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Research Article

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Structural, vibrational, and electronic properties of Succinimide, N-Hydroxy Succinimide and N-Methyl Succinimide by density functional theory: A comparative study

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ABSTRACT

A comparative study of structure, energies and spectral analysis of Succinimide, N-hydroxy-succinimide (NHS) and N-methyl-succinimide (NMS) has been carried out using density functional method (DFT/B3LYP) with 6-311++G(d,p) as basis set. To determine lowest-energy molecular conformation of NHS and NMS molecule, the selected torsion angle is varied and molecular energy profile is calculated. The molecular electrostatic potential surface, electric dipole moment, polarizability and the first hyperpolarizability values of Succinimide, NHS and NMS have been calculated at the same level of theory and basis set. The thermodynamic properties of the studied compounds at different temperatures were also calculated.

Keywords: Vibrational analysis, HOMO-LUMO and MESP.

INTRODUCTION

Succinimide and its N-substituted derivatives are significant structural units in many important compounds [1,2] including plant growth stimulators [3], additives for lubricating oils [4], corrosion inhibitors [5], sychoanaleptic agents [6], drugs for memory enhancement [7], antitumor representatives such as epipodophyllotoxin glycoside [8,9]. N-hydroxy-succinimide (NHS) and its acylated derivatives are useful reagents for the synthesis of peptides and antibiotics. NHS is also used for the preparation of active esters and as an additive to suppress racemisation in peptide coupling [10]. NHS can selectively deliver an attached moiety to mild nucleophilic species (amino acids, amines and thiols) under relatively mild reaction conditions. Thescaffold may then be used as a basis for the separation and subsequent detection of the nucleophile [11].

The present communication deals with the comprehensive comparative study of the structural, electronic and vibrational properties of Succinimide, N-Hydroxy-succinimide (NHS) and N-Methyl-succinimide (NMS) due to their biological and medical importance. The structure and harmonic wave numbers were determined and analyzed at the density functional theory (DFT) level employing the basis set 6-311++G(d,p). The optimized geometry of all the three molecules and their molecular properties such as equilibrium energy, frontier orbital energy gap, molecular electrostatic potential (MESP) energy map, dipole moment, polarizability and first static hyperpolarizability were calculated and discussed. A complete vibrational analysis of the molecules were performed by combining the experimental IR spectroscopic data and the quantum chemical calculations. DFT based calculations provide not only the qualitative but also the quantitative understanding of energy distribution of each vibrational mode on the basis of potential energy distribution (PED)[12-14]. The thermodynamic properties of the studied compounds at different temperatures were also calculated.

COMPUTATIONAL AND EXPERIMENTAL DETAILS

The molecular structure optimization of the three compounds and corresponding vibrational harmonic wavenumbers were calculated using DFT with Becke-3-Lee-Yang-Parr (B3LYP) functional[15,16] with 6-311++G(d,p) basis sets using GAUSSIANO9W [17] program package. Initial geometry for succinimide, N-hydroxy-succinimide (NHS) and N-methyl-succinimide (NMS) were generated from standard geometrical parameters [18]. As Succinimide has no flexible side chain, conformational search is not required as such for it.The structure of later two were obtained with the help of potential energy surface scan at B3LYP level, adopting the standard 6-31G(d) basis set. This geometry was then re-optimized at B3LYP level, using basis set 6-311++G (d,p).The optimized geometrical parameters, rotational constants, fundamental vibrational wavenumbers, IR intensity, molecular orbitals and other thermodynamic parameters were also calculated.

The experimental FT-IR spectrum of the Succinimide, NHS and NMS were obtained from NIST website [19]. To calculate analytically the dipole moment (μ), mean polarizability <α>, anisotropy of the polarizability (Δα), and the total first static hyperpolarizability (β)[20,21], finite field approach was used and B3LYP/6-311++G(d,p) basis set was employed. The total dipole moment μ, mean polarizability <α>, the anisotropy of the polarizability Δα, and the total first static hyperpolarizability β and are given in terms of x, y, z components by the following equations $\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$

$<\alpha> = 1/3\ [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$,
$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + 6\alpha^2_{xx} + 6\alpha^2_{xy} + 6\alpha^2_{yz}]^{1/2}$

The total intrinsic hyperpolarizability β_{TOTAL}[22] is define as $\beta_{TOTAL} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$

Where, $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$; $\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx}$; $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$

The β components of Gaussian output are reported in atomic units and, therefore the calculated values are converted into e.s.u. units (α; 1 a.u. = 0.1482 x 10^{-24}e.s.u., β; 1 a.u. = 8.3693 x 10^{-33}e.s.u.)

RESULTS AND DISCUSSION

3.1.Potential Energy Scan and Molecular Geometry:

Conformational search is not required in the case of Succinimide as it contains no side chain with flexible dihedral angles. PES scan has been performed for NHS and NMS molecules at B3LYP/6-31G(d) level of theory and are shown in Fig. 1 and Fig. 2

The dihedral angle C3-N9-O12-H13 and C4-N9-C12-H13 are relevant coordinates for conformational flexibility within NHS and NMS molecules respectively. These dihedrals determine the orientation of hydroxyl / methyl group with respect to the Succinimide ring. In case of NHS, all the geometrical parameters were simultaneously relaxed while dihedral angle C3-N9-O12-H13 was varied in step of 10° ranging from -180° to +180°.

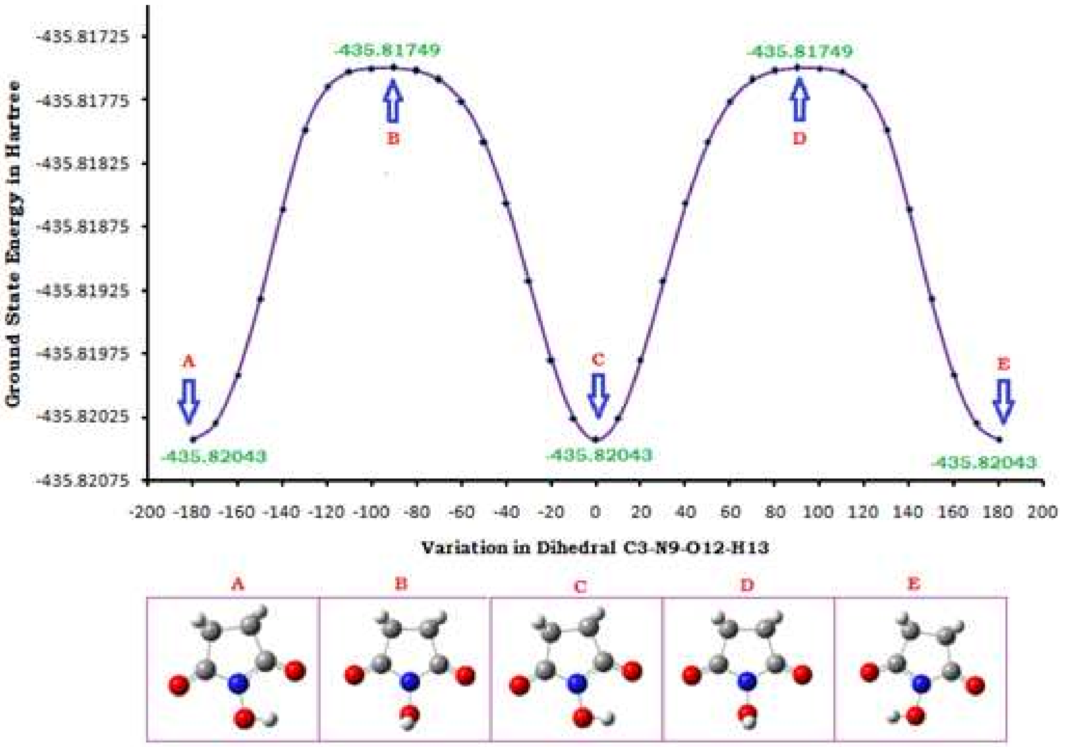

Fig.1.The potential energy curves of NHS along the C3-N9-O12-H13 dihedral

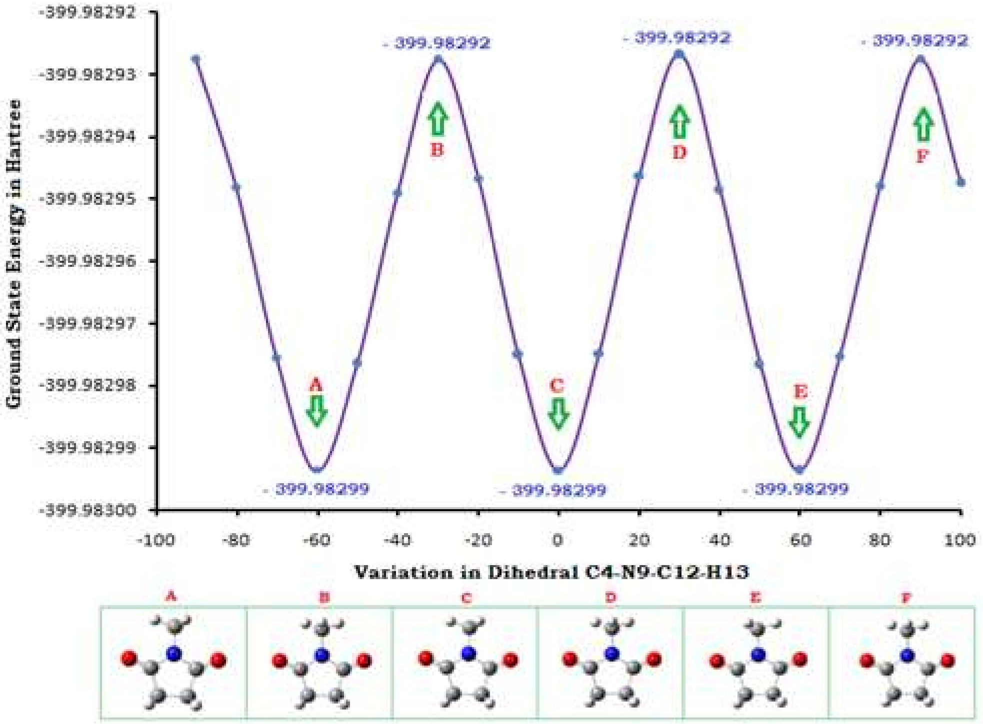

Fig.2.The potential energy curves of NMS along the C4-N9-C12-H13 dihedral

Similarly, dihedral angle C4-N9-C12-H13 was varied in step of 10° ranging from -90° to +90° for NMS. For C3-N9-O12-H13 rotation, three true local minima in PES for NHS were determined at -180°, 0° and +180°, all having equal energy at -435.82043 Hartree. Whereas, for C4-N9-C12-H13 rotation, three true local minima of NMS were determined at -60° , 0° and +60° with same energy value at -399.98299 Hartree. Structure corresponding to the minima at the potential energy scan has been used as the starting point for optimization of structure at the higher level of the basis set.

