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DFT and Experimental studies of N-(4-nitrophenyl) maleimide

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ABSTRACT

N-(4-nitrophenyl) maleimide was synthesized from the maleic anhydride and 4-nitroaniline followed by characterization using IR and NMR spectroscopic techniques. Quantum chemical calculations were performed to optimize geometry of the title compound by density functional theory method at B3LYP level and 6-311++G(d, p), 6-31++G (d, p), 6-31+G (d, p) and 6-31+G (d) as basis set. ^{1}HNMR and fundamental vibrational frequencies were calculated theoretically by DFT and HF method and compared with experimental data. The small difference between observed and scaled theoretical frequencies were recorded. Thermodynamic properties like zero-point energy, entropy, heat capacity and dipole moment have been recorded at B3LYP/6-3++G (d, p). Absorption maxima (λmax) is calculated with the help of HOMO-LUMO energy gap. Small energy gap implies an electron density transfer from HOMO to LUMO and also implies the reactivity of the title compound.

Keywords: DFT study, HOMO-LUMO, IR spectrum, 4-nitrophenyl maleimide, vibrational frequencies.

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 pharmacology [1-6], biology [7-13], synthetic chemistry [14-16], polymer chemistry [17-18] as well as material science[19].

Ab initio and Density Functional Theory (DFT) methods have become a powerful tool to investigate molecular structure and vibrational spectra in most of the chemical studies. Traditional ab initio methods have been used for many years and there is number of evidence of computational data from which researchers can choose a proper theory level that predicts the physical and chemical properties of the system under consideration [20]. DFT methods can produce good optimization of the chemical system [21]. N Sundaraganesan et al. [22] reported the optimized geometry and vibrational frequencies, of 2,4,6-triaminopyrimidine by HF and density functional B3LYP method with the 6-31G (d, p) basis set. S Chandra et al. [23] reported IR and Raman spectra and HOMO-LUMO energy gap of 1,3-dimethyl barbituric acid experimentally and theoretically by DFT method at B3LYP level using 6-31 G (d, p) basis set. V. L. Siji et al. [24] reported FT-IR and FT-Raman spectral studies and DFT calculations of keto-enol tautomers of benzaldehyde –N (4)-phenyl semicarbazone using B3LYP method with 6-311++G** basis set. A. B. Sawant et al. [25] synthesized 2-[5-(4-chlorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl] phenol from chalcone and investigated the molecular structure and vibrational spectra of the same by *Ab initio* (RHF and MP2) and Density Functional Theory (DFT) method at B3LYP level using 6-31+G (d), 6-31++ G (d, p), 6-311G (d, p), 6-311++G (d, p) basis sets. Sundaraganesan et al. [26] have been studied molecular structure and vibrational spectra of 2-chlorobenzoic acid by density functional theory and *Ab initio* Hartree-Fock calculations using 6-311++G (d, p) basis set.Singh et al. [27] reported molecular structure and vibrational spectra of 2-hydroxy-5-methyl-3-nitropyridine by HF and DFT using 6-311G (d) and 6-311G (3d, 2p) basis sets.

Literature survey reveals that, optimization and vibrational frequencies for N-(4-nitrophenyl) maleimide have not been reported so far. Therefore, the N-(4-nitrophenyl) maleimidewas synthesized by the recent method [28]. The optimized geometries and vibrational frequencies of the title compound was carried out by density functional theory method at B3LYP level using 6-311++G (d, p) basis set.These frequencies were analysed and compared with the experimental data. HOMO and LUMO energy have been used to calculate absorption maxima of the molecule.

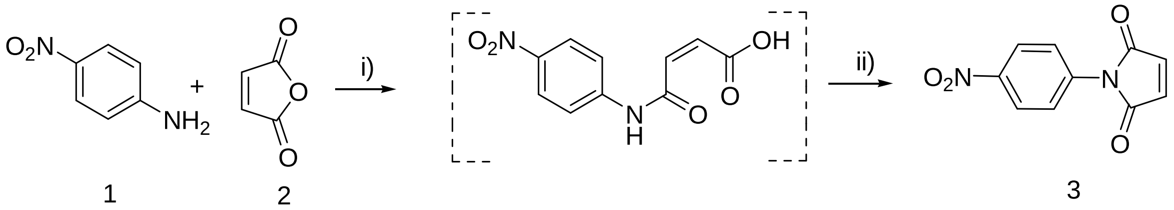
MATERIALS AND METHODS

The reagents required for the synthesis of N-(4-nitrophenyl) maleimide (3) were analytical grade purchased from Sigma Aldrich and S.D. Fine chemicals and were used without further purification. Melting point was determined on a Gallenkamp melting point apparatus and it was uncorrected.IR spectrum was recorded as KBr pellets on a Shimadzu FTIR-408 spectrophotometer. The ^{1}H-NMR spectrum was recorded on Bruker 300 MHz, NMR spectrometer using $CDCl_3$ as solvent and TMS as in internal standard. Peak values are shown in δ (ppm).

