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Vibrational Spectral Investigations, HOMO- LUMO, First-Hyperpolarizability Analyses of 2,4-Dimethoxybenzonitrile by *ab initio* and Density Functional Method

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ABSTRACT

In the present study, the FT-IR and FT-Raman spectra of 2,4-dimethoxybenzonitrile have been recorded in the region 4000–400 cm^{-1} and 3500–50 cm$^{-1,}$ respectively. The fundamental modes of vibrational frequencies of (24DMBN) are assigned. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of *ab initio* Hartree–Fock (HF) and density functional theory (DFT) gradient calculations with complete relaxation in the potential energy surface using 6-311++G(d,p)) basis set. The vibrational frequencies which were determined experimentally from the spectral data are compared with those obtained theoretically from *ab initio* and DFT calculations. A close agreement was achieved between the observed and calculated frequencies by refinement of the scale factors. The infrared and Raman spectra were also predicted from the calculated intensities. Thermodynamic properties like entropy, heat capacity, zero point energy, have been calculated for the molecule. The calculated HOMO–LUMO energy gap reveals that charge transfer occurs within the molecule. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED).

1.Introduction

Benzonitrile is a phenyl cyanide compound which is derived mainly from benzoic acid reaction with lead thiocynate by heating. It is a colourless liquid having a smell of bitter almonds. It reacts violently with strong acids to produce toxic hydrogen cyanide and it decomposes on heating, producing very toxic fumes of hydrogen cyanide and nitrous oxides [1]. Benzonitrile is used as a solvent and chemical intermediate for synthesis of pharmaceuticals, dye stuffs and rubber chemicals through the reaction of alkylation, condensation, hydrolysis, halogenations or nitration. Benzonitrile and its derivatives are used in the manufacturing of lacquers, polymers and anhydrous metallic salts as well as intermediates for pharmaceuticals, agrochemicals and other organic chemicals. Many derivatives of benzonitrile are used in medicine as urinary antiseptic in the form of a salt and in vapour form for disinfecting bronchial tubes. These are also used in dye industry for making aniline blue and for preserving food products [2].

Density functional theoretical modeling of substituted benzene as benzonitrile has been reported by Fleming *et al.* [3,4]. Sundaraganesan *et al.* [5] have reported the molecular structure and vibrational spectra of 3-chloro-4-fluorobenzonitrile. F- and Cl- mono substituted benzonitrile derivatives have been investigated by vibrational spectroscopy [6,7] and in some cases also by ultraviolet absorption spectroscopy [8]. Chloro-disubstituted [9] benzonitrile and chloro and methyl-disubstituted [10-12] benzonitrile have been studied by infrared spectroscopy. Now-a-days, NMR, Raman spectroscopy combined with quantum chemical computation has been recently used as an effective tool in the vibrational analysis of drug molecules [13], biological compounds [14] and natural product [15].

However, the detailed HF/B3LYP comparative studies on the complete FT-IR and FT-Raman spectra of 2,4-dimethoxybenzonitrile (**24DMBN**) have not been reported so far. In the present investigation, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for HF and B3LYP at 6-311++G(d,p) basis set are compared. The vibrational assignments have been performed based on total energy distribution (TED).

2. Experimental Procedure

2,4-dimethoxybenzonitrile (24DMBN) molecule under investigation was purchased from Lancaster Chemical Company, UK, and used as such without further purification to record FT-IR and FT-Raman spectra. The Fourier transform infrared spectrum of 24DMBN was recorded in the range between 400–4000 cm^{-1} with a BRUKER IFS 66V model spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source. The FT-Raman spectrum of 24DMBN was recorded on a computer interfaced BRUKER IFS 66V model interferometer equipped with FRA-106 FT-Raman accessories. The spectrum was measured in the Stokes region 3500–50 cm^{-1} using Nd:YAG laser operating at 200 mW power continuously with 1064 nm excitation. The reported wavenumbers are expected to be accurate within ± 1 cm^{-1}.

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3. Computational Procedure

The entire calculations are performed at Hartree-Fock (HF) and B3LYP levels using GAUSSIAN 09W [16] program package, invoking gradient geometry optimization [17] for calculating both structure and vibrational spectra of 24DMBN. The optimized structural parameters are used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 24DMBN are used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and force constants. The density functional theory (DFT) [18] with the Becke three-parameter hybrid functional (B3) [19] have been used for the exchange part and the Lee-Yang-Parr (LYP) correlation function [20], accepted as a cost effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structure. Among the best performing levels, the frequency data to calculate the TEDs using the MOLVIB package [21] has been arbitrarily chosen. TEDs has been calculated in the following way: the geometries and Cartesian force constants from archive file have been extracted and used them as input in the MOLVIB package. The package generated the internal coordinates via a transformation, which in the second stage computed internal force constants from a similarity transformation of the *ab initio* force constant matrix (the Hessian). Finally, TEDs are calculated in internal coordinates.

4. Results and Discussion

4.1. Molecular geometry

Molecular geometry is a sensitive indicator of intra and intermolecular interactions. The molecular structure of 24DMBN belongs to C_1 point group symmetry. For C_1 symmetry there would not be any relevant distribution. The molecule consists of 21 atoms and expected to have 57 normal modes of vibrations of the same species ‘A’. These modes are found to be IR and Raman active suggesting that the molecule possesses a non-centro symmetric structure, which recommends 24DMBN for non-linear optical applications. The optimized molecular structure of 24DMBN is shown in Fig. -1.