The final optimized molecular geometry at B3LYP/6-311++G(d,p) of Succinimide, NHS and NMS are given in **Fig. 3**. The optimized geometric parameters are given in **Table 1**.

The bond lengths C1-C4 and C2-C3 are found shorter than C1-C2 in all the three molecules. This shortening of the bond lengths may be due to the electronegative Oxygen atom attached at C3 and C4 atoms.

Table 1 :Optimized Geometric Parameters for Succinimide, N-Hydroxy-succinimide and N-Methyl-succinimide computed at B3LYP/6-311++G(d,p)

Succinimide		N-Hydroxy-succinimide		N-Methyl-succinimide	
Parameter	**Calculated**	**Parameter**	**Calculated**	**Parameter**	**Calculated**
Bond Length (A^0)		**Bond Length (A^0)**		**Bond Length (A^0)**	
C1-C2	1.538	C2-H8	1.092	C3-O10	1.208
C1-C4	1.526	C3-N9	1.380	C4-N9	1.393
C1-H5	1.092	C3-O11	1.203	C4-O11	1.208
C1-H6	1.092	C4-N9	1.395	N9-C12	1.456
C2-C3	1.526	C4-O10	1.201	C12-H13	1.091
C2-H7	1.092	N9-O12	1.374	C12-H14	1.089
C2-H8	1.092	O12-H13	0.977	C12-H15	1.091
C3-N10	1.392	**Bond Angle (in degree)**		**Bond Angle (in degree)**	
C3-O12	1.206	C2-C1-C4	106.3	C2-C1-C4	105.1
C4-N10	1.392	C2-C1-H5	113.1	C2-C1-H5	113.6
C4-O11	1.206	C2-C1-H6	113.1	C2-C1-H6	113.6
H9-N10	1.012	C4-C1-H5	108.4	C4-C1-H5	108.6
Bond Angle (in degree)		C4-C1-H6	108.4	C4-C1-H6	108.6
C2-C1-C4	105.4	H5-C1-H6	107.4	H5-C1-H6	107.1
C2-C1-H5	113.5	C1-C2-C3	105.0	C1-C2-C3	105.3
C2-C1-H6	113.6	C1-C2-H7	113.3	C1-C2-H7	113.6
C4-C1-H5	108.5	C1-C2-H8	113.3	C1-C2-H8	113.6
C4-C1-H6	108.5	C3-C2-H7	108.9	C3-C2-H7	108.5
H5-C1-H6	107.1	C3-C2-H8	108.9	C3-C2-H8	108.6
C1-C2-C3	105.4	H7-C2-H8	107.3	H7-C2-H8	107.1
C1-C2-H7	113.6	C2-C3-N9	106.9	C2-C3-N9	107.8
C1-C2-H8	113.6	C2-C3-O11	130.7	C2-C3-O10	127.3
C3-C2-H7	108.5	N9-C3-O11	122.3	N9-C3-O10	124.8
C3-C2-H8	108.5	C1-C4-N9	105.1	C1-C4-N9	108.0
H7-C2-H8	107.1	C1-C4-O10	128.9	C1-C4-O11	127.6
C2-C3-N10	107.0	N9-C4-O10	126.0	N9-C4-O11	124.3
C2-C3-O12	127.9	C3-N9-C4	116.7	C3-N9-C4	113.7
N10-C3-O12	125.2	C3-N9-O12	120.6	C3-N9-C12	123.6
C1-C4-N10	107.0	C4-N9-O12	122.7	C4-N9-C12	122.7
C1-C4-O11	127.9	N9-O12-H13	102.4	N9-C12-H13	110.1
N10-C4-O11	125.2	**Dihedral Angle (in degree)**		N9-C12-H14	107.7
C3-N10-C4	115.2	C4-C1-C2-C3	0.0	N9-C12-H15	110.1
C3-N10-H9	122.4	C4-C1-C2-H7	-118.7	H13-C12-H14	110.2
C4-N10-H9	122.4	C4-C1-C2-H8	118.7	H13-C12-H15	108.7
Dihedral Angle (in degree)		H5-C1-C2-C3	118.8	H14-C12-H15	110.2
C4-C1-C2-C3	0.0	H5-C1-C2-H7	0.1	**Dihedral Angle (in degree)**	
C4-C1-C2-H7	-118.7	H5-C1-C2-H8	-122.5	C4-C1-C2-C3	0.1
C4-C1-C2-H8	118.6	H6-C1-C2-C3	-118.8	C4-C1-C2-H7	-118.5
H5-C1-C2-C3	118.6	H6-C1-C2-H7	122.5	C4-C1-C2-H8	118.8
H5-C1-C2-H7	0.0	H6-C1-C2-H8	-0.1	H5-C1-C2-C3	118.8
H5-C1-C2-H8	-122.7	C2-C1-C4-N9	0.0	H5-C1-C2-H7	0.2
H6-C1-C2-C3	-118.7	C2-C1-C4-O10	180.0	H5-C1-C2-H8	-122.6
H6-C1-C2-H7	122.6	H5-C1-C4-N9	-121.9	H6-C1-C2-C3	-118.5
H6-C1-C2-H8	0.0	H5-C1-C4-O10	58.1	H6-C1-C2-H7	122.9
C2-C1-C4-N10	0.0	H6-C1-C4-N9	121.9	H6-C1-C2-H8	0.2
C2-C1-C4-O11	-180.0	H6-C1-C4-O10	-58.1	C2-C1-C4-N9	-0.1
H5-C1-C4-N10	-122.0	C1-C2-C3-N9	0.0	C2-C1-C4-O11	179.9
H5-C1-C4-O11	58.0	C1-C2-C3-O11	180.0	H5-C1-C4-N9	-122.0
H6-C1-C4-N10	122.0	H7-C2-C3-N9	121.6	H5-C1-C4-O11	58.0
H6-C1-C4-O11	-58.0	H7-C2-C3-O11	-58.4	H6-C1-C4-N9	121.8
C1-C2-C3-N10	0.0	H8-C2-C3-N9	-121.7	H6-C1-C4-O11	-58.2
C1-C2-C3-O12	-180.0	H8-C2-C3-O11	58.3	C1-C2-C3-N9	-0.1
H7-C2-C3-N10	122.0	C2-C3-N9-C4	0.0	C1-C2-C3-O10	179.9
H7-C2-C3-O12	-58.0	C2-C3-N9-O12	-180.0	H7-C2-C3-N9	121.8
H8-C2-C3-N10	-122.0	O11-C3-N9-C4	180.0	H7-C2-C3-O10	-58.1
H8-C2-C3-O12	58.0	O11-C3-N9-O12	0.0	H8-C2-C3-N9	-122.1
C2-C3-N10-C4	0.0	C1-C4-N9-C3	0.0	H8-C2-C3-O10	57.9
C2-C3-N10-H9	180.0	C1-C4-N9-O12	180.0	C2-C3-N9-C4	0.0
O12-C3-N10-C4	180.0	O10-C4-N9-C3	-180.0	C2-C3-N9-C12	-180.0
O12-C3-N10-H9	0.0	O10-C4-N9-O12	0.0	O10-C3-N9-C4	-180.0
C1-C4-N10-C3	0.0	C3-N9-O12-H13	0.0	O10-C3-N9-C12	0.0
C1-C4-N10-H9	180.0	C4-N9-O12-H13	-180.0	C1-C4-N9-C3	0.0

O11-C4-N10-C3	180.0
O11-C4-N10-H9	0.0

N-Hydroxy-Succinimide

Parameter	**Calculated**
Bond Length (A^0)	
C1-C2	1.543
C1-C4	1.527
C1-H5	1.091
C1-H6	1.091
C2-C3	1.515
C2-H7	1.092

N-Methyl-Succinimide

Parameter	**Calculated**
Bond Length (A^0)	
C1-C2	1.535
C1-C4	1.523
C1-H5	1.092
C1-H6	1.092
C2-C3	1.523
C2-H7	1.092
C2-H8	1.092
C3-N9	1.395
C1-C4-N9-C12	-180.0
O11-C4-N9-C3	-180.0
O11-C4-N9-C12	0.0
C3-N9-C12-H13	-120.0
C3-N9-C12-H14	0.1
C3-N9-C12-H15	120.3
C4-N9-C12-H13	60.0
C4-N9-C12-H14	-179.9
C4-N9-C12-H15	-59.7

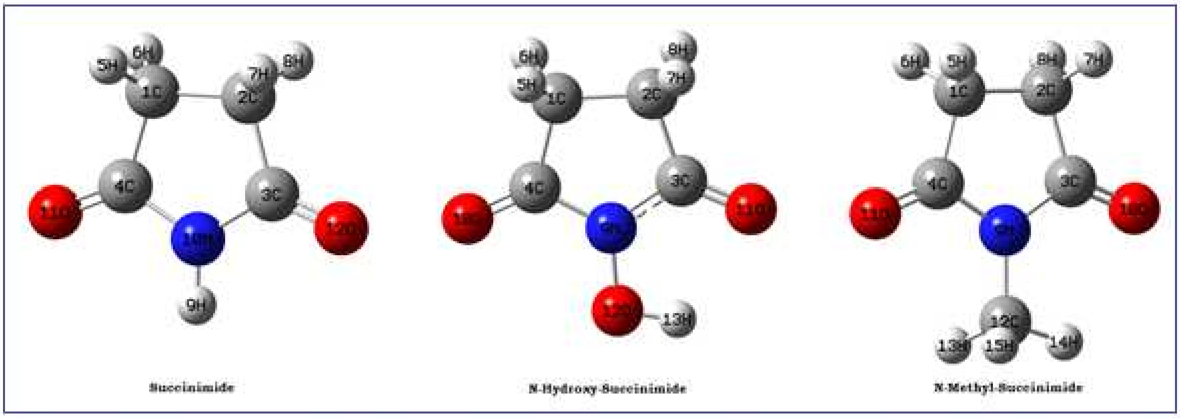

Fig.3. Theoretical optimized possible geometric structure with atoms numbering of Succinimide, NHS and NMS calculated at B3LYP/6-311++G(d,p) level of theory.

