Computational and Experimental Study on *N*-(4-Chlorobenzoyl)-Anthranilic Acid

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Abstract

The crystal of *N*-(4-Cholorobenzoyl)-anthranilic acid has been synthesized and characterized by X-Ray, ^{1}H-NMR, ^{13}C-NMR and IR techniques. Its molecular geometry was also optimized using HF and DFT/B3LYP theories with the 6−31G(d) and 6−31G+(d,p) basis sets and compared with the experimental data. The calculated results show that the optimized geometry can well reproduce the crystal structure, and the theoretical vibrational frequencies and chemical shift values show good agreement with experimental values.

Keywords: FT-IR; Hartree-Fock method; anthranilic acid; DFT

1. Introduction

The formation of amides has attracted considerable interest owing to their importance in bioorganic and organic chemistry, their value as intermediates in organic synthesis and a wide range of applications in the chemical industry [1].

Amide bond structure of amide derivatives often plays a key role in functions such as molecular recognition events or biological activities [2]. Amide bonds continue attracting the attention of the chemists, biologists because of their profound importance in living systems; such as, they determine the interactions of biologically active structures like peptides [3].

In this context, we would like to report the preparation of *N*-(4-cholorobenzoyl)-anthranilic acid crystal and their characterization with the help of X-Ray, ^{1}H-NMR, ^{13}C-NMR and IR techniques. Furthermore, theoretical calculations have been performed using the Gaussian 03 program [4] at various levels of theory to investigate the structural and physical properties of title compound [5].

2. Experimental and Computational

2.1 Material and Measurements

All chemicals were purchased from Sigma–Aldrich or Fluka Chemical Company with a stated purity of greater than 99% and it was used as such without further purification. The FT-IR spectra were recorded in the region of 400–4000 cm^{-1} on Perkin-Elmer Spektrum 100 BX, FT-IR spectrophotometer. ^{1}HNMR spectra were recorded indeuterated chloroform using tetra methyl silane (TMS) as an internal reference standard on BRUKER DPX-400 NMR spectrometer.

2.2. Computational details

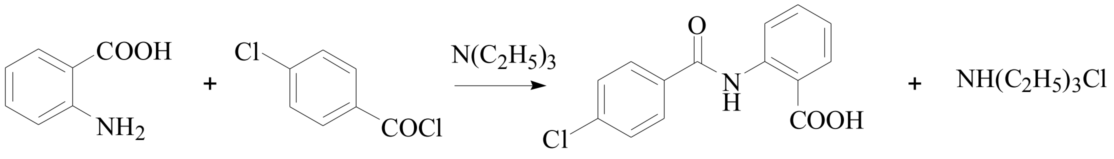
The structural and geometrical features of the hydrogen bonded compound of the title compound is studied extensively in this work by ab initio and DFT calculations with various basis sets: 6-31G(d) and 6-31G+(d,p) using the GAUSSIAN 03 series of programs [4].

2.3. X-ray structure determination

Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The intensity data were integrated using the SAINT program [6]. Absorption corrections were applied based on equivalent reflections using SADABS [7]. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXL [8]. The program ORTEP-3 [9] for Windows was used preparation of the figures. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

2.4. Synthesis of N-(4-Cholorobenzoyl)-anthranilic acid

N-(4-cholorobenzoyl)-anthranilic acid (**1**): A solution of anthranilic acid (10 mmol) in THF (50 ml) was added dropwise a THF solution of 4-choloro benzoyl chloride (10 mmol) at room temperature and then triethylamine (10 mmol) added. The reaction mixture was stirred for 15 h. It was poured and then 100 ml water was added. The crude product was crystallized from acetonitrile.



(**1**)

Scheme 1

Yield: 82 %; IR : ν 3311 (N-H), 3102 (Ar-H), 2650 (OH-C=O), 1692 (C=O), 1659 (C=O, first amide band), 1587 (C=O, secondary amid band), 1488-1468 (C=C), cm^{-1}; ^{1}H-NMR (400 MHz, DMSO *d*$_6$): δ=12.2 (s, 1H, H$_2$, OH), 8.7 (t, 1H, H$_1$N, NH), 8.1-7.2 (m, 8H, Ar-H)); ^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ (ppm) :169.98 (ArC-O-NH-), 163.54 (ArC-O-), 140.88-116.16 (ArC- H)

