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A density functional approach to pharmaceutical intermediate n-(methyl) phthalimide to yield complete vibrational assignments and HOMO-LUMO energy gap

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ABSTRACT
The understanding of optimized molecular geometry, vibrational analysis of the heterocyclic organic compounds plays a vital role in the process of drug discovery. The present work provides geometrical parameters, vibrational assignments for pharmaceutical intermediate N-(Methyl)phthalimide (NMP). Moreover, the present study aims to illustrate how intramolecular interactions appear within the molecule on account of HOMO-LUMO studies. In addition to these, Mullikan's Atomic charges associated with each atom of the stable conformer are also reported. Entire vibrational, geometrical parameters, Mullikan's Atomic charges and HOMO-LUMO Energy gap of NMP were predicted with the aid of B3LYP level of theory with 6-311++G(d,p) basis set on a quantum chemical software Gaussian 03W. In view of visual inspection, 51 normal modes of vibrations contributed to NMP were found out. HOMO-LUMO studies provided information about occupied and unoccupied molecular orbitals and intramolecular interactions of NMP. Mullikan's Atomic charge on each atom of NMP shows Charge-stability relations.

Introduction

Phthalimide and its derivatives is very important compound in various fields. In pharmaceutical, they are used as an intermediate material.

In medical field, phthalimide analogues are used in the synthesis of antimicrobial activity, androgens and other agents for treating tumor necrosis factor [1]. In medicinal chemistry, phthalimide analogues play a vital role as anti-convulsant, anti-inflammatory, analgesic, hypolipidimic and immunomodulatory activities [2].

Certain phthalimide derivatives are used as herbicides and for reducing bacterial contamination. In industry, they are widely used in the production of pesticides, dyes, plastics, high performance ion exchange resins, surfactants.

Because of its wide applications in various fields, Phthalimide and its nitro derivatives have been extensively investigated earlier. V. Krishnakumar et al [1,3] reported the vibrational assignments of N-bromophthalimide and N-hydroxyphthalimide, respectively.

Literature survey reveals that to the best of our knowledge no DFT calculations have been performed on account of NMP so far. Therefore, the present work was undertaken.

The main objective of this investigation is to calculate optimized molecular geometry, vibrational frequencies and vibrational assignments associated with N-(Methyl) phthalimide. In addition to these, HOMO-LUMO studies were also performed to enumerate the presence of intramolecular interactions within the molecule. Moreover, Mullikan's charges on each atom of the title molecule were also presented to illustrate charge-stability relations.

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Materials and Methods

The sample NMP in the solid form was purchased from the Lancaster Chemical Company, (UK) with a purity of greater than 98% and it was used as such without further purification. The FT-IR spectrum of NMP was recorded in the frequency region 400□4000 cm^{-1} on a NEXUS 670 spectrophotometer equipped with an MCT detector, a KBr pellet technique. The FT-Raman spectrum of NMP also has been recorded in the frequency region 100□3500 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory with Nd:YAG laser operating at 1.5W power continuously with 1064 nm excitation. The entire vibrational assignments and measurements were performed by means of Density Functional B3LYP method combining Becke's three-parameter hybrid functional method [4] with Lee-Yang-Parr's correlation functional (LYP) [5,6] with the standard high level 6-311++G(d,p) basis set in Gaussian 03W Quantum chemical software package [7]. In the calculations, the molecular geometry was optimized by assuming Cs point group symmetry. Charge of each point is taken as zero and the spin multiplicity is taken as one.

Results and Discussion

Molecular Geometry

Figure 1. Optimized Molecular Geometry of NMP

The title compound NMP is shown in Figure 1 has 19 atoms which belong to N-Substituted heterocyclic aromatic organic compound. The optimized geometrical parameters of NMP calculated by B3LYP/6-311++G(d,p) level are presented in Table 1. In the six member ring, the average C-C bond length is of the range ~1.3935Å. Introduction of substituent in the N-substituted phthalimide ring leads to significant variation in charge distribution in the molecule. Consequently, this greatly affects the molecular geometrical parameters of the five member ring. Hence the average C□C bond length in the five member ring observed in the range ~1.4942 Å. The average C□H bond length in the aromatic ring calculated by B3LYP/6-311++G(d,p) is ~1.0837Å whereas in the methyl group; the average C□H bond length is of ~1.0905Å. C□N bond lengths such as C7□N9, C8□N9 are found to be equal i.e 1.4028Å. But outside the ring, N9□C15 bond length (1.4538Å) slightly varies from that of ring C□N. Due to high symmetry of the benzene ring, its bond angles and dihedral angles are almost equal. Therefore, the average bond angles corresponding to aromatic C□C□H calculated at B3LYP/6-311++G(d,p) is 120.3823°. The substituent does not affect bond angles and dihedral angles of the NMP. Moreover, the dihedral angles of aromatic C□C□C□H angles are found to be ~180°. In other words, consecutive C□C and C□H bond lengths are co-planar.

