RESEARCH PAPER | Chemistry | Volume : 3 | Issue : 5 | May 2013 | ISSN - 2249-555X

Computational investigations of oxazole, thiazole and carbazole having pesticide utility in agriculture by Ab-initio and DFT Methods

KEYWORDS: Ab-initio, DFT, log p, pesticide

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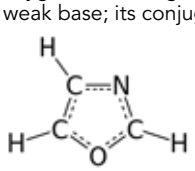
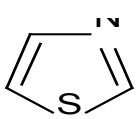
ABSTRACT *The geometric, electronic structure, effect of the substitution and structure physical-chemistry relationship for oxazole, thiazole and carbazole has been studied by Ab-initio and DFT methods. In the present work, the calculated values namely dipole moments, λmax values and QSAR properties, are reported and discussed in terms of the reactivity of oxazole, thiazole and carbazole (log P) as pesticide. As compared oxazole has maximum log P value which shows that this can be best used in the pesticide utilization.*

The emerging resistance to disease causing parasites demands the synthesis of new remedies for agricultural pesticides, which are effective against organisms resistant to currently available pesticides (Bakhotmah, Reda, Abdul, Mohammad, Mohamed & Mansor, 2011). Oxazole have an important role in the synthesis of potential pesticides (Robertson, 2005).

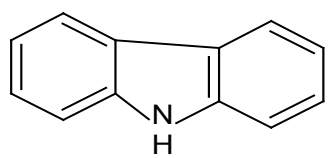
Oxazole is the parent compound for a vast class of heterocyclic aromatic organic compounds. These are azoles with oxygen and nitrogen separated by one carbon. Oxazole is a weak base; its conjugate acid has a pKa of 0.8.



Thiazole is a heterocyclic compound that contains both sulfur and nitrogen; the term thiazole also refers to a large family of derivatives. Thiazole itself is a pale yellow liquid with a pyridine-like odor and the molecular formula C_3H_3NS (Shaffer, Wierschke, 1993).



Carbazole is an aromatic heterocyclic organic compound. It has a tricyclic structure, consisting of two six-membered benzene ring fused on either side of a five-membered nitrogen-containing ring.



Computational Methods

All calculations were performed by using HyperChem 8.0 software (HyperChem, 2007). The geometries of oxazole and their derivatives were first fully optimized by molecular mechanics, with MM+ force-field (rms=0.001 Kcal/Å). The calculation of QSAR properties were performed by the module (QSAR Properties, version 8.0). QSAR Properties is a module that, together with HyperChem, allows several properties commonly used in QSAR studies to be calculated.

Ab-initio methods are characterized by the introduction of an arbitrary basis set for expanding the molecular orbitals and then the explicit calculation of all required integrals involving this basis set. Density functional theory (DFT) methods are often considered to be Ab-initio methods for determining the molecular electronic structure, even though many of the most common functional use parameters derived from empirical data, or from more complex calculations. In DFT, the total energy is expressed in terms of the total one-electron density rather than the wave function.

Results and Discussion

HOMO-LUMO orbitals energies are calculated in table 1 along with λ_{max} value for all the molecules. Higher is the HOMO-LUMO energy gap, lesser is the flow of electrons to the higher energy state, making the molecular hard and less reactive.

Table 1 Orbital Energies of HOMO-LUMO with λ_{max} in Oxazole, Thiazole and Carbazole

Method	Ab initio			DFT		
	Oxazole	Thiazole	Carbazole	Oxazole	Thiazole	Carbazole
HOMO in eV	-9.219681	-20.237945	-1.755530	-9.221693	-16.038302	18.530087
LUMO in eV	3.825516	-11.329380	5.808741	3.823328	-7.487877	18.918472
λ_{max}	94nm	138 nm	163 nm	94nm	144 nm	3187 nm

As evident from table1, the least difference in HOMO-LUMO values was in carbazole both with Ab initio and DFT methods followed by thiazole. But the maximum difference was found in case of oxazole, which shows that molecules are hard and less reactive.

Values of λ_{max} for oxazole were the same with both Ab-initio and DFT methods. These values were closer to each other in

Volume : 3 | Issue : 5 | May 2013 | ISSN - 2249-555X

case of thiazole with both methods. HOMO-LUMO energy gap is affected by substituents on double bond. As HOMO- LUMO energy gap decreases (smaller ΔE), λ_{max} shifts to longer wavelength. Extending conjugation has larger effects on λ_{max}; shift is again to longer wavelength.

Table 2 Different Energies of Oxazole, Thiazole and Carbazole molecule

Method	Ab initio			DFT		
	Oxazole	Thiazole	Carbazole	Oxazole	Thiazole	Carbazole
Dipole Moment	1.417670D	2.737873D	3.095025	1.417862D	1.569925D	0.963221
Total Energy	-153502.2424879 (kcal/mol)	-374085.7667376 (kcal/mol)	-107794.7261582 (kcal/mol)	-153502.7600895 (kcal/mol)	-501309.0675937 (kcal/mol)	-46074.4594417 (kcal/mol)

Study of structure physical-chemical property relationship for oxazole, thiazole and carbazole has been studied by HyperChem software.

Ab-initio and DFT method show close results in case of oxazole while, there is large variation in dipole moment and total energy values in the case of thiazole and carbazole (Table 3).

Table 3 QSAR Properties

Methods	Oxazole Value	Thiazole Value	Carbazole Value
Partial Charge	0.00e	0.00e	0.00e
Surface area (approx)	176.50A^2	147.74 A^2	247.51 A^2
Volume	261..39 A^3	174.70 A^3	541.13 A^3
Hydration Energy	-7.98kcal/ mol	-3.63 kcal/mol	-4.85 kcal/mol
Log P	-0.79	-0.45	-0.07
Refractivity	17.77 A^3	24.21 A^3	61.72 A^3
Polarizability	6.88 A^3	9.25 A^3	20.67 A^3
Mass	69.06amu	85.12amu	167.21amu

By comparing QSAR properties of the three compounds (table 3), it has elicited that carbazole has maximum area, volume, refractivity, polarizability and mass. In QSAR properties all three compounds shows no net charge values. Log P value of these compounds shows solubility in organic vs. water for oxazole (-0.79), thiazole (-0.45) and carbazole is (-0.07), which shows that oxazole have more solubility than thiazole and carbazole. As compared oxazole has maximum log P value which shows that this can be best used in the pesticide production. Derivatives of oxazole show herbicidal effect in agriculture. Carbazole shows less value of Log P, which means it, is least soluble. Polarizability value of carbazole is higher than thiazole and oxazole.

Compounds with high log P values and low H bonding capacity can readily get past ester/phosphate groups in skin membranes. High Log P values which are still soluble on account of their low melting point (Earll, 2006). Similarly it is possible to have a low Log P compound with a high melting point, which is very insoluble.

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