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Conformational, vibrational, NMR and DFT studies of N-methylacetanilide

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HIGHLIGHTS

- ► FTIR, FT-Raman and NMR spectral studies of *N*-methylacetanilide were carried out.
- The non-hydrogen atoms excluding the phenyl group are almost coplanar.
- The CNC angle reveals less steric hindrance and more stability in *cis*isomer.
- ► The E_{LUMO} E_{HOMO} orbital energy gap in case of *cis*- isomer is found to be 5.8753 eV.
- ► The $n_N \rightarrow \pi^*_{CO}$ interaction has strong stabilisation energy of 61.53 kJ mol⁻¹.

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The FT-IR, FT-Raman, ¹H, ¹³C and NMR spectral measurements of *N*-methylacetanilide and complete assignments of the observed spectra have been elaborated. DFT calculations have been performed and the structural parameters of the *cis*- and *trans*-isomers of the compound were determined from the optimised geometry with 6-31G(d,p), 6-311++G(d,p) and cc-pVTZ basis sets and giving energies, harmonic vibrational frequencies, depolarisation ratios, IR and Raman intensities. The geometric parameters, harmonic vibrational frequencies and chemical shifts were compared with the experimental data of the molecules. The influences of various factors regarding the stability and the conformational state of the *cis*- isomer have been discussed. A detailed natural bond orbital analysis was carried out.



ABSTRACT

A detailed conformational, vibrational, NMR and DFT studies of *N*-methylacetanilide have been carried out. In DFT, B3LYP method have been used with 6-31G**, 6-311++G** and cc-pVTZ basis sets. The vibrational frequencies were calculated resulting in IR and Raman frequencies together with intensities and Raman depolarisation ratios. The dipole moment derivatives were computed analytically. Owing to the complexity of the molecule, the potential energy distributions of the vibrational modes of the compound are also calculated. Isoelectronic molecular electrostatic potential surface (MEP) and electron density surface were examined. ¹H and ¹³C NMR isotropic chemical shifts were calculated and the assignments made are compared with the experimental values. The energies of important MO's of the compound were also determined from TD-DFT method.

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Introduction

Amides are of fundamental chemical interest as conjugation between nitrogen lone-pair electrons and the carbonyl π -bond, results in distinct physical and chemical properties. A planar structure of secondary amide group has been confirmed by measurement with X-rays and the *trans*- configuration is the most stable [1–8]. Three different conformational forms of the amide group are possible: *trans*, *cis* (planar) and non-planar. The –CO–NH– group adopts a planar 'peptide-like' conformation, as in the case of formamide [9], methyl hydrazinocarboxylate [10], *N*-methylformamide [11], *o*-methyl acetanilide [12] and formanilide [13,14].

Many acetanilide derivatives exhibit fungicidal, herbicidal and pharmacological activities which further stimulated the recent interest in their chemistry. Anilide herbicides such as alachlor, acetochlor, metolachlor, pretilachlor and butachlor are promising weed control agents for a wide variety of economically important crops including rice, cotton, potatoes and corns [14–17]. The choloroacetanilide herbicide alachlor is one of the most extensively used agro chemical [18,19]. Propanil (3,4-dichloropropioanilide) is a selective contact anilide herbicide used for the control of broad leveled and grass weeds. Acetanilide is used in medicine under the name antifebrin, as a febrifuge and it has pain relieving properties [20]. Acetanilide is a useful intermediate in various reactions of aniline in which it is desirable to protect the amino group. The 3-(*N*-phenylacetylamino)-2,6-piperidinedione, Antineoplaston A10, is used as antitumour drug [21].

The stereochemistry of the amide bond is an important in biological and medicinal chemistry. Many experimental and theoretical studies on the *cis-trans* stereochemistry of the amide bond have been made [22–24]. The stereochemistry is critical in determining the biological activity of the amide compounds. The relative stability of *trans*- and *cis*-amide conformation is affected by *N*-methylation, without change of the apparent planar amide structures. As amides are the simplest model for peptides and also due to the fungicidal, herbicidal and several pharmacological activities of many acetanilide derivatives, their exact structure has been the subject of many experimental and theoretical studies [25–27].

The amide structures of *N*-methylanilide and three of their derivatives are *cis*- in the crystal, whereas those of the corresponding *N*—H amide compounds (secondary amides) are *trans* [28,29]. The *N*-methylanilides with various aliphatic groups at the carbonyl end, such as isopropyl, cyclopropyl, isopropenyl and t-butyl adopted the *cis*- amide structure in the crystal [30]. Thus, it was proved that *cis*-amide structure is more stable than the *trans*-structure in *N*-methylacetanilide.

Thus, the stabilities of *trans*- and *cis*-amide models for *N*-methylacetanilide were compared by using DFT studies. The conformation of secondary amides: derivatives of formanilide, acetanilide and benzylamides were carried out [12]. The molar Kerr constants of acetanilide and certain *N*- and *p*-substituted acetanilides are analysed to indicate that (*a*) the preferred solute conformations of the molecules $X-C_6H_4-NH-CO-CH_3$ (X = -H, $-CH_3$, -CI, or —Br), examined in benzene or dioxan, are defined by a planar, *cis*- arrangement of the group C_{ar} —N—C=O and dihedral angles of $38^{\circ} \pm 6^{\circ}$ (standard deviation) between the amide group plane and that of the aromatic ring, and that (*b*) in *N*-methylacetanilide the C=O is *trans* to the phenyl group.

Many research works have been carried out on the spectroscopic and nonlinear properties of molecular crystals of *N*-phenylacetamide derivatives [31–35]. The vibrational spectroscopic analysis of acetanilide derivative particularly the *N*-methylacetanilide has not been studied. Thus, owing to the vast biological significance and applications of *N*-methylacetanilide in an enormous field and in continuation of earlier studies on *N*-(chloro substituted phenyl)-2,2-dichloroacetamides [36] and *N*-(methylphenyl)-2,2dichloroacetamides [37–39], we have carried out an extensive spectroscopic and quantum chemical studies on *N*-methylacetanilide in an effort to provide explanations for the conformational, vibrational frequencies and to understand the effect of methyl group on the frequencies of amide group.

Experimental

A chloroform solution containing acetyl chloride (1.57 g, 0.02 mol) was added drop wise to a solution of *N*-methylaniline (2.14 g, 0.02 mol) and pyridine (2.37 g, 0.03 mol) in chloroform (20 ml) under stirring on an ice-water bath. The reaction mixture was stirred at room temperature for 3–5 h. A solid product was separated from the solution by suction filtration, purified by successive washing with ordinary water, 0.5 mol/L HCl, 0.5 mol/L NaOH and distilled water, respectively. The crude sample was allowed to dry at room temperature. The yield of the product is about 69%. The product was recrytallised with ethanol and dried in air. The melting point of *N*-methylacetanilide is 101 °C. All elemental analysis (C, H, N) were carried out on a Perkin Elmer 2400 CHN elemental analyser. The calculated (found)% for $C_9H_{11}NO$: C, 72.46 (72.48); H, 7.43 (7.41) and N, 9.39 (9.32). Scheme 1 depicts the preparation of the compound under investigation.

The FTIR spectrum of the compound was recorded in the solid phase by KBr disc method in a Bruker IFS66V spectrometer equipped with a Globar source, Ge/KBr beam splitter and a TGS detector in the range of 4000–400 cm⁻¹. The spectral resolution was 2 cm⁻¹. The FT-Raman spectrum of the compound was also recorded with the same instrument with FRA 106 Raman module. The Raman spectrum was obtained in the wavenumber range 4000–100 cm⁻¹ with a scanning speed of 30 cm⁻¹ min⁻¹. The light scattering was excited using a low-noise diode pumped Nd:YAG laser source operating at 1.064 µm with 200 mW power. A special (enhanced) liquid nitrogen cooled germanium detector was used. The frequencies of all sharp bands are accurate to 2 cm⁻¹.

