_{19}-N_{20}-C_{32}	**128.98**
	N_{20}-C_{32}	1.47	N_{20}-C_32-C_{33}	105.16
	N_{21}-C_{22}	**1.50**	N_{21}-C_{22}-C_{28}	111.12

Table 3. Bond lengths and bond angles of atoms of F1 molecule.

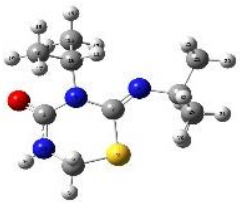
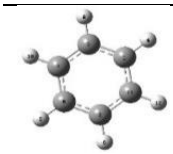
F1	Bond Length	(Å)	Bond Angle	(º)
	C_1-N_{33}	1.37	C_1-N_{33}-C_4	122.39
	O_2-C_1	1.22	O_2-C_1-N_9	123.16
	S_3-C_7	1.82	S_3-C_7-N_8	125.41
	C_4-S_3	1.84	C_4-S_3-C_7	96.17
	C_7-N_8	1.26	C_7-N_8-C_{20}	129.27
	N_8-C_{20}	1.47	N_8-C_{20}-C_{25}	112.17
	N_9-C_{10}	1.50	N_9-C_{10}-C_{16}	111.16
	C_{10}-C_{12}	1.53	C_{10}-C_{12}-H_{15}	109.43
	C_{12}-H_{15}	1.10	C_1-N_{33}-H_{34}	114.43
	N_{33}-H_{34}	1.01		

Table 4. Bond lengths and bond angles of atoms of F2 molecule.

F2	Bond Length	(Å)	Bond Angle	(º)
	C_1-C_{11}	1.40	C_1-C_{11}-H_{12}	120.0
	C_2-C_5	1.40	C_2-C_5-H_9	119.99
	C_3-C_7	1.40	C_3-C_7-C_5	119.99
	H_4-C_1	1.09	H_4-C_1-C_{11}	119.99
	C_5-H_9	1.09	C_2-C_5-H_9	119.99

For the fragments in Table 7, the energy values in the gaseous and aqueous phase were examined. The lowest energy level, in other words the degradation path, starting from the most stable fragment for Buprofezin in Figure 1, was determined both in the light of the above mentioned predictions and by the analysis of the energy values of each fragment in Table 7.

Table 5. Bond lengths and bond angles of atoms of F3 molecule.

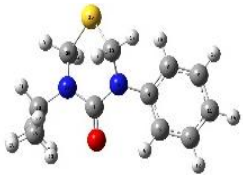
F3	Bond Length	(Å)	Bond Angle	(°)
		1.22	O_2-C_1-N_3	123.77
	N_3-C_1	1.40	C_4-N_3-C_1	122.66
	C_4-N_3	1.43	C_5-C_4-N_3	118.80
	C_5-C_4	1.40	C_6-C_9-C_{11}	120.34
	C_6-C_9	1.39	S_{15}-C_{16}-N_3	113.26
	S_{15}-C_{16}	1.85	N_{19}-C_{30}-H_{31}	108.41
	N_{19}-C_{30}	1.46	C_{20}-N_{19}-C_1	119.98
	C_{20}-N_{19}	1.49	C_{22}-C_{20}-C_{26}	112.47
	C_{22}-C_{20}	1.54		
	C_{26}-H_{28}	1.09		

Table 6. Bond lengths and bond angles of atoms of F4 molecule.

