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Vibrational spectroscopic studies and DFT calculations of 4-fluoro-*N*-(2-hydroxy-4-nitrophenyl)benzamide

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Fourier transform infrared (FT-IR) and FT-Raman spectra of 4-fluoro-*N*-(2-hydroxy-4-nitrophenyl)benzamide were recorded and analyzed. The vibrational wavenumbers and corresponding vibrational assignments were examined theoretically using the Gaussian03 set of quantum chemistry codes. The red-shift of the NH-stretching wavenumber in the infrared (IR) spectrum from the computed wavenumber indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom. The simultaneous IR and Raman activation of the C═O-stretching mode gives the charge transfer interaction through a π-conjugated path. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

KEYWORDS: benzamide; FT-IR spectra; FT-Raman spectra; DFT calculations

INTRODUCTION

In the past few decades, the dramatically rising prevalence of multidrug-resistant microbial infections has become a serious healthcare problem. In particular, the emergence of multidrug-resistant strains of Gram-positive bacterial pathogens such as methicillin-resistant *Staphylococcus aureus* and *Staphylococcus epidermis* and vancomycin-resistant *Enterococcus* is a problem of ever-increasing significance.[1–5] Benzamide derivatives exhibit various types of biological properties such as anthelmentic, antihistaminic, antifungal, and antibacterial.[6–14] 6-*N*-(2-hydroxy-3,5-dichlorophenyl)-2-hydroxy-3,5,6-trichlorobenzamide (oxyclozanide), which has a benzamide structure, was discovered in 1969 as an anthelmentic agent effective against *Fasciola* hepatica for the treatment of liver fluke infection.[6] 3,4-Dihydroxy-6-(*N*-ethylamino)benzamide is a natural product that has been found in green pepper (*Piper nigrum L.*) as an antibacterial by Pradhan *et al.*[11] Additionally, a benzamide derivative, BAS-118, has been found to be a novel anti-*Helicobacter pylori* agent with a potent and selective antibacterial activity, which includes clarithromycin (CAM)- and metronidazole (MNDZ)-resistant isolates.[15] Yalcin *et al.*[10] and Aki-Sener *et al.*[12–14] reported some novel microbiologically active *N*-(2−hydroxy-5-substituted phenyl) benzamide/phenyl acetamide/phenoxy acetamide/thiophenoxy acetamide derivatives. The synthesis and biological evaluation of *N*-(2-hydroxy-4(or 5)-nitro/aminophenyl) benzamides and phenyl acetamides as antimicrobial agents are reported by Ertan *et al.*[16] However, there is no report on the infrared (IR) and Raman spectra of 4-fluoro-*N*-(2-hydroxy-4-nitrophenyl) benzamide. Computational 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 IR, Raman and theoretical calculations of the wavenumbers of the title compound are reported.

EXPERIMENTAL

The chemicals were purchased from commercial vendors and were used without purification. The reactions were monitored and the purity of the product was checked by thin layer chromatography (TLC). Silica gel 60 F_{254} chromatoplates were used for TLC. The solvent systems were chloroform/methanol (15 : 1). The final compound was purified by recrystallization using an appropriate solvent. The melting point was measured with a capillary melting point apparatus (Buchi SMP 20 and Electrothermal

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9100) and are uncorrected. The yield was calculated after recrystallization. The Fourier transform infrared (FT-IR) spectrum (Fig. S1, Supplementary Materials) was recorded on a Jasco FT/IR-420 spectrometer with KBr pellets. The FT-Raman spectrum (Fig. 1) 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, measurement on solid sample. The ^{1}H NMR spectra was recorded employing a VARIAN Mercury 400 MHz FT spectrometer, chemical shifts (δ) are in parts per million relative to TMS, and coupling constants (J) are reported in Hertz. Elemental analyses were taken on a Leco 932 CHNS-O analyzer. The results of the elemental analyses (C, H, N) were within ±0.4% of the calculated amounts.

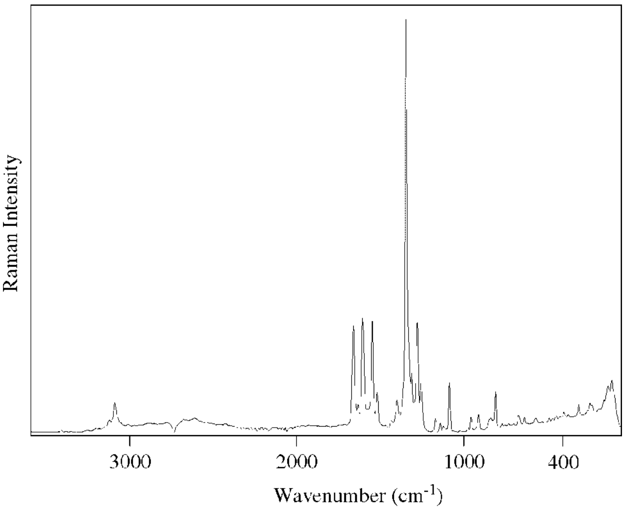

Figure 1. FT-Raman spectrum.