Computational details

Since the amide group is a highly polarisable, the DFT study is essential for the purpose of getting the structural parameters in



N-methylacetanilide

precision with the standard 6-31G^{**}, high level 6-311++G^{**} and the triple zeta cc-pVTZ basis sets incorporating both diffuse and polarisation functions. Thus, the gradient corrected density functional theory (DFT) [40] with the three-parameter hybrid functional Becke3 (B3) [41,42] for the exchange part and the Lee–Yang–Parr (LYP) correlation functional [43], calculations have been carried out in the present investigation, using 6-31G^{**}, 6-311++G^{**} and cc-pVTZ basis sets with Gaussian-09 [44] program. The harmonic vibrational frequency calculations were carried out resulting in IR and Raman frequencies together with intensities and Raman depolarisation ratios. The dipole moment derivatives and polarizability derivatives were computed analytically. Owing to the complexity of the molecule, the potential energy distribution of the vibrational modes of the compound are also calculated using Fuhrer et al. program [45].

Isoelectronic molecular electrostatic potential surfaces (MEP) and electron density surfaces [46] were calculated using 6-311++G(d,p) basis set. The molecular electrostatic potential (MEP) at a point 'r' in the space around a molecule (in atomic units) can be expressed as:

$$V(r) = \sum_{A} \frac{Z_{A}}{|R_{A} \to -r \to |} - \int \frac{\rho(r^{*} \to) dr^{*}}{|r^{*} \to -r \to |}$$

where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electronic density function for the molecule. The first and second terms represent the contributions to the potential due to nuclei and electrons, respectively. V(r) is the resultant at each point r, which is the net electrostatic effect produced at the point r by both the electrons and nuclei of the molecule. The molecular electrostatic potential (MEP) serves as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecules including biomolecules and drugs [47]. Structures resulting from the plot of electron density surface mapped with electrostatic potential surface depict the shape, size, charge density distribution and the site of chemical reactivity of a molecule. Gauss View 5.0.8 visualisation program [48] has been utilised to construct the MEP surface, the shape of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals.

The B3LYP method allows calculating the shielding constants with accuracy. The ¹H and ¹³C NMR isotropic shielding were calculated using the GIAO method [49,50] using the optimised parameters obtained from B3LYP/6-311++G(d,p) method. The effect of solvent on the theoretical NMR parameters was included using the PCM model. The isotropic shielding constant values were used to calculate the isotropic chemical shifts δ with respect to tetramethylsilane (TMS). $\delta_{iso}(X) = \sigma_{TMS}(X) - \sigma_{iso}(X)$, where δ_{iso} – isotropic chemical shift and σ_{iso} – isotropic shielding constant.

Results and discussion

Conformational analysis

The amide (—CONH—) group is planar, or nearly so [30,36,38,39, 51–53], giving rise to two isomers (*cis*- and *trans*-). The planes of the amide-group and the benzene ring can make an arbitrary angle with each other and on two main effects: π -electron communication and steric interactions between the benzene ring and the acetamido-group. It was found that the unmethylated acetamido-groups were preferentially in the conformation with the carbonyl oxygen (C=O) *trans*- to *N*—H, this conformation has been named *endo- or trans*- (*I*). When the acetamido group is methylated, however, the other conformation, named *exo-* or *cis*- (1*I*) is found to be the most stable.



The NMR spectrum of the *N*-methylacetanilide molecules in pyridine and dipole moment in dioxane solutions are in the conformation with the *N*-methylacetamido group in the *exo-* or *cis-* configuration (II) and with the plane of the group —CONR— orthogonal to the benzene ring.

In acetanilide the acetamido group is in the endo-configuration (I), and the plane of the acetamido group and the benzene ring is making an angle of 38°. But, the stable conformation of N-methylacetanilide is completely different from the conformation of acetanilide. It is difficult to understand why the methylation of acetanilide should completely reverse the relative stability of the exo- and the endo- isomer. The angle between the acetamido group and the benzene ring is larger when the acetamido group is in the exo- configuration than in the endo-configuration. The van der Waals radius of a carbonyl oxygen is about 1.5 Å, while the van der Waals radius of a methyl group is 2.0 Å. Furthermore, the methyl group is closer to the benzene ring as the C–C distance is 0.3 Å longer than the C–O distance. The increase in the angle from 38° to 90° must therefore be ascribed to larger van der Waals interaction between the benzene ring and the exo-acetamido group than between the benzene ring and the endo-acetamido group. The carbon atom in the benzene ring closest to the carbonyl oxygen is forced a little out of the ring plane due to van der Waals interaction between these two atoms. Similarly, in N-methylacetanilide the bond between the benzene ring and the nitrogen atom is bent about 6°, revealing the existence of strain in the molecule induced by the van der Waals interaction between the methyl group and the benzene ring. The non-hydrogen atoms excluding the phenyl group are almost coplanar. The dihedral angle formed between this plane and the benzene ring of cis-N-methylacetanilide is 85.47° and is well correlated with the 2-chloro-N-methyl-N-phenylacetamide, 87.07° molecule [54].

The conformational analysis was carried out through the potential surface scan the with B3LYP method using 6-31G^{**} basis set in order to ascertain most stable geometry of NMA. During the scan,



Fig. 1. Potential energy surface of N-methylacetanilide.



Fig. 2. (a) *cis*-Amide conformation of *N*-methylacetanilide and (b) the plane of the ring and the plane of amido group in *cis*-amide are perpendicular to each other and (c) trans-amide conformation of *N*-methylacetanilide.



Fig. 3. Optmised structure of the most stable cis-N-methylacetanilide.

all the geometrical parameters were simultaneously relaxed while the dihedral angle O9–C8–N7–C11 is varied in steps of 15° ranging from 0° to 360°. For O9–C8–N7–C11 rotation a true local minima of *cis-N*-methylacetanilide having energy –479.70168 Hartrees was determined. The potential energy barrier obtained by the rotation of the amide group with the dihedral angle O9–C8–N7–C11 is depicted in Fig. 1. The various conformers of *N*-methylacetanilide are depicted in Fig. 2a–c. The compound has two different conformers namely *cis*- and *trans-N*-methylacetanilide. The *cis-N*-methylacetanilide conformer is more stable than the *trans-N*-methylacetanilide by 2.29 kcal mol⁻¹. The O9–C8–N7–C11 dihedral angle of the most stable geometry of *cis-N*-methylacetanilide determined by B3LYP/6-311++G^{**} method is 0.1°. This confirms the existence of the amido group in the *cis*conformation.

Structural properties

The optimised molecular geometry and atom numbering scheme of the compounds under investigation is shown in Fig. 3.

The optimised structural parameters bond lengths and the bond angles for the thermodynamically preferred geometry of *cis*- and *trans-N*-methylacetanilide conformers at B3LYP levels with 6-31G**, 6-311++G** and cc-pVTZ basis sets are presented in Table 1. It is observed that the mean C—C bond distance calculated between the ring carbon atoms of *cis*- and *trans-N*-methylacetanilide by B3LYP/6-311++G** method is 1.395 Å, and thus the C—C and C—H bond lengths are found to be not significantly deviated.

The bond distance of the compounds *cis*- and *trans-N*-methylacetanilide determined at the DFT level of theory are in good agreement with the structural parameters of 2-chloro-*N*-methyl-*N*-phenylacetamide [54] and *N*-(3-hydroxyphenyl)acetamide [55] where the mean bond distance of C—C (ring) is found to be 1.3798 Å. The C1—N7 bond distance increases in the order *trans*-< *cis*-*N*-methylacetanilide. The bond length between the amide nitrogen and the carbonyl group, N7—C8 of *cis*-*N*-methylacetanilide is 0.007 Å shorter than the *trans*- isomer. The angle at C1—N7—C11of *cis*- isomer (120.6°) is more than the *trans*- isomer (117.4°). This shows the more stability and less steric hindrance in the *cis*- isomer. But the angle C8—N7—Cl1 in *cis*- isomer (119.7°) is less than the *trans*- isomer (121.6°). The dihedral angles C1—N7—C8—O9 of cis- and trans- isomers are 179° and 4°, respectively.

