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A comparison between different properties of bromoxynil and dichlobenil by DFT Method

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Abstract

In this work, we perform a set of quantum mechanical calculations on compounds bromoxynil and Dichlobenil. Various properties bond length, dipole moment, energy, HOMO-LUMO energy gap studied by using DFT method in Gaussian calculations. The stability and chemical reactivity have been studied.

Key words : DFT, Nitrile Herbicides, Dipole moment, HOMO-LUMO.

INTRODUCTION

Herbicides are the chemicals used to kill the plants that interfere in the growth of desired plants. Herbicides do not affect the required plants. Herbicides may be selective or non selective. Selective herbicides kill unwanted plants only whereas non selective herbicides kill all the plants in the place where it applied. After application of herbicides, different herbicides chose different mechanism for their action. Herbicides grouped in to following types on the basis of their mode of action.

- Growth Regulator Herbicides: They act as auxinic herbicides used for control of broadleaf weeds in cereal crops [1]. They mimic natural plant auxins, causing abnormal growth and disruption of the conductive tissues of the plant.

- The inhibitors of amino acid synthesis: These herbicides inhibit certain enzyme activities to the production of amino acids. Amino acids are the building blocks of proteins. Once protein production stops, growth stops [2].

- Cell membrane disrupters: These herbicides enter through leaves and damage membrane [3].

- Lipid biosynthesis inhibitor: Herbicides in this family move in both the xylem and phloem of the plant and inhibit enzymes activity in the production of lipids [4].

- Herbicides which disrupt cell division: These herbicides inhibit cell division or mitosis, except pronamide and napropamide which stop cell division before mitosis [5].

- Inhibitors of photosynthesis: They block the electron transport system of photosynthesis, causing a buildup of destructive high energy products which destroy chlorophyll and ultimately the leaf tissues [6-8].

Here two nitrile herbicides Bromoxynil and Dichlobenil will be compared by using DFT. Bromoxynil is a nitrile herbicide. It is used as post emergent herbicide for the control of annual broad leaves. Bromoxynil inhibits the process of photosynthesis by inhibiting electron transfer process in photosystem II of undesired plants [9]. As the half life period of bromoxynil in soil is few days so it is observed that bromoxynil is safe to use for broad leaf control in wheat during spring fall season [10]. Dichlobenil inhibits cellulose synthesis [11]. Dichlobenil is a pre emergence cellulose biosynthesis inhibitor used for the destruction of broad leaves weeds. The pre emergence action of dichlobenil is based on the impairment of seedling growth more than on the inhibition of seed germination [12]. Gaussian is used to study various properties of Bromoxynil (3,5-Dibromo-4-hydroxy benzonitrile)and Dichlobenil (2,6-dichlorobenzonitrile). The method opted is DFT. With this method Dipole moment, HOMO, LUMO Energy will be studied.

Effect of electronegative atoms on above mentioned properties will be studied. Effect of electronegative atoms on above mention properties is being studied.

Dipole moment decides the reactive nature of the herbicide and retention time of the agrochemical. More the dipole moment more will be the polarity and lesser will the retention time of the herbicide [13-14]. By DFT method various studies have been done. DFT is the most trustworthy method for theoretical study. The reliability has been studied for number of chemicals. The calculated values by DFT have good correlation with experimental data [15-17].

Theoretical study of bis (N-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl) ethanimidamidato) M complexes (M= Co, Ni, Cu, Zn, Pd, Cd) have been carried out for their structural electronic and optical properties [18]. Theoretical results are in good agreement with experimental data. Study of 4-(2, 3-Dihydroxy benzylideneaminol)-3-methyl-1H-1.2.4-triazol-5(4H)-one has been done by DFT computational modeling [19]

Computational Methods

We first perform the calculations to generate the structure of minimum energy using energy optimization of the compound. Energy optimization is done to get the geometrically most stable form of the compound. This calculation is done for frequency and energy optimization. The method used is DFT with basis set 6-31G/B3LYP. With this method and basis set calculations have been done for both the compounds Bromoxynil and Dichlobenil. From these calculations we infer the dipole moment, HOMO-LUMO energy. Here we will discuss the effect of electronegative atoms present in both the chemicals on above calculated

Table 1:

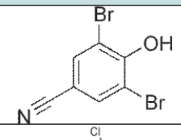
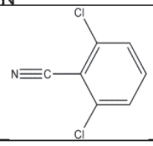
IUPAC Name of the Compound	Structure	Molecular Weight
Bromoxynil (3,5-Dibromo-4-hydroxy benzonitrile)		274.85814 amu.
Dichlobenil (2,6-dichlorobenzonitrile)		170.96425 amu.