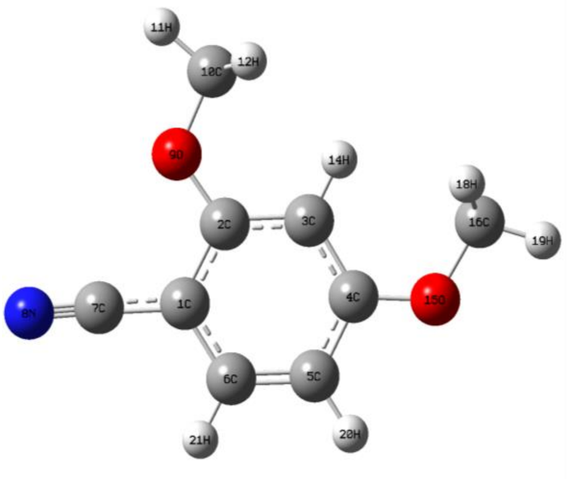

Fig 1. Molecular structure of 2,4-dimethoxybenzonitrile

The optimized structure parameters of 24DMBN is calculated by *ab initio* (HF) and DFT (B3LYP) levels with the 6-311++G(d,p) basis set are listed in Table -1. Molecular geometries can be specified in terms of bond lengths, bond angles and torsional angles. It can be inferred that for a bond to be stronger, the overlap should be greater, which in turn would shorten the distance between the nuclei i.e. bond length. A stronger bond has therefore, a shorter bond length [25]. Internal and symmetric co-ordinates of 24DMBN are tabulated in Tables -2 and 3.

4.2. Vibrational spectra

The spectral analysis of title compound is done by HF and DFT method using the basis set 6-311++G(d,p). The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2 and 3 respectively. The experimental and theoretical fundamental modes of vibrations of 24DMBN are represented in Table -4.

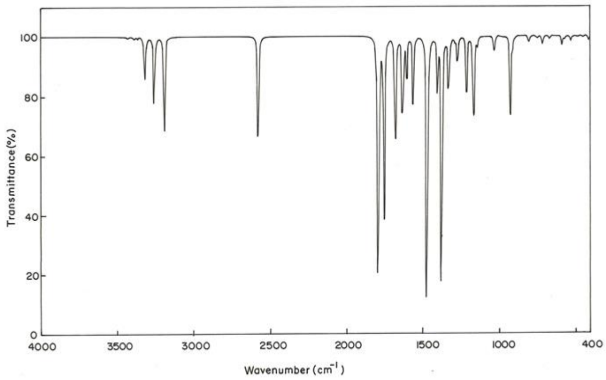

Fig 2. FT-IR spectrum of 2,4-dimethoxybenzonitrile.

Methyl group vibrations.

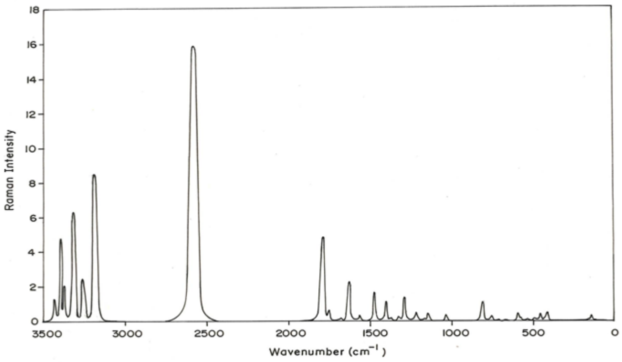

Fig 3. FT-Raman spectrum of 2,4-dimethoxybenzonitrile.

For the assignment of CH_3 group frequencies one can expect nine fundamentals to be associated with each CH_3 group, namely the symmetrical stretching in CH_3 (CH_3 sym. stretching), asymmetrical stretching (i.e. in-plane hydrogen stretching mode), the symmetrical (CH_3 sym deformation) and asymmetrical (CH_3 asy deformation) deformation modes, the in-plane rocking (CH_3 ipr), out-of-plane rocking (CH_3 opr) and twisting (CH_3 twist) modes. In addition to that, CH_3 ops, out-of-plane stretch and CH_3 opb, out-of-plane bending modes of the CH_3 group would be expected to be depolarized for asymmetry species. The C–H stretching in CH_3 occurs at lower frequencies than those of the aromatic ring (3100–3000 cm^{-1}). The vibrations of the methyl group in 24DMBN are observed in the typical range reported [26,27]. The symmetric stretching vibrations are observed at 3178, 3160 cm^{-1} in FT-IR and FT-Raman spectra, respectively, for 24DMBN. For methyl substituted benzene derivatives, the asymmetric and symmetric bending vibrations of methyl groups normally appear in the regions 1465–1440 cm^{-1} and 1400–1370 cm^{-1}, respectively. The torsional mode is expected below 400 cm^{-1}. The Raman peaks at 124 and 102 cm^{-1} for 24DMBN is assigned to the CH_3 torsional vibrations. The comparative results between the experimental and theoretical wavenumbers gave a full description of the vibrational properties of 24DMBN molecule. Detailed assignments of CH_3 group of 24DMBN are listed in Table -4.

Table 1.Optimized geometrical parameters of 2,4-dimethoxybenzonitrile obtained by B3LYP and HF methods with 6-311++G(d,p) basis set.

