

Experimental and Computational Studies of N-(4-Bromophenyl) Maleanilic Acid and N-(4-Bromophenyl) Maleimide

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Abstract

N-(4-bromophenyl) maleanilic acid and *N*-(4-bromophenyl) maleimide were synthesized from the maleic anhydride and 4-bromoaniline followed by characterization using FT-IR and ¹HNMR spectroscopic techniques. Theoretical calculations were performed to optimize geometry of these compounds by DFT/B3LYP level using 6-311++G(d, p) as basis set. ¹HNMR and fundamental vibrational frequencies were calculated theoretically by the same method and basis set and were compared with experimental data. The small difference between experimental and scaled theoretical frequencies were recorded. Thermodynamic properties like zero-point energy, entropy, heat capacity and dipole moment have also been recorded by the same method and basis set. Absorption maxima (λ_{max}) 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-bromophenyl) maleimide.

Keywords: Computational study, N-(4-bromophenyl) maleanilic acid, chemical reactivity.

Introduction

N-substituted 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 Synthetic Chemistry¹⁻³, Pharmacology⁴⁻⁷, Polymer Chemistry⁸⁻⁹, Biology¹⁰⁻¹⁴ as well as Material Science¹⁵. Traditional *ab initio* methods have been used for many years and there is number of evidences of computational data from which researchers can choose a proper theory level that predicts the physical and chemical properties of the system under consideration¹⁶. *Ab initio* method of computation like DFT have become a powerful tool to produce good optimization of the chemical system¹⁷ and investigate molecular structure, vibrational spectra in most of the chemical studies.

Many researchers have reported the *ab initio* Hartree-Fock calculations and DFT study of different heterocyclic compounds¹⁸⁻²¹ and reported FT-IR, 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. Computational study of some N-aryl maleimides have been reported earlier²².

According to the literature survey, optimization and vibrational frequencies for maleanilic acid and maleimide under investigation have not yet been reported.

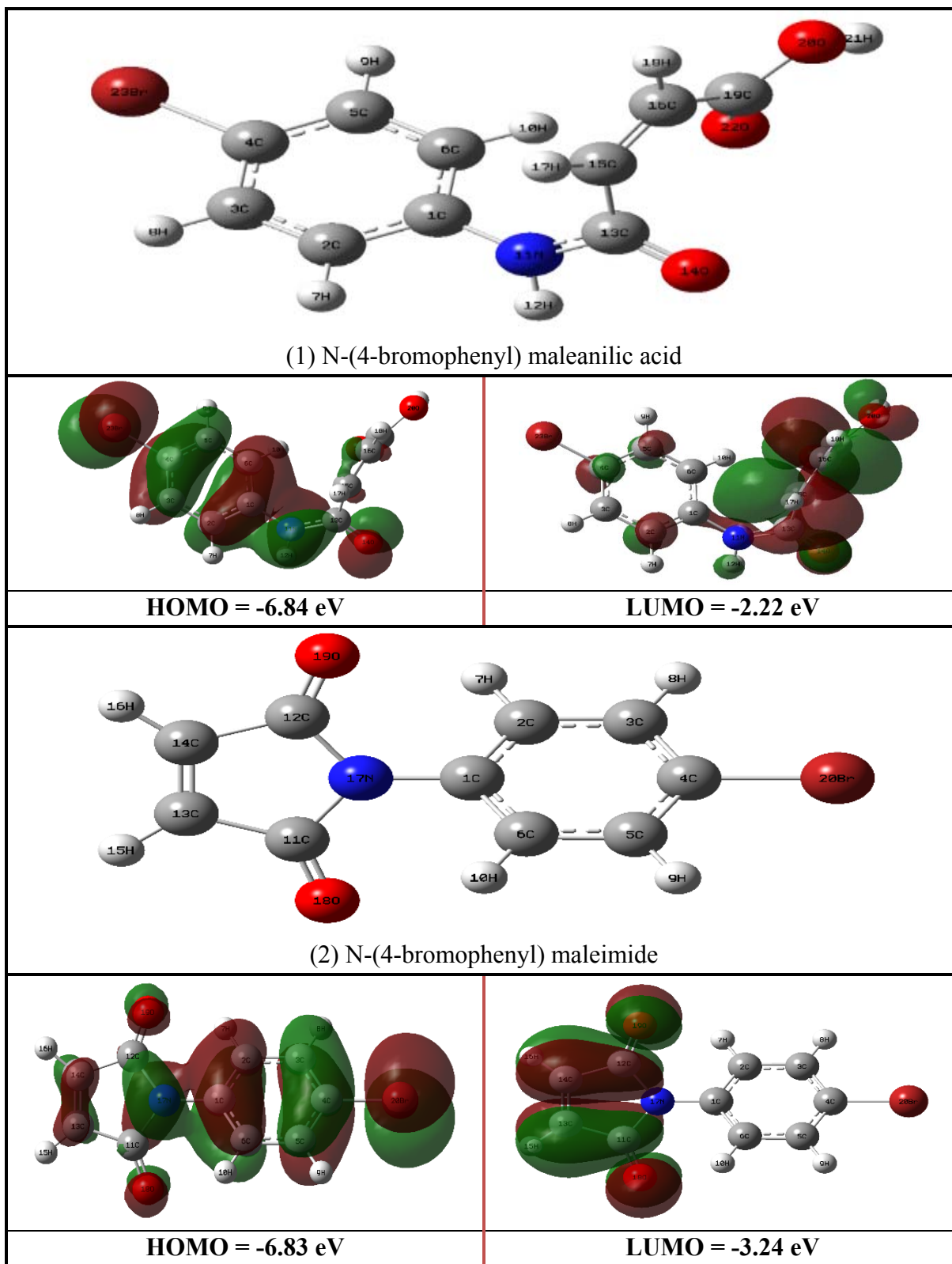
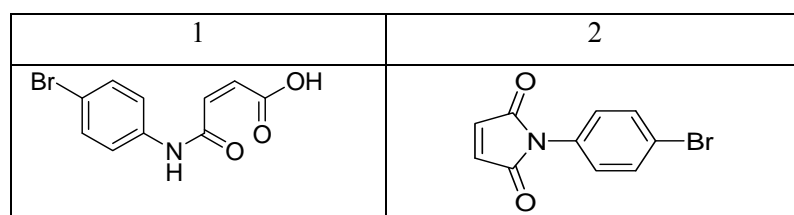


