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Theoretical Studies on Structure of the Soil Contaminating Phenylurea Herbicides

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The use of herbicides has intensively increased mainly due to their massive pollution of the soil and environment. As these herbicides are directly or indirectly toxic to a wide range of organisms, their potential for contaminating soil, surface water and groundwater makes these xenobiotics of special interest from a health and environmental point of view. In this work, the sum of total energy (E_T), NBO charge on atoms, dipole moment, differences between HOMO and LUMO and geometrical parameters are calculated for difenoxuron (**Dif**), diuron (**Diu**), linuron (**L**) and metoxuron (**M**), at B3LYP/6-311++G (3df,2p) level of theory. Among these herbicides, linuron (**L**) is more effective and powerful, whereas metoxuron is the least effective herbicide. The highest HOMO-LUMO gap for **L** shows their high stability among these herbicides.

Key Words: Difenoxuron, Diuron, Linuron, Metoxuron, *Ab initio*, DFT calculation.

INTRODUCTION

In the past decades, the various herbicides are produced. The aim of these productions is to increase yields and improve the quality of agricultural production. These products, indispensable in a modern, profitable agricultural context, are nevertheless a major source of contamination of the natural environment, especially in intensive agricultural areas[1], but also they have relevance in the industrial emissions during their production. The biosphere has the potential for simultaneous or sequential exposure to these intentionally introduced environmental xenobiotics and is subjected to their toxic effects. Unfortunately, nontarget organisms, including humans, are affected by these compounds[2,3]. Therefore, exact knowledge of their toxic effects is a need in order to plan for environmental remediation, particularly for soils, where they accumulate. Over the past few decades, extensive work has been devoted to identify the precise biochemical mechanisms underlying insecticide toxicity. Defined acute biochemical interactions have only been assigned to organophosphorus and carbamate compounds[4,5]. Because of the lipophilicity of most of these compounds, a

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possible target of their interaction with living organisms is represented by biomembranes where they may induce physical and chemical perturbations and consequently, alterations of the native properties of biomembranes. Several studies demonstrate that insecticides induce perturbations of membrane fluidity and enzyme dynamics and that among these compounds, the most powerful toxicant is also the most effective in inducing membrane perturbations. On the other hand, the least toxic affects the membrane structure to a lesser extent. The insecticides possessing intermediate toxicity have shown to have some intermediate effects[6-8]. Phenylurea derivatives are extensively used as herbicides. These substances are well-known to inhibit photosynthesis by entering the plants *via* the root. They are principally employed for selective control of germinating grass and broad-leaved weeds in many crops, but some of them are also used for total weed control of noncultivated areas such as roads, railways and parks. In this work, theoretical studies are done on structure of the soil contaminating phenylurea herbicides. The structure of four herbicides, difenoxuron (**Dif**), diuron (**Diu**), linuron (**L**) and metoxuron (**M**), was investigated (Fig. 1).

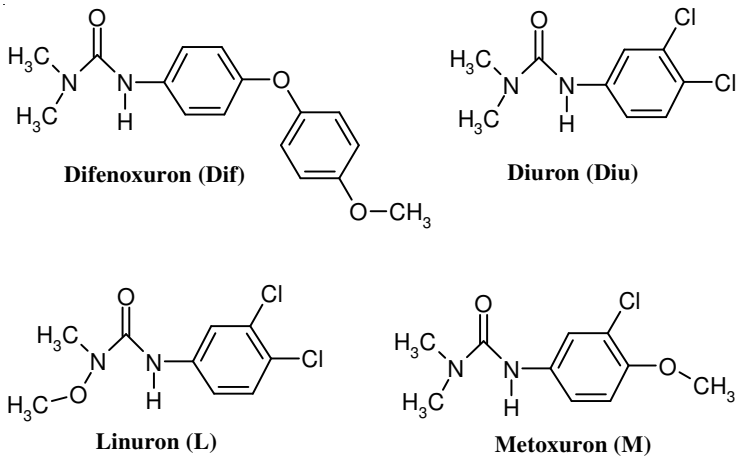


Fig. 1. Structure of difenoxuron, diuron, linuron and metoxuron

EXPERIMENTAL

The Gaussian 98 system of programs are employed for the geometry optimizations on 4 herbicides, difenoxuron, diuron, linuron and metoxuron, at B3LYP/6-311++G (3df,2p) level of theory[9-11]. The former optimized geometrical outputs are used as inputs for the B3LYP/6-311++G (3df,2p)

calculations; obtaining more accurate values of activation electronic energies (E), enthalpies (H) and Gibbs free energies (G). In order to find energy minima, keyword FOPT is used. This keyword requests that a geometry optimization be performed. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations, using redundant internal coordinates[12]. For minimum state structures, only real frequency values are accepted. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions obtained through frequency calculations are multiplied by the scaling factor of 0.89 suggested by Hehre *et al.*[13] for HF/6-311++G (3df,2p); and by 0.99 scaling factor of Rauhut and Pulay[14] for B3LYP/6-311++G (3df,2p).