Normal Coordinate Analysis

The molecule belongs to Cs point group symmetry and the group theory analysis of NMP indicates that, 51 normal modes of vibrations are distributed among the symmetry species as Γvib= 35A'(In-plane vibrations)+16A"(Out-of plane vibrations). From the structural point of view of the molecule, 19 In-plane stretching vibrations, 16 in-plane bending vibrations and 16 out-of plane bending vibrations are contributed to NMP. Detailed description of the vibration modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full sets of 72 standard internal coordinate [containing 21 redundancies] are defined as given in the Table 2.

Local Symmetry Coordinates

From 72 full sets of internal co-ordinates, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates followed by the recommendations of Fogarasi and Pulay [8,9]. The local symmetry co-ordinates corresponding to probable degrees of freedom of NMP were presented in Table 3.

Observed & Calculated Vibrational Spectra

The experimentally observed FT-IR and FT-Raman spectra of NMP along with the calculated spectra are shown in Figs 2 and 3, respectively. The calculated spectra were drawn with the aid of origin graphics program. Theoretically calculated IR intensities and Raman activities were taken as an input data for drawing calculated IR and Raman spectra respectively. This shows that, the theoretical computation by density functional B3LYP/6-311++G(d,p) level were good agreement with the experimental spectral data.

CH3 vibrations

For the assignments of CH3 group frequencies one can expect nine fundamentals can be associated with each CH3 group, namely CH3 ss (symmetric stretching), CH3 as (asymmetric stretching), CH3 ips (in-plane stretching), CH3 ops (out-of-plane stretching), CH3 ipb (in-plane bending), CH3 opb (out-of-plane bending), CH3 ipr (in-plane rocking), CH3 opr (out- of- plane rocking) and tCH3 (twisting) modes. The asymmetric stretching and asymmetric deformation modes of the methyl group are expected to be depolarized for A□ symmetry species [10]. The C□H stretching in CH3 occurs at lower frequencies than those of the aromatic ring 3000–2900 cm-1 [11-14]. In the present investigation, the asymmetric and symmetric stretching vibrations are observed in the ranges 2988–2881 cm-1 at FT-Raman spectrum. The theoretically computed value by B3LYP/6-311++G(d,p) method at 3085 cm-1 (see mode no: 6 in Table 4) assigned to CH3 asymmetric stretching vibration is over estimated by ~85 cm-1 when compared to the literature as well as recorded spectrum.

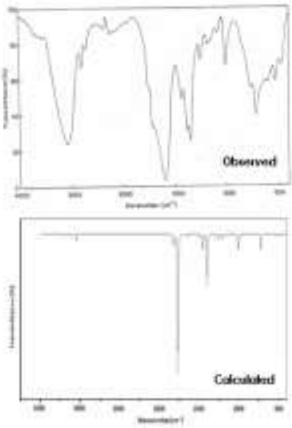


Fig.2 Observed and calculated IR

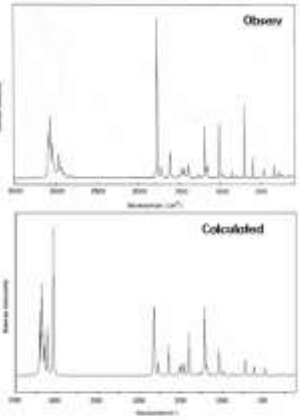


Fig.3 Observed and calculated Raman

For methyl substituted benzene derivatives, the asymmetric and symmetric bending vibrations of methyl group normally appear in the regions 1400□1370 cm-1 [15]. The bands observed at 1414 and 1394 cm-1 in the FT-Raman spectrum were attributed to asymmetric and symmetric deformations of methyl group respectively. The theoretically computed values of 1470 and 1454 cm-1 (see mode no: 15, 16 in Table 4) by B3LYP/6-311++G(d,p) method. The computed results are also in good agreement with the literature as well as recorded spectrum.

Generally aromatic compounds [16] display a methyl rock (□CH3) in the neighbourhood of 1045 cm-1. The second rock in the region 970±70 cm-1 is more difficult to find among C□H out of plane deformations. For the title compound, (□CH3) mode is calculated at 1099 cm-1 and (δCH3) mode calculated at 1035 cm-1. The weak band observed at 1084 cm-1 in the FT-IR is identified as (□CH3) mode. The strong peak at 1014 cm-1 in the FT-Raman spectrum is identified as (δCH3) mode. The assignment of the band at 108 cm-1 in the Raman is attributed to Butterfly motion. The experimental counterpart belongs to Butterfly and twisting (τCH3) modes are possible only in far IR spectra.

