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Stability of some Organophosphorus Pesticides in Water

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Abstract

Quantum mechanical calculations were carried out to study the molecular geometry and electronic structure of organophosphorus pesticides compounds (dichlorvos, meinphos and parathion). The parathion is more stable, needs low heat of formation, and has more activity and low toxicity compared to the others. The strongest reactivity effect with LUMO was predicted for parathion bearing the benzene ring and sulfur atom of parathion. The molecule of water shows affects on HOMO and LUMO energies. The spatial distribution of HOMO and LUMO compresses and disappears around some atoms for each pesticide due to the water effect. We have been found that only the parathion spatial distribution extends and increases in HOMO and LUMO case. Dichlorvos was more hydrolysis in water. The magnetic field strength has attenuations on the binding energies between dichlorvos and water, while due to other pesticides there increases with the meinphos and parathion.

Keywords: Pesticide, HOMO-LUMO, Toxicity, Molecular quantum, QSAR, Reactivity.

الخلاصة

الحسابات الميكانيكية الكمية نُفِّذتْ لدراسة الهندسة الجزيئية والتركيبِ الإلكتروني لمركبات المبيدات الفسفورية العضوية (دايكلورافوس، مينافوس، باراثيون). الباراثيون أكثر استقراراً، ويحتاج لحرارة تكوين قليلة، ولَه نشاطُ أكثر ومستوى سمية واطئُ مقَارن مع الآخرين. جزيئة الماء اظهرت تاثيرات علي طاقة اعلى مستوي جزيئي مملوء واوطئ مستوي جزيئي فارغ. التوزيع المكاني لاعلى مستوي جزيئي مملوء واوطئ مستوي جزيئي فارغ يضغطانِ وينتشران حول بعض الذرات لكُلّ مبيد بسبب تأثيرِ الماء. وجدنا ان التوزيع المكاني لباراثيون ممتد وزيادة في حالة اعلى مستوي جزيئي مملوء واوطئ مستوي جزيئي فارغ. دايكلورافوس كَان أكثر تحلل في الماء. قوة المجال المغناطيسي لَها تخفيض على طاقات الترابط بين دايكلورافوس وماء، بينما للمبيدات الأخرى هنالك تَزايد مع باراثيون وميناقوس.

Introduction

The use of pesticides in agriculture to boost food production is a major factor contributing to the degradation of our environment. The implementation of appropriate management strategies requires that adequate information to be developed regarding the types, physical and chemical properties, and fate and pesticides toxicity. Organophosphorus and other herbicides constitute a group of chemically similar compounds used to control certain annual broadleaf weeds and grasses in South of Iraq and throughout the world. They are used primarily in corn, but also in sorghum, sugarcane, cotton, macadamia orchards, pineapple, asparagus, other crops, and landscape vegetation, to some extent. Herbicides such as atrazine have been estimated to be the most heavily used herbicide in the United States in 1987-89, with its most extensive use for corn and soybeans in several states [R.A. Grover, 1995]. All the triazine herbicides including atrazine, cyanazine, and propazine may be released into the environment through effluents discharge from manufacturing facilities, and through their use as herbicides. Some pesticides are considered to be somewhat persistent in water, and mobile in soil. Because of their water solubility, they may leach into the ground water [E.M. Thurman *et al.*,1991, E.M. Thurman, *et al.*, 1992], as well as be transported in surface runoff [R.A. Grover, 1988]. Photo-degradation and volatilization are of little significance under most field conditions. In some countries, monitoring studies of surface waters as well as ground waters have shown widespread detection of these herbicides [E.M. Thurman *et al.,* 1991, E.M. Thurman, *et al*., 1992, R. H. Coupe *et al*., 1998, D. W. Kolpin *et al*., 1997, D. W. Kolpin *et al*., 1998, P.J. Squillace, *et al*., 1993, P.J. Squillace *et al*., 1992]. As an example, surface water test collected from 149 sites in 122 Midwestern river basins indicated that 52% of the sites exceeded the United States Environmental. The U.S. considers atrazine as a systemic toxicant that has a potential of causing a variety of acute health effects including: congestion of the heart, lungs, and kidneys, hypotension, antidiuresis, muscle spasms, weight loss, and adrenal degeneration. Upon chronic exposure, atrazine also has the potential of causing weight loss, cardiovascular damage, retinal degeneration, and mammary tumors. Similar health effects have been reported with exposure to other pesticide compounds [U.S. EPA., 1996]. Because of the increase in incidence of mammary gland tumors in female laboratory animals exposed to some kinds of herbicides and are therefore considered as possible human cyanazine, respectively. The oral reference dose is set at 0.035 mg/kg/day. In many agricultural areas, triazine metabolites and transformation products such as desethyl atrazine and deisopropyl atrazine are also commonly found in surface and ground waters, together with their parent compounds [D. W. Kolpin *et al*., 1997, Thurman *et al*., 1994. In a regional study of nine rivers in the Midwest Corn Belt, [Thurman *et al*., 1994] pointed out that desethyl atrazine and deisopropyl atrazine occur frequently in surface water that receive runoff from two parent triazine herbicides, atrazine and cyanazine. However, little is known about the toxicological effects of triazine metabolites, and how their toxicity compares to that of the parent triazines. Moreover, no conceptual model has been developed to predict the toxicity of this important group of herbicides.

