



IR, Raman and DFT Calculations of 5,6-benzo-2-pyrone

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(Received: February 15, 2012; Accepted: March 28, 2012)

ABSTRACT

FTIR and FT-Raman spectrum of 5,6-benzo-2-pyrone 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 phenyl and pyrone ring modes are identified and assigned. The predicted infrared intensities and Raman activities are reported.

Key words: FTIR, FT-Raman, DFT calculations, pyrone.

INTRODUCTION

Coumarins are interesting heterocycles because of their photochemical and photophysical properties¹, leading to numerous industrial and laser dye applications². It is well known that coumarins increase their dipolar moment when excited. Coumarins comprise a group of natural compounds found in a variety of plant sources. The very long association of plant coumarins with various animal species and other organisms throughout evolution may account for the extraordinary range of biochemical and pharmacological activities of these chemicals in mammalian and other biological systems³. Rao and Vasantham⁴ reported the nitroketene dithioacetal chemistry and synthesis of coumarins incorporating nitrothiophene moiety. Pyrone group is a constituent of the structures of a series of natural products^{5,6} with interesting biological and pharmacological activities⁷ such as anti-coagulant, anticancer,

spasmolytic, anti-anaphylactic, etc.⁸. Further more, these compounds can be employed as pigments⁹, photoactive materials¹⁰ and utilized as potential biodegradable agrochemicals^{11,12}. *Ab initio* quantum mechanical method is at present widely used for simulating IR spectra. 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 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 and 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 program¹³ 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 wavenumbers¹⁴.

RESULTS AND DISCUSSION

The observed IR, Raman and calculated (scaled) wavenumbers and the assignments are given in Table 1. The carbonyl group vibration gives rise to characteristic bands in vibrational spectra. The intensity of these bands can increase owing to conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads to intensification of IR bands. The carbonyl absorption $\delta\text{C}=\text{O}$ of six membered ring¹⁵ occurs in the region 1750–1650 cm^{-1} and in the present case, the band observed at 1671 in the IR spectrum, 1708 in the Raman spectrum and at 1695 cm^{-1} (DFT) is assigned as C=O stretching band. The deviation of the calculated wavenumber for this mode can be attributed to the underestimation of the large degree of δ -electron delocalization due to conjugation in the molecule. The deformation bands of the C=O are also identified at 467 cm^{-1} in the IR spectrum, 462 cm^{-1} in the Raman spectrum and at 744, 470 cm^{-1} theoretically¹⁶.

Pyrone ring stretching modes are reported at 1073, 1008, 880 cm^{-1} in the IR spectrum and at 1070, 1011, 881 cm^{-1} in the Raman spectrum and at 1068, 1000, 937, 905 cm^{-1} theoretically^{17,18}. We have observed the pyrone string stretching modes at 1622, 1231, 910, 834 cm^{-1} in the IR spectrum, 1621, 1218, 1055, 895 cm^{-1} in the Raman spectrum and the DFT calculations give these modes at 1612, 1227, 1056, 900, 838 cm^{-1} . For the pyrone ring, the in-plane CH deformation bands are assigned at 1403 cm^{-1} in IR, 1236 cm^{-1} in Raman and at 1400, 1240 cm^{-1} theoretically and the out-of-plane CH deformations bands are assigned at 995 cm^{-1} in IR, 990 cm^{-1} in Raman and at 999, 825 cm^{-1} theoretically. The in-plane ring deformations δPy are reported at 729 cm^{-1} in the IR spectrum and at 706, 523 cm^{-1} in the Raman spectrum and at 851, 513 cm^{-1} by *ab initio* calculations^{17,18}. In the present case the bands at 738 cm^{-1} (IR), 738 cm^{-1} in Raman and 743, 293 cm^{-1} (DFT) are assigned as the in-plane ring deformation bands of the pyrone ring. The out-of-plane and twisting modes of the pyrone ring are reported at 638 cm^{-1} (Raman), 626 cm^{-1} (theoretical) and 481 cm^{-1} (IR), 450, 480 cm^{-1} (Raman), 410, 483 cm^{-1} (theoretical), respectively¹⁸⁻¹⁹. In the present case the bands at 668 (IR), 376 (Raman), 665, 375 cm^{-1} (DFT) and 159, 99 cm^{-1} (DFT) are assigned as the out-of-plane ring deformation δPy and the twisting mode τPy of the pyrone ring, respectively. The C=C stretching mode of the pyrone ring is reported at 1694, 1634 cm^{-1} in the IR spectrum, 1690 cm^{-1} in the Raman spectrum and at 1732, 1674 cm^{-1} by HF calculations¹⁸⁻¹⁹. The C=C stretching mode of unconjugated alkenes usually shows moderate to weak absorption in the range¹⁵ 1667–1640 cm^{-1} . In lactones, when the double bond is adjacent to the –O–, a strong C=C absorption is observed¹⁵ in the 1685–1660 cm^{-1} . For the title compound the C=C stretching mode is assigned at 1612 cm^{-1} (DFT) and at 1622 cm^{-1} in IR spectrum and at 1621 cm^{-1} in the Raman spectrum.



