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### Vibrational analysis and physical property studies of 6-Methoxy-2-[(E)phenyliminomethyl]-phenol in the THz, IR and UV-Visible spectral regions.

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#### <u>Abstract</u>

Bulk single crystals of 6-Methoxy-2-[(*E*)-phenyliminomethyl]phenol were grown after preparing the material by Schiff base condensation of ortho-vanillin alternatively called 2hydroxy-3-methoxybenzaldehyde and aniline. The three dimensional molecular and crystal structure of the title compound is confirmed by X-ray diffraction. Molecules crystallized in the orthorhombic crystal system and noncentrosymmetric space group  $P2_12_12_1$ . Geometry optimization, vibrational analysis, Calculation of HOMO-LUMO band gap and molecular hyperpolarizability of the proposed material have been carried out. Terahertz time domain spectroscopic studies have been performed and the refractive index and absorption coefficient of material is calculated in the THz regime. Molecular vibrations responsible for different THz phonon modes are identified with the help of density functional theory based calculations.

Keywords: Crystal growth, Nonlinear optics, Second harmonic generation, Organic materials, THz spectroscopy, Density functional theory.

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#### **1.Introduction**

Low cost organic nonlinear optical (NLO) materials are being considered as efficient substitutes to their inorganic counterparts because of their large values of hyperpolarizability and less complex crystal growth process [1, 2]. Since organic materials exhibit superior electro-optic response, they are also potential alternatives to inorganic materials for terahertz (THz) generation and subsequent applications[3]. Major drawback of the organic NLO materials reported so far is their low stability under laser action and moisture. The highly efficient, well established organic NLO material DAST cannot be used for second harmonic generation (SHG) using the technologically important widespread Nd:YAG laser of wavelength 1064 nm because of its absorption edge in 560 nm and high absorbance at 532 nm [4, 5]. Researchers are working towards developing high efficient NLO organic noncentrosymmetric materials with higher laser damage threshold. Materials are also supposed to be possessed with the property of low absorption in the optically important spectral regions so that they can be potentially applied to second harmonic and THz generation purposes. This can be achieved by constructing new organic molecules with donor- $\pi$ -acceptor (D- $\pi$ -A) system comprising different functional groups which have lesser absorption bands in the THz and visible regions [6, 7]. But most of the time the chiral molecular structures built in this way will crystallize in a centrosymmetric fashion which cannot be used for second order nonlinear optical processes [8]. In that sense it is easy and important to study the physical properties related to nonlinear optical performance of organic materials for which noncentrosymmetric crystal structure is already reported.

Schiff base condensation is a well used chemical process for design and synthesis of organic NLO materials. It's an easily feasible chemical reaction to add or substitute electron accepting or donating organic functional groups to the parent molecule and also to establish  $\pi$ -bridges in it[9-11]. The large optical nonlinearity and high second harmonic generation (SHG) efficiency of the organic material vanillin and its derivatives and that of the derivative of aniline are well known [12]. m-nitroaniline, 2-methyl-4-nitroaniline, etc are some very familiar examples. m-nitroanilin is reported for its terahertz generation as well [13, 14]. Vanillylideneaniline (VAN) also called 2-methoxy-4(phenyliminomethyl) phenol formed through Schiff base condensation of vanillin and aniline has been already reported for its SHG and high nonlinear optical activity [15, 16]. The authors have reported its detailed infrared and

Raman spectroscopic analysis along with computational details in [9]. In this report, we are introducing another NLO crystal for second order processes which is obtained by transferring the hydroxyl group of aldehyde moiety of VAN from para position to ortho position (Compare the molecular structure given under geometry optimization section of this manuscript with figure 4 of reference [9]). Here the title material 6-Methoxy-2-[(E)-phenyliminomethyl]-phenol is synthesized by Schiff base condensation of 2-Hydroxy-3-methoxybenzaldehyde alternatively called ortho-Vanillin with aniline. The synthesis procedure and noncentrosymmetric crystal structure is already reported by Yu-Ye Yu [17]. We have grown a bulk crystal of the material with a dimension of size 7 X 4 X 3 mm<sup>3</sup> by slow evaporation solution growth technique and its structure is confirmed by single crystal X-ray diffraction method. A study on physical properties which affects the nonlinear optical performance of the material and detailed vibrational analysis has been carried out along with theoretical calculations. Refractive index and absorption coefficient of the material in the technically important 0-2THz region is also studied. Molecular vibrations responsible for THz phonon mode absorption in this range are investigated as well. The first order molecular hyperpolarizability calculation and experimentally observed SHG show that the grown crystal is a potential candidate for second order nonlinear optical processes.

