

Molecular geometry, ab initio and density functional theory calculations of Linuron (3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea)

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Abstract The geometric optimization of Linuron was done in gas-phase and in water-phase with HF and DFT quantum chemical methods with 6-31G(d,p) basis sets. The electrostatic potential was calculated. It was found that the formation of hydrogen bonds gives sp^2 hybridization of the nitrogen atom bonded to the aryl substituent. The dimer was optimized in the gas-phase by HF/6-31G(d,p). The orders of the bonds and the net atomic charges of the atoms in the molecule were determined.

Key words: Linuron, quantum chemical calculations, geometry optimization, electrostatic potential

INTRODUCTION

Linuron is foliar absorbed and residual, selective systematic herbicide to control most of the annual broadleaf weeds in broadleaf crop sites. It is a representative of a large group of structurally similar herbicides [11]. They affect the light stage of photosynthesis by inhibiting the Hill reaction in the photosystem II [9] and the oxidation phosphorylation [2].

Linuron is kept in aqueous suspension which is required to be stable for at least two years. One of the main factors affecting the stability is the process of dissolution of smaller crystals and growth of larger crystals (recrystallization). The process is deterred by substances sorbing onto crystal surfaces. To find such substances, it is necessary to know the nature of their interaction with Linuron molecules placed in crystal surface. Major factors controlling this process are molecules geometry and their electron structure. Besides, the biological activity of the pesticides depends on these factors.

An effective method for studying the reaction behavior of molecules is the measuring of their electrostatic potential – $V(r)$. The electrostatic potential $V(r)$ that is created by the nuclei and electrons of a molecule in the surrounding space is given by:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (1)$$

where Z_A is the charge on nucleus A, located at R_A , and $\rho(r')$ is the electron density function calculated from the molecule wave function. The sign of $V(r)$ is a physical observable, which can be obtained experimentally by diffraction techniques as well as computationally. The electrostatic potential is widely used to predict the reactivity of numerous chemical systems in electron- and nucleophilic reactions, for studying biological systems and hydrogen bonds [8].

The aim of the present work is using quantum chemical methods to determine the geometric and electronic structure of Linuron in gas-phase and in water-phase, calculate its electrostatic potential.

COMPUTATIONAL METHODS

The full optimization of 3-(3,4-Dichlorophenyl)-1-Methoxy-1-Methyl Urea was done in gas-phase and in water-phase with Hartree-Fock (HF) and Density Functional Theories (DFT) at the B3LYP level with 6-31G(d,p) basis sets, using the Gaussian 03 software [3]. All calculations were converged to 10^{-8} a.u. Vibration frequencies were also calculated to the structures with optimized geometry and no imaginary frequency were obtained, so the stationary points correspond to the minima of the potential energy surface.

To take into account the effect of the solvent by self-consistent reaction field (SCRF) the method of Onsager was used [7]. The Onsager model places the solute in a spherical cavity within the solvent reaction field. The solvent is treated as polarizable continuum with a dielectric constant - ϵ , instead of explicit solvent molecules. The charge distribution of the solute polarizes the solvent producing a reaction potential. The reaction potential of

solvent alters the solute. This interaction is represented by a Hamiltonian containing the solvent reaction potential.

The electrostatic potential of Linuron was calculated by ab initio HF method with 6-31G(d,p) basis sets.

In order to characterize the electronic population on each atomic centre a Mulliken population analysis [6] was carried out for the Linuron.

The software packages HyperChem 5.0 [4] and Molekel 5.4 [10] were used for data preparation and visualization of the results obtained.

RESULTS AND DISCUSSIONS

The visualization of the optimized geometrical structure and atomic labeling of Linuron are presented in Fig.1.

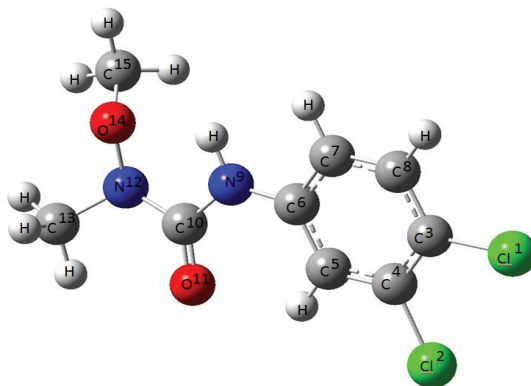


Fig. 1. Optimized geometrical structure and atomic labeling of Linuron.

The main results from the Linuron geometry optimization, the net charges of the heteroatoms and the orders of the bonds are shown in Tables 1-3.

Table.1. Optimized geometrical parameters of Linuron.

