



Vibrational Spectroscopic Investigations of 4-nitroprocatechol

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ABSTRACT

The IR and Raman spectra of 4-nitroprocatechol have been recorded and analyzed. The harmonic vibrational wavenumbers were calculated theoretically using Gaussian03 software. Calculations were performed by the DFT level using the standard 6-31G* basis. The calculated wavenumbers agree well with the observed wavenumbers. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands found in the IR and Raman spectra of the title compound. The predicted infrared intensities and Raman activities are reported.

Key words: IR, Raman, DFT, Nitroprocatechol.

INTRODUCTION

Catechol, also known as pyrocatechol or 1,2-dihydroxybenzene, is an organic compound with the molecular formula $C_6H_4(OH)_2$. It is the ortho isomer of the three isomeric benzenediols. This colorless compound occurs naturally in trace amounts. Catechol occurs as feathery white crystals that are very rapidly soluble in water. Catechol occurs in free form naturally in kino and in beechwood tar; its sulfonic acid has been detected in the urine of horse and humans¹. Small amounts of catechol occur naturally in fruits and vegetables, along with the enzyme polyphenol oxidase (also known as catecholase, or catechol oxidase). Upon mixing the enzyme with the substrate and exposure to oxygen (as when a potato or apple is cut and left out), the colorless catechol oxidizes to reddish-

brown melanoid pigments, derivatives of benzoquinone. The enzyme is inactivated by adding an acid, such as lemon juice, and slowed with cooling. Excluding oxygen also prevents the browning reaction. Benzoquinone is said to be antimicrobial, which slows the spoilage of wounded fruits and other plant parts. Catechol moieties are also found widely within the natural world. Arthropod cuticle consists of chitin linked by a catechol moiety to protein. The cuticle may be strengthened by cross-linking, in particular, in insects, and of course by biomineralization². Catechols are produced through the metabolism of cholesterol by bacteria such as mycobacterium tuberculosis³. Urushiols are naturally existing organic compounds that have the catechol skeleton structure and diphenol functionality but with alkyl groups substituted onto the aromatic ring. Urushiols are the skin-irritating

poisons found in plants like poison ivy, etc. Catecholamines are biochemically significant hormones/neurotransmitters that are phenethylamines in which the phenyl group has a catechol skeleton structure. Parts of a molecule of catechin, another natural compound presents in tea, has the catechol skeleton structure in it. Approximately 50% of synthetic catechol is consumed in the production of pesticides, the remainder being used as a precursor to fine chemicals such as perfumes and pharmaceuticals¹. It is a common building block in organic synthesis⁴. Several industrially significant flavors and fragrances are prepared starting from catechol. Guaiacol is prepared by methylation of catechol and is then converted to vanillin. The related monoethyl ether of catechol, guethol, is converted to ethylvanillin, a component of chocolate confectioneries. 3-Trans-Isocamphylcyclohexanol, widely used as a replacement for sandalwood oil, is prepared from catechol via guaiacol and camphor. Piperonal, a flowery scent, is prepared from the methylene diether of catechol followed by condensation with glyoxal and decarboxylation⁵. Catechol is used as a black-and-white photographic developer, but, except for some special purpose applications, its use until recently was largely historical. Research shows that catechol and catechols with electron donating substituents, specially in acidic and neutral media, show one anodic peak and a corresponding cathodic one, which correspond to the transformation of catechol to o-benzoquinone and vice versa. In the present

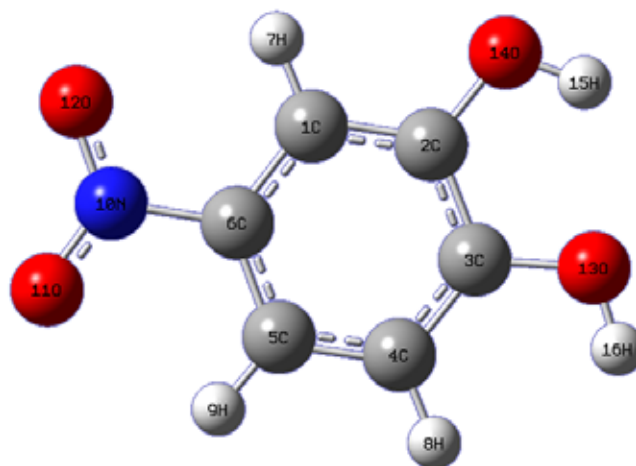
study the FT-IR and FT-Raman and theoretical calculations of the wavenumbers of the title compound are reported.