Synthesis of N-(4-nitrophenyl) maleimide

N-(4-nitrophenyl) maleimide (3) was synthesized from corresponding aniline (1) and maleic anhydride (2) by following **scheme-1** as per therecently reported one pot efficient procedure [28]. The solid product obtained was purified by crystallisation using ethyl alcohol.

Scheme-1

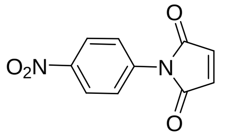


Reagents and Conditions: **i**) AcOH, r.t., 10 min. **ii**) Conc. H_2SO_4, 60^{o}C, 2.5 hr.

Spectral Data

The spectral data of the synthesized compound is as follow. The experimental ^{1}H-NMR and IR spectral data of the title compound is listed in **Table-1** and **fig. 1** shows experimental (a) and theoretical (b& c) IR spectrum.

Table1: Experimental and theoretical spectral data of N-(4-nitrophenyl) maleimide

 Mol. Formula: $C_{10}H_6N_2O_4$	**Experimental data**	**Theoretical data**
^{1}HNMR data δ (ppm)	(300 MHz, $CDCl_3$) 6.94 (2H, s, 2 X =CH), 7.68 (2H,d, J = 9.3 Hz, ArH), 8.07 (2H, d, J = 9.3 Hz, ArH).	H16 and H17 (2H): 6.66 H7 and H10 (2H): 7.79 H8 and H9 (2H): 8.54
IR data cm^{-1}	1716: imide C=O stretch. 1583:C=C stretch. 1533, 1348: NO_2 stretch. 1143,831,694.	1713: imide C=O stretch. 1585, 1573: C=C stretch. 1516: NO_2 stretch.

Computational Details:

All computational calculations were performed on an Intel, Core i3 personal computer using the Gaussian 09W program[29] package without any constraint on the geometry. Geometries of the titled compound were optimized by DFT/B3LYP at 6-311++G(d, p), 6-31++G (d, p), 6-31+G (d, p) and 6-31+G (d) as basis sets in gas phase. Optimized geometry parameters were used in vibrational frequency calculations by DFT/B3LYP level and by HF method at 6-311++G(d, p) to confirm the structure as minima. Absence of imaginary frequency confirms the energy minima. The vibrational frequency assignments and other parameters were made using Gauss View 5.0molecular visualization program.

RESULTS AND DISCUSSION

Molecular geometry

The optimized geometrical parameters (bond lengths, bond angles and dihedral angles) of the title compound are listed in **Table-2, 3 and 4** according to the numbering reported in optimized structure of the title compound in **fig.2**. Comparison of experimental and the computational data showed good agreement for peak with high relative intensities. C1 point group symmetry showed the planer structure of the title compound. There are 22 atoms in the molecule of title compound, so 60 normal modes of fundamental vibrations are expected. The vibrational frequencies computed at the HF level contain known systematic error due to the neglect of electron correlation resulting in overestimations of about 10 to 20%, therefore it is usual to scale frequencies predicted at HF and DFT/B3LYP level by an empirical factor [30] of 0.8929 and 0.9613 respectively. The use of factors proved to produce good agreement with experiment for wide range of chemical system. The scaled vibrational frequencies are listed in **Table-5**.

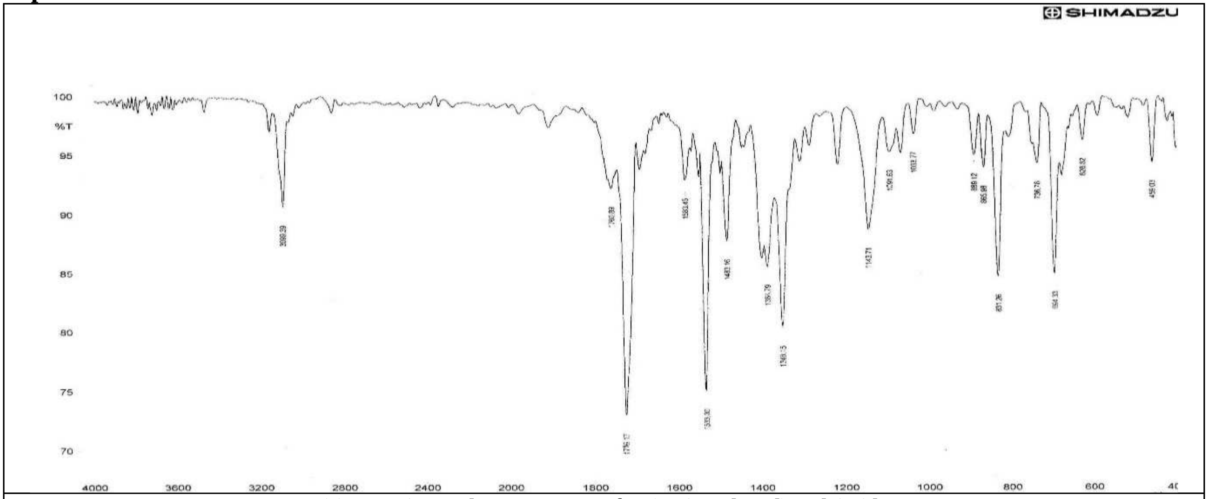
Vibrations of imide >C=O group: Anamide carbonyl group absorbs strongly in the 1630-1690 cm^{-1} region. For imide carbonyl, experimental vibration is reported at 1716 cm^{-1} while computed C=O stretching frequency is obtained at 1713 cm^{-1} by DFT and 1631 cm^{-1} by HF methods respectively. So vibrational assignments predicted by DFT method is very close to that of the experimental value for the title compound.