Bond Length	Value (Å)		Bond angle	Value (◦)		Dihedral Angle	Value (◦)	
	DFT/ 6-311++G(d,p)	HF/ 6-311++G(d,p)		DFT/ 6-311++G(d,p)	HF/ 6-311++G(d,p)		DFT/ 6-311++G(d,p)	HF/ 6-311++G(d,p)
C1-C2	1.4132	1.41	C2-C1-C6	118.9063	118.902	C6-C1-C2-C3	-0.0007	181.6387
C1-C6	1.407	1.4036	C2-C1-C7	120.5746	120.5842	C6-C1-C2-O9	179.9969	180.0005
C1-C7	1.4288	1.4249	C6-C1-C7	120.5191	120.5077	C7-C1-C2-C3	179.999	-0.0005
C2-C3	1.4014	1.3984	C1-C2-C3	120.1907	120.1129	C7-C1-C2-O9	-0.0034	179.9881
C2-C9	1.3546	1.352	C1-C2-O9	115.9302	115.9966	C2-C1-C6-C5	0.0006	179.9921
C3-C4	1.4025	1.3993	C3-C2-O9	123.879	123.8904	C2-C1-C6-H21	-179.9998	-0.0005
C3-H14	1.0802	1.0786	C2-C3-C4	119.5662	119.6737	C7-C1-C6-C5	180.0009	179.9881
C4-C5	1.4041	1.4008	C2-C3-H14	119.9347	119.8746	C7-C1-C6-H21	0.0005	179.9921
C4-C15	1.3598	1.3574	C4-C3-H14	120.4992	120.4517	C1-C2-C3-C4	0.0004	-0.0192
C5-C6	1.3854	1.3818	C3-C-C5	120.7156	120.6127	C1-C2-C3-H14	-180.0007	0.00035
C5-H20	1.0838	1.0819	C3-C4-O15	123.6587	123.683	O9-C2-C3-C4	-179.997	-180.0021
C6-H21	1.0848	1.083	C5-C4-O15	115.6257	115.7043	O9-C2-C3-H14	0.002	-179.9891
C7-N8	1.1648	1.1565	C4-C5-C6	119.2818	119.3254	C1-C2-O9-C10	-180.03	0.0052
O9-C10	1.4244	1.4236	C4-C5-H20	119.1316	119.0922	C3-C2-O9-C10	-0.0325	0.0022
C10-H11	1.09	1.088	C6-C5-H20	121.5866	121.5825	C2-C3-C4-C5	0.0	-180.0057
C10-H12	1.0966	1.0948	C1-C6-C5	121.3393	121.3672	C2-C3-C4-O15	180.0017	-179.9855
C10-H13	1.0966	1.0948	C1-C6-H21	118.6485	118.6276	H14-C3-C4-C5	180.0011	0.0066
C15-C16	1.4244	1.4234	C5-C6-H21	120.0122	120.0052	H14-C3-C4-O15	0.0027	179.9505
C16-H17	1.0968	1.0949	C2-O-C10	119.5762	119.6048	C3-C4-C5-C6	-0.0001	-0.0614
C16-H18	1.0968	1.0949	O9-C10-H11	105.4733	105.5066	C3-C4-C5-H20	180.0	-0.0068
C16-H19	1.0902	1.0883	O9-C10-H12	111.2429	111.2624	O15-C4-C5-C6	-180.0017	180.0116
			O9-C10-H13	111.2432	111.2665	O15-C4-C5-H20	-0.0015	180.0011
			H11-C10-H12	109.4457	109.4022	C3-C4-O15-C16	-0.0215	0.0196
			H11-C10-H13	109.4447	109.3962	C5-C4-O15-C16	-180.0199	0.0098
			H12-C10-H13	109.8829	109.8964	C4-C5-C6-C1	-0.0002	-179.9909
			C4-O15-C16	119.3565	119.3509	C4-C5-C6-H21	180.0002	179.9927
			O15-C16-H17	111.2824	111.3179	H20-C5-C6-C1	-180.0003	-0.008
			O15-C16-H18	111.2821	111.3131	H20-C5-C6-H21	0.0	-0.0546
			O15-C16-H19	105.6612	105.6957	C2-O9-C10-H11	180.0264	179.9631
			H17-C16-H18	109.7762	109.7821	C2-O9-C10-H12	-61.4039	-0.0081
			H17-C16-H19	109.3688	109.311	C2-O9-C10-H13	61.4578	-180.0024
			H18-C16-H19	109.3683	109.3161	C4-O15-C16-H17	-61.3709	-180.0074
						C4-O15-C16-H18	61.4092	-0.0017
						C4-O15-C16-H19	-179.9812	-179.9359
						C2-O9-C10-H12	-61.3881	-61.3881
						C2-O9-C10-H13	61.5214	61.5214
						C4-O15-C16-H17	-67.3679	-67.3679
						C4-O15-C16-H18	61.4674	61.4674
						C4-O15-C16-H19	179.9485	-179.9485

Table 2.Definition of internal coordinates of 2,4-dimethoxybenzonitrile.

No.(i)	Symbol	Type	Definition[a]
Stretching			
1-7	T_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1, C1-C7
8	Q_i	C≡N	C7≡N8
9-11	r_i	C-H	C3-H14, C5-H20, C6-H21
12-17	r_i	C-H (methyl)	C10-H11, C11-H12, C11-H13, C16-H17, C16-H18, C16-H19
18-21	P_i	C-O	C2-O9, C11-O9, C4-O15, C16-O15
In-plane bending			
22-27	β_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
28-29	α_i	C-C-C	C6-C1-C7, C2-C1-C7
30	θ_i	C-C≡N	C1-C7≡N8
31-36	σ_i	C-C-H	C2-C3-H14, C4-C3-H14, C4-C5-H20,C6-C5-H20, C1-C6-H21, C5-C6-H21
37-40	δ_i	C-C-O	C2-C3-O9, C1-C2-O9, C3-C4-O15,C5-C4-O15
41-42	ρ_i	C-O-C	C3-O9-C11, C4-O15-C16
43-48	ν_i	O-C-H	O9-C10-H11, O9-C10-H12, O9-C10-H13, O15-C16-H17, O15-C16-H18, O15-C16-H19
49-54	λ_i	H-C-H	H11-C10-H12, H12-C10-H13, H13-C10-H11, H17-C16-H18, H18-C16-H19, H17-C16-H19
Out-of-plane bending			
55	ω_i	C-C	C7-C1-C6-C2
56	ψ_i	C≡N	N8-C7-C1-C2
57-59	π_i	C-H	H14-C3-C2-C4, H20-C5-C4-C6, H21-C6-C5-C1
60-61	Σ_i	C-O	O9-C2-C3-C4, O9-C10-C3-C4
62-63	Φ_i	O-C	O9-C10-C2-C3, O15-C16-C4-C5
Torsion			
64-69	τ_i	tRing	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
70-71	τ_i	tC-OCH3	(C1, C3)-C3-O9-C10-(H11, H12, H13),(C3, C5)-C4-O15-C16-(H17, H18, H19)

[a] For numbering of atoms refer Fig. 1.