The synthesis was performed by reacting 5-nitro-2-aminophenols with appropriate 4-fluorobenzoic acid chloride, obtained in turn by treating 4-fluorobenzoic acid with thionyl chloride. Thionyl chloride (1.5 ml) and 4-fluorobenzoic acid (0.5 mmol) were refluxed in benzene (5 ml) at 80 °C for 3 h, and then excess thionyl chloride was removed in vacuo. The residue was dissolved in ether (10 ml) and the solution added during 1 h to a stirred, ice-cold mixture of 5-nitro-2-aminophenol (0.5 mmol), sodium bicarbonate (0.5 mmol), diethyl ether (10 ml) and water (1 ml). The mixture was stirred overnight at room temperature and filtered. After the precipitate was washed with water, 2 N HCl and water, respectively, and finally with ether, the title compound was obtained. The crude product was purified by recrystallization from ethanol. The crystals were dried *in vacuo*.

Yield 33%, m.p. 244–245 °C, elemental analysis: calculated/found: C 56.53/56.97; H 3.28/3.268; N 10.14/10.08. ^{1}H NMR (DMSO-d_0) δ ppm J = Hz: 7.34–7.38 (m, 2H, 10-H, 7-H); 7.70 (d, 1H, $J_m = 2.8$, 19-H); 7.76 (dd, 1H, $J_0 = 8.8$ and $J_m = 2.8$, 18-H); 8.01–8.05 (m, 2H, 9-H, 8-H); 8.14 (d, 1H, $J_0 = 8.8$, 15-H); 9.65 (s, 1H, OH).

COMPUTATIONAL DETAILS

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer.[17] The density functional theoretical (DFT) computations were performed at the B3LYP/6–31G* level of theory to get the optimized geometry (Fig. 2) and vibrational wavenumbers of the normal modes of the title compound. The DFT partitions the electronic energy $E = E_T + E_V + E_J + E_{XC}$, where E_T, E_V and E_J are electronic kinetic energy, electron nuclear attraction and electron–electron repulsion terms, respectively. The electron correlation is taken into account in the

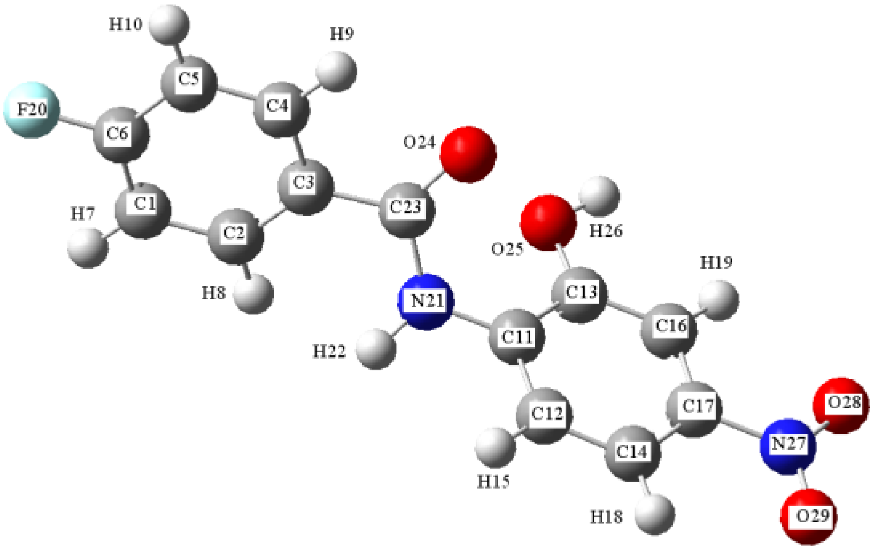

Figure 2. Optimized geometry of the molecule. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

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DFT via the exchange-correlation term E_{XC}, which includes exchange energy arising from the antisymmetry of quantum mechanical wavefunction and dynamic correlation in the motion of individual electrons, and it makes DFT dominant over the conventional Hartree–Fock (HF) procedure.[18] DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures (Table S1, Supplementary Materials) were confirmed to be minimum-energy conformations. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The DFT hybrid B3LYP functional method tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data.[19] Thus, a scaling factor of 0.9613 has been uniformly applied to the B3LYP calculated wavenumbers.[18] The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry.[20] The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes.[21,22]

RESULTS AND DISCUSSION

The observed IR and Raman bands with their relative intensities and calculated wavenumbers and assignments are given in Table 1.