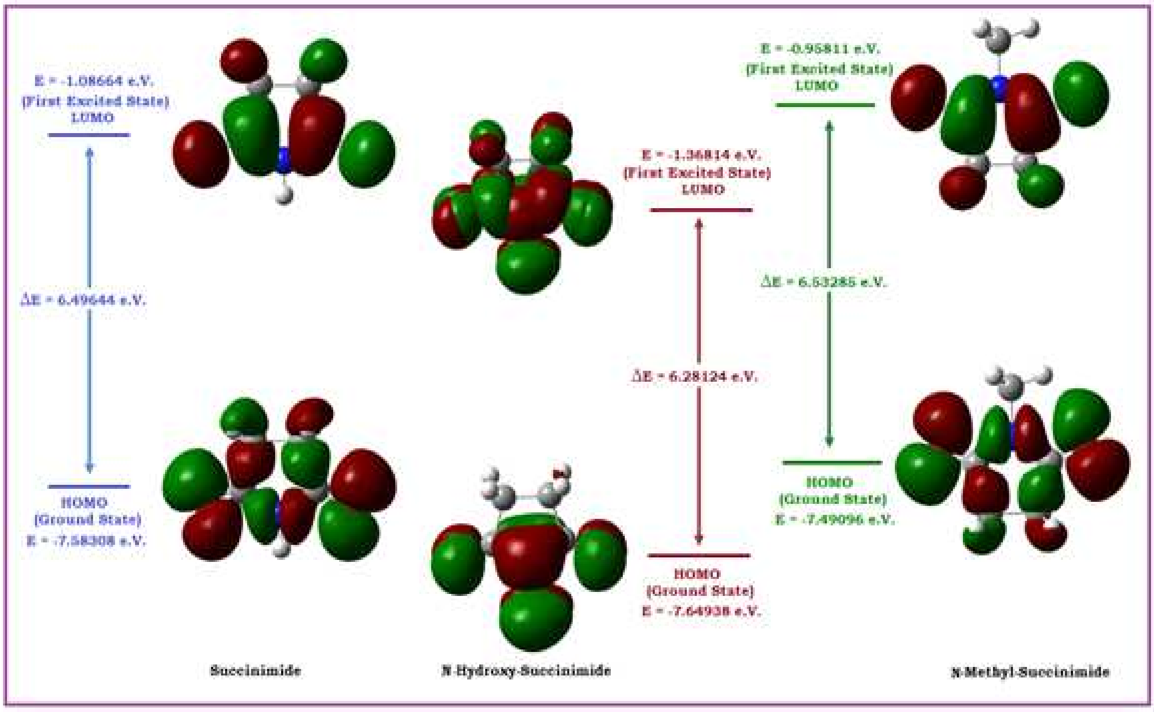

Fig. 4. Patterns of the principle highest occupied and lowest unoccupied molecular orbitals of *Succinimide, NHS and NMS* obtained with TD-DFT/B3LYP/6-311++G(d,p) method.

The calculated C=O bond lengths in all the three molecules vary from 1.201-1.208A^o and are close to standard values 1.220A^o [23,24]. The C-H bond lengths remained between 1.091 Å and 1.092 Å in all three molecules under investigation. The calculated bond lengths are in good agreement with those reported in [1]. The interior C-C-C angles in Succinimide and the two derivatives vary from 105.0^o - 105.4^o except the one C2-C1-C4 (106.3^o) in NHS. The calculated values of C-N-C angle in NMS (113.7^o) are found shorter than Succinimide and NHS which are

115.2^{o} and 116.7^{o} respectively. In NHS, the angle O11-C3-N9 (122.3^{o}) is found to be smaller than angle O10-C4-N9 (126.0^{o}) which shows a strong possibility of hydrogen bonding between the partially negative oxygen atom O11 of the carbonyl group and the hydrogen atom H13 of the OH group attached to nitrogen N9.

3.2 Electronic Properties

The most important orbitals in a molecule are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way how molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability so termed as soft molecule [25].

The 3D plots of frontier molecular orbitals shown in **Fig. 4** predict that HOMO is covers the entire molecule except methyl group (in NMS) and two CH_2 groups in NHS. The LUMO in all the three cases have more anti-bonding character. The lower value of the frontier orbital gap in NHS (6.28124 eV) than Succinimide (6.49644 eV) and NMS (6.53285 eV) clearly shows that NHS is more polarizable and chemically reactive than both its parent molecule Succinimideand NMS.

The MESP, which is a plot of electrostatic potential mapped onto the constant electron density surface of Succinimide, NHS and NMS are shown in **Fig. 5**. The molecular electrostatic potential surfaces make clear that even when the two molecules are structurally very similar; this similarity does not carry over into their electrophilic/nucleophilic reactivities. The resulting molecular electrostatic potential surface mapped in terms of colour grading and is very useful tool in investigation of correlation between molecular structure and the physiochemical property relationship of molecules including biomolecules and drugs [26-32]. The variation in electrostatic potential produced by a molecule is largely responsible for the binding of a drug to its receptor binding sites, as the binding site in general is expected to have opposite areas of electrostatic potential.The MESP map, in case of Succinimide, NHS and NMS clearly suggests that a large potential swings towards the two C=O groups (dark red) from CH_2 group (blue). The region around oxygen atoms reflects the most electronegative region and has excess negative charge, whereas the two CH_2 groups bear the brunt of positive charge (blue region). The MESP of NHS reveals larger electron rich area due to additional hydroxy group as compared to its parent molecule Succinimide and NMS.

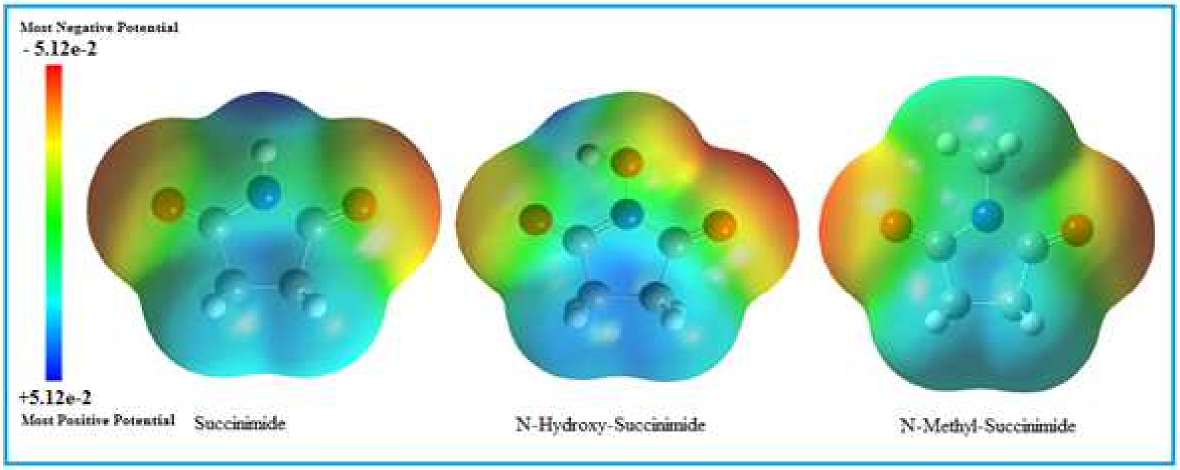

Fig. 5 : The MESP Surface of *Succinimide, NHS and NMS*

3.3 Electric moments

The dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole-dipole interactions, because higher the dipole moment, stronger will be the intermolecular interactions. The calculated value of dipole moment in case of NHS is found to be almost 2.27 times higher than that of the NMS and 1.64 times higher than that of parent molecule Succinimide **(Table 2).** The lower frontier orbital energy gap and high dipole moment for NHS shows its higher activity and lesser stability as compared to Succinimide and NMS.

Table 2 : Polarizability data and hyperpolarizability data for Succinimide, NHM and NMS

Components	B3LYP/6-311++G(d,p)		
	Succinimide	N-Hydroxy-succinimide	N-Methyl-succinimide
Dipole Moment			
(μ)	2.2211 D	3.6449 D	1.6039 D
Polarizability (α)			
α_{xx}	76.932	82.571	85.724
α_{yy}	58.039	69.071	75.536
α_{zz}	38.853	41.186	48.508
<α>	8.5869 x 10^{-24}e.s.u.	9.5257 x 10^{-24}e.s.u	10.3625 x 10^{-24}e.s.u
Hyperpolarizability (β)			
β_{xxx}	-1.4834	-80.4053	-24.2773
β_{xxy}	30.7814	-0.0008	-0.0271
β_{xyy}	32.7351	92.7204	-19.4235
β_{yyy}	-117.7550	163.6410	-152.1101
β_{xxz}	-2.0287	0.0040	0.2509
β_{xyz}	20.4557	0.0016	0.0001
β_{yyz}	-20.6531	33.0832	-6.7455
β_{xzz}	-23.6013	0.0014	-0.0138
β_{yzz}	0.9238	0.7654	-12.9586
β_{zzz}	0.1176	41.6361	-12.1304
β_{TOTAL}	0.7472 x 10^{-30}e.s.u.	1.5149 x 10^{-30}e.s.u.	1.4378 x 10^{-30}e.s.u.

The determination of electric polarizability and hyperpolarizability is of fundamental importance to study the phenomenon induced by intermolecular interactions, simulation studies and nonlinear optical effects. In the absence of experimental data, the values of polarizability and hyperpolarizability calculated at the same level of theory and the same basis set for the title molecules, can provide a satisfactory comparison of these quantities. The mean polarizability of NMS (10.3625 x 10^{-24}e.s.u.) is found to be higher than that of Succinimide (8.5869 x 10^{-24}e.s.u.) and NHS (9.5257 x 10^{-24}e.s.u.). Urea is one of the prototypical molecules used in the study of the Non linear optical properties of molecular systems. Therefore, it is used frequently as a threshold value for comparative purposes. All the three molecules under investigation (Succinimide/NHS/NMS) has large β_{TOTAL} value (0.7472/1.5149/1.4378 x 10^{-30}e.s.u) than urea (almost 3.84/7.78/7.38 times greater than urea), that indicates, they are good candidates for NLO material.

