Commun. Comput. Chem
doi: 10.4208/cicc.2018.v6.n1.1

Vol.6, No.1, pp.1-12
Apr. 2018

REGULAR ARTICLE

Semi-Empirical and HOMO, LUMO Studies of Some Chlorinated Pesticides Compounds

Mamoun S.M. Abd El-Kareem[*], M.A. Rabbih, E.T.M.Selim

Molcular and atomic physics unit., Experimental Nuclear Physics Dept., Nuclear Research Centre, Egyptian Atomic Energy Authority, Inshas, Cairo, Egypt

Received 7 Feb. 2018; Accepted (in revised version) 10 Apr. 2018

Abstract: Theoretical studies on some chlorinated pesticides compounds namely: Heptachlor, Heptachlorepoxide and Chlordane as a first group, Aldrin and Endrin as a second group, and DDT, Methoxychlor as a third group, were performed using semi-empirical quantum chemical calculation. Modified Neglect of Diatomic Overlap MNDO method was used to investigate the effect of positional variation of chlorine and oxygen atoms on the electronic and structure properties of the studied chlorinated pesticides. The structure optimization of some electronic parameters such as heats of formation, total energies, electronic energy, binding energy, nuclear energy, ionization energies, electron affinities and dipole moment were calculated and discussed. The energy of the Highest Occupied Molecular Orbital (HOMO) and the energy of the Lowest Unoccupied Molecular Orbital (LUMO) are also calculated. The LUMO - HOMO energy gap have been calculated and discussed. The stability and activity of the studied compounds based on the obtained values have been investigated.

Keyword: Semi-empirical calculations, HOMO & LUMO calculations and chlorinated pesticides.

1. INTRODUCTION

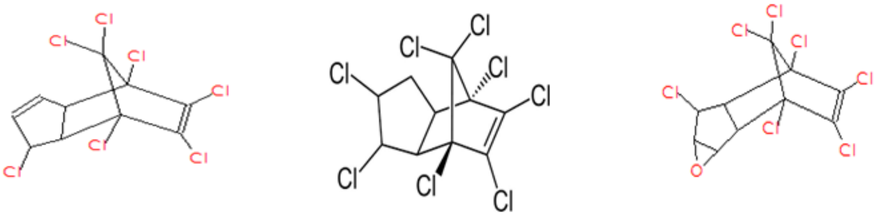
Pesticides found their way into wide applications and have played a significant part in constantly boosting agricultural and animal production. The hazards have brought along

---

[*] Corresponding author:mamoun_sarhan@yahoo.com

with them to food safety and human health has increasingly become the focus of world attention.[1-3]

Organochlorine pesticides are of great concern due to their occurrence at high concentrations in aquatic ecosystems; despite bans on production and usage.4 Many of the organochlorine compounds are substances that have high toxicity. They accumulated in organisms and biomagnified through the food chain, so consumption of fish from contaminated areas may be a real health risk for the consumers.[5]Most of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of wildlife and believed to be possible carcinogens or mutagens.[6]



Heptachloro
$C_{10}H_5Cl_7$

Chlordane
$C_{10}H_6C_{18}$

Heptachlor-
epoxide
$C_{10}H_5Cl_7O$

Figure 1: The chemical structures of Group (I).

Semi-empirical, Density Functional Theory, Molecular Mechanics and Ab-initio methods are often employed to investigate fundamental problems and to calculate geometrical and substantial parameters of theses chlorinated pesticides. These methods give information on the total energy, electron affinity, proton affinity, molecular geometry, heats of formation, charge densities, dipole moments, population analysis, chemical reaction pathways and thermodynamic properties. Semi-empirical methods provide the information of Primary calculations of different chemical properties using several methods viz. MNDO (Modified Neglect of Diatomic Overlap), AM1, PM3 and ZINDO9. [7-8]

Since the other quantum chemical calculation methods are time consuming, so, semi-empirical MNDO use with reasonably good results.[9] Also, authors have been used MNDO method in the investigation of the volatile components in basil oil and ginger extract.[10-11]

The frontier molecular orbital such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the chemical species are serious in defining organic compounds reactivity. [12-13]