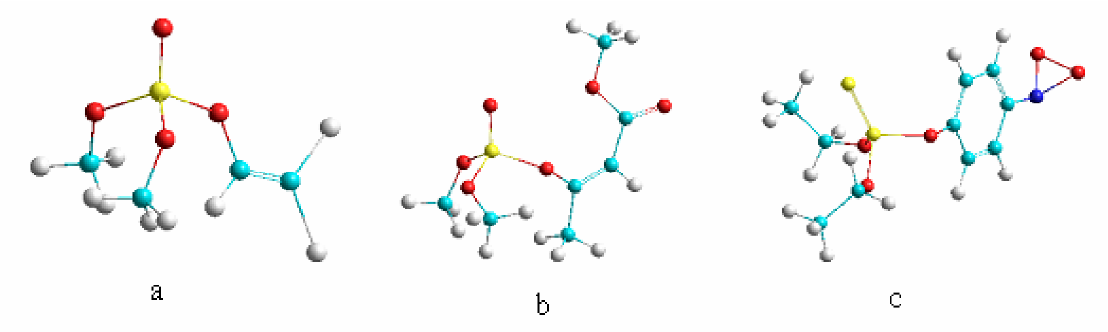
The aims of this research were to assess the relative stability of organophosphorus insecticides in water and some of their physical properties. Study the magnetic field effect on organophosphorus pesticide reactivity. Moreover, to have a theoretical protocol for the quantum mechanical estimation of pesticide for an initial recognition of the reactivity of given compounds.

Computational Details

Theoretical calculations are used to bridge gaps in understanding the experimental results. In many cases the results of the experimental methods are unable to accurately describe small components of complex biochemical system. The methods of molecular quantum mechanics can be used to investigate properties beyond the scope of current crystallographic methods. The molecular quantum mechanic provides the interaction energies that are not provided by the x-ray and NMR experiments. The theoretical methods can be used to further investigation and to predict the physical and chemical nature of hydrogen bonding interactions. To investigate the structural and electronic properties of organophosphorus, we use PM3 [J. J. Stewart, 1989]. PM3 is a semi-empirical SCF method for chemical calculations. PM3 is a reparametrization of the AM1 method [M. Dewar *et al*., 1977]. PM3 and AM1 are generally the most accurate methods in HyperChem. PM3 has been parameterized for many main group elements and some transition metals. The resolution of PM3 as implemented in the HyperChem^{TM} Release 7.52 for Windows Molecular Modeling System program package [www.hyperchem] was employed for the geometry optimizations.

Results and Discussion

Molecular quantum mechanical calculations were carried out to study the molecular geometry and electronic structure of organophosphorus pesticides compounds, see scheme 1, using the HyperChem^{TM} 7.52 package [15].



Scheme 1. Structure of organophosphorus pesticides compounds (a-dichlorvos, b-meinphos and c-parathion respectively).

