Available online at www.elixirpublishers.com (Elixir International Journal)

Vibrational Spectroscopy



Elixir Vib. Spec. 65B (2013) 20204-20211

Scaled Quantum Chemical Studies of the Structure, Vibrational Spectra, Force Constants and First-Order Hyperpolarizability of 3,5-Dimethylpyridine

P.Vennila¹, M.Govindaraju^{2,*} and G.Venkatesh³ ¹Research and Development Centre, Bharathiar University, Coimbatore - 641 046, India. ²Department of Chemistry, Kongu Polytechnic College, Erode- 638052, India. ³Department of Chemistry, VSA Group of Institutions, Salem, Tamilnadu, India.

ARTICLE INFO

Article history: Received: 20 October 2013; Received in revised form: 25 November 2013; Accepted: 7 December 2013;

Keywords

Normal Coordinate Analysis, FT-IR, Density Functional Theory, HOMO, LUMO, Force constants, First-order Hyperpolarizability, Electronic Excitation Energy.

ABSTRACT

The molecular vibrations of 3,5-dimethylpyridine (35DMP) were investigated at room temperature by Fourier transform infrared (FTIR) and FT-Raman spectroscopy. The spectra of the above compounds have been recorded in the region 4000-400, 4000-100 cm , respectively. They were interpreted with the aid of normal coordinate analysis following full structure optimization and force field calculations based on density functional theory (DFT) using B3LYP /6-31G* and B3LYP/6-311+G** methods and basis set combinations. The results of the calculations were applied to simulated infrared and Raman spectra of the title compound, which showed excellent agreement with the observed spectra. The vibrational force constants were also performed by using DFT calculations. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. The values of the total dipole moment (μ) and the first-order hyperpolarizability (β) of the investigated compound were computed using DFT calculations. The calculated results also show that the 35DMP might have microscopic nonlinear optical (NLO) behavior with non-zero values. A detailed interpretation of the infrared and Raman spectra of 35DMP is also reported based on total energy distribution (TED). Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method were also calculated for the molecule.

© 2013 Elixir All rights reserved.

Introduction

Pyridine is a very stable compound with a great deal of aromatic character. Pyridine has been extensively studied from the spectroscopic point of view, due in part to its presence in many chemical structures of high interest in a variety of biomedical and industrial fields. Pyridine has the intrinsic interest of being the azine nearest to benzene. Compounds containing the pyridine ring systems are widely distributed in nature. Some examples are Vitamin B6 and nicotinamide adenine which are of great interest in biochemical and pharmaceutical fields. In pyridine, pyrazine and in related sixmembered heterocyclic molecules, resonance occurs as in benzene, causing the molecule to be planar and stable. The vibrational spectra of substituted pyridine have been the subject of several investigations [1,2]. 3,5-dimethylpyridine is used to the intermediate of medicine, pesticides etc.

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra. A significant advance in this area was made by scaled quantum mechanical (SQM) force field method [3-6]. In scaled quantum mechanical (SQM) approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules [7,8] and were recommended for general use. Recent spectroscopic studies on these materials have been motivated because the vibrational spectra are very useful for the understanding of specific biological process and in the analysis of relatively complex systems.

In the present study, we report the vibrational analysis of 3,5-dimethylpyridine (35DMP) using the SQM force field

method based on density functional theory (DFT) calculations. The calculated infrared and Raman spectra of the title compounds were simulated utilizing the scaled force fields and the computed dipole derivatives for IR intensities and polarisability derivatives for Raman intensities.

Experimental Details

The compound 35DMP was purchased from the Sigma– Aldrich Chemical Company (USA) with a stated purity of greater than 98% and it was used as such without further purification. The FT-Raman spectrum of 35DMP has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 4000-100 cm⁻¹ on a Brucker model IFS 66V spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FT-IR spectrum of this compound was recorded in the region 4000–400 cm⁻¹ on IFS 66V spectrophotometer.