C=O vibrations

If a compound contains a carbonyl group, the absorption generally among the strongest presents [17]. Accordingly the FT-Raman bands observed at 1759 and 1719 cm-1 in the title compound have been assigned to C=O stretching modes of vibrations. The assignments of C=O in-plane and out-of-plane bending vibrations are strongly coupled with the ring torsion modes also and the vibrations made in this study were given in Table 4 and the tabulated values are supported by the literature [18-20].

C□N vibrations

The identification of C□N stretching vibration is a rather difficult task since there are problems in identifying these frequencies from other vibrations in FT-Raman. In the present work, the band observed at 1380, 1359 cm-1 in the FT-IR and 1385, 1365 cm-1 in the FT-Raman have been assigned to C□N stretching vibration. The theoretically computed value of C□N stretching vibrations at 1400, 1382 cm-1 is in excellent agreement with experimental observation. The band at 290 cm-1 in the FT-Raman is assigned to C□N out-of-plane bending vibration.

C□C vibrations

In our title molecule, there are six equivalent C□C bonds in the ring1 possesses six C□C stretching vibrations. However, due to high symmetry of benzene, many modes of vibrations are infrared inactive [21]. In general, the bands around 1650 to 1350 cm-1 in benzene derivatives are assigned to skeletal stretching C□C bands. The bands observed at 1432, 1594 cm-1 in FT-IR spectrum and 1609, 1582, 1468, 1433 in FT-Raman spectrum of N-(Methyl) phthalimide is identified as C□C stretching vibrations. The theoretically predicted C□C stretching vibrations by B3LYP/6-311++G(d,p) method are 1647, 1625, 1496, 1484 cm-1 corresponding to the mode no: 10,11,13,14 as listed in Table 4. The C□C aromatic stretch [22] known as semi circle stretching observed at 1609 cm-1 in FT Raman and 1594 cm-1 in FT-IR spectrum.

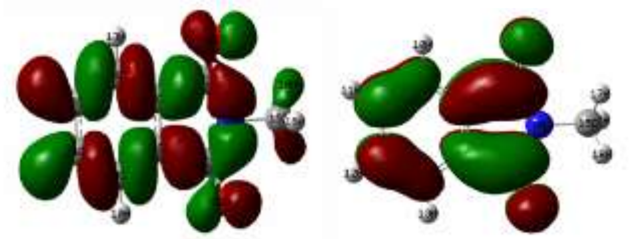
C□H vibrations

The hetero aromatic structure displays the presence of C□H stretching vibrations in the region 3100□3000 cm-1 which is the characteristic region for the ready identification of C□H stretching vibrations [11]. In this region, the bands are not affected appreciably by the nature of substituent. In the present study, these bands observed at 3022–3083 cm-1 in the FT-Raman spectrum have been assigned as aromatic C□H stretching vibrations. The recorded values are also in good agreement with the literature.

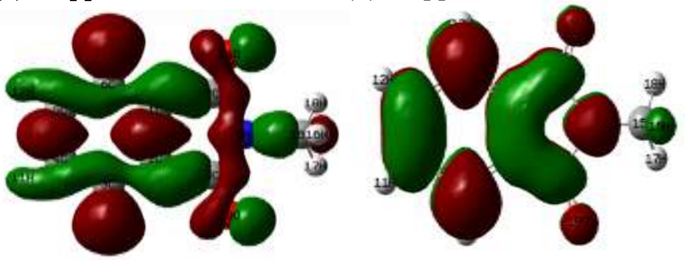
The aromatic C□H in-plane bending modes of benzene and its derivatives are observed in the region 1300□1000 cm-1 [11]. In the present work the bands corresponding to the aromatic C□H in-plane bending modes observed at 1249, 1183 cm-1 in FT-IR whereas in FT-Raman the same modes observed in the region 1315□1170 cm-1. The theoretically computed B3LYP/6-311++G(d,p) method at 1310-1189cm-1 shows good agreement with the recorded data. The C□H out of plane deformation modes of benzene [23, 24] are expected to occur in the region 1000□600 cm-1. Hence, in the present study these bands observed at 977, 908, 871, 799 cm-1(see mode no: 30, 31, 32, 34 in Table 4) by B3LYP/6-311++G(d,p) method show excellent correlation with recorded FT-IR and FT-Raman bands.