#### 2.Synthesis and crystallization

The title material, 6-Methoxy-2-[(E)-phenyliminomethyl]phenol (OVAN) is prepared by condensation of Schiff base ortho-vanillin alternatively called 2-hydroxy-3methoxybenzaldehyde and aniline. Measured amount of ortho-vanillin is diluted in 20 ml of ethanol and stirred for 10 minutes. Equimolar amount of aniline is added to this drop by drop using a micropipette. The solution is stirred and refluxed for two hours and then set to cool. It is then transferred to a beaker and covered with perforated aluminum foil. The prepared solution is thus allowed for slow evaporation to form the crystals of red colour. This is recrystallised several times to get the purest crystal. Finally crystal of the size 7 X 4 X 3 mm<sup>3</sup> has been harvested. Photograph of the as grown crystal is shown in Fig.1a. Reaction scheme of the title material is given in Fig. 1b.



**Fig. 1: a)** Photograph of as grown OVAN crystal. **b)** Schiff's base condensation reaction of ortho-vanillin and Aniline in ethanol solvent to form 6-Methoxy-2-[(*E*)-phenyliminomethyl]phenol.

#### **3.Experimental details**

Single crystal X-ray diffraction experiment was performed on a Rigaku Saturn724 diffractometer using graphite monochromated Mo-Ka radiation at a temperature of 296 K. A complete data set was processed using Crystal Clear software. Perkin Elmer Frontier FTIR/FIR spectrometer was used to record FTIR spectrum in the wavenumber range of 4000 cm<sup>-1</sup> - 400 cm<sup>-1</sup>. JASCO V670 UV-vis-NIR spectrophotometer was used to record the UV-Visible absorption spectrum in the range 200 -1000 nm. Kurtz-Perry powder technique was employed to make a qualitative measurement of SHG efficiency. THz time domain spectroscopic studies (THz-TDS) were carried out using a TERA K8 terahertz spectrometer manufactured by Menlosystems. To decrease the absorption of THz radiation by water vapor, nitrogen gas was filled in to the spectrometer till the humidity reads less than 7%. The refractive index and absorption coefficient of VAN in the 0-2 THz regime were calculated by inbuilt software TeraMat attached with the spectrometer setup.

#### **4.Computational details**

Optimized molecular geometry of OVAN is computed using B3LYP (Becke, threeparameter, Lee-Yang-Parr) functional with 6-311++g(d,p) basis set. Gaussian 16, revision B.01 software package was used for computation and GaussView 06 program for visualization. [18, 19]. Most stable conformation obtained out of geometry optimization was further confirmed by a potential energy scanning over the possible dihedral angles. A vibrational analysis was carried out using the same level of theory and the FTIR spectrum of the material is simulated. VEDA 04

program was used to calculate the potential energy distribution of vibrational wavenumbers in the IR and THz region.

#### 5. Results and discussions

#### 5.1. X-ray diffraction analysis and geometry optimization

CCDC number	1914825
Empirical formula	C <sub>14</sub> H <sub>13</sub> NO <sub>2</sub>
Formula weight	227.25
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
a/Å	6.0826(5)
b/Å	9.1620(8)
c/Å	21.0100(16)
$\alpha/^{\circ}$	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1170.87(16)
Z	4
$\rho_{calc}g/cm^3$	1.289
$\mu/\text{mm}^{-1}$	0.087
F(000)	480.0
Crystal size/mm <sup>3</sup>	$0.33 \times 0.29 \times 0.23$
Radiation	MoKa ( $\lambda = 0.71073$ )
20 range for data collection/°	3.878 to 50.054
Index ranges	$-7 \le h \le 6, -10 \le k \le 10, -25 \le l \le 25$
Reflections collected	9765
Independent reflections	2057 [ $R_{int} = 0.0663$ , $R_{sigma} = 0.0467$ ]
Data/restraints/parameters	2057/0/156
Goodness-of-fit on F <sup>2</sup>	1.079
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0805, wR_2 = 0.2182$
Final R indexes [all data]	$R_1 = 0.1068, wR_2 = 0.2575$
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.28
Flack parameter	0.3(10)

Table 1. Crystal data and structure refinement for OVAN.



Fig. 2: Crystal packing view of OVAN along a-axis

Synthesis and crystal structure of the material OVAN is already reported[17]. To confirm the crystal structure we carried out single crystal X-ray diffraction experiment on the grown samples and the structure details obtained were found to be in agreement with the earlier structure report [17]. Also the crystallographic data obtained is in accordance with the 'Tables of bond lengths determined by X-ray and neutron diffraction. part 1 .bond lengths in organic compounds' by Frank H. Allen et. al [20]. The details of the crystal data and structure refinement is presented in Table 1. Fig. 2 shows the crystal packing view of the grown crystals along a-axis. As shown in Table 1, the material is found to be crystallized in orthorhombic crystal system with noncentrosymmetric space group  $P2_12_12_1$ .

