

## FT-IR Spectroscopic Studies and Gaussian 03 Calculations of 2, 2'-Ethylenebis(nitrilomethylidene)diphenol

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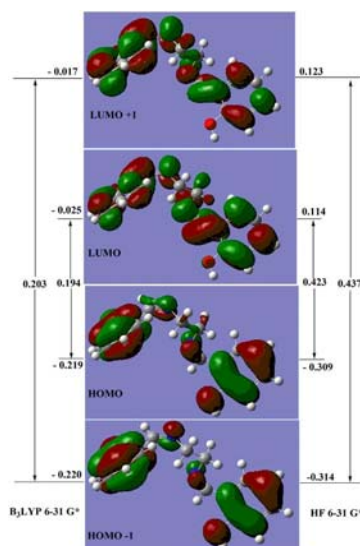
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### ABSTRACT

The vibrational wavenumbers and corresponding vibrational assignments of 2,2'-Ethylene bis(nitrilomethylidene) diphenol are examined theoretically using the Gaussian03 set of quantum chemistry codes. Comparison of the observed IR spectra with the calculated results by Hartree-Fock and B<sub>3</sub>lyp method is found in agreement with the experimental data. Theoretical infrared and Raman intensities are reported. The atomic orbital compositions of the frontier molecular orbital for SalenH<sub>2</sub> molecule is shown by the following figure.



**Keywords:** Schiff base, IR, Raman, Gaussian 03, Vibration, Strength, Bending.

## INTRODUCTION

Schiff base ligands represent one of the most widely utilized classes of ligands in coordination chemistry.<sup>1</sup> Their complexes find many important catalytic applications ranging from asymmetric epoxidation,<sup>2</sup> Lewis acid assisted organic transformations,<sup>3</sup> ring opening of epoxides,<sup>4</sup> to various types of polymerization,<sup>5-8</sup> as well as their widespread use as model compounds for the study of the active sites of metallo-enzymes<sup>9</sup> and other applications such as; solid phase extraction of metal ions,<sup>10</sup> preparation of the ion selective electrodes<sup>11-15</sup> and etc. With attention to the importance of these ligands, each year many literatures have been published from synthesis of these compounds through two component reactions to their application in different fields for various purposes.

Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wave number, phase or other physical properties.<sup>16</sup> Organic molecules, able to manipulate photonic signals efficiently, are of importance in technologies such as optical communication, optical computing and dynamic image processing.<sup>17,18</sup> Phenyl substituent's can increase molecular hyperpolarizability, a result described as surprising.<sup>19,20</sup>

Many organic molecules, containing conjugated  $\pi$  electrons and characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy.<sup>21</sup> *ab initio* quantum mechanical method is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the theoretical calculations of the wavenumbers and first hyperpolarizability of the title compound are reported and compared with experimental data.

## EXPERIMENTAL

All reagents and solvents were obtained from Merck Chemical Inc. were purchased and used as received. The FT-IR spectrum was recorded using

KBr on a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI). The spectral resolution was  $4\text{ cm}^{-1}$ .

## Synthesis of 2,2'-Ethylenebis (nitrilomethylidene)diphenol:

To the stirred solution of Salicylaldehyde (4 mmol) in 5ml MeOH Ethylendiamine (2 mmol) was added at room temperature. The reaction was continued for 3.4 min. The progress of the reaction was monitored by TLC. After the reaction was completed, the brown oil was collected and dissolved in hot petroleum ether. After cooling yellow solid product was obtained. The precipitate was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, 2,2'-Ethylene bis(nitrilomethylidene) diphenol was obtained in 99% yield, m.p.=127-128°C.

## Computational details

Calculations of the title compound were carried out with Gaussian03 program<sup>22</sup> using the HF/6-31G\* and B3lyp/6-31G\* basis set to predict the molecular structure and wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wave number values computed at the Hartree-Fock and DFT level contain known systematic errors due to the negligence of electron correlation<sup>23</sup>. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G\* and B3lyp/6-31G\* basis set.<sup>23</sup> Parameters corresponding to optimized geometry of 2,2'-Ethylene bis (nitrilomethylidene)diphenol (Scheme.1) are given in Table 1. The absence of imaginary wave number on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