C-H Vibrations: Aromatic C-H stretching occurs at the 3100-3000 cm^{-1} while olefin C-H stretching occurs in the 3010-3095 cm^{-1} range. For the title imide compound aromatic C-H stretching is obtained at 3094- 3096 cm^{-1} by DFT and at 2947-2948 cm^{-1} by HF method while olefin C-H stretching is obtained at 3106 cm^{-1} by DFT and at 2959 cm^{-1} by HF method. C-H stretching predicted by DFT method is found to be nearly close to the literature and experimentally reported value.

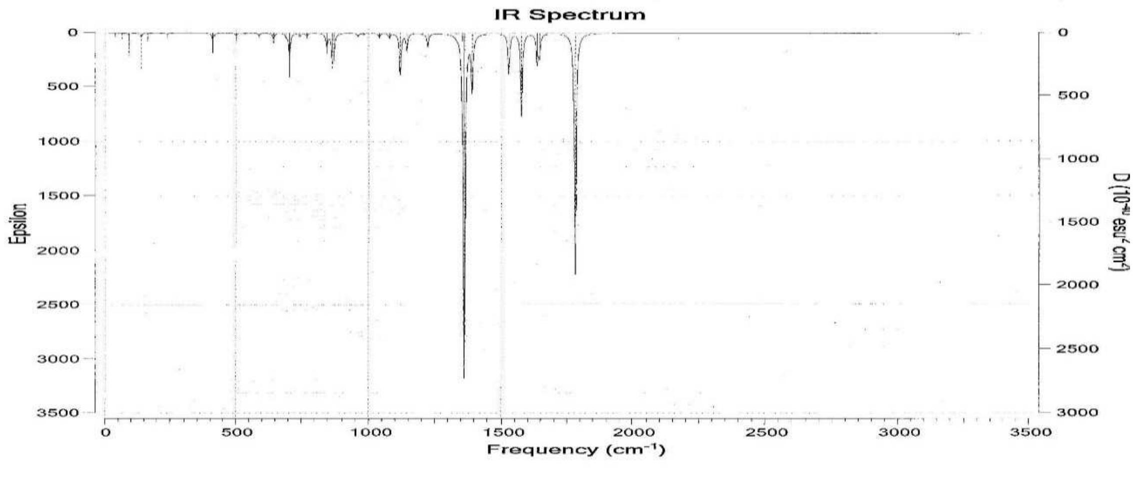
C=C vibrations: The region of C=C stretching vibrations were given in literature in the range of 1660-1580 cm^{-1}. Theoretically the vibrations were predicted at 1573- 1585 cm^{-1}by DFT and at 1548-1569 cm^{-1}by HF method for aromatic and olefin C=C. The experimental values were assigned at1598 cm^{-1}.Computational vibrational frequencies were obtained by DFT are in good agreement with the experimental values.

*N-O vibration*s: The region of N-O stretching vibration was 1550-1350 cm^{-1}. The experimental stretching vibration of the title compound was found at 1508 cm^{-1}. Theoretically it was predicted at 1516 cm^{-1} by DFT/B3LYP and at 1338 cm^{-1} by HF method.