Fig. 3a shows the optimized molecular arrangement of OVAN molecule in gas phase. Fig. 3b shows the orientation of a single molecule in the crystalline unit cell which is deduced out of the single crystal X-ray diffraction structure solution. Fig. 3a is generated using density functional theory (DFT) calculations in Gaussian software. This is the most stable conformation of the molecule's geometry which is confirmed after a potential energy surface scanning over the possible dihedral angles. Fig. 4 shows the variation of potential energy of the molecule when the dihedral angles C21-C20-N19-C17, C2-C3-O9-C10, H8-O7-C2-C1 are rotated through 360° with rotation steps of 10°. In all the three cases the lowest energy value is found as -746.705 Hartree. In all this three cases molecular orientation is similar to that obtained from the self consistent field equation solution which is shown in Fig. 3a. A comparison of the DFT optimized geometrical parameters with the experimental values has been carried out. Details are tabulated as Table A1 in appendix. The calculated geometrical parameters are found to be in good

agreement with the single crystal XRD measurements output. Most of the calculated bond lengths are same as the experimental observations up to two decimal places. C-H bond lengths are calculated to be 1.08 Å but it is found as 0.93 Å and 0.96 Å experimentally. This is expected as the DFT calculations are done in gas phase without considering intermolecular crystalline effects. Bond length O7-H8 has been calculated as 0.99 Å is found experimentally only of length 0.82 Å. This is the shortest bond because it makes an intermolecular hydrogen bonding with the nitrogen atom N19 [9]. It must be also in intermolecular hydrogen bonding relationships with the neighboring molecules in the unit cell. This is further confirmed by the difference in the simulated and experimental values of dihedral angle C1-C2-O7-H8 = 0.36 (simulated) and -138.0 (experimental) as visible in Fig. 3a and 3b. Also there exists a strong intramolecular hydrogen bonding between H8--O9 atoms in the molecule. The crystal packing diagram in Fig. 2 shows the unit cell of the crystal comprise of 4 molecules also linked through an intermolecular hydrogen boding between O9--H29 between neighboring molecules. This O9--H29 hydrogen bonding can be further confirmed by the abnormal difference in the simulated and experimental bond angle value of O9-C10-H11 = 105.74 (simulated) and 109.5 (experimental). The existence of C17-N19 bond of length 1.28 Å is a confirmation of the occurrence of intended Schiff base condensation reaction between the ortho-vanillin and aniline moieties of the title material. Different dihedral angle values will help us to see how planar the molecule is. The two rings in the molecule exist in different planes. The difference in the dihedral angle values C17-N19-C20-C25 = 144.14, C2-C1-C17-N19 = -0.62 confirms that the two rings are not coplanar. But the bridge atoms connecting the two rings C1, C17, N19 and C20 are sharing almost the same spatial plane as the dihedral angle C1-C17-N19-C20 value reads 177.23. The dihedral angle C2-C1-C17-N19 = -0.62 also show that first three of the above mentioned bridge atoms lie in the same plane of ortho-vanillin ring. The dihedral angle values C2-C3-O9-C10 = -179.80, C4-C3-O9-C10 = 0.2 shows that the carbon atom C10 of the methoxy group lies in the same plane of the ring. This in turn enlights into the vibrational analysis of the molecule. It is proved that the methoxy group lying in the same plane with the attached ring structure may cause a higher wavenumber value for its asymmetric and symmetric stretching. This is discussed in the section methoxy group vibration in vibrational analysis part in this report. The dihedral angle value C3-O9-C10-H11 = 179.87 shows even the hydrogen atom H11 is also in the same plane of the ring and methoxy carbon. But the other two hydrogen atoms of the methoxy group lies out of plane

from the ring. This is evident from the dihedral angle values C3-O9-C10-H12 = 61.16, C3-O9-C10-H13 = -61.42. C1-C17 is the largest C-C bond length observed which is equal to 1.45 Å. Most of the other C-C bond lengths are around 1.41 Å. This shows that the molecule is highly conjugated and there is a large delocalization of  $\pi$  electrons. C3-C4 (1.39 Å), C5-C6 (1.38 Å), C21-C22 (1.39 Å), C22-C23 (1.39 Å), C23-C24 (1.39 Å), C24-C25 (1.39 Å), are the shortest C-C bonds observed. It means  $\pi$  electron population is higher at these positions. The largest  $\pi$  electron concentration is located at C17-N19 where we have the shortest bond length of 1.28 Å. The bond lengths C2-O7 (1.34 Å) and C3-O9 are also comparatively shorter as the two oxygen atoms make major contribution to the  $\pi$  electron delocalization in the ring.