Full geometry optimization was performed by the semi-empirical PM3 method at the Unrestricted Hartree-Fock level theory. The binding energy and the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and heat of formation finally were calculated LogP, see Table 1. The energy calculations of conformers (dichlorvos, meinphos and parathion) show that parathion is lower in energy than the other two pesticides, which show an increase of parathion stability and binding more than the other. The heat of formation calculations for parathion compound shows low heating to deformation comparism with other compounds. The spatial distribution and positions of HOMO (Figure 1, Figure 2 and Figure 3) and LUMO (Figure 4, Figure 5 and Figure 6) of dichlorvos, meinphos and parathion provide information on the reactivity of the pesticides. The Quantitative Structure-Activity Relationship (QSAR) was studied by semi-empirical PM3 quantum mechanical calculations. The QSAR shows that toxicity of parathion, approximately, lower than other pesticides.

Table 1. HOMO and LUMO energies, HOMO-LUMO energy gaps (ΔE_g) in eV, heat of formation, binding energy, total energy (E_T) and QSAR for dichlorvos, meinphos and parathion using PM3 method.

	dichlorvos	meinphos	parathion
LUMO (eV)	-0.32	-0.579	-2.003
HOMO (eV)	-8.979	-9.574	-9.491
ΔE_g (eV)	8.659	8.995	7.488
H.F (Kcal/mol)	-227.298	-297.428	-50.684
B. E (Kcal/mol)	-1647.357	-2603.908	-3041.777
E_T (Kcal/mol)	-57965.730	-67233.977	-76861.398
LogP	1.38	0.2	0.0

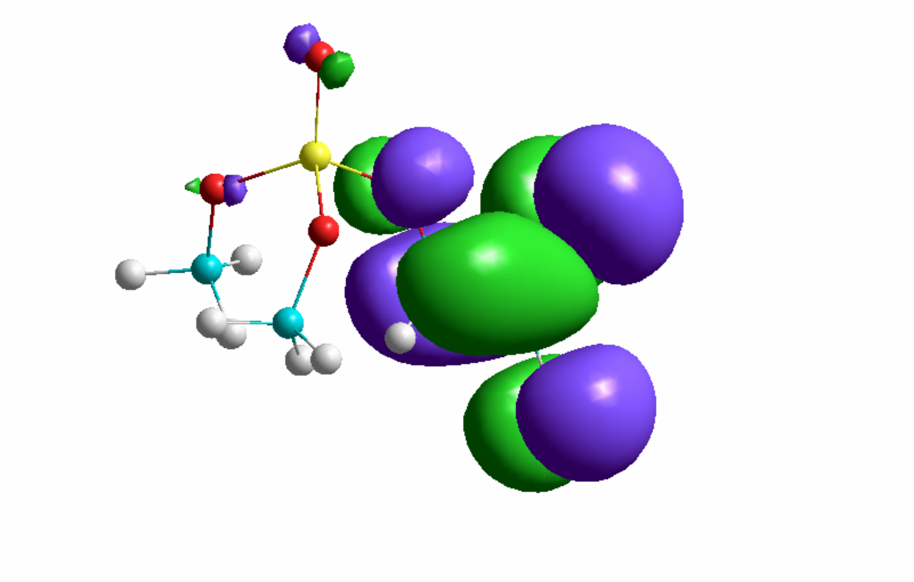


Figure 1. Optimized geometry and spatial distribution of HOMO for dichlorvos using PM3 method.

