

Computational Study on the Structure of N-(2-Amino-benzoyl)-N'-phenyl hydrazine

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Abstract

The hydrazide compound N-(2-Amino-benzoyl)-N'-phenyl hydrazine has been synthesized and characterized by ¹H-NMR, ¹³C-NMR, IR and X-Ray determination. The molecular geometry and vibrational frequency values in the ground state have been calculated using the density functional methods HF and B3LYP with the 6-31G(d) and 6-31G+(d,p) basis sets. 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; Hydrazide

1. Introduction

Hydrazides are a class of compounds with wide applications especially as a ligand in preparation of new complexes [1]. These compounds can be used in synthesis of novel heterocyclic compounds [2], pharmaceutical chemistry [3] and many other applications [4]. The chemistry of hydrazide derivatives has been investigated intensively in the last decade owing to antituberculosis activity [5] and vibrational analysis[6] as well as their use in analytical chemistry[7].

Understanding the conformational behavior and spectral properties of hydrazides would give detailed information about their chemical and biological activity. Because of the biological significance particularly in medicinal and enzyme chemistry hydrazides have recently become attractive to theoreticians as well as experimentalists. Experimental and theoretical research may become a very useful methodology to describe reaction mechanisms in organic chemistry [8]. The C-N rotational barrier in hydrazide was predicted to be about 28–30 kcal/mol which is indicative of a significant partial p double-bond character of the C-N peptide linkage and an sp² nature of the central nitrogen atom, which would stabilize the planar structure of the molecules [9,10].

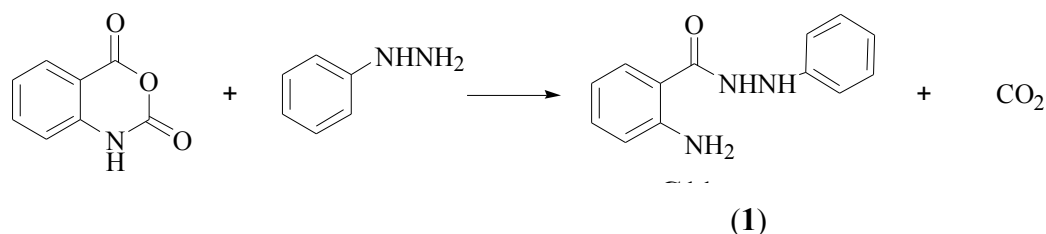
In this paper, we report the synthesis, characterisation and crystal structure of N-(2-amino-benzoyl)-N'-phenyl hydrazine, (C₁₃H₁₃N₃O), as well as theoretical studies using the HF and DFT/B3LYP levels of theory using the 6-31G(d) and 6-31G+(d,p) basis sets. We aimed to describe and characterize the molecular structure, and chemical shifts of N-(2-amino-benzoyl)-N'-phenyl hydrazine, both experimentally and theoretically. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift-molecular structure relationship.

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. The spectrum was recorded at room temperature, with scanning speed of $30 \text{ cm}^{-1} \text{ min}^{-1}$ and the spectral resolution of 2.0 cm^{-1} . Melting points were determined in open capillary tubes using Electrothermal IA-9200. $^1\text{H-NMR}$ spectra were recorded in deuterated chloroform using tetra methyl silane (TMS) as an internal reference standard on BRUKER DPX-400 NMR spectrometer.



Scheme 1

2.2. Synthesis of *N*-(2-Amino-benzoyl)-*N'*-phenyl hydrazine

A solution of (0.1 mol) phenyl hydrazine in water and (0.1 mol) of isatoic anhydride was added and stirred for 4 hr. The mix was stirred and the temperature raised slowly until a moderate evolution of CO_2 gas occurred. This was usually between 60°C and 70°C . After letting the mixture cool to room temperature, it was poured over crushed ice. The solid product were collected by filtration then fractionally recrystallized from dilute dioxane to give of dark brown crystals of the title compound suitable for X-ray analysis.

