

Synthesis & Determination of Isomeric form of “2-[(3-Bromophenyl) hydrazono] 3- oxo- Butanoic Acid”

by X- Ray diffraction technique & confirmation by experimental method

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I. Introduction

The Bromine derivative of phenyl hydrazine has been studied for its insecticidal properties¹. It has also found numerous applications in analytical chemistry²⁻⁴, chemotherapy⁵⁻⁸ and as chromogenic reagents⁹. It has been synthesised by Dr A Sahay and his co-workers as part of their project to study the crystal structure of a series of phenylhydrazones and their stereochemistry the crystal structure of the title compound has been determined¹⁰⁻¹³. Earlier I reported the structure of “2-[(p-Bromophenyl) hydrazono]-3-ethoxy-3-oxo-propanoic acid” (SINHA K et al., 2012).

Table 1: Crystal data and structure refinement details

Crystal description	Light yellow, elongated needle
Empirical formula	Br.C ₁₀ H ₉ N ₂ O ₃
Formula weight	285.10
Temperature	293 ^o K
Crystal system space group	Monoclinic, P2 ₁ /n
Unit cell dimensions	a = 20.213 (9), b = 4.540 (1) c = 12.640 (6) Å β = 110.99(5)
Z, volume, calculated density	4, 1083 Å ³ , 1.933 g cm ⁻³
Absorption coefficient	53.25 cm ⁻¹
F (000)	568
Crystal size	0.87 X 0.62 X 0.37 mm ³
Radiation wavelength (λ)	1.5418 Å
θ range for data collection	1- 70°
Index ranges	0 < h < 23, 0 < k < 5, -15 < l < 14
No. of reflections collected/unique	2192/2054
Data/restraints/parameters	939/ 0/181
Difference peaks and holes	1.754 < p < -1.105 e Å ³
Final R indices [F0>3 F0]	0.0828
R indices (all data)	0.0910
R _w	0.0739
Goodness of fit	4.609

II. Materials and Methods

Arylhydrazone was prepared from arylamine (with about 90% yield). The yellow arylhydrazone was converted into orange red compound by using perchloric acid. Purity of the compound was ascertained by TLC.

The bromine derivative of the above compound was synthesized using bromine solution in acetic acid, by dissolving 6 ml of bromine in 44ml of glacial acetic acid.

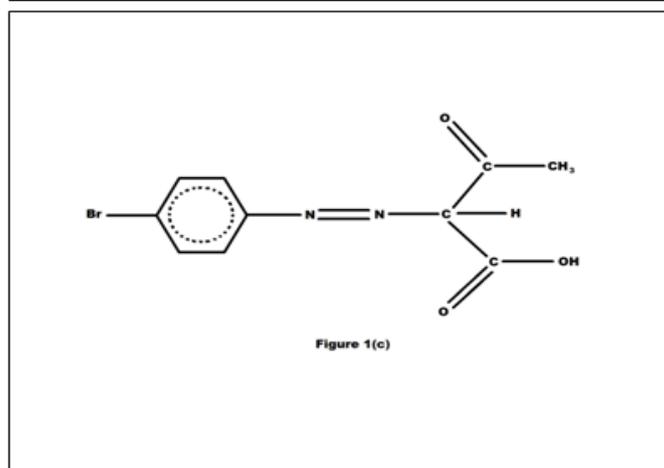
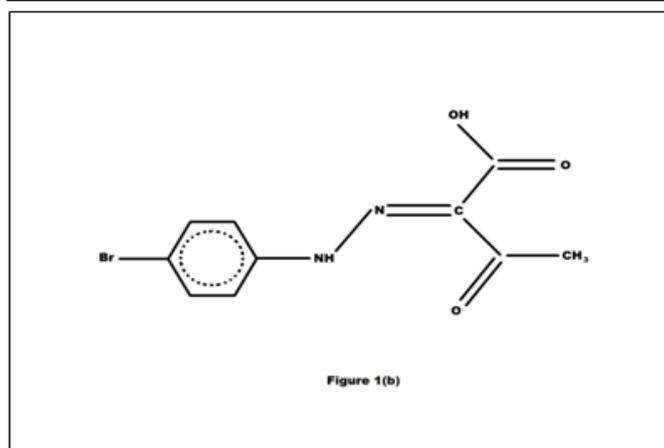
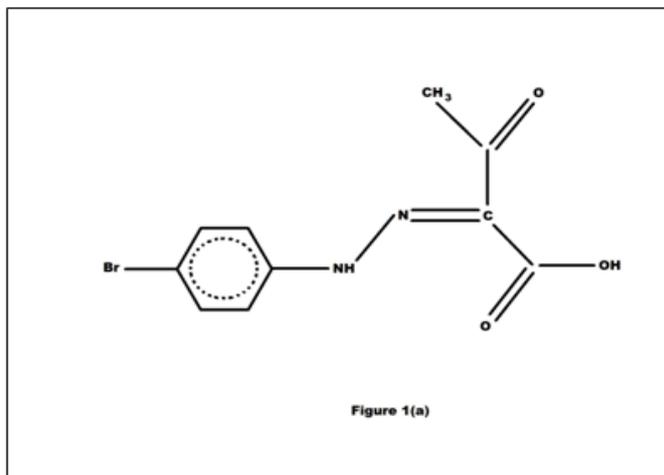
0.001 mol of compound (prepared above) was dissolved in 10 ml of acetic acid and to it was added bromine solution in acetic acid (0.001mol). Bromine derivative slowly separated out.