Few papers are dealing with pesticides structural elucidation, understanding its structure- activity relationship using quantum chemical calculations (semi-empirical methods) to predict their physical or thermochemical properties. The work of ZHU XiuHua et al used quantum chemical descriptors computed by the semi-empirical PM6 for monitoring of organochlorine pesticides in Alps air,[14] while Aleksandra Nestorovska-Krsteska and Zoran Zdravkovski [15] were used semi-empirical (AM1 and PM3) and hybrid density functional (B3LYP) methods to study of the Diastereofacial Isomers of Aldrin and Dieldrin. Also, the mass spectra of some chlorinated pesticides compounds have been investigated by Damico et al. [16]

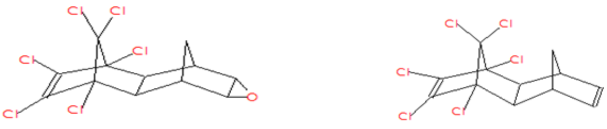
Knowledge of physical and thermochemical properties and the reactivity of the chlorinated pesticides are essential to understanding environmental behaviour of these compounds. Our present study focuses on using MNDO method in HypeChem7.5 program package [17] to report and discuss some of their physical and thermochemical data using MNDO semi-empirical method.

Table 1. Computed HOMO, LUMO energies, energy gap, ionization energy (IE), electron affinity (EA) and dipole moment for Group (I).

Energy (eV)	Heptachlor	Heptachlor- epoxide	Chlordane
HOMO (ground state)	-10.88848	-11.17524	-11.18567
LUMO(ground state)	-0.99057	-1.15238	-1.18726
Energy gap = LUMO–HOMO	9.89790	10.02285	9.99840
Ionization energy	9.93	10.10	10.10
Electron affinity	1.87	1.91	1.91
Dipole moment (Deby)(ground state)	2.4	2.3	1.4

2. THEORETICAL METHOD

The MNDO quantum chemical method in HyperChem 7.5 package software was used to calculate the molecular geometry, Net atomic charge, electron density, Frontier Molecular Orbital energies (HOMO–LUMO) and total energy. Structures of the studied compounds were drawn on the same program and then were optimised. All these calculations were done on the Core i3 machine with configuration: Core i3 /Win7 Professional 4 GB Ram 500 GB Hard Desk.



Endrin
$C_{12}H_8Cl_6O$
MW 378

Aldrin
$C_{12}H_8Cl_6$
MW 362

Figure2: The chemical structures of Group (II)

3. RESULTS AND DISCUSSION

The molecular structures of the studied compounds are shown in **figures 1-3**.The computed thermochemical data such as HOMO & LUMO energies, ionization energy, electron affinities, binding energy, total energy, heats of formation and dipole moment of the studied compounds have been calculated and reported as shown in **Tables** (**1-6**).

In this study, the compounds are divided to three groups, the first group (I) are tricyclic compounds contain Heptachlor and its metabolite Heptachlorepoxide and Chlordane. The second group (II) are tetracyclic compounds contains Aldrin and Endrin. While the third group (III) are biphenyl compounds, contain DDT and Methoxychlor.

T**able 2**. The computed heat of formation, binding energy and total energy for Group (I).

Energy (kcal.mol^{-1})	**Heptachlor**	**Heptachlor- epoxide**	**Chlordane**
Heat of formation $\Delta H_f(M)$(neutral)	25		-3
Heats of formation $\Delta H_f(M)^{-1}$(anion)	-17	-39	-47
Heat of formation $\Delta H_f(M)^{+\bullet}$(cation)	254	238	230
Binding energy(ground state)	-2147	-2227	-2360
Total energy			
(neutral)	-88311	-95721	-97491
(cation)	-88082	-95488	-97258
(anion)	-88354	-95765	-97536

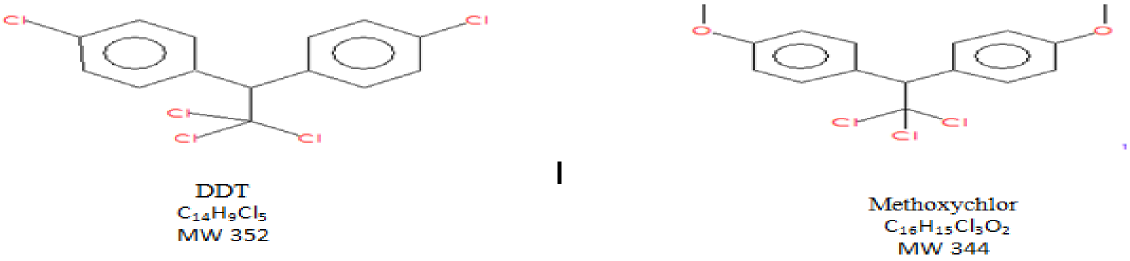


Figure3: The chemical structures of Group (III).

