Research Article

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Theoretical Study of the Reduction Reaction and Conformational Analysis of Paraquat by Density Functional Theory

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Abstract

Calculations of the reduction reaction and conformations of the paraquat have been studied theoretically within the method of density functional theory using the B3LYP functional and 6-31++G(d,p) basis sets. Through of the conformational analysis it was possible to evaluate the relative stability of the conformational isomers obtained by rotating around the C4C3 bond, from systematic variations of the C17C4C3C2 dihedral. The paraquat is found to be twisted about the inter-ring bond. With results of lowest unoccupied molecular orbital and natural bond orbital atomic partial charges it was possible to identify the atoms N7 or N19 as is the most likely region for reduction and a mechanism has been proposed.

Key words: *DFT; Paraquat; Reduction; Conformational*

Abbreviations: HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; DFT: density functional theory; HF: Hartree Fock; NBO: natural bond orbital; B3LYP: Becke, three-parameter; EA: electron affinity; ESCF: self-consistent field energy.

Introduction

The modern agriculture is heavily dependent on the use of pesticides as protective agents against all sorts of plant diseases. The paraquat (1, 1'-dimethyl-4,4'-bipyridylium ion) whose molecular structure is shown in Figure 1 is the most toxic herbicide, the third most widely used in the world, almost more than 120 countries and used for more than 50 plants for both terrestrial and aquatic [1, 2, 3].
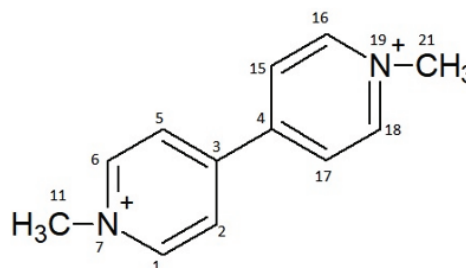

Figure 1: Structure of the paraquat.

Conformational analysis is the study of molecular conformations and their influences on the physicochemical properties of this molecule. This analysis is usually done by performing a rotation around a single bond, varying the dihedral angle of the bonds. The conformational preference of bipyridiniums depend on electronic structure [4] and according to Calderbrank [5] has been implicated as a property which determines their suitability as electron relays.

Through the atomic charges and frontier molecular orbitals: HOMO and LUMO [6], giving an estimate of likely atoms involved process of oxidation or reduction, and represent the ability of a chemical to donate or accept electrons. The HOMO energy is directly related to the ionization potential, while the LUMO energy is related to the electron affinity.

We conducted DFT conformational analyses and calculations of determining exactly the atoms where occurs the reduction the likely mechanism of paraquat. A theoretical study similar was used successfully on the proposition of the mechanism of reduction of berenil [7].

Computational Details

All Calculations on the paraquat molecule in the ground state and reduced form have been performed using DFT with the B3LYP functional [8, 9] and the 6-31+G(d,p) basis set as implemented in the Gaussian 09 program [10].

The electron affinity can be obtained by two procedures: the first through Koopmans' theorem states that the EA [11] can be expressed in terms of the ELUMO (Eq. 1) and the second through ΔESCF method [12] (Eq. 2).

$$EA = -E_{LUMO}, \qquad (1)$$

$$EA = E_{SCF} (N \text{ electrons}) - E_{SCF} (N + 1 \text{ electrons}), \qquad (2)$$

Results and Discussion

Geometric analysis

The optimized energy (total energy of the paraquat) calculations, in atomic units is -574.6903186. The most stable state that the total energy from HF and DFT calculations (-570.966455395 a.u and -569.609154759 a.u respectively) obtained of Kreisig [3].

The geometric optimization is an important step for obtaining correct of the partial atomic charges, frontier molecular orbitals and

conformers isomers. The Table 1 shows the molecular geometry parameter of the paraquat. The calculated bond length (in Å) and bond angles (in o) is in a good agreement with the experimental values [13].