Fig. 1: Optimized geometry and HOMO, LUMO plots of N-(4-bromophenyl) maleanilic acid (1) and maleimide (2)

Materials and Method:

N-(4-bromophenyl) maleanilic acid (1) and maleimide (2) were synthesized²³ in the laboratory. Reagents and chemicals required for their synthesis were obtained from S. D. Fine Chemicals and were used without purification. Melting points were determined using Gallenkamp melting point apparatus and it was uncorrected. Products were purified by crystallisation and characterised by FT-IR and ¹H-NMR spectroscopic techniques. Infrared spectra was recorded on Shimadzu FTIR-408 spectrophotometer and ¹H-NMR spectrum was recorded on Bruker 300 MHz spectrometer using dimethyl sulphoxide and CDCl₃ as solvent.

Computational calculations were carried out on an Intel, Core i3 personal computer using the Gaussian 09W program²⁴ package. Geometries of the molecules were optimized by DFT/B3LYP at 6-311++G (d, p) basis set. The optimized geometry parameters were used in vibrational frequency calculations to confirm the structure as minima. Absence of imaginary frequency confirms the energy minima. Gauss View 5.0 molecular visualization program was used for assigning the vibrational frequency and other parameters. These frequencies were analysed and compared with the experimental data. HOMO and LUMO energy have been used to calculate absorption maxima of the molecule.



The experimental ¹H-NMR and FT-IR spectral data of the maleanilic acid and maleimide were listed in Table 1 and spectra are shown in figure 2 and 3.

Table 1: Experimental ¹H-NMR and FT-IR spectral data of 1 and 2.

Comp.	Spectral data	
1	¹ H-NMR (DMSO): 6.32 δ (d, 1H, HC=, J=12 Hz), 6.47 δ (d, 1H, HC=, J=12 Hz), 7.39 δ (d, 2H, Ar-H, J=8.7 Hz), 7.65 δ (d, 2H, Ar-H, J=8.6 Hz), 10.49 δ (s, 1H, NH), 13.1 δ (bs, 1H, OH).	IR: 1627, 1705, 3070, 3271 cm ⁻¹ .
2	¹ H NMR (300 MHz, CDCl ₃): 6.85 (2H, s, 2 X =CH) 7.25 (2H, d, J=8.7 Hz, ArH), 7.58 (2H, d, J=8.7 Hz, ArH).	IR: 1716, 1587, 1143, 825, 684.

Results and Discussion

Molecular geometry

Theoretical calculations related to geometry optimization were performed by DFT method with the B3LYP level at 6-311G++ (d, p) basis set in the ground state.

According to the numbering reported in optimized structure (Figure 1) of the compounds 1 and 2, the optimized geometry parameters (bond lengths and bond angles) are listed in Table 2. The self-consistent field (SCF) energy of 1 and 2 was found to be -3240.64 a.u. and -3164.18 a.u., while dipole moment was found 2.1221 and 3.1642 D respectively.