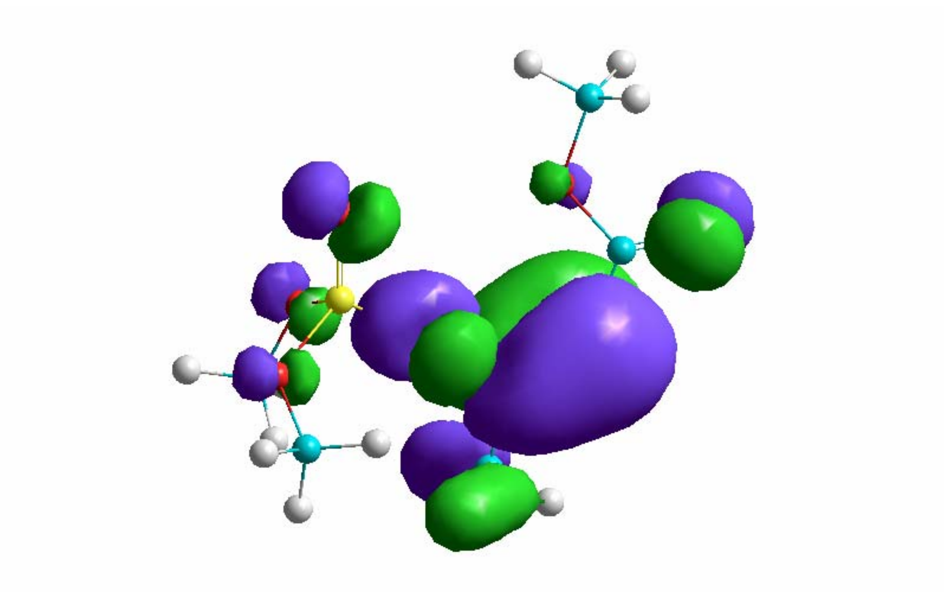


Figure 2. Optimized geometry and spatial distribution of HOMO for meinphos using PM3 method.

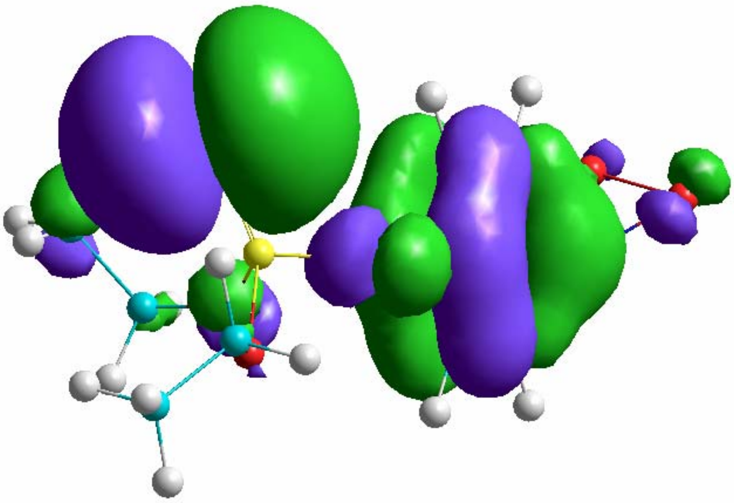


Figure 3. Optimized geometry and spatial distribution of HOMO for parathion using PM3 method.

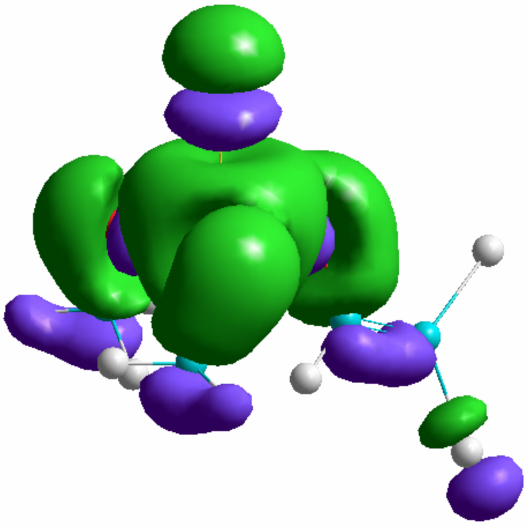


Figure 4. Optimized geometry and spatial distribution of LUMO for dichlorvos using PM3 method.

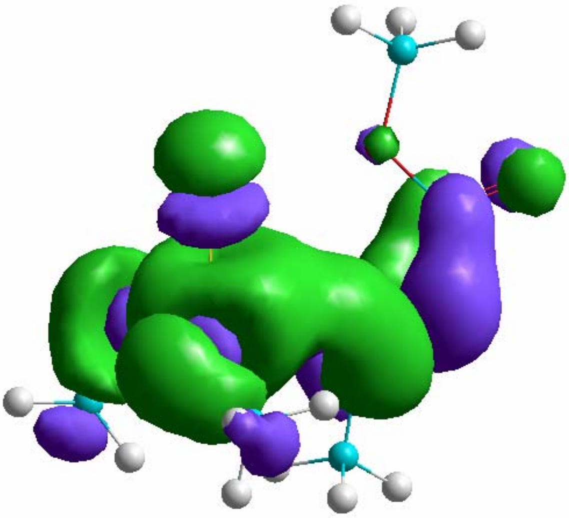


Figure 5. Optimized geometry and spatial distribution of LUMO for meinphos using PM3 method.