The most characteristic bands in the spectra of nitro compounds are due to NO_2-stretching vibrations, which are the two most useful group wavenumbers, not only because of their spectral position but also for their strong intensity.[23] In nitro compounds the antisymmetric NO_2-stretching vibrations[23] are located in the region 1580 ± 80 cm^{-1}. The symmetric NO_2-stretching vibrations[23] are expected in the region 1380 ± 20 cm^{-1}. In substituent nitrobenzenes, $\upsilon_s NO_2$ appears strongly at 1345 ± 30 cm^{-1}, in 3-nitropyridine[24] at 1350 ± 20 cm^{-1} and in conjugated nitroalkenes[25] at 1345 ± 15 cm^{-1}. In the present case, the bands observed at 1548 cm^{-1} in the IR spectrum and 1541 cm^{-1} in the Raman spectrum are assigned as asymmetric NO_2 modes. The $\upsilon_s NO_2$ mode is observed at 1340 cm^{-1} in the Raman spectrum as a very strong band. The DFT calculations give 1564 and 1345 cm^{-1} as asymmetric and symmetric NO_2-stretching modes, respectively.

Table 1. Calculated vibrational wavenumbers, measured infrared, Raman band positions and assignments for 4-Fluoro-*N*-(2-hydroxy-4-nitrophenyl)benzamide

$\upsilon_{(calculated)}$ (cm^{-1})	$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	IR intensity (km mol^{-1})	Assignments
3610			62.52	υOH
3464	3403 s		17.63	υNH
3136		3140 vw	1.86	υCH II
3109			3.47	υCH I
3104			3.65	υCH II
3103			3.73	υCH I
3097	3092 mbr		1.78	υCH I
3077		3084 w	10.12	υCH I
3074	3000 w	3000 vw	9.29	υCH II
	2933 wbr			Combination bands
	2889 w			
	2844 w			
	2644 wbr	2659 w		
	2556 w	2606 w		
	2311 w			
1716	1653 s	1653 s	165.07	υC=O
1612	1628 w		15.52	υPh I
1601	1604 s	1599 s	105.51	υPh II
1588			43.91	υPh II
1578			6.71	υPh I
1564	1548 s	1541 s	215.60	$\upsilon_{as}NO_2$
1501		1511 w	50.54	υPh II
1500	1502 s		81.66	υPh I
1470			315.52	δNH
1406	1424 s	1420 vw	231.82	υPh II, δOH
1395	1390 s	1391 w	15.71	υPh I
1345		1340 vvs	19.24	$\upsilon_s NO_2$
1339	1345 s		528.52	υCN
1307		1304 w	0.54	υPh I
1280			132.71	υPh II
1275	1268 s	1271 s	191.35	δCH I, II
1263			24.14	υCN
1242		1250 m	51.47	υCF
1236	1249 s		135.06	$\upsilon(C–O)_h$
1212	1196 w		252.45	δNH
1153	1160 m	1163 w	83.70	ρNH, δCH I
1144		1139 vw	72.84	δCH II
1106	1098 w	1102 vw	42.77	δCH II
1089		1079 m	5.13	δCH I
1073	1077 w		112.40	δCH I
1059			46.09	υCC
994	1013 w	1000 vw	10.39	δCH I
946	946 w	948 w	0.94	γCH I
937			16.55	γCH I
922			0.22	γCH I
919	902 w	904 w	0.23	γCH II
882	873 m		9.08	ωNH

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Table 1. (*Continued*)

