A computational study of 2-Nitro-N-(4-nitrophenyl)benzamide

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ABSTRACT

The vibrational frequencies of 2-Nitro-N-(4-nitrophenyl)benzamide were calculated using Gaussian03 software package and the fundamental modes are assigned. The predicted infrared intensities and Raman activities are reported. The calculated geometrical parameters are in agreement with reported values. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

Key words: Hartree-Fock, hyperpolarizability, benzamide

INTRODUCTION

The benzanilide core is present in compounds with such wide ranging biological activity that it has been called a privileged structure. Benzanilides serve as intermediate towards benzothiadiazin-4-ones[1], quinazoline-2,4-diones[2], benzodiazepine-2,5-ones[3], and 2,3-disubstituted 3H-quinazoline-4-ones[4]. In the fast 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 Staphylocccus aureus and Staphylococcus epidermis and vancomycin-resistant Enterococcus is a problem of ever increasing significance[5-9]. Benzamide derivatives exhibit various types of biological properties such as anthelmentic, antihistaminic, antifungal, and antibacterial[10-15]. 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 vibrational frequencies are calculated theoretically. The geometrical parameters obtained are compared with experimental data given by Saeed *et al*.[16] and the hyperpolarizability value is also calculated.

Computational details

Calculations of the title compound were carried out with Gaussian 03 program[17] using the HF/6-31G* basis set to predict the molecular structure and wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation.[18] We

therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The IR and Raman bands and their assignments are given in Table 1. The most characteristic bands in the spectra of nitro

Table 1 : Calculated vibrational wavenumbers and band assignments

$\upsilon_{(HF)}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	Force constants	Assignments
3418	229.65	146.97	9.33	υNH
3104	6.56	42.65	7.80	υCH
3066	2.79	66.12	7.61	υCH
3063	2.96	98.82	7.60	υCH
3062	2.02	50.05	7.58	υCH
3053	1.79	112.07	7.56	υCH
3038	8.12	131.99	7.47	υCH
3023	2.89	67.40	7.36	υCH
3016	5.60	58,44	7.35	υCH
1671	216.79	108.76	4.51	υC=O
1628	106.48	176.21	9.99	υPh
1613	10.80	100.27	10.99	υPh
1606	211.68	251.20	11.60	υPh
1580	81.88	33.63	8.46	υPh
1564	428.42	66.80	6.88	$\upsilon_{as}NO_2$
1510	103.82	0.04	3.82	$\upsilon_{as}NO_2$
1492	27.73	5.11	3.82	υPh
1457	318.72	3.71	5.45	υPh
1438	452.33	13.57	7.35	δNH
1434	195.43	5.73	4.77	υPh
1390	101.73	1.20	5.12	υPh
1337	282.79	64.49	5.62	υ_sNO_2
1329	18.14	31.23	2.43	υ_sNO_2
1316	339.99	348.38	5.85	υCN, υPh
1305	620.89	464.08	3.96	υCN, δCH
1290	15.81	28.63	2.34	υPh
1235	6.73	3.93	4.36	δCH
1227	66.30	0.82	2.45	υCN
1214	22.58	8.35	5.39	δNH
1193	75.29	56.28	1.36	δCH
1161	19.12	15.00	1.71	δCH
1138	1.75	8.45	2.13	δCH, ρNH
1128	19.21	10.00	1.56	δCH
1116	39.82	17.19	1.75	υCX(X)
1108	18.30	109.25	3.00	υCX(X)
1079	2.09	0.67	1.72	δCH
1069	3.24	1.25	2.42	δCH
1064	2.27	3.63	1.17	υCX(X)

Table 1. Cont.

1046	1.42	3.44	1.15	υCX(X)
1038	5.42	26.84	1.50	δCH
1029	4.54	21.42	1.63	δCH
1010	0.48	12.88	2.28	δCH
952	6.24	4.31	1.06	γCH
925	223.91	1.19	1.08	γCH
889	35.11	4.69	2.53	γCH
884	31.56	7.91	0.83	γCH
842	22.11	29.43	2.34	ωNH
828	26.96	5.30	1.80	γCH
826	6.05	1.55	1.56	γCH
818	64.43	1.90	1.07	γCH
797	43.68	3.84	2.35	γNH, υPh(X)
786	107.09	2.62	0.88	γCH, δNO$_2$
747	5.10	7.73	1.32	γPh, δNO$_2$
719	19.21	3.20	1.61	υPh(X)
714	28.37	1.40	1.99	γPh
694	31.21	1.38	1.61	δPh(X)
691	6.54	1.19	1.56	ωNO$_2$
660	6.79	3.73	2.13	ωNO$_2$
640	1.87	3.14	2.12	δC=O, δPh
626	0.11	6.04	1.94	ρNO$_2$
581	0.89	0.99	1.07	δPh(X), ñNO$_2$
524	21.09	2.33	0.64	γPh(X)
519	6.42	1.36	1.20	γPh(X)
499	7.08	2.13	0.91	γPh(X)
436	14.89	1.98	0.81	γPh, γC=O
426	0.62	0.23	0.40	γPh(X)
419	0.92	3.22	1.00	δPh(X)
400	17.99	1.54	0.68	γPh
385	20.43	1.68	0.7048	δPh(X)
345	1.36	1.14	0.70	δCX(X)
329	4.99	1.46	0.45	δCX(X)
292	3.56	2.17	0.40	δCX(X)
244	9.06	3.58	0.42	δCX(X)
211	5.78	5.76	0.28	γCX(X)
201	2.93	4.45	0.22	γCX(X)
167	2.80	1.62	0.18	γCX(X)
138	1.42	2.11	0.10	γCX(X)
114	0.49	4.54	0.05	τC=ONH
78	2.21	4.03	0.05	τPh
63	1.20	0.38	0.03	τNO$_2$
56	6.71	0.53	0.02	τNO$_2$
51	4.00	2.53	0.02	τPh
27	0.27	6.75	0.01	τPh
21	2.09	2.43	0.01	τPh