Table2: Optimized geometrical parameters (bond lengths and bond angles) of 1 and 2

Bond length (Å) For N-(4-bromophenyl) maleanilic acid (1)					
Bond	Bond length	Bond	Bond length	Bond	Bond length
C1-C2	1.398	C4-Br23	1.916	C15-C16	1.334
C1-C6	1.397	C5-C6	1.393	C15-H17	1.087
C1-N11	1.423	C5-H9	1.082	C16-H18	1.084
C2-C3	1.392	C6-H10	1.083	C16-C19	1.480
C2-H7	1.084	N11-H12	1.013	C19-O20	1.354
C3-C4	1.392	N11-C13	1.370	C19-O22	1.210
C3-H8	1.082	C13-O14	1.218	O20-H21	0.969
C4-C5	1.391	C13-C15	1.509		
Bond length (Å) For N-(4-bromophenyl) maleimide (2)					
C1-C2	1.396	C4-C5	1.391	C11-O18	1.205
C1-C6	1.396	C4-Br20	1.916	C12-C14	1.499
C1-N17	1.426	C5-C6	1.392	C12-N17	1.412
C2-C3	1.392	C5-H9	1.082	C12-O19	1.205
C2-H7	1.081	C6-H10	1.081	C13-C14	1.331
C3-C4	1.391	C11-C13	1.499	C13-H15	1.080
C3-H8	1.082	C11-N17	1.412	C14-H16	1.080
Bond angles of N-(4-bromophenyl) maleanilic acid (1)					
Bond angle	Value	Bond angle	Value	Bond angle	Value
C2-C1-C6	119.6	C5-C4-Br23	119.4	N11-C13-C15	117.7
C2-C1-N11	119.4	C4-C5-C6	119.5	O14-C13-C15	119.7
C6-C1-N11	120.9	C4-C5-H9	120.4	C13-C15-C16	126.9
C1-C2-C3	120.5	C6-C5-H9	120.1	C13-C15-H17	113.8
C1-C2-H7	119.7	C1-C6-C5	120.1	C16-C15-H17	118.7
C3-C2-H7	119.8	C1-C6-H10	119.4	C15-C16-H18	120.5
C2-C3-C4	119.1	C5-C6-H10	120.3	C15-C16-C19	122.9
C2-C3-H8	120.3	C1-N11-H12	118.1	H18-C16-C19	116.4
C4-C3-H8	120.5	C1-N11-C13	128.2	C16-C19-O20	111.4
C3-C4-C5	121.0	H12-N11-C13	113.6	C16-C19-O22	125.7
C3-C4-Br23	119.5	N11-C13-O14	122.0	O20-C19-O22	122.8
				C19-O20-H21	107.3
Bond angles of N-(4-bromophenyl) maleimide (2)					
Bond angle	Value	Bond angle	Value	Bond angle	Value
C2-C1-C6	120.0	C5-C4-Br20	119.4	C14-C12-O19	127.5
C2-C1-N17	119.9	C4-C5-C6	119.4	N17-C12-O19	126.3
C6-C1-N17	119.9	C4-C5-H9	120.5	C11-C13-C14	109.0
C1-C2-C3	120.0	C6-C5-H9	120.0	C11-C13-H15	121.3
C1-C2-H7	120.2	C1-C6-C5	120.1	C14-C13-H15	129.5
C3-C2-H7	119.7	C1-C6-H10	120.2	C12-C14-C13	109.0
C2-C3-C4	119.4	C5-C6-H10	119.7	C12-C14-H16	121.3
C2-C3-H8	120.0	C13-C11-N17	106.1	C13-C14-H16	129.6
C4-C3-H8	120.5	C13-C11-O18	127.5	C1-N17-C11	125.1
C3-C4-C5	121.0	N17-C11-O18	126.3	C1-N17-C12	125.2
C3-C4-Br20	119.4	C14-C12-N17	106.1	C11-N17-C12	109.6

Table 3: Experimental and theoretical (scaled) selected fundamental vibrations calculated by DFT/B3LYP/6-311++G(d,p) basis set for 1 and 2

Selected normal mode	Calculated IR frequencies cm^{-1} (scaled)	IR Intensities (km) mol	Experimental IR frequencies cm^{-1}	Assignments
N-(4-bromophenyl) maleanilic acid (1)				
63	3582	104.09	3070	O-H str.(carboxyl)
62	3426	45.94	3271	N-H str. (2° amide)
59	3061	1.99		Ar-H str. (asym.)
57	3044	4.54		Ar-H str. (asym.)
56	3018	0.32		=C-H str. (asym.)
55	1679	232.56	1705	C=O str. (carboxyl)
54	1632	587.71	1627	C=O str. (amide)
53	1616	50.95		C=C str. (olefin)
52	1560	10.46		Ar. C=C str.
51	1541	1.17	1543	Ar. C=C str.
50	1462	157.20		Ar-H (ip) bending
49	1413	15.87	1388	N-H bending
48	1382	215.49		=C-H (ip) bending
47	1362	10.27		Ar-H (ip) bending
46	1292	116.50		C-N str. (amide)
45	1278	8.50		Ar-H (ip) bending
44	1260	195.54		O-H bending
43	1248	6.40		Ring deformation
42	1191	16.10		Ar-N str.
41	1172	18.69		=C-H (ip) bending
40	1156	1.57		Ar-H (ip) bending
39	1114	542.16	1010	C-OH str. (carboxyl)
23	648	10.89	678	C-Br str.
N-(4-bromophenyl) maleimide (2)				
54	3123	0.02		C-H str. (sym.) (olefin)
53	3103	0.00		C-H str. (asym.) (olefin)
52	3092	0.69		Ar-H str. (sym.)
51	3091	0.68	3086	Ar-H str. (asym.)
48	1762	0.30		C=O str. (sym.)
47	1708	661.06	1712	C=O str. (asym.)
46	1584	3.55		C=C str. (olefin)
45	1566	0.35	1489	Ar C=C str.
41	1081	34.66		C-N str. (imide)
34	1340	463.50	1381	Ar-N str.
21	713	12.39	702	C-Br (halogen)

