Investigation of Bond Lengths, Bond Angles, Thermodynamic Properties and Chemical Reactivity of N-(4-Methoxyphenyl) Maleanilic Acid, and N-(4-Methoxyphenyl) Maleimide by DFT Method

D. D. LOKHANDE[1], A. M. BHAGARE[2], J. S. AHER[3*]

[1]Department of Chemistry, KPG Arts, Commerce and Science College, Igatpuri, Nashik (MS), India.
[2]Dpeartment of Chemistry, Arts, Commerce and Science College Ozar (Mig), Nashik (MS), India.
[3*]Department of Chemistry, K. T. H. M. College, Nashik 422 002, (MS), India.
Corresponding Author Email: ddlokhande1175@gmail.com

Abstract:
Geometry optimization calculation for N-(4-methoxyphenyl) maleanilic acid and N-(4-methoxyphenyl) maleimide were performed by DFT/B3LYP level using 6-311++G (d, p) as basis set. Absorption maxima (λmax) and chemical reactivity were compared using highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap. Small energy gap implies more reactivity of N-(4-methoxyphenyl) maleimide. Thermodynamic properties like Total thermal energy, entropy, heat capacity, zero-point energy, and dipole moment have also been calculated by the same method and basis set.
Keywords: Maleimide, Thermodynamic property, Chemical reactivity, DFT

INTRODUCTION

Cyclic maleimide is an important heterocyclic moiety that has attracted the attention of researchers in the field of synthetic Organic Chemistry because of its long history of applications in Pharmacology[1-3], Synthetic Chemistry[4-6], Biology[7-9], and Polymer Chemistry[10-11]. Researchers can choose a proper computational method that predicts the physical and chemical properties of the compounds under investigation[12]. *Ab initio* method of computation like DFT have become a powerful tool to produce good optimization of the chemical system[13] and to investigate molecular structure, thermodynamic properties and chemical reactivity. Many researchers have reported the *ab initio* Hartree-Fock calculations and DFT study of different heterocyclic compounds[14-16] and reported HOMO-LUMO energy and other thermodynamic properties at B3LYP level using 6-31+G (d), 6-31++ G (d, p), 6-311G (d, p), 6-311++G (d, p) basis sets. Authors have been reported the computational study of few derivatives of N-aryl maleanilic acids and N-aryl maleimides earlier[17-19].

Present study is the extension of previous work in which optimized bond lengths, bond angles, chemical reactivity and thermodynamic properties of N-(4-methoxyphenyl) maleanilic acid and N-(4-methoxyphenyl) maleimide have reported.

EXPERIMENTAL WORK

Materials and Method

All calculations were carried out on an Intel, Core i3 personal computer using the Gaussian 09 program[20] package. Geometries of the molecules were optimized by DFT/B3LYP at 6-311++G (d, p) basis set. The optimized geometry parameters were used to confirm the structure as minima. Absence of imaginary frequency confirms the energy minima. Gauss View 5.0 molecular visualization program was used for HOMO, LUMO plots and energy have been used to calculate absorption maxima and the chemical reactivity of the molecule.

RESULTS AND DISCUSSION

Molecular geometry

Geometry optimization related calculations were performed by DFT method with the B3LYP level at 6-311G++ (d, p) basis set in the ground state. Optimized geometry and HOMO-LOMO plots of the compounds 'a' and 'b' are given in Table 1 and 2 while optimized geometry parameters (bond lengths and bond angles) are listed in Table 3 and 4 respectively. Optimized C-C bond lengths in benzene ring of compound 'a' and 'b' falls in the range of 1.385 to 1.399 Å which shows double bond character. The optimized C-H, C-N, C=O, C=C, C-C and C-H bond lengths in maleimide ring fall in the range of 1.081, 1.409-1.429, 1.206, 1.332, 1.500 and 1.080 Å respectively.

HOMO-LUMO energy, absorption maxima:

The highest occupied molecular orbital (HOMO) which acts as an electron donor and the lowest unoccupied molecular orbital (LUMO) that acts as an electron acceptor. HOMO-LUMO energy gap can be used to predict the absorption maxima (λmax) of the molecules[21] by using following equations[22].