On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of these are examined and proposed.

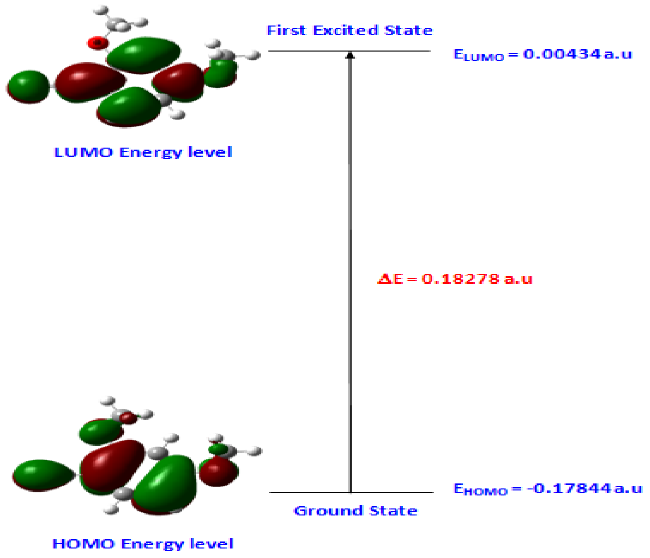

Fig 4. HOMO-LUMO energy gap of 2,4-dimethoxybenzonitrile.

Table 3. Definition of local symmetry co-ordinates of 2,4-dimethoxybenzonitrile.

No.(i)	Symbol[a]	Definition[b]
1-7	CC	$T_1, T_2, T_3, T_4, T_5, T_6, T_7$
8	CN	Q_8
9-11	CH	r_9, r_{10}, r_{11}
12-13	CH3 ss	$(r_{12} + r_{13} + r_{14})/\sqrt{3}$, $(r_{15} + r_{16} + r_{17})/\sqrt{3}$
14-15	CH3 ips	$(2r_{12} + r_{13} + r_{14})/\sqrt{6}$, $(2r_{15} + r_{16} + r_{17})/\sqrt{6}$
16-17	CH3 ops	$(r_{13} - r_{14})/\sqrt{2}$, $(r_{16} - r_{17})/\sqrt{2}$
18-21	CO	$P_{18}, P_{19}, P_{20}, P_{21}$
22	Rtrigd	$(\beta_{22} - \beta_{23} + \beta_{24} - \beta_{25} + \beta_{26} - \beta_{27})/\sqrt{6}$
23	Rsymd	$(-\beta_{22} - \beta_{23} + 2\beta_{24} - \beta_{25} - \beta_{26} + 2\beta_{27})/\sqrt{12}$
24	Rasymd	$(\beta_{22} - \beta_{23} + \beta_{25} - \beta_{26})/2$
25	bCCN	$(\alpha_{28} - \alpha_{29})/\sqrt{2}$
26	bCN	θ_{30}
27-29	bCH	$(\sigma_{31} - \sigma_{32})/\sqrt{2}$, $(\sigma_{33} - \sigma_{34})/\sqrt{2}$, $(\sigma_{35} - \sigma_{36})/\sqrt{2}$
30-31	bCO	$(\delta_{37} - \delta_{38})/\sqrt{2}$, $(\delta_{39} - \delta_{40})/\sqrt{2}$
32-33	bOC	ρ_{41}, ρ_{42}
34-35	CH3 sb	$(-\nu_{43} - \nu_{44} - \nu_{45} + \lambda_{49} + \lambda_{50} + \lambda_{51})/\sqrt{6}$, $(-\nu_{46} - \nu_{47} - \nu_{48} + \lambda_{52} + \lambda_{53} + \lambda_{54})/\sqrt{6}$
36-37	CH3 ipb	$(-\lambda_{49} - \lambda_{50} - 2\lambda_{51})/\sqrt{6}$, $(-\lambda_{52} - \lambda_{53} - 2\lambda_{54})/\sqrt{6}$
38-39	CH3 opb	$(\lambda_{49} - \lambda_{50})/\sqrt{2}$, $(\lambda_{52} - \lambda_{53})/\sqrt{2}$
40-41	CH3 ipr	$(2\nu_{43} - \nu_{44} - \nu_{45})/\sqrt{6}$, $(2\nu_{46} - \nu_{47} - \nu_{48})/\sqrt{6}$
42-43	CH3 opr	$(\nu_{44} - \nu_{45})/\sqrt{2}$, $(\nu_{47} - \nu_{48})/\sqrt{2}$
44	ωCCN	ω_{55}
45	ωCN	ψ_{56}
46-48	ωCH	$\pi_{57}, \pi_{58}, \pi_{59}$
49-50	ωCO	Σ_{60}, Σ_{61}
51-52	ωOC	Φ_{62}, Φ_{63}
53	tRtrigd	$(\tau_{64} - \tau_{65} + \tau_{66} - \tau_{67} + \tau_{68} - \tau_{69})/\sqrt{6}$
54	tRsymd	$(\tau_{64} - \tau_{66} + \tau_{67} - \tau_{69})/\sqrt{2}$
55	tRasymd	$(-\tau_{64} + 2\tau_{65} - \tau_{66} - \tau_{67} + 2\tau_{68} - \tau_{69})/\sqrt{12}$
56-57	tOCH3	τ_{70}, τ_{71}

[a] These symbols are used for description of the normal modes by TED.