For 1 and 2 the optimized bond lengths of C-C bond in benzene ring fall in the range of 1.391 to 1.398 Å which shows double bond character and the optimized bond lengths of C-H, C-N, C=O, C=C, C-C and C-H in imide ring fall in the range of 1.080, 1.412, 1.205, 1.331, 1.499 and 1.080 Å respectively. C-Br length in 1 and 2 was 1.916 Å. C=O length in 1 was 1.210 to 1.218 while C-O bond length was 1.354 Å.

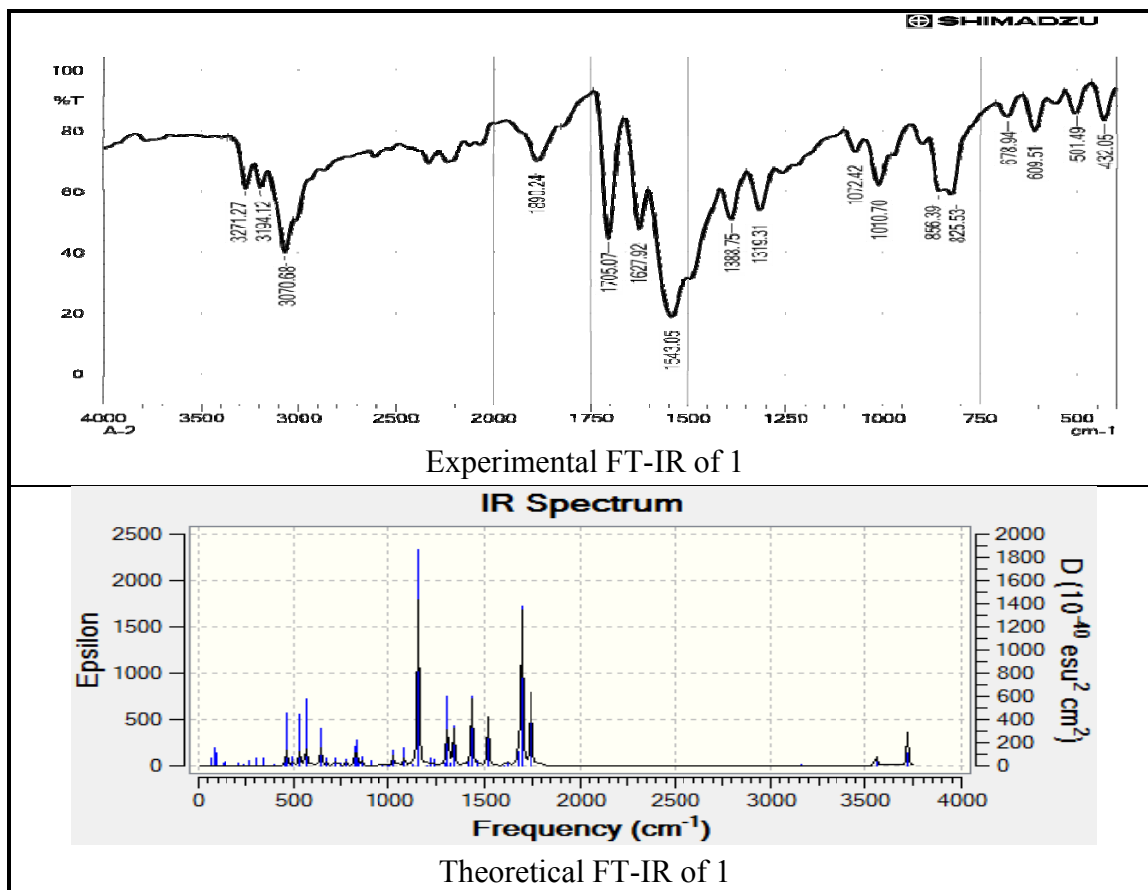


Table 4: Experimental and theoretical ¹H-NMR chemical shifts (δ) in ppm of 1 and 2