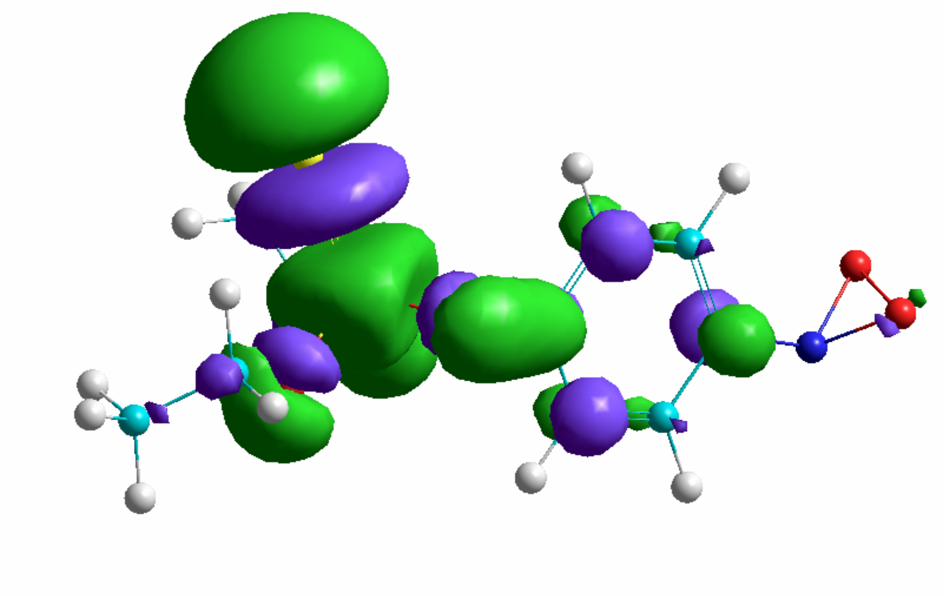


Figure 6. Optimized geometry and spatial distribution of LUMO for parathion using PM3 method.

From HOMO and LUMO energies of dichlorvos, meinphos and parathion (Table 1), the parathion shown decreased HOMO-LUMO gaps compared to the other two. Energy gap reduction is caused by a strong decrease of LUMO energies while HOMO energies increase slightly. Also the dichlorvos leads to smaller band gap than meinphos, but the LUMO energy for meinphos is lower than dichlorvos compound. One can therefore identify for parathion the low-lying LUMO, as a site will be most likely involved in reactions comparative with other compounds. Since the structure of parathion leads to strongest reactivity effect was

predicted for the benzene ring and sulfur atom of parathion if the reaction is reduced, see figure 3. The spatial distribution of LUMO, see Figure 6, was concentrated around sulfur atom of parathion and the reactivity effect, oxidation reaction, was predicted due to the sulfur atom. The geometry optimization for the three pesticide compounds with molecule of water was performed by the semi-empirical PM3 method at the UHF level of theory. The calculation results are shown in Table 2. The energy calculations of conformers show that increases in the stability of meinphos (1.796 Kcal/mol) in water then parathion (0.563 Kcal/mol) and no interested change with dichlorvos. Note that the good pesticide properties must be having low hydrolysis. The heat of formation and binding energy of meinphos shows increases compare with dichlorvos and parathion. According to these results the meinphos pesticide has poor properties comparable with other pesticides. This point leads to deduce that the meinphos has the most stability in water. The binding energy of the pesticides with molecule of water dichlorvos was estimated as $B.E^{pesticide+H_2O} = \left(E^{pesticide} + E^{H_2O}\right) - E^{pesticide+H_2O}$. The binding energy of dichlorvos with H_2O was more than other compounds, since dichlorvos more hydrolysis in water as mention above. We can note the effect of applied external magnetic field on the binding between the pesticide and molecule of water. The applied two level of magnetic field strength shown attenuations on the binding energies between dichlorvos and water, while there increases with the meinphos and parathion.

Table 2. The change in HOMO and LUMO energies, HOMO-LUMO energy gaps (ΔE) in eV, heat of formation, binding energy, total energy (E_T) for dichlorvos, meinphos and parathion with water using PM3 method.

	dichlorvos	meinphos	parathion
LUMO (eV)	-0.307	-0.497	-1.974
HOMO (eV)	-8.992	-9.672	-9.483
ΔE_g (eV)	8.685	9.175	7.509
H. F (Kcal/mol)	-227.360	-299.225	-51.243
B. E (Kcal/mol)	-1647.361	-2605.705	-3042.336
E_T (Kcal/mol)	-57965.734	-67235.773	-76861.961
B.E with H_2O	-2.585	-1.043	-1.917
B.E with H_2O*	-2.565	-1.660	-2.099
B.E with H_2O**	-2.557	-2.176	-2.224

* applied external magnetic field equal to 1.0 (a.u), ** applied external magnetic field equal to 10 (a.u).