3.4 Thermo dynamical Properties

The values of some thermodynamic parameter (such as zero-point vibrational energy, thermal energy, specific heat capacity, rotational constant and entropy) at standard temperature (298.15 K) for Succinimide, NHS and NMS molecules computed at DFT/B3LYP with 6-311G++(d,p) methods are listed in **Table 3**. On the basis of vibrational analysis, the standard statistical thermodynamic functions : heat capacity ($C^0_{p,m}$), entropy (S^0_m), and enthalpy change (ΔH^0_m) for the Succinimide, NHS and NMS molecules were obtained from the theoretical harmonic frequencies and listed in **Table 4**.

Table 3 : The calculated thermo dynamical parameters of Succinimide, NHS and NMS at 298.15K in ground state

Basis Set	B3LYP/6-311++G(d,p)		
	Succinimide	N-Hydroxy-succinimide	N-Methyl-succinimide
SCF energy (a.u.)	-360.7794	-435.9608	-400.1022
E_{HOMO} (e.V.)	-7.58308	-7.64938	-7.49096
E_{LUMO} (e.V.)	-1.08664	-1.36814	-0.95811
$E_{LUMO-HOMO}$ (e.V.)	6.49644	6.28124	6.53285
Zero point energy (kcal mol^{-1})	57.51037	59.67621	74.8866
Rotational Constants (GHz)	5.91626	3.20566	3.09283
	2.25578	2.25041	2.23509
	1.66658	1.34413	1.32949
Specific heat (C_v) (cal mol^{-1} K^{-1})	21.351	25.834	26.827
Entropy (S) (cal mol^{-1} K^{-1})	78.220	84.230	88.065
Dipole moment (Debye)	2.2211	3.6449	1.6039

Table 4: Thermodynamic properties at different temperatures at the B3LYP/6-311++G(d,p) level for Succinimide, NHS and NMS

T (K)	Heat Capacity ($C_p{}^0{}_m$)			Entropy ($S^0{}_m$)			Enthalpy ($H^0{}_m$)		
	Succinimide	N-Hydroxy-Succinimide	N-Methyl-Succinimide	Succinimide	N-Hydroxy-Succinimide	N-Methyl-Succinimide	Succinimide	N-Hydroxy-Succinimide	N-Methyl-Succinimide
100	9.631	11.654	13.116	60.918	63.025	65.816	0.971	1.034	1.163
200	14.686	18.739	19.459	70.336	74.628	78.155	2.359	2.748	2.979
298.15	21.351	25.834	26.827	78.22	84.23	88.065	4.319	5.132	5.44
400	28.027	32.709	34.623	86.031	93.387	97.635	7.042	8.323	8.776
500	33.605	38.472	41.453	93.348	101.769	106.558	10.332	12.089	12.787
600	38.151	43.192	47.196	100.253	109.577	115.001	14.126	16.379	17.427
700	41.846	47.037	51.964	106.728	116.84	122.952	18.331	21.096	22.591

From **Table 4**, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 700K due to the fact that the molecular vibrational intensities increase with temperature [33,34]. The correlation equations among heat capacities, entropies, enthalpy change and temperatures were fitted by quadratic, linear and quadratic formulas. The corresponding fitting equations, fitting factors (R^2) for these thermodynamic properties and the correlation graphics of Succinimide, NHS and NMS are shown in **Fig. 6**.

All the thermodynamic data supplied are helpful information for further study of Succinimide, NHS and NMS. These can be used to compute the other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermo chemical field [35]. It is important to mention here that all thermodynamic calculations were done in gas phase and they could not be used in solution.

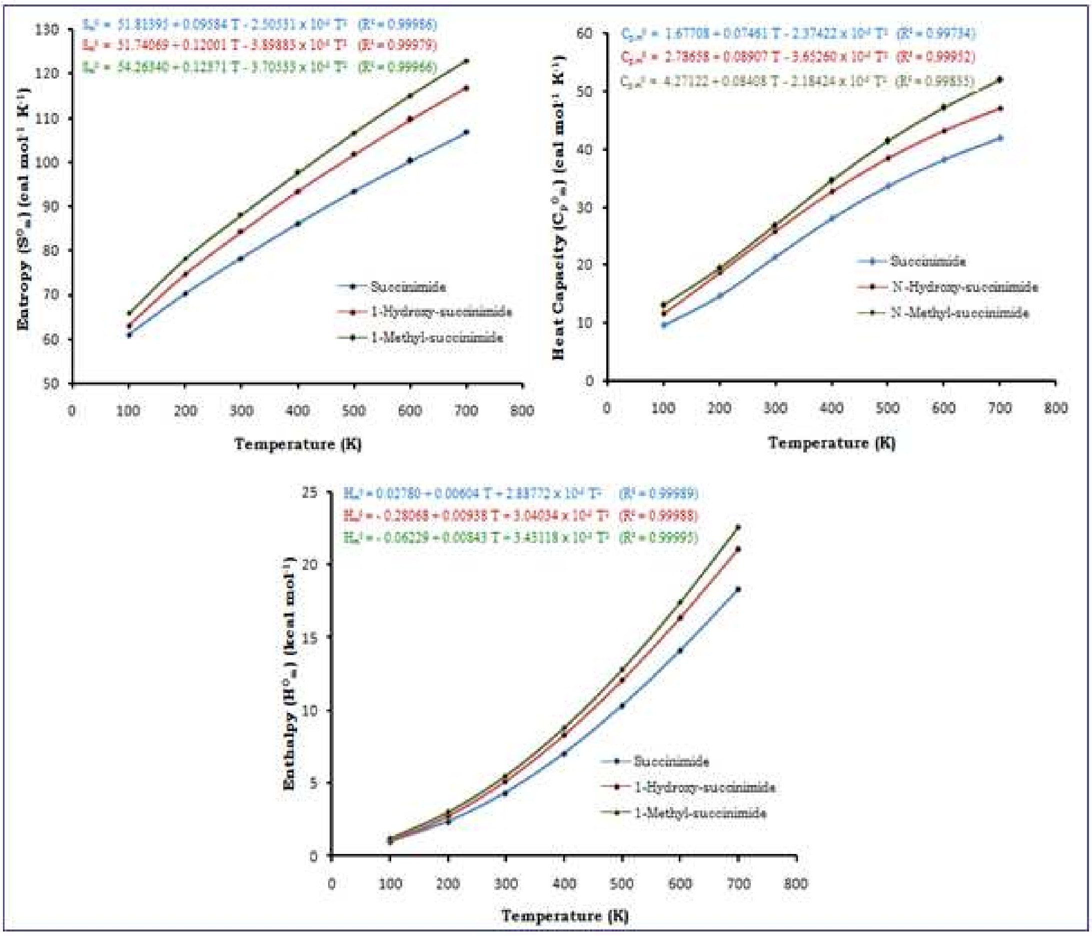

Fig.6 : The temperature dependence correlation graph of heat capacity, entropy, and enthalpy for Succinimide, NHS and NMS.

3.5 Vibrational Analysis

DFT based calculations provide not only the qualitative but also the quantitative understanding of energy distribution of each vibrational mode on the basis of potential energy distribution (PED) and lead to an additional interpretation of the vibrational spectroscopic data as demonstrated in studies conducted by various groups [36-39]. For normal coordinate analysis of Succinimide, NHS and NMS, the complete set of 41, 45 and 56 standard internal coordinates have been defined respectively (**Table 5**).[45,46] were used.

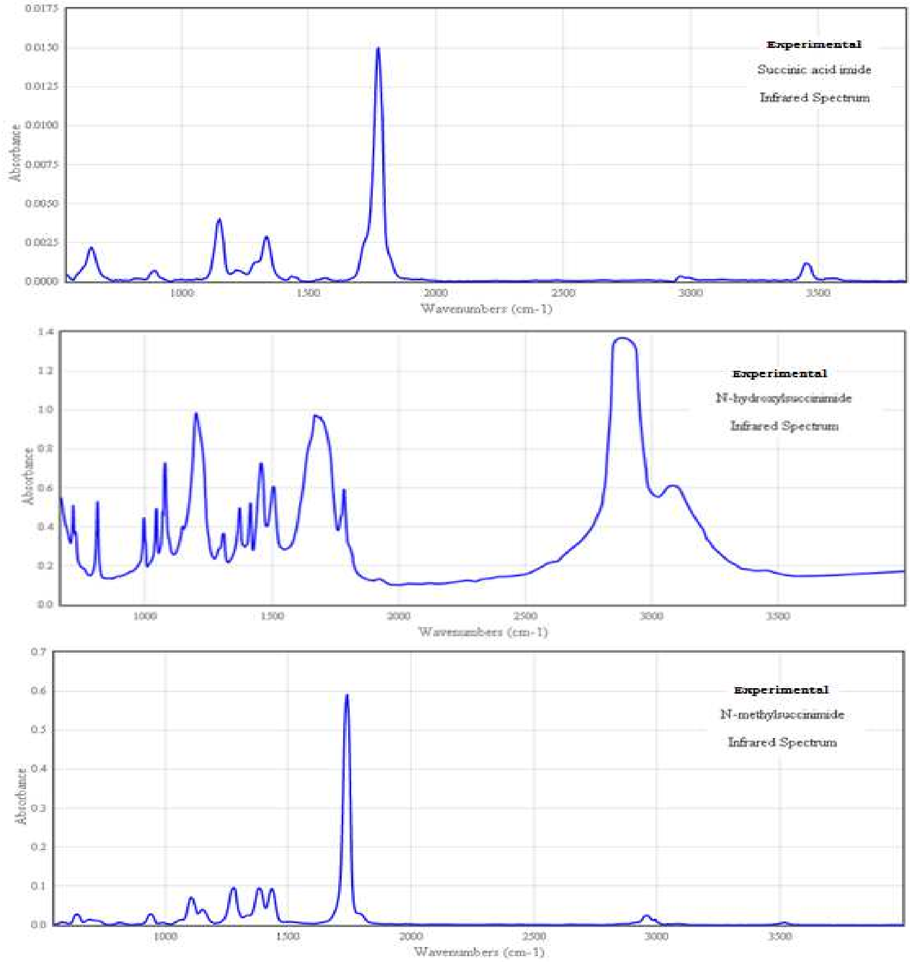

Fig.7 :Experimental FT-IR spectra of Succinimide, NHS and NMS

Using these internal coordinates, a non redundant set of 30, 33, 39 (i.e. 3n-6) local symmetry coordinates (**Table 6**) are constructed on the basis of recommendations of the G. Fogarasi et al [40-41] . The theoretical vibrational assignment of the title compounds using percentage potential energy distribution (PED) have been done with the MOLVIB program (version V7.0-G77) written by T. Sundius [42-44].In general, DFT harmonic treatments overestimate the observed vibrational wavenumbers owing to neglecting of anharmonic corrections and incompleteness of basis set. In this work, we have adopted the scaling approach to offset the systematic errors, an empirical uniform scaling factor of 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1}. The experimental and computed vibrational wavenumbers, their IR intensities and the detailed description of normal modes of vibration of title compounds Succinimide, NHS and NMS in terms of their contribution to the potential energy are given in **Table 7, 8 and 9** respectively. The experimental and theoretical IR spectrum of title molecules are shown in **Fig. 7 and 8** respectively. For complete vibrational analysis of all the three title molecules, the vibrational modes are discussed hereunder five heads: (i) CH_2 vibrations (iii) CH_3 vibrations (iii) C=O stretch(iv) OH vibrations (v) Ring vibrations.