From the calculated data of the studied compounds (**Tables 1-6**), we have obtained the values of heats of formation, total energies, binding energy and HOMO, LUMO energies of the neutral and charged molecules besides energy gap (LUMO – HOMO) as well as ionization energy, electron affinity and dipole moment. These thermochemical data are necessary in the description of the conformational properties of the studied compounds and may not publish before as our knowledge.

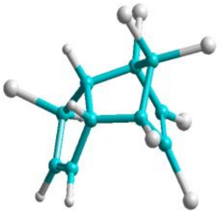
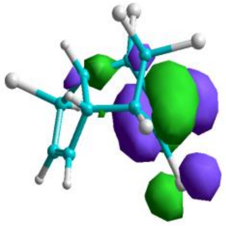
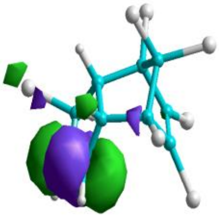
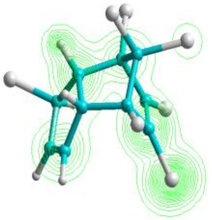
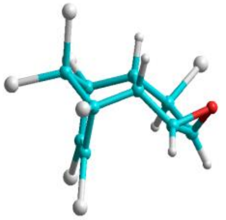
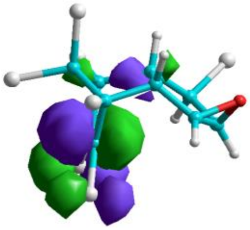
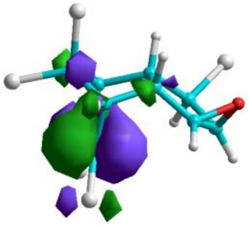
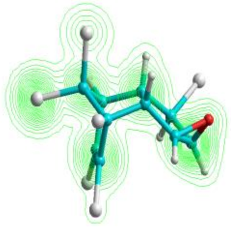
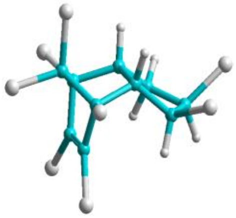
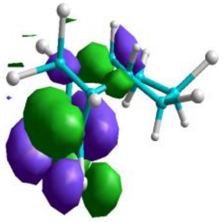
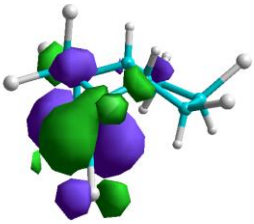
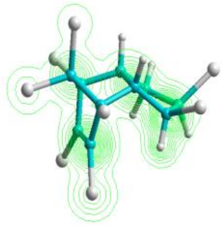
Optimized Structures	HOMO (3D isosurface)	LUMO (3D isosurface)	Total charge density(2D contours)
 **Heptachlor**			
 **Heptachlorepoxide**			
 **Chlordane**			

Figure 4: The optimized molecular structures, HOMO, LUMO and total electron density of the group (I).