Table 1: Vibrational assignments of 5,6-benzo-2-pyrone

B3LYP/6-31G* $\nu(\text{cm}^{-1})$	IR intensity	Raman activity	IR $\nu(\text{cm}^{-1})$	Raman $\nu(\text{cm}^{-1})$	Assignments
3128	1.43	145.23	-	-	ν CHPy
3121	4.44	161.37	-	-	ν CHPh
3105	20.20	172.00	-	-	ν CHPh
3089	11.39	100.33	-	-	ν CHPh
3079	10.80	105.22	3062	3072	ν CHPy
3076	0.44	16.26	3039	3065	ν CHPh
1695	505.07	96.22	1671	1708	ν C=O
1612	53.84	129.56	1622	1621	δ C=C
1599	57.58	39.24	1608	1605	ν Ph
1550	26.93	102.85	1565	1567	ν Ph
1479	2.59	18.71	1488	1489	ν Ph
1447	22.34	10.43	1454	1456	ν Ph
1400	9.48	5.69	1403	-	δ CHPy
1339	0.48	71.24	-	1327	ν Ph
1277	8.96	4.43	1279	1268	δ CHPh
1240	30.94	8.23	-	1236	δ CHPy
1227	10.83	35.39	1231	1218	ν COC
1175	16.30	13.83	1178	1179	δ CHPh
1166	2.68	34.30	1155	1159	δ CHPh
1113	15.89	10.09	1110	1106	δ CHPh
1056	77.88	30.33	-	1055	ν COC
1021	1.05	16.64	-	-	ν Ph
999	0.51	2.31	995	990	γ CHPy
986	0.25	0.07	-	-	γ CHPh
947	4.45	0.39	953	948	γ CHPh
900	17.69	1.57	910	895	ν CC
872	1.46	4.93	870	-	γ CHPh
838	52.45	1.57	834	-	ν CC
825	70.60	0.60	-	-	γ CHPy
760	35.43	1.18	762	755	γ CHPh
744	1.27	6.70	-	-	ν C=O
743	19.03	3.72	738	738	γ Ph, δ Py
717	4.36	20.97	-	-	δ Py
665	3.16	5.68	668	-	γ Py
604	9.88	0.42	612	-	δ Py
538	0.05	1.02	-	-	γ Ph
524	5.55	3.95	526	529	δ Ph
470	5.09	3.28	467	462	γ C=O
457	3.03	0.82	-	-	γ Ph
433	1.19	23.07	-	-	δ Py
375	0.73	4.71	-	376	γ Py
293	1.09	1.26	-	-	δ Py, δ Ph
259	0.08	1.21	-	-	γ Ph, γ Py
159	5.77	0.85	-	-	tPh tPy
99	1.09	0.39	-	96	γ Py

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; t-twisting; Ph-phenyl ring; Py-Pyrone ring.

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 stretch²⁰. In the present case, the DFT calculations give the δCH modes in the range $3121\text{--}3076\text{ cm}^{-1}$. The bands observed at 3039 cm^{-1} in the IR spectrum and at 3065 cm^{-1} in the Raman spectrum were assigned as νCH modes of the benzene rings. 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 vibrations. 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 high¹⁶. 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 the ortho disubstituted benzene¹⁶, νPh modes are expected in the region $1620\text{--}1260\text{ cm}^{-1}$. The νPh modes are observed at 1608 , 1565 , 1488 , 1454 cm^{-1} in the IR spectrum, 1605 , 1567 , 1489 , 1456 , 1327 cm^{-1} in the Raman spectrum and 1599 , 1550 , 1479 , 1447 , 1339 cm^{-1} theoretically. In ortho disubstitution, the ring breathing mode has three wavenumber intervals depending on whether both substituents are heavy; or one of them is heavy, while the other is light; or both of them are light. In the first case, the

interval is $1100\text{--}1130\text{ cm}^{-1}$; in the second case $1020\text{--}1070\text{ cm}^{-1}$; while in the third case it is between²¹ 630 and 780 cm^{-1} . For the title compound, the ring breathing mode of the phenyl ring Ph is assigned at 1021 cm^{-1} theoretically. The ring breathing mode of ortho substituted benzene ring is reported at 1013 cm^{-1} theoretically²².

The in-plane bending δCH modes¹⁶ of the phenyl ring are expected above 1000 cm^{-1} . Bands observed at 1279 , 1178 , 1155 , 1110 cm^{-1} in the IR spectrum and 1268 , 1179 , 1159 , 1106 cm^{-1} in the Raman spectrum are assigned as δCH modes of the ortho substituted benzene ring. The DFT calculations give these modes at 1277 , 1175 , 1166 , 1113 cm^{-1} . The CH out-of-plane deformations¹⁶ 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 $\tilde{\alpha}\text{CH}$ modes are observed at 953 , 870 , 762 cm^{-1} (IR), 948 , 755 (Raman), 986 , 947 , 872 , 760 cm^{-1} (DFT). The deformations bands of the phenyl and pyrone rings are also identified and assigned (table 1) and some of the modes are not pure, but contains contributions from other modes also.

CONCLUSION

The IR and Raman spectra of 5,6-benzo-2-pyrone were recorded and analyzed. The frequencies are calculated theoretically using Gaussian03 software package. The calculated frequencies are found to be in agreement with the experimental values. The predicted infrared intensities and Raman activities are reported.

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