



## FTIR, FT-Raman and DFT Calculations of 5-nitro-1,3-Benzodioxole

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### ABSTRACT

FTIR and FT-Raman spectrum of 5-nitro-1,3-benzodioxole were recorded and analyzed. The vibrational wavenumbers were examined theoretically using the Gaussian03 set of quantum chemistry codes. The experimental frequencies are in agreement with the calculated (B3LYP) scaled values. The predicted infrared intensities and Raman activities are reported.

**Key words:** FTIR, FT-Raman, DFT, benzodioxole.

### INTRODUCTION

The benzodioxole ((methylenedioxy) benzene) group is present in a number of endothelin receptor antagonists. Endothelins are 21-amino acid bicyclic peptides originally isolated from the supernatant of cultured porcine endothelial cells<sup>1</sup>. There have been many studies about the molecular conformations of indan-like benzene fused ring molecules<sup>2-4</sup>. These molecules have received considerable attention due to their interesting conformational properties. Laane et al. reported the infrared, Raman, electronic UV absorption, and laser induced fluorescence excitation spectra of two oxygen containing indan-like molecule, phthalan<sup>5-7</sup> and 1,3-benzodioxole<sup>8,9</sup>. 1,3-benzodioxole has been studied extensively by several spectrographic

and theoretical methods owing to its propensity for large amplitude motion<sup>10-12</sup>. It is believed that the molecule has a nonplanar structure in its electronic ground state. While the aromatic ring is planar, the five member ring is puckered, with the oxygen atoms and the CH<sub>2</sub> group on opposite side of the aromatic plane. In the present work, the vibrational spectroscopic analysis of 5-nitro-1,3-benzodioxole is reported, experimentally and theoretically.

### EXPERIMENTAL

The FT-IR spectrum was recorded on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets, number of scans 16, resolution 2 cm<sup>-1</sup>. The FT-Raman spectrum was obtained on a BRUKER RFS 100/S, Germany. For excitation of the spectrum the

emission of a Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2  $\text{cm}^{-1}$ .

### COMPUTATIONAL DETAILS

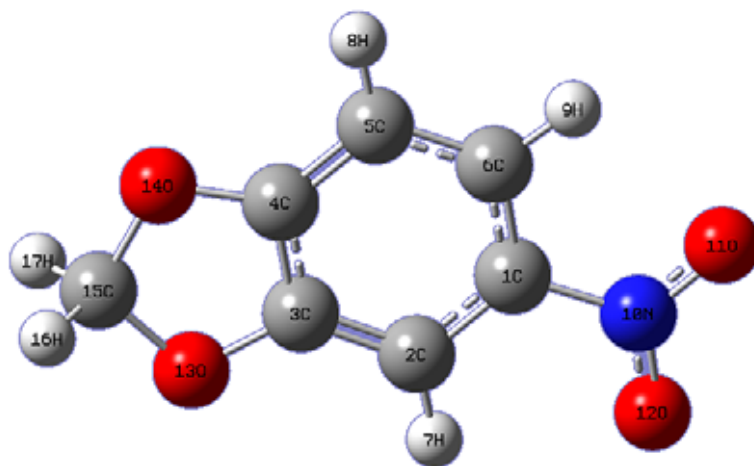
Calculations of the title compound were carried out with Gaussian03 software program<sup>13</sup> using the B3LYP/6-31G\* basis sets to predict the molecular structure and vibrational wavenumbers. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Therefore, a scaling factor of 0.9613 was uniformly applied to the DFT calculated wavenumbers<sup>14</sup>. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes<sup>15,16</sup>.

### RESULTS AND DISCUSSION

The observed IR, Raman and calculated (scaled) wavenumbers and the assignments are given in Table 1. In nitro compounds,  $\nu_{\text{as}}\text{NO}_2$  are located in the region  $1580 \pm 80 \text{ cm}^{-1}$ . The nitro benzene derivatives<sup>17</sup> shows  $\nu_{\text{as}}\text{NO}_2$  in the region  $1535 \pm 30 \text{ cm}^{-1}$  and the 3-nitropyridine at  $1530 \pm 20 \text{ cm}^{-1}$ . In the present case,  $\nu_{\text{as}}\text{NO}_2$  are obtained at 1596 theoretically and at  $1609 \text{ cm}^{-1}$  in IR spectrum.