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^{-1} . 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 cm^{-1} .

Computational details

Calculations of the title compound were carried out with Gaussian03 software program⁶ 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 wavenumbers⁷. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{8,9}.



RESULTS AND DISCUSSION

The observed IR, Raman and calculated (scaled) wavenumbers and the assignments are given in Table 1. The DFT calculations give the OH stretching bands at 3618, 3573 cm^{-1} and strong bands are observed in the IR spectrum at 3388, 3300 cm^{-1} . The in-plane deformation¹⁰ is expected in the region $1400 \pm 40 \text{ cm}^{-1}$ and the bands at 1444, 1380 cm^{-1} in the IR spectrum and at 1446, 1382 cm^{-1} in the Raman spectrum are assigned as the in-plane deformation of OH band. The calculated values are 1451 and 1372 cm^{-1} . The stretching mode of the hydroxyl group with respect to the phenyl moiety C-O appears at 1251, 1185 cm^{-1} in the IR spectrum, 1184 cm^{-1} in the Raman spectrum and the calculated value are 1232, 1179 cm^{-1} . This band is expected in the region^{11, 12} $1220 \pm 40 \text{ cm}^{-1}$. El-Shahway *et al.*¹³ reported C-O stretching at 1240 cm^{-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 show $\nu_{\text{as}}\text{NO}_2$ in the region¹⁰ $1535 \pm 30 \text{ cm}^{-1}$ and the 3-nitropyridine at $1530 \pm 20 \text{ cm}^{-1}$. In the present case, $\nu_{\text{as}}\text{NO}_2$ are obtained at 1601 cm^{-1} theoretically (DFT) and at 1592 cm^{-1} in IR and at 1597 cm^{-1} in Raman spectrum. In nitro compounds, $\nu_{\text{s}}\text{NO}_2$ are located in the region 1300-1360 cm^{-1} . The nitrobenzene derivatives show $\nu_{\text{s}}\text{NO}_2$ in $1345 \pm 30 \text{ cm}^{-1}$ and the 3-nitropyridines in $1350 \pm 20 \text{ cm}^{-1}$. For the title compound, $\nu_{\text{s}}\text{NO}_2$ is observed at 1341 cm^{-1} (DFT), 1327 cm^{-1} (IR) and 1327 cm^{-1} (Raman). In the aromatic nitro compounds, bands are usually seen at $855 \pm 40 \text{ cm}^{-1}$ (NO_2 scissors deformation δNO_2), $760 \pm 30 \text{ cm}^{-1}$ (NO_2 out of plane wag ωNO_2), $540 \pm 30 \text{ cm}^{-1}$ (NO_2 in-plane rock νNO_2) and $70 \pm 20 \text{ cm}^{-1}$ (tNO_2). In the present case, the observed values for δNO_2 are 901 cm^{-1} (DFT); ωNO_2 is 784 cm^{-1} (DFT); νNO_2 are 549 cm^{-1} (DFT), 546 cm^{-1} (IR) and 551 cm^{-1} (Raman) and tNO_2 is at 61 cm^{-1} (DFT). Panicker *et al.*¹⁴ reported the NO_2 deformation bands at 800, 724, 534 cm^{-1} (theoretically) and 809, 727, 717, 524 cm^{-1} (experimentally). Sundaraganesan *et al.*¹⁵ reported the NO_2 deformation bands at 839, 744 and 398 cm^{-1} experimentally and 812, 716, 703 and 327 cm^{-1} theoretically.

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 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch¹⁶⁻¹⁷. In the present case, the DFT calculations give the νCH modes in the range 3137-3062 cm^{-1} . The band observed at 3067 cm^{-1} in the IR spectrum is assigned as νCH 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 cm^{-1}) are good group vibrations¹⁰. In the absence of ring conjugation, the band near 1580 cm^{-1} is usually weaker than that at 1600 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 high¹⁰. The sixth ring stretching vibration or ring breathing mode appears as a weak band near 1000 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 νPh modes¹⁰ are seen in the region 1640 – 1110 cm^{-1} and these modes are observed at 1628, 1511, 1284, 1121 cm^{-1} in the IR spectrum, 1505, 1279, 1129 cm^{-1} in the Raman spectrum and at 1614, 1564, 1498, 1281, 1139 cm^{-1} (DFT) theoretically. In asymmetric tri-substituted benzenes, when all the three substituents are light, the wavenumber interval of the breathing mode¹¹ is between 500 and 600 cm^{-1} .