**Fig. 3: a).**Optimized molecular structure of 6-Methoxy-2-[(*E*)-phenyliminomethyl]phenol using B3LYP/6-311++G(d,p) level of DFT. **b**) Orientation of a single molecule in the crystal unit cell obtained from single crystal



Fig. 4: Two dimensional potential energy scan curves of OVAN at B3LYP/6-311++G(d,p) level

#### 5.2. Vibrational analysis



Fig. 5: a) Simulated B3LYP/6-311++G(d, p) level IR spectrum. b) FT-IR spectrum of OVAN recorded in the range 4000-400 cm<sup>-1</sup>

#### 5.2.1. Hydroxyl group vibrations

Fig. 5a and 5b show the simulated and experimental IR absorption bands for OVAN. Major absorption peaks and vibrational assignments are detailed in Table 2. The sharp band at 3065 cm<sup>-1</sup> in the simulated spectrum stands for the absorption due to O-H stretching vibrations. Experimentally a very weak absorption band is found at 3080 cm<sup>-1</sup>. This is usually expected in and around 3600 cm<sup>-1</sup> without the influence of intra/inter- molecular hydrogen bonds[21, 22]. The experiment was performed using solid powder sample which has all its crystalline nature prevalent. Therefore in the experimentally observed spectrum O-H stretching band is found to be weakened and shifted towards a lower wavenumber. This is due to the effect of strong intramolecular N19-H8 and intermolecular C-H--O hydrogen bonds[17]. The sharp band at 1195 cm<sup>-1</sup> supports this argument as it confirms the existence of strong intermolecular hydrogen bonding[23]. Absorption due to O-H in-plane and out-of-plane bending vibrations are observed at 1443 cm<sup>-1</sup> and 690 cm<sup>-1</sup> respectively. The out-of-plane bending vibration can vary from 800 cm<sup>-1</sup> to 300 cm<sup>-1</sup> according to the strength of prevailing hydrogen bonds with the O-H atoms[24].

Therefore the O-H out-of-plane bending vibration located at 694 cm<sup>-1</sup> further reaffirms the existence of strong hydrogen bonds in the crystal.

#### 5.2.2. Methoxy group vibrations

The dihedral angle value C2-C3-O9-C10 = -179.80 shows that carbon atom of methoxy group lies in the plane of phenyl ring. This indicates that the asymmetric and symmetric stretching wavenumbers of methoxy group will possess a high value. This is found to be satisfied as we observed two clear absorption peaks at 2956 cm<sup>-1</sup> and 2837 cm<sup>-1</sup> corresponding to –CH3 asymmetric and symmetric stretching respectively. Presence of a methoxy group can be confirmed with the existence of the –CH3 symmetric stretching band in between 2840 cm<sup>-1</sup> to 2815 cm<sup>-1</sup> [23]. Sharp peak at 1464 cm<sup>-1</sup> and 1409 cm<sup>-1</sup> is attributed to the asymmetric and symmetric deformation of methoxy group respectively[9, 24]. C-O-C stretching vibration associated with methoxy group (C10-O9-C3) is expected in the range 1310 cm<sup>-1</sup> – 1020 cm<sup>-1</sup> [24]. In the experimental spectrum asymmetric and symmetric C-O-C stretching is found at 1251 cm<sup>-1</sup> and 1075 cm<sup>-1</sup> respectively. Absorption bands in the region 580 cm<sup>-1</sup> to 505 cm<sup>-1</sup> is a specification of aromatic compounds with methoxy group. This is spotted as the C-O-C in-plane deformation bands at 549 cm<sup>-1</sup> and 555 cm<sup>-1</sup> in the experimental spectrum.

#### 5.2.3. C=N Vibrations

In case of the title material, a characteristic peak for C=N vibration can show that the proposed chemical reaction has occurred and the synthesis procedure is successful. The sharp peak is found experimentally at  $1613 \text{ cm}^{-1}$ .

Scaled Wavenumber <sup>a</sup> (cm <sup>-1</sup> )	Experimental IR Wavenumber (cm <sup>-1</sup> )	Relative Intensity <sup>b</sup> (Calculated)	Assignments
3065	3080	88.52	O7-H8 stretching
2957	2956	12.77	CH <sub>3</sub> asymmetric stretching.
2914	2837	20.56	CH <sub>3</sub> symmetric stretching.
1619	1613	45.22	C=N vibrations
1470	1464	5.26	O-CH <sub>3</sub> asymmetric deformation
1448	1443	2.33	O-H in plane bending
1413	1409	6.70	O-CH <sub>3</sub> Symmetric deformation
1358	1361	7.79	CH <sub>3</sub> in-plane bending
1251	1251	100	Asymmetric C-O-C stretching
1186	1195	32.33	Strong intermolecular hydrogen bonds,
			O-H bending.
1094	1091	5.61	C-O asymmetric stretching
1072	1075	7.25	Symmetric C-O-C stretching
680	690	8.13	O-H out of plane deformation
569	549	2.49	C-O-C in plane deformation
542	535	0.68	C-O-C in plane deformation

**Table 2.** Calculated vibrational wavenumbers and measured IR band positions and assignments for VAN <sup>*a*</sup>Obtained from the wave numbers calculated at B3LYP/6-311++G(d,p) using scaling factors 0.9673 <sup>*b*</sup>Relative absorption intensities normalized with highest peak absorption equal to 100.