2.2.1. Compound

Dark brown crystals, yield 85%. Anal. Calc. for C, 68,70; H, 5,77; N, 18,49; O, 7,04. Found: C, 67,6; H, 5,34; N, 18,39; O, 7,01 IR: ν 3429 (NH_2), 3334 (N-H), 3025 (Ar-H), 1642 (C=O), 1584 (C=O), 1492-1443 (C=C), cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 10.1 (s, 1H, NH), 8.7-6.4 (m, 8H, Ar-H), 3.4 (s, 2H, NH_2); $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ (ppm) :168 (ArC-O-NH-), 148.5-114.5 (ArC- H)

2.3. 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 [11]. Full geometry optimisation of the studied hydrogen-bonded complexes was performed. The optimised geometrical parameters were compared with the available experimental data in order to establish the accuracy for the prediction of the geometrical parameters of hydrogen-bonded complexes. The density functional (DFT) calculations in this work were carried out in the framework of Kohn–Sham density-functional theory [12] (DFT) with the nonlocal three-parameter gradient corrected exchange-correlation functional of Becke and Lee, Yang and Parr including partially exact HF-exchange (B3LYP) [13].

2.4. X-ray structure determination

Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The intensity data were integrated using the SAINT program [14]. Absorption corrections were applied based on equivalent reflections using SADABS [15]. The structures were solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXL [16]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealised positions with isotropic displacement parameters constrained to 1.5 times the U_{equiv} of their attached carbon atoms for all others. The program ORTEP-3 [17] for Windows was used for preparation of the figures. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

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

Empirical formula	C ₁₃ H ₁₃ N ₃ O
Formula weight (g.mol ⁻¹)	227.26
T(K)	293(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
a (Å)	6.1188 (3)
b (Å)	19.8850 (11)
c (Å)	9.6347 (4)
α (°)	90
β (°)	94.042 (4)
γ (°)	90
V (Å ³)	1169.36 (10)
Z	4
ρ _{calc} (g.m ⁻³)	1.291
μ (mm ⁻¹)	0.09
F(000)	480
θ range for data collection (°)	32.3
Index ranges	-9 ≤ h ≤ 8 -29 ≤ k ≤ 23 -13 ≤ l ≤ 13
Reflections collected	8813
Independent reflections (R _{int})	0.034
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3743/ 0 /154
Goodness-of-fit (GOF) on <i>F</i> ²	S=0.82
R indices [I > 2σ(I)]	R ₁ = 0.051 wR ₂ = 0.153
Largest difference in peak and hole (eÅ ⁻³)	0.38 and -0.41
CCDC deposition no.	769530

3. Results and discussion

The selected bond distances are summarized in Table 1. It is obvious that the C11–O30 with a bond length of 1.24 Å is in good agreement with the C=O double bond [18]. The calculated C11–O30 bond distance by HF/6-31G(d), HF/6-31+G(d,p), B3LYP/6-31G(d), B3LYP/6-31+G(d,p) methods is 1.21 Å, 1.21 Å, 1.24 Å, 1.24 Å, respectively. The C11–N26 bond distance value of 1.35 Å consists well with the C=N double bond distance. C11–N26 bond distance demonstrate that the keto tautomer is favoured over the enol form for the title compound. While the C12–N28 bond distance is 1.41 and C1–N23 bond distance is 1.39 Å similar normal C–N bond distance. Similarly, C–C bond lengths except C10–C11 are between 1.36–1.40 Å which is indicative of significant conjugate double bond character. The longer C10–C11 bond distance (1.48 Å) shows that there is no delocalization of the nitrogen lone pair of electrons towards the ring. From the structural data given in Table 2 it is observed that the various ring C–C bond distances and the C–H bond lengths of the title compound are found to be almost same at all levels of calculations.

N–N– bond distance equals to 1.39 Å. The influence of the substituents on the skeletal molecular parameters of the title compound seems to be negligibly small. The bond lengths determined from B3LYP methods are slightly higher than that obtained from HF method.