The energies and thermodynamic parameters of the *cis*- and *trans*- conformers have also been computed at B3LYP methods with 6-31G**, 6-311++G** and cc-pVTZ basis sets and are presented in Table 2. The frequency calculations compute the zero point energies, thermal correction to internal energy, enthalpy, Gibbs free energy and entropy as well as the heat capacity for a molecular system. The calculated SCF energy of the compounds clearly indicates that the *cis*- isomer (-479.70168 Hartrees) is more stable than *trans*- isomer (-479.69762 Hartrees). The larger total dipole moment of *cis*- isomer (4.24 D) than *trans*- (3.76 D) molecule leads to more charge separation.

Analysis of molecular electrostatic potential

The molecular electrostatic potential surface (MEP) displays electrostatic potential (electron + nuclei) distribution, molecular shape, size and dipole moments of the molecule and it provides a visual method to understand the relative polarity [56]. The total electron density mapped with electrostatic potential surface of *cis-N*-methylacetanilide constructed by B3LYP/6-311++G^{**} method [57,58] is shown in Fig. 4.

Molecular electrostatic potential (MEP) mapping is very useful in the investigation of the molecular structure with its physio-

Table 1

Structural parameters of the stable *Cis-amide* and *Trans-amide* conformations of *N*-methylacetanilide employing B3LYP method with 6-31G**, 6-311++G** and cc-pVTZ basic sets.

Structural parameters	trans-Amide			cis-Amide			Experimental ^a
F	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**	
Internuclear distance (Å)	20211/0 010	boblingee prind	20211/0 011 0	20211/0 010	bobiii/ee prib	20211/0 011 0	
C1–C2	1.403	1.396	1.399	1.4	1.393	1.397	1.384
C1-C6	1.402	1.396	1.398	1.4	1.393	1.397	1.380
C1N7	1.431	1.429	1.433	1.433	1.431	1.435	1.437
C2-C3	1.393	1.387	1.391	1.395	1.39	1.394	1.379
C2—H12 C2—C4	1.081	1.077	1.080	1.086	1.082	1.084	0.93
C3-H13	1.596	1.591	1.595	1.596	1.59	1.594	0.93
C4C5	1.394	1.388	1.392	1.396	1.39	1.394	1.373
C4-H14	1.086	1.082	1.084	1.086	1.082	1.084	0.93
C5–C6	1.395	1.390	1.394	1.395	1.39	1.393	1.382
C5—H15	1.086	1.082	1.084	1.086	1.082	1.084	0.93
C6—H16	1.085	1.081	1.084	1.086	1.082	1.084	0.93
N7-C8 N7-C11	1.392	1.380	1.388	1.384	1.378	1.381	1.345
C8-09	1.223	1.217	1.219	1.225	1.219	1.222	1.220
C8–C10	1.524	1.519	1.521	1.521	1.517	1.519	1.509
C10-H17	1.094	1.090	1.093	1.094	1.09	1.092	0.97
C10-H18	1.089	1.085	1.088	1.094	1.09	1.093	0.97
C10-H19	1.096	1.091	1.094	1.089	1.085	1.088	0.97
CTI-H20 CTI_H21	1.098	1.094	1.096	1.096	1.092	1.094	0.96
C11—H21 C11—C22	1.090	1.086	1.089	1.089	1.085	1.088	0.96
	1.031	1.007	1.005	1.050	1.032	1.034	0.50
Bond angle (°)	110.1	110.1	110.2	110.6	110 5	110.6	120.7
$C_{2} = C_{1} = C_{0}$	119.1	119.1	179.3	119.6	119.5	119.0	120.7
C6-C1-N7	119.6	119.7	119.7	120.5	120.2	120.3	119.3
C1-C2-C3	119.9	120.0	120.0	119.1	119.2	119.3	119.3
C1-C2-H12	119.7	119.7	119.7	120.1	120.2	120.1	120.4
C3-C2-H12	120.4	120.2	120.3	120.1	120.2	120.2	120.4
C2-C3-C4	120.9	120.8	120.7	119.1	119.2	119.3	120.2
C2-C3-H13	119.1	119.2	119.2	123.6	123.6	123.5	119.9
$C_4 - C_5 - C_5$	120.0	120.0	120.0	117.1	120.6	120.6	120.2
C3-C4-H14	120.4	120.4	120.3	120.1	120.1	120.1	119.9
C5-C4-H14	120.4	120.4	120.3	119.8	119.8	119.8	119.9
C4-C5-C6	120.3	120.3	120.3	120.1	120.1	120.1	122.3
C4-C5-H15	120.3	120.3	120.3	119.9	119.8	119.8	119.8
C6-C5-H15	119.3	119.4	119.5	120.1	120.1	120.1	119.8
C1-C6-H16	120.5	120.5	120.4	120.1	120.1	120.1	119.3
C5-C6-H16	119.3	119.3	119.5	120.1	120.1	120.1	120.4
C1-N7-C8	120.9	120.8	120.4	119.8	119.8	119.8	123.1
C1-N7-C11	117.3	117.3	117.4	120.7	120.5	120.6	116.6
C8–N7–Cl1	121.2	121.3	121.6	119.3	119.5	119.7	120.1
N7-C8-09	122.7	122.7	122.5	121.8	121.9	121.8	123.1
N/-C8-C10 09-C8-C10	116.9	116.9	116.8	110.5	110.7	110.7	1 14.8 122 1
C8-C10-HI7	112.6	112.4	112.3	107.6	108	108.1	109.1
C8-C10-H18	106.9	107.1	107.2	110.7	110.7	110.6	109.1
C8-C10-H19	111.6	111.5	111.4	121.6	121.4	121.5	109.1
H17-C10-H18	109.3	109.3	109.3	111.6	111.7	111.8	107.8
H17-C10-H19	107.7	107.7	107.8	111.4	111.3	111.1	107.8
H18-C10-H19 N7-C11-H20	108./	108.9	108.8	107.6	107.7	107.7	107.8
N7-C11-H21	112.5	112.5	112.7	109.2	107.2	107.5	109.5
N7-C11-H22	108.9	108.9	108.7	109.4	109.4	109.2	109.5
H20-C11-H21	108.3	108.3	108.4	109.7	109.6	109.6	109.5
H20-C11-H22	108.4	108.4	108.5	108.4	108.4	108.6	109.5
H21-C11-H22	107.8	107.8	107.8	109.7	109.6	109.5	109.5
C6-C1-C2-C3	-U.I 170.2	-U.I 170.4	-U.I 170.2	-U./ 170.4	-0.8 170.4	-U./ 170.4	
0-01-02-H12 N7-01-02-03	-179.5 -178.2	-1/9.4 -178.4	–179.5 –178.5	179.4 	1/9.4 	1/9.4 _178.8	
N7-C1-C2-H12	2.6	2.3	2.3	1.5	1.4	1.4	
C2-C1-C6-C5	-0.3	-0.2	-0.3	0.6	0.7	0.6	
C2-C1-C6-H16	178.9	179.1	179.1	-179.6	-179.6	-177.9	
N7-C1-C6-C5	177.8	178.2	178.1	178.6	178.7	178.6	
N7-C1-C6-H16	-3.0	-2.5	-2.5	-1.7	-1.6	-1.7	
$C_2 - C_1 - N_2 - C_3$	-43.5 144.6	-46.1 141 0	-49.9 138.6	-88.2 91.6	-88.7 91.2	-85.7 92.5	
$C_2 = 0.7 - 0.11$ C6-C1-N7-C8	138.4	135.6	131.7	93.9	93.4	96.5	
C6-C1-N7-C11	-33.5	-36.5	-39.8	-86.3	-86.7	-86.7	

Table 1 (continued)