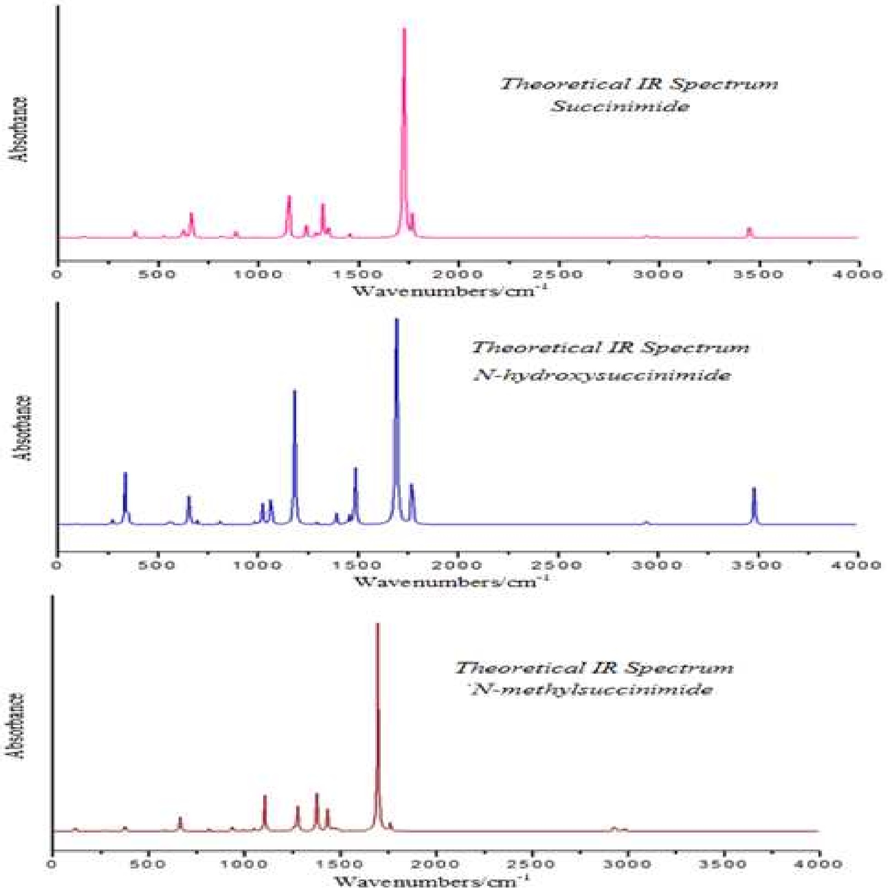

Fig.8 :.Theoretically simulated vibrational spectra of Succinimide, NMS and NHS

3.5.1 CH_2 vibrations

All the three molecules (Succinimide, NHS and NMS) under investigation possess two methylene groups which accounts for two stretching and four bending normal modes. The four bending vibrations of methylene group found in the IR spectrum are CH_2 scissoring/rocking/wagging and twisting. The CH_2 asymmetric stretching vibrations are generally observed in the region 3000-2900 cm^{-1}, while the CH_2 symmetric stretch appears between 2900 and 2800 cm^{-1} [47,48]. In the present work, CH_2 asymmetric stretching vibrations are observed at 2979, 3037 and 2980 cm^{-1} (FTIR) in Succinimide, NHS and NMS molecules respectively. The calculated asymmetric CH_2 stretching vibrations of the two methylene groups in Succinimide/NHS/NMS are found at (2986, 2971)/(2988,2973)/(2984,2969) cm^{-1} by B3LYP method respectively with more than 97% contribution to PED. Similarly, the calculated symmetric CH_2 stretching vibrations of the methylene groups are at (2946,2939)/(2947,2940)/(2945, 2938) cm^{-1} respectively. No bands could be assigned to CH_2 symmetric stretching vibrations in the experimental FT-IR spectra of any of the title molecules.

The general order for CH_2 deformation are CH_2(scis)> CH_2(wag)> CH_2(twist)> CH_2(rock). The two methylene scissoring modes in Succinimide/NHS/NMS are calculated at (1454,1434)/ (1456,1435)/(1456,1436) cm^{-1} respectively with more than 80% contribution to PED. These vibrations are well supported by the two bands observed at 1462/1454 cm^{-1}(FTIR) in Succinimide/NHS molecules respectively. From the theoretical calculations, the CH_2 wagging modes are predicted at (1225, 1149)/(1296,1255)/(1293,1255) cm^{-1} as a mixed mode with C-C stretch for Succinimide/NHS/NMS. It shows a good correlation with the FTIR bands at 1155, 1310 cm^{-1} for Succinimide/NHS respectively. In NHS and NMS, CH_2 twisting vibrational modes are found as pure modes at (1222,1148) / (1225,1148) cm^{-1}, whereas in Succinimide, they are found as a mixed mode with CH_2wagging modes at 1225 and 1149 cm^{-1}.

Table 5 : Definition of Internal Coordinates of Succinimide, N-Hydroxy-Succinimide (NHS), N-Methyl-Succinimide (NMS)

No.	Symbol	Type	Definitions
Succinimide			
Streching			
1-3	r_i	C-C	C1-C2, C2-C3, C4-C1
4-5	r_i	C-N	C3-N10, C4-N10
6-7	r_i	C-O	C3-O12, C4-O11
8	r_i	N-H	N10-H9
9-12	r_i	C-H	C1-H5, C1-H6, C2-H7, C2-H8
In-Plane Bending			
13-14	α_j	C-C-C	C1-C2-C3, C4-C1-C2
15-17	α_j	C-C-N	C1-C4-N10, C2-C3-N10, C3-N10-C4
18-19	α_j	H-C-H	H5-C1-H6, H7-C2-H8
20-27	α_j	C-C-H	C4-C1-H5, C4-C1-H6, C2-C1-H5, C2-C1-H6, C3-C2-H7, C3-C2-H8, C1-C2-H7, C1-C2-H8
28-29	α_j	C-C-O	C1-C4-O11, C2-C3-O12
30-31	α_j	N-C-O	N10-C4-O11, N10-C3-O12
32-33	α_j	C-N-H	C3-N10-H9, C4-N10-H9
Out-of-Plane Bending			
34	γ_k	O-C-N-C	O11-C4-N10-C1
35	γ_k	O-C-C-N	O12-C3-C2-N10
36	γ_k	H-N-C-C	H9-N10-C3-C4
Torsion/ Twisting			
37	τ_i	C-C-C-C	C4-C1-C2-C3
38-41	τ_i	C-C-C-N	C1-C2-C3-N10, C2-C3-N10-C4, C3-N10-C4-C1, N10-C4-C1-C2
N-Hydroxy-Succinimide			
Streching			
1-3	r_i	C-C	C1-C2, C2-C3, C4-C1
4-5	r_i	C-N	C3-N9, C4-N9
6-7	r_i	C-O	C3-O11, C4-O10
8	r_i	N-O	N9-O12
9	r_i	O-H	O12-H13
10-13	r_i	C-H	C1-H5, C1-H6, C2-H7, C2-H8
In-Plane Bending			
14-15	α_j	C-C-C	C1-C2-C3, C4-C1-C2
16-23	α_j	C-C-H	C4-C1-H5, C4-C1-H6, C2-C1-H5, C2-C1-H6, C3-C2-H7, C3-C2-H8, C1-C2-H7, C1-C2-H8
24-25	α_j	H-C-H	H5-C1-H6, H7-C2-H8
26-28	α_j	C-C-N	C1-C4-N9, C2-C3-N9, C3-N9-C4
29-30	α_j	C-C-O	C1-C4-O10, C2-C3-O11
31-32	α_j	N-C-O	N9-C4-O10, N9-C3-O11
33-34	α_j	C-N-O	C3-N9-O12, C4-N9-O12
35	α_j	N-O-H	N9-O12-H13
N-Hydroxy-Succinimide			
Out-of-Plane Bending			
36	γ_k	O-C-N-C	O10-C4-N9-C1
37	γ_k	O-C-C-N	O11-C3-C2-N9
38	γ_k	O-N-C-C	O12-N9-C3-C4
39-40	γ_k	C-N-O-H	C3-N9-O12-H13, C4-N9-O12-H13
Torsion/ Twisting			
41	τ_i	C-C-C-C	C4-C1-C2-C3
42-45	τ_i	C-C-C-N	C1-C2-C3-N9, C2-C3-N9-C4, C3-N9-C4-C1, N9-C4-C1-C2
N-Methyl-Succinimide			
Streching			
1-3	r_i	C-C	C1-C2, C2-C3, C4-C1
4-6	r_i	C-N	C3-N9, C4-N9, C12-N9
7-8	r_i	C-O	C3-O10, C4-O11
9-12	r_i	C-H (CH_2)	C1-H5, C1-H6, C2-H7, C2-H8
13-15	r_i	C-H (CH_3)	C12-H13, C12-H14, C12-H15
In-Plane Bending			
16-17	α_j	C-C-C	C1-C2-C3, C4-C1-C2
18-19	α_j	C-C-N	C1-C4-N9, C2-C3-N9
20-22	α_j	C-N-C	C3-N9-C4, C4-N9-C12, C3-N9-C12
23-24	α_j	C-C-O	C1-C4-O11, C2-C3-O10
25-32	α_j	C-C-H	C4-C1-H5, C4-C1-H6, C2-C1-H5, C2-C1-H6, C3-C2-H7, C3-C2-H8, C1-C2-H7, C1-C2-H8
33-34	α_j	H-C-H	H5-C1-H6, H7-C2-H8
35-37	α_j	H-C-H	H13-C12-H14, H14-C12-H15, H15-C12-H13
38-39	α_j	N-C-O	N9-C4-O11, N9-C3-O10
40-42	α_j	N-C-H	N9-C12-H13, N9-C12-H14, N9-C12-H15
Out-of-Plane Bending			
43	γ_k	O-C-N-C	O11-C4-N9-C1
44	γ_k	O-C-C-N	O10-C3-C2-N9
45	γ_k	C-N-C-C	C12-N9-C3-C4
Torsion/ Twisting			
46	τ_i	C-C-C-C	C4-C1-C2-C3
47-50	τ_i	C-C-C-N	C1-C2-C3-N9, C2-C3-N9-C4, C3-N9-C4-C1, N9-C4-C1-C2
51-56	τ_i	C-N-C-H	C4-N9-C12-H13, C4-N9-C12-H14, C4-N9-C12-H15,C3-N9-C12-H13, C3-N9-C12-H14, C3-N9-C12-H15