[b] The internal coordinates used here are defined in Table .2.

C≡N vibrations

For the aromatic compound which bears a C≡N group attached to the ring, a band of very good intensity has been observed in the region 2240–2221 cm^{-1} and it is being attributed to C≡N stretching vibrations [28]. The strong bands obtained at 2587 cm^{-1} in IR and 2589 cm^{-1} in Raman spectrum are assigned to C≡N stretching vibration of 24DMBN and the corresponding force constant contribute 86% to the TED. The in-plane and out-of-plane bending modes of C≡N group are strongly coupled with C–C–C bending modes. They are due to the out-of-plane aromatic ring deformation with in-plane deformation of the C≡N vibration and in-plane bending of the aromatic ring with the C–C≡N bending. The FT-Raman bands at 498 and 275 cm^{-1} are assigned to the individual in-plane and out-of-plane deformation of C≡N vibration, respectively.

Table 4. The Experimental and calculated frequencies (cm^{-1}), IR intensity ($Km\ mol^{-1}$), Raman activity ($A^4\ amu^{-1}$) and probable assignments (characterized by TED) of 2,4-dimethoxybenzonitrille using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) level calculations.

S. No.	Observed frequency (cm^{-1})		HF/6-311++G(d,p)						DFT/6-311++G(d,p)						Assignment % of TED
	FT-IR	FT-Raman	Calculated frequencies (cm^{-1})		Reduced Mass	Force Constants	IR Intensity	Raman Activity	Calculated frequencies (cm^{-1})		Reduced Mass	Force Constants	IR Intensity	Raman Activity	
			Unscaled	Scaled					Unscaled	Scaled					
1	-	3305	3238	3297	1.0887	6.7265	1.4498	51.8546	3257	3299	1.0889	6.8089	1.8105	131.27	νCH(99)
2	3292	-	3209	3284	1.0952	6.6468	1.2029	154.212	3227	3280	1.0952	6.7226	1.5783	62.381	νCH(98)
3	-	3287	3192	3279	1.0891	6.5397	1.5672	56.5632	3210	3282	1.0893	6.6144	1.8736	52.936	νCH(96)
4	3219	-	3144	3210	1.0995	6.4065	12.0399	107.668	3163	3212	1.1002	6.4859	11.9226	132.71	CH_{3ips}(92)
5	-	3210	3140	3200	1.0994	6.3870	17.7747	135.426	3158	3203	1.1001	6.4679	17.5989	57.0101	CH_{3ips}(91)
6	3178	-	3073	3171	1.1066	6.1612	37.9344	60.2343	3091	3173	1.1068	6.2327	40.5775	160.50	CH_{3ss}(89)
7	-	3160	3071	3152	1.1066	6.1504	25.7520	40.3504	3089	3155	1.1067	6.2227	25.4830	676.8936	CH_{3ss}(90)
8	3104	-	3011	3097	1.0345	5.5281	72.1959	234.979	3024	3100	1.0342	5.5740	79.5695	199.744	CH_{3ops}(87)
9	-	3082	3009	3073	1.0344	5.5108	22.9967	81.0928	3022	3075	1.0342	5.5667	23.2303	2.3475	CH_{3ops}(88)
10	2587	2589	2325	2580	12.763	40.3762	85.9532	626.936	2327	2582	12.6755	40.4592	86.8935	3.3460	νCN(86)
11	1793	1794	1643	1785	6.0719	9.6588	270.472	154.351	1651	1788	6.01782	9.6741	280.31	6.4543	νCC(85)
12	1749	1747	1604	1740	7.8860	11.9632	94.2008	5.2967	1612	1742	7.9276	12.1476	97.0155	14.9844	νCC(83)
13	1690	-	1536	1681	2.5673	3.5716	98.4444	15.4292	1544	1683	2.6370	3.7059	95.5059	5.9583	νCC(86)
14	1646	-	1505	1638	1.1169	1.4908	51.3075	3.2482	1509	1641	1.1436	1.5359	55.9154	14.0114	νCC(81)
15	-	1638	1500	1630	1.0741	1.4249	58.1304	5.2532	1504	1633	1.0729	1.4317	53.4539	18.439	νCC(80)
16	1617	-	1496	1611	1.0454	1.3802	19.3348	14.9099	1502	1613	1.046	1.3904	18.2228	24.1057	νCC(82)
17	1573	-	1494	1565	1.0453	1.3755	1.9879	11.1526	1500	1568	1.4039	1.8613	15.5672	16.1677	νCC(84)
18	-	1560	1491	1549	1.3907	1.8292	16.5466	6.3073	1499	1552	1.0459	1.3859	1.1311	30.1765	CH_{3ipb}(81)
19	1485	-	1473	1474	1.1780	1.5064	30.1601	0.9721	1477	1481	1.1730	1.5097	29.0465	6.9585	CH_{3ipb}(83)
20	-	1466	1441	1454	2.4560	3.0072	37.6916	6.3003	1448	1459	2.3582	2.9140	38.3296	3.2203	CH_{3sb}(84)
21	1411	-	1351	1400	5.8570	6.2991	121.675	30.6755	1365	1403	6.2963	6.9160	111.7057	1.8997	CH_{3sb}(83)
22	-	1388	1314	1375	4.1175	4.1949	158.822	6.9270	1327	1377	4.3893	4.5577	183.4604	21.3398	νCO(81)
23	1382	-	1294	1373	1.7417	1.7200	57.6655	27.4193	1297	1379	1.6455	1.6327	40.6611	1.5731	νCO(80)
24	1352	-	1236	1341	2.2939	2.0649	204.572	1.2256	1246	1343	2.4195	2.2139	221.0732	3.4590	bCH(79)
25	1323	-	1218	1311	2.6366	2.3070	1.6872	26.1642	1222	1314	2.4741	2.1779	1.1228	0.1461	bCH(76)
26	-	1279	1204	1267	1.3998	1.1966	0.0001	1.3197	1207	1271	1.3920	1.1957	0.0652	0.0704	CH_{3opb}(82)
27	1249	-	1193	1237	1.5487	1.2987	31.3989	4.3656	1198	1240	1.5724	1.3316	17.8241	0.2439	bCH(75)
28	-	1201	1168	1190	1.2708	1.0226	0.8415	3.4103	1172	1196	1.2692	1.0274	1.4598	27.4689	CH_{3opb}(80)
29	1190	-	1167	1179	1.2720	1.0216	0.3581	1.6018	1171	1182	1.2701	1.0273	0.3089	0.2468	CH_{3opr}(79)
30	1175	-	1135	1163	1.7041	1.2946	61.2126	9.2156	1139	1165	1.6653	1.2734	52.0056	3.84936	CH_{3opr}(77)
31	-	1123	1057	1110	6.5453	4.3152	93.5161	2.9238	1064	1116	6.3079	4.2101	88.8188	0.5533	νOC(79)
32	1073	-	1052	1061	3.6905	2.4106	21.0697	5.2332	1057	1064	3.7171	2.4477	20.2194	1.4777	νOC(81)
33	-	1014	967	1001	1.3166	0.7254	0.7197	0.1296	966	1007	1.3113	0.7212	0.4830	6.2735	CH_{3ipr}(74)
34	955	-	955	942	4.5993	2.4730	22.6063	6.4223	959	947	4.5768	2.4813	21.1223	2.7476	CH_{3ipr}(73)
35	838	-	836	823	2.0603	0.8486	54.8866	0.0484	835	826	1.8103	0.7440	63.3356	3.8785	Rtrigd(70)
36	-	795	824	783	1.6835	0.6738	6.7467	0.1731	823	787	1.5990	0.6384	2.2382	1.4007	Rsymd(68)
37	779	-	762	767	5.7091	1.9569	6.3516	20.9967	763	770	5.7505	1.9756	6.0884	4.4031	Rasymd(69)
38	749	-	743	732	2.1453	0.6988	0.3284	0.5019	731	733	2.6971	0.8493	0.0947	4.0052	bCCN(67)