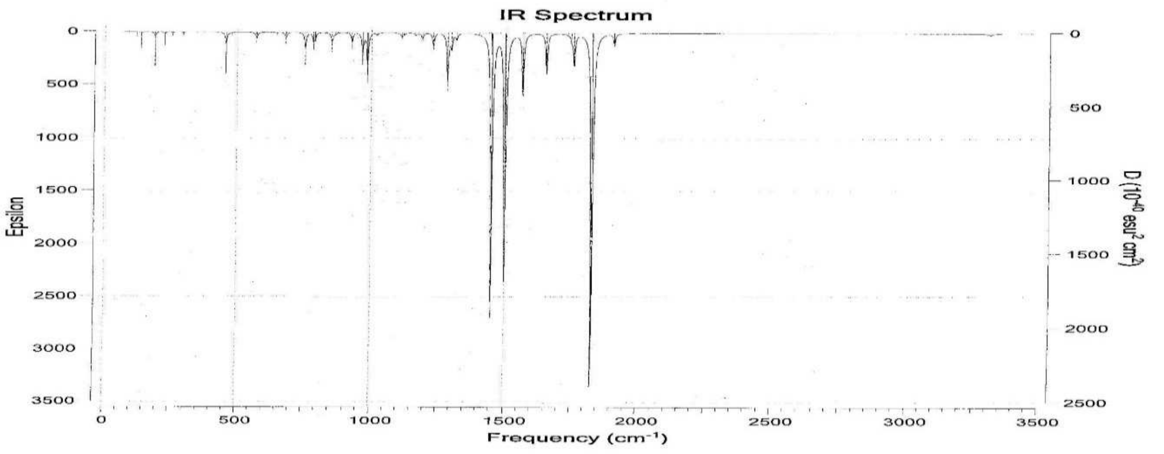
IR Spectrum



(a) Experimental IR Spectrum of N-(4-nitrophenyl) maleimide



(b) IR Spectrum by DFT/B3LYP at 6-311++G (d, p)



(c) IR Spectrum by HF/6-311++G (d, p)

Fig. 1-IR spectrum (Experimental and Theoretical) of N-(4-nitrophenyl) maleimide.

Optimized molecule and HOMO-LUMO plots of N-(4-nitrophenyl) maleimide

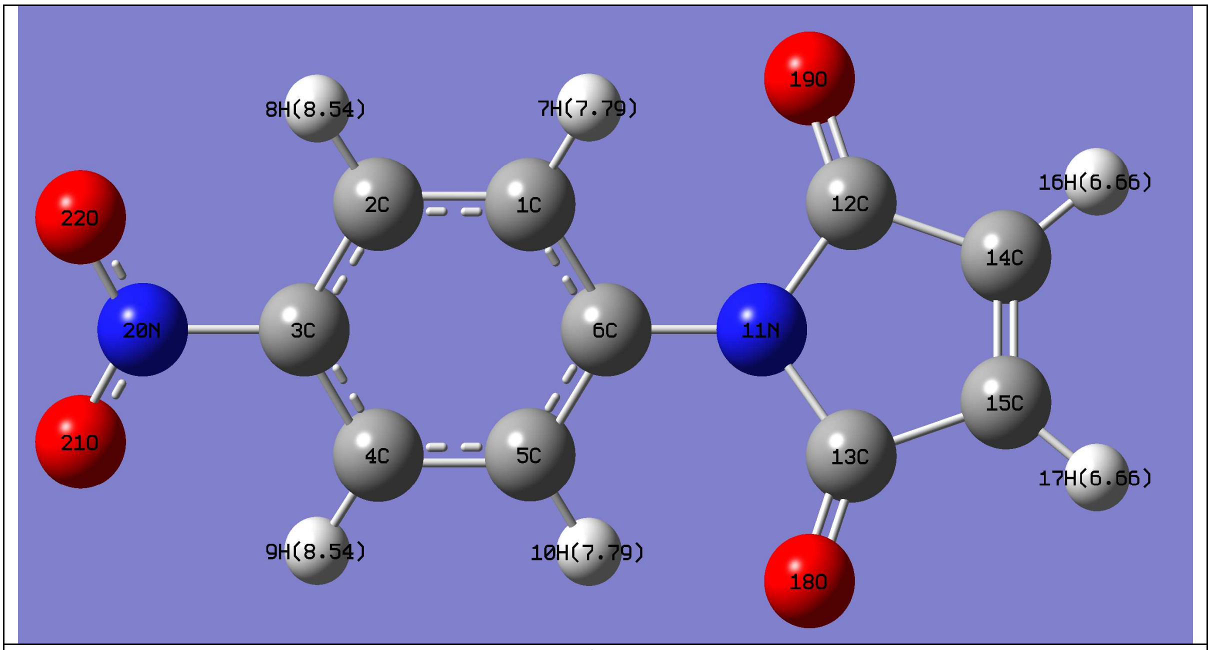
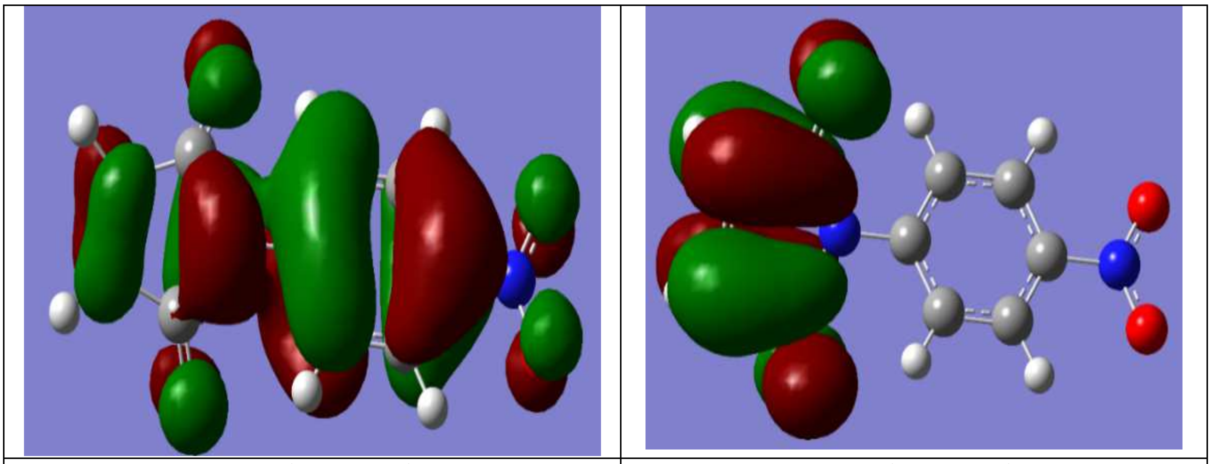