Parameter	Bond length	Experimental
N7-C11	1.49	1.47
N7-C6	1.35	1.36
N7-C1	1.35	1.34
C6-C5	1.39	1.37
C5-C3	1.40	1.38
C3-C2	1.41	1.41
C2-C1	1.38	1.38
C3-C4	1.49	1.49
C4-C15	1.40	1.38
C15-C16	1.39	1.37
N19-C16	1.35	1.36
N19-C18	1.35	1.34
N19-C21	1.49	1.47
C18-C17	1.38	1.38
C17-C4	1.41	1.41
Parameter	Bond angle	Experimental
N7-C6-C5	121	119-121
C6-C5-C3	120	119-122
C5-C3-C2	118	117-120
C3-C2-C1	120	119-122
C2-C1-N7	121	119-121
C6-N7-C1	120	119-123
N19-C16-C15	121	119-121
C16-C15-C4	120	119-122
C15-C4-C17	118	117-120
C4-C17-C18	120	119-122
C17-C18-N19	121	119-121
C18-N19-C16	120	119-123

Table 1: *Geometrical parameters calculated for paraquat.*

Conformational

The rotational energy barrier related to the rotation around the C3C4 bond was investigated in paraquat. From systematic variations of the C17C4C3C2 dihedral angle, the relative energy curve (Figure 2) showed the existence of a minimum structure (more

stable conformational isomer) and a maximum structure (less stable conformational isomer). The planar structure (0°) is estabilized by resonance interactions between the two aromatic rings and resides on top of maximum. The orthogonal structure (90°) also represents a maximum. This potential curve exhibiting a minimum at 41o very similar to 40o obtained by Kleier [4].
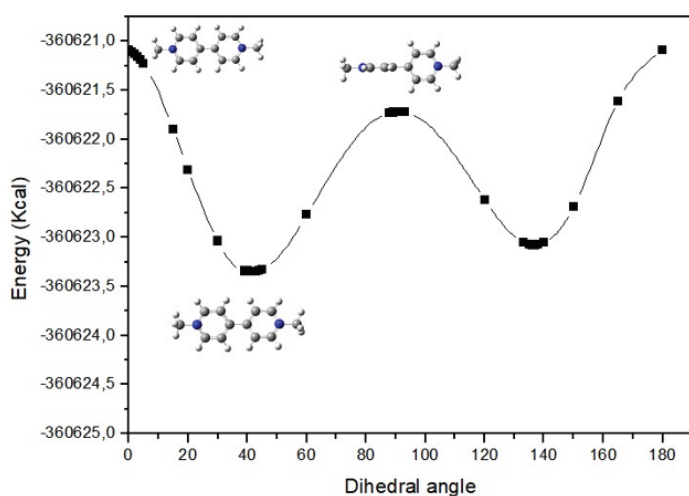

Figure 2: Torsional potential for paraquat.

Reduction Reaction

The reduction of paraquat showed a reaction with the entry 1e- [5]. An electron is added to the paraquat (charge +2) yielding reduced paraquat (charge +1).

The EA was calculated by Koopmans' theorem (-E_{LUMO} = 236.96 Kcal/mol) and by the ΔE_{SCF} method (207.74 Kcal/mol) by difference between the total energy of the paraquat (charge +2) and the paraquat (charge +1). In this case, the paraquat (charge +2) was been optimized at the same level of theory as the paraquat (charge +1). These results show the stability of the reduction reaction and according to Sadi [14] the procedure second that was chose gives more accurate results that Koopmans approach.