#### 5.3. THz spectroscopy



**Fig. 6: a)** THz transmission signal recorded in the time domain with and without the sample. **b)** Fast Fourier transformed frequency domain spectrum obtained by dividing amplitude of the transmitted wave through the sample by reference amplitude. Y-axis is plotted on a logarithmic scale to the base 10

Fig. 6a shows the amplitude of transmitted THz signal in the time domain. Black line represents blank measurements and red line shows the measurement on the sample. Fig. 6b shows the measured THz absorption spectrum in the frequency domain which is calculated by dividing the amplitude of THz signal transmitted through the sample by the amplitude obtained in the blank measurements. Three major absorption dips are found in this spectrum at 0.89 THz, 1.19 THZ and at 1.55 THz. In many cases it has been reported that absorptions in the range 0-2 THz is due to intermolecular vibrations and their assignments are generally difficult [25-27]. Jongtaek Kim et al reported assignments for molecular vibrations of OH1 crystal for its THz absorption [7]. In their report it was shown that vibrational absorption spectrum calculated in the gas phase for a single molecule of OH1 is showing considerable similarity to the absorption spectrum calculated for OH1 crystal [7]. Based on this we have performed calculations of THz phonon mode vibrations of OVAN in the gas phase and tried to assign them to its THz absorption modes. THz phonon mode vibrations of OVAN was simulated by Gaussian software package[18]. The simulated vibrations were visualized using GaussView program[19]. The phonon mode absorptions were assigned to different molecular vibrations using VEDA 04 program[28]. In the simulation THz phonon mode absorptions are found at 1.00 THz, 1.34 THz and at 1.84 THz. This can be considered analogous to the experimental THz absorption values mentioned above as 0.89 THz, 1.19 THz and at 1.55 THz. The small shift in the calculated value

Frequency in THz		Relative	Vibrational assignments (PED %)
		Intensity <sup>b</sup>	Only contributions $\geq 10\%$ are listed
Calculated <sup>a</sup>	Observed	(Calculated)	
			Ó
0.99	0.89	0.11	τC17-N19-C20-C25(37), τC2-C1-
			C17-N19 (15), TC1-C17-N19-C20
			(20),
1.34	1.19	0.68	τC17-N19-C20-C25(32), τC5-C6-
			С1-С17 (16), тС1-С17-N19-С20
		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	(18),
1.84	1.55	0.13	δ C17-N19-C20(33), δ C1-C17-N19
		$\circ$	(21),

is due to the non consideration of crystalline effects. According to the Gaussian outputs the observed THz absorptions are attributed to different molecular vibrations as in Table 3.

**Table 3.** Calculated THz vibrational wavenumbers, measured THz absorption band positions (cm<sup>-1</sup>) and assignments for OVAN *Abbreviations:*  $\delta$ : *bending,*  $\tau$ : *torsion* 

<sup>a</sup>Obtained from the wave numbers calculated at B3LYP/6-311++G(d,p) using scaling factors 0.9673

<sup>b</sup>*Relative absorption intensities normalized with highest peak absorption equal to 100.* 



**Fig. 7: a)** Absorption coefficient of OVAN in the 0-2THz range. **b)** Refractive index of OVAN in the 0-2 THz region **c)** Extinction coefficient of OVAN in the 0-2 THz region.

Absorption coefficient and THz refractive index of the material is given in Fig. 7a and 7b as obtained from the TeraMat software. There is a moderate absorption of THz radiation after 0.5 to 2 THz by the title material. Fig. 7a shows that maximum THz absorption is found as 49 cm<sup>-1</sup> at 1.54 THz. There are three peak values of absorption coefficient 30 cm<sup>-1</sup>, 36 cm<sup>-1</sup>, and 49 cm<sup>-1</sup> at 0.89 THz, 1.19 THz, 1.55THz which correspond to the phonon mode absorptions we already discussed. Refractive index of the material in the 0.2 to 2 THz regime is found varying in the range 1.85 to 2.0. The imaginary part of refractive index (Extinction coefficient) is calculated and depicted in Fig. 7c. From Fig. 7a and 7c, we can see that behavior of variation of extinction coefficient varies in the range 0.1 to 0.8.

#### 5.4. UV-Visible spectroscopy

Absorbance in the UV-Visible spectral range has been measured using a UV spectrometer from 200nm to 800nm wavelength region. The calculated % transmittance and the Tauc plot has been given in Fig. 8a and 8b [29, 30]. In Fig. 8a the lower transmission cut off is marked at 500nm. It means the absorption of light is maximum by the material below this value. The material is nearly 80% transparent to light above 500 nm. The material's good transparency of green light (> 500 nm) makes it suitable for second harmonic generation using the widespread 1064 nm Nd-YAG lasers. We extrapolated the  $(\alpha h\nu)^2$  Vs hv graph shown in the Fig. 8b to the X –axis to meet it at the value of 2.01 eV which represents the optical band gap of the material. The optical band gap of VAN which has a very close structure with the title material was reported as 3.49 eV in [15].