Table 1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{14}H_{10}ClNO_3$
Formula weight (g.mol^{-1})	275.68
T(K)	100 (2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	6.6989 (5)
b (Å)	7.2140 (6)
c (Å)	25.1489 (18)
α (°)	90
β (°)	92.624 (4)
γ (°)	90
V (Å^3)	1214.07 (16)
Z	4
μ (mm^{-1})	0.32
T_{min}, T_{max}	0.666, 0.746
Reflections collected	2991
Independent reflections (R_{int})	0.024
Refinement method	Full-matrix least-squares on F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.087, 1.06
Largest difference in peak and hole (eÅ^{-3})	0.42 and −0.22
CCDC deposition no.	759152

3. Results and discussion

The selected bond lengths are summarized in Table 2. It is obvious that the C19–O5 and C18–O2 with a bond length of 1.22 Å and 1.23 Å are in good agreement with the C=O double bond [18]. The calculated C19–O5 and C18–O2 bond length by HF/6-31G(d), HF/6-31+G(d,p), B3LYP/6-31G(d), B3LYP/6-31+G(d,p) methods are 1.20 Å, 1.20 Å, 1.22 Å, 1.22 Å, and 1.20 Å, 1.20 Å, 1.23 Å, 1.23 Å, respectively.

The C19–N6 bond length is 1.37 Å and C8–N6 bond length is 1.40 Å similar normal C–N bond distance. The difference in calculated C-N bond length of 0.01 Å is due to the repulsion between the lone pair of electron on the oxygen and the nitrogen atoms [5]. It is observed that the various ring C–C bond lengths and the C–H bond lengths of the title compound are found to be almost same at all levels of calculations. The calculated C25-Cl1 bond length is nearly equal to experimental.

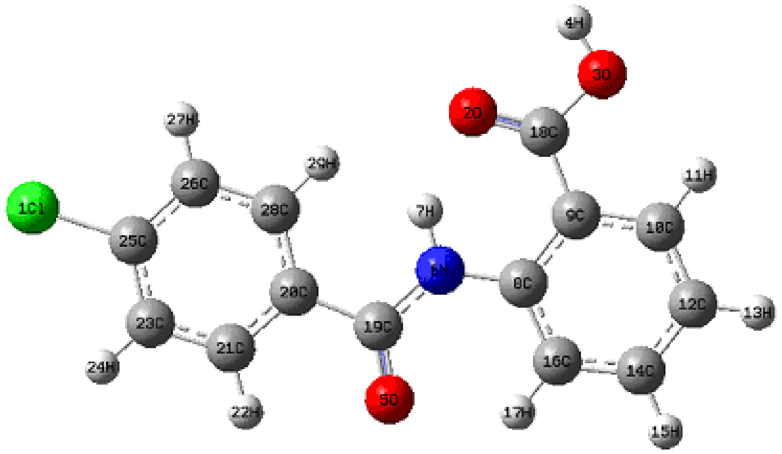


Fig. 1. Molecular model of *N*-(4-Cholorobenzoyl)-anthranilic acid with numbering of atoms.

Table 2. Experimental and optimized bond length of *N*-(4-Cholorobenzoyl)-anthranilic acid calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	Exp.	ab-initio		DFT	
		HF/6-31G(d)	HF/6-31G+(d.p)	B3LYP/6-31G(d)	B3LYP/6-31G+(d.p)
N6-H7	0.84	0.99	0.99	1.01	1.01
N6-C19	1.37	1.36	1.36	1.38	1.38
N6–C8	1.40	1.39	1.39	1.39	1.39
O3-H4	0.84	0.95	0.95	0.97	0.97
C19-O5	1.22	1.20	1.20	1.22	1.22
C19-C20	1.51	1.50	1.50	1.50	1.50
C25-C23	1.39	1.38	1.38	1.39	1.39
C18-O2	1.23	1.20	1.20	1.23	1.23
Cl1-C25	1.74	1.73	1.74	1.75	1.75
R^2		0.9751	0.9732	0.9753	0.9753

For numbering of atoms refer Fig. 1

The selected bond angles are summarized in Table 3. The bond angle O5–C19–N6 is 124.7°. The bond angle O5–C19–N6 calculated by HF/6-31G(d), HF/6-31+G(d,p), B3LYP/6-31G(d), B3LYP/6-31+G(d,p) methods is 123.9°, 124.4°, 123.5°, 123.6°, respectively. The bond angles determined from HF methods are slightly higher than that obtained from B3LYP methods.