Computational Details

Quantum chemical methods based on density functional theory are now widely used for calculations of the structure and vibrational frequencies of molecules [9]. The molecular geometry optimizations, energy and vibrational frequency calculations were carried out for 35DMP with the GAUSSIAN 09W software package [10] using the B3LYP functionals [11,12] combined with the standard 6-31G* and 6-311+G** basis sets. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to SQM procedure [13] using selective scaling in the natural internal coordinate representation [14,15]. Transformations of the force field and the subsequent normal

20204

reality

coordinate analysis including the least square refinement of the scaling factors, calculation of the total energy distribution (TED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program written by Sundius [16].

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using the standard procedure [17] of decomposing the traces of the symmetry operation into the irreducible representations. The symmetry analysis for the vibrational mode of 35DMP is presented in some details in order to describe the basis for the assignments. By combining the results of the GAUSSVIEW program [18] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence.

The Raman activities (Si) calculated with the GAUSSIAN 09W program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering [19-21].

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hcv_{i} / KT)]} - \dots - (1)$$

Where υ_0 is the exciting frequency (in cm⁻¹), υ_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Essentials of nonlinear optics related to **B**

The nonlinear response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor expansion of the total dipole moment μ_t induced by the field:

$$\mu_{t} = \mu_{0} + \alpha_{ij} E_{i} + \beta_{ijk} E_{i} E_{j} + \dots$$

Where α is linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first-order hyperpolarizability tensor components. The components of first-order hyperpolarizability can be determined using the relation

$$\beta_{i} = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x, y and z components the magnitude of the total static dipole moment (μ), isotropic polarizability (α_0), first-order hyperpolarizability (β_{total}) tensor, can be calculated by the following equations:

$$\mu_1^{0} = (\mu_x^{2} + \mu_y^{2} + \mu_z^{2})^{1/2}$$

$$\beta_{\text{tot}} = (\beta_x^{2} + \beta_y^{2} + \beta_z^{2})^{1/2}$$

The complete equation for calculating the first-order hyperpolarizability from GAUSSIAN 09W output is given as follows:

 $\beta_{\text{tot}} = [(\beta_{\text{xxx}} + \beta_{\text{xyy}} + \beta_{\text{xzz}})^2 + (\beta_{\text{yyy}} + \beta_{\text{yzz}} + \beta_{\text{yxx}})^2 + (\beta_{\text{zzz}} + \beta_{\text{zxx}} + \beta_{\text{zyy}})^2]$

The β components of GAUSSIAN 09W output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u= 8.3693 x10⁻³³ esu).

Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations.

An optimization is complete when it has converged. i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules. This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry. At the optimized structure, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The electric dipole moment and dispersion free first-order hyperpolarizibility were calculated using finite field method. The finite field method offers a straight forward approach to the calculation of hyperpolarizabilities.

All the calculations were carried out at the DFT level using the three-parameter hybrid density functional B3LYP and a $6-311+G^{**}$ basis set.

Results and discussion Molecular geometry

The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 2. The optimized molecular structure of 35DMP was shown in Fig 1.



Fig 1.The optimized molecular structure of 35DMP Table 1. Total energies of 35DMP, calculated at DFT B3LYP/6-31G* and B3LYP/6-311+G** level

Method	Energies (Hartrees)
6-31G*	-326.85672721
6-311+G**	-326.93507469

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 58 standard internal coordinates containing 13 redundancies were defined as given in Table 3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al [22] are summarized in Table 4.

The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

Analysis of vibrational spectra

The 45 normal modes of 35DMP are distributed among the symmetry species as Γ_{3N-6} = 31 A' (in-plane) + 14 A" (out-of-plane), and in agreement with C_s symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A") to depolarized band.

The detailed vibrational assignments of fundamental modes of 35DMP along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were reported in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of 35DMP are produced in a common frequency scales in Fig 2 & Fig 3.



Fig 2. FT-IR spectra of 35DMP (a)Observed (b) Calculated with B3LYP/6-311+G**



Fig 3. FT-Raman spectra of 35DMP (a) Observed (b) Calculated with B3LYP/6-311+G**

Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n} \left(\upsilon_{i}^{calc} - \upsilon_{i}^{exp}\right)^{2}}$$

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G^{**}) of 35DMP was found to be 96 cm⁻¹. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 7.82 cm⁻¹ between the experimental and scaled frequencies of the title compound.