It was recrystallized at room temperature by slow evaporation for 72 hours using methanol as a solvent system. The crystal intensity data was collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromator with CuKα radiation (λ=1.5418Å). ω-2θ scan mode was employed for 2192 reflections in the theta range 1-70°. The crystal exists in monoclinic system with space group P2₁/n. The crystallographic data and structure refinement details are presented in Table 1.

The crystals obtained were transparent, light yellowish in colour, elongated needle in shape.

III. Results and discussions

The compound $\text{Br C}_{10}\text{H}_9\text{N}_2\text{O}_3$ (mol. mass = 285) may exist in the following three forms [fig 1(a), 1(b) and 1(c)]



Since Bond length, bond angles and torsion angles are approximately the same, so it may be concluded that both forms may be E- isomer or Z isomer as shown in in fig[1(a) and 1(b)]. It has been found that both forms always exist in equilibrium mixture in solution. Hence both forms are inter-convertible. However in solid state the compound exists in pure single isomer, Z isomer.

Attempts to isomerise the pure isomer to other form by shining UV light or heat or alkali treatment were unsuccessful.¹⁵ Hydrolysis of hydrazone in boiling methanolic sodium hydroxide gave mixture of products from which pure E-isomer could not be separated.

Crystallisation of this crude alkaline hydrolysis product always resulted in the isolation of pure single isomer identical with the keto acid obtained by direct acid hydrolysis of the hydrazone. The acids, both half

esters and acid ketones seem to exist in Z- configuration and failure of transforming this into the E form is presumably due to locking of configuration by due to either strong hydrogen bonding with the acid carbonyl or by electrostatic attraction due to inner salt.

Thus Experimentally found results by chemistry persons confirmed the existence of only z isomeric form. The present study of the compound by X- ray analysis also shows that the compound can exist only in Z isomeric due to the magnitude of torsion present around the N(2) –C(7) bond.. The result of X-ray analysis of gives the torsion angle for N(1)-N(2)-C(7)-C(8) as 1.0(6)° and for N(1)-N(2)-C(7)-C(9) as 179(13)° which fixes the conformation around -N=C < and confirms that the molecule is the first space isomer i.e Z isomer as shown in Fig 1(a). Refinement of the diffraction data gives the final atomic position and equivalent isotropic displacement parameters for all the non- hydrogen atoms , which are listed in Table 2. Bond lengths and Bond angles are listed in Table 3.