Structural parameters	trans-Amide			cis-Amide			Experimental ^a
	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**	
C1-C2-C3-C4	0.4	0.2	0.4	0.4	0.4	0.4	
C1-C2-C3-H13	180.0	180.0	179.9	-179.7	-179.7	-179.7	
H12-C2-C3-C4	179.6	179.5	179.6	-179.7	-179.8	-179.7	
H12-C2-C3-H13	-0.8	-0.7	-0.7	0.2	0.2	0.2	
C2-C3-C4-C5	-0.3	-0.1	-0.2	0.0	0.1	0.0	
C2-C3-C4-H14	179.8	179.9	179.8	180.0	179.9	179.9	
H13-C3-C4-C5	-179.8	-179.8	-179.9	-179.9	-179.9	-179.9	
H13-C3-C4-H14	0.2	0.2	0.1	0.1	0.1	0.1	
C3-C4-C5-C6	-0.2	-0.2	-0.2	-0.1	0.2	0.1	
C3-C4-C5-H15	-179.7	-179.7	-179.7	179.9	179.9	180.0	
H14-C4-C5-C6	179.8	179.8	179.8	179.9	179.9	179.9	
H14-C4-C5-H15	0.3	0.3	0.3	0.0	0.0	0.0	
C4-C5-C6-C1	0.5	0.4	0.5	-0.2	-0.2	-0.2	
C4-C5-C6-H16	-178.8	-179.0	-178.9	-179.9	-179.9	-179.9	
H15-C5-C6-C1	180.0	179.9	179.9	179.7	179.7	179.7	
H15-C5-C6-H16	0.8	0.6	0.6	0.0	0.0	0.0	
C1-N7-C8-09	4.9	3.9	4.0	-179.6	-179.7	-179.0	
C1-N7-C8-C10	-175.4	-176.1	-176.2	0.4	0.3	1.7	
C11-N7-C8-09	176.5	175.7	175.2	0.2	0.2	0.1	
C11-N7-C8-C10	-3.8	-4.4	-5.0	-179.7	-179.8	-176.0	
C1-N7-C11-H20	88.8	90.0	90.8	59.3	59.0	60.1	
C1-N7-C11-H21	-149.8	-148.6	-147.7	-179.7	-178.9	-180.0	
C1-N7-C11-H22	-31.6	-30.4	-29.5	-60.9	-61.2	-60.0	
C8-N7-C11-H20	-83.1	-82.0	-80.6	-118.9	-118.7	-114.4	
C8-N7-C11-H21	38.3	39.4	40.9	0.9	1.2	5.5	
C8-N7-C11-H22	156.5	157.6	159.1	120.8	121.1	125.3	
N7-C8-C10-H17	55.3	55.9	55.8	-57.0	-57.0	-59.6	
N7-C8-C10-H18	175.3	176.0	175.8	62.7	-62.8	-60.1	
N7-C8-C10-H19	-66.0	-65.0	-65.2	-177.4	-177.3	-179.8	
09-C8-C10-H17	-125.0	-124.1	-124.4	122.9	123.0	121.3	
09-C8-C10-H18	-5.0	-4.0	-4.4	-177.4	-117.2	-119.0	
09-C8-C10-H19	113.7	115.0	114.6	2.6	2.6	1.1	

^a Values taken from Ref. [54,55].

Table 2

The calculated thermodynamic parameters of the stable *cis-amide* and *trans-amide* conformations of *N*-methylacetanilide employing B3LYP method with 6-31G^{**}, cc-pVTZ and 6-311++G^{**} basis sets.

Thermodynamic parameters (298 K)	trans-Amide			cis-Amide		
	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**	B3LYP/6-31G**	B3LYP/cc-pVTZ	B3LYP/6-311++G**
SCF energy, (Hartrees)	-479.58091	-479.73854	-479.69762	-479.58465	-479.74234	-479.70168
Total energy (thermal), E_{total} (kcal mol ⁻¹)	121.68	121.18	120.94	121.52	121.05	120.83
Vibrational Energy, $E_{\rm vib}$ (kcal mol ⁻¹)	119.90	119.40	119.17	119.74	119.27	119.06
Zero point vibrational energy (kcal mol ⁻¹)	115.20	114.67	114.38	114.72	114.26	113.98
Heat capacity, C_v (cal mol ⁻¹ K ⁻¹)	31.10	39.31	39.12	39.34	39.30	39.47
Entropy, S (cal mol ⁻¹ K ⁻¹)	99.63	100.53	99.99	34.52	105.71	107.95
Rotational constants (GHz)						
X	2.44	2.46	2.44	2.29	2.30	2.29
Y	0.75	0.75	0.74	0.71	0.71	0.71
Ζ	0.61	0.61	0.61	0.67	0.68	0.67
Dipole moment (Debye)						
μ _x	-0.73	-0.71	-0.69	3.93	4.01	4.24
μ_{v}	3.28	3.30	3.45	0.84	0.09	0.10
μ_z	1.12	1.20	1.34	0.0	0.0	0.0
μ_{total}	3.54	3.58	3.76	3.93	4.01	4.24
E_{LUMO+1} (eV)			-0.4933			-0.9143
E_{LUMO} (eV)			-0.6735			-0.9881
$E_{\rm HOMO}$ (eV)			-6.3398			-6.8633
$E_{\rm HOMO-1}$ (eV)			-6.9251			-6.9033
E _{LUMO-HOMO} (eV)			5.6663			5.8753

chemical property relationships [57–59]. The electrostatic potential contour map and the surface for positive and negative potentials are shown in Figs. 5 and 6, respectively.

The colour scheme for the MESP surface is red¹, electron rich, partially negative charge; blue, electron deficient, partially positive

charge; light blue, slightly electron deficient region; yellow, slightly electron rich region; green, neutral; respectively. It is obviously from the Figs. 4 and 5 that the region around oxygen atoms linked with carbon through double bond represents the most negative potential region (red). The hydrogen atoms attached to the ends of methyl group posses the maximum positive charge. The predominance of green region in the ring surfaces corresponds to a potential halfway between the two extremes red and dark blue colour. Thus, the total

 $^{^{1}\,}$ For interpretation of colour in Figs. 4–6, the reader is referred to the web version of this article.

V. Arjunan et al. / Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 104 (2013) 182-196



Fig. 4. Total electron density mapped with electrostatic potential surface of *cis-N*-methylacetanilide.



Fig. 5. Electrostatic potential contour surface of cis-N-methylacetanilide.

electron density surface mapped with electrostatic potential clearly reveals the presence of high negative charge on the carbonyl oxygen and in part of the ring while more positive charge around the $-CH_3$ region.

Frontier molecular orbitals

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry [60]. The energies of HOMO LUMO, LUMO+1 and HOMO-1 and their orbital energy gaps are calculated using B3LYP/6-311++G^{**} method and the pictorial illustration of the frontier molecular orbitals are shown in Fig. 7. Molecular orbitals provide insight into the nature of reactivity, conjugation, aromaticity, lone pairs and some of the structural and physical properties of molecules. The region of HOMO spread over the entire molecule while in the LUMO the ring part has more overlapping. The frontier molecular orbital energies of *trans*- and *cis-N*methylacetanilide are presented in Table 2. The energy gap between HOMO and LUMO is a critical parameter in determining



Fig. 6. Electrostatic potential surface of *cis-N*-methylacetanilide.

electrical transport properties [61]. The frontier orbital energy gap ($E_{HOMO} - E_{LUMO}$) in case of *cis*- isomer is found to be 5.8753 eV.

Natural bond orbital (NBO) analysis

The atomic charges of *cis*-*N*-methylacetanilide calculated by NBO analysis using the B3LYP 6-311++ G^{**} method are presented in Table 3. Among the ring carbon atoms C1 has a positive charge while others have negative charge. The positive charge of C1 is due to the attachment of highly electronegative nitrogen atom (N7) to it. The negative charge of N7 is also due to the electron donating nature of the methyl groups by means of hyper conjugative effect. The very high positive charge on the amide carbon C8 is due to the partial polar nature of C=O group. This also leads to a high negative charge on the oxygen atom O9. The methyl group carbon atoms C10 and C11 have high negative charge because of no bond resonance.

The NBO method demonstrates the bonding concepts like atomic charge, Lewis structure, bond type, hybridisation, bond order, charge transfer and resonance possibility. Table 4 depicts the bonding concepts such as type of bond orbital, their occupancies, the natural atomic hybrids of which the NBO is composed, giving the percentage of the NBO on each hybrid, the atom label, and a hybrid label showing the hybrid orbital (sp^x) composition (the amount of s-character, p-character, etc.) of *cis-N*-methylacetanilide determined by B3LYP/6-311++G^{**} method. The occupancies of NBOs reflecting their exquisite dependence on the chemical environment. The NBO energy values show the corresponding spatial



Fig. 7. Frontier molecular orbitals of *cis-N*-methylacetanilide.