39	-	733	707	721	6.1058	1.8014	4.7986	5.8889	706	724	6.1642	1.8145	4.7227	0.3748	bCO(69)
40	705	-	649	692	3.4243	0.8520	8.1149	0.3025	648	696	3.5022	0.8670	7.4947	0.5688	bCO(68)
41	-	684	629	672	6.2424	1.4585	1.9605	1.5602	622	674	6.1221	1.3996	1.5787	1.6817	bOC(65)
42	-	625	541	613	5.8831	1.0157	2.7620	2.7303	540	616	5.8825	1.0129	2.5636	1.2317	bOC(66)
43	617	-	540	610	6.8123	1.1721	6.8170	2.8350	533	603	6.6156	1.1108	7.0599	3.4834	ωCH(59)
44	610	-	504	592	4.7513	0.7121	5.1213	1.9969	503	594	4.7685	0.7128	5.3380	0.0866	ωCH(58)
45	-	577	4650	562	3.2866	0.3935	0.7985	1.0855	452	569	3.3291	0.4012	0.5061	0.7544	ωCH(59)
46	-	570	428	560	6.5780	0.7126	0.9237	6.1223	424	561	6.6316	0.7307	0.5904	0.4587	tRtrigd(56)
47	558	-	395	547	6.8664	0.6332	4.0442	8.6676	394	549	6.9489	0.6378	4.0414	1.2543	tRsymd(55)
48	-	535	287	522	3.4702	0.1686	6.5753	1.9250	287	527	3.4606	0.1687	6.7571	0.4521	tRasymd(57)
49	-	498	282	481	2.9409	0.1380	0.0498	0.1838	287	487	2.5764	0.1253	0.1317	0.2635	bCN(64)
50	485	-	268	468	2.1426	0.0911	1.0106	0.0306	272	471	2.1521	0.0942	0.7063	0.7823	ωCCN(56)
51	-	436	226	421	1.2219	0.0369	0.4214	0.5048	233	425	1.2523	0.0401	0.3911	0.1469	ωCO(54)
52	415	-	186	401	1.6396	0.0337	0.4100	0.9715	189	403	1.7147	0.0363	0.4065	0.2658	ωCO(55)
53	-	390	175	376	3.2415	0.0586	0.3237	1.2408	175	380	3.2431	0.0591	0.3060	0.7852	ωOC(52)
54	-	335	134	321	8.7298	0.0935	4.0651	3.5205	132	323	8.7973	0.0909	4.1317	2.7812	ωOC(53)
55	-	275	125	260	4.3107	0.0400	9.8657	0.8662	129	262	4.2504	0.0417	10.0535	7.5843	ωCN(54)
56	-	124	90	115	3.6118	0.0176	1.7379	0.4146	94	116	3.5729	0.0188	1.7997	21.0354	tOCH$_3$(51)
57	-	102	65	85	3.7651	0.0096	0.14970	0.4512	67	91	3.8804	0.0104	0.1631	0.1873	tOCH$_3$(52)

C–H vibrations

The aromatic structure shows the presence of C–H stretching vibration in the region 3000–3100 cm^{-1} [29]. There are three stretching vibrations identified for C–H stretching at 3305, 3287 in Raman and 3292 cm^{-1} in FT-IR spectrum. The theoretically computed (scaled) values for C–H vibrations using B3LYP/6-311++G method show a good agreement with recorded spectrum. The bands due to the ring C–H in-plane bending are usually observed in the region 1000–1300 cm^{-1}. In the title compound, these vibrations are observed at 1352, 1323 and 1249 cm^{-1} in FT-IR spectrum. The C–H out-of plane bending vibrations are usually observed between 750 and 1000 cm^{-1} [30]. In the present compound, these vibrations are observed at 617, 610 and 577 cm^{-1} in FT-IR and FT-Raman spectra respectively.