Kleier [4] suggest that the reduction occurs (C3-C4 carbons) of the paraquat molecule. However, they don't show the mechanism of the reduction reaction. In order to identify the most probable sites for the reduction reaction of the molecule, a LUMO contour map (Figure 3) analysis are obtained for paraquat in the ground state (charge +2).
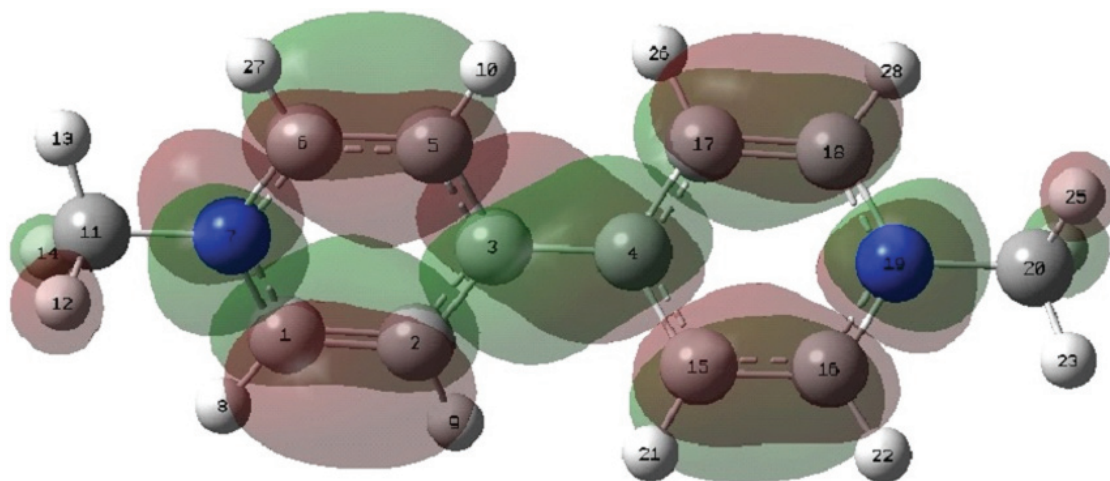

*Figure 3: LUMO contour map of the paraquat in the ground state.*

The orbital LUMO provides evidence on the sites of reduction of a molecule as this orbital is responsible for entry of electrons. As can be seen in the Figure 3, the orbitals located in the atoms C1, C2, C3, C4, C5, C6, N7, C15, C16, C17, C18 and N19 offer contributions to form the LUMO. Hence, those regions must be directly involved in the reduction process.

To realm the evidences observed from the LUMO analysis, NBO atomic charges [15] were calculated for two states paraquat: ground state (charge +2) and reduced form (charge +1). This calculation allowed evaluating the change in electron density before and after the reduction of the molecule. The values of the atomic charge calculated are indicated in Table 2.

Atoms	Paraquat (+2)	Paraquat (+1)
C1	0.09	0.03
C2	-0.21	-0.24
C3	0.01	-0.07
C4	0.01	-0.02
C5	-0.21	-0.22
C6	0.10	0.02
N7	-0.29	-0.36
C15	-0.21	-0.25
C16	0.10	0.03
C17	-0.21	-0.25
C18	0.09	0.03
N19	-0.29	-0.36

Table 2: *Calculated atomic charges for the paraquat molecule in the ground state and reduced form.*

The Table 2 shows that the inclusion of one electron in the paraquat (+2), leads to an increase in the electronic density of the atoms C1, C2, C3, C4, C5, C6, N7, C15, C16, C17, C18 and N19. As C3 and C6 atoms, are located in aromatic rings, the delocalization of charges in these regions explains the variations found out thus they are not expected to represent sites of reduction. It is also observed in Table 2 the largest variations in charge density occurred in the N7 or N19 (-0.29 in the ground state and -0.36 after reduction). Thus, in the mechanism is the entrance of an electron in the atom N7 or N19 in the sequence there is a rearrangement and the electron is then transferred to one of the pyridinium rings yelding a free radical (scheme 1).
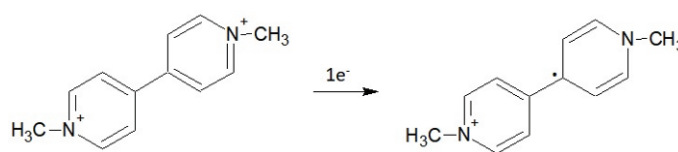
Scheme 1: *Paraquat reduction mechanism.*

Conclusion

The conformational analysis it was possible to evaluate the relative stability of the conformational isomers. These calculations conformations show preference for a twisted conformational isomer (41°) rather than a planar structure isomer.

The LUMO contour map of the paraquat and the atomic charges of the paraquat molecule in the ground state and after the reduction, reveals large variations in charge densities for nitrogen atoms, indicating these atoms as the site of reduction in the molecule. A possible mechanism for the reaction of reduction of paraquat was suggested.

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