Fig. 2 Optimized molecular structure and NMR shielding of N-(4-nitrophenyl) maleimide at DFT/B3LYP)/6-311++G (d, p)



HOMO (-0.28034 a.u.) **LOMO (-0.13056 a.u.)**

Fig. 3 HOMO, LUMO plots of N-(4-nitrophenyl) maleimide at DFT/B3LYP)/6-311++G(d, p)

Bond lengths

Table 2- Optimized geometrical parameter,bond lengths (A^o) of N-(4-nitrophenyl) maleimide by DFT method at B3LYP level using different basis sets

Parameter **Bond length** (A^o)	6-311++G (d, p)	6-31++G(d, p)	6-31+G(d, p)	6-31+G(d)
	Bond lengths			
C1-C2	1.388	1.3914	1.3914	1.3916
C1-C6	1.3997	1.4033	1.4033	1.4032
C1-H7	1.0802	1.0819	1.0819	1.0829
C2-C3	1.3905	1.3943	1.3943	1.3946
C2-H8	1.081	1.0828	1.0828	1.0835
C3-C4	1.3905	1.3943	1.3943	1.3946
C3-N20	1.4772	1.4713	1.4713	1.4712
C4-C5	1.388	1.3914	1.3914	1.3916
C4-H9	1.081	1.0828	1.0828	1.0835
C5-C6	1.3997	1.4033	1.4033	1.4032
C5-H10	1.0802	1.0819	1.0819	1.0829
C6-N11	1.4212	1.4219	1.4219	1.4218
N11-C12	1.4164	1.417	1.417	1.4171
N11-C13	1.4164	1.417	1.417	1.4171
C12-C14	1.4967	1.497	1.497	1.497
C12-O19	1.2042	1.2121	1.2121	1.2121
C13-C15	1.4967	1.497	1.497	1.497
C13-O18	1.2042	1.2121	1.2121	1.2121
C14-C15	1.3315	1.3364	1.3364	1.3366
C14-H16	1.0801	1.082	1.082	1.083
C15-H17	1.0801	1.082	1.082	1.083
N20-O21	1.2249	1.2324	1.2324	1.2324
N20-O22	1.2249	1.2324	1.2324	1.2324

Bond angles

Table 3- Optimized geometrical parameter, bond angles (^{o}) of N-(4-nitrophenyl) maleimide by DFT method at B3LYP level using different basis sets

Parameter **Bond angles**(A^{o})	6-311++G (d, p)	6-31++G(d, p)	6-31+G(d, p)	6-31+G(d)
	Bond angles			
C2-C1-C6	119.8944	119.8718	119.8717	119.8972
C2-C1-H7	119.8750	119.8737	119.8737	119.8173
C6-C1-H7	120.2269	120.25	120.25	120.2824
C1-C2-C3	119.0664	119.0867	119.0868	119.1018
C1-C2-H8	121.1682	121.1017	121.1017	120.9713
C3-C2-H8	119.7639	119.81	119.8101	119.9253
C2-C3-C4	121.7871	121.759	121.7589	121.7084
C2-C3-N20	119.1064	119.1207	119.1207	119.1457
C4-C3-N20	119.1064	119.1203	119.1203	119.1459
C3-C4-C5	119.0664	119.0879	119.0879	119.1016
C3-C4-H9	119.7639	119.8091	119.809	119.9255
C5-C4-H9	121.1683	121.1016	121.1016	120.9713
C4-C5-C6	119.8945	119.8705	119.8705	119.8974
C4-C5-H10	119.8750	119.8728	119.8728	119.8174
C6-C5-H10	120.2268	120.2521	120.2521	120.2821
C1-C6-C5	120.2875	120.3203	120.3203	120.2895
C1-C6-N11	119.8562	119.838	119.8379	119.8552
C5-C6-N11	119.8562	119.8417	119.8418	119.8553
C6-N11-C12	125.2781	125.3631	125.3631	125.3436
C6-N11-C13	125.2778	125.3637	125.3637	125.3443
C12-N11-C13	109.4442	109.2732	109.2731	109.312
N11-C12-C14	106.1462	106.3624	106.3625	106.3351
N11-C12-O19	126.2664	126.211	126.211	126.2058
C14-C12-O19	127.5868	127.426	127.4259	127.4584
N11-C13-C15	106.1462	106.3625	106.3625	106.3351
N11-C13-O18	126.2664	126.2108	126.2108	126.2058
C15-C13-O18	127.5869	127.4261	127.4261	127.4583
C12-C14-C15	109.1317	109.001	109.001	109.0088
C12-C14-H16	121.2991	121.3453	121.3453	121.3065
C15-C14-H16	129.5689	129.6536	129.6536	129.6846
C13-C15-C14	109.1317	109.0007	109.0006	109.0089
C13-C15-H17	121.2991	121.346	121.346	121.3064
C14-C15-H17	129.5689	129.6532	129.6532	129.6846
C3-N20-O21	117.6457	117.7513	117.7512	117.7517
C3-N20-O22	117.6457	117.7509	117.7509	117.7517
O21-N20-O22	124.7087	124.4978	124.4978	124.4966