C-H vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region $3300-3000 \text{ cm}^{-1}$ due to aromatic C–H stretching vibrations. Accordingly, in the present study the C–H vibrations of the title compounds are observed at 3163, 3159 and 3153 cm⁻¹ in the FTIR spectrum and 3149, 3148 and 3143 cm⁻¹

in Raman for 35DMP. The bands due to C–H in-plane ring bending vibration interacting some what with C–C stretching vibration are observed as a number of m-w intensity sharp bands in the region 1300–1000 cm⁻¹. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm⁻¹ [23]. The in-plane and out-of-plane bending vibrations of C–H have also been identified for the title compound.

C-C vibrations

The ring C-C stretching vibrations [24], known as semicircular stretching usually occur in the region 1300-1100 and 1700-1480 cm⁻¹. The C-C stretching vibrations of 35DMP are observed 1659, 1628, 1473 and 1470 in the FT-IR spectrum and 1654, 1633, 1629 and 1474 cm⁻¹ in FT-Raman spectrum. In accordance with above literature data in our present study, the bands for C-C stretching vibrations are observed at 1308, 1303, 1305, 1302, 1193 and 1198 cm⁻¹ in FT-IR spectrum. These observed frequencies show that, the substitutions in the ring to some extent about the ring mode of vibrations. The comparison of the theoretically computed values are in good agreement theoretical values obtained by B3LYP/6-311+G** method.

C-N vibrations

The identification of C-N vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of force field calculations, the C-N vibrations are identified and assigned in this study. The slight shift in wavenumber in due to the fact that force constants of the C-N bond increases due to resonance with the ring. Absorbances are also observed at 1700–1620 cm⁻¹, 1580–1210 cm⁻¹, 1000–960 cm⁻¹ and 825–775 cm⁻¹. Accordingly the bands observed at 1659, 1654, 1633, 1628, 1478, 1472, 1369, 1363, 1207 and 1201 cm⁻¹ have been assigned to C-N stretching modes and their corresponding TED modes are, respectively.

Methyl group vibrations

For the assignments of CH₃ group frequencies, basically nine fundamentals can be associated to each CH₃ group namely, CH₃ ss, symmetric stretch; CH₃ ips, inplane stretch (ie, in-plane hydrogen stretching modes); CH₃ ipb, in-plane-bending (i.e., hydrogen deformation modes); CH₃ sb, symmetric bending; CH₃ ipr, in-plane rocking; CH₃ opr, out-of-plane rocking and tCH₃, twisting hydrogen bending modes. In addition to that, CH₃ ops, out-of-plane stretch and CH₃ opb, out-of plane bending modes of the CH₃ group would be expected to be depolarised for A' symmetry species. The CH₃ ss frequency is established at 3046, 3042 and 3041 cm⁻¹ in IR and CH₃ ips is assigned at 3108, 3107 and 3103 cm⁻¹ in IR respectively, for 35DMP. These assignments are also supported by the literature [25] in addition to TED output. We have observed the symmetrical methyl deformation mode CH₃ sb, at 1435, 1431 and 1426 cm⁻¹ in the infrared and Raman, and in-plane-bending methyl deformation mode CH_3 ipb, at 1430 cm⁻¹ in the Raman. The band at 3045, 3042, 3046, 3041 and 1078, 1071, 1067, 1045, 1042 cm^{-1} in infrared is attributed to CH₃ ops and CH₃ opb, respectively, in the A' species. The methyl deformation modes mainly coupled with the in-plane-bending vibrations. The bands obtained at 965 cm^{-1} and 951 cm^{-1} in IR and Raman are assigned to CH_3 inplane and out-of-plane rocking modes. The assignment of the band at 196 cm⁻¹ in IR is attributed to methyl twisting mode. Vibrational force constants

Quantum-mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr² units. These force constants were transformed to the force fields in internal local-symmetry coordinates.