Fig. 8: a) UV transmission spectrum of OVAN measured in the range 200-800 nm. b) Tauc plot of OVAN

#### 5.5. Frontier Molecular orbital calculations

A molecular orbital is a mathematical function that describes the behavior of an electron or pair of electrons with in a molecule. These functions are typically plotted as surfaces around the molecular structure. Although these orbitals are actually mathematical conveniences and not physical quantities, they are very useful for qualitative description of bonding and reactivity[31]. While designing materials for nonlinear optical applications, material structures with relatively low HOMO-LUMO band gap is usually preferred. High charge transfer is associated with such molecules of low HOMO-LUMO band gap and hence high nonlinear optical response is observed with them. The exact correlation functional to calculate HOMO eigenvalue, LUMO eigenvalue and the value of energy gap between them is not known. It has been reported that more accurate LUMO eigenvalues can be calculated by first calculating HOMO-LUMO energy gap and adding HOMO eigenvalue to it. Zhang and Musgrave reported a linear correlation equation to get corrected values of these parameters. Here we performed the frontier molecular orbital calculation using the B3LYP functional and 6-311++g(d,p) basis set of DFT. The output obtained is then corrected using the correlation equation (1) introduced by Zhang and Musgrave[32]. The results are tabulated in Table 4 comparing with the geometrically similar material VAN for which the calculations are already reported by the authors in [9]. Fig. 9(a) and 9(b) shows the distribution of HOMO and LUMO orbitals over the molecular structure. They are shown as transparent surfaces in order to see their orientation more easily. The positive and negative orbital lobes are displayed in different colors. It can be seen that a major part of HOMO orbital surface is distributed over the ortho-vanillin moiety of the title material whereas LUMO is distributed uniformly over both the rings. But there is no contribution from the methoxy ring towards the LUMO orbital. As per Table 4 corrected HOMO, LUMO eigenvalues and their band gap are found as -8.49 eV, -5.88 eV and 2.6 eV respectively. The HOMO-LUMO band gap of 2.6 eV is quite small and it favors good intermolecular charge transfer and hence high nonlinear optical performance as well. This electronic band gap was reported as 2.85 eV for the geometrically similar VAN. The colour difference of the two crystals VAN and OVAN can be accounted by this difference of 0.25 eV in the electronic band gap. The only difference in the molecular structure of VAN and OVAN is the position of -OH group in the vanillin moiety.

$$-HOMO_{corr} = A + B x (-HOMO_{cal})$$
(1)



Fig. 9: a) HOMO plot of OVAN. b) LUMO plot of OVAN. Both generated using B3LYP functional and 6-311++g(d,p) basis set.

	Calculated	l value (eV)	Corrected v	value (eV)
	OVAN	VAN	OVAN	VAN
HOMO eigen value	-5.89	-5.92	-8.49	-8.52
LUMO eigen value	-1.99	-1.76	-5.88	-5.68
HOMO-LUMO energy	3.90	4.16	2.60	2.85
gap				

**Table. 4:** HOMO energy, LUMO energy and HOMO-LUMO gap values calculated using B3LYP functional and corrected by equation (1).

#### 5.6. Hyperpolarizability calculations and second harmonic generation

The search for materials suitable for nonlinear optical applications focuses on ones having a very large hyperpolarizability. The dynamic first order hyperpolarizability of the molecule at a specified input laser wavelength will represent the second harmonic generation efficiency of the material with the same wavelength of incident light. But computing the nonlinear optical related properties of organic molecules is computationally intensive. Conventional hybrid DFT functionals perform adequately with for compounds with moderate electron delocalization. However they are known to overestimate these properties for systems

with significant electron delocalization. In order to ameliorate this effects we used the Coulombattenuating model employing B3LYP hybrid functional (CAM-B3LYP) in our calculations along with 6-311++g(d,p) basis set. When comparing the observed experimental values with this predicted hyperpolarizability values from Gaussian, we multiply the predicted values by a factor of  $\frac{1}{2}$  [31]. Therefore both these values are separately shown in Table 5. Table 5 also shows a comparison of dipole moment, polarizability and wavelength dependent hyperpolarizability at 1064 nm of the title material with those of the geometrically similar VAN and the benchmark urea. Dipole moment of OVAN molecule is 1.8 times higher than that of VAN, but it is 1.8 times lesser than that of urea. Polarizability of OVAN is exactly similar to that of VAN and it is 6 times higher than that of urea. Interestingly molecular hyperpolarizability of OVAN is 10 times higher than that of urea. But it is found 2.5 times lesser than that of geometrically similar VAN. A semi-qualitative measurement of the second harmonic generation efficiency of the material was calculated employing the widely used Kurtz-Perry powder technique [33]. The powdered sample was filled in a capillary tube and placed in the beam path of a 1064 nm laser radiation with a pulse width of 10 ns and repetition rate of 10 Hz comprising an input energy of 1.2 mj/pulse. The observed SHG intensity is tabulated in Table 5 comparing with VAN and Urea along with their hyperpolarizability values. As expected from the hyperpolarizability values the observed second harmonic generation output for OVAN is lesser than that for VAN.