Dihedral angles

Table 4- Optimized geometrical parameter, dihedral angles (°) of N-(4-nitrophenyl) maleimideby DFT method at B3LYP level using different basis sets.

Dihedral angles	6-311++G (d, p)	6-31++G(d, p)	6-31+G(d, p)	6-31+G(d)
	Dihedral angles			
C6-C1-C2-C3	0.5597	0.5771	0.5771	0.5958
C6-C1-C2-H8	-179.8803	-179.865	-179.8651	-179.8694
H7-C1-C2-C3	179.8667	179.8044	179.8044	179.9608
H7-C1-C2-H8	-0.5733	-0.6377	-0.6377	-0.5045
C2-C1-C6-C5	-0.2841	-0.2935	-0.2934	-0.3024
C2-C1-C6-N11	179.7165	179.7062	179.7062	179.6976
H7-C1-C6-C5	-179.5887	-179.5178	-179.5178	-179.6643
H7-C1-C6-N11	0.4119	0.4818	0.4817	0.3357
C1-C2-C3-C4	-0.2814	-0.2897	-0.2896	-0.2996
C1-C2-C3-N20	179.7185	179.7104	179.7104	179.7003
H8-C2-C3-C4	-179.8477	-179.8534	-179.8533	-179.8393
H8-C2-C3-N20	0.1522	0.1467	0.1467	0.1606
C2-C3-C4-C5	-0.2816	-0.2913	-0.2913	-0.2997
C2-C3-C4-H9	-179.8479	-179.8539	-179.8538	-179.8395
N20-C3-C4-C5	179.7185	179.7087	179.7087	179.7004
N20-C3-C4-H9	0.1522	0.1461	0.1462	0.1606
C2-C3-N20-O21	-179.895	-179.68	-179.68	-179.6554
C2-C3-N20-O22	0.1063	0.3194	0.3194	0.3337
C4-C3-N20-O21	0.1049	0.32	0.32	0.3445
C4-C3-N20-O22	-179.8938	-179.6806	-179.6806	-179.6664
C3-C4-C5-C6	0.5597	0.5774	0.5774	0.5958
C3-C4-C5-H10	179.8666	179.8042	179.8042	179.9607
H9-C4-C5-C6	-179.8803	-179.8659	-179.8659	-179.8694
H9-C4-C5-H10	-0.5734	-0.6391	-0.6391	-0.5045
C4-C5-C6-C1	-0.284	-0.2924	-0.2924	-0.3022
C4-C5-C6-N11	179.7154	179.708	179.708	179.6979
H10-C5-C6-C1	-179.5884	-179.5162	-179.5162	-179.6641
H10-C5-C6-N11	0.411	0.4841	0.4842	0.3359
C1-C6-N11-C12	-38.6802	-37.4738	-37.4737	-38.5986
C1-C6-N11-C13	141.3173	142.5472	142.5473	141.4031
C5-C6-N11-C12	141.3204	142.5259	142.5259	141.4013
C5-C6-N11-C13	-38.6821	-37.4531	-37.4531	-38.5969
C6-N11-C12-C14	-179.9675	-179.9443	-179.9444	-179.9618
C6-N11-C12-O19	-0.2412	-0.2094	-0.2094	-0.2656
C13-N11-C12-C14	0.0347	0.0375	0.0375	0.0367
C13-N11-C12-O19	179.761	179.7725	179.7725	179.7329
C6-N11-C13-C15	-179.9916	-179.9709	-179.9709	-179.9658
C6-N11-C13-O18	-0.2242	-0.2375	-0.2375	-0.2677
C12-N11-C13-C15	0.0062	0.472	0.0472	0.0358
C12-N11-C13-O18	179.7736	179.7806	179.7806	179.7338
N11-C12-C14-C15	-0.0679	-0.1193	-0.1193	-0.1048
N11-C12-C14-H16	179.7536	179.7706	179.7705	179.7804
O19-C12-C14-C15	-179.7894	-179.8501	-179.85	-179.796
O19-C12-C14-H16	0.0321	0.0398	0.0398	0.0891
N11-C13-C15-C14	-0.0505	-0.1253	-0.1253	-0.1042
N11-C13-C15-H17	179.7717	179.7629	179.7629	179.781
O18-C13-C15-C14	-179.8139	-179.8544	-179.8544	-179.7973
O19-C13-C15-H17	0.0083	0.0338	0.0338	0.0879
C12-C14-C15-C13	0.0722	0.1487	0.1488	0.1272
C12-C14-C15-H17	-179.7308	-179.7272	-179.7272	-179.7454
H16-C14-C15-C13	-179.73	-179.7291	-179.7291	-179.7453
H16-C14-C15-H17	0.4671	0.3949	0.3949	0.3822