Table 3

Atomic charges of the stable *cis-amide* and *trans-amide* conformations of *N*-methy-lacetanilide by NBO analysis using B3LYP/6-311++G^{**} method.

Atom	trans-Amide	cis-Amide
C1	0.1689	0.1560
C2	-0.1905	-0.2041
C3	-0.1927	-0.1941
C4	-0.2109	-0.1982
C5	-0.1959	-0.1941
C6	-0.2287	-0.2041
N7	-0.5162	-0.5326
C8	0.6940	0.6950
09	-0.6160	-0.6358
C10	-0.6650	-0.6625
C11	-0.3581	-0.3535
H12	0.2268	0.2135
H13	0.2058	0.2077
H14	0.2050	0.2074
H15	0.2043	0.2077
H16	0.2062	0.2136
H17	0.2140	0.2195
H18	0.2342	0.2201
H19	0.2162	0.2291
H20	0.1852	0.1870
H21	0.2032	0.2351
H22	0.2106	0.1870

Table 4
Bond orbital analysis of <i>N</i> -(methylacetanilide) by B3LYP/6-311++ G^{**} method.

Bond	Occupancy	Atom	cis-N-methylacetan	ilide
orbital			Contribution from parent NBO (%)	Atomic hybrid contributions (%)
C1=C2	1.9731	C1	52.37	s(36.47) + p1.74(63.49)
		C2	49.63	s(35.76) + p1.80(64.20)
C1=C2	1.6668	C1	51.56	s(0.00) + p1.00(99.96)
		C2	48.44	s(0.00) + p1.00(99.95)
C1-C6	1.9732	C1	50.36	s(36.43) + p1.74(63.53)
		C6	49.64	s(35.75) + p1.80(64.21)
C1N7	1.9832	C1	38.12	s(26.97) + p2.70(72.93)
		N7	61.88	s(33.90) + p1.95(66.06)
C2-C3	1.9768	C2	50.35	s(35.90) + p1.78(64.06)
		C3	49.65	s(35.67) + p1.80(64.28)
C3–C4	1.9794	C3	50.09	s(35.87) + p1.79(64.09)
		C4	49.91	s(35.69) + p1.80(64.27)
C3=C4	1.6588	C3	49.94	s(0.00) + p1.00(99.96)
		C4	50.06	s(0.00) + p1.00(99.96)
C4–C5	1.9794	C4	49.91	s(35.68) + p1.80(64.27)
		C5	50.09	s(36.85) + p1.79(64.10)
C5–C6	1.9768	C5	49.65	s(35.68) + p1.80(64.27)
		C6	50.35	s(35.90) + p1.78(64.06)
C5=C6	1.6593	C5	50.50	s(0.00) + p1.00(99.95)
		C6	49.95	s(0.00) + p1.00(99.96)
N7-C8	1.9849	N7	63.94	s(35.41) + p1.82(64.55)
		C8	36.06	s(30.88) + p2.24(69.02)
N7-C11	1.9806	N7	63.67	s(30.67) + p2.26(69.30)
		C11	36.33	s(23.57) + p 3.24(76.30)
C8—09	1.9930	C8	35.34	s(32.76) + p2.05(67.07)
		09	64.66	s(41.09) + p1.43(58.80)
C8=09	1.9896	C8	29.08	s(0.00) + p1.00 (99.49)
		09	70.92	s(0.00) + p1.00(99.88)
C8–C10	1.9832	C8	49.27	s(36.32) + p1.75(63.64)
		C10	50.73	s(27.36) + p2.65(72.57)

Table 5

Second order perturbation theory analysis of Fock matrix of *cis*-*N*-methylacetanilide using NBO analysis using B3LYP/6-311++G** method.

$E^{(2)a}$	$E(j)-E(i)^{b}$	$F(i,j)^{e}$
(KJ IIIOI)	(a.u.)	(a.u.)
19.87	0.29	0.068
20.49	0.29	0.069
4.28	1.11	0.062
4.66	1.10	0.064
20.97	0.28	0.069
20.51	0.28	0.068
4.26	1.11	0.062
21.59	0.28	0.070
20.40	0.28	0.068
4.65	1.10	0.064
4.63	0.97	0.060
4.54	0.54	0.047
4.49	0.96	0.060
4.19	0.91	0.055
6.37	0.82	0.069
6.33	0.82	0.069
61.53	0.28	0.0117
4.99	0.65	0.055
5.24	0.65	0.056
25.55	0.70	0.121
18.66	0.63	0.099
	$E^{(2)a}$ (kJ mol ⁻¹) 19.87 20.49 4.28 4.66 20.97 20.51 4.26 21.59 20.40 4.65 4.63 4.54 4.54 4.49 4.19 6.37 6.33 61.53 4.99 5.24 25.55 18.66	$\begin{array}{cccc} E^{(2)a} & E(j)-E(i)^b \\ (kJ \mbox{mol}^{-1}) & (a.u.) \\ \\ 19.87 & 0.29 \\ 20.49 & 0.29 \\ 4.28 & 1.11 \\ 4.66 & 1.10 \\ 20.97 & 0.28 \\ 20.51 & 0.28 \\ 4.26 & 1.11 \\ 21.59 & 0.28 \\ 20.40 & 0.28 \\ 20.40 & 0.28 \\ 4.65 & 1.10 \\ 4.63 & 0.97 \\ 4.54 & 0.54 \\ 4.49 & 0.96 \\ 4.19 & 0.91 \\ 6.37 & 0.82 \\ 6.33 & 0.82 \\ 6.33 & 0.82 \\ 61.53 & 0.28 \\ 4.99 & 0.65 \\ 5.24 & 0.65 \\ 5.24 & 0.65 \\ 25.55 & 0.70 \\ 18.66 & 0.63 \\ \end{array}$

LP – lone pair.

^a Stabilisation (delocalisation) energy.

^b Energy difference between i (donor) and j (acceptor) NBO orbitals.

^e Fock matrix element *i* and *j* NBO orbitals.

symmetry breaking in the direction of unpaired spin. The Lewis structure that is closest to the optimised structure is determined.

For example, the bonding orbital for N7–C8 with 1.9849 electrons has 63.94% N7 character in a $sp^{1.82}$ hybrid and has 36.06% C8 character in a $sp^{2.24}$ hybrid orbital. In the case of C8=O9 bond-

ing orbital with 1.9856 electrons has 29.08% C8 character in a $sp^{1.0}$ hybrid and has 70.92% O9 character in a $sp^{1.0}$ hybrid orbital. A bonding orbital for N7—C11 with 1.9806 electrons has 63.67% N7 character in a $sp^{2.26}$ hybrid and has 36.33% C11 character in a $sp^{3.24}$ orbital. The C1—N7 with 1.9832 electrons has 38.12% C1 character in a $sp^{2.70}$ hybrid and has 61.88% N7 character in a $sp^{1.95}$ orbital. The C—C bonds of the aromatic ring posses more p character than s character. This is clearly indicates the delocalisation of π electrons among all the carbon atoms. Similarly C1—N7 bond has also posses more p character.

Donor-acceptor interactions: Perturbation theory energy analysis

Strong electron delocalisation in the Lewis structure also shows up as donor–acceptor interactions. This bonding–anti bonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy $E^{(2)}$ [58–61]. This energy represents the estimate of the off-diagonal NBO Fock matrix element. The stabilisation energy $E^{(2)}$ associated with *i*(donor) \rightarrow *j*(acceptor) delocali-

sation is estimated from the second-order perturbation approach [62] as given below

$$E^{(2)} = q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_i}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) and F(i,j) is the off-diagonal Fock matrix element.