P.Vennila et al./ Elixir Vib. Spec. 65B (2013) 20204-20211

Table 2. Optimized geometrical parameters of 35DMP obtained by B3LYP/6-311+G** density functional calculations

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-N1	1.33663	C3-C2-N1	124.22228	C4-C3-C2-N1	0.00000
C3-C2	1.40062	C4-C3-C2	116.81639	C5-C4-C3-C2	0.00000
C4-C3	1.39777	C5-C4-C3	120.51536	C6-N1-C2-C3	0.00000
C5-C4	1.39777	C6-N1-C2	117.40714	H7-C2-N1-C6	180.00000
C6-N1	1.33664	H7-C2-N1	116.12730	H8-C3-C4-C2	180.00000
H7-C2	1.08984	H8-C4-C3	119.74236	H9-C6-N1-C2	180.00000
H8-C4	1.08899	H9-C6-N1	116.12678	C10-C3-C2-N1	180.00000
H9-C6	1.08983	C10-C3-C2	121.36898	C11-C5-C4-C3	180.00000
C10-C3	1.50849	C11-C5-C4	121.81374	H12-C10-C3-C2	0.00000
C11-C5	1.50850	H12-C10-C3	111.22826	H13-C10-C3-C2	-120.22653
H12-C10	1.09338	H13-C10-C3	111.40564	H14-C10-C3-C2	120.22653
H13-C10	0.09590	H14-C10-C3	111.40564	H15-C11-C5-C4	-59.77323
H14-C10	1.09590	H15-C11-C5	111.40571	H16-C11-C5-C4	180.00000
H15-C11	1.09590	H16-C11-C5	111.22830	H17-C11-C5-C4	59.77323
H16-C11	1.09338	H17-C11-C5	111.40571		
H17-C11	1.09590				

*for numbering of atom refer Fig 1

Table 3. Definition of internal coordinates of 35DMP

No(i)	symbol	Туре	Definition	
Stretching 1-6	r _i	C-C	C2-C3,C3-C4,C4-C5,C5-C6,C3-C10, C5-C11	
7-8	Si	C-N	N1-C2,N1-C6	
9-11	pi	C-H	С2-Н7,С4-Н8,С6-Н9	
12-14	Pi	C-H	С10-Н12,С10-Н13,С10-Н14	
15-17	n _i	C-H	C11-H15,C11-H16,C11-H17	
Bending	a	CCN	N1-C2-C3,C2-C3-C4,C3-C4-C5,	
18-23	α _i	C-C-N	C4-C5-C6,C5-C6-N1,N6-N1-C2	
24-29	θ_{i}	N-C-H	N1-C2-H7,C3-C2-H7,C3-C4-H8, C5-C4-H8,C5-C6-H9,N1-C6-H9	
30-31	βi	C-C-C	C10-C3-C2, C10-C3-C4	
32-33	Φ_{i}	C-C-C	C11-C5-C6, C11-C5-C4	
34-36	γ _i	H-C-H	H12-C10-H13, H13-C10-H14, H14-C10-H12	
37-39	μ	C-C-H	С3-С10-Н12, С3-С10-Н13, С3-С10-Н14	
40-42	vi	H-C-H	H15-C11-H16, H16-C11-H17, H17-C11-H15	
43-45	ϕ_i	C-C-H	C5-C11-H15, C5-C11-H16, C5-C11-H17	
Out-of-plane 46-48	ω _i	C-H	H7-C2-N1-C3, H8-C4-C3-C5, H9-C6-C5-N1.	
49-50	ξi	C-C	C10-C3-C2-C4,C11-C5-C4-C6	
Torsion 51-56	τ_i	τC-N	N1-C2-C3-C4,C2-C3-C4-C5, C3-C4-C5-C6,C4-C5-C6-N1, C5-C6-N1-C2,C6-N1-C2,C3	
57	τ	τC-C-H	C2-C3-C10-(H12,H13,H14)	
58	τ	τC-C-H	C6-C5-C11-(H15,H16,H17)	