## RESULTS AND DISCUSSION

The aromatic compounds, the asymmetric stretching vibrations of  $\text{CH}_2$  are expected in the range of  $2905\text{-}3000\text{ cm}^{-1}$  and symmetric  $\text{CH}_2$  vibrations in the range of  $2860\text{-}2870\text{ cm}^{-1}$ .<sup>24,25</sup> The asymmetric stretching modes of the methyl group

are calculated to be at 2940, 2895  $\text{cm}^{-1}$  and the symmetric mode at 2847  $\text{cm}^{-1}$ . Two bending vibrations can occur within a methylene group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending vibration, involves out-of phase bending of the C-H bonds. The asymmetrical deformations are expected in the range<sup>24</sup> of 1400-1485  $\text{cm}^{-1}$ . The calculated values of  $\delta_{\text{as}}\text{CH}_2$  modes are 1462 and 1429  $\text{cm}^{-1}$ . In many molecules, the symmetric deformation  $\delta_{\text{as}}\text{CH}_2$  are expected in the region<sup>24</sup> 1380  $\pm$ 25  $\text{cm}^{-1}$ .

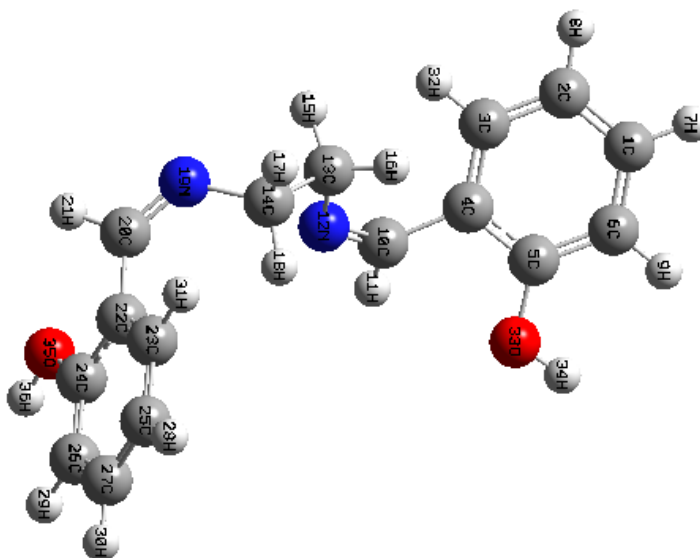
The HF calculations give  $\delta_{\text{as}}\text{CH}_2$  at 1465  $\text{cm}^{-1}$ . The bands observed at 1499, 1462 and 1420  $\text{cm}^{-1}$  in the IR spectrum are assigned as deformation bands of the methylene group. Aromatic molecules display a methyl rock<sup>24</sup> in the neighborhood of 1051  $\pm$ 100  $\text{cm}^{-1}$ . The second methyl rock<sup>24</sup> in the region 945  $\pm$ 10  $\text{cm}^{-1}$  is more difficult to find among the C-H out-of-plane deformations. For the title compound, these modes  $\rho\text{CH}_2$  are calculated at 1215 and 1199  $\text{cm}^{-1}$ . The band observed at 1116 and 1107  $\text{cm}^{-1}$  in the IR spectrum is assigned as methyl rocking vibration.

The broad band observed in the IR spectrum at 3450  $\text{cm}^{-1}$  is assigned to the asymmetric stretching mode<sup>26</sup> of OH. The OH stretching modes are expected in the region<sup>24</sup> 3250-3480  $\text{cm}^{-1}$ .

Primary aromatic amines with nitrogen directly attached to the ring absorb in the region 1260  $\pm$ 60  $\text{cm}^{-1}$  due to the stretching vibration of the phenyl carbon-nitrogen bond<sup>25, 27, 28</sup>. We have observed this  $\nu\text{CN}$  mode at 1294, 1285, 1249, 1221 and 1200  $\text{cm}^{-1}$  in the IR spectrum and at 1313, 1312, 1297, 1296 and 1299  $\text{cm}^{-1}$  theoretically. The phenyl CH stretching vibrations occur above 3000  $\text{cm}^{-1}$  and is typically exhibited as multiplicity of weak to moderate bands, compared with the aliphatic CH stretching.<sup>29</sup> In the present case, the HF calculations give  $\nu\text{CH}$  modes in the range 3280  $\pm$ 80  $\text{cm}^{-1}$ . The bands observed at 3100 and 3050  $\text{cm}^{-1}$  in the IR spectrum is assigned as phenyl CH stretching modes. For tri-substituted phenyl ring,  $\nu\text{Ph}$  modes<sup>24</sup> are seen in the Range 1640-1400  $\text{cm}^{-1}$ . In the present case, the  $\nu\text{Ph}$  modes are observed at 1673, 1501, 1467 and 1465  $\text{cm}^{-1}$  in the IR spectrum and at 1578, 1499, 1462 and 1420  $\text{cm}^{-1}$  theoretically.