In nitro compounds,  $\nu_s\text{NO}_2$  are located in the region  $1400 \pm 40 \text{ cm}^{-1}$ . For the title compound,  $\nu_s\text{NO}_2$  is observed at  $1427 \text{ cm}^{-1}$  (DFT),  $1437 \text{ cm}^{-1}$  (IR) and  $1430 \text{ cm}^{-1}$  (Raman). In the aromatic nitro compounds, bands are usually seen at  $855 \pm 40 \text{ cm}^{-1}$  ( $\text{NO}_2$  scissors deformation  $\delta\text{NO}_2$ ),  $760 \pm 30 \text{ cm}^{-1}$  ( $\text{NO}_2$  out of plane wag  $\omega\text{NO}_2$ ),  $580 \pm 30 \text{ cm}^{-1}$  ( $\text{NO}_2$  in-plane rock  $\sigma\text{NO}_2$ ) and  $70 \pm 20 \text{ cm}^{-1}$  ( $\tau\text{NO}_2$ ). In the present case, the observed values for  $\delta\text{NO}_2$  are 917 (DFT), 920 (IR)  $\text{cm}^{-1}$ ;  $\omega\text{NO}_2$  is  $803 \text{ cm}^{-1}$  (DFT);  $\sigma\text{NO}_2$  are 666 (DFT) and  $\tau\text{NO}_2$  is at  $21 \text{ cm}^{-1}$  (DFT). Panicker *et al.*<sup>18</sup> reported the  $\text{NO}_2$  deformation bands at 800, 724,  $534 \text{ cm}^{-1}$  (theoretically) and 809, 727, 717,  $524 \text{ cm}^{-1}$  (experimentally). Sundaraganesan *et al.*<sup>19</sup> reported the  $\text{NO}_2$  deformation bands at 839, 744 and  $398 \text{ cm}^{-1}$  experimentally and 812, 716, 703 and  $327 \text{ cm}^{-1}$  theoretically.

For methylene groups<sup>20</sup>, the  $\text{CH}_2$  vibrations are observed in the region 2800-3000, 1200-1400, 875-1150 and  $600-950 \text{ cm}^{-1}$ . The vibrations of the  $\text{CH}_2$  group (the asymmetric stretch  $\nu_{\text{as}}\text{CH}_2$ , symmetric stretch  $\nu_s\text{CH}_2$ , the scissoring vibration and wagging vibration) appear in the regions 2940-3005, 2870-2940, 1420-1480 and  $1320-1380 \text{ cm}^{-1}$ , respectively<sup>17, 21</sup>. The stretching bands of the  $\text{CH}_2$  groups are observed at  $2925 \text{ cm}^{-1}$  in the IR spectrum and at 2992,  $2942 \text{ cm}^{-1}$  theoretically for the title compound. According to literature<sup>22-23</sup> scissoring mode of the  $\text{CH}_2$  group give rise to characteristic band near  $1485 \text{ cm}^{-1}$  in IR and Raman spectra. This mode is observed at  $1489 \text{ cm}^{-1}$  in the IR spectrum and at  $1474 \text{ cm}^{-1}$  theoretically. The wagging mode