*for numbering of atom refer Fig 1

Table 4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for 35DMP

		33D MI	
No.(i)	Symbol ^a	Definition ^b	Scale factors used in calculation
1-6	C-C	r1,r2,r3,r4,r5,r6	0.914
7-8	C-N	\$7,\$8	0.914
9-11	C-H	p9, p10, p11	0.992
12	mss1	(P12+P13+P14)/ \sqrt{3}	0.992
13	mips1	(2P13-P12-P14)/ √6	0.992
14	mops1	(P13-P14)/ V2	0.992
15	mss2	$(n15+n16+n17)/\sqrt{3}$	0.992
16	mips2	(2n16-n15-n17)/ √6	0.992
17	mops2	(n16-n17)/ $\sqrt{2}$	0.992
18	C-C-N	$(\alpha 18 - \alpha 19 + \alpha 20 - \alpha 21 + \alpha 22 - \alpha 23)/\sqrt{6}$	0.992
19	C-C-N	$(2\alpha 18 - \alpha 19 - \alpha 20 + 2\alpha 21 - \alpha 22 - \alpha 23)/\sqrt{12}$	0.992
20	C-C-N	(α19-α20+α22-α23)/2	0.992
21-23	N-C-H	$(\theta 24 - \theta 25)/\sqrt{2}, (\theta 26 - \theta 27)/\sqrt{2}, (\theta 28 - \theta 29)/\sqrt{2}$	0.916
24	C-C-C	(β30-β31)/√2	0.923
25	C-C-C	(Ф32-Ф33)/√2	0.923
26	msb1	(γ34+γ35+γ36-µ37-µ38-µ39)/ √6	0.990
27	mipb1	(2736-734-735)/ 16	0.990
28	mopb1	(y34-y36)/ √2	0.990
29	mipr1	(2µ38-µ37-µ39)/ √6	0.990
30	mopr1	(µ37-µ39)/ √2	0.990
31	msb2	(v40+v41+v42-φ43-φ44-φ45)/ √6	0.990

P.Vennila et al./ Elixir Vib. Spec. 65B (2013) 20204-20211

32	mipb2	(2v42-v40-v41)/ V6	0.990
33	mopb2	(v40-v42)/ ¹ / ₂	0.990
34	mipr2	(2φ44-φ43-φ45)/ √6	0.990
35	mopr2	(φ43-φ45)/ √2	0.990
36-38	C-H	ω46, ω47, ω48	0.994
39-40	C-C	ξ49, ξ50	0.962
41	tring	$(\tau 51 - \tau 52 + \tau 53 - \tau 54 + \tau 55 - \tau 56)/\sqrt{6}$	0.994
42	tring	$(\tau 51 - \tau 53 + \tau 54 - \tau 56)/2$	0.994
43	tring	$(-\tau 51+2\tau 52-\tau 53-\tau 54+2\tau 55-\tau 56)/\sqrt{12}$	0.994
44	C-C-H	τ57/2	0.979
45	C-C-H	τ58/2	0.979

^a These symbols are used for description of the normal modes by TED in Table 5. ^b The internal coordinates used here are defined in Table 3.

Table 5. Detailed assignments of fundamental vibrations of 35DMP by normal mode analysis based on SQM force field