Energy gap (eV) = Energy gap (Hartree or a.u.) x 27.2113834 and λ_{max} =1240/Energy gap (eV).

For the compounds 'a' and 'b' HOMO-LUMO energy and λmax calculated and was found at 278 nm and 376 nm respectively shown in Table 5.

Chemical Reactivity Indices:

The chemical reactivity indices such as total energy (**E**), global chemical hardness (**η**), softness (**σ**), electronic chemical potential (**μ**), electronegativity (**χ**) and electrophilicity index (**ω**) were calculated by using HOMO-LUMO energy gap and which provides information about reactivity of molecules. The values of all these indices are listed in Table 4.

Global chemical hardness (η): It is associated with the stability and reactivity of the chemical system. It measures the resistance to change in the electron distribution or charge transfer.

Chemical hardness is calculated using following equation. Softness is the reciprocal of global chemical hardness given by the equation $\eta = ((E_{LUMO} - E_{HOMO}))/2$. Where, E_{LUMO} and E_{HOMO} are the LUMO and HOMO energies. The larger the HOMO-LUMO energy gap, the harder and more stable/less reactive the molecule. Thus compound 'a' is less reactive than compound 'b'.

Electronegativity (χ): The concept of electronegativity was put forward by Pauling[23]. It is the power of an atom in a molecule to attract electrons towards itself. Higher is the electronegativity of the species, greater is its electron accepting power and greater is the electrophilicity. It was determined using following equation. $\chi = -(E_{LUMO} + E_{HOMO}))/2$

Electronic chemical potential (μ): It describes the escaping tendency of electrons from an equilibrium system[24] and is same in magnitude to that of the electronegativity with opposite sign[25] or half of the sum of HOMO and LUMO energy and it was determined using equation. $\mu = -\chi$ or $\mu = (E_{LUMO} + E_{HOMO}))/2$. Greater the electronic chemical potential, less stable or more reactive is the compound.

Global electrophilicity index (ω): It was introduced by Paar and is measure of the capacity or propensity of a chemical species to accept electrons[26-27] and stabilization in energy when chemical system accepts additional amount of electronic charge from the environment[28-29]. Global electrophilicity index was calculated by using the electronic chemical potential and chemical hardness by following equation and maleimide (b) is found to more electrophilic than acid maleanilic acid (a). $\omega = \mu^2/2\eta$

Ionization energy (I) and electron affinity (A): Gas phase ionization energies (I) and electron affinities (A) of the isomers are related to the HOMO and LUMO energies according to the Koopmans' theorem by the following equation. $A = -E_{LUMO}$ and $I = -E_{HOMO}$

Electron affinity is the capability of a ligand to accept precisely one electron from a donor. Ionization energy was found to be more for imide than acid while electronic affinity was nearly equal for both compounds.

Thermodynamic properties: The standard thermodynamic functions such as total thermal energy (E), total molar heat capacity at constant volume (Cv), total Entropy (S), dipole moment, molar mass and Zero-point vibrational energy (Kcal/mol) were obtained and reported in Table 6.

Table 1: Optimized geometry and HOMO, LUMO plots of N-(4-methoxyphenyl) maleanilic acid (a)