One can observe that the calculated values for the total energies for the first group (**Figure 1**) at the ground state are (Heptachlor = -88311 kcal.mol^{-1}, Heptachlorepoxide = -95721kcal.mol^{-1}, Chlordane = -97491 kcal.mol^{-1}) (**Table 2**). Also, the calculated values of the heats of formation at the ground state of these group are equal (Heptachlor = 25 kcal.mol^{-1}, Heptachlorepoxide = 5 kcal.mol-1and Chlordane = - kcal.mol^{-1}) (**Table 2**). From these values of the total energy and the heats of formation, one can observe that the chlordane compound has the smallest values. This means that Chlordane is the more stable than the other two compounds heptachlor and heptachlorepoxide. This difference is explained on the basis of substituted chlorine and oxygen atoms and changes in their configuration. On the other hand, from the values of dipole moment of the first group at the ground state are (Heptachlor = 2.4 Debye (D), Heptachlorepoxide = 2.3 D and Chlordane = 1.4 D) (**Table1**) and one can note that the chlordane compound has the less polarizability than the other two compounds in this group. The presence of double bond for Heptachlor compound and oxygen atom for Heptachlorepoxide are affecting the reactive site for these two compounds while for Chlordane compound the substituent of chlorine in five cyclic rings reduces the dipole moment as listed in **Table 1**. Also, the stabilities of the two metabolites of the heptachlor compound (Heptachlorepoxide and Chlordane) are clear from the values of binding energy of the three compounds of the first group (Heptachlor = -2147 kcal.mol^{-1}, Heptachlorepoxide = -2227 kcal.mol^{-1}and Chlordane = -2360 kcal.mol^{-1}) Hence, the chlordane has the less value of binding energy follow by heptachlor epoxide and heptachlor. As shown as in **Table 1**. On the other hand, One can note that the first Group compounds have nearly the same values of ionization energy (Heptachlor = 9.93 eV, Heptachlorepoxide = 10.10 eV and Chlordane = 10.12 eV). This is may be due to the presence of π bond in these compounds in which the ionization occurs from it, and the geometry of the tricyclic configuration of the chlorine atoms has a small effect on ionization energy. Also, they have nearly the same values of electron affinity (1.9 eV) as listed in **Table 1**. On the other hand, the difference is clear in the dipole moment values, since Heptachlor and Heptachlorepoxide have nearly the same value (2.35 D) while Chlordane has 1.4 D. This may be due to that Chlordane compound has no double bond and oxygen atom in his structure than the other two compounds (**Table 1**), as describe before.

The calculated values of the thermochemical data of the second group (II) Aldrin and Endrin (as in **Table 3-4**) show that the two compounds have the values of heats of formation which equal to 73 and 45 kcal.mol^{-1} respectively. The positive values of the heats of formation indicate that these two compounds have relatively low stabilities with in accordance to group (I). The low value of the heat of formation of Endrin than Aldrin due to the substituent of the oxygen atom on the double bond in its structure (**Figure 2**). The total energy values of Aldrin and Endrin at the ground states are -86971 and -94389 kcal.mol^{-1} respectively. From these, values one can note that Endrin is more stable than Aldrin

Table 3. Computed HOMO, LUMO energies, energy gap, ionization energy (IE), electron affinity (EA) and dipole moment for Group (II).

Energy (eV)	**Aldrin**	**Endrin**
HOMO (ground state)	-10.10377	-10.84611
LUMO(ground state)	-0.70630	-0.84558
Energy gap = LUMO–HOMO	9.39746	10.00052
Ionization energy	9.00	9.76
Electron affinity	1.90	1.65
Dipole moment (Deby)(ground state)	3.5	4.1

compound which is due to the presence of oxygen atom in its structure and evaporates of the double bond as shown as in **figure 2**. The highest value of ionization energy of Endrin (9.76 eV) than Aldrin (9.00 eV) and the electron affinity- value of Endrin (1.65 eV) are small than it for Aldrin (1.90 eV) as shown as in **Tables 3-4**. Also, the energy gap of Endrin is greater than it for Aldrin (10.00053 and 9.39747 eV) which increases its reactivity. On the other hand, the calculated dipole moment values are 4.1 and 3.5 D for Endrin and Aldrin respectively. The dipole moment of the molecule gives information on the polarity of these molecules. The large dipole moment may increase its reactivity. This means, Endin and Aldrin have a tendency to interact with other molecules.