υ(calculated) (cm^{-1})	υ(IR) (cm^{-1})	υ(Raman) (cm^{-1})	IR intensity (km mol^{-1})	Assignments
851	852 m	848 vw	23.81	γCH I
830	817 m		36.94	Ring breath I
819			22.76	γCH I
805		802 m	1.33	γCH II
800	798 w		22.96	γCH II
792	760 m		37.77	δNO_2
773		761 vw	4.16	γNH
733			39.42	γPh I, δPh(X) II
722	718 m	724 vw	31.00	ωNO_2
686		694 vw	4.62	γPh II
663		662 w	10.37	Ring breath II
654	651 w		4.85	δC=O
621		625 vw	0.05	γOH
590	618 m		30.17	δPh I
564	561 m	564 vw	2.83	δPh(X) II
548			0.78	γPh(X) II
538			4.99	ρNO_2
505	520 w		3.38	γPh(X) I
478		477 vw	107.35	γC=O
457			7.64	γPh(X) II
450			11.86	δPh(X) I
418			1.98	γPh I
410			0.92	δCX(X)
387		386 vw	7.53	δCF
368		364 vw	11.45	δPh(X) II
346			5.03	δCC(X) I
321			12.69	γPh I
293		301 w	66.68	δCO(X) II
277			9.22	δCN(X) II
249		234 wbr	16.76	δCN(X) II
210			3.54	δCF(X) I
205			1.58	γCO(X) II
159		159 w	7.99	γCN(X) II
114		130 w	1.51	γCN(X) II
109			3.91	tC=ONH
99		103 m	2.00	γCF(X) I
62			0.37	tPh
41			0.22	tPh
35			0.63	tPh
26			0.23	tPh

υ, stretching; δ, in-plane deformation; γ, out-of-plane deformation; ρ, rocking; t, torsional; ω, wagging; Ph, phenyl; I, Ph attached to fluorine; II, Ph attached to nitro group; v, very; s, strong; m, medium; w, weak; br, broad; X, substituent sensitive; subscripts : as, asymmetric; s, symmetric.

According to some investigators,[26–28] the NO_2 scissors[23] occur in the region 850 ± 60 cm^{-1} when conjugated to C=C or aromatic molecules, with a contribution of the υCN, which is expected to be near 1120 cm^{-1}. For nitrobenzene, δNO_2 is reported[23] at 852 cm^{-1}, for $H_2C{=}CHNO_2$ at 890 cm^{-1} and for 1,3dinitrobenzene at 904 and 834 cm^{-1}. For the title compound, the DFT calculations give the band at 792 cm^{-1} as the deformation band of NO_2. The band observed at 760 cm^{-1} in the IR spectrum is assigned as δNO_2. In aromatic compounds, the wagging mode, ωNO_2, is assigned at 740 ± 50 cm^{-1} with a moderate to strong intensity, a region in which γCH is also active.[23] ωNO_2 is reported at 701 and 728 cm^{-1} for 1,2-dinitrobenzene and at 710 and 772 cm^{-1} for 1,4-dinitrobenzene.[23] For the title compound, the band at 718 cm^{-1} in the IR spectrum, 724 cm^{-1} in the Raman spectrum and 722 cm^{-1} (DFT) is assigned as ωNO_2 modes. In aromatic compounds, the rocking mode ρNO_2 is active in the region 545 ± 45 cm^{-1}. Nitrobenzene[23] shows this rocking mode at 531 cm^{-1}. In the present case, the DFT calculations give rocking mode of NO_2 at 538 cm^{-1}. Sundaraganesan *et al.*[29] reported the NO_2 deformation bands at 839, 744 and 398 cm^{-1} (experimental), and 812, 716, 703 and 327 cm^{-1} theoretically.

The OH group provides three normal vibrations υOH, δOH and γOH, of which both the stretching vibration and the out-of-plane deformations are good group vibrations. The DFT calculations give the υOH band at 3610 cm^{-1}. The in-plane OH deformation[23] is expected in the region 1400 ± 40 cm^{-1} and the band at 1424 cm^{-1} (IR), 1420 cm^{-1} (Raman) and 1406 cm^{-1} (DFT) is assigned as this mode is not pure, but contains significant contribution from phenyl ring-stretching modes. The stretching of the hydroxyl group with respect to the phenyl moiety υ$(C–O)_h$ appears at 1249 cm^{-1} in the IR spectrum and the calculated value is 1236 cm^{-1}. This band is expected[30–32] in the region 1220 ± 40 cm^{-1}. The out-of-plane OH deformation is observed at 625 cm^{-1} in the Raman spectrum and at 621 cm^{-1} theoretically, which is expected[23] in the region 650 ± 80 cm^{-1}. For paracetamol, υ$(C–O)_h$ and γOH are reported at 1240 and 620 cm^{-1}, respectively.[33]

The NH-stretching vibration[23] appears strongly and broadly in the region 3390 ± 60 cm^{-1}. For the title compound, the strong band at 3403 cm^{-1} in the IR spectrum is assigned as υNH mode. The calculated value for this mode is 3464 cm^{-1}. The NH-stretching wavenumber is red-shifted by 61 cm^{-1} in the IR spectrum with a strong intensity from the computed wavenumber, which indicates the weakening of the N–H bond resulting in proton transfer to the neighboring oxygen.[34]