In asymmetric tri-substituted benzene, when all the three substituent's are light, the wave number interval of ring breathing mode<sup>35</sup> is between 500 and 600  $\text{cm}^{-1}$ . In the case of mixed substituent's, the wave number is expected<sup>35</sup> to appear between 600 and 750  $\text{cm}^{-1}$ .

When all the three substituent's are heavy, the ring breathing mode is expected around 1100  $\text{cm}^{-1}$ . For the title compound, the band calculated at



**Scheme.1: Optimized of 2,2'-Ethylene bis (nitrilomethylidene)diphenol**

**Table 1: Calculated vibrational wave numbers (scaled), measured infrared band positions and assignments for 2,2'-Ethylene bis (nitrilomethylidene)diphenol**

$\nu$ (cm <sup>-1</sup> )	HF/6-31G*		B3LYP/6-31G*			$\nu_{(IR)}$ (cm <sup>-1</sup> )	Assignments
	IR Intensity	Raman Activity	$\nu$ (cm <sup>-1</sup> )	IR Intensity	Raman Activity		
3887.42	104.877	117.87	3831.98	57.83	147.93		$\nu$ OH
3885.53	101.59	114.08	3828.97	56.97	145.39	3450 b	$\nu$ OH
3433.33	12.05	133.78	3358.52	11.25	152.57		$\nu$ CH <sub>Ph</sub>
3426.79	19.20	188.25	3353.54	17.19	198.99		$\nu$ CH <sub>Ph</sub>
3418.95	28.64	123.97	3346.08	20.88	112.94		$\nu$ CH <sub>Ph</sub>
3413.61	28.27	62.57	3340.67	21.01	60.57		$\nu$ CH <sub>Ph</sub>
3403.45	9.37	88.80	3333.14	7.41	95.13		$\nu$ CH <sub>Ph</sub>
3401.03	6.37	83.42	3331.02	3.98	84.01	3100 w	$\nu$ CH <sub>Ph</sub>
3383.48	16.33	81.48	3313.62	15.80	87.41	3050 w	$\nu$ CH <sub>Ph</sub>
3383.33	14.41	75.74	3313.52	13.98	82.13		$\nu$ CH <sub>Ph</sub>
3373.62	21.27	70.91	3294.4	21.94	75.24		$\nu$ CH <sub>C=N</sub>
3367.53	30.01	112.14	3288.19	29.60	119.85	2728 m	$\nu$ CH <sub>C=N</sub>
3294.76	48.55	15.98	3229.99	31.32	21.86	2930 m	$\nu_{as}$ CH <sub>2</sub>
3281.51	13.20	70.92	3219.68	11.03	67.31	2901 m	$\nu_s$ CH <sub>2</sub>
3231.14	64.06	148.82	3162.57	38.57	157.11	2870 m	$\nu$ CH <sub>2</sub>
3215.04	12.84	26.83	3148.66	16.46	36.93		$\nu$ CH <sub>2</sub>
1910.83	140.35	264.09	1822.63	108.8	221.33		$\nu$ Ph
1901.78	232.67	207.66	1815.34	137.56	229.85		$\nu$ Ph
1823.73	42.33	67.61	1709.31	39.73	72.79		$\nu$ Ph
1821.66	54.12	63.72	1708.75	39.88	107.53		$\nu$ Ph
1797.53	15.29	8.94	1695.54	23.08	13.28		$\nu$ Ph
1796.96	13.13	9.51	1694.97	20.77	16.08		$\nu$ Ph
1673.25	16.09	2.24	1560.13	21.95	9.35	1658 s	$\nu_{C=N}$
1672.87	15.87	2.85	1559.06	20.13	11.48	1611 s	$\nu_{C=N}$
1629.19	12.42	12.36	1515.27	50.64	1.64	1578 s	$\nu$ Ph
1620.74	64.18	1.2	1514.9	51.33	1.58		$\tau$ Ph
1620.17	64.59	1.53	1480.04	16.59	10.75		$\tau$ Ph
1618.37	18.20	8.34	1466.06	21.23	6.55		$\omega$ Ph
1545.50	8.48	6.73	1442.54	12.70	14.94		$\omega$ Ph
1542.51	10.01	14.40	1441.61	13.76	14.63		$\omega$ Ph
1526.85	2.09	6.20	1403.48	10.97	3.52		$\omega$ Ph
1501.01	92.32	4.10	1400.08	11.66	5.08	1499 s	$\delta_{as}$ CH <sub>2</sub>
1467.41	133.71	0.82	1363.19	69.80	27.59	1462 s	$\delta_{as}$ CH <sub>2</sub>
1465.98	128.40	0.82	1349.99	55.55	5.50	1420 s	$\delta_{as}$ CH <sub>2</sub>
1400.51	4.46	21.08	1323.79	53.45	0.82		$\delta$ CH <sub>2</sub>
1381.10	41.09	22.05	1322.31	50.45	1.36		$\delta$ CH <sub>2</sub>
1380.15	41.20	12.44	1292.64	2.85	42.83	1372 s	$\nu$ C-O
1361.15	50.41	27.12	1290.03	2.06	35.49	1318	$\nu$ C-O
1353.46	42.82	27.19	1266.63	2.06	17.06		$\nu$ C-O
1349.54	12.52	4.32	1226.63	3.75	40.92		$\nu$ C-O
1313.30	26.42	1.16	1226.78	4.25	18.01		$\tau$ CH <sub>2</sub>
1312.92	0.92	0.28	1220.77	3.21	5.16		$\tau$ CH <sub>2</sub>
1297.27	20.02	4.75	1211.06	4.14	9.54	1294 m	$\nu$ C-C-N
1296.74	27.84	3.55	1172.91	50.63	9.06	1285 m	$\nu$ C-C-N
1296.36	26.13	13.60	1172.31	56.50	6.05	1249 m	$\nu$ C-C-N