Sr. No	Experimental ¹ H-NMR chemical shifts (δ) in ppm (300MHz, DMSO)	Theoretical ¹ H-NMR chemical shifts (δ) in ppm (B3LYP/6-311++G(d,p) level using GIAO method)
1	7.39 (2H d J=8.7, Ar-H)	H7:7.31, H8:7.73, (Ar-H)
	7.65 (2H d J=8.6, Ar-H)	H9:7.69, H10:8.05, (Ar-H)
	10.49 (1H, s, NH)	H12: 7.02, (NH)
	6.32 (1H d, =CH) 6.47 (1H d, =CH)	H17: 6.81, H18: 6.37, (=CH)
	13.1 (1H, bs, OH)	H21: 6.42, (OH)
2	7.25 (2H d J=8.7, Ar-H)	H7: 7.45, H10: 7.45, (Ar-H)
	7.58 (2H d J=8.7, Ar-H)	H8: 7.55, H9: 7.55, (Ar-H)
	6.85 (2H s =CH)	H15: 6.60, H16: 6.60, (=CH)

Vibrational assignments:

Depending on the geometry of molecule fundamental modes of vibrations are calculated for linear and non-linear molecule using the formula $3N-5$ and $3N-6$ respectively. Both 1 and 2 compounds have non-linear geometry and they contain 23 and 20 atoms, therefore they show 63 and 54 fundamental modes of vibrations respectively.

The *ab initio* HF and DFT potentials systematically overestimates the vibrational wave numbers²⁵. These discrepancies are corrected either by computing anharmonic corrections explicitly or by introducing a scaled field²⁶ or directly scaling the calculated wavenumbers with the proper factor²⁷. The scaling factor of 0.9631 was used for B3LYP method. Selected scaled fundamental modes of vibrations and FT-IR spectrum (experimental and theoretical) for 1 and 2 are given in Table3.