Parameters	Linuron in gas-phase		Linuron in water-phase		dimer in gas-phase	Linuron in solid-phase
	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	HF/6-31G(d,p)	Exp.[1]
Bond length (Å)						
C ¹⁰ -N ⁹	1.360	1.375	1.365	1.384	1.358	1.361
C ¹⁰ -O ¹¹	1.198	1.223	1.201	1.226	1.200	1.196
C ¹⁰ -N ¹²	1.392	1.411	1.382	1.397	1.392	1.395
C ¹³ -N ¹²	1.452	1.460	1.454	1.460	1.451	1.433
C ¹⁵ -O ¹⁴	1.410	1.433	1.415	1.439	1.410	1.417
C ³ -Cl ¹	1.735	1.749	1.741	1.757	1.737	1.690
C ³ -C ⁴	1.384	1.400	1.383	1.398	1.383	1.407
C ³ -C ⁸	1.385	1.396	1.385	1.396	1.386	1.372
C ⁴ -Cl ²	1.734	1.749	1.741	1.759	1.736	1.727
C ⁴ -C ⁵	1.387	1.395	1.385	1.393	1.387	1.353
C ⁵ -C ⁶	1.387	1.401	1.390	1.405	1.388	1.437
C ⁶ -C ⁷	1.393	1.404	1.394	1.406	1.393	1.407
C ⁶ -N ⁹	1.402	1.403	1.395	1.394	1.404	1.365

C ⁷ -C ⁸	1.376	1.388	1.376	1.387	1.377	1.363
N ¹² -O ¹⁴	1.382	1.425	1.380	1.420	1.379	1.435
Bond angle (grad)						
N ¹² -C ¹⁰ -O ¹¹	120.2	120.4	121.0	121.5	119.8	119.7
N ⁹ -C ¹⁰ -O ¹¹	125.2	125.9	124.6	125.0	125.2	125.8
C ⁴ -C ³ -Cl ¹	122.4	122.1	122.5	122.2	122.4	121.9
C ³ -C ⁴ -Cl ²	121.3	121.1	121.2	120.9	121.3	119.5
C ⁵ -C ⁶ -N ⁹	123.9	123.3	124.0	123.3	123.9	122.0
C ⁷ -C ⁶ -N ⁹	117.0	117.5	117.1	117.8	117.0	119.8
C ¹⁰ -N ¹² -C ¹³	117.4	117.3	118.0	118.5	117.4	119.5
C ¹⁰ -N ¹² -O ¹⁴	114.4	113.9	114.4	114.1	114.4	115.6
C ¹³ -N ¹² -O ¹⁴	111.3	111.1	111.7	112.1	111.2	114.9
C ¹⁰ -N ⁹ -C ⁶	127.5	127.7	127.5	127.6	126.5	126.8
C ¹⁵ -O ¹⁴ -N ¹²	110.7	109.3	111.2	110.1	111.2	109.2
Dihedral angle (grad)						
C ¹⁰ -N ¹² -O ¹⁴ -C ¹⁵	120.2	122.7	123.3	126.8	118.5	119.1
N ⁹ -C ¹⁰ -N ¹² -C ¹³	-149.9	-149.7	-151.6	-153.1	-152.8	-157.5
O ¹¹ -C ¹⁰ -N ¹² -C ¹³	32.7	33.5	30.7	29.8	29.7	27.0
C ¹³ -N ¹² -O ¹⁴ -C ¹⁵	-103.8	-102.2	-99.4	-95.1	-105.6	-95.3
C ⁶ -N ⁹ -C ¹⁰ -O ¹¹	0.6	1.3	0.5	0.5	5.2	-0.6
C ⁶ -N ⁹ -C ¹⁰ -N ¹²	-176.7	-175.3	-177.0	-176.5	-172.1	-175.7
C ⁸ -C ³ -C ⁴ -Cl ²	179.9	-179.9	180.6	-179.9	-179.9	179.4
N ⁹ -C ¹⁰ -N ¹² -O ¹⁴	-16.8	-17.5	-17.1	-17.6	-19.7	-13.6
O ¹¹ -C ¹⁰ -N ¹² -O ¹⁴	165.8	165.7	165.3	165.1	162.8	170.9

The results obtained from the geometry optimizations of Linuron in gas-phase and in water-phase cannot be verified experimentally. Only the solid state structure was studied by X-ray diffraction [1]. The fragment O¹¹C¹⁰N⁹N¹² is planar (within accuracy of 2 grad). The angles at N¹² showed that their structure is pyramidal. The orders of the bonds C¹⁰-N⁹ and C¹⁰-N¹² are 1.27 and 1.20 Å, respectively (Table 2) which indicates that the orientation of the electron couple allows conjugation with C=O. Such effect of conjugation was observed also between the chlorine atoms and the benzene ring.