When all the three substituents are heavy, the wavenumber appears above 1100 cm^{-1} . In the case of mixed substituents, the wavenumber is expected¹¹ to appear between 600 and 750 cm^{-1} . For the title compound the phenyl ring breathing mode is observed at 653 cm^{-1} in the IR spectrum, 656 cm^{-1} in the Raman spectrum and at 666 cm^{-1} theoretically. Mary *et al.*¹⁸ reported the ring breathing mode of tri-substituted benzene ring at 733 cm^{-1} in the IR spectrum and at 738 cm^{-1} theoretically. The in-plane bending δCH modes¹⁰ of the phenyl ring are expected above 1000 cm^{-1} . For the tri-substituted benzene ring these modes are observed at 1185, 1081 cm^{-1} in IR, 1184, 1081

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
3618	92.31	162.63	3388		νOH
3573	90.16	69.54	3300		νOH
3137	5.80	53.13			νCH
3135	2.45	62.87			νCH
3062	12.01	102.69	3067		νCH
1614	4.07	2.96	1628		νPh
1601	44.90	103.87	1592	1597	$\nu_{\text{as}}\text{NO}_2$
1564	265.60	7.93			νPh
1498	114.85	1.87	1511	1505	νPh
1451	26.73	7.34	1444	1446	δOH
1372	1.21	1.83	1380	1382	δOH
1341	328.11	281.00	1327	1327	$\nu_{\text{s}}\text{NO}_2$
1307	221.65	20.73		1308	νCN
1281	287.39	39.09	1284	1279	νPh
1232	39.54	9.99	1251		νCO
1179	45.63	6.06	1185	1184	$\nu\text{CO}, \delta\text{CH}$
1139	63.75	2.53	1121	1129	νPh
1099	50.48	1.61	1081	1081	δCH
1057	92.15	20.72			δCH
929	31.50	5.18	947	935	γCH
901	1.55	1.98			δNO_2
876	19.50	1.20	871		γCH
795	16.09	5.67	788	794	γCH
784	14.54	3.15			ωNO_2
773	37.71	22.90	746	750	γOH
721	35.31	2.35	722		γPh
666	0.90	0.18	653	656	νPh
632	23.78	2.24		632	$\delta\text{Ph(X)}$
574	7.82	6.76			γOH
549	0.06	0.21	546	551	σNO_2
532	1.86	0.64			$\gamma\text{Ph(X)}$
442	5.65	0.91		448	$\gamma\text{Ph(X)}$
416	3.46	3.36			$\delta\text{Ph(X)}$
412	56.47	1.11			$\delta\text{Ph(X)}$
347	0.14	2.42		351	$\delta\text{CX(X)}$
333	2.22	1.60			$\delta\text{CX(X)}$
302	5.41	0.33			$\delta\text{CX(X)}$
282	189.45	2.76			$\gamma\text{CX(X)}$
208	0.86	0.33		210	$\gamma\text{CX(X)}$
207	2.49	2.25			$\gamma\text{CX(X)}$
114	0.38	0.48		111	tPh
61	0.25	0.08			tNO ₂

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; ω -wagging; σ -rocking; t-torsion; as-asymmetric; s-symmetric; Ph-phenyl ring; X-substituent sensitive.

cm⁻¹ in Raman and at 1179, 1099, 1057 cm⁻¹ theoretically. The CH out-of-plane deformations¹⁰ are observed between 1000 and 700 cm⁻¹. Generally the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. These γ CH modes are observed at 947, 788 (IR), 935, 794 (Raman), 929, 876, 795 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 IR and Raman spectra of 4-nitroprocatechol have been recorded and analyzed. The harmonic vibrational wavenumbers were calculated theoretically using Gaussian03 software. Calculations were performed by the DFT level using the standard 6-31G* basis. The calculated wavenumbers agree well with the observed wavenumbers. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands found in IR and Raman spectra of the studied molecule.

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