The carbonyl-stretching C=O vibrations[23,34] are expected in the region 1715–1680 cm^{-1} and in the present study this mode appears at 1653 cm^{-1} in both spectra as a strong band. The DFT calculations give this mode at 1716 cm^{-1}. El-Shahawy *et al.*[33] reported a value 1640 cm^{-1} in the IR spectrum as υC=O for paracetamol. The deviation of the calculated wavenumber for this mode can be attributed to the underestimation of the large degree of π-electron delocalization due to conjugation of the molecule.[35] The intensity of the carbonyl group can increase because of conjugation or

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formation of hydrogen bonds. The increase in conjugation, therefore, leads to the intensification of the Raman lines as well as increased IR band intensities. The conjugation and influence of intermolecular hydrogen bonding result in the lowering of the stretching wavenumbers. The bands associated with the C=O-stretching mode are found to be strongly and simultaneously active in both IR and Raman spectra. This phenomenon is unusual, since, generally, even in the absence of inversion symmetry, the IR and Raman spectra are complementary; in most cases, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. However, the Intramolecular charge transfer (ICT) from the donor to acceptor group through a single-double bond conjugate path can induce large variations of both the molecular dipole moment and molecular polarizability, making the IR and Raman activities strong at the same time. Thus in the title compound, simultaneous IR and Raman activation of C=O-stretching mode clearly explains a charge transfer interaction between donor and acceptor through the π-conjugated path.[36,37] The δC=O in-plane deformation[23] has been found in the region $625 \pm 70\ \mathrm{cm^{-1}}$ and the band at $651\ \mathrm{cm^{-1}}$ in the IR spectrum and $654\ \mathrm{cm^{-1}}$ (DFT) is assigned as this mode. The C=O out-of-plane deformation[23] is in the range $540 \pm 80\ \mathrm{cm^{-1}}$, and the DFT calculations give this mode at $478\ \mathrm{cm^{-1}}$, and a very weak band is observed in the Raman spectrum at $477\ \mathrm{cm^{-1}}$.

The CNH vibration in which N and H atoms move in opposite direction of carbon atoms in the amide moiety appears at $1470\ \mathrm{cm^{-1}}$ theoretically, and the CNH vibration in which N and H atoms move in the same direction of carbon atoms in the amide group appears at $1196\ \mathrm{cm^{-1}}$ (IR) and $1212\ \mathrm{cm^{-1}}$ (DFT).[30,31,33] The NH rock in the plane is observed at $1160\ \mathrm{cm^{-1}}$ (IR), $1163\ \mathrm{cm^{-1}}$ (Raman) and at $1153\ \mathrm{cm^{-1}}$ theoretically.[33] The out-of-plane wagging[23] of NH is moderately active with a broad band in the region $790 \pm 70\ \mathrm{cm^{-1}}$ and the band at $761\ \mathrm{cm^{-1}}$ in the Raman spectrum and $773\ \mathrm{cm^{-1}}$ (DFT) is assigned as this mode. El-Shahawy *et al.*[33] reported a value $720\ \mathrm{cm^{-1}}$ for this mode. The C–N-stretching vibration,[23] coupled with the δNH, is moderately to strongly active in the region $1275 \pm 55\ \mathrm{cm^{-1}}$. El-Shahawy *et al.*[33] observed a band at $1320\ \mathrm{cm^{-1}}$ in the IR spectrum as this υC–N mode. In the present case, the band at $1268\ \mathrm{cm^{-1}}$ in the IR spectrum is assigned as this mode. The DFT calculations give the corresponding band at $1263\ \mathrm{cm^{-1}}$.

Fluorine atoms directly attached to the aromatic ring give rise to bands[31] in the region $1270–1100\ \mathrm{cm^{-1}}$. Many of these compounds, including the simpler ones with one fluorine only on the ring, absorb near $1230\ \mathrm{cm^{-1}}$.[31] The υC–F is reported at $1157\ \mathrm{cm^{-1}}$ and at $1223\ \mathrm{cm^{-1}}$ (IR), $1244\ \mathrm{cm^{-1}}$ (HF).[38,39] For the title compound, the band observed at $1250\ \mathrm{cm^{-1}}$ in the Raman spectrum is assigned as υC–F mode. The DFT calculations give this mode at $1242\ \mathrm{cm^{-1}}$. The substitution of fluorine in the phenyl ring shortens the C–C bond lengths $C_1–C_6$ and $C_5–C_6$ of the benzene ring. Fluorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from the neighboring atoms, which move close together in order to share the remaining electrons more easily as a result. Due to this, the bond angle A(1,6,5) is found to be 122.2° in the present case, which is 120° for normal benzene. Similarly, the bond lengths $C_1–C_6$ and $C_5–C_6$ are 1.3907 and 1.3922 Å, respectively, which is 1.3864 Å for normal benzene.[39]