Vibrational assignments

Table 5- Fundamental scaled vibrational frequencies of N-(4-nitrophenyl) maleimide calculated by DFT/B3LYP and Hartree Fock methods at 6-311++G(d, p) basis set with their assignments.

Normal mode	DFT/B3LYP/6-311++G (d, p)		HF/6-311++G(d, p)		Assignments
	Calculated scaled frequencies cm^{-1}	IR intensity	Calculated scaled frequencies	IR intensity	
60	3124	0.3302	2974	1.0434	Sym. olefin C-H stretching
59	3107	2.8093	2960	2.8905	Sym. Ar-H stretching
58	3106	1.9564	2959	2.3711	Asym. Ar-H stretching
57	3105	0.1395	2956	1.1084	Asym. olefin C-H stretching
56	3096	1.1468	2948	1.0458	Sym. Ar-H stretching
55	3094	0.9613	2947	1.4849	Asym. Ar-H stretching
54	1766	0.0340	1703	32.9328	Sym. C=O stretch. Imide
53	1713	645.34	1631	973.76	Asym. C=O stretch. Imide
52	1585	4.1985	1548	02.104	C=C Stretching (olefin)
51	1582	54.234	1560	17.940	C=C Stretching (aromatic)
50	1573	76.858	1569	85.274	C=C Stretching (aromatic)
49	1516	221.72	1338	298.967	Asym. N-O stretching
48	1470	107.64	1476	111.828	C-H in plane bending(olefin)
47	1392	0.5882	1397	166.858	C-H bending aromatic
46	1337	147.53	1339	434.9412	C-N stretching (C-N) imide
45	1308	951.09	1299	700.634	C-N stretching (C-NO$_2$)
44	1301	22.160	1295	17.5315	C=C (aromatic ring deform.)
43	1279	2.8877	1292	51.8615	C-H in plane bending (arom.)
42	1274	0.9762	1290	0.5996	C-H wagging olefin
41	1175	36.195	1174	16.5380	C-N stretching (C-N) arom.
40	1159	2.5063	1145	125.8279	C-H aromatic scissoring sym.
39	1100	44.773	1120	4.25611	C-H aromatic scissoring asym.
38	1076	67.534	1061	16.5225	C-N stretching (C-NO$_2$)
37	1076	43.977	1097	36.7234	C-N stretching imide asym.
36	1037	11.938	1048	4.0520	C-H scissoring olefin
35	1000	10.186	1038	7.5510	C-H wagging arom
34	992	1.5533	1012	0.0950	C-H bending in plane arom.
33	977	0.0036	1000	6.1539	C-H bending(arom)
32	955	3.9269	980	1.4863	C-H twisting arom.
31	942	0.1315	979	0.0631	C-H twisting olefin
30	923	8.5279	90	5.4561	Arom. Ring deformation
29	836	52.599	872	24.864	N-O scissoring
28	831	62.078	864	0.3015	C-H out pf plane bending
27	812	35.118	863	52.7806	C-H olefin wagging
26	805	1.2424	827	24.8642	C-H arom. wagging
25	739	7.9574	772	4.4950	Imide ring deformation
24	714	4.4679	761	27.9871	Ring vibrations
23	712	5.6904	705	12.1064	Ring deformation
22	676	61.370	699	23.9054	Ring deformation
21	664	8.3939	673	43.5295	Imidering deformation
20	619	3.1175	661	0.0600	Imide ring bending
19	617	12.993	610	3.0721	Ring deformation
18	606	1.5620	607	13.7668	Ring bending imide
17	565	6.0321	576	3.4384	Ring vibrations
16	513	1.0171	511	6.0562	Ring vibrations
15	500	1.6807	509	10.4150	Ring deformation
14	482	7.7905	498	1.3700	Imide ring deformation
13	404	2.6320	424	2.5169	Aromatic ring deformation
12	395	16.415	407	31.4707	Ring deformation
11	368	0.0488	383	0.0198	Ring deformation
10	308	0.1123	331	0.9939	Ring vibrations
9	273	0.0032	325	0.0008	Ring deformation
8	227	1.8119	263	1.7219	Ring vibrations
7	227	2.4395	226	1.5804	Ring vibrations
6	156	2.6879	200	4.9462	Ring vibrations
5	132	10.078	187	0.0001	NO$_2$group vibrations
4	85	4.0253	168	10.6263	Ring vibrations
3	60	0.8006	120	3.7044	Ring vibrations
2	50	0.0228	104	0.8961	Ring vibrations
1	35	0.2763	85	0.0398	Ring vibrations