C–C vibrations

The ring stretching vibrations are very much important in the spectrum of benzene and its derivatives, and are highly characteristic of the aromatic ring itself. The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650–1400 cm^{-1} are good group vibrations [31]. Socrates [32] mentioned that the presence of conjugate substituent such as C=C causes a heavy doublet formation around the region 1625-1575 cm^{-1}. As predicted in the earlier studies, in this investigation, the bands observed at 1793, 1749, 1690, 1646, 1617, 1573 cm^{-1} in IR spectrum and Raman bands at 1794, 1747, 1638 cm^{-1} have been assigned to C–C stretching modes of 24DMBN. The corresponding ring in-plane bending and out-of-plane vibrations are shown in Table - 4.

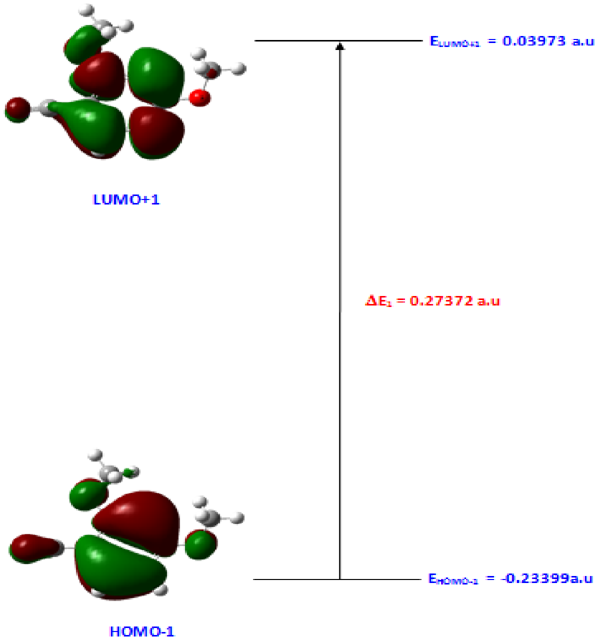

Fig 5. HOMO-1-LUMO+1 energy gap of 2,4-dimethoxybenzonitrile.

5. Other Molecular Properties

5.1. HOMO-LUMO analysis

The HOMO−LUMO energy gap of 24DMBN is calculated at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels and are shown in Table -5. reveals that the energy gap reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. Therefore, an electron density transfer occurs from the more aromatic part of the π-conjugated system in the electron-donor side to its electron-withdrawing part. Moreover, a lower HOMO−LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule. The positive phase is red and the negative one is green. It is clear from the figure that, the HOMOs are localized mainly on the nitrile and CH_3 group. On the other hand, the LUMOs are localized mainly on C−C bond of the benzene ring. The HOMO−LUMO energy levels of 24 DMBN are shown in Fig. 6.

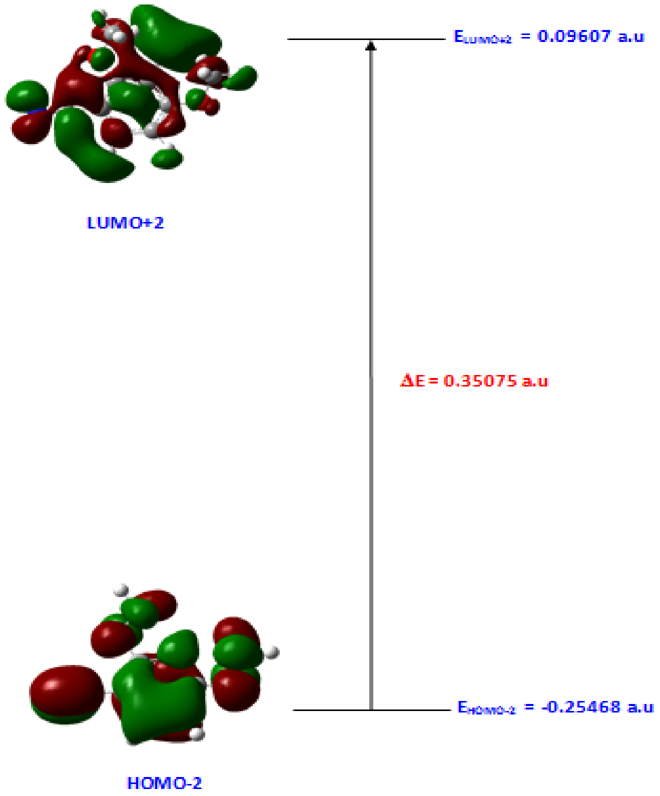

Fig 6. HOMO-2-LUMO+2 energy gap of 2,4-dimethoxybenzonitrile.

Using Koopman’s theorem for closed-shell compounds, global hardness η and electronic chemical potential μ can be defined as

$$\eta = \frac{I - A}{2}$$

$$\mu = \frac{-(I + A)}{2}$$

where I and A are the ionization potential and electron affinity of the compound, respectively. Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor.

Parr *et al.* [33] have defined a new descriptor to quantify the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a compound. Parr *et al.* have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as follows:

$$\omega = \frac{\mu^2}{2\eta}$$

The usefulness of this new reactivity quantity has been recently demonstrated

in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity. The calculated value of electrophilicity index describes the biological activity of 24DMBN. All the calculated values of hardness, potential, and electrophilicity index are shown in Table .5.