C=O bond lengths (O30- C11) should be elongated when the hydrogen bond to N23–H25, N26–H27 and N28–H29 is formed in the crystal structure – the experimental value is therefore larger than calculated. It is possible that the crystal formation may introduce their significant strain because of intermolecular interactions.

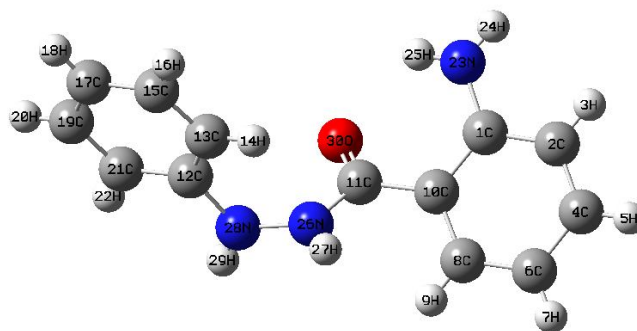


Fig. 1. Molecular model of N-(2-amino-benzoyl)-N'-phenyl hydrazine with numbering of atoms.

Table 2. Experimental and optimized bond length of N-(2-Amino-benzoyl)-N'-phenyl hydrazine calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	HF		B3LYP		
	Exp.	6-31G(d)	6-31G+(d,p)	6-31G(d)	6-31G+(d,p)
C11-N26	1.35	1.36	1.36	1.38	1.38
C11-O30	1.24	1.21	1.21	1.24	1.24
N26-H27	0.86	0.99	0.99	1.01	1.01
C10-C11	1.48	1.49	1.49	1.49	1.49
C10-C1	1.40	1.41	1.41	1.43	1.43
C1-N23	1.39	1.38	1.37	1.37	1.37
N23-H25	0.86	1.00	1.00	1.01	1.01
C1-C2	1.39	1.40	1.40	1.41	1.41
C8-C10	1.40	1.40	1.40	1.41	1.41
N26-N28	1.39	1.38	1.38	1.40	1.39
N28-H29	0.86	1.00	1.00	1.02	1.02
N28-C12	1.41	1.41	1.41	1.42	1.42
C13-H14	0.93	1.07	1.07	1.08	1.08
C13-C12	1.38	1.39	1.39	1.40	1.40

For numbering of atoms refer Fig. 1

The selected bond angles are summarized in Table 3. A deviation in the bond angle of C10–C1–C2 from the rest of the ring bond angles (118.9°) where the substituent group attached at C1 is observed. The calculated C10–C1–C2 bond angle by HF/6-31G(d), HF/6-31+G(d,p), B3LYP/6-31G(d), B3LYP/6-31+G(d,p) methods is 118.2°, 118.1°, 118.3°, 118.3°, respectively. In the case of N-(2-Amino-benzoyl)-N'-phenyl hydrazine the bond angle O30–C11–N26 is calculated as 120.9°, 120.9°, 119.4°, 119.4°, respectively. This variation in bond angle depends on the electronegativity of the central atom. If the electronegativity of the central atom decreases, bond angle decreases. The C10-C11-N26 angle is 115.5° as for an sp² hybridized C(11) carbon and almost similar calculated values (116°-117.1°). This indicates the delocalization of π electrons in the central part of the molecule [19]. 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-(2-Amino-benzoyl)-N'-phenyl hydrazine calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	Exp.	HF		B3LYP	
		6-31G(d)	6-31G+(d,p)	6-31G(d)	6-31G+(d,p)
C10-C1-C2	118.9	118.2	118.1	118.3	118.3
C10-C1-N23	121.9	122.3	122.3	121.8	122.0
C1-N23-H25	120.0	116.3	116.3	115.7	117.0
H24-N23-H25	120.1	114.9	114.9	117.0	118.4
C1-C10-C11	120.9	119.9	119.9	119.4	119.5
C10-C11-O30	123.3	123.1	123.1	123.9	123.5
C10-C11-N26	115.5	116.0	116.0	116.8	117.1
N26-C11-O30	121.2	120.9	120.9	119.4	119.4
H27-N26-C11	119.0	121.8	121.8	121.4	121.3
H27-N26-N28	119.0	116.0	116.0	115.0	115.2
C11-N26-N28	122.0	122.0	122.0	120.3	120.6
N26-N28-H29	121.5	110.5	110.5	108.8	109.6
N26-N28-C12	116.8	117.8	117.8	116.9	117.3
H29-N28-C12	121.6	112.4	112.4	111.3	112.1
N28-C12-C21	117.8	118.1	118.1	118.1	118.1
C21-C12-C13	119.0	119.4	119.4	119.4	119.5