The Fock matrix analysis yield different types of donor–acceptor interactions and their stabilisation energy. All lone pair-bond pair interactions with more than 4 kJ mol⁻¹ stabilisation energies are listed in Table 5. In *cis*- isomer of the molecule, the lone pair donor orbital, $n_N \rightarrow \pi^*_{CO}$ interaction between the nitrogen lone pair and the C8–O9 antibonding orbital is seen to give a strong stabilisation, 61.53 kJ/mol. The $n_O \rightarrow \sigma^*_{CN}$ stabilisation energy of lone pair of electrons present in the oxygen atom (O9) to the antibonding orbital (σ^*) of N7–C8 is equal to 25.55 kJ/mol. The bond pair donor orbital, $\pi_{CC} \rightarrow \pi^*_{CC}$ interaction between the C3–C4 bond pair and the C1–C2 antibonding orbital



Fig. 8. (a) The ¹H NMR (b) ¹³C NMR spectra of *cis-N*-methylacetanilide.

Table 6
The experimental and calculated ¹ H and ¹³ C isotropic chemical shifts (δ_{iso} , ppm) with respect to TMS and isotropic magnetic shielding constants (σ_{iso}) of <i>cis</i> -N-methylacetanilide.

Assignment	$\sigma_{ m iso}$ (¹³ C)	Cal. (δ_{iso})	Expt. (δ_{iso})	Assignment	$\sigma_{\rm iso}$ (¹ H)	Cal. (δ_{iso})	Expt. (δ_{iso})
C1	31.31	153.22	144.59	H12	24.50	7.47	7.21
C2	48.82	135.71	127.03	H13	24.25	7.72	7.39
C3	48.61	135.92	129.70	H14	24.34	7.62	7.38
C4	50.14	134.39	127.65	H15	24.29	7.68	7.39
C5	48.40	136.13	129.70	H16	24.51	7.46	7.21
C6	48.79	135.74	127.03	H17	30.37	1.60	1.88
C8	8.67	175.86	170.32	H18	30.27	1.70	1.88
C10	159.32	25.21	22.37	H19	30.49	1.48	1.88
C11	146.71	37.82	37.08	H20	29.46	2.51	3.27
				H21	27.17	4.79	3.27
				H22	29.45	2.52	3.27



Fig. 9. Correlation of (a) 1 H and (b) 13 C experimental and theoretical NMR chemical shift of *N*-methylacetanilide.

give more stabilisation of 20.97 kJ mol⁻¹ while between the C3—C4 bond pair and the C5—C6 antibonding orbital has 20.51 kJ mol⁻¹.

NMR spectral investigations

The observed ¹H and ¹³C NMR spectra of the compound are given in the Fig. 8a and b, respectively. The ¹H and ¹³C theoretical and experimental chemical shifts, isotropic shielding constants and the assignments are presented in Table 6. Aromatic carbons give signals with chemical shift values from 100 to 200 ppm [63–



Fig. 10. Correlation of (a) ¹H and (b) ¹³C experimental NMR chemical shift and shielding constant of *cis*-N-methylacetanilide.

65]. The observed experimental chemical shift positions of ring carbons atoms lie in the range 144.59–127.03 ppm. The -I effect of nitrogen (N7) reduces the electron density of the carbon atom C1, thus its NMR signal is observed in the very downfield at 144.59 ppm. Due to the symmetry of the phenyl ring the carbon atoms C2, C6 and C3, C5 are attributed to the downfield NMR signals 127.03 and 129.70 ppm, respectively. The carbonyl carbon atom C8 is significantly observed in the downfield with chemical shift value 170.32 ppm reveals the presence of partially positive charge on the carbon atom. Comparing the chemical shift positions of ring carbon atoms with that of methyl carbon atoms, C10 and C11, the upfield chemical shift 22.37 and 37.08 ppm, respectively



Fig. 11. (a) FTIR (b) FT-Raman spectra of cis-N-methylacetanilide.

is due to the electron donating effect of methyl groups. The peak observed at 77 ppm belongs to the solvent CDCl₃ peak.

¹H chemical shifts were obtained by complete analysis of the NMR spectrum to quantify the possible different effects acting on the shielding constant of protons. The hydrogen atoms present in the benzene ring shows NMR peaks in the narrow range 7.21–7.39 ppm. The C-methyl hydrogen atoms are observed in the upfield at 1.88 ppm while the *N*-methyl hydrogen atoms shows the peaks at 3.27 ppm shows that these protons are under high magnetic shielding. The calculated and experimental chemical shift values are given in Table 6 shows a good agreement with each other. The linear regression between the experimental and theoretical ¹H and ¹³C NMR Chemical shifts are represented in Fig. 9. The correlations of the experimental chemical shift with that of the shielding constants are illustrated in Fig. 10.

Vibrational analysis

The FTIR and FT-Raman spectra of *cis-N*-methylacetanilide are shown in Fig. 11a and b. All the observed wavenumbers are assigned in terms of fundamentals, overtones and combination bands. The observed and calculated frequencies along with their relative intensities, probable assignments and potential energy distributions (PED) are presented in Table 7. The geometry of the molecule is considered by possessing C₁ point group symmetry. The 60 fundamental vibrations of each *N*-methylacetanilide are distributed into the irreducible representations under C₁ symmetry as 40 in-plane and 20 out of plane vibrations of 'A' species. All the vibrations are active in both IR and Raman.

Carbon-carbon vibrations

The aromatic carbon–carbon stretching vibrations of the molecule are found in the IR spectrum at 1599, 1584, 1496 and 1324 cm⁻¹ as strong to weak bands and at 1600 and 1586 cm⁻¹ in Raman. Similarly the very weak and medium intensity lines observed in the infrared spectrum at 995 and 972 cm⁻¹ and the corresponding band in Raman spectrum is seen at 975 cm⁻¹ are ascribed to the C–CH₃ and N–CH₃ stretching modes. In the present work the bands occurring at 1007 and 720 cm⁻¹ in Raman spectrum are assigned to the CCC in-plane trigonal bending and ring breathing vibrations, respectively. These frequencies appear in the respective range [37–39]. The CCC in-plane bending and out of plane vibrations are described as mixed modes as there are about 12–24% PED contributions mainly from C–H in-plane bending and out of plane bending vibrations, respectively. The C–N in-plane and out of plane bending modes also coupled to some extent with that of C=O bending vibrations.

C—H vibrations

The C—H bond present in the phenyl group of the compound gives medium and very weak bands at 3047, 3029 and 3012 cm⁻¹ in IR spectrum is attributed to the C—H stretching vibrations of the phenyl group. The PED contribution of the aromatic C—H stretching modes indicates that these are also highly pure modes as carbon–carbon stretching. The aromatic C—H inplane bending modes are observed at 1162, 1143 and 1086 cm⁻¹ in the IR spectrum. The C—H out of plane bending modes of the present compound are observed in the said region [37–39] and presented in the Tables 6 and 7. Since the alkyl C—H in-plane bending modes are observed in the same region of C—C stretching, significant overlapping occurs. The aromatic C—H in-plane and out of plane bending vibrations have substantial contribution from the ring CCC in-plane and out of plane bending, respectively.

Amide group vibrations

The very strong doublet in IR spectrum observed at 1667/ 1657 cm^{-1} are assigned to the amide-I, the C=O stretching band of the molecule. The NCA shows that the amide-I, band is to be pure even though it has slightly mixed with the amide-III, C–N stretching mode by about 10–15%. The C–N stretching mode, the amide-III band is assigned to the wave number observed at 1352 and 1356 cm⁻¹ in the infrared and Raman spectra, respectively. The amide-IV, C=O in-plane bending is found at 770 cm⁻¹ in the IR spectrum. The amide-VI, C=O out of plane bending is observed at 560 cm⁻¹ in IR.

Methyl group (-CH₃) vibrations

The symmetric stretching, $v_s(CH_3)$ frequencies are determined theoretically as 2895 and 2871 cm⁻¹ by B3LYP/6-311++G^{**} method. The antisymmetric stretching $v_a(CH_3)$ are assigned to the wavenumbers 2969 and 2937 cm⁻¹. The methyl symmetric deformation modes are assigned to the frequencies at 1421 and 1388 cm⁻¹ in IR spectrum. The corresponding asymmetric deformation vibration is ascribed to the band at 1453 cm⁻¹ in the IR spectrum. The presence of the bands at 1075 and 1029 cm⁻¹ in infrared spectrum is assigned to the methyl rocking fundamentals. The calculated band at 1274 and 1266 are assigned to the methyl wagging mode of the compound. The assignments are agreed well with reported literature values [37–39]. All other observed fundamental modes are given in Table 7.