HOMO-LUMO Energy gap

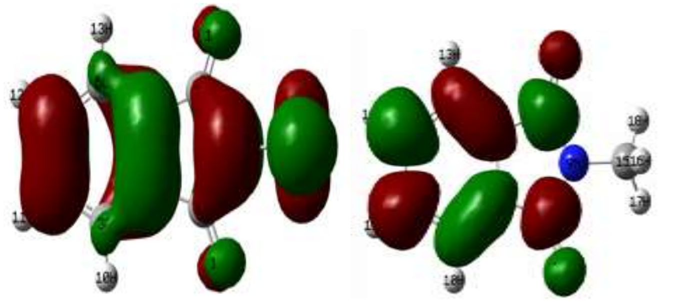
The Figure 4 shows that the orbitals from HOMO□2 to LUMO+2 of NMP are well localized within the phthalimide ring, but all the LUMO surfaces have no amplitude [25] on methyl group linked to five member ring. In HOMO and HOMO□1, the orbital has higher amplitude in C7=O14 and C8=O19. In HOMO□2, the orbitals have well localized on methyl group of NMP. In other words, each valence electron in H16, H17, H18 highly delocalized or coupled with C15 of the methyl group. The rest of the valence electron in C15 is delocalized on N9 in HOMO□1 orbital as shown in Figure 4(c). The presence of intramolecular charge transfer from donor to acceptor group within molecule can identify by finding the co-existence of IR and Raman activity [26]. It is also observed that in our title molecule the bands at 3096, 1713, 1432, 1380, 1249, 1183 and 603 cm-1 in FT-IR spectrum have their counterparts in FT-Raman at 3083, 1719, 1433, 1385, 1252, 1187 and 604 cm-1 show that the relative intensities in IR and Raman are comparable resulting from the electron cloud movement through single-double bond π conjugated path from donor to acceptor groups. The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground state to the first exited state and is mainly described by one-electron excitation from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). The HOMO, LUMO energies of NMP has been calculated at B3LYP/6-311++G(d,p) level is presented in Table 5. The energy gap presented in Table 6 reflects the chemical activity of the molecule. HOMO represents the ability to donate an electron and LUMO represents the ability to accept an electron. Among the six subsequent exited states calculated, the strongest transitions appear between HOMO → LUMO orbitals. The numerical value of energy gap between HOMO-LUMO orbitals calculated at B3LYP level is □0.18393a.u. The energy gaps for other possible energy transitions are presented in Table 6.



(a) Mapped surface of HOMO (b) Mapped surface of LUMO



(c) Mapped surface of HOMO□1 (d) Mapped surface of LUMO+1



(e) Mapped surface of HOMO□2 (f) Mapped surface of LUMO+2

Fig 4. Selected molecular orbital contours of NMP from HOMO□2 to LUMO+2

Other Molecular Properties

In addition to the vibrational assignments, several thermodynamic parameters are also calculated [27] on the basis of vibrational analysis at B3LYP/6-311++G(d,p).

The calculated thermodynamic properties are presented in the Table 7.

The self consistent field (SCF) energy, zero point vibrational energies (ZPVE), rotational constants, dipole moment and entropy SVib(T) are calculated to the extent of accuracy and the variations in the ZPVEs seem to be insignificant. The total energies and change in total entropy of N-(Methyl) phthalimide at room temperature are only marginal.

Mullikan's Atomic Charges

The values of the Mullikan's atomic charges [28] on each atom of the title compound were also obtained with the help of B3LYP level of the theory incorporating 6-311++G(d,p) basis set. The Mullikan's atomic charges on each atom of the title compound are presented in Table 8. Moreover, Mullikan's atomic charges of NMP were found to be equal. This shows that, there is no correlation between charge and Stability of the molecule.

Conclusion

The normal mode frequencies and corresponding vibrational assignments of the title compound were theoretically performed using B3LYP/6-311++G(d,p) level in Gaussian 03W software package. The computed normal mode frequencies were compared with those observed experimentally. The vibrational frequency analysis of the N-(Methyl) phthalimide by B3LYP method agrees satisfactorily with experimental results. During the present investigation, few of the experimental observations were found to be in disagreement with the computed data. However, the vibrational assignments made during the present investigation can be put on a greater confidence level because these are visualized in three dimensions using a Gauss view program. The calculated HOMO-LUMO energies showed that charge transfer occur with the molecule and strongest energy transition (EHOMO□ELUMO= □0.18393a.u) takes place between HOMO-LUMO orbitals. The Mullikan's atomic charge studies showed that, there is no correlation between charge and stability of the molecule. In addition, thermodynamic functions of NMP were also presented.