Table 1 continued...

1227.68	26.27	14.95	1170.98	84.03	7.37	1221 m	$\nu$ C-C-N
1215.42	8.93	3.92	1169.40	72.60	2.16	1200 m	$\nu$ C-C-N
1199.42	38.90	4.92	1112.24	6.03	0.31	1151 m	$\rho$ CH <sub>2</sub>
1198.63	38.70	3.85	1110.50	2.91	5.64	1116 m	$\rho$ CH <sub>2</sub>
1035.73	8.22	15.09	1102.96	1.21	13.32	1107 m	$\rho$ Ph
961.28	8.63	0.83	1085.12	7.76	18.04	1043 m	$\rho$ Ph
955.41	7.58	6.98	1083.44	1.55	10.21	982 m	$\rho$ Ph
947.24	2.89	4.21	1024.25	2.53	14.92	972 m	$\rho$ Ph
938.65	18.65	8.26	1016.17	2.55	1.22	937 m	$\gamma$ CH <sub>2</sub>
899.59	22.54	5.03	924.33	5.76	0.68	900 m	$\gamma$ CH <sub>2</sub>
895.77	18.03	4.73	922.01	12.98	8.21		$\gamma$ CH
886.38	11.39	9.18	911.03	16.63	3.10	874 m	$\gamma$ Ph
869.69	4.21	26.15	909.99	14.26	2.91	858 m	$\gamma$ Ph
838.21	66.18	2.47	881.37	8.45	7.98	775 m	$\gamma$ Ph
837.22	81.22	1.97	870.54	8.10	10.70	750 s	$\gamma$ Ph
797.48	5.18	3.89	860.01	7.52	11.81		$\rho$ CH
794.52	3.67	8.82	849.05	21.22	8.25		$\rho$ Ph
755.22	24.37	0.89	848.24	4.56	19.30	744 m	$\rho$ Ph
724.98	6.43	1.67	845.50	2.59	7.02		$\rho$ Ph
653.07	9.52	7.45	820.79	2.78	3.29	648 m	$\rho$ Ph
616.29	0.29	3.41	811.87	1.57	4.04		$\rho$ CH <sub>2</sub>
613.26	7.07	5.80	790.44	4.05	9.07		$\rho$ CH <sub>2</sub>
602.98	1.27	4.45	786.23	10.84	1.96		$\gamma$ CH <sub>2</sub>
589.92	86.93	4.94	719.73	55.26	1.19		$\gamma$ CH <sub>2</sub>
585.10	81.92	2.49	718.84	16.88	5.83		$\rho$ OH
565.90	66.38	2.22	699.43	16.97	8.03		$\rho$ OH
561.26	82.43	1.95	691.40	15.59	2.22		$\tau$ Ph
561.54	9.47	3.41	676.39	4.80	2.42		$\tau$ Ph
535.14	8.30	3.74	659.12	0.28	6.93		$\tau$ Ph
504.68	5.94	2.27	587.38	1.86	5.62		$\delta$ CX(X)
469.20	1.90	1.45	567.62	0.79	1.93		$\delta$ CX(X)
462.78	7.24	1.21	564.56	8.39	1.10		$\bar{a}$ CX(X)
450.33	3.08	1.42	537.77	0.79	0.61		$\bar{a}$ CX(X)
374.05	4.71	0.85	514.83	8.39	5.45		$\delta$ C-C-N
321.56	3.30	0.72	512.85	14.16	8.85		$\delta$ C-C-N
306.98	0.65	2.56	481.30	30.81	4.62		$\delta$ C=N-C
290.98	0.32	3.43	462.68	14.67	1.14		$\delta$ C=N-C
245.43	2.85	1.29	439.16	5.68	1.62		$\gamma$ C=N-C
226.28	0.33	2.07	400.87	5.75	1.56		$\gamma$ C=N-C
220.54	0.37	2.44	393.35	2.43	1.22		$\rho$ CX(X)
177.10	0.59	3.16	385.21	5.17	1.02		$\rho$ CX(X)
130.09	0.09	2.50	325.16	6.30	3.79		t Ph
108.36	0.05	4.41	261.77	5.06	1.3		t Ph
76.65	0.25	0.62	243.27	2.40	0.78		t CNC
67.86	0.51	2.38	241.36	0.60	2.03		t CNC
30.04	0.74	5.39	192.48	7.95	2.14		t CCN
13.90	0.85	6.97	174.34	3.21	1.72		t CCN