Table 3. Experimental and optimized bond angle of *N*-(4-Cholorobenzoyl)-anthranilic acid calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	Exp.	HF/6-31G(d)	HF/6-31G+(d,p)	B3LYP/6-31G(d)	B3LYP/6-31G+(d,p)
H4-O3-C18	109.4	108.1	108.3	106.4	106.5
O3-C18-O2	122.2	120.1	120.1	119.8	119.8
C9-C8-N6	118.8	119.1	119.2	118.9	118.9
C8-N6-H7	114.0	113.5	113.9	112.8	112.6
C8-N6-C19	129.1	128.9	128.9	129.0	129.0
H7-N6-C19	116.0	117.4	117.2	118.1	118.3
N6-C19-O5	124.7	123.9	124.4	123.5	123.6
O5-C19-C20	121.0	120.1	120.4	120.7	120.7
H29-C28-C26	119.7	117.1	117.9	117.2	117.3
Cl1-C25-C23	119.3	119.5	119.5	119.5	119.5
R^2		0,9555	0,9673	0,9356	0,9339

For numbering of atoms refer Fig. 1

The selected dihedral angles are summarized in Table 4. The chlorine connected phenyl ring is planar with carbonyl connected phenyl ring which is evident from the dihedral angle of C20-C19-N6-C28 177.2°. The torsion angles determined from B3LYP methods are slightly higher than that obtained from HF methods.

Table 4. Experimental and optimized dihedral angle of *N*-(4-Cholorobenzoyl)-anthranilic acid calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	Exp.	HF/6-31G(d)	HF/6-31G+(d,p)	B3LYP/6-31G(d)	B3LYP/6-31G+(d,p)
H4-O3-C18-O2	-4,3	0,0	0,2	0,0	0,0
O3-C18-C9-C10	5,8	0,0	-0,6	0,0	0,0
H4-O3-C18-C9	175,5	179,9	-179,9	180,0	-179,9
C8-N6-C19-O5	-2,0	0,0	3,8	-0,0	0,0
H7-N6-C19-O5	176	-180,0	-174,1	179,9	-179,9
O5-C19-C20-C28	-176,0	180,0	-160,1	-179,9	-179,9
Cl1-C25-C23-H24	-0,2	0,0	0,0	0,0	0,0
Cl1-C25-C23-C21	179,8	-180,0	179,8	180,0	180,0
Cl1-C25-C26-C28	-0,5	180,0	179,8	-180,0	-180,0
C20-C19-N6-C28	177,2	180,0	-176,9	-179,9	-179,9
C9-C10-C12-C14	0,4	0,0	-0,04	0,0	0,0
R^2		0.1036	0.0131	0.3587	0.007

For numbering of atoms refer Fig. 1

The observed and calculated frequencies of *N*-(4-Cholorobenzoyl)-anthranilic acid are summarised in Table 5. According to calculated correlation coefficient values, B3LYP/6-31G+(d,p) method is in better agreement with the experimental than other methods. As can be seen from R^2 values depicted in Tables 5, we found good agreement between calculated and experiment. All experimental and theoretical vibrational frequencies in the infrared spectra are consistent with each other. Theoretical (NH) stretching frequencies are slightly larger than experimental data. Differences can be explained by electronic correlation effects since polarization functions not included in theoretical calculations.

Table 5. Experimental and calculated level vibrational frequencies (cm^{-1}), and probable assignments of *N*-(4-Cholorobenzoyl)-anthranilic acid.

Exp.	HF/6-31G(d)	HF/6-31G+(d,p)	B3LYP/6-31G(d)	B3LYP/6-31G+(d,p)
1247	1233	1228	1271	1268
1313	1314	1312	1328	1323
1488	1441	1508	1490	1484
1659	1634	1664	1659	1653
1692	1928	1719	1730	1729
3102	3369	3355	3193	3191
3311	3874	3355	3495	3482
R^2	0.9895	0.995	0.999	0.9992

4. Conclusions

We have carried out DFT and ab initio calculations on the structure and vibrational spectrum of *N*-(4-Cholorobenzoyl)-anthranilic acid. Comparison between the calculated and experimental structural parameters for bond lengths, R^2 values of B3LYP/6-31G(d) and B3LYP/6-31G+(d,p) are found to be similar. Bond lenghts and dihedral angles indicates that B3LYP results are in good agreement with experimental values. The parameters for bond angles indicates that HF results are in good agreement with experimental values. Vibrational frequencies, Infrared intensities calculated by B3LYP/6-31G+(d,p) method agree very well with experimental results.

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