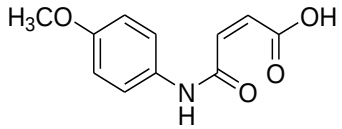
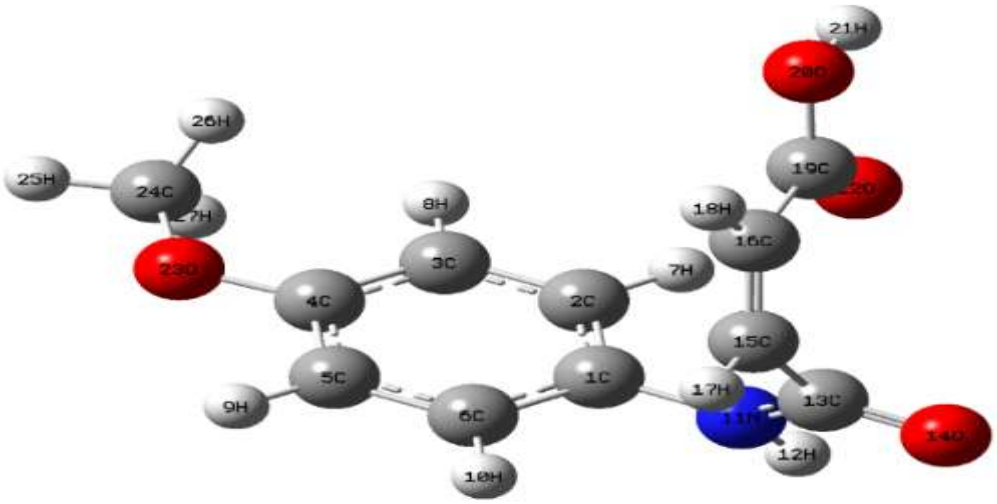
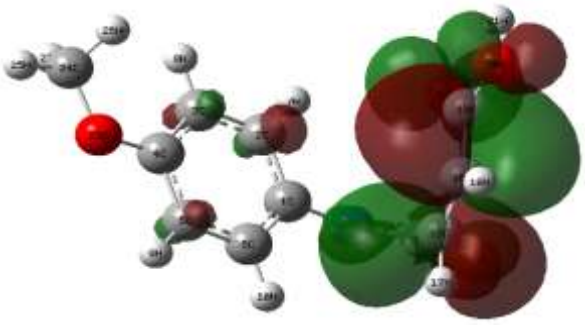
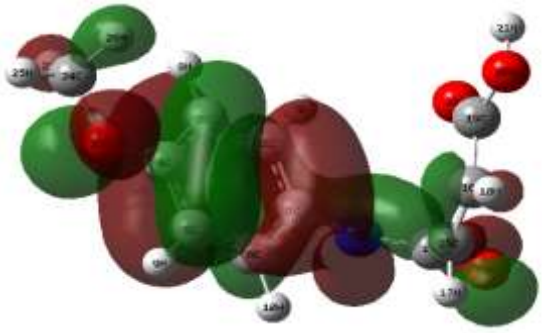
(a) **N-Phenyl-(4-methoxy maleanilic acid)**/ (Z)-3-(4-methoxyphenylcarbamoyl) acrylic acid	
	
	
Optimized molecular structure	
	
LUMO = -1.9769 eV	**HOMO = -6.4327 eV**

Table 2: Optimized geometry and HOMO, LUMO plots of N-(4-methoxyphenyl) maleimide (b)