Table 2: For the chemical Bromoxynil

Name of the bond	Bond length (before optimization)	Bond length (After optimization)
C1-C2	1.39516	1.38541
C2-C3	1.39471	1.40281
C3-C4	1.39543	1.40183
C4-C5	1.39483	1.38619
C5-C6	1.39514	1.40910
C1-H7	1.09961	1.08211
C2-Br10	1.91000	1.94682
C3-O11	1.43000	1.36677
O11-H12	0.96000	0.98130
C4-Br9	1.91000	1.92468
C5-H8	1.09976	1.08221
C6-C13	1.54000	1.42885
C13-N14	1.14660	1.17430

properties. Here the molecular structures of these two chemicals have been used as an input in Gauss View 3.09 which is based on Gaussian. The IUPAC name, structure, and molecular weight of these compounds are given in Table 1.

RESULTS

The structures of bromoxynil and Dichlobenil have been used as input for the Gaussian. First calculations have been done for optimization and frequency. The optimized structure is the structure most stable structure of that compound. The optimized structures for both the chemicals are shown in fig.1 and fig. 2. The bond lengths for both the chemicals have been calculated for normal structure and optimized structure. The bond lengths are given in Table 2 and Table 3.

Other factor affects the reactivity of chemical is energy gap of HOMO and LUMO. By using DFT method and basis set 6-31G/B3LYP energy of HOMO and LUMO have been calculated for both the chemicals is shown in table 4. The calculated values of three reactivity parameters Chemical hardness, Electronic chemical potential and electrophilicity are given in table 5.

DISCUSSION

Dipole moment has been calculated for both the compounds. The values of dipole moment have been compared with each other. The calculated values for dipole moment are given in table 4. Dipole moment explains the retention time of the agrochemical [20]. The more the dipole moment more will be the solubility of herbicide in water. Hence the chemical with more value of dipole moment will be removed easily and its contamination in soil and food materials will be less. As per results mentioned in table Dichlobenil will have less contamination in soil and food materials as compare to bromoxynil. On the other hand it is observed that more the electron withdrawing groups attached strong will be the herbicidal action. It is studied in the case of Twenty-one N-phenyl heteroarylamine analogues of fluazinam for its fungicidal action [21]. It is found that with the introduction of electron withdrawing group fungicidal effect get optimized. In both the chemicals taken electron withdrawing groups are present. In bromoxynil two bromine and one hydroxyl groups are attached and in Dichlobenil two Chlorine atoms are present. As Cl is more electronegative than Br and OH act as electron releasing

Table 3: For the chemical Dichlobenil

Name of the bond	Bond length (before optimization)	Bond length (After optimization)
C1-C2	1.39576	1.39059
C2-C3	1.39471	1.39857
C3-C4	1.39543	1.39858
C4-C5	1.39483	1.39058
C5-C6	1.39514	1.41044
C1-Cl13	1.76000	1.81123
C2-H7	1.09966	1.08229
C3-H8	1.09968	1.08416
C4-H9	1.09968	1.08229
C5-Cl12	1.76000	1.81123
C6-C10	1.54000	1.42645
C10-N11	1.14660	1.17306

Table 4 :

Name of the Compound	**Dipole moment (Debye)**	**HOMO (au)**	**LUMO (au)**	**Energy gap (ΔE)**
Bromoxynil	3.4320	-0.307	-0.195	-0.112
Dichlobenil	5.9445	-0.325	-0.195	-0.130

Table 5 :

Name of the chemical	Chemical hardness (η)	Electronic chemical potentials (μ)	Electrophilicity (ω)
Bromoxynil	0.056	0.251	0.0563
Dichlobenil	0.065	0.26	0.52