Table6: Definition of local symmetry coordinates of Succinimide, N-Hydroxy-Succinimide (NHS) and N-Methyl-Succinimide (NMS)

No.	Symbol	Definitions
		Succinimide
1-3	ν(C-C)	r_1, r_2, r_3
4-5	ν(C-N)	r_4 , r_5
6-7	ν(C-O)	r_6 , r_7
8	ν(N-H)	r_8
9	$\nu_s(CH_2)$(C1)	$r_9 + r_{10}$
10	$\nu_{as}(CH_2)$(C1)	$r_9 - r_{10}$
11	$\nu_s(CH_2)$(C2)	$r_{11} + r_{12}$
12	$\nu_{as}(CH_2)$(C2)	$r_{11} - r_{12}$
13-14	β(C-O)	$\alpha_{30} - \alpha_{28}, \alpha_{29} - \alpha_{31}$
15	β(N-H)	$\alpha_{32} - \alpha_{33}$
16	Sis. (CH_2)(C1)	$\alpha_{18} - \alpha_{14}$
17	$\rho(CH_2)$(C1)	$\alpha_{22} - \alpha_{23} + \alpha_{20} - \alpha_{21}$
18	Wag.(CH_2)(C1)	$\alpha_{22}+\alpha_{23} - \alpha_{20}-\alpha_{21}$
19	twist (CH_2)(C1)	$\alpha_{22}-\alpha_{23} - \alpha_{20}+\alpha_{21}$
20	Sis. (CH_2)(C2)	$\alpha_{19} - \alpha_{23}$
21	$\rho(CH_2)$(C2)	$\alpha_{24} - \alpha_{25} + \alpha_{26} - \alpha_{27}$
22	Wag.(CH_2)(C2)	$\alpha_{24}+\alpha_{25} - \alpha_{26} - \alpha_{27}$
23	twist (CH_2)(C2)	$\alpha_{24} - \alpha_{25} - \alpha_{26}+\alpha_{27}$
24	δ R	$\alpha_{14} + a\ (\alpha_{13} + \alpha_{15}) + b\ (\alpha_{16} + \alpha_{17})$
25	δ' R	$(a-b)\ (\alpha_{13} - \alpha_{15}) + (1-a)\ (\alpha_{16} - \alpha_{17})$
26-27	γ(C-O)	γ_{34}, γ_{35}
28	γ (N-H)	γ_{36}
29	τ R	$b(T_{37} + T_{41}) + a(T_{38} + T_{40}) + T_{39}$
30	τ' R	$(a-b)(T_{40} - T_{38})+(1-a)(T_{41} - T_{37})$
		N-Hydroxy-Succinimide
1-3	ν(C-C)	r_1, r_2, r_3
4-5	ν(C-N)	r_4 , r_5
6-7	ν(C-O)	r_6 , r_7
8	ν(N-O)	r_8
9	ν(O-H)	r_9
10	$\nu_s(CH_2)$(C1)	$r_{10} + r_{11}$
11	$\nu_{as}(CH_2)$(C1)	$r_{10} - r_{11}$
12	$\nu_s(CH_2)$(C2)	$r_{12} + r_{13}$
13	$\nu_{as}(CH_2)$(C2)	$r_{12} - r_{13}$
14-15	β(C-O)	$\alpha_{31} - \alpha_{29}, \alpha_{30} - \alpha_{32}$
16	β(N-O)	$\alpha_{33} - \alpha_{34}$
17	Sis. (CH_2)(C1)	$\alpha_{24} - \alpha_{15}$
18	$\rho(CH_2)$(C1)	$\alpha_{18} - \alpha_{19} + \alpha_{16} - \alpha_{17}$
19	Wag.(CH_2)(C1)	$\alpha_{18}+\alpha_{19} - \alpha_{16}-\alpha_{17}$
20	twist (CH_2)(C1)	$\alpha_{18}-\alpha_{19} - \alpha_{16}+\alpha_{17}$
21	Sis. (CH_2)(C2)	$\alpha_{25} - \alpha_{14}$
22	$\rho(CH_2)$(C2)	$\alpha_{20} - \alpha_{21} + \alpha_{22} - \alpha_{23}$
23	Wag.(CH_2)(C2)	$\alpha_{20}+\alpha_{21} - \alpha_{22} - \alpha_{23}$
24	twist (CH_2)(C2)	$\alpha_{20} - \alpha_{21} - \alpha_{22}+\alpha_{23}$
25	δ R	$\alpha_{15} + a\ (\alpha_{14} + \alpha_{26}) + b\ (\alpha_{27} + \alpha_{28})$
26	δ' R	$(a-b)\ (\alpha_{14} - \alpha_{26}) + (1-a)\ (\alpha_{27} - \alpha_{28})$
27	β(O-H)	α_{35}
28-29	γ(C-O)	γ_{36}, γ_{37}
30	γ (N-O)	γ_{38}
31	τ C-N-O-H	$\gamma_{39} + \gamma_{40}$
32	τ R	$b(T_{41} + T_{45}) + a(T_{42} + T_{44}) + T_{43}$
33	τ' R	$(a-b)(T_{44} - T_{42})+(1-a)(T_{45} - T_{41})$
		N-Methyl-Succinimide
1-3	ν(C-C)	r_1, r_2, r_3
4-6	ν(C-N)	r_4 , r_5,r_6
7-8	ν(C-O)	r_7 , r_8
9	$\nu_s(CH_2)$(C1)	$r_9 + r_{10}$
10	$\nu_{as}(CH_2)$(C1)	$r_9 - r_{10}$
11	$\nu_s(CH_2)$(C2)	$r_{11} + r_{12}$
12	$\nu_{as}(CH_2)$(C2)	$r_{11} - r_{12}$
13	$\nu_s(CH_3)$	$r_{13} + r_{14} + r_{15}$
14	$\nu_{as}(CH_3)$	$r_{13} - r_{14} - r_{15}$
15	$\nu_{as}'(CH_3)$	$r_{14} - r_{15}$
16	Sis. (CH_2)(C1)	$\alpha_{33} - \alpha_{17}$
17	$\rho(CH_2)$(C1)	$\alpha_{27} - \alpha_{28} + \alpha_{25} - \alpha_{26}$
18	Wag.(CH_2)(C1)	$\alpha_{27}+\alpha_{28} - \alpha_{25}-\alpha_{26}$
19	twist (CH_2)(C1)	$\alpha_{27}-\alpha_{28} - \alpha_{25}+\alpha_{26}$
20	Sis. (CH_2)(C2)	$\alpha_{34} - \alpha_{16}$
21	$\rho(CH_2)$(C2)	$\alpha_{29} - \alpha_{30} + \alpha_{31} - \alpha_{32}$
22	Wag.(CH_2)(C2)	$\alpha_{29}+\alpha_{30} - \alpha_{31}-\alpha_{32}$
23	twist (CH_2)(C2)	$\alpha_{29}-\alpha_{30} - \alpha_{31}+\alpha_{32}$
24	δ R	$\alpha_{17} + a\ (\alpha_{16} + \alpha_{18}) + b\ (\alpha_{19} + \alpha_{20})$
25	δ' R	$(a-b)\ (\alpha_{16} - \alpha_{18}) + (1-a)\ (\alpha_{19} - \alpha_{20})$
26-27	β(C-O)	$\alpha_{39} - \alpha_{24}, \alpha_{38} - \alpha_{23}$
28	β(N-C)	$\alpha_{22} - \alpha_{21}$
29	$\delta_s(CH_3)$	$\alpha_{35} + \alpha_{36} + \alpha_{37} - \alpha_{40} - \alpha_{41} - \alpha_{42}$
30	$\delta_{as}(CH_3)$	$2\ \alpha_{35} - \alpha_{36} - \alpha_{37}$
31	$\delta_{as}'(CH_3)$	$\alpha_{36} - \alpha_{37}$
32	$\rho(CH_3)$	$2\ \alpha_{41} - \alpha_{42} - \alpha_{40}$
33	ρ' (CH_3)	$\alpha_{42} - \alpha_{40}$
34-35	γ(C-O)	γ_{43}, γ_{44}
36	γ (N-C)	γ_{45}
37	$\tau(CH_3)$	$T_{54} + T_{55} + T_{56} - T_{51} - T_{52} - T_{53}$
38	τ R	$b(T_{46} + T_{50}) + a(T_{47} + T_{49}) + T_{48}$
39	τ' R	$(a-b)(T_{49} - T_{47})+(1-a)(T_{50} - T_{46})$

$a = \cos 144^0$; $b = \cos 72^0$

3.5.2 CH_3 vibrations

The N-methyl-succinimide (NMS) holds a CH_3 group substituted for the H atom attached with the N atom in the succinimide ring. For assignments of CH_3 group frequencies, one can expect that nine fundamental vibrations can be associated to CH_3 group.The asymmetric stretch is usually at higher wavenumber than the symmetric stretch. The asymmetric C-H vibration for methyl group is usually occur in the region between 2975 and 2920 cm^{-1} [49-51] and the symmetric C-H vibrations for methyl group is usually occur in the region of 2870-2840 cm^{-1}. In the present work, asymmetric CH_3 stretching vibrations are observed at 3021 and 2986 cm^{-1} and will complemented with a band observed at 2980 cm^{-1} in FTIR. The CH_3 symmetric stretching mode is calculated at 2925 cm^{-1} as a pure mode with more than 95% contribution to PED. The asymmetric and symmetric deformation vibrations of methyl group appear in the region 1465-1440 cm^{-1} and 1390-1370 cm^{-1}[52]. The modes calculated at 1483 and 1465 cm^{-1} are assigned to CH_3 symmetric deformation vibrations with more than 70% contribution to PED in NMS. No bands which could be assigned to CH_2 symmetric deformation vibrations were registered in the experimental FTIR spectrum of NMS molecule. The methyl rocking mode vibration usually appears within the region of 1070-1010 cm^{-1} [53-56]. The out-of-plane CH_3 rocking mode is theoretically calculated using B3LYP/6-311++G(d,p) at 1130 cm^{-1} with 80% contribution to PED.