Scale factors

Computed harmonic frequencies typically overestimate vibrational fundamentals due to basis set truncation and neglect of elec-

Table 7

The observed FTIR, FT-Raman and calculated frequencies determined by B3LYP method with 6-31G^{**}, 6-311++G^{**} and cc-pVTZ basis sets along with their relative intensities, probable assignments and potential energy distribution (PED) of cis-*N*-methylacetanilide.^a

Observed wave	number (cm ⁻¹)	B3LYP/6-3	11++G** (calculated wav	enumber (cm ⁻¹)	B3LYP/6-31C	G** calculated v	wavenumber (cm ⁻¹)	B3LYP/cc-pV	TZ calculated	wavenumber (cm ⁻¹)	Assignment	%PED
FTIR	FT-Raman	Unscaled	Scaled	IR intensity	Raman Activity	Unscaled	Scaled	IR intensity	Unscaled	Scaled	IR intensity		
3047 m	3058 m	3193	3034	8.14	335.16	3211	3035	10.09	3195	3035	8.99	vCH	90v _{nh}
3029 vw		3185	3026	16.77	7.72	3203	3027	21.49	3187	3028	18.25	νCH	93v _{CH}
		3179	3020	11.69	73.57	3198	3022	15.36	3181	3022	12.20	νCH	91v _{CH}
3012 vw		3171	3012	1.20	113.90	3189	3014	1.68	3173	3014	1.07	νCH	$94v_{CH}$
		3165	3006	1.53	20.98	3182	3007	1.44	3166	3008	1.62	vCH	90v _{CH}
		3151	2993	2.80	78.74	3177	3002	11.55	3152	2994	4.69	$v_a CH_3$	92v _{CH}
		3151	2993	9.85	67.82	3176	3002	1.04	3151	2993	8.05	V _a CH ₃	93v _{CH}
2969 vw		3106	2951	6.80	29.90	3129	2957	7.32	3106	2951	6.88	V _a CH ₃	91v _{CH}
2937 w	2937 w	3073	2919	25.47	65.91	3092	2922	26.70	3069	2916	24.83	V _a CH ₃	92v _{CH}
		3048	2895	5.75	133.54	3064	2896	5.36	3050	2898	5.71	$v_s CH_3$	95v _{CH}
		3022	2871	48.32	152.73	3037	2870	50.61	3023	2872	47.75	v _s CH ₃	90v _{CH}
1667/1657 vs		1725	1673	442.18	16.16	1772	1675	349.27	1735	1683	377.25	vC=0	95v _{c=0}
1599 s	1600 m	1637	1588	40.73	29.71	1655	1588	26.23	1640	1591	33.88	vCC	89vcc
1584 m	1586 w	1621	1573	3.05	8.92	1638	1573	3.46	1625	1576	3.56	vCC	85vcc
1496 s		1527	1481	66.52	2.49	1540	1479	61.41	1534	1488	60.96	vCC	86vcc
		1510	1465	6.90	10.31	1524	1463	6.26	1513	1468	9.12	vCC	84vcc
1453 m		1501	1456	13.93	8.03	1514	1453	11.07	1503	1458	11.36	δ ₂ CH ₃	876снз
		1484	1440	15.97	4.60	1497	1437	13.39	1487	1442	12.33	δ ₃ CH ₃	85бснз
		1477	1433	0.27	1.67	1489	1429	0.38	1483	1439	2.16	VCC	86vcc
1421 s		1471	1427	17.09	5.93	1483	1423	11.04	1472	1428	14.86	δ _c CH ₂	898cua
1388 s		1440	1397	25 31	5.93	1445	1387	39.20	1442	1399	25.77	δ _c CH ₂	908cH3
1352 m	1356 w	1401	1359	114 03	3.01	1412	1356	128.08	1402	1360	102.71	vCv	87VcN
1324 w	1550 W	1378	1336	117.08	18 21	1387	1331	82.81	1378	1337	115.23	VCC	85Vcc
1299 m	1301 m	1346	1305	0 39	0.55	1353	1299	0.70	1352	1311	0 39	vC—nh	83Vcc
1200 111	1501 111	1314	1274	1 78	0.59	1326	1273	1 36	1314	1275	1 69	mCH ₂	600 cup + 22 t cup
		1305	1266	72.07	23 23	1318	1265	75 52	1305	1266	74 20	OCH2	$62\omega_{cH3} + 18\tau_{cH3}$
1162 m	1164 w	1193	1157	1 30	3 30	1197	1149	1.62	1197	1161	1 12	BCH	618cu + 218ccc
1102 m	1155 w	1182	1146	0.07	2.68	1187	1140	0.02	1185	1149	0.04	всн	70Bcu + 14Bccc
1115111	1155 W	1164	1129	72.89	6.67	1171	1174	71 74	1167	1132	69.45	всн	678cu + 168ccc
		1147	1112	1 23	1 30	1155	1109	1 14	1153	1112	1 38	всн	65Bcu + 15Bcc
1086 vw	1087 w	1101	1068	27.52	4 16	1108	1063	24.42	1102	1069	26.26	всн	608 au + 228 au
1075 w	1007 W	1095	1062	676	0.32	1100	1055	4 87	1099	1066	6.00	oCH _o	620mm + 188mm
1075 W	1031 vw	1055	1002	3.67	0.52	1052	1010	4.67	1054	1022	3 34	oCH _o	600 mm + 268 mm
1023 11	1007 vs	1045	1020	12 30	11 93	1052	1009	7.95	1049	1022	834	вссс	57Base + 22Bas
995 vw	1007 13	1045	989	0.03	37.45	1019	978	0.91	1025	994	0.06	vC-CH ₂	59Bcc + 18Bco
972 m	975 m	1015	975	0.002	0.08	1013	962	0.01	1013	983	0.00	vN-CH ₂	68Vuc + 14Bccc
572 m	575 m	988	958	0.002	0.04	984	944	22.80	994	964	0.03	VCH	$60_{NL} + 18_{Vecc}$
945 w		979	949	27 55	3 76	976	937	0.84	979	950	27.45	VCH	$56\gamma_{cH} + 24\gamma_{cec}$
924 w	924 m	038	010	1 11	1.65	030	902	3 22	946	018	0.49	VCH	50 / CH + 24 / CCC
524 W	524 III	920	001	7.10	5 30	933	805	1.46	031	903	7.68	γCH γCH	$32\gamma_{CH} + 26\gamma_{CCC}$
		929	000	0.02	0.97	952	833	4.40	961	925	0.02	VCH	$\frac{40}{100}$ $\frac{10}{100}$ $\frac{10}{100}$ $\frac{10}{100}$
777 m		700	766	12 91	0.87	700	750	11.02	707	772	10.00		547CH + 207CCC
717 m	720 s	722	700	165	13.85	724	695	2 35	724	702	5 92	BCCC	53Basa + 21B
706 s	120 3	71/	602	1.05	0.10	716	687	2.55	720	608	38 33	вссс	578+ 188
626 w	623 m	634	615		4.19	634	609	20.12	636	617	0.15	вссс	558+228
020 W	025 111	621	612	6.24	-1.27 A AD	622	606	6.00	620	612	6.21	vece	$5 J_{PCCC} + 2 Z_{PCH}$
502 w		504	576	0.22	4.42	500	564	0.90	505	577	4.25	PCN	$J \rightarrow \gamma CCC = 10 \gamma CH$
592 W		594	570	4.04	0.20	300 EC9	504	3.39 21.40	595	577	4.20		$53p_{CN} + 20p_{CC}$
200.2		JO7 452	420	20.00	0.09	300 4E 4	343 425	21.40	J/2 4E4	333	21.22 E 97	YC-U	$OU\gamma_{C=0} \neq 21\gamma_{NC}$
		433	439	0.15 0.16	1.40	404	433	0.02	404	440	J.8/	YCIN PC ph	$60^{\circ}\gamma_{CN} + 10^{\circ}\gamma_{C=0}$
	402 104	422	410	1.62	0.51	420	40ð	0.05	420	415	0.14	pc-pn	50p _{CC} = 24p _{CH}
	403 VW	421	40ð	1.03	0.10	41ð	401	2.40	424	411	1.51	$pC - CH_3$	$52p_{CC} + 20p_{CN}$
		401	389	J./ð	3.82	402	380	2.02	403	221	2.29	$p_U - UH_3$	$31\beta_{CC} + 19\beta_{CO}$