**Table 1 :Calculated (scaled) wavenumbers, IR, Raman bands and assignments**

B3LYP/6-31G* $\nu(\text{cm}^{-1})$	IR intensity	Raman activity	IR $\nu(\text{cm}^{-1})$	Raman $\nu(\text{cm}^{-1})$	Assignments
3145	6.64	54.46			$\nu\text{CH}$
3134	2.48	77.13			$\nu\text{CH}$
3110	1.89	92.31	3119		$\nu\text{CH}$
2992	40.89	163.43			$\nu_{\text{as}}\text{CH}_2$
2942	115.42	250.34	2925		$\nu_{\text{s}}\text{CH}_2$
1619	25.45	11.34	1632	1620	$\nu\text{Ph}$
1596	15.65	73.75	1609		$\nu_{\text{as}}\text{NO}_2$
1563	189.45	6.23	1551		$\nu\text{Ph}$
1515	1.32	38.51	1516		$\nu\text{Ph}$
1474	302.11	0.49	1489		$\delta\text{CH}_2$
1427	20.57	33.63	1437	1430	$\nu_{\text{s}}\text{NO}_2$
1395	3.13	12.10	1381		$\nu\text{Ph}$
1372	13.89	12.77		1378	$\omega\text{CH}_2$
1336	428.93	404.83	1345	1333	$\nu\text{Ph}$
1260	375.73	26.55	1270	1272	$\nu\text{CN}$
1224	40.89	6.75			$\nu\text{COC}$
1160	0.01	9.54	1171		$\nu\text{COC}$
1144	4.87	2.59			$\delta\text{CH}$
1103	10.66	0.97	1120	1128	$\delta\text{CH}$
1100	16.73	1.37	1115		$\tau\text{CH}_2$
1046	22.51	17.81	1066	1051	$\nu\text{COC}$
1027	145.43	3.68	1036	1028	$\nu\text{COC}, \delta\text{CH}$
936	32.58	8.05	930	932	$\gamma\text{CH}$
917	0.56	2.32	920		$\delta\text{NO}_2$
907	29.56	7.10			$\sigma\text{CH}_2$
864	24.85	1.08	872		$\gamma\text{CH}$
806	13.30	2.52	810	809	$\gamma\text{CH}$
803	1.55	6.40		805	$\omega\text{NO}_2$
796	33.34	23.60			$\nu\text{Ph}$
721	31.63	2.05	719	725	$\gamma\text{CH}$
715	3.60	11.80			$\gamma\text{Ph}$
678	0.79	0.23	686		$\delta\text{Ph(X)}$
666	10.98	2.14			$\sigma\text{NO}_2$
570	5.99	7.14	574		$\gamma\text{Ph(X)}$
544	0.13	0.10	546		$\delta\text{Ph(X)}$
528	3.82	0.92			$\gamma\text{Ph(X)}$
411	0.58	0.50			$\delta\text{Ph(X)}$
394	2.81	3.46			$\delta\text{CX(X)}$
339	0.01	2.62			$\delta\text{CX(X)}$
316	0.36	2.33			$\gamma\text{CX(X)}$
224	0.13	2.51			$\gamma\text{CX(X)}$
203	1.18	1.15		208	$\delta\text{CX(X)}$
119	4.59	0.02			$\gamma\text{CX(X)}$
63	0.17	0.17		75	tPh
21	6.43	0.69			tNO <sub>2</sub>

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\omega$ -wagging;  $\sigma$ -rocking; t-torsion; as-asymmetric; s-symmetric; Ph-phenyl ring; X-substituent sensitive.

is observed at  $1378\text{ cm}^{-1}$  in the Raman spectrum and at  $1372\text{ cm}^{-1}$  theoretically. The twisting and rocking vibrations of the  $\text{CH}_2$  group appear in the region<sup>17</sup> of  $1200\text{-}1280$  and  $740\text{-}900\text{ cm}^{-1}$ , respectively. These modes are also assigned. For the title compound the twisting vibration is observed at  $1115\text{ cm}^{-1}$  in the IR spectrum and at  $1100\text{ cm}^{-1}$  theoretically. The rocking deformation is assigned at  $907\text{ cm}^{-1}$  theoretically.

The asymmetric and symmetric C-O-C stretching vibrations are expected to appear at  $1150\text{-}1250$  and  $1000\text{-}1050\text{ cm}^{-1}$ <sup>22</sup>. In the present case the DFT calculations give these modes at  $1224$ ,  $1160$ ,  $1046$  and  $1027\text{ cm}^{-1}$ . The bands at  $1171$ ,  $1066$ ,  $1036$  (IR) and  $1051$ ,  $1028\text{ cm}^{-1}$  (Raman) are assigned as C-O-C symmetric stretching modes. The C-O-C stretching modes are reported at  $1250$ ,  $1073\text{ cm}^{-1}$  for 2-mercaptobenzoxazole<sup>23</sup>,  $1263$ ,  $1055\text{ cm}^{-1}$  for 5-methyl-2-(p-fluorophenyl)benzoxazole<sup>24</sup>.