3.5.3 C=O vibrations

The appearance of a strong band in IR spectra between 1790-1810 cm^{-1} show the presence of carbonyl group in the molecule and is due to the C=O stretch [57]. The frequency of the stretch due to carbonyl group mainly depends on the bond strength which in turn depends upon inductive, conjugative, field and steric effects. As usual, the modes calculated at higher wavenumber (1769/1771/1759 cm^{-1}) and the one at lower wavenumber (1725/1692/1695 cm^{-1}) have been identified as the symmetric and asymmetric stretching modes of two C=O groups for Succinimide/NHS/NMS respectively. The electron withdrawing nitrogen atom attached to carbonyl group increases the strength of the C=O bonds causing the vibrations to occur at a relatively higher value. For this reason, strong bands appear in FTIR of Succinimide/NHS/NMS at 1735/1685/1702 cm^{-1} assigned to C=O stretch vibrations. The bands calculated at 557,531/565,552/570,565 cm^{-1} in case of Succinimide/NHS/NMS respectively, are identified as C=O out-of-plane bending modes and are supported by a weak intensity band in FTIR at 556 cm^{-1} for NMS.

Table 7 : Theoretical and Experimental wavenumbers in cm^{-1} of Succinimide

S. No.	Calculated Wavenumbers		Experimental Wavenumber	IR Intensity	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
	Unscaled in cm^{-1}	Scaled in cm^{-1}	FTIR in cm^{-1}		
1	3603	3452	3456	61.89	ν(N10-H9) (93)
2	3117	2986	2979	4.84	$\nu_{as}(CH_2)$(C1) (50) + $\nu_{as}(CH_2)$ (C2)(50)
3	3101	2971		0.00	$\nu_{as}(CH_2)$(C1) (50) + $\nu_{as}(CH_2)$ (C2)(50)
4	3075	2946		0.64	$\nu_{s}(CH_2)$(C1) (48) + $\nu_{s}(CH_2)$ (C2)(48)
5	3068	2939		12.90	$\nu_{s}(CH_2)$(C1) (49) + $\nu_{s}(CH_2)$ (C2)(49)
6	1847	1769		75.42	δ R (34) + ν(C3-O12) (15) + ν(C4-O11) (15) + δ' R (11) + ν(C-C) (10)
7	1801	1725	1735	954.20	δ' R (59) + ν(C4-O11) (10) + ν(C3-O12) (10) + ν(C-C) (8) +ν(C3-N10) (8)
8	1479	1454	1462	17.88	Sis. (CH_2) (C1) (40) + Sis. (CH_2) (C2) (40) + ν(C-C) (8)
9	1459	1434		0.05	Sis. (CH_2) (C1) (46) + Sis. (CH_2) (C2) (46)
10	1372	1349	1358	48.21	ν(C3-N10) (39) + δ' R (30) + β (N10-H9) (22)
11	1344	1321	1326	109.04	δ' R (61) + ν(C3-N10) (19) + ν(C-C) (7)
12	1313	1290		21.82	ν(C-C) (40) + δ' R (26) + Wag. (CH_2) (C1) (13) + Wag. (CH_2) (C2) (13)
13	1259	1238	1242	51.47	ν(C-C) (43) + δ R (13) + δ' R (12) + ν(C3-N10) (9) + ν(C4-N10) (7)
14	1246	1225		0.00	Wag. (CH_2) (C2) (48) + twist (CH_2) (C1) (48)
15	1169	1149		2.70	ν(C3-N10) (53) +ν(C-C) (33) + ν(C4-N10) (6)
16	1168	1149	1155	215.39	Wag. (CH_2) (C2) (43) + twist (CH_2) (C1) (43)
17	1026	1008		0.00	ρ (CH_2) (C2) (36) + ρ (CH_2) (C1) (36) + γ (C4-O11) (10) + γ (C3-O12) (10)
18	1007	990		3.36	ν(C-C) (64) + δ' R (17) + δ R (15)
19	904	889	875	22.90	δ' R (63) + ν(C-C) (22) + ν(C3-N10) (11)
20	843	828		5.90	ν(C-C) (69) + δ R (14) + δ' R (10) + ν(C3-N10) (6)
21	828	814		8.30	ρ (CH_2) (C2) (22) + ρ (CH_2) (C1) (22) + γ (C4-O11) (12) + γ (C3-O12) (12))
22	678	667		112.55	γ (N10-H9) (81) + τ' R (7) + γ (C4-O11) (5) + γ (C3-O12) (5)
23	638	628	626	38.36	δ' R (72) + ν(C-C) (21)
24	630	619		5.51	δ R (51) + δ' R (33) + ν(C3-N10) (9)
25	567	557		0.00	γ (C3-O12) (35) + γ (C4-O11) (35) + ρ (CH_2) (C2) (10) + ρ (CH_2) (C1) (10)
26	541	532		5.44	δ' R (54) + ν(C-C) (30) + β (C4-O11) (7) + β (C3-O12) (7)
27	540	531		5.58	γ (C4-O11) (23) + γ (C3-O12) (23) + τ' R (18) + ρ (CH_2) (C1) (15)
28	391	384		22.68	δ' R (63) + ν(C3-N10) (11) + ν(C-C) (5)
29	134	132		8.89	τ' R (60) + γ (N10-H9) (39)
30	80	79		0.00	τ R (60) + τ' R (20) + ρ (CH_2) (C2) (8) + ρ (CH_2) (C1) (8)

ν –> stretching; ν_s –> symmetric stretching ; ν_{as} –> asymmetric stretching ; ρ–> rocking ; δ –>deformation ; β –>in-plane bending ; γ–> out-of-plane bending ; Sis –> scissoring ; Wag. –> wagging; twist –> twisting; τ –> Torsion ; R –> Ring

3.5.4 OH vibrations

The title molecule, N-hydroxy-succinimide (NHS) holds a hydroxy group substituted at the N atom in the Succinimide ring. The OH stretching vibrations are generally observed in the region around 3200-3650 cm^{-1}. The characteristic peak calculated at 3481 cm^{-1} is pure O-H stretching vibration and contributes 100% to the P.E.D. The band observed at 1495 cm^{-1} in FTIR is assigned to OH in-plane bending vibration in NHS while corresponding band calculated theoretically by B3LYP/6-311++G(d,p) at wavenumber 1487 cm^{-1}. The OH twisting mode is calculated at 337 cm^{-1} and contributes 82% to the total P.E.D.

Table 8 : Theoretical and Experimental wavenumbers in cm^{-1} of N-Hydroxy-succinimide

S. No.	Calculated Wavenumbers		Experimental Wavenumber	IR Intensity	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
	Unscaled in cm^{-1}	Scaled in cm^{-1}	FTIR in cm^{-1}		
1	3634	3481		85.03	ν (O12-H13) (100)
2	3119	2988	3037	3.53	ν_{as}(CH$_2$)(C1) (66) + ν_{as}(CH$_2$) (C2)(34)
3	3103	2973		0.08	ν_{as}(CH$_2$) (C2)(65) + ν_{as}(CH$_2$)(C1) (34)
4	3076	2947		2.03	ν_s(CH$_2$) (C1)(74) + ν_s(CH$_2$) (C2)(22)
5	3069	2940		10.81	ν_s(CH$_2$) (C2)(76) + ν_s(CH$_2$) (C1)(23)
6	1849	1771	1777	145.30	δ' R (26) + δ R (24) + ν(C4-O10) (23) + ν(C-C) (16) + ν(C3-O11) (5)
7	1767	1692	1685	816.24	δ' R (48) + ν(C3-O11) (20) + ν(C3-N9) (10) + ν(C-C) (8) + ν(C4-O10) (5)
8	1513	1487	1495	133.88	β(O12-H13) (54) + ν(C3-N9) (18) + ν(C4-N9) (10) + δ R (9)
9	1481	1456	1454	19.85	Sis. (CH$_2$) (C2) (38) + Sis. (CH$_2$) (C1) (34) + ν(C-C) (8) + δ R (7) + ν(C3-N9) (7)
10	1460	1435		3.86	Sis. (CH$_2$) (C1) (45) + Sis. (CH$_2$) (C2) (38) + δ' R (8) + ν(C3-N9) (5)
11	1415	1391	1408	25.90	δ' R (59) + ν(C3-N9) (26)
12	1318	1296	1310	5.65	δ' R (40) + ν(C-C) (33) + Wag. (CH$_2$)(C2) (13) + Wag. (CH$_2$)(C1) (12)
13	1277	1255		1.55	ν(C-C) (43) + δ R (19) + Wag. (CH$_2$)(C1) (14) + Wag. (CH$_2$)(C2) (12)
14	1243	1222		0.00	twist (CH$_2$)(C1) (50) + twist (CH$_2$)(C2) (46)
15	1205	1184	1202	289.09	ν(C3-N9) (63) + ν(C-C) (14) + ν(C4-N9) (10)
16	1168	1148		1.60	twist (CH$_2$)(C2) (45) + twist (CH$_2$)(C1) (41)
17	1085	1067	1073	79.37	ν(C-C) (69) + ν(N9-O12) (9) + δ' R (7)
18	1041	1023	1039	48.92	δ' R (50) + ν(C-C) (38)
19	1022	1004		0.10	ρ (CH$_2$)(C1) (36) + ρ (CH$_2$)(C2) (36) + γ(C3-O11) (10) + γ(C4-O10) (9) + τ R (6)
20	999	982	992	7.45	ν(C-C) (61) + δ' R (20) + δ R (16)
21	824	810	819	11.32	ρ (CH$_2$)(C1) (25) + ρ (CH$_2$)(C2) (24) + τ' R (12) + γ(C3-O11) (11) + γ(C4-O10) (10)
22	708	696		9.50	ν(C-C) (67) + ν(C3-N9) (22)
23	669	657	668	70.80	ν(C3-N9) (55) + ν(C4-N9) (17) + β(C4-O10) (8) + β(C3-O11) (5)
24	598	588		0.33	δ R (48) + δ' R (43)
25	575	565		9.50	γ(C3-O11) (61) + ρ (CH$_2$)(C2) (16) + τ' R (8) + γ(N9-O12) (7)
26	567	557		0.80	δ' R (59) + ν(C-C) (33)
27	561	552		4.15	γ(C4-O10) (44) + τ' R (24) + ρ (CH$_2$)(C1) (13) + γ(N9-O12) (13)
28	359	353		18.52	δ' R (67) + ν(C3-N9) (9) + δ R (6)
29	343	337		115.04	τ CN-OH (82) + γ(C3-O11) (9)
30	277	272		11.75	β(N9-O12) (39) + δ' R (31) + β(C3-O11) (7) + ν(C3-N9) (6) + β(C4-O10) (5)
31	227	223		0.04	γ(N9-O12) (85) + τ' R (8)
32	104	102		1.73	γ(N9-O12) (42) + τ' R (36) + τ R (15)
33	90	88		1.89	τ' R (58) + τ R (24) + γ(N9-O12) (13)