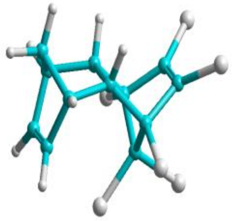
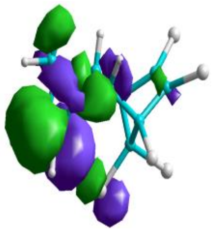
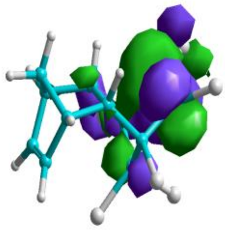
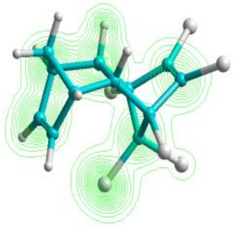
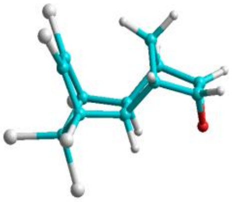
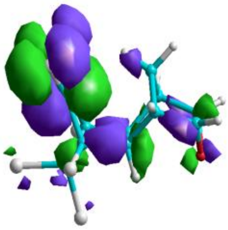
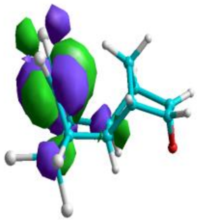
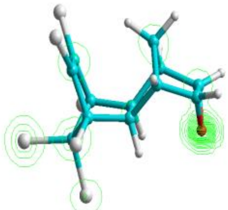
Optimized Structures	**HOMO (3D isosurface)**	**LUMO (3D isosurface)**	**Total charge density (2D contours)**
 **Aldrin**			
 **Endrin**			

Figure 5: The optimized molecular structures, HOMO, LUMO and total electron density of the group (II).

For the third group (III) which contains the DDT and Methoxychlor compounds as shown as in **Figure 3**, the calculated thermochemical data are listed in **Tables** (**5-6**). The total energies at the ground state are -85077 and -91436 kcal.mol-1for DDT and Methoxychlor respectively. From these values, one can note that Meythoxychlor is more stable than DDT, this is confirmed by the values of the heats of formation at the ground state 21 and -44 kcal.mol^{-1} for DDT and Methoxychlor respectively. The negative value of the heat of formation of Methoxychlor indicates its stability than DDT which has the positive value. This may be due to the presence of the two methoxy groups coupled with the two phenyl rings in Methoxychlor. Also, the stability of Methoxychlor compound is clear also from the calculated values of the ionization energy and the electron affinity, hence Methoxychlor has the less value of ionization energy than DDT (8.2 eV for Methoxychlor and 9.2 eV for DDT). The ionization of the methoxychlor compound may occur from a π orbital of the benzene rings or a localized electron (pair electron) on the oxygen atom. This leads to decrease the ionization energy of Methoxychlor than DDT. The highest value of electron affinity (1.7 eV for Methoxychlor and 1.4 eV for DDT) as shown as in **Tables** (5).