The identification of C–N vibrations is a difficult task, since mixing of several bands are possible in this region. Silverstein and Webster[40] assigned the C–N-stretching absorption in the region $1382–1266\ \mathrm{cm^{-1}}$ for aromatic amines. The C–N-stretching mode is reported at $1368\ \mathrm{cm^{-1}}$ for benzamide,[41] at 1382, $1307\ \mathrm{cm^{-1}}$ for benzotriazole[29] and at 1335, $1331\ \mathrm{cm^{-1}}$ for 2,4-dinitrophenylhydrazine.[29] Primary aromatic amines with nitrogen directly on the ring absorb strongly at $1330–1260\ \mathrm{cm^{-1}}$ due to stretching for the phenyl carbon nitrogen band.[31] The υC–N is reported at $1340\ \mathrm{cm^{-1}}$ (Raman), $1325\ \mathrm{cm^{-1}}$ (calculated),[42] $1318\ \mathrm{cm^{-1}}$[43] and at $1332\ \mathrm{cm^{-1}}$ (IR), $1315\ \mathrm{cm^{-1}}$ (Raman), $1315\ \mathrm{cm^{-1}}$ (HF).[39] For the title compound, the DFT calculation gives this mode at $1339\ \mathrm{cm^{-1}}$ and the very strong band at $1345\ \mathrm{cm^{-1}}$ in the IR spectrum is assigned as υC–N.

Since the identification of all the normal modes of vibration of large molecules is not trivial, we tried to simplify the problem by considering each molecule as a substituted benzene. Such an idea has already been successfully utilized by several workers for the vibrational assignment of molecules containing multiple homo- and heteroaromatic rings.[39,44–48] In the following discussion, the phenyl rings attached with fluorine and nitro groups are designated as ring I and II, respectively. The modes in the two phenyl rings will differ in wavenumber, and the magnitude of splitting will depend on the strength of interaction between different parts (internal coordinates) of the two rings. For some modes, this splitting is so small that they may be considered as quasi-degenerate, while for other modes a significant amount of splitting is observed.[44–46,49]

The aromatic CH-stretching vibrations[23] absorb weakly to moderately between 3120 and $3000\ \mathrm{cm^{-1}}$. The DFT calculations give bands in the range $3074–3136\ \mathrm{cm^{-1}}$ as υCH-stretching modes. Experimentally, we have observed bands at 3092, $3000\ \mathrm{cm^{-1}}$ in the IR spectrum and at 3140, 3084, $3000\ \mathrm{cm^{-1}}$ in the Raman spectrum.

The benzene ring possesses six ring-stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and $1440\ \mathrm{cm^{-1}}$ are good group vibrations.[23] With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader the absorption regions.[23] In the case of C=O substitution, the band near $1490\ \mathrm{cm^{-1}}$ can be very weak.[23] The fifth ring-stretching vibration is active near $1315 \pm 65\ \mathrm{cm^{-1}}$, a region that overlaps strongly with that of the CH in-plane deformation.[23] In the sixth ring-stretching vibration, the ring-breathing mode appears as a weak band near $1000\ \mathrm{cm^{-1}}$

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in mono-, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from other modes.