Fig. 1: Optimized Structure of Bromoxynil

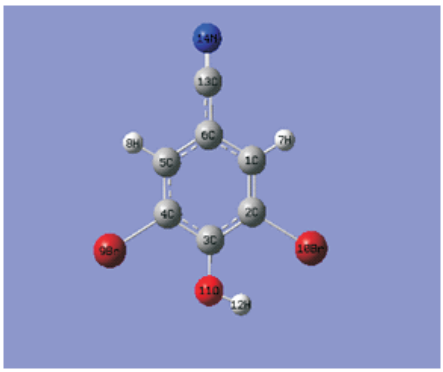


Fig. 2: Optimized Structure of Dichlobenil

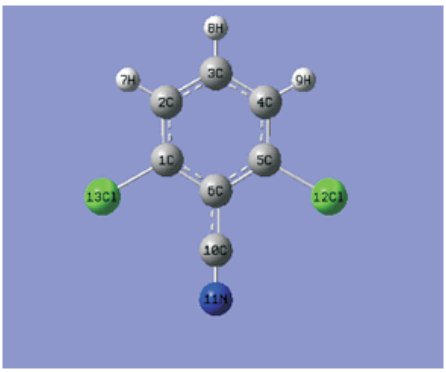


Fig. 3: HOMO Bromoxynil

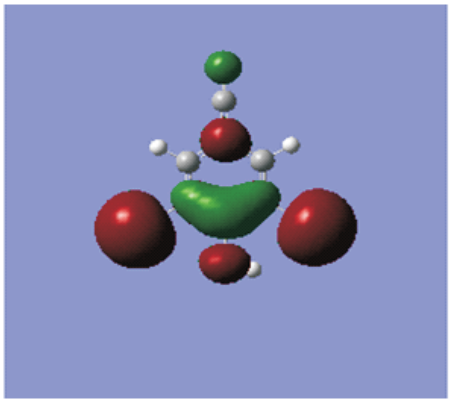


Fig. 4: LUMO Bromoxynil

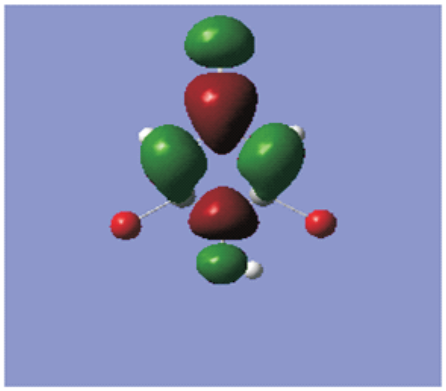


Fig. 5: HOMO Dichlobenil

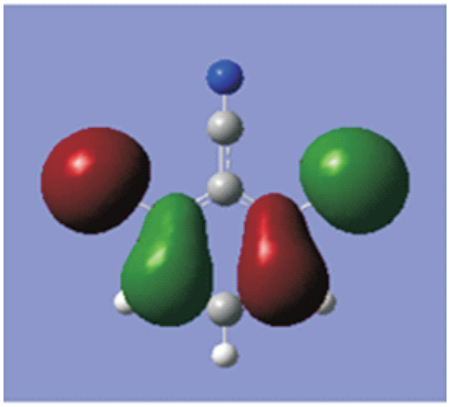
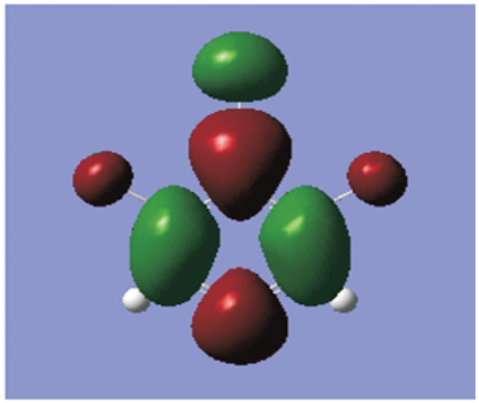


Fig. 6: LUMO Dichlobenil



group when attached to benzene ring so here dichlobenil is more effective herbicide than bromoxynil.

The HOMO-LUMO energy gap estimates the reactivity of the compounds. Here ΔE for Dichlobenil is less than bromoxynil. It shows dichlobenil requires less energy for the excitation of the electron. Here we found that dichlobenil is more reactive than bromoxynil. HOMO and LUMO structures also explain the electron density. The structures of HOMO and LUMO for bromoxynil are given in Fig 3 and Fig 4.

HOMO and LUMO energy used to measure some reactivity parameters named chemical hardness (η), electronic chemical potentials (μ) and electrophilicity (ω). All the three parameters explain the stability and reactivity of the chemical. More the value of chemical hardness less will be the stability. Smaller the value of chemical potential more will be the stability. Smaller the value of electrophilicity more will be the stability [22-23].These parameters calculated as:

Chemical hardness (η) = $1/2(E_{LUMO} - E_{HOMO})$ Electronic chemical potentials (μ) = $-(E_{LUMO} + E_{HOMO})/2$Electrophilicity (ω) = $\mu^2/2\eta$

From results it is found that the chemical hardness of bromoxynil is less than dichlobenil so here bromoxynil is more stable than and less reactive than dichlobenil. Electronic chemical potential of bromoxynil is less than dichlobenil so it is more stable and less reactive than dichlobenil. Similarly like electric chemical potential, electrophilicity of bromoxynil is less than dichlobenil so it is more stable than dichlobenil and its reactivity will be lesser than dichlobenil.

CONCLUSION

A comparative study of two nitrile herbicides has been carried out. Mode of action for both the herbicides is different. From all above calculations done by using DFT/B3LYP it is found than dichlobenil is more reactive than bromoxynil. More electronegative chlorine present in dichlobenil made it more effective than bromoxynil.

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