Material	Dipole	Polarizability	Hyperpolarizability	Hyperpolarizability/2	Observed
	moment	(esu)	at 1064 nm. (esu)	(esu)	SHG
	(esu)				Intensity
		<u>)</u>			(mV)
OVAN	2.428 x 10 <sup>-</sup> 18	3.0005 x 10 <sup>-</sup> 23	9.7316 x 10 <sup>-30</sup>	4.8658 x 10 <sup>-30</sup>	5
VAN	1.3625 x 10 <sup>-</sup> 18	3.056 x 10 <sup>-23</sup>	2.434 x 10 <sup>-29</sup>	1.217 x 10 <sup>-29</sup>	10
Urea	4.4755 x 10 <sup>-</sup> 18	4.906 x 10 <sup>-24</sup>	9.49 x 10 <sup>-31</sup>	4.745 x 10 <sup>-31</sup>	12

**Table. 5:** Comparison of dipole moment, polarizability, hyperpolarizability and experimental second harmonic generation output values of OVAN, VAN and urea.

#### 6. Conclusion

Bulk single crystals of 6-Methoxy-2-[(*E*)-phenyliminomethyl]phenol is grown by slow evaporation solution growth technique using ethanol solvent. Theoretically simulated vibrational bands in the IR region are found in good agreement with the experimental output. The material is transparent to wavelength above 500 nm enabling it for second harmonic generation using widespread 1064 nm Nd:YAG lasers. The optical band gap of the material is obtained as 2.01 eV. THz refractive index of the material is found varying in the range 1.85 to 2.0. Material shows moderate absorption of THz in the measured range of 0-2 THz. The HOMO-LUMO energy gap of the material is only 2.6 eV. This is close to the value of geometrically similar VAN. First order molecular hyperpolarizability is calculated as 9.7316 x  $10^{-30}$  which is 10 times higher than that of urea. The low HOMO-LUMO band gap and high hyperpolarizability value shows that the material can be used for second order nonlinear optical processes including second harmonic generation. Kurtz-Perry experimental results shown in Table 5 confirm the good second harmonic generation capability of the material.

Bond length		Bond Angle		Dihedral Angle				
Parameters	Calc	XRD	Parameters	Calc	XRD	Parameters	Calc	XRD
C1-C2	1.413	1.401	C2-C1-C6	119.78	118.7	C6-C1-C2-C3	0.17	0.7
C1-C6	1.412	1.383	C2-C1-C17	120.8	120.5	C6-C1-C2-O7	-179.78	-179.2
C1-C17	1.45	1.436	C6-C1-C17	119.41	120.5	C17-C1-C2-C3	-179.89	174.7
C2-C3	1.417	1.394	C1-C2-C3	119.24	118.8	C17-C1-C2-O7	0.16	-5.2
C2-O7	1.337	1.347	C1-C2-O7	122.52	121.4	C2-C1-C6-C5	-0.17	-1.0
C3-C4	1.39	1.361	C3-C2-O7	118.23	119.8	C2-C1-C6-H16	179.88	178.4
C3-O9	1.359	1.368	C2-C3-C4	119.64	120.4	C17-C1-C6-C5	179.89	-175.5
C4-C5	1.405	1.393	C2-C3-O9	115.17	114.5	C17-C1-C6-H16	-0.06	4.0
C4-H14	1.082	0.930	C4-C3-O9	125.19	125.0	C2-C1-C17-H18	-179.74	179.8
C5-C6	1.378	1.34	C3-C4-C5	120.94	120.7	C2-C1-C17-N19	-0.62	-0.1
C5-H15	1.083	0.931	C3-C4-H14	119.95	119.6	C6-C1-C17-H18	0.21	-6.0
C6-H16	1.085	0.931	C5-C4-H14	119.11	119.6	C6-C1-C17-N19	179.33	173.9
O7-H8	0.994	0.820	C4-C5-C6	119.93	118.8	C1-C2-C3-C4	-0.06	-1.1
O9-C10	1.42	1.43	C4-C5-H15	119.45	120.5	C1-C2-C3-O9	179.94	-177.6
C10-H11	1.089	0.960	C6-C5-H15	120.61	120.7	07-C2-C3-C4	179.89	178.8