The ring-breathing mode for the parasubstituted benzenes with entirely different substituents[30] has been reported to be strongly IR active with typical bands in the interval 780–840 cm^{-1}. For the title compound, this is confirmed by the strong band in the IR spectrum at 817 cm^{-1}, which finds support from the computational results. The ring-breathing mode of parasubstituted benzenes is reported at 804, 792 cm^{-1} experimentally and at 782, 795 cm^{-1} theoretically.[50,51] In asymmetric trisubstitued benzenes, when all the three substituents are light, the wavenumber interval of the breathing mode[30] 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 expected[30] to appear between 600 and 750 cm^{-1}. For the title compound, the phenyl ring II breathing mode is observed at 663 cm^{-1} theoretically. For parasubstituted benzenes, the δCH modes are seen in the range 995–1315 cm^{-1}, and for trisubstituted benzenes these modes are in the range 1290–1050 cm^{-1}.[23] Bands observed at 1160, 1098, 1077 and 1013 cm^{-1} in the IR spectrum, and at 1271, 1163, 1139, 1102, 1079 and 1000 cm^{-1} in the Raman spectrum are assigned as δCH modes. The DFT calculation gives these modes at 1275, 1153, 1144, 1106, 1089, 1073 and 994 cm^{-1}, as these modes and some of the bands are not pure but contain significant contribution from other modes. The CH out-of-plane deformations[23] 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 γCH modes are observed at 946, 902, 852 and 798 cm^{-1} in the IR spectrum, and at 948, 904, 848 and 802 cm^{-1} in the Raman spectrum. The strong CH out-of-plane deformation band occurring at 840 ± 50 cm^{-1} is typical for 1,4-disubstituted benzenes.[23] For the title compound, a strong band is observed at 852 cm^{-1} in the IR spectrum. Again, according to literature,[23,31] a lower γCH absorbs in the neighborhood 820 ± 45 cm^{-1}, but is much weaker or IR inactive. The DFT calculations give a γCH at 819 cm^{-1} and no band is experimentally observed for this mode. In the case of trisubstituted benzenes, two γCH bands are observed at 890 ± 50 and 815 ± 45 cm^{-1} in the IR spectrum. The bands observed at 902 cm^{-1} (IR), 904 and 802 cm^{-1} (Raman) and 919 and 805 cm^{-1} (DFT) are assigned as these modes.

The carbon–oxygen (phenolate) $C_{13}-O_{25}$ distance 1.356 Å is in agreement with the average distance of 1.362 Å found among phenols.[52] The DFT calculations give shortening of the angles $C_{14}-C_{17}-N_{27}$ by 0.7° and $C_{16}-C_{17}-N_{27}$ by 1.5° from 120° at C_{17} position and $C_{17}-N_{27}-O_{28}$, $C_{17}-N_{27}-O_{29}$ by 2.3° from 120° at N_{27} position. This reduction in angles reveals the hydrogen bonding with H_{19} and H_{18} which is evident from the enlargement in the angles $C_{16}-C_{17}-C_{14}$ by 2.2° and $O_{28}-N_{27}-O_{29}$ by 4.6°. Also at C_1 position, the angles $C_4-C_3-C_{23}$ are reduced by 2.7°, $C_2-C_3-C_{23}$ are increased by 3.5° from 120°, and this asymmetry of exocyclic angles reveals the interaction between O_{24} and the phenyl ring I. The C–C bond lengths in the phenyl ring I lie between 1.3907 and 1.4030 Å, while for the phenyl ring II, the range is 1.4146–1.3914 Å. The CH bond lengths lie between 1.0848 and 1.0862 Å for phenyl ring I, and 1.0820 and 1.0846 Å for phenyl ring II. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere in between the normal values for a single (1.54 Å) and a double (1.33 Å) bond.[53]

The IR bands in the 2311–2933 cm^{-1} region and their large broadening support the intramolecular hydrogen bonding between the C=O and OH groups.[54]