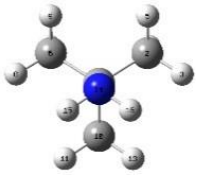
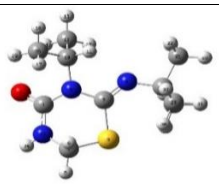
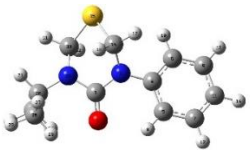
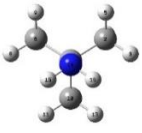
F4	Bond Length	(Å)	Bond Angle	(°)
	C_2-C_1	1.54	C_2-C_1-N_{14}	107.26
	H_3-C_2	1.10	H_3-C_2-C_1	110.92
	H_4-C_2	1.09	H_4-C_2-C_1	111.08
	H_5-C_2	1.09	H_5-C_2-C_1	110.36
	C_6-C_1	1.54	C_6-C_1-N_{14}	107.26
	H_7-C_6	1.09	H_7-C_6-C_1	111.08
	H_8-C_6	1.10	H_8-C_6-H_9	107.96
	H_9-C_6	1.09	H_9-C_6-C_1	110.35
	C_{10}-C_1	1.54	C_{10}-C_1-N_{14}	112.46
	H_{11}-C_{10}	1.10	H_{11}-C_{10}-C_1	110.79
	H_{12}-C_{10}	1.10	H_{12}-C_{10}-H_{13}	107.67
	H_{13}-C_{10}	1.10	H_{15}-N_{14}-H_{16}	105.58
	N_{14}-C_1	1.48		
	H_{15}-N_{14}	1.02		
	H_{16}-N_{14}	1.02		

Table 7. Energy values at gaseous and aqueous phase of fragments of Buprofezin molecule at ground state.

Fragments	Gaseous Phase (kcal × mol^{-1})	Aqueous Phase (kcal × mol^{-1})
 F1	ΔE = -646259.269 ΔH =-646258.677 ΔG = -646297.31	-646265.554 -646264.962 -646303.707
 F2	ΔE = -145672.145 ΔH =-145671.552 ΔG =-145692.13	-145673.825 -145673.232 -145693.807
 F3	ΔE = -658603.816 ΔH =-658603.224 ΔG =-658640.648	-658610.321 -658609.729 -658647.481
 F4	ΔE =-134065.437 ΔH =-134064.845 ΔG = -134087.851	-134068.225 -134067.632 -134090.657

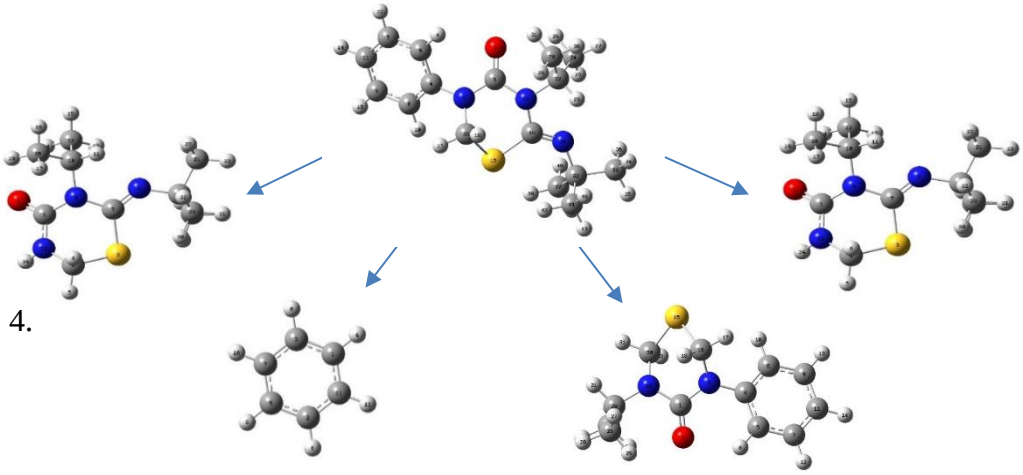


Figure 2. Optimized geometric structures of four fragments of the Buprofezin molecule. (grey, C; white, H; blue,N; red, O; yellow, S)

CONCLUSIONS

In this study, the possible reaction paths between the pesticide Buprofezin molecule and the OH radical were determined. For this purpose, geometry optimization of the molecules was made, then the most appropriate quantum mechanical method was determined and the possible products were theoretically predicted. The fragmentation reaction requires energy, OH radicals are used to degrade pesticide molecules. The lowest energy molecule has the most stable structure. Accordingly, we list the pesticide molecules from the most stable to the most unstable: F4, F2, F1, F3, Buprofezin. Our goal was to break down pesticide molecules molecules down to the smallest harmless substances. As can be seen from the results, this fragmentation took place theoretically. These results will guide experimental studies and determine the fragmentation mechanism.

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