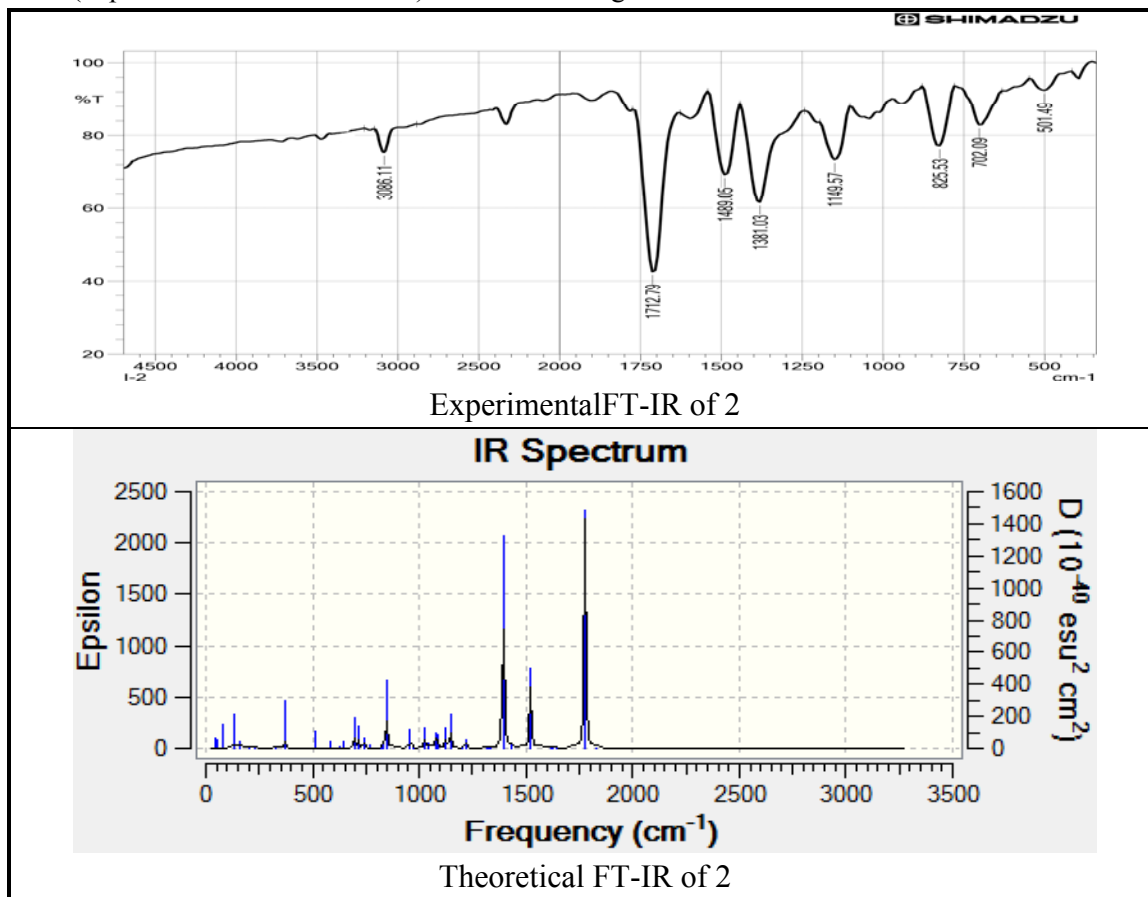


Figure 2: Experimental and theoretical FT- IR spectrum of 1 and 2

Vibrations of imide $>C=O$ group: An amide carbonyl group absorbs strongly in the $1630-1690\text{ cm}^{-1}$ region²⁸⁻²⁹. Experimentally amide carbonyl and carboxyl carbonyl of an acid showed absorption at 1627 and 1705 cm^{-1} whereas theoretically it was at 1632 and 1679 cm^{-1} respectively. For imide carbonyl, experimental vibration was reported at 1712 cm^{-1} and computed $C=O$ stretching frequency was obtained at 1708 cm^{-1} .

C-H Vibrations: Aromatic C-H stretching occurs at the $3100-3000\text{ cm}^{-1}$ whereas olefin C-H stretching occurs in the $3010-3095\text{ cm}^{-1}$ range. For the title compounds aromatic C-H stretching was obtained at $3073-3061$ and $3092-3091\text{ cm}^{-1}$ whereas olefin C-H stretching is observed at $3057-3018$ and $3123-3103$

cm^{-1} by DFT method. C-H stretching vibrations calculated was found to be nearly close to the literature and experimentally reported value.

C=C vibrations: The region of C=C stretching vibrations were given in literature in the range of 1660-1580 cm^{-1} . Theoretically the vibrations were predicted in a range 1616 to 1541 cm^{-1} for aromatic and olefin C=C. The experimental values were assigned in the range 1543 to 1489 cm^{-1} .

C-N vibrations: The region of C-N stretching vibration is 1550-1350 cm^{-1} . Theoretically it was predicted at 1292 cm^{-1} for acid and at 1340 cm^{-1} for imide by DFT/B3LYP method. Computational vibrational frequencies obtained by DFT were found in good agreement with the experimental values. Theoretically C-Br stretching was observed in the range 713 to 648 cm^{-1} . Theoretical $^1\text{H-NMR}$ chemical shifts (δ) in ppm calculated by B3LYP/6-311++G(d,p) level using GIAO method are shown in Table 4. Experimental and computational FT-IR and $^1\text{H-NMR}$ spectra are shown in figure 2 and 3 respectively.