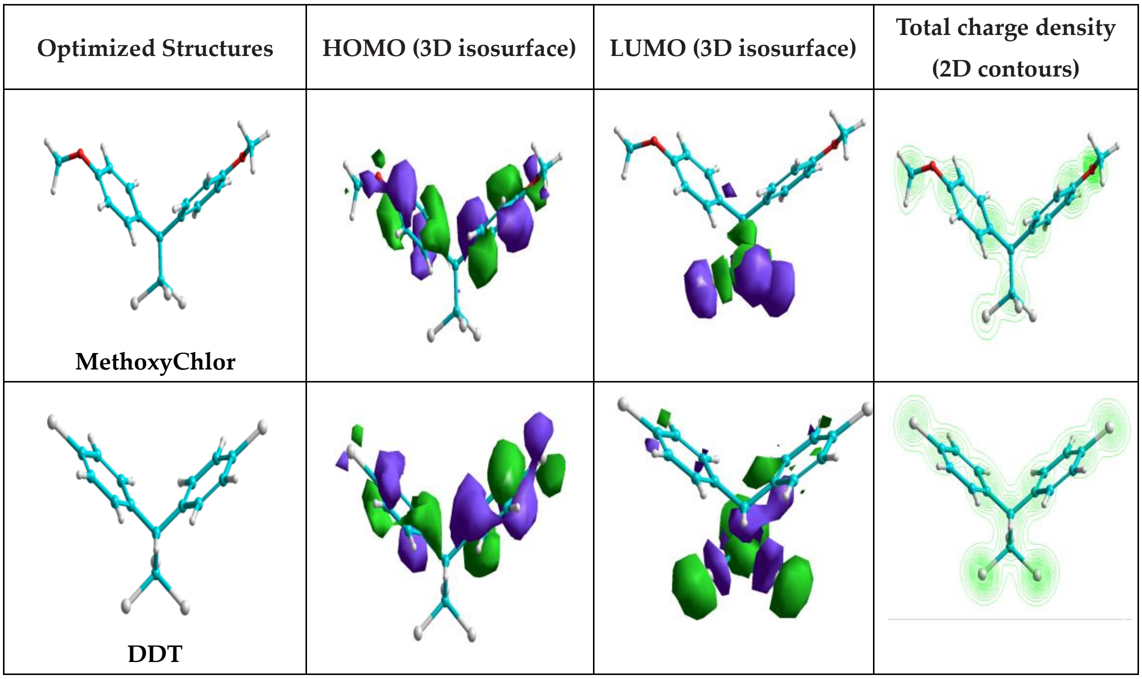


Figure 6: The optimized molecular structures, HOMO, LUMO and total electron density of the group (III).

The dipole moments of the third group are 1.2 and 0.8 D for DDT and Methoxychlor respectively. The difference may be due to in part to their polarizability (charge distributions and bond lengths) of side groups –Cl and –OCH3. In general, the lower values of dipole moments for the two compounds are due to the interaction of the chlorine atoms in aromatic rings. The lowest values of the dipole moment of this group may give low tendency to interact with other molecules.

The data observed for Group (III) suggest that, the positioning of the methoxy group has a large effect on the heats of formation. On the other hand, a small effect of the chlorine and methoxy substituents on the electron affinity and dipole moment, which they have lone pairs that may interest with aromatic π systems.

Frontier Molecular Orbital (FMO) Analysis

Quantum chemical parameters such as the energy of the Highest Occupied Molecular Orbital (HOMO), the energy of the Lowest Unoccupied Molecular Orbital (LUMO), energy gap [LUMO - HOMO], the dipole moment (D) and the charges density are often sighted among the most important quantities that provide information on the reactivity of the compounds under consideration.[18]

HOMO and LUMO orbital energies and total charge density of the three groups under study are obtained from the quantum chemical calculations using MNDO method at the ground state which is listed in **Tables** (**1-6**). While the optimised molecular structures, HOMO, LUMO and total charge density of the studied molecules using MNDO method were given in **Figures** (**4-6**).

The values of the HOMO and LUMO orbital energies at the ground state of the first group are equal to (Heptachlor = -10.88848 eV, Heptachlorepoxide = -11.17524 eV and Chlordane = -11.18567 eV). While the values of LUMO energies are equal to (Heptachlor = -0.9905704 eV, Heptachlor epoxide = -1.152387eV and Chlordane = -1.18726 eV)

The energies of HOMO and LUMO are not activity descriptors but can be connected to the activity of molecules under study. Higher HOMO energies indicate better electron-donating properties of a molecule and the lower is connected with the lower activity of the molecule. [19] The values of HOMO, LUMO and energy gap of the first group listed in **Table 1**. One can note that heptachlor compound has the better electron donating properties and lower activity than the other two compounds in the same group.

The HOMO and LUMO for the studied molecules together with the total charge density are shown in **figure** (**4-6**). In the first group molecules, the HOMO and the LUMO of Heptachlor compound are delocalized throughout the system with the HOMO having the maximum amplitude on the fifth cyclic ring which has one double bond and coupled with one chlorine atom as shown as in **figure 4**. While the LUMO has the maximum amplitude at the other side at the six cyclic ring which has the double bond with two chlorine atoms. The total charge density shows that the molecule appears to have a neutral distribution of charges (green lines **figure 4**).From the values of HOMO and LUMO energies of the other compounds in the first group Heptachloroepoxide and Chlordine one can note it have the

T**able 4**. The computed heat of formation, binding energy and total energy for Group (II).