	calculation							
S.	Symmetry species	Observed (cm ⁻¹)	frequency	Calculated B3LYP/6-	l frequen 311+G ^{**} t	cy (cm ⁻¹) force field	with l	TED (%) among type of internal coordinates ^c
INO.	Č _s	Infrared	Raman	Unscaled	Scaled	IR ^a A _i	Raman ^b I _i	
1	Α'			3167	3161	18.440	80.250	CH(99)
2	Α'	3153		3163	3159	26.499	104.874	CH(98)
3	Α'		3149	3148	3143	23.900	159.472	CH(99)
4	Α'	3127		3133	3128	27.769	189.384	mips2(47),mops1(37),mips1(12)
5	Α'			3118	3114	6.318	62.517	mips2(50),mops1(35),mips1(12)
6	Α'			3112	3107	14.840	106.704	mops2(100)
7	A'	3108		3107	3103	46.427	73.698	mips1(74),mops1(25)
8	Α'			3045	3042	16.178	81.472	mss1(49),mss2(49)
9	Α'	3042		3046	3041	17.484	87.273	mss2(49),mss1(49)
10	Α'		1654	1659	1654	1.332	17.924	CC(46),bCH(20),CN(17),bring(10),CCm(6)
11	Α'	1628		1633	1629	6.509	16.682	CC(47),bCH(16),CN(13),bring(9)
12	Α'		1522	1528	1523	10.511	15.416	bmopb2(49),bmipb2(37)
13	Α'			1519	1515	16.815	9.968	bmipb1(36),bmopb2(34),bmipb2(17)
14	Α'		1502	1508	1504	9.333	21.477	bmipb2(36),bmipb1(23),bmopb2(10),bmopb1(9),bmopr2(5)
15	Α'	1501		1503	1500	7.232	15.518	bmopb1(60),bmipb1(38)
16	Α'			1478	1472	18.253	0.892	bmipb2(31),bCH(18),bmopb2(17),CN(14),CC(13)
17	Α'		1474	1473	1470	0.733	12.375	bmipb2(39),bmopb2(22),CC(14),bmipb1(8),bCH(7)
18	A'	1430		1435	1431	0.339	24.298	bmsb1(81),CCm(8)
19	A'			1430	1426	0.248	22.154	bmsb2(74),bmipb2(7),CCm(7)
20	A'	1380	1385	1369	1363	5.175	0.107	bCH(83),CN(6)
21	Α'			1308	1303	3.655	4.641	CC(52),CN(38)
22	Α'	1303		1305	1302	0.927	11.185	CCm(35),bCH(24),CC(18),bring(17)
23	A'			1207	1201	15.304	7.568	CN(66),bCH(17),CCm(9)
24	A'		1200	1198	1196	1.505	0.864	bCH(48),CCm(28),CC(18)
25	A''			1078	1071	8.025	0.161	gCH(27),bmopr2(16),bmipr1(12),tring(10),bmopb1(10),gCC(9)
26	A''	1068		1071	1067	0.261	0.225	gCC(41),bmipr1(19), bmopr2(9),gCH(7),bmopb1(7),bmipb1(6)
27	A'		1049	1056	1050	7.669	16.675	bring(38),bmipr2(23),CC(20),bmipb2(7),bmopb2(5)
28	A'	1043		1045	1042	2.070	7.149	bmipr2(20),CC(19),bring(18),bmopr1(18),bmipb2(6),CCm(6)
29	A'	1012	1004	1008	1003	0.518	1.406	bmopr1(36),bmipr2(20),CC(12),bring(8),bmipr1(7),bmipb2(5)
30	A''			965	960	0.001	3.519	gCH(88)
31	A''	960		956	951	0.072	3.618	gCH(90)
32	A''			952	950	0.036	0.607	gCH(33),CC(25),bring(16),bmopr1(8), CCm(6)
33	A''		881	886	880	7.814	0.251	gCH(68),tring(18)
34	A''			726	731	10.674	0.420	tring(81),gCC(17)
35	A'	724	717	733	728	6.098	12.409	bring(48),CCm(23),CC(20),CN(8)
36	A''			555	549	0.986	4.241	gCC(72),CCm(16), bring(7)
37	A'	533	543	542	538	0.713	8.091	bring(67),CCm(21),CC(10)
38	A''			518	513	0.000	0.440	gCC(58),tring(36)
39	A''	452		456	451	0.332	0.224	tring(59),gCC(30),gCH(9)
40	A'			460	397	0.730	0.195	bCC2(45),bCC1(38)
41	A'		276	275	270	0.509	1.682	bCC1(45),bCC2(36)
42	A''	104	233	238	232	0.000	4.041	tring(77),gCC(10),gCH(9)
43	A''	196		198	195	1.120	1.203	gCC(47),tring(31),gCH(17)
44	A''			56	50	0.097	0.106	tm2(56),tm1(19),gCC(9)
45	A''			50	45	0.006	0.190	tm1(45),tm2(16),gCC(13),bmopb1(10),bmipb1(8),tring(5)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;

^a Relative absorption intensities normalized with highest peak absorption

^bRelative Raman intensities calculated by Eq 1 and normalized to 100.

^c For the notations used see Table 4.