The spatial distribution and positions of HOMO (Figure 7, Figure 8 and Figure 9) and LUMO (Figure 4, Figure 5 and Figure 6) of dichlorvos, meinphos and parathion with H_2O provide information on the reactivity of the molecules. From the comparison of HOMO and LUMO spatial distribution for each pesticide alone with same pesticide under water effect, the spatial distribution compress and disappear around some atoms according to water effect. Only the parathion spatial distribution extends and increases in HOMO and LUMO case. This may reflect that the activity of parathion pesticide increase in water.

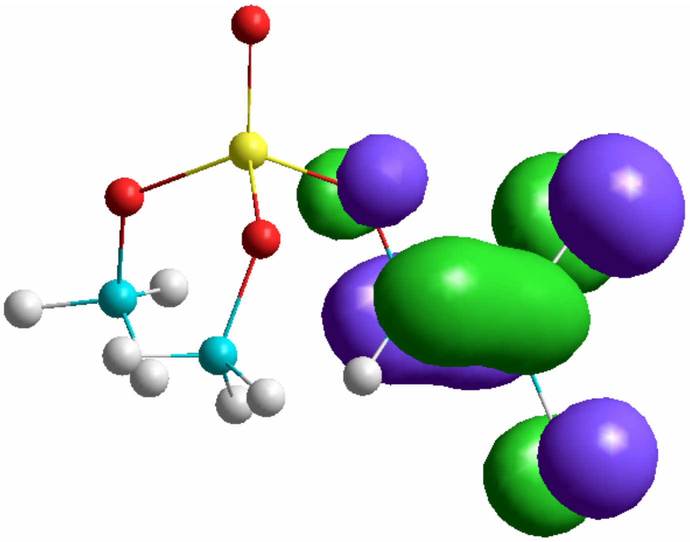


Figure 7. Optimized geometry and spatial distribution of HOMO for dichlorvos under water influence using PM3 method.

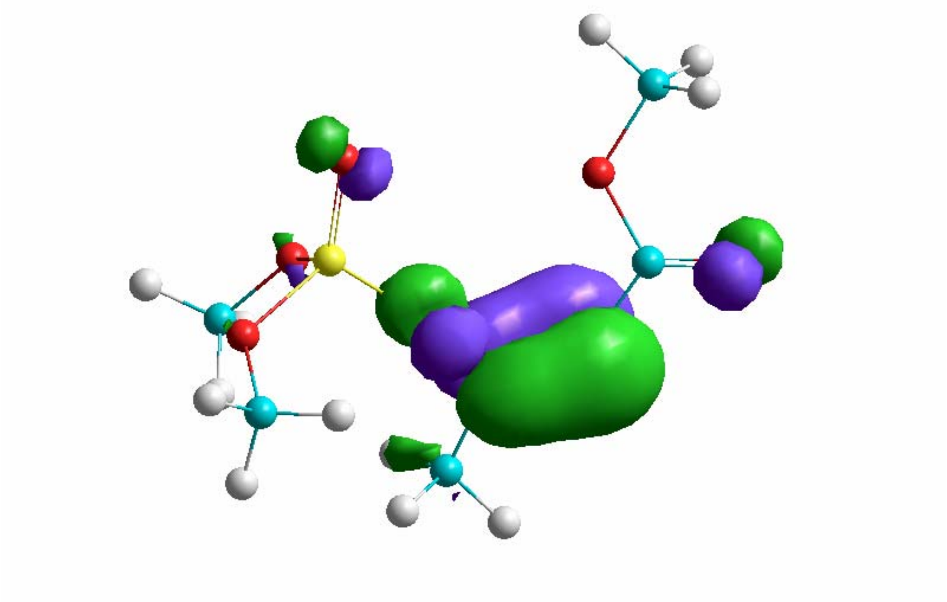


Figure 8. Optimized geometry and spatial distribution of HOMO for meinphos using PM3 method.