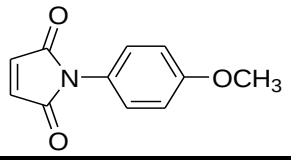
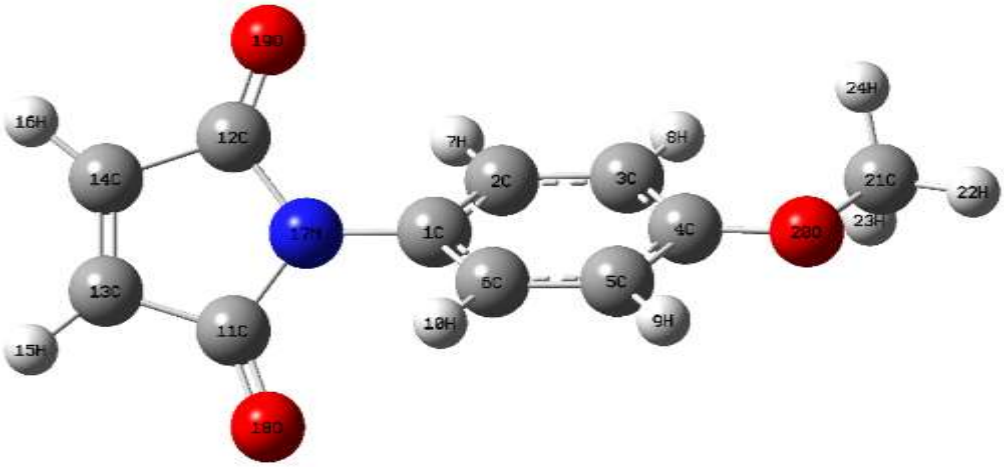
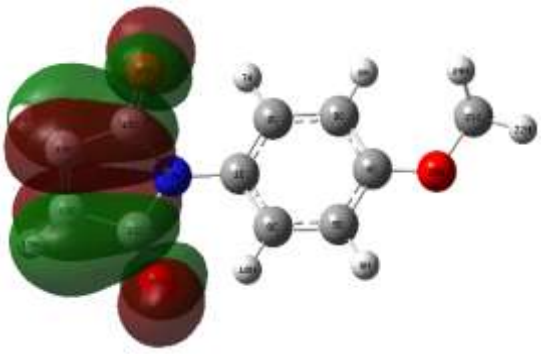
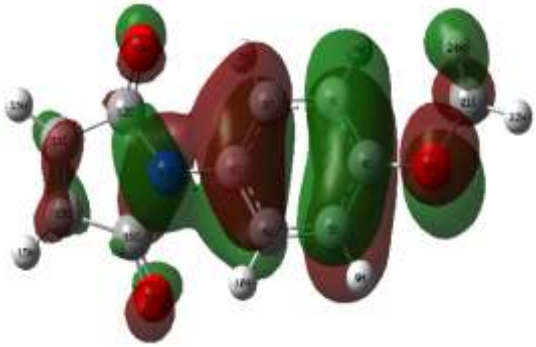
(b) **N-Phenyl-(4-methoxy maleimide)/** 1-(4-methoxyphenyl)-1*H*-pyrrole-2,5-dione	
	
	
Optimized molecular structure	
	
LUMO = -2.9910 eV	**HOMO = -6.2844 eV**

Table 3: Optimized geometry parameters (bond lengths and bond angles) of 'a'

Bond length (Å) For N-(4-methoxyphenyl) maleanilic acid (a)					
Bond	Bond length	Bond	Bond length	Bond	Bond length
C1-C2	1.392	C5-C6	1.386	C16-H18	1.083
C1-C6	1.399	C5-H9	1.083	C16-C19	1.477
C1-N11	1.431	C6-H10	1.084	C19-O20	1.359
C2-C3	1.395	N11-H12	1.013	C19-O22	1.209
C2-H7	1.083	N11-C13	1.364	O20-H21	0.969

C3-C4	1.398	C13-O14	1.220	O23-C24	1.422
C3-H8	1.082	C13-C15	1.508	C24-H25	1.087
C4-C5	1.401	C15-C16	1.334	C24-H26	1.095
C4-O23	1.363	C15-H17	1.087	C24-H27	1.095
Bond angles of N-(4-methoxyphenyl) maleanilic acid (a)					
Bond angle	Value	Bond angle	Value	Bond angle	Value
C2-C1-C6	119.2	C6-C5-H9	121.1	C15-C16-C19	123.5
C2-C1-N11	120.3	C1-C6-C5	120.5	H18-C16-C19	116.2
C6-C1-N11	120.4	C1-C6-H10	119.4	C16-C19-O20	110.9
C1-C2-C3	120.7	C5-C6-H10	120.0	C16-C19-O22	126.6
C1-C2-H7	119.2	C1-N11-H12	118.4	O20-C19-O22	122.3
C3-C2-H7	120.0	C1-N11-C13	127.1	C19-O20-H21	107.0
C2-C3-C4	119.7	H12-N11-C13	113.6	C4-O23-C24	118.7
C2-C3-H8	119.2	N11-C13-O14	123.0	O23-C24-H25	105.7
C4-C3-H8	121.1	N11-C13-C15	118.3	O23-C24-H26	111.3
C3-C4-C5	119.7	O14-C13-C15	118.4	O23-C24-H27	111.3
C3-C4-O23	124.6	C13-C15-C16	127.4	H25-C24-H26	109.3
C5-C4-O23	115.8	C13-C15-H17	113.7	H25-C24-H27	109.3
C4-C5-C6	120.1	C16-C15-H17	118.4	H26-C24-H27	109.5
C4-C5-H9	118.6	C15-C16-H18	120.2		