P.Vennila et al./ Elixir Vib. Spec. 65B (2013) 20204-20211

Reduced masses (AMU)	Force constants (mDyne/A)
1.02	0.00
1.05	0.00
2.86	0.06
2.73	0.08
2.53	0.10
2.58	0.23
3.80	0.45
2.96	0.45
4.86	0.83
5.10	0.91
7.15	2.22
2.63	0.82
1.34	0.61
3.20	1.70
1.32	0.70
1.38	0.74
1.50	0.89
1.56	1.00
4.07	2.64
1.51	1.01
1.54	1.04
1.55	1.30
2.47	2.10
2.39	2.38
7.35	7.35
1.27	1.39
1.24	1.49
1.26	1.52
1.95	2.48
2.19	2.80
1.04	1.38
1.04	1.38
1.16	1.57
1.33	1.81
4.86	7.60
5.77	9.30
1.03	5.65
1.03	5.65
1.10	6.22
1.10	6.22
1.10	6.34
1.10	6.34
1.08	6.35
1.09	6.39
1.09	6.41
	•

Table 6. Diagonal force constants (10² Nm⁻¹) of 35DMP

Table 7. The dipole moment (μ) and first-order hyperpolarizibility (β) of 35DMP derived from DFT calculations

β _{xxx}	22.827
β_{xxy}	3505.9
β_{xyy}	800.09
β_{yyy}	36878
β_{zxx}	25.022
β_{xyz}	4035.3
β_{zyy}	22.611
β_{xzz}	462.16
β_{yzz}	-2727.7
β_{zzz}	-36.112
β_{total}	37.275
μ_{x}	0.66423494
$\mu_{\rm y}$	4.5407
μ_z	0.29264854
μ	0.97822742

Dipole moment (μ) in Debye, hyperpolarizibility $\beta(-2\omega; \omega, \omega) \ 10^{-30}$ esu.

Table 8. Computed absorption wavelength (λ_{ng}) , energy (E_{ng}) , oscillator strength (f_n) and its major contribution

n	λ_{ng}	Eng	f _n	Major contribution			
1	202.7	6.12	0.1219	H-0->L+0(+78%), H-1->L+1(+19%)			
2	200.7	6.18	0.0104	H-2->L+0(+86%)			
3	3 190.5 6.51 0.0248 H-0->L+1(+53%), H-1->L+0(43%)						
((Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)						

The force field determined was used to calculate the vibrational potential energy distribution among the normal coordinate. The local-symmetry coordinates defined in terms of the internal valence coordinates following the IUPAC recommendations are given in Table 6 for the title compounds. **First-order hyperpolarizability calculations**

The first-order hyperpolarizibility (β_{iik}) of the novel molecular system of 35DMP is calculated using B3LYP/6-311+G** basis set based on finite field approach. Hyperpolarizibility is a third rank tensor that can be described by a 3 x 3 x 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman [26] symmetry. The calculated first-order hyperpolarizability (β_{total}) of 35DMP is 37.275×10^{-30} esu, which is greater than that of urea (0.1947 x 10) 30 esu). The calculated dipole moment (µ) and first-order hyperpolarizibility (β) are shown in Table 7. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{yyy} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated, in general, with even larger projection of β_{total} quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as β_{total} values. The connection between the electric dipole moments of an organic molecule having donor-acceptor substituent and first-order hyperpolarizability is widely recognized in the literature [27]. The maximum β was due to the behavior of nonzero µ value. One of the conclusions obtained from this work is that non-zero μ value may enable the finding of a non-zero β value. Of course Hartee-Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Fig 4 shows the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) of 35DMP. There is an inverse relationship between hyperpolarizability and HOMO-LUMO.

HOMO energy = -0.32589 a.u LUMO energy = 0.13254 a.u HOMO-LUMO energy gap = 0.45843 a.u



Fig 4. Representation of the orbital involved in the electronic transition for (a) HOMO (b) LUMO (c) Virtual

Electronic excitation mechanism

The static polarizability value [28-29] is proportional to the optical intensity and inversely proportional to the cube of transition energy. With this concept, larger oscillator strength (f_n) and $\Delta \mu_{gn}$ with lower transition energy (E_{gn}) is favourable to obtain large first static polarizability values. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method and are summarized in Table 8. Representation of the orbital involved in the electronic transition was shown in Fig 5.