For numbering of atoms refer Fig. 1

The bond angles and also the torsion angles C12–N28–N26–C11, N28–N26–C11–C10, and N28–N26–C11–O30 of -89° , -172.1° and 5.9° , respectively, show that the molecule itself is not planar.

The torsion angles N23–C1–C10–C8 = -177.8° , C10–C11–N26–N28 = -172.1° and N28–C12–C21–H22 = -3.5° , H25–N23–C1–C10 = -3.9° reveal that O23 and C8 are *trans* to each other, C10 and N28 are *trans* to each other and N28 and H22 are *cis* to each other, C10 and H25 are *cis* to each other.

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-(2-Amino-benzoyl)-N'-phenyl hydrazine calculated by B3LYP and HF methods using 6-31G(d) and 6-31+G(d,p) basic sets.

	HF			B3LYP	
	Exp.	6-31G(d)	6-31G+(d,p)	6-31G(d)	6-31G+(d,p)
H25-N23-C1-C10	-3.9	-25.7	-25.4	-20.3	-17.6
N23-C1-C10-C8	-177.8	-178.6	-178.9	-179.3	-179.6
N23-C1-C10-C11	3.7	3.2	2.8	2	1.3
C1-C10-C11-O30	36.1	33.3	33.1	23.3	20.8
C1-C10-C11-N26	-145.9	-146.9	-147.1	-156.2	-158.7
C8-C10-C11-N26	35.7	34.9	34.7	25.2	22.2
C8-C10-C11-O30	-142.2	-144.9	-145.2	-155.3	-158.4
C10-C11-N26-N28	-172.1	-174.9	-174.8	-169.5	-170.7
C10-C11-N26-H27	7.8	-0.5	-0.9	-11.1	-10.8
C11-N26-N28-H29	91.0	49.4	49.1	32.3	34.6
O30-C11-N26-N28	5.9	4.9	5.1	11	9.8
H29-N28-N26-H27	-88.9	-125.4	-125.2	-127.4	-126.5
H27-N26-N28-C12	91.0	104.5	103.7	105.5	104.2
H29-N28-C12-C21	-12.4	31.1	30.4	35.7	35.0
H29-N28-C12-C13	162.5	-152.8	-153.3	-148.4	-148.8
C19-C21-C12-C13	1.4	0.3	0.3	0.2	0.2

For numbering of atoms refer Fig. 1

As seen from Table 2, most of the optimized bond lengths are slightly longer than the experimental values, the bond angles and dihedral angles are slightly different from the experimental angles. We note that the experimental results are for the solid phase and the theoretical calculations are for the gas phase. In the solid state, the existence of a crystal field along with the intermolecular interactions connect the molecules together, which results in the differences in bond parameters between the calculated and experimental values [20].

3.2. Vibrational analysis

The observed and calculated frequencies using HF/6-31G(d), HF/6-31+G(d,p), B3LYP/6-31G(d) and B3LYP/6-31+G(d,p) methods along with their relative probable assignments of N-(2-Amino-benzoyl)-N'-phenyl hydrazine are summarised in Tables 5. The maximum number of values determined by B3LYP/6-31G(d) method is well agreed with the experimental values and is also confirmed by the scale factors used to get the scaled frequencies.

The aromatic ring carbon–carbon stretching modes are expected in the range from 1650 to 1200 cm^{-1} . Benzene has two degenerate modes at 15984 cm^{-1} and 1492 cm^{-1} . Similarly the frequency of two non-degenerate modes observed at 1307 cm^{-1} and 1031 cm^{-1} in benzene. The actual positions of these modes are determined not so much by the nature of the substituents but by the form of substitution around the ring. The frequency of degenerate pair in benzene is fairly insensitive to substitution.