#### Appendix

C10-H12	1.096	0.960	C1-C6-C5	120.46	122.5	07-C2-C3-O9	-0.11	2.3
С10-Н13	1.096	0.960	C1-C6-H16	118.92	118.8	С1-С2-О7-Н8	0.36	-138.0
C17-H18	1.096	0.931	C5-C6-H16	120.62	118.7	С3-С2-О7-Н8	-179.6	42.1
C17-N19	1.288	1.285	С2-О7-Н8	107.14	109.5	C2-C3-C4-C5	-0.05	2.0
N19-C20	1.409	1.420	C3-O9-C10	118.38	117.0	C2-C3-C4-H14	-179.98	-177.7
C20-C21	1.403	1.399	O9-C10-H11	105.74	109.5	O9-C3-C4-C5	179.95	-178.3
C20-C25	1.402	1.383	O9-C10-H12	111.46	109.4	O9-C3-C4-H14	0.02	-2.0
C21-C22	1.393	1.367	O9-C10-H13	111.46	109.5	C2-C3-O9-C10	-179.8	164.6
C21-H30	1.084	0.930	H11-C10-H12	109.33	109.5	C4-C3-O9-C10	0.2	-11.7
C22-C23	1.394	1.37	H11-C10-H13	109.33	109.5	C3-C4-C5-C6	0.06	-3.0
C22-H29	1.084	0.931	H12-C10-H13	109.43	109.5	C3-C4-C5-H15	-179.96	176.9
C23-C24	1.395	1.38	C1-C17-H18	116.24	118.3	H14-C4-C5-C6	179.99	176.9
C23-H28	1.084	0.930	C1-C17-N19	122.74	123.4	H14-C4-C5-H15	-0.03	-3.0
C24-C25	1.391	1.38	H18-C17-N19	121.02	118.3	C4-C5-C6-C1	0.05	3.0
C24-H27	1.084	0.930	C17-N19-C20	121.18	121.0	C4-C5-C6-H16	-180	-177.3
C25-H26	1.084	0.931	N19-C20-C21	122.84	124.0	H15-C5-C6-C1	-179.93	-177.3
-	-	-	N19-C20-C25	118.0	117.1	H15-C5-C6-H16	0.02	3.0
-	-	-	C21-C20-C25	119.12	119.0	C3-O9-C10-H11	179.87	-170.2
-	-	-	C20-C21-C22	120.18	121.2	С3-О9-С10-Н12	61.16	69.8
-	-	-	C20-C21-H30	119.84	119.3	С3-О9-С10-Н13	-61.42	-50.2
-	-	-	C22-C21-H30	119.94	119.3	C1-C17-N19-C20	177.23	-175.8
-	-	-	C21-C22-C23	120.43	119.7	H18-C17-N19-C20	-3.69	4.3
-	-	-	C21-C22-H29	119.53	120.2	C17-N19-C20-C21	-38.26	30.7
-	-	-	С23-С22-Н29	120.03	120.2	C17-N19-C20-C25	144.14	-150.8
-	-	-	C22-C23-C24	119.54	119.3	N19-C20-C21-C22	-179.17	-179.1
-	-	-	С22-С23-Н28	120.2	120.3	N19-C20-C21-H30	-1.32	1.0
-	-	-	C24-C23-H28	120.25	120.4	C25-C20-C21-C22	-1.59	2.5
-	-	-	C23-C24-C25	120.35	121.8	С25-С20-С21-Н30	176.26	-177.5
-	-	-	C23-C24-H27	120.05	119.1	N19-C20-C25-C24	179.82	-178.7
-	-	-	C25-C24-H27	119.6	119.1	N19-C20-C25-H26	-0.97	-1.0
-	-		C20-C25-C24	120.35	118.9	C21-C20-C25-C24	2.12	-2.8
	-	-	C20-C25-H26	118.75	120.4	С21-С20-С25-Н26	-178.67	177.4
	-		C24-C25-H26	120.9	120.5	C20-C21-C22-C23	0.18	-1.0
-	-	-	-	-	-	С20-С21-С22-Н29	179.37	179.0
-	-	-	-	-	-	H30-C21-C22-C23	-177.67	179.0
-	-	-	-	-	-	H30-C21-C22-H29	1.52	-1.0
-	-	-	-	-	-	C21-C22-C23-C24	0.72	0.0
-	-	-	-	-	-	С21-С22-С23-Н28	179.8	179.8
-	-	-	-	-	-	H29-C22-C23-C24	-178.47	179.8
-	-	-		-	-	H29-C22-C23-H28	0.61	0.0
-	-	-		-	-	C22-C23-C24-C25	-0.18	0.0
-	-	-	-	-	-	C22-C23-C24-H27	179.35	179.9

-	-	-	-	-	-	H28-C23-C24-C25	-179.26	179.9
-	-	-	-	-	-	H28-C23-C24-H27	0.27	0.0
-	-	-	-	-	-	C23-C24-C25-C20	-1.25	2.0
-	-	-	-	-	-	С23-С24-С25-Н26	179.55	-178.5
-	-	-	-	-	-	H27-C24-C25-C20	179.21	-178.4
-	-	-	-	-	-	H27-C24-C25-H26	0.02	1.0

Table A1. DFT optimized and experimental geometrical parameters

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Graphical abstract



#### <u>Highlights</u>

- Good quality NLO crystals of 6-Methoxy-2-[(E)-phenyliminomethyl]-phenol
- THz spectroscopic studies have been carried out in the 0-2 THz region
- Molecular vibrations responsible for THz phonon modes have been identified
- THz Absorption coefficient and refractive index of the material is calculated.
- An organic material with HOMO-LUMO energy gap of only 2.6 eV.

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