Table 5. HOMO–LUMO energy and other related properties of 2,4-dimethoxybenzonitrille in a.u obtained by B3LYP and HF methods with 6-311++G(d,p) basis set.

Parameters	**B3LYP/6-311++G(d,p)**	**HF/6-311++G(d,p)**
HOMO	-0.23546	-0.23741
LUMO	-0.04524	-0.04683
Global hardness (η)	0.09511	0.09529
Electronic chemical potential (μ)	-0.14035	-0.14212
Electrophilicity index (ω)	0.103554	0.10598
Ionization energy (I)	0.23546	0.23741
Electron affinity (A)	0.04524	0.04683

5.2. First Hyperpolarizability Calculation – A NLO property

The electronic and vibrational contributions to the first hyperpolarizability have been studied theoretically for many organic and inorganic systems. The values of the first hyperpolarizability were found to be quite large for the so-called push-pull molecules, i.e. p-conjugated molecules with the electron donating and the electron withdrawing substituents attached to a ring, compared to the monosubstituted systems [34]. This type of functionalization of organic materials, with the purpose of maximizing NLO properties, is still commonly followed route.

The first hyperpolarizability of title compound is calculated using DFT and HF methods with 6-311++G(d,p) basis set. In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability (β) is a third rank tensor that can be described by 3 × 3 × 3 matrices. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + ...$$

... (4.1)

where E^0 is the energy of the unperturbed molecule, F_α is the field at the origin, and $\mu_{\alpha,}$ $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first order hyperpolarizability, respectively. The total static dipole moment (μ) and the mean first hyperpolarizability (β) using the x, y, z components, they are defined as:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

$$\beta = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Since the value of hyperpolarizability (β) of the GAUSSIAN 09W output is reported in atomic units (a.u.), the calculated values should have been converted into electrostatic units (esu) (β: 1 a.u. = 8.639 × 10^{-33} e.s.u). The total molecular dipole moment and first hyperpolarizability are 7.2326 Debye and 2.7124 × 10^{-30} e.s.u, respectively and are depicted in Table 4.6. Total dipole moment of title compound is approximately five times greater than those of urea and first hyperpolarizability of title compound is 7 times greater than those of urea (μ and β of urea are 1.3732 Debye and 0.3728 × 10^{-30} e.s.u obtained by DFT/6-311++G(d,p) method). The results obtained by DFT/6-311++G(d,p) and HF/6-311++G(d,p) methods are listed in Table 4.6.

Table6.Nonlinear optical properties of 2,4-dimethoxybenzonitrille obtained by B3LYP and HF methods with 6-311++G(d,p) basis set.

NLO Behaviour	**B3LYP/6-311++G(d,p)**	**HF/6-311++G(d,p)**
Dipole moment (μ)	7.2326 Debye	7.2087 Debye
Mean polarizability (α)	0.7702809474×10^{-30} esu	1.063354781×10^{-30} esu
Anisotropy of the polarizability (Δα)	2.628007605×10^{-30} esu	3.418336395×10^{-30} esu
First hyperpolarizability (β)	2.7124360596×10^{-30} esu	2.969282183×10^{-30} esu
Energy	553.57172266 a.u	-553.69142547 a.u

5.3. Thermodynamical parameters

Several calculated thermodynamical parameters, rotational constants, rotational temperature and vibrational temperature have been presented in Table -7. The zero-point vibration energies, the entropy and the molar capacity at constant volume were calculated. The variations in the zero-point vibration energies seem to be insignificant. The changes in the total entropy of 24DMBN at room temperature at DFT/6-311++G(d,p) and HF/6-311++G(d,p) methods are only marginal .

Table 7. Theoretically computed zero point vibrational energy (kcal mol^{-1}), rotational constant (GHz), rotational temperature (kelvin), thermal energy (kcal mol-1), molar capacity at constant volume (cal mol^{-1} kelvin^{-1}), entropy (cal mol^{-1} kelvin^{-1}) of 2,4-dimethoxybenzonitrille obtained by B3LYP and HF methods with 6-311++G(d,p) basis set.

Parameter	**B3LYP/6-311++G(d,p)**	**HF/6-311++G(d,p)**
Zero point vibrational energy	103.03004	102.62
Rotational constant	1.52067 0.66904 0.46741	1.52568 0.67239 0.46951
Rotational temperatures	0.07298 0.03211 0.02243	0.07322 0.03227 0.02253
Energy		
Total	110.115	109.72
Translation	0.889	0.889
Rotational	0.889	0.889
Vibrational	108.338	107.946
Molar capacity at constant volume		
Total	41.664	41.696
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	35.703	35.735
Entropy		
Total	103.989	104.234
Translational	41.176	41.176
Rotational	30.892	30.879
Vibrational	31.921	32.179

Conclusion

The FT-IR and FT-Raman spectra of 2,4-dimethoxybenzonitrile have been studied. The equilibrium geometries, harmonic wavenumbers and HF and DFT calculations for 2,4-dimethoxybenzonitrile are carried out for the first time.

Optimized geometrical parameters of the title compound are calculated. B3LYP/6-311++G(d,p) calculations are shown better correlation with the experimental data than other calculations. The calculated vibrational values are in good agreement when they are compared with IR and Raman experimental data. Frontier molecular orbital analysis, and NLO properties and other molecular properties of the title compound are also studied at DFT/6-311++G(d,p) and HF/6-311+G(d,p) levels. The results of this study will help researches to design and synthesis of new materials. Decrease in HOMO and LUMO energy gap, explains the eventual charge transfer within the molecule which is responsible for the chemical reactivity of the molecule. These calculations are carried out in ground state by using *ab initio* and Density functional theory.

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