Mulliken atomic charges:

Atomic charges depend on how the atoms are defined. It also plays an important role in the application of quantum chemical calculations to molecular system. Natural Population Analysis (NPA) is used to generate 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-6**. More positive charge is present on H8 (0.255197) and H9 (0.255200)while more negative charge is present on C3 (-0.464664) and C6 (-0.356796).

Table 6- Optimized geometrical parameters of N-(4-nitrophenyl) maleimide.
Mulliken atomic charges by DFT method at B3LYP level at 6-311++G (d, p)basis sets.

Atom	Charge	Atom	Charge	Atom	Charge (a.u.)
C1	0.133118	H9	0.255200	H17	0.230427
C2	-0.113407	H10	0.224442	O18	-0.252248
C3	-0.464664	N11	0.222042	O19	-0.252245
C4	-0.113277	C12	-0.039283	N20	-0.179205
C5	0.132980	C13	-0.039481	O21	-0.005227
C6	-0.356797	C14	-0.043730	O22	-0.005223
H7	0.224460	C15	-0.043511		
H8	0.255197	H16	0.230430		

HOMO-LUMO energy and absorption maxima:

The HOMO is a highest occupied molecular orbital that can act as an electron donor and the LUMO is lowest unoccupied molecular orbital that can accept electron. **Fig.3** shows the HOMO-LUMO plot for the title compoundwhich clearly indicates that electron cloud moves from aromatic ring to imide ring.The small energy difference (0.150 a.u. or 4.07 eV) between HOMO and LUMO indicates their closeness. HOMO-LUMO energy gap can be used to predict the absorption maxima (λmax) of the molecules[31] by following formula [32].

$$\text{Energy gap (eV)} = \text{Energy gap (Hartree or a.u.)} \times 27.2113834$$
$$\lambda_{max} = 1240/\text{Energy gap (eV)}$$

For the title compound λmax was determined and found to be 304nm given in **Table-7**.

Table 7-HOMO, LUMO (a.u.), λmax, dipole moment (D) and SCF energy (a.u.) values of
N-(4-nitropheyl) maleimide by DFT method at B3LYP level using 6-311++G (d, p) basis set.

Basis set	HOMO Energy	LUMO Energy	Energy Gap (a.u. or Hartree)	Energy Gap (eV)	λmax (nm)	Dipole moment Debye	E(RB3LYP) (a.u)
6-311++G (d, p)	-0.28034	-0.13056	0.14978	4.075	304	6.8827	-795.20274114

Thermochemical parameters:

Table 8- Theoretically computed energy (a.u.), zero-point vibrational energy, (Kcal/mol),
rotational constant (GHz), entropy (Cal/mole) of N-(4-nitrophenyl) maleimide by DFT/B3LYP at 6-311++G (d, p)

Parameters	**Values**
Total E (Thermal) Kcal/mol.	102.362
Translational	0.889
Rotational	0.889
Vibrational	100.585
Total (Cv) Cal mol^{-1} Kelvin^{-1}	47.369
Translational	2.981
Rotational	2.981
Vibrational	41.407
Total Entropy (S) Cal mol^{-1} Kelvin^{-1}	113.895
Translational	42.042
Rotational	32.463
Vibrational	39.391
Zero point vibrational energy (Kcal/mol)	94.49428
Rotational constant (GHz)	1.47585 0.27609 0.24021
Dipole moment (D)	6.8827

CONCLUSION

N-(4-nitrophenyl) maleimide was synthesized and characterised by the ^{1}HNMR and IR spectroscopy. The optimized geometries were computed by DFT/ B3LYP at different basis sets using Gaussian 09W package and Gauss view A-5.0. Vibrational assignments were examined by DFT and HF methods of computation and the values predicted by

DFT/B3LYP at 6-31++G (d, p) were found to be nearly in good agreement with the experimental values of the title compound. The absorption maxima of the synthesized molecule are obtained from HOMO-LUMO energy gap.

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