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-torsion; rocking; ω -wagging; X-substituent sensitive; Ph-Phenyl; subscripts: as - asymmetric, s- symmetric.

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[19]. In nitro compounds, the asymmetric and symmetric NO_2 stretching vibrations are expected in the regions, 1580 ± 80 and 1380 ± 20 cm^{-1}, respectively[19]. For the title compound, the HF calculations give 1564, 1510 cm^{-1} and 1337, 1329 cm^{-1}, as asymmetric and symmetric stretching vibrations of nitro group. According to some investigators[20-22], the NO_2 scissors occur in the region 850 ± 60 cm^{-1} when conjugated to C=C or aromatic molecules and the

wagging mode ωNO_2 in the region 740 ± 50 cm^{-1} [19]. In aromatic compounds the rocking mode ρNO_2 is active in the region 545 ± 45 cm^{-1} [19]. All these modes are identified and assigned (Table 1).

The carbonyl stretching C=O vibration are expected in the region 1715-1680 cm^{-1} and in the present study the HF calculation give this mode at 1671 cm^{-1} with strong IR and Raman activity[19,23]. The in-plane δC=O has been found in the region 625 ± 70 cm^{-1} and the out-of-plane deformation γC=O in the region 540 ± 80 cm^{-1} [19]. These deformation bands are assigned at 640 and 436 cm^{-1}.
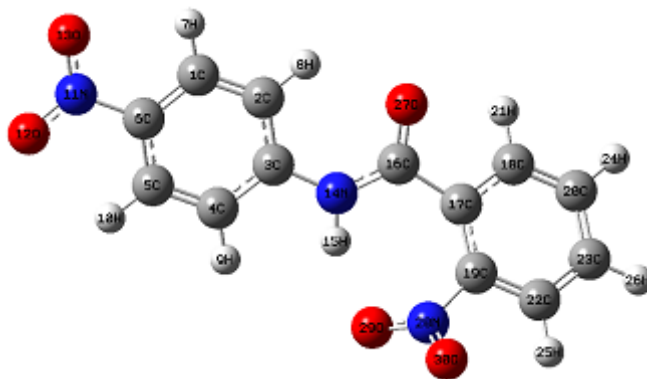
The CNH vibration in which N and H atoms move in opposite direction of the carbon atom in the amide moiety appears at 1430 cm^{-1} theoretically and the CNH vibration in which N and H atoms move in the same direction of the carbon atom appear at 1214 cm^{-1} [24-26]. The NH rock[26] in the plane is calculated to be at 1138 cm^{-1} and the out-of-plane wagging mode ωNH is expected in the region 790 ±70 cm^{-1} and the band at 842 cm^{-1} is assigned as this mode[19]. The HF calculations give the C-N stretching modes[19] at 1222, 1315 and 1326 cm^{-1}.

The phenyl CH stretching vibrations, ring CC vibrations – νPh, the in-plane and out-of-plane CH deformations, and ring deformations are also assigned (Table 1) . Some modes are not pure but contains significant contributions from other modes also.

For the title compound, according to Saeed *et al.*[16], the bond lengths C_{16}-O_{27} =1.2132, N_{11}-O_{13}= 1.2292, N_{11}-O_{12}=1.2252, N_{28}-O_{29}=1.2242, N_{28}-

O_{30}=1.2182, N_{14}-C_{16}=1.3612, N_{14}-C_3=1.4092, N_{11}-C_6=1.4632, N_{28}-C_{19} =1.4712Å. In the present calculation the corresponding lengths are, 1.2279, 1.2274, 1.2281, 1.2353, 1.2148, 1.3522, 1.4031, 1.4416 and 1.4587 Å. In the present case, the bond angles C_{16}-N_{14}-C_3 =128.1, O_{12}-N_{11}-O_{13} =123.3, O_{12}-N_{11}-C_6 =118.3, O_{13}-N_{11}-C_6 =118.4, O_{30} 30-N_{28}-O_{29} =123.3, O_{30}-N_{28}-C_{19} =18.0, O_{29}-N_{28}-C_{19} =118.6, C_2-C_3-C_4 =119.7, C_2-C_3-N_{14} =124.3 and C_4-C_3-N_{14} =116.0°. The corresponding reported values[16] are 127.5, 123.5, 118.7, 117.9, 123.9, 118.0, 118.1, 120.4, 123.3 and 116.4°.

Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research[27]. 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, by analyzing the vibrational modes using the IR and

Raman spectrum. The calculated first hyperpolarizability of the title compound is 7.08 × 10^{-30} esu, which is comparable with the reported values of similar derivates[28].We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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