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Table 1. Optimized bond lengths, bond angles and dihedral angles of NMP based on B3LYP/6311++G(d,p)

Parameters[a]	Bond length(Å)	Parameters[a]	Bond angle(^{0})	Parameters[a]	Dihedral angle(^{0})
$C_1 - C_2$	1.3939	$C_2 - C_1 - C_6$	121.5291	$C_6 - C_1 - C_2 - C_3$	-0.0004
$C_1 - C_6$	1.3850	$C_2 - C_1 - C_7$	108.2490	$C_6 - C_1 - C_2 - C_8$	179.9682
$C_1 - C_7$	1.4942	$C_6 - C_1 - C_7$	130.2219	$C_7 - C_1 - C_2 - C_3$	-179.996
$C_2 - C_3$	1.3850	$C_1 - C_2 - C_3$	121.5291	$C_7 - C_1 - C_2 - C_8$	-0.001
$C_2 - C_8$	1.4942	$C_1 - C_2 - C_8$	108.2491	$C_2 - C_1 - C_6 - C_5$	0.0312
$C_3 - C_4$	1.3994	$C_3 - C_2 - C_8$	130.2218	$C_2 - C_1 - C_6 - H_{13}$	-179.97
$C_3 - H_{10}$	1.0834	$C_2 - C_3 - C_4$	117.4031	$C_7 - C_1 - C_6 - C_5$	179.9928
$C_4 - C_5$	1.3981	$C_2 - C_3 - H_{10}$	120.9915	$C_7 - C_1 - C_6 - H_{13}$	-0.0084
$C_4 - H_{11}$	1.084	$C_4 - C_3 - H_{10}$	121.6054	$C_2 - C_1 - C_7 - N_9$	0.1406
$C_5 - C_6$	1.3994	$C_3 - C_4 - C_5$	121.0678	$C_2 - C_1 - C_7 - O_{14}$	179.9226
$C_5 - H_{12}$	1.0840	$C_3 - C_4 - H_{11}$	119.5721	$C_6 - C_1 - C_7 - N_9$	-179.825
$C_6 - H_{13}$	1.0834	$C_5 - C_4 - H_{11}$	119.3601	$C_6 - C_1 - C_7 - O_{14}$	-0.043
$C_7 - N_9$	1.4028	$C_4 - C_5 - C_6$	121.0678	$C_1 - C_2 - C_3 - C_4$	-0.0306
$C_7 - O_{14}$	1.2092	$C_4 - C_5 - H_{12}$	119.3601	$C_1 - C_2 - C_3 - H_{10}$	179.9699
$C_8 - N_9$	1.4028	$C_6 - C_5 - H_{12}$	119.5721	$C_8 - C_2 - C_3 - C_4$	-179.9916
$C_8 - O_{19}$	1.2092	$C_1 - C_6 - C_5$	117.4031	$C_8 - C_2 - C_3 - H_{10}$	0.0089
$N_9 - C_{15}$	1.4538	$C_1 - C_6 - H_{13}$	120.9916	$C_1 - C_2 - C_8 - N_9$	-0.139
$C_{15} - H_{16}$	1.0931	$C_5 - C_6 - H_{13}$	121.6053	$C_1 - C_2 - C_8 - O_{19}$	-179.9241
$C_{15} - H_{17}$	1.0892	$C_1 - C_7 - N_9$	105.6138	$C_3 - C_2 - C_8 - N_9$	179.826
$C_{15} - H_{18}$	1.0892	$C_1 - C_7 - O_{14}$	129.1102	$C_3 - C_2 - C_8 - O_{19}$	0.0408
		$N_9 - C_7 - O_{14}$	125.2756	$C_2 - C_3 - C_4 - C_5$	0.0306
		$C_2 - C_8 - N_9$	105.6138	$C_2 - C_3 - C_4 - H_{11}$	-179.9599
		$C_2 - C_8 - O_{19}$	129.1093	$H_{10} - C_3 - C_4 - C_5$	-179.9698
		$N_9 - C_8 - O_{19}$	125.2765	$H_{10} - C_3 - C_4 - H_{11}$	0.0406
		$C_7 - N_9 - C_8$	112.2738	$C_3 - C_4 - C_5 - C_6$	0.0
		$C_7 - N_9 - C_{15}$	123.8606	$C_3 - C_4 - C_5 - H_{12}$	-179.9893
		$C_8 - N_9 - C_{15}$	123.8617	$H_{11} - C_4 - C_5 - C_6$	179.9895
		$N_9 - C_{15} - H_{16}$	111.0850	$H_{11} - C_4 - C_5 - H_{12}$	0.0002
		$N_9 - C_{15} - H_{17}$	108.6724	$C_4 - C_5 - C_6 - C_1$	-0.0308
		$N_9 - C_{15} - H_{18}$	108.6750	$C_4 - C_5 - C_6 - C_{13}$	179.9704
		$H_{16} - C_{15} - H_{17}$	108.9905	$H_{12} - C_5 - C_6 - C_1$	179.9585
		$H_{16} - C_{15} - H_{18}$	108.9896	$H_{12} - C_5 - C_6 - H_{13}$	-0.0403
		$H_{17} - C_{15} - H_{18}$	110.4272	$C_1 - C_7 - N_9 - C_{15}$	-179.5391
				$O_{14} - C_7 - N_9 - C_8$	179.9686
				$O_{14} - C_7 - N_9 - C_{15}$	0.6681
				$C_2 - C_8 - N_9 - C_7$	0.238
				$C_2 - C_8 - N_9 - C_{15}$	179.5385
				$O_{19} - C_8 - N_9 - C_7$	-179.9662
				$O_{19} - C_8 - N_9 - C_{15}$	-0.6657
				$C_7 - N_9 - C_{15} - H_{16}$	89.5866
				$C_7 - N_9 - C_{15} - H_{17}$	-150.5166
				$C_7 - N_9 - C_{15} - H_{18}$	-30.3109
				$C_8 - N_9 - C_{15} - H_{16}$	-89.6339
				$C_8 - N_9 - C_{15} - H_{17}$	30.2629
				$C_8 - N_9 - C_{15} - H_{18}$	150.4686