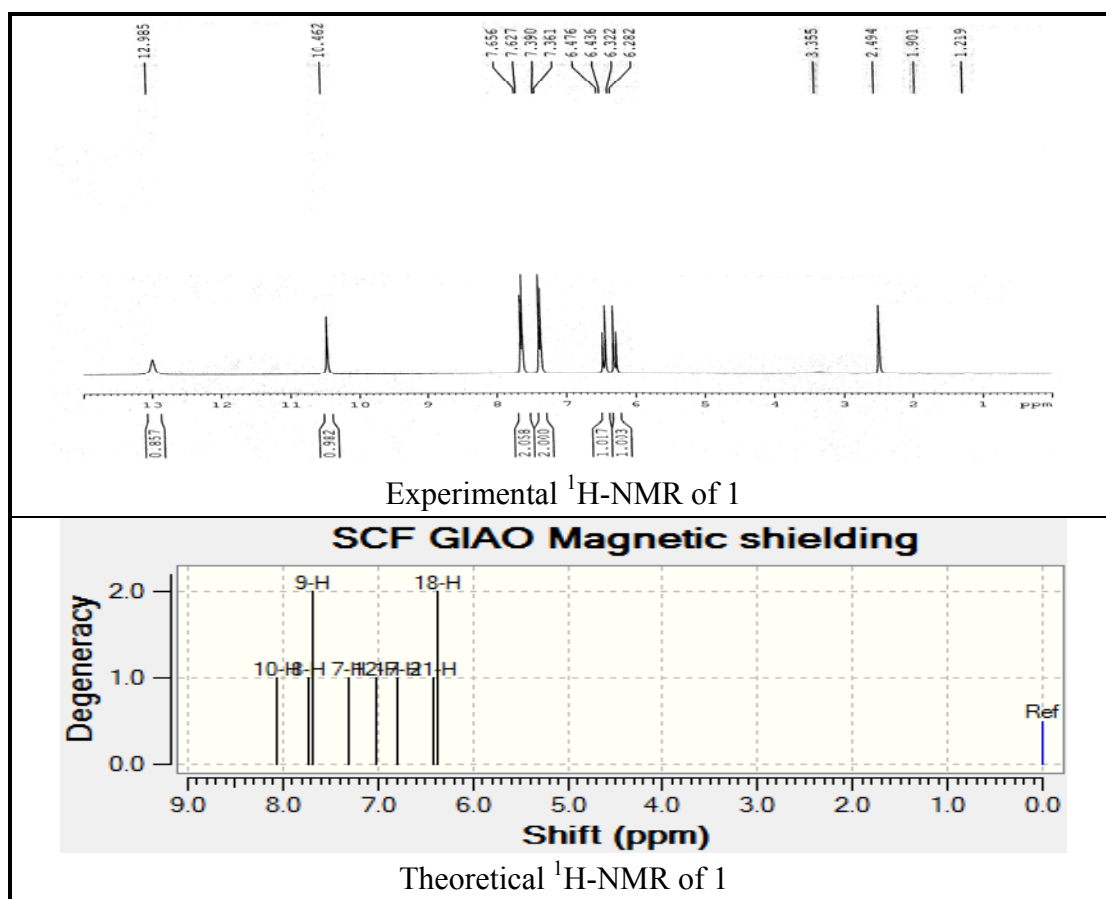


Figure 3: Experimental and theoretical $^1\text{H-NMR}$ spectrum of 1

Mulliken atomic charges

Atomic charges play an important role in the application of quantum chemical calculations to molecular system. It is used to get information on the electron densities of the atoms. Atomic charges were obtained using the NPA based on the DFT/B3LYP/6-311++G (d, p) wave function are listed in Table 5. All hydrogen atoms have positive charges. More positive charge was found to present on H12 (0.327) in 1 and H8 and H9 (0.232) in 2 but more negative charge (-0.442 and -0.374) was present on C1 in both 1 and 2 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 (λ_{\max}) of the molecules³⁰ by using equation 1³¹. Energy gap (eV) = Energy gap (Hartree or a.u.) x 27.2113834

$$\lambda_{\max} = 1240 / \text{Energy gap (eV)} \text{ ----- 1}$$

For the compounds 1 and 2 HOMO-LUMO energy and λ_{\max} calculated and was found at 268 nm and 347nm respectively shown in Table 6. HOMO-LUMO plots are given in figure 1.

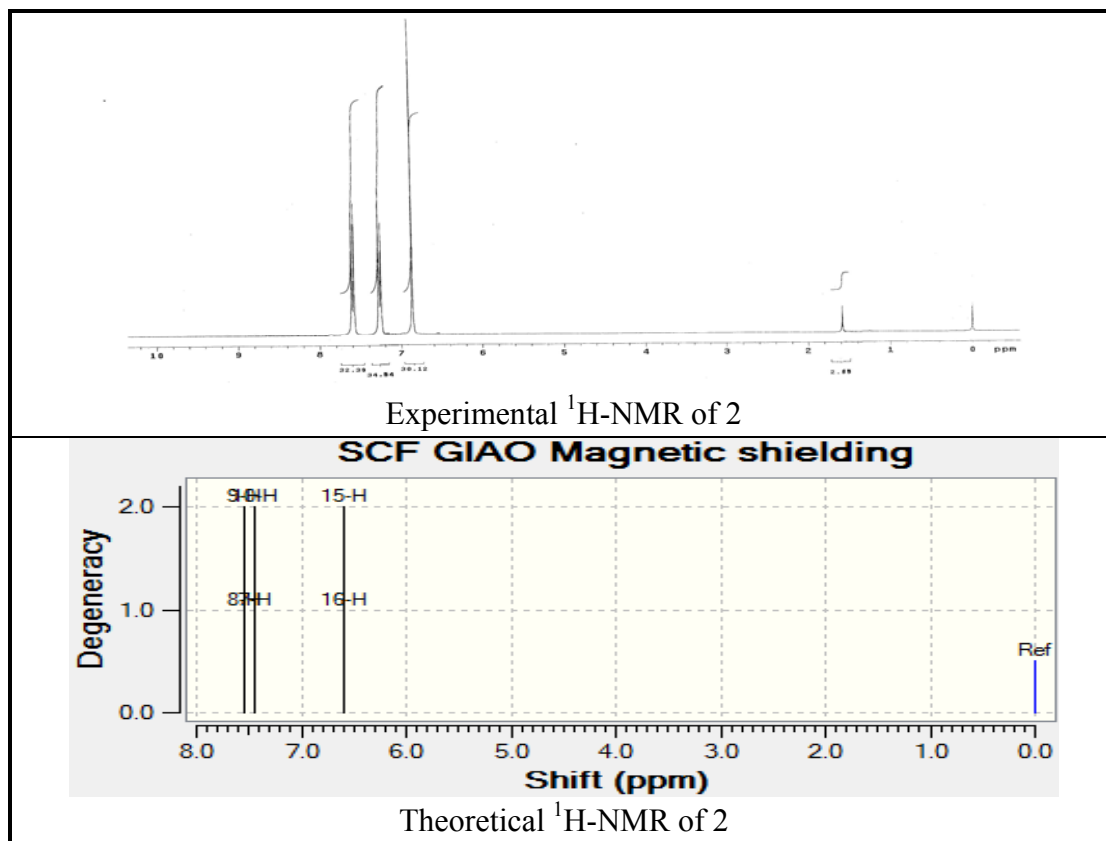


Figure 3: Experimental and theoretical ¹H-NMR spectrum of 2

Chemical Reactivity:

The chemical reactivity descriptors such as total energy (E), 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 descriptors are listed in Table 6.