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structure parameters of related molecules.[55–57] According to Noveron *et al.*[55] for complexes of *N*-(4-pyridyl)benzamide, the bond lengths for $C_{11}-N_{21}$, $C_{23}-O_{24}$, $C_{23}-N_{21}$, $C_{23}-C_3$, C_3-C_2, C_3-C_4 and $N_{21}-H_{22}$ are 1.3953, 1.2253, 1.3703, 1.4943, 1.3923, 1.3933 and 0.773 Å, respectively, and the corresponding values for the title compound are 1.4093, 1.2195, 1.3958, 1.4977, 1.4029, 1.4030 and 1.0115 Å. For *N*-(2-pyridyl)benzamide complexes,[56] the bond lengths for $C_{23}-O_{24}$, $N_{21}-C_{23}$, $N_{21}-C_{11}$ and $C_{23}-C_3$ are 1.2445, 1.3646, 1.4156 and 1.4816 Å, respectively, while in the present case, these bond lengths are 1.2195, 1.3958, 1.4093 and 1.4977 Å. Saeed *et al.*[57] reported $C_{25}-O_{23}$, $N_{27}-O_{28}$, $N_{27}-O_{29}$, $N_{21}-C_{23}$, $N_{21}-C_{11}$ and $N_{27}-C_{17}$ bond lengths as 1.2132, 1.2292, 1.2252, 1.3612, 1.4092 and 1.4632 Å for 2-nitro-*N*-(4-nitrophenyl)benzamide. For the title compound, we have obtained these bond lengths as 1.2195, 1.2321, 1.2311, 1.3958, 1.4093 and 1.4677 Å. For the benzamide moiety of the title compound, the calculated values of the bond angles $C_{23}-N_{21}-C_{11}$, $C_{12}-C_{11}-N_{21}$, $O_{24}-C_{23}-N_{21}$, $O_{24}-C_{23}-C_3$, $N_{21}-C_{23}-C_3$, $C_4-C_3-C_{23}$ and $C_2-C_3-C_{23}$ are 123.3°, 120.3°, 122.4°, 122.6°, 115.0°, 123.5° and 117.3°, respectively. Sun *et al.*[56] reported the corresponding angles as 124.7°, 116.6°, 123.1°, 118.7°, 118.3°, 124.3° and 115.6° for benzamide complexes. The bond angles of the NO_2 group of the title compound $O_{28}-N_{27}-O_{29}$ 124.6°, $O_{29}-N_{27}-C_{17}$ 117.7° and $O_{28}-N_{27}-C_{17}$ 117.7° are in agreement with the values 123.5°, 118.7° and 117.9° given by Saeed *et al.*[57] Also, DFT calculations give the torsional angles, $C_{14}-C_{12}-C_{11}-N_{21}$, $N_{21}-C_{11}-C_{13}-C_{16}$, $O_{24}-C_{23}-C_3-C_2$, $N_{21}-C_{23}-C_3-C_2$, $O_{24}-C_{23}-C_3-C_4$ and $N_{21}-C_{23}-C_3-C_4$ around the benzamide group as 178.4°, −179.7°, −22.5°, 158.2°, 158.9° and −20.4°, which are in agreement with the reported values[55] 178.5°, −178.9°, −16.8°, 163.8°, 161.6° and −17.8°.

In order to investigate the performance and vibrational wavenumbers of the title compound, root mean square (RMS) value and correlation coefficient between calculated and observed wavenumbers were calculated (Fig. 3). RMS

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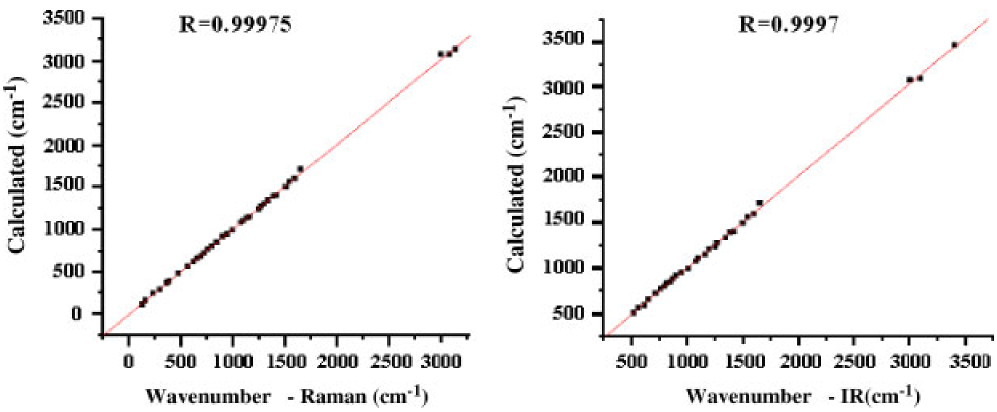

Figure 3. Correlation graphs of calculated and experimental wavenumbers. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

values of wavenumbers were evaluated using the following expression.[58]

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}(\upsilon_i^{\text{calc}} - \upsilon_i^{\text{exp}})^2} \qquad (1)$$

The RMS error of the observed Raman bands, IR bands and scaled wavenumbers are found to be 18.9 and 25.2, respectively. 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 IR wavenumbers and intensities of many other modes. Also, we state that experimental results belong to the solid phase, and theoretical calculations belong to the gaseous phase.

CONCLUSION

The FT-IR and FT-Raman spectra of 4-fluoro-*N*-(2-hydroxy-4-nitrophenyl)benzamide were studied. The molecular geometry and wavenumbers have been calculated using the B3LYP/6–31G* basis set. The observed wavenumbers are found to be in agreement with the calculated values. The red-shift of NH-stretching wavenumber in the IR spectrum from the computed wavenumber indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom. The simultaneous IR and Raman activation of the C=O-stretching mode gives the charge transfer interaction through a π-conjugated path.

Supporting Information

Supporting information may be found in the online version of this article.

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