[a]For numbering of atom refer Figure 1.

Table 2. Definition of internal coordinates of NMP

Internal co-ordinates	Symbol	Type	Definition[a]
In-plane Stretching			
1-4	r_i	C-H (Aromatic)	C_3-H_{10}, C_4-H_{11},C_5-H_{12}, C_6-H_{13}
5-6	R_i	C=O	C_7-O_{14}, C_8-O_{19}
7-9	t_i	C-N	C_8-N_9, C_7-N_9, C_{15}- N_9
10-12	r_i	C-H (Methyl)	C_{15}-H_{16}, C_{15}-H_{17}, C_{15}-H_{18}
13-20	P_i	C-C (Aromatic)	C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, C_5-C_6, C_6-C_1, C_1-C_7, C_2-C_8.
In-plane Bending			
21-28	δ_i	C-C-H	C_1-C_6-H_{13}, C_5-C_6-H_{13}, C_6-C_5-H_{12},C_4-C_5-H_{12}, C_5-C_4-H_{11}, C_3-C_4-H_{11}, C_2-C_3-H_{10}, C_4-C_3-H_{10}.
29-32	ρ_i	C(N)-C-O	C_1-C_7-O_{14}, N_9-C_7-O_{14}, C_2-C_8-O_{19}, N_9-C_8-O_{19}.
33-38	β_i	t (Ring 1)	C_6-C_1-C_2, C_1-C_2-C_3, C_2-C_3-C_4, C_3-C_4-C_5, C_4-C_5-C_6, C_5-C_6-C_1.
39-43	β_i	t (Ring 2)	C_7-C_1-C_2, C_1-C_2-C_8, C_2-C_8-N_9, C_8-N_9-C_7, N_9-C_7-C_1.
44-45	λ_i	C-N-C	C_7-N_9-C_{15}, C_8-N_9-C_{15}
46-48	σ_i	N-C-H	N_9-C_{15}-H_{16}, N_9-C_{15}-H_{17}, N_9-C_{15}-H_{18}.
49-51	α_i	H-C-H	H_{16}-C_{15}-H_{17}, H_{17}-C_{15}-H_{18}, H_{16}-C_{15}-H_{18}.
Out-of plane Bending			
52-55	ω_i	C_{ar}-H	H_{10}-C_3-C_2-C_4, H_{11}-C_4-C_3-C_5, H_{12}-C_5-C_4-C_6, H_{13}-C_6-C_5-C_1.
56-57	ω_i	C_{ar}-O	O_{14}-C_7-C_1-N_9, O_{19}-C_8-C_2-N_9.
58	ω_i	C-N	C_{15}-N_9-C_7-C_8.
59	τ_i	t(N)-CH_3	(C_7,C_8)-N_9-C_{15}-(H_{16},H_{17},H_{18}).
60-65	τ_i	t(Ring1)	C_1-C_2-C_3-C_4, C_2-C_3-C_4-C_5, C_3-C_4-C_5-C_6, C_4-C_5-C_6-C_1, C_5-C_6-C_1-C_2, C_6-C_1-C_2-C_3.
66-70	τ_i	t(Ring2)	C_1-C_7-N_9-C_8, C_7-N_9-C_8-C_2, N_9-C_8-C_2-C_1, C_8-C_2-C_1-C_7, C_2-C_1-C_7-N_9.
71-72	τ_i	Butterfly	C_6-C_1-C_2-C_8, C_7-C_1-C_2-C_3.

[a]For numbering of atom refer Figure 1.