Observed wavenumber (cm ⁻¹) B3LYP/	5-311++G**	calculated wave	enumber (cm ⁻¹)	B3LYP/6-31G**	calculated wa	avenumber (cm ⁻¹)	B3LYP/cc-pVTZ	calculated wa	avenumber (cm ⁻¹)	Assignment	%PED
FTIR FT-Rai	nan Unscale	d Scaled	IR intensity	Raman Activity	Unscaled	Scaled	IR intensity	Unscaled	Scaled	IR intensity		
	322	312	0.27	0.50	323	310	0.22	323	313	0.31	γαα	$47\gamma_{ccc}$ + $26\gamma_{CH}$
276 vi	v 260	252	4.55	1.93	262	252	4.61	262	254	4.34	γC—ph	$46\gamma_{cc}$ + $18\gamma_{ccc}$
	158	153	4.14	0.20	158	152	3.47	158	153	3.47	$\gamma C-CH_3$	$52\gamma_{cc} + 20\gamma_{cN}$
	117	113	0.35	0.08	127	121	0.002	125	121	0.16	γCCH ₃	$55\gamma_{cc}$ + $15\gamma_{co}$
	101	98	0.34	3.97	104	100	1.33	103	100	0.32	γссс	$46\gamma_{ccc} + 16\gamma_{cH}$
	89	87	1.64	0.47	102	98	0.76	95	92	1.08	γссс	$44\gamma_{ccc} + 18\gamma_{cH}$
	56	55	1.77	1.79	65	62	1.52	68	66	2.18	CH ₃ torsion	
	9	9	0.15	6.35	14	14	0.12	12	12	0.13	CH ₃ torsion	

Table 7 (continued)

^a v-Stretching: β -in-plane bending: δ -deformation; ρ -rocking; γ -out of plane bending and ω -wagging.

tron correlation and mechanical anharmonicity [56]. To compensate these shortcomings and to correlate the experimentally observed and theoretically computed frequencies for each vibrational modes of the compound under B3LYP methods, scale factors are introduced. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different types of fundamental vibrations. To determine the scale factors, the procedure used previously [57– 74] have been followed that minimises the residual separating experimental and theoretically predicted vibrational frequencies.

V. Arjunan et al. / Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 104 (2013) 182–196



Fig. 12. The correlation diagram for the calculated and the experimental frequencies of *cis-N*-methylacetanilide.

The optimum scale factors for vibrational frequencies were determined by minimising the residual

$$\Delta = \sum_{i}^{N} \left(\lambda \omega_{i}^{\text{Theor}} - v_{i}^{\text{Expt}} \right)^{2}$$

where ω_i^{Theo} and v_i^{Expt} are the *i*th theoretical harmonic frequency and *i*th experimental fundamental frequency (in cm⁻¹), respectively and *N* is the number of frequencies included in the optimisation which leads to

$$RMS = \sqrt{\frac{\varDelta}{N}}$$

The scale factors used in this study minimised the deviations between the computed and experimental frequencies. A uniform scaling factor is recommended for all frequencies <1800 cm⁻¹ at the B3LYP method with $6-31G^{**}/6-311++G^{**}$ basis sets and is adopted in this study. Due to the large anharmonicities of C—H and *N*—H stretching frequencies >2700 cm⁻¹ were scaled by two different scale factors [72,73].

Initially, all scaling factors have been kept fixed at a value of 1.0 to produce the pure DFT calculated vibrational frequencies (unscaled) which are given in Table 7. Subsequently, the scale factors 0.95 and 0.945 for C—H and CH₃ vibrations determined with 6-311++G^{**} and 6-31G^{**} basis sets. The correction factors 0.945 for C—H/CH₃ vibrations with cc-pVTZ basis set. For all other vibrations 0.97 and 0.96 were used to produce the scaled wavenumber. The resultant scaled frequencies are also listed in Table 7. These are much closer to unity and thus the vibrational frequencies calculated by using the B3LYP functional with 6-311++G^{**} basis set can be utilised to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra. The correlation diagram for the calculated and the experimental frequencies are shown in Fig. 12.

Conclusions

The structural parameters, thermodynamic properties and vibrational frequencies of the optimised geometry of *cis and trans*-amide form of *N*-methylacetanilide have been determined from DFT-B3LYP methods. The effects of substituents (methyl and phenyl group) on the amide vibrational frequencies were analysed. ¹H and ¹³C NMR isotropic chemical shifts were calculated and the assignments made are compared with the experimental values. The energies of important MO's of the compound were also determined from TD-DFT method. The total electron density and electrostatic potential of the compound were determined by natural bond orbital analysis.

The following observations are made from the complete vibrational assignment and analysis of the FTIR, FT-Raman and FT-NMR spectra of *cis-N*-methylacetanilide.

- (i) The unmethylated acetamido-groups were preferentially in the conformation with the carbonyl oxygen (C=O) *trans*- to *N*—H, this conformation has been named *endo- or trans*-. When the acetamido group is methylated, however, the other conformation, named *exo-* or *cis-* is found to be the most stable.
- (ii) The *cis*-amide conformer of *N*-methylacetanilide is more stable than the *trans* amide form by 2.36 kcal mol⁻¹.
- (iii) In acetanilide the acetamido group is in the endo-configuration (I), and the plane of the acetamido group and the benzene ring is making an angle of 38°. But, the stable conformation of *N*-methylacetanilide is completely different from the conformation of acetanilide and has the corresponding angle of 90°.

- (iv) The conformational state of the molecule depends on several intramolecular factors: resonance effect between the amide group and the aromatic ring, steric interaction between various substituents around the --NH--CO- grouping in the aromatic ring, conjugation between the carbonyl bond and the nitrogen lone pair as well as direct field influences inside the amide group.
- (v) The non-hydrogen atoms excluding the phenyl group are almost coplanar. The dihedral angle formed between this plane and the benzene ring is 87.07°.
- (vi) The C1—N7 bond distance increases in the order *trans- < cis-N*-methylacetanilide. The bond length between the amide nitrogen and the carbonyl group, N7—C8 of *cis-N*-methylacetanilide is 0.007 Å shorter than the *trans-* isomer.
- (vii) The angle at C1–N7–C11of *cis* isomer (120.6°) is more than the *trans*- isomer (117.4°). This shows the more stability and less steric hindrance in the *cis*- isomer.
- (viii) The total electron density surface mapped with electrostatic potential clearly reveals the presence of high negative charge on the carbonyl oxygen and in part of the ring while more positive charge around the –CH₃ region.
- (ix) The NBO analysis confirms the presence of resonance structures and reveals the exact *s* and *p* character of each bond. The lone pair donor orbital, $n_N \rightarrow \pi^*_{CO}$ interaction between the nitrogen lone pair and C8=O9 antibonding orbital is seen to give a strong stabilisation, 61.53 kJ/mol.
- (x) The frontier orbital energy gap $(E_{\text{HOMO}} E_{\text{LUMO}})$ in case of *cis* isomer is found to be 5.8753 eV. The $n_{\text{O}} \rightarrow \sigma_{\text{NC}}^*$ stabilisation energy of lone pair of electrons present in the oxygen atom (O9) to the antibonding orbital (σ^*) of N7–C8 is equal to 25.55 kJ/mol.
- (xi) The carbonyl carbon atom C8 is significantly observed in the downfield with chemical shift value 170.32 ppm reveals the presence of partially positive charge on the carbon atom. The -*I* effect of nitrogen (N7) reduces the electron density of the carbon atom C1, thus its NMR signal is observed in the very downfield at 144.59 ppm.
- (xii) The very strong doublet in IR spectrum observed at 1667/ 1657 cm⁻¹ are assigned to the amide-I, the C=O stretching band of the molecule.

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