RESULTS AND DISCUSSION

The structures of the four soil contaminating phenylurea herbicides are considered. The different effects exerted by these herbicides on their effective behaviour can be attributed to some particular structural features. Metoxuron, bears a chloro and a methoxy group in positions 3 and 4 of the aromatic ring, respectively, which make it different from diuron which instead bears two -Cl groups. The presence of the chlorine (the only difference between the two molecules) seems to make diuron more able than metoxuron to powerful herbicide. This is still true when linuron is considered; this molecule also possesses two -Cl groups on the aromatic ring like diuron. A comparison of the diuron and linuron structures shows that they are identical, apart from the presence of a *N*-methoxy and a *N*-methyl group on the linuron molecule instead of two *N*-methyl groups of diuron. The fact that linuron exerts a stronger effect than diuron on the effective behaviour can be related to the presence of the methoxy group. However, the different effect of linuron on effective behaviour is due not only to the methoxy group but also to its location, as difenoxuron and metoxuron also contain methoxy groups.

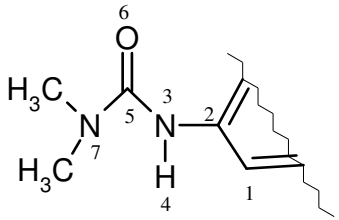
In this work, the sum of total energy (E_T), NBO charge on atoms, dipole moment and differences between HOMO and LUMO of 4 herbicides, difenoxuron, diuron, linuron and metoxuron are calculated at B3LYP/6-311++G (3df,2p) level of theory (Table-1). Geometrical parameters including bond lengths (R), bond angles (A) and dihedral angles (D) are calculated for these herbicides at B3LYP/6-311++G (3df,2p) level (Table-2, Fig. 2). The results of HF/6-311++G (3df,2p) are omitted for sake of brevity.

The negative charge on N_3 for **Dif, Diu, L** and **M** is more than on N_7 (Table-1). Lower the charge on N_7 respect to N_3 may be attributed to more conjugation of non-bonding electrons of N_7 with carbonyl group. The negative charge on N_3 decreases on going from **Dif** to **Diu** (passing through **M** and **L**), demonstrating that electron withdrawing substituents decrease the

TABLE-1
SUM OF TOTAL ENERGY (E_T), NBO CHARGE ON ATOMS, DIPOLE MOMENT (DEBYE) AND DIFFERENCES BETWEEN HOMO AND LUMO (eV) FOR DIFENOXURON, DIURON, LINURON AND METOXURON AT B3LYP/6-311++G (3df,2p)

Compound(s)	Energy (E_T)	Charge				Dipole moment	HOMO	LUMO	$\Delta_{LUMO-HOMO}$
		N_3	C_5	O_6	N_7				
Difenoxuron	-599728.499	-0.695	0.806	-0.642	-0.531	2.760	-0.212	-0.032	0.180
Diuron	-912469.625	-0.548	0.825	-0.669	-0.531	7.337	-0.229	-0.032	0.197
Linuron	-959639.021	-0.645	0.810	-0.644	-0.234	6.675	-0.234	0.010	0.244
Metoxuron	-695934.767	-0.684	0.818	-0.653	-0.531	1.947	-0.231	-0.035	0.196

TABLE-2
BOND LENGTHS (Å), BOND ANGLES (DEGREE) AND DIHEDRAL ANGLES (DEGREE) AT B3LYP/6-311++G (3df,2p) FOR DIFENOXURON, DIURON, LINURON AND METOXURON



Compound(s)	Bond length (Å)					Bond angles (º)			Dihedral angles (º)		
	C_2N_3	N_3H_4	N_3C_5	C_5O_6	C_5N_7	$C_2N_3C_5$	$N_3C_5O_6$	$N_7C_5O_6$	$C_1C_2N_3H_4$	$H_4N_3C_5O_6$	$C_2N_3C_5N_7$
Difenoxuron	1.424	1.014	1.402	1.232	1.376	127.812	119.888	122.888	50.377	9.013	45.270
Diuron	1.407	1.001	1.393	1.230	1.382	128.012	122.486	122.724	0.117	176.668	177.461
Linuron	1.405	1.013	1.375	1.225	1.411	128.028	125.536	120.314	1.200	172.110	174.699
Metoxuron	1.417	1.014	1.407	1.230	1.374	128.514	119.631	123.215	42.520	11.364	46.684