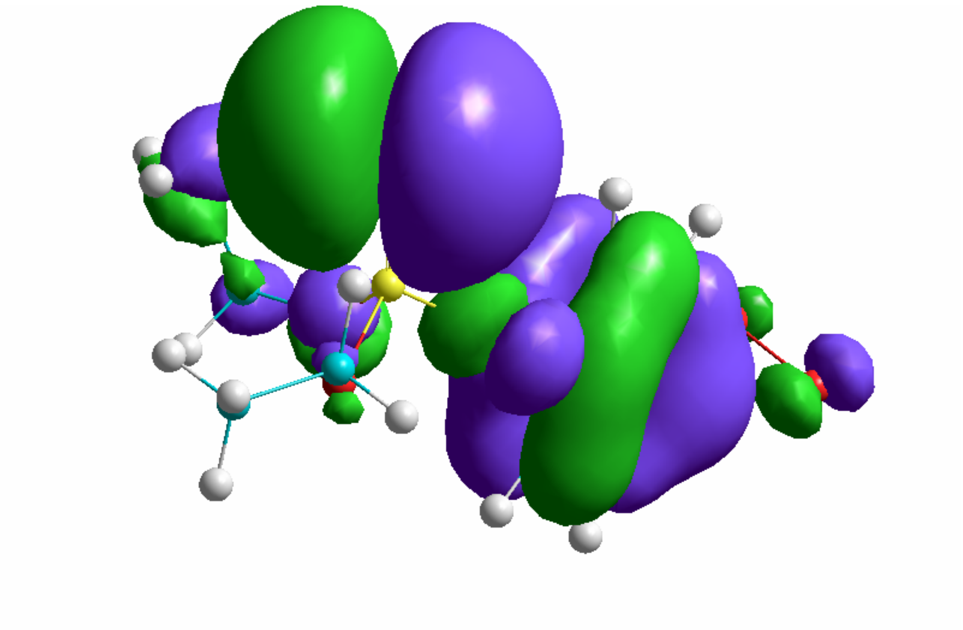


Figure 9. Optimized geometry and spatial distribution of HOMO for parathion using PM3 method.

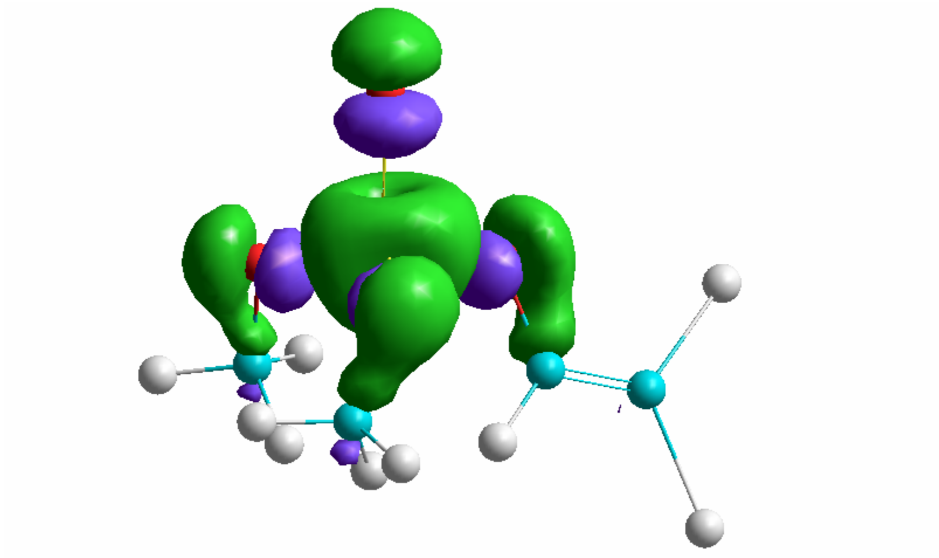


Figure 10. Optimized geometry and spatial distribution of LUMO for dichlorvos using PM3 method.