Table 4: Optimized geometry parameters (bond lengths and bond angles) of 'b'

Bond length (Å) For N-(4-methoxyphenyl) maleimide (b)					
Bond	Bond length	Bond	Bond length	Bond	Bond length
C1-C2	1.390	C5-C6	1.385	C12-O19	1.206
C1-C6	1.399	C5-H9	1.083	C13-C14	1.332
C1-N17	1.429	C6-H10	1.082	C13-H15	1.080
C2-C3	1.395	C11-C13	1.500	C14-H16	1.080
C2-H7	1.082	C11-N17	1.409	O20-C21	1.422
C3-C4	1.397	C11-O18	1.206	C21-H22	1.089
C3-H8	1.081	C12-C14	1.500	C21-H23	1.095
C4-C5	1.401	C12-N17	1.409	C21-H24	1.095
C4-O20	1.363				
Bond angles of N-(4-methoxyphenyl) maleimide (b)					
Bond angle	Value	Bond angle	Value	Bond angle	Value
C2-C1-C6	119.7	C6-C5-H9	120.9	C12-C14-C13	108.9
C2-C1-N17	120.2	C1-C6-C5	120.1	C12-C14-H16	121.4
C6-C1-N17	120.1	C1-C6-H10	119.9	C13-C14-H16	129.5
C1-C2-C3	120.4	C5-C6-H10	119.9	C1-N17-C11	125.0
C1-C2-H7	119.9	C13-C11-N17	106.1	C1-N17-C12	125.1
C3-C2-H7	119.5	C13-C11-O18	127.4	C11-N17-C12	109.8
C2-C3-C4	119.8	N17-C11-O18	126.3	C4-O20-C21	118.6
C2-C3-H8	118.9	C14-C12-N17	106.1	O20-C21-H22	105.8
C4-C3-H8	121.2	C14-C12-O19	127.4	O20-C21-H23	111.3
C3-C4-C5	119.5	N17-C12-O19	126.4	O20-C21-H24	111.3
C3-C4-O20	124.6	C11-C13-C14	108.9	H22-C21-H23	109.3

C5-C4-O20	115.8	C11-C13-H15	121.5	H22-C21-H24	109.3
C4-C5-C6	120.3	C14-C13-H15	129.6	H23-C21-H24	109.5
C4-C5-H9	118.7				

Table 5: HOMO-LUMO energy gap, λmax and chemical reactivity indices of 'a' and 'b'

Chemical Reactivity Indices	**a**	**b**
HOMO energy (eV)	-6.43	-6.28
LUMO energy (eV)	-1.98	-2.99
Energy Gap (eV)	4.45	3.29
λmax (nm)	278	376
Global chemical hardness (η) eV	2.23	1.65
Chemical softness (σ) eV	0.45	0.60
Electronegativity χ (eV)	4.21	4.64
Electronic chemical potential μ (eV)	-4.21	-4.64
Electrophilicity index ω (eV)	3.97	6.53
Electron affinity A (eV)	1.98	2.99
Ionization energy I (eV)	6.43	6.28

Table 6: Thermodynamic properties of 'a' and 'b' calculated by DFT/B3LYP at 6-311++G(d,p) basis set.

Property	**a**	**b**
Total Energy (Thermal) Kcal/Mol.	139.024	121.132
Total heat capacity (Cv) Cal Mol^{-1} $Kelvin^{-1}$	55.473	48.048
Total Entropy (S) Cal mol^{-1} $Kelvin^{-1}$	123.478	113.439
Zero-point vibrational energy (Kcal/mol)	129.7478	113.180
Dipole moment	5.0279	1.3417
Molar Mass	221.068	203.058

CONCLUSION

The geometry optimization were done by DFT/ B3LYP at 6311G++d,p basis sets using Gaussian 09 package programme and Gauss view A-5.0. The small HOMO-LUMO energy gap, chemical hardness, softness and λ_{max} values shows that the compound b is more reactive than a. The thermodynamic parameters also showed the reactivity difference of the two compounds.

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