Energy (kcal.mol^{-1})	**Aldrin**	**Endrin**
Heat of formation $\Delta H_f(M)$(neutral)	73	45
Heats of formation $\Delta H_f(M)^{-1}$(anion)	29	7
Heat of formation $\Delta H_f(M)^{+\bullet}$(cation)	281	270
Binding energy(ground state)	-2568	-2656
Total energy		
(neutral)	-86971	-94389
(cation)	-86762	-94164
(anion)	-87015	-94427

approximately the same values as listed in **Table 1**. (Heptachlorepoxide = -11.17524 eV, Chlordane = -11.18567eV for HOMO) and (Heptachlor epoxide = -1.152387 eV, Chlordane = -1.187264 eV for LUMO) and also, they have approximately the same energy gap values (Heptachlorepoxide = 10.022853 and Chlordane = 9.998406 eV). From these values of HOMO, LUMO and energy gap, one can say that these two compounds have the same activity. The total charge density shows that Heptachloroepoxide and Chlordane appear to have a neutral distribution of charges (green lines **figure 4**).

From the second group (Aldrin and Endrin) calculated values of HOMO and LUMO orbital energies, one can observe that the two compounds have approximately the same values of HOMO energies (Aldrin = -10.10377 and Endrin = -10.84611) that confirmed the same activity of the two compounds. The total charge density shows that Aldrin appears to have a neutral distribution of charges. While in the case of the Endrin the charge density concentrates on the only oxygen atom in its structure (green lines **figure 5**).

The calculated values of HOMO energies of the third group compounds (DDT and Methoxychlor) show that DDT has the highest value (-10.14146 eV) than Methoxychlor (-9.649988) that indicates the relatively higher activity of DDT than Methoxychlor compound. This also confirmed by the value of energy gap as listed in **Table 5**.

The total charge density shows that DDT appears to have a neutral distribution of charges and the charge density concentrates on the down three chlorine atoms. In the case of the methoxychlor, the charge density concentrates on the two oxygen atoms in its structure as shown as in **figure 6**).

From the heats of formation of the all studied compounds, one can observe that methoxychlor compound is the most stable compounds. This is due to the presence of the two methoxy group in its structure coupled with the two phenyl rings.

Also, a comparison of the dipole moments, one can say that the second group (II) have the greater values of dipole moment which have greater tendency to interact with other molecules. For that, the other follows group (II) > group (I) > group (III).

Table 5. Computed HOMO, LUMO energies, energy gap, ionization energy (IE), electron affinity (EA) and dipole moment for Group (III).

Energy (eV)	DDT	Methoxychlor
HOMO (ground state)	-10.14146	-9.64998
LUMO(ground state)	-0.66552	-0.49155
Energy gap = LUMO–HOMO	9.47593	9.15843
Ionization energy	9.24	8.20
Electron affinity	1.39	1.74
Dipole moment (Deby)(ground state)	1.2	0.8

The energy gap for the group (I) and group (II) the presence of adding the oxygen atom or double bond decreases the energy gaps.

The electron affinities of these groups have values less than 2 eV. The interaction of electrons with molecules leads to negative ion.

The highest values of ionization energy of these groups which have the follow order I > II > III show that, these need high energy to become cation. On the other hand the electron affinity has the order I > II > III for these groups which the energy required for a molecule to accept electron as shown as in **tables** (**1-6**).

T**able 6**. The computed- heats of formation binding energy and total energy for Group (III).

Energy (kcal.mol-1)	**DDT**	**Methoxychlor**
Heats of formation $\Delta H_f(M)$(neutral)	21	-44
Heats of formation $\Delta H_f(M)^{-1}$(Anion)	-10	-83
Heats of formation $\Delta H_f(M)^{+\bullet}$(cation)	233	146
Binding energy(ground state)	-2985	-3765
Total energy		
(neutral)	-85077	-91436
(cation)	-84864	-91247
(anion)	-85109	-91476

4. CONCLUSION

Pesticides have played a critical role in the development of the agriculture and are still irreplaceable until the present time (1). The thermochemical data of the studied molecules have been investigated employing the MNDO method. These thermochemical data are relevant in the description of the conformational properties of the studied compounds. Based on the obtained results one can conclude that:

-For the first group: Heptachlor and its metabolite Heptachlorepoxide and Chlordane are not stable compounds this confirmed by the values of its heats of formation while Chlordane is the more stable one due to the negative value of its heats of formation. The stability and activity of these compounds are discussed. Heptachlor compound has the better electron donating properties and lower activity than the other two compounds in the same group based on HOMO and LUMO calculations.