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 equation 2. Softness is the reciprocal of global chemical hardness.

$$\eta = ((E_{\text{LUMO}} - E_{\text{HOMO}})) / 2 \text{ ----- 2}$$

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 2 is more reactive than compound 1.

Electronegativity(χ): The concept of electronegativity was put forward by Pauling³². 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 equation 3.

$$\chi = -(E_{LUMO} + E_{HOMO})/2 \text{-----} 3$$

Electronic chemical potential (μ): It is same in magnitude to that of the electronegativity with opposite sign³³ or half of the sum of HOMO and LUMO energy and it was determined using equation 4.

$$\mu = -\chi \text{ or } \mu = (E_{LUMO} + E_{HOMO})/2 \text{-----} 4$$

Physically ' μ ' describes the escaping tendency of electrons from an equilibrium system³⁴. Greater the electronic chemical potential, less stable or more reactive is the compound.

Global electrophilicity index (ω): It was introduced by Paarand is measure of the capacity or propensity of a chemical species to accept electrons^{35, 36} and stabilization in energy when chemical system accepts additional amount of electronic charge from the environment^{37, 38}. Global electrophilicity index was calculated by using the electronic chemical potential and chemical hardness by following equation 5.

$$\omega = \mu^2 / 2 \eta \text{-----} 5$$

Imide was found to be more electrophilic than maleanilic acid.

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 equation 6.

$$A = -E_{LUMO} \text{ and } I = -E_{HOMO} \text{-----} 6$$

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

On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions such as total thermal energy (E), total molar heat capacity at constant volume (Cv), total Entropy (S), rotational constant (G Hz) and Zero-point vibrational energy (Kcal/mol) were obtained and reported in Table 7.

Table 5: Mulliken atomic charges of 1 and 2

Atom	Charge		Atom	Charge		Atom	Charge	
	1	2		1/2	1		2	1/2
C1	-0.442	-0.374	H9	0.242	0.232	H/N17	0.227	0.235
C2	0.025	0.076	H10	0.191	0.197	H/O18	0.220	-0.261
C3	-0.177	-0.266	N/C11	-0.110	-0.090	C/O19	-0.145	-0.261
C4	0.136	0.125	H/C12	0.327	-0.090	O/Br20	-0.146	-0.178
C5	-0.336	-0.267	C13	-0.141	-0.017	H/C21	0.287	--
C6	0.077	0.076	O/C14	-0.267	-0.017	O/H22	-0.260	--
H7	0.177	0.197	C/H15	0.147	0.225	Br/H23	-0.175	--
H8	0.226	0.232	C/H16	-0.084	0.225	H24		--

Table 6: HOMO, LUMO energy gap (a.u.), λ_{\max} and SCF energy (a.u.) and global chemical hardness values of 1 and 2

Parameters	1	2
HOMO energy (eV)	-6.84	-6.83
LUMO energy (eV)	-2.22	-3.24
Energy Gap (eV)	4.62	3.57
λ_{\max} (nm)	268	347
E(RB3LYP) (a.u. or Hartree)	-3240.64	-3164.18
Global chemical hardness (η) eV	2.30	1.79
Chemical softness (σ) eV	0.43	0.55
Electronegativity χ (eV)	4.53	5.04
Electronic chemical potential μ (eV)	-4.53	-5.04
Electrophilicity index ω (eV)	4.45	7.09
Electron affinity A (eV)	2.22	3.24
Ionization energy I (eV)	6.84	6.83

Table 7: Thermodynamic parameters of 1 and 2

Parameters	1	2
Total E (Thermal) Kcal/mol.	111.784	93.791
Total (Cv) Cal mol ⁻¹ Kelvin ⁻¹	50.472	43.052
Total Entropy (S) Cal mol ⁻¹ Kelvin ⁻¹	120.827	109.670
Zero point vibrational energy (Kcal/mol)	103.382	86.591
Dipole moment (D)	2.1221	3.1642
Molecular mass	268.969	250.958

Conclusion

N-(4-bromophenyl) and N-(4-methoxyphenyl) maleimides were synthesized and characterised by the FT-IR and ¹HNMR spectroscopy. The optimized geometry parameters were computed by DFT/ B3LYP at 6311G++d,p basis sets using Gaussian 09W package and Gauss view A-5.0. Vibrational assignments examined by DFT methods of computation were found to be nearly in good agreement with the experimental values of both the compounds. The small HOMO-LUMO energy gap, chemical hardness, softness and λ_{\max} values shows that the compound 2 is more reactive than 1. The thermodynamic parameters also showed the reactivity difference of the two compounds.

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