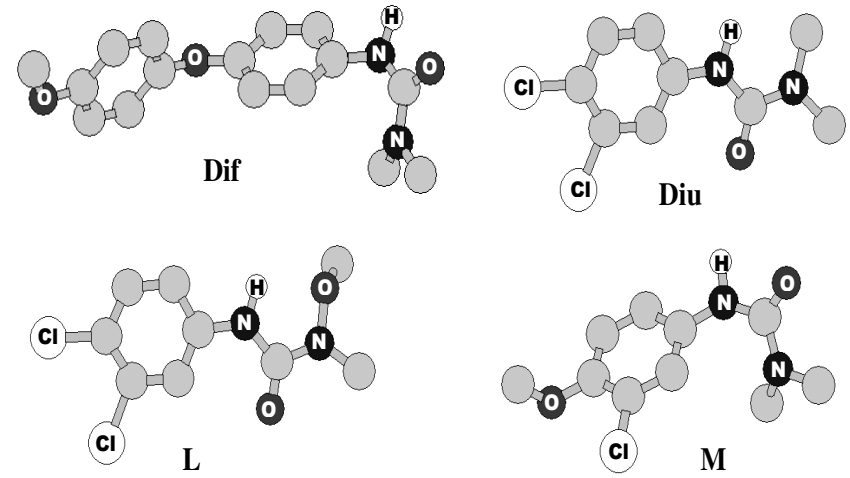


Fig. 2. Most stable conformation of four herbicides, difenoxuron (**Dif**), diuron (**Diu**), linuron (**L**) and metoxuron (**M**). Only one of hydrogen is shown

charge on N_3. The change order of negative charge on N_3 is: **Diu** (-0.548) < **L** (-0.645) < **M** (-0.684) < **Dif** (-0.695).

It was reported that among these herbicides, **L** is the most effective in perturbing the ordinate structure of vesicles forming phospholipids, effective biomembrane penetration, whereas **M** is the least effective and the others exert an intermediate effect. Despite of the highest biomembrane penetration, the high dipole moment for **L** explains that, **L** is the rather effectual and powerful among four herbicides. Also, the lowest biomembrane penetration and the lowest dipole moment of **M** lead to a powerless herbicide.

The HOMO-LUMO energy separation has been used as a simple indicator of kinetics stability (Table-2)[15]. A large HOMO-LUMO gap implies high kinetic stability and low chemical reactivity, because it is energetically favour to add electrons to a high-lying LUMO, to extract electrons from a low-lying HOMO and so to form activated complex of any potential reaction. The highest HOMO-LUMO gap for **L** shows their high stability among of four herbicides. The change order of HOMO-LUMO gap is: **L** (0.244) > **Diu** (0.197) > **M** (0.196) > **Dif** (0.180).

The bond length of C_2-N_3 is smaller for **L** and **Diu** respect to **Dif** and **M** due to presence of electron withdrawing substituent on the phenyl ring, leading more electron resonance sharing of nitrogen atom with phenyl ring (Table-2). Except for **L**, the bond length of C_5-N_7 is smaller than C_5-N_3 for **Diu**, **Dif** and **M** due to more conjugation of non-bonding electrons of N_7 with carbonyl group. Except for **L**, the bond angle of N_7-C_5-O_6 is larger than N_3-C_5-O_6 for **Diu**, **Dif** and **M** due to more steric effect of methyl groups.

Dihedral angles C_1-C_2-N_3-H_4, H_4-N_3-C_5-O_6 and C_2-N_3-C_5-N_7 of **Dif** and **M** as well as **Diu** and **L** are similar. With respect to dihedral angles, the most stable conformer of **Dif** and **M** is non-planar while the most stable conformer of **Diu** and **L** is planar (Fig. 2).

Conclusions

The sum of total energy (E_T), NBO charge on atoms, dipole moment, differences between HOMO and LUMO and geometrical parameters are calculated for difenoxuron, diuron, linuron and metoxuron, at B3LYP/6-311++G (3df,2p) level of theory. Linuron (**L**) is the rather effective and powerful, while metoxuron is the least effective herbicide. The change order of HOMO-LUMO gap and/or stability is: **L** (0.244) > **Diu** (0.197) > **M** (0.196) > **Dif** (0.180).

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