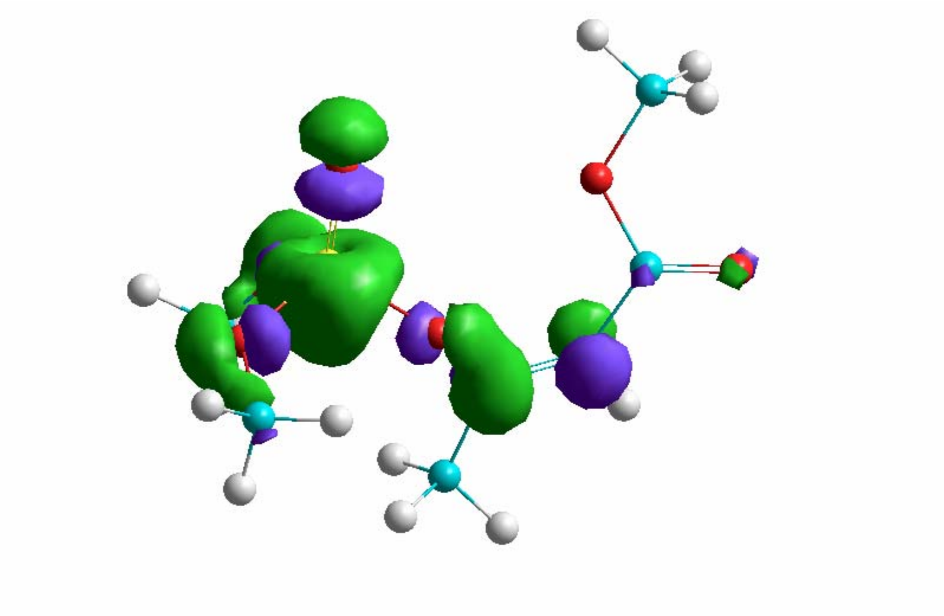


Figure 11. Optimized geometry and spatial distribution of LUMO for meinphos using PM3 method.

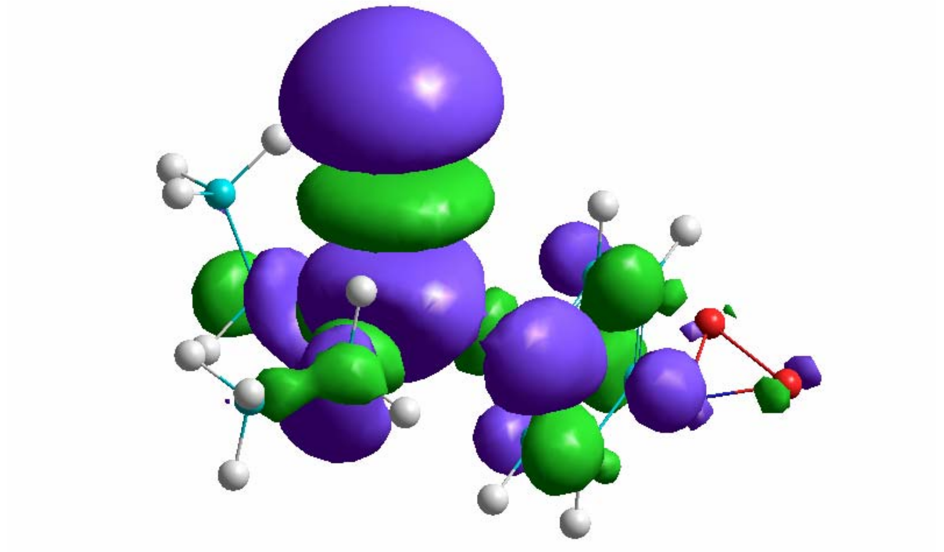


Figure 12. Optimized geometry and spatial distribution of LUMO for parathion using PM3 method.

Conclusions

Results of quantum chemical calculations provide information about the reactivity of organophosphorus pesticides (dichlorvos, meinphos and parathion). The parathion more stable, need low heat of formation, more active and has low toxicity compared with the others. The parathion has smaller HOMO-LUMO energy gap than in case of dichlorvos and meinphos. Energy gap reduction is caused by the strong decrease of LUMO energies. The strongest reactivity effect with LUMO was predicted for parathion bearing the benzene ring and sulfur atom of parathion. The molecule of water shows affects on HOMO and LUMO energies. The spatial distribution compresses and disappears around some atoms for each pesticide according to water effect. Only the parathion spatial distribution extends and increases in HOMO and LUMO case. This may be reflect that the activity of parathion pesticide increase in water. Dichlorvos was more hydrolysis in water. The magnetic field strength causes attenuations on the binding energies between dichlorvos and water, while there increases in the cause of the meinphos and parathion.

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