ν –> stretching; ν_s –> symmetric stretching ; ν_{as} –> asymmetric stretching ; ρ –> rocking ; δ –>deformation ; β –>in-plane bending; γ–>out-of-plane bending ; Sis –>scissoring ; Wag. –> wagging; twist –> twisting; τ–> Torsion ; R –> Ring

3.5.5 Ring vibrations

The ring spectral region for Succinimide, NHS and NMS predominantly involves C-C, C-N stretching, and ring deformation and tortional vibrational modes. The identification of C–N vibrations is a very difficult task sincemixing of several bands is possible in this region. In the present study, computed wavenumbers for the C-C stretching modes are found as mixed mode with C-N stretching modes at (1290,1238,990,828)/(1255,1067,696)/(1255, 1105,1052,993) cm^{-1} for Succinimide/NHS/NMS and correspond to the experimentally observed bands in FTIR at 1242/1073/1103cm^{-1} respectively. The FTIR bands observed at 1358/1202/1285 cm^{-1} have been assigned to C-N stretching vibrations for Succinimide/NHS/NMS and the predicted values of these vibrations are 1349/1184/1277 cm^{-1} respectively. The torsional modes appear below 531/565/570 cm^{-1} in case of Succinimide/NHS/NMS respectively.

Table 9 : Theoretical and Experimental wavenumbers in cm^{-1} of N-Methyl-succinimide

S. No.	Calculated Wavenumbers		Experimental Wavenumber	IR Intensity	Assignment of dominant modes in order of decreasing potential energy distribution (PED)
	Unscaled in cm^{-1}	Scaled in cm^{-1}	FTIR in cm^{-1}		
1	3154	3021		0.45	ν_{as}' (CH_3) (73) + ν_{as} (CH_3) (24)
2	3117	2986	2980	12.23	ν_{as} (CH_3) (74) + ν_{as}' (CH_3) (25)
3	3115	2984		5.69	ν_{as} (CH_2) (C1) (50) + ν_{as} (CH_2) (C2)(50)
4	3099	2969		0.00	ν_{as} (CH_2) (C2)(50) + ν_{as} (CH_2) (C1) (49)
5	3074	2945		1.76	ν_s (CH_2) (C1) (50) + ν_s (CH_2) (C2) (48)
6	3067	2938		13.75	ν_s (CH_2) (C2) (50) + ν_s (CH_2) (C1) (49)
7	3053	2925		22.36	ν_s (CH_3) (97)
8	1836	1759	1768	32.76	δ R (25) + ν(C3-O10) (24) + ν(C4-O11) (24) + δ' R (10) + ν(C-C) (7)
9	1769	1695	1702	864.26	δ' R (49) + ν(C4-O11) (18) + ν(C3-O10) (17) + ν(C-C) (5)
10	1509	1483		18.19	δ_{as}' (CH_3) (56) + δ_{as} (CH_3) (18) + ρ (CH_3) (13)
11	1491	1465		11.53	δ_{as} (CH_3) (68) + δ_{as}' (CH_3) (22) + ρ' (CH_3) (13)
12	1482	1456		5.68	Sis. (CH_2) (C1) (44) + Sis. (CH_2) (C2) (40) + ν(C-C) (6)
13	1461	1436		3.82	Sis. (CH_2) (C2)(47) + Sis. (CH_2) (C1) (37) + δ' R (6)
14	1457	1432	1430	79.53	δ' R (42) + δ_s (CH_3) (26) + ν(C4-N9) (11) + δ R (6)
15	1400	1376	1372	142.93	δ' R (50) + ν(C4-N9) (14) + δ_s (CH_3) (8) + ν(N9-C12) (7) + δ R (6)
16	1315	1293		2.53	δ' R (36) + Wag. (CH_2) (C1) (20) + Wag. (CH_2) (C2) (19) + ν(C-C) (20)
17	1299	1277	1285	144.81	ν(C4-N9) (47) + δ' R (20) + ν(C3-N9) (10) + ρ (CH_3) (9)
18	1277	1255		13.74	ν(C-C) (35) + Wag. (CH_2) (C2) (21) + Wag. (CH_2) (C1) (20) + δ R (11)
19	1246	1225		0.01	twist (CH_2) (C2) (48) + twist (CH_2) (C1) (47)
20	1168	1148	1155	0.89	twist (CH_2) (C1) (41) + twist (CH_2) (C2) (39)
21	1150	1130		0.89	ρ' (CH_3) (80) + δ_{as} (CH_3) (6)
22	1124	1105	1103	139.79	ν(C-C) (36) + ν(C4-N9) (20) + δ' R (12) + ρ (CH_3) (8) + ν(C3-N9) (6)
23	1070	1052		17.42	ν(C-C) (73) + ν(N9-C12) (18)
24	1027	1009		0.00	ρ (CH_2) (C1) (35) + ρ (CH_2) (C2) (35) + γ(C3-O10) (10) + γ(C4-O11) (10)
25	1010	993		6.20	ν(C-C) (65) + δ' R (18) + δ R (11)
26	955	939	942	25.85	δ' R (60) + ν(C-C) (9) + ν(C4-N9) (9) + ρ (CH_3) (6)
27	831	817	805	9.90	ρ (CH_2) (C2) (21) + ρ (CH_2) (C1) (21) + τ R (13) + γ(C3-O10) (12) + γ(C4-O11) (12)
28	707	695		0.26	ν(C-C) (60) + ν(C4-N9) (22) + ν(N9-C12) (8) + ν(C3-N9) (5)
29	676	665	652	54.21	ν(C4-N9) (34) + δ' R (14) + δ R (14) + ν(C3-N9) (10) + β(C3-O10) (8) + β(C4-O11) (7)
30	595	585		5.27	δ R (56) + δ' R (31)
31	580	570		3.85	γ(C4-O11) (36) + τ R (20) + ρ (CH_2) (C1) (17) + γ(N9-C12) (11) + γ(C3-O10) (7)
32	574	565	556	0.46	γ(C3-O10) (52) + ρ (CH_2) (C2) (17) + γ(C4-O11) (13) + τ R (7)
33	564	554		0.22	δ' R (64) + ν(C-C) (22) + β(C3-O10) (5) + β(C4-O11) (5)
34	385	378		24.45	δ' R (57) + δ R (10) + β(C3-O10) (9) + β(C4-O11) (7) + ν(N9-C4) (7)
35	281	276		5.01	β(N9-C12) (44) + δ' R (38) + β(C4-O11) (6)
36	218	214		1.19	γ(N9-C12) (78) + τ R (14)
37	120	118		16.32	τ R (82) + γ(N9-C12) (14)
38	87	86		0.00	τ' R (64) + τ R (20) + ρ (CH_2) (C2) (6) + ρ (CH_2) (C1) (6)
39	41	41		0.00	τ (CH_3) (60) + ρ' (CH_3) (23) + δ_{as} (CH_3) (11)

ν –> stretching; ν_s –> symmetric stretching ; ν_{as} –> asymmetric stretching ; ρ –> rocking ; δ –>deformation ; β –>in-plane bending; γ–>out-of-plane bending ; Sis –>scissoring ; Wag. –> wagging; twist –> twisting; τ–> Torsion ; R –> Ring

CONCLUSION

The comprehensive investigation of the ground state structural, spectral and electronic properties of Succinimide, N-hydroxy-succinimide (NHS) and N-methyl-succinimide (NMS) have been performed using B3LYP/6-311++G (d,p) level of theory. The complete vibrational assignment and analysis of the fundamental modes of all the three title molecules were carried out using theoretical and experimental FTIR spectral data.The frontier orbital energy gap, dipole moment, MESP surface and first static hyperpolarizability of Succinimide, NHS and NMS were also calculated.The lower value of the frontier orbital gap in NHS (6.28124 eV) than Succinimide (6.49644 eV) and NMS

(6.53285 eV) clearly shows that NHS is more polarizable and chemically reactive than its parent molecule Succinimide and NMS. The MESP map shows the negative potential sites are on oxygen atoms as well as the positive potential sites are around the hydrogen atoms. The thermodynamic properties of the studied compounds at different temperatures were also calculated.

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