Table 3. Definition of local symmetry coordinates for NMP

Possible local symmetric co-ordinates	Type	Definition[a]
1-4	CH_{ar}	$r_1, r_2, r_3, r_4.$
5-6	CO	$R_5, R_6.$
7-9	CN	$t_7, t_8, t_9.$
10	CH_3(ss)	$(r_1+r_2+r_3)/\sqrt{3}$
11	CH_3(ips)	$(2r_{10}-r_{11}-r_{12})/\sqrt{6}$
12	CH_3(ops)	$(r_{11}-r_{12})/\sqrt{2}$
13-20	CC_{ar}	$P_{13}, P_{14}, P_{15}, P_{16}, P_{17}, P_{18}, P_{19}, P_{20}.$
21-24	bCH	$(\delta_{21}-\delta_{22})/\sqrt{2}, \quad (\delta_{23}-\delta_{24})/\sqrt{2}, \quad (\delta_{25}-\delta_{26})/\sqrt{2}, \quad (\delta_{27}-\delta_{28})/\sqrt{2}.$
25-26	bCO	$(\rho_{29}-\rho_{31})/\sqrt{2}, \quad (\rho_{30}-\rho_{32})/\sqrt{2}.$
27	Ring 1	$(\beta_{33}-\beta_{34}+\beta_{35}-\beta_{36}+\beta_{37}-\beta_{38})/\sqrt{6}$
28	Ring 2	$(-\beta_{33}-\beta_{34}+2\beta_{35}-\beta_{36}+\beta_{37}-2\beta_{38})/\sqrt{12}$
29	Ring 3	$(\beta_{33}-\beta_{34}-\beta_{36}-\beta_{37})/2$
30	Ring 4	$\beta_{39}+a(\beta_{40}+\beta_{43})+b(\beta_{41}+\beta_{42})$
31	Ring 5	$(a-b)(\beta_{39}-\beta_{42})+(1-a)(\beta_{40}-\beta_{41})$
32	bCN	$(\lambda_{44}-\lambda_{45})/\sqrt{2}$
33	CH_3 sb	$(-\sigma_{46}-\sigma_{47}-\sigma_{48}+\sigma_{49}+\sigma_{50}+\sigma_{51})/\sqrt{6}$
34	CH_3 ipb	$(-\alpha_{49}-\alpha_{50}+2\alpha_{51})/\sqrt{6}$
35	CH_3 opb	$(\alpha_{49}-\alpha_{50})/\sqrt{2}$
36	CH_3 ipr	$(2\sigma_{46}-\sigma_{47}-\sigma_{48})/\sqrt{6}$
37	CH_3 opr	$(\sigma_{47}-\sigma_{48})/\sqrt{2}$
38-41	ωCH	$\omega_{52}, \omega_{53}, \omega_{54}, \omega_{55}.$
42-43	ωCO	$\omega_{56}, \omega_{57}.$
44	ωCN	$\omega_{58}.$
45	τCH_3	$\tau_{59}.$
46	t Ring1	$(\tau_{60}-\tau_{61}+\tau_{62}-\tau_{63}+\tau_{64}+\tau_{65})/\sqrt{6}$
47	t Ring2	$(\tau_{60}-\tau_{61}+\tau_{63}-\tau_{65})/2$
48	t Ring3	$(-\tau_{60}+2\tau_{61}-\tau_{62}-\tau_{63}+2\tau_{64}-\tau_{65})/\sqrt{12}$
49	t Ring4	$b(\tau_{66}+\tau_{70})+a(\tau_{67}+\tau_{69})+\tau_{68}$
50	t Ring5	$(a-b)(\tau_{70}-\tau_{66})+(1-a)(\tau_{69}-\tau_{67})$
51	Butterfly	$(\tau_{71}-\tau_{72})/\sqrt{2}$

[a]For numbering of atom refer Figure 1.

Table 4. Comparison of experimental and theoretical frequencies of N-(Methyl) phthalimide along with their theoretical reduced masses and force constants