Table.2. Bond orders of Linuron.

Bond	Bond order	Bond	Bond order
C ¹⁰ – O ¹¹	2.09	C ⁵ – C ⁴	1.44
C ¹⁰ – N ⁹	1.27	C ⁴ – C ³	1.43
C ¹⁰ – N ¹²	1.20	C ⁴ – Cl ²	1.20
N ¹² – O ¹⁴	1.20	C ³ – Cl ¹	1.19
O ¹⁴ – C ¹⁵	1.13	C ³ – C ⁸	1.43
N ¹² – C ¹³	1.07	C ⁸ – C ⁷	1.50
N ⁹ – C ⁶	1.14	C ⁷ – C ⁶	1.39
C ⁶ – C ⁵	1.42		

Fig.2 shows the molecular electrostatic potential of Linuron calculated by ab initio HF method with 6-31G(d,p) basis sets in gas-phase. The red colored surface areas show the most negative molecular electrostatic potential while dark blue areas – the most positive one. It can be seen that there is a prerequisite for the formation of hydrogen bond N – H.....O. Similar phenomenon was observed also in non-substituted carbamide [5]. There, the crystallization is a result from the formation of hydrogen bonds. With crystalline Linuron, there is a π-π interaction between the benzene rings situated one above the other together with the formation of hydrogen bonds.

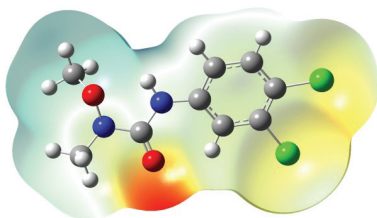


Fig. 2. Calculated HF/6-31G(d,p) electrostatic potential on the 0.001 electrons/bohr³ molecular surface of Linuron.

To inspect the influence of hydrogen bonds in Linuron geometry, the dimer was calculated by the ab initio HF method with 6-31G(d,p) basis sets. The optimized dimer geometry is presented in Fig.3 and the results from its geometry optimization – in Table 1. The participation of hydrogen atom in a hydrogen bond indicates that the atom N⁹ is with sp² hybridization.

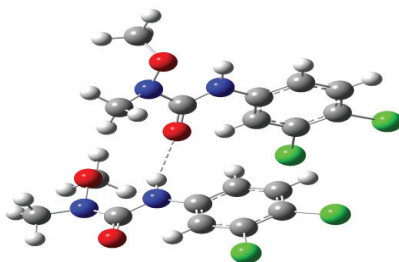


Fig. 3. Optimized geometry of the dimer.

The quantum-chemical calculations provide possibility to estimate the net atomic charges - q localized at the corresponding atoms as a result of the redistribution of the electrons in the molecule. Despite that they are neither experimentally observed nor connected with some physical property, they allow revealing the distribution of electron density in a system of interconnected atoms and predicting some chemical properties of the molecule. The net atomic charges were obtained by the Mulliken population analysis [6] with Hartree-Fock (HF) and Density Functional Theories (DFT) methods with 6-31G(d,p) basis sets.

Table 3. Mulliken atomic charges of Linuron.

atom	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	atom	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
C ³	-0.159	-0.091	O ¹¹	-0.627	-0.523
C ⁴	-0.139	-0.112	N ¹²	-0.365	-0.260
C ⁵	-0.114	-0.070	C ¹³	-0.131	-0.166
C ⁶	0.339	0.328	O ¹⁴	-0.514	-0.407
C ⁷	-0.189	-0.127	C ¹⁵	-0.004	-0.057
C ⁸	-0.098	-0.074	Cl ¹	0.041	0.007
N ⁹	-0.856	-0.666	Cl ²	0.034	0.015
C ¹⁰	1.04	0.787			

The net atomic charges of the heteroatoms (Table 3) show that the highest electron density is located at the nitrogen atom bonded to the benzene ring. It indicates that the conjugation of the free electron couple with the ring is comparatively weak which was confirmed also by the value of the order of the bond N⁹-C⁶ (Table 2). The Mulliken population analysis shows charge transfer from the chlorine atoms to aromatic ring.

CONCLUSIONS

The geometric parameters were determined – lengths, angles and bond orders, as well as the net atomic charges of Linuron in gas-phase and in water-phase by Hartree-Fock (HF) and Density Functional Theories (DFT) at the B3LYP level with 6-31G(d,p) basis sets. The electrostatic potential was calculated. It was found that hydrogen bonds are formed which results in sp^2 hybridization of the nitrogen atom bonded to the aryl substituent. The molecule of the dimer was optimized in gas-phase by HF method with 6-31G(d,p) basis sets.

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