The existence of one or more aromatic rings in a structure is normally readily determined from the C-H and C=C-C related vibrations. The C-H stretching occurs above  $3000\text{ cm}^{-1}$  and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch<sup>25</sup>. In the present case, the DFT calculations give the  $\nu\text{CH}$  modes at  $3145$ ,  $3134$  and  $3110\text{ cm}^{-1}$ . The band observed at  $3119\text{ cm}^{-1}$  in the IR spectrum is assigned as  $\nu\text{CH}$  mode of the benzene ring. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring near  $1600$ ,  $1580$ ,  $1490$  and  $1440\text{ cm}^{-1}$ ) are good group vibrations<sup>17</sup>. In the absence of ring conjugation, the band near  $1580\text{ cm}^{-1}$  is usually weaker than that at  $1600\text{ cm}^{-1}$ . The fifth ring stretching vibration which is active near  $1335 \pm 35\text{ cm}^{-1}$  a region which overlaps strongly with that of the CH in-plane deformation and the intensity is in general, low or medium high<sup>17</sup>. The sixth ring stretching vibration or ring breathing mode appears as a weak band near  $1000\text{ cm}^{-1}$  in mono, 1,3-di and 1,3,5-trisubstituted benzenes. In the other wise substituted benzene, however, this vibration is substituent sensitive and difficult to distinguish from the ring in-plane deformation. For tri-substituted phenyl ring the  $\nu\text{Ph}$  modes<sup>17</sup> are seen in the region  $1640 - 1250\text{ cm}^{-1}$  and these modes

are observed at  $1632$ ,  $1551$ ,  $1516$ ,  $1381$ ,  $1345\text{ cm}^{-1}$  in the IR spectrum,  $1620$ ,  $1333\text{ cm}^{-1}$  in the Raman spectrum and at  $1619$ ,  $1563$ ,  $1515$ ,  $1395$ ,  $1336\text{ cm}^{-1}$  (DFT) theoretically. In asymmetric tri-substituted benzenes, when all the three substituents are light, the wavenumber interval of the breathing mode<sup>26</sup> is between  $500$  and  $600\text{ cm}^{-1}$ . When all the three substituents are heavy, the wavenumber appears above  $1100\text{ cm}^{-1}$ . In the case of mixed substituents, the wavenumber is expected<sup>26</sup> to appear between  $600$  and  $750\text{ cm}^{-1}$ . For the title compound the phenyl ring breathing mode is assigned at  $796\text{ cm}^{-1}$  theoretically. Mary *et al.*<sup>27</sup> reported the ring breathing mode of tri-substituted benzene ring at  $733\text{ cm}^{-1}$  in the IR spectrum and at  $738\text{ cm}^{-1}$  theoretically. The in-plane bending  $\delta\text{CH}$  modes<sup>17</sup> of the phenyl ring are expected above  $1000\text{ cm}^{-1}$ . For the tri-substituted benzene ring these modes are observed at  $1120$ ,  $1036\text{ cm}^{-1}$  in IR,  $1128$ ,  $1028\text{ cm}^{-1}$  in Raman and at  $1144$ ,  $1103$ ,  $1027\text{ cm}^{-1}$  theoretically. The CH out-of-plane deformations<sup>17</sup> are observed between  $1000$  and  $700\text{ cm}^{-1}$ . Generally the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These  $\gamma\text{CH}$  modes are observed at  $872$ ,  $810$ ,  $719$  (IR),  $809$ ,  $725$  (Raman),  $864$ ,  $806$ ,  $721\text{ cm}^{-1}$  (DFT). The in-plane and out-of-plane substituent modes of the phenyl ring are also identified and assigned (Table 1).

## CONCLUSION

The FTIR and FT-Raman spectra of 5-nitro-1,3-benzodioxole were recorded and analyzed. The harmonic vibrational wavenumbers were calculated theoretically using Gaussian03 set of quantum chemistry codes. The calculated wavenumbers (B3LYP) agree well with the observed wavenumbers. The small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the infrared wavenumbers and intensities of many other modes. Also we state that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

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