-For the second group: Aldrin and Endrin have relatively low stabilities, this confirmed by the positive values of its heats of formation and they have the nearly same activity based on HOMO and LUMO calculations.

-For the third group: The DDT and Methoxychlor are noted that Methoxychlor compound is the more stable compound from all studied compounds due to the lowest value of its heats of formation. From the calculated values of HOMO energies, one can observe that DDT has the higher activity than Methoxychlor. This due to the presence of chlorine atoms bonded to the phenyl groups.

References

[1] Pang, G. F.; Cao, Y. Z.; Zhang, J. J.; Fan, C. L.; Liu, Y. M.; Li, X. M. J. Chromatogr. A. 1125(2006) 1.

[2] Aysal, P.; Ambrus, A.; Lehotay, S. J.; Cannavan, A. J. Environ. Sci. Health B. 42(2007) 481.

[3] Hercegova, A.; Domotorova, M.; Kruzˇlicova, D.; Matisova, E. J. Sep. Sci. 29 (2006) 1102.

[4] Guruge, K. S. ; Tanabe, S. Mar. Pollut. Bull. 42 (2001) 179.

[5] Bayarri, S; Baldassarri, L. T.; Iacovella, N.; Ferrara, F.; Di Domenico, A. Chemosphere.43(2001) 601.

[6] Colborn, T; Vom Saal, F. S.; Soto, A.M. Environ. Health. Perspect. 101 (1993) 101, 378.

[7] Sewariya Vinod; Shrivastava Richa; Prasad G.B.K.S.; Arora Kishor. Int. J. Pharm. Bio. Sci.3B(3) (2012) 910.

[8] Priyakumar; Deva, U.; Sastry,G; Narahari. Indian J. Chem.39A (2000), 39(A), 92.

[9] Arora K.; Singh B. Res.J.chem.sci.3(10) (2013) 36.

[10] Mamoun S. M. Abd El-Kareem; Mohamed Abd El Fattah Rabbih; Ezzat Taha Mohamed Selim; Elsherbiny Abd El-monem Elsherbiny; Ayman Yasen El Khateeb; International Journal of Analytical Mass Spectrometry and Chromatography(IJAMSC). 4 (2016) 14.

[11] Mamoun S.M. Abd El-Kareem; M.A.Rabbih; E.T.M.Selim. International Journal of Physical Research (IJPR).4 (2016) 20.

[12] Fukui K., Yonezaw T., Shingu,H. J. Chem. Phy. 20 (1952) 722.

[13] Huizar Luis Humberto-Mendoza; Reyes Clara Hilda Rios. J.Mex. Chem. Soc., 55(3) (2011) 142.

[14] ZHU XiuHua; DING GuangHui; LEVY Walkiria; JAKOBI Gert, OFFENTHALER Ivo; MOCHE Wolfang; WEISS Peter; SCHRAMM Karl-Werner. Chinese Sci. Bull. 56(18) (2011) 1884.

[15] Aleksandra Nestorovska-Krsteska ; Zoran Zdravkovski. Int. J. Mol. Sci. 7 (2006) 35.

[16] Damico, J. N., Barron, R. P.; Ruth, J. M. Org. Mass Spectrom. 1 (1968) 331.

[17] HyperChemTM, Release 7.5 Pro for Windows, “Molecular Modeling System”, Hypercube, User Evaluation copy, Organization: Evaluation copy, Dealer: Copyright©2002 Hypercube,Inc, Serial No.99-999-9999999999.

[18] Eno E. Ebenso; Mwadham M. Kabanda; Taner Arslan; Murat Saracoglu; Fatma Kandemirli, Lutendo C. Murulana; Ashish K. Singh; Sudhish K. Shukla; B. Hammouti, K.F. Khaled; M.A. Quraishi; I.B. Obot; N.O. Eddy. Int. J. Electrochem. Sci. 7 (2012) 5643.

[19] S. Sebastian; N. Sundaraganesan; S. Manoharan.. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.74 (2009) 312.