$\nu$ -stretching;  $\omega$ -wagging;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\rho$ -rocking;  $\tau$ -twisting; t-torsional; m-medium; w-weak; s-strong; b-broad; subscript : as-asymmetric; s-symmetric; Ph-phenyl ring; X-substituent sensitive

750  $\text{cm}^{-1}$  is assigned as the ring breathing mode of the phenyl ring. The in-plane bending  $\delta\text{CH}$  modes<sup>24</sup> are expected above 1000  $\text{cm}^{-1}$ . In the present case, these modes are observed at 1111, 1162, 1219  $\text{cm}^{-1}$  in the IR spectrum and at 1113, 1171, 1209  $\text{cm}^{-1}$  theoretically. The CH out-of plane deformations<sup>24</sup> are observed between 1000 and 700  $\text{cm}^{-1}$ . Generally, the CH out-of plane deformations with the highest wave numbers have a weaker intensity than those absorbing at lower wave numbers. These  $\gamma\text{CH}$  modes are observed at 937, 900, 874 and 858  $\text{cm}^{-1}$  in the IR spectrum and at  $895\pm 60$   $\text{cm}^{-1}$  theoretically.

In the imine group, the nitrogen atom is likely out-of-plane, with a torsional angle C-C-C-N around  $175.3^\circ$  or (around  $4.7^\circ$ ). Existence of this angle has interpreted to be caused by the asymmetric interaction between the OH group and the benzene ring plane. This interaction is common to all aniline derivatives<sup>27, 30</sup>. The C=N distance in the present case is 1.256 Å, which is similar to the measured value in imine<sup>31</sup>. Analysis of organic molecules having conjugated  $\delta$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research.<sup>32</sup> The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement. The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system is calculated using HF method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a  $3\times 3\times 3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry<sup>33</sup>. The calculated first hyperpolarizability of the title compound is  $1.386 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives and experimental evaluation of this data is not readily available.

### CONCLUSION

In this work, we have performed the theoretical and experimental vibrational analysis of 2,2'-Ethylene bis (nitriolomethylidene)diphenol. The theoretical study gave a description of the

geometry and vibrational wave numbers of the title compound. The calculated (scaled) wave numbers are in good agreement with the experimental values obtained for the investigated molecule.

The observed discrepancies between the theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum mechanical methods to overestimate the force constants at the exact equilibrium geometry. From the calculated hyperpolarizability value, we conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

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