Mode	Symmetry species	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1})	Reduced mass (amu	Force constants (mdyne/A)	Vibrational assignments[a]
		IR	Raman				
1	A'	3096	3083	3200	1.097	6.617	υCH_{ar}
2	A'	-	3063	3197	1.094	6.586	υCH_{ar}
3	A'	-	3039	3185	1.091	6.520	υCH_{ar}
4	A'	-	3022	3173	1.087	6.446	υCH_{ar}
5	A'	-	2988	3151	1.106	6.469	$\upsilon_{as}CH$ in CH_3
6	A"	-	2958	3085	1.096	6.263	$\upsilon_{as}CH$ in CH_3
7	A'	-	2881	3044	1.039	5.671	$\upsilon_{s}CH$ in CH_3
8	A'	-	1759	1824	12.256	24.014	υC=O
9	A'	1713	1719	1770	12.802	23.620	υC=O
10	A'	-	1609	1647	6.919	11.058	υCC
11	A'	1594	-	1625	7.168	11.424	υCC
12	A'	-	1532	1514	1.049	1.417	βCH_3
13	A'	-	1468	1496	2.388	3.149	υCC
14	A'	1432	1433	1484	1.954	2.569	υCC
15	A"	-	1414	1470	1.291	1.689	γCH_3
16	A'	-	1394	1454	1.324	1.648	βCH_3
17	A'	1380	1385	1400	3.806	4.393	υCN
18	A'	1359	1365	1382	6.507	7.320	υCN
19	A'	-	1315	1310	1.597	1.616	βCH
20	A'	1249	1252	1270	2.516	2.390	βCH
21	A'	1183	1187	1211	3.754	3.243	βCH
22	A'	-	1170	1189	1.157	1.795	βCH
23	A'	-	1157	1181	1.176	0.966	υCC
24	A'	-	-	1149	1.306	1.015	υCC
25	A'	1084	-	1099	2.447	1.740	σCH_3
26	A"	-	1014	1035	2.008	1.267	δCH_3
27	A'	1006	-	1012	2.520	1.522	υCC
28	A'	-	-	1009	1.321	0.793	υCC
29	A'	-	965	982	1.399	0.796	υCN
30	A"	-	-	977	6.909	3.882	γCH
31	A"	-	858	908	1.354	0.658	γCH
32	A"	762	796	871	4.926	2.204	γCH
33	A'	-	-	801	1.917	0.726	βCN
34	A"	-	-	799	6.374	2.396	γCH
35	A'	-	709	727	2.356	0.734	βRing1
36	A'	714	-	718	6.460	1.964	βRing2
37	A'	-	-	709	6.500	1.925	βRing3
38	A'	603	604	680	4.961	1.352	βRing4
39	A'	-	-	610	10.965	2.406	βCO
40	A"	527	-	537	7.235	1.230	γCO
41	A"	470	472	477	5.639	0.757	γCO
42	A'	-	-	465	4.889	0.622	βRing5
43	A"	-	-	415	3.095	0.314	τRing1
44	A'	-	352	352	11.351	0.826	βCO
45	A"	-	290	278	3.867	0.177	γCN
46	A"	-	239	236	4.385	0.144	τRing2
47	A"	-	171	233	4.950	0.158	τRing3
48	A"	-	131	154	10.578	0.147	τRing4
49	A"	-	115	137	5.006	0.056	τRing5
50	A"	-	108	108	3.575	0.025	Butterfly
51	A"	-	-	29	1.021	0.003	τCH_3

[a] υ_s, symmetry stretching; υ_{as}, anti-symmetic stretching; β, In-plane bending;
γ, Out-of-plane bending; σ, In-plane rock; δ, Out-of-plane rock; τ, torsion.

Table 5 HOMO, LUMO energies of NMP

S.No	Molecular Orbitals	Energy a.u
1.	HOMO	−0.27913
2.	HOMO−1	−0.28308
3.	HOMO−2	−0.28997
4.	LUMO+2	−0.01396
5.	LUMO+1	−0.05693
6.	LUMO	−0.09520

Table 6. Selected HOMO–LUMO energy gap

S.No	Energy transitions	Energy gap a.u
1.	HOMO → LUMO	–0.18393
2.	HOMO–1→ LUMO	–0.18788
3.	HOMO–2 →LUMO	–0.19477
4.	HOMO → LUMO+1	–0.22220
5.	HOMO–1→ LUMO+1	–0.22615
6.	HOMO–2 →LUMO+1	–0.23304
7.	HOMO → LUMO+2	–0.26517
8.	HOMO–1→ LUMO+2	–0.26912
9.	HOMO–2 →LUMO+2	–0.27601

Table 7. Thermodynamic properties of N-(Methyl) phthalimide.

Parameter	B3LYP/6-311G++(d,p)
Self Consistent Field energy	–552.55965 a.u
Zero point vibrational energy	89.80434 (Kcal/Mol)
Rotational constants	1.73207 GHz
	0.86367 GHz
	0.57839 GHz
Entropy	92.751 Cal/Mol-Kelvin
Specific heat capacity at constant volume	34.485 Cal/Mol-Kelvin
Translational energy	41.139 Cal/Mol-Kelvin
Rotational energy	30.297 Cal/Mol-Kelvin
Vibrational energy	21.315 Cal/Mol-Kelvin
Dipole moment	2.4023 debye

Table 8. Atomic charges on each atom of NMP

S.No	Atom	B3LYP/6-311G++(d,p)
1.	C_1	0.661206
2.	C_2	0.661202
3.	C_3	–0.604069
4.	C_4	–0.177594
5.	C_5	–0.177510
6.	C_6	–0.604092
7.	C_7	–0.074142
8.	C_8	–0.073931
9.	N_9	–0.000273
10.	H_{10}	0.190851
11.	H_{11}	0.178403
12.	H_{12}	0.178403
13.	H_{13}	0.190849
14.	O_{14}	–0.312071
15.	C_{15}	–0.288152
16.	H_{16}	0.193415
17.	H_{17}	0.184793
18.	H_{18}	0.184789
19.	O_{19}	–0.312078