Amides ($-\text{C}=\text{O}$) vibrations generally show IR absorption at 1750–1650 cm^{-1} . Conjugation, ring size, hydrogen bonding, steric and electronic effects often result in significant shifts in $-\text{C}=\text{O}$ absorption frequencies [21]. In the frequency of the carbonyl stretching vibration is absorbed at 1642 cm^{-1} in the infrared spectrum, the reason being that the double bond character of the $-\text{C}=\text{O}$ group is less due to the nitrogen lone pair electron being delocalized towards the carbonyl end.

In the experimental frequencies observed at 3429 cm^{-1} in the infrared spectrum are assigned to the asymmetric stretching modes of N-(2-Amino-benzoyl)-N'-phenyl hydrazine. Among the other vibrations of amino group, the very strong band in IR at 1612 cm^{-1} is assigned to the $-\text{NH}_2$ deformation mode. The N–H stretching vibration of hydrazide group appears at 3334 cm^{-1} and two different frequencies are calculated at this value. The in-plane bending vibration of the same is observed at 1584 cm^{-1} in the IR spectrum. This vibration is overlapped with the C–N in-plane bending absorptions. On the other hand, the two NH_2 stretching modes were assigned to the calculated whole methods. The strong vibrational frequency observed at 668 cm^{-1} in the infrared spectrum is assigned to the N–H out of plane bending mode of N-(2-Amino-benzoyl)-N'-phenyl hydrazine. The experimental values at all levels of calculations become slightly lower than the theoretical N–H stretching frequencies. The theoretical values are given in Table 5.

Generally, the calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra of the title compound. The first is caused by the environment and second reason is the fact that the experimental value is an anharmonic frequency and while the calculated value is a harmonic one.

Table 5. Experimental and calculated level vibrational frequencies (cm^{-1}), and probable assignments of N-(2-Amino-benzoyl)-N'-phenyl hydrazine.

Observed wavenumber(cm^{-1})	HF		B3LYP		Assignment	
	FTIR	6-31G(d)	6-31G+(d,p)	6-31G(d)		6-31G+(d,p)
668		651	648	681	673	γNH , γCH
747		733	729	758	755	$\delta_{\text{oop}}\text{CH}$ (phenyl C1-C10)
857		853	848	865	858	$\delta_{\text{oop}}\text{CH}$ (phenyl C12- C21)
903		905	901	919	912	γNH , γCH
1031		1008	1004	1056	1047	νCC
1106		1113	1114	1104	1109	βCH
1153		1160	1154	1191	1181	$\delta_{\text{ip}}\text{CH}$ (phenyl)
1239		--	--	1273	1263	νCN , δNH , δC H
1307		1338	1333	1313	1304	νCC (phenyl); δCH
1492		1477	1468	1500	1500	νCC , νCH
1584		1610	1597	1571	1552	δNH (amide νCC
1612		1616	1604	1647	1625	δNH_2
1642		1928	1903	1735	1706	$\nu\text{C}=\text{O}$ + $\nu\text{C}-\text{N}$ + δNH (amide I, associated)
3234		3348	3335	3216	3216	νCH
3334		3813	3826	3516	3543	$\nu\text{NH}(\text{N}28)$
3334		3921	3927	3635	3650	$\nu\text{NH}(\text{N}26)$
3429		3808	3812	3529	3537	$\nu_{\text{as}}\text{NH}_2$

v, stretching; δ , deformation; as, antisymmetrical; oop, out of plane; β , in-plane bending; γ out of plane bending

4. Conclusions

We have carried out DFT and ab initio calculations on the structure and vibrational spectrum of N-(2-Amino-benzoyl)-N'-phenyl hydrazine. Comparison between the calculated

and experimental structural parameters for bond lengths and torsion 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) method agree very well with experimental results.

Acknowledgments

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