Fig 5. Representation of the orbital involved in the electronic transition for (a) HOMO-0 (b) LUMO+0 (c) HOMO-1 (d) LUMO+1 (e) HOMO-2

Conclusions

IR and Raman Spectra were obtained for 35DMP, in which all of the expected 45 normal modes of vibration were assigned. The optimized molecular geometry, force constants and vibrational frequencies were calculated using DFT techniques in the B3LYP approximation. Taking the observed frequencies as a basis corresponding to the fundamental vibrations, it was possible to proceed to a scaling of the theoretical force field. The resulting SQM force field served to calculate the potential energy distribution, which revealed the physical nature of the molecular vibrations, and the force constants in internal coordinates, which were similar to the values obtained before for related chemical species. The first-order hyperpolarizibility (β_{iik}) of the novel molecular system of 35DMP is calculated using B3LYP/6-311+G** basis set based on finite field approach. The calculated first-order hyperpolarizability (β_{total}) of 35DMP is 37.275×10^{-30} esu, which is greater than that of urea (0.1947×10^{-30}) esu). The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . It is noticed that in β_{yyy} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method.

References

- 1. A. Topacli, S. Bayari, Spectrochim. Acta Part A 57 (2001) 1385.
- 2. R.N. Medhi, R. Barman, K.C. Medhi, S.S. Jois, Spectrochim. Acta Part A 56 (2000) 1523.
- 3. I. Lopez Tocon, M.S. Wolley, J.C. Otero, J.I. Marcos, J. Mol. Struct. 470 (1998) 241.
- 4. B.A. Hess Jr., J. Schaad, P. Carsky, R. Zahraduik, Chem. Rev. 86 (1986)

709.

- 5. P. Pulay, X. Zhou, G. Fogarasi, in: R. Fransto (Ed.), NATO AS Series, Vol. C, 406, Kluwer, Dordrecht, 1993, p. 99.
- 6. W.J. Hehre, L. Random, P.V.R. Schleyer, J.A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1986.
- 7. G.R. De Mare, Y.N. Panchenko, C.W. Bock, J. Phys. Chem. 98 (1994) 1416.
- 8. Y. Yamakita, M. Tasuni, J. Phys. Chem. 99 (1995) 8524.
- 9. G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.
- 10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
- M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Ivengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 11. A.D. Becke, J. Chem. Phys., 98 (1993) 5648.

- 12. C. Lee, W. Yang, R.G. Parr, Phys. Rev., B37 (1988) 785.
- 13. P. Pulay, G. Fogarasi, G.Pongor, J. E. Boggs, A. Vargha, J. Am. Chem. Soc., 105 (1983) 7037.
- 14. G. Fogarasi, P. Pulay, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, vol. 14, Elsevier, Amsterdam, 1985.
- 15. G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay, J. Am. Chem. Soc. 114 (1992) 8191.
- 16. T. Sundius, J. Mol. Struct. 218 (1990) 321.
- 17. F.A. Cotton, Chemical Applications of Group Theory, Wiley Interscience, New York, 1971.
- 18. A. Frisch, A.B. Nielson, A.J. Holder, Gaussview Users Manual, Gaussian Inc., Pittsburgh, PA, 2000.
- 19. P.L. Polavarapu, J. Phys. Chem. 94, 8106 (1990).
- 20. G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.V. Wang, J.R. Durig, Spectrochim. Acta 49A,2007 (1993).
- 21. G. Keresztury, in: J.M. Chalmers and P.R. Griffiths(Eds), Handbook of Vibrational Spectroscopy vol.1, John Wiley & Sons Ltd. p. 71, (2002).
- 22. P. Pulay, G. Fogarasi, F. Pong, J.E. Boggs, J. Am. Chem. Soc., 101 (1979) 2550.
- 23. M. Silverstein, G. Clayton Bassler, C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1981.
- 24. B.A. Hess Jr., J. Schaad, P. Carsky, R. Zahraduik, Chem. Rev. 86 (1986) 709.
- 25. S. Dheivamalar and V. Silambarasan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 96 (2012) 480-484.
- 26. D.A. Kleinman, Phys. Rev. 1962;126,1977.
- 27. P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1991.
- 28. K. Wu, C. Liu, C. Mang, Opt. Mater. 29 (2007) 1129-1137.
- 29. S. Iran, W.M.F. Fabian, Dyes Pigments 70 (2006) 91-96.