Table 2 Final atomic fractional coordinates x, y, z and *Biso (Å²) with e.s.d's in the parentheses for the non hydrogen atoms

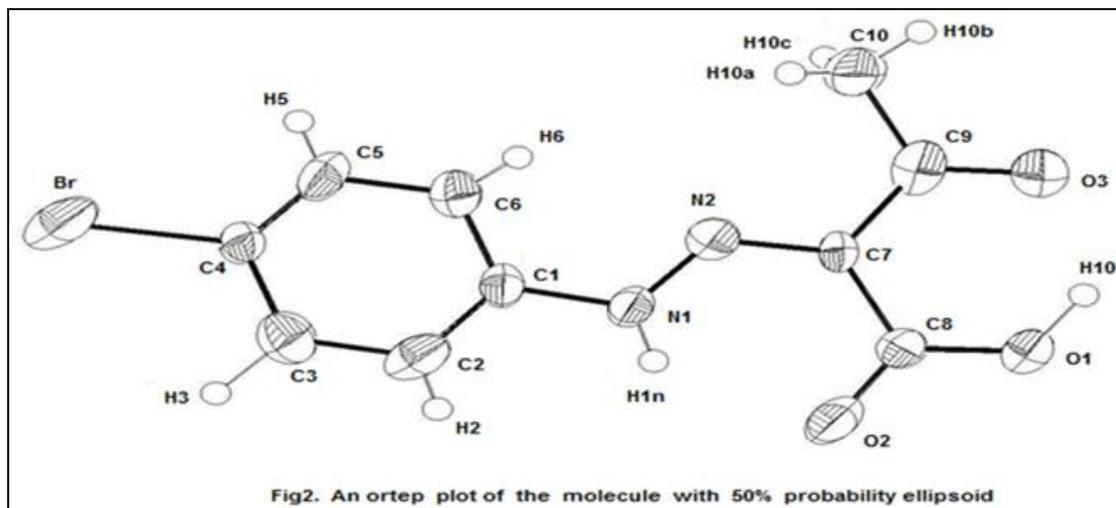
Atom	x	y	z	Biso (Å ²)
BR	.11871(9)	-.2584(5)	-.01566(14)	5.86(10)
O1	.0358 (4)	.2333(24)	.5740 (6)	3.8 (5)
O2	.0804 (5)	.5647(22)	.7112 (7)	4.4 (5)
O3	.1820 (4)	.8730(21)	.7095 (7)	4.1 (5)
N1	.0924 (4)	.209 (3)	.4147 (7)	2.8 (5)
N2	.1344 (5)	.4071(23)	.4725 (7)	2.6 (5)
C1	.1151 (6)	-.105 (3)	.1216 (9)	3.3 (7)
C2	.1588 (7)	.080 (3)	.1824 (10)	4.2 (8)
C3	.1550 (7)	.187 (3)	.2836 (10)	4.3 (8)
C4	.1004 (6)	.102 (3)	.3179 (9)	2.9 (6)
C5	.0521 (7)	-.081 (4)	.2523 (11)	4.5 (8)
C6	.0582 (7)	-.190 (3)	.1545 (11)	4.7 (8)
C7	.1312 (6)	.522 (3)	.5663 (9)	2.6 (6)
C8	.0782 (6)	.432 (3)	.6184 (10)	3.3 (7)
C9	.1833 (6)	.741 (4)	.6234 (8)	3.2 (7)
C10	.2400 (7)	.814 (3)	.5769 (11)	4.4 (8)

* Biso is the mean of the Principal axes of the Thermal- ellipsoid

Table 3 Bond distances (Å) bond angles (°) and torsion angle (°) for non-hydrogen atoms (e.s.d's are given in parantheses)

Br-C(1)	1.897(11)	C(1)-C(2)	1.258(19)
O(1)-C(8)	1.232(15)	C(1)-C(6)	1.409(17)
O(2)-C(8)	1.306(14)	C(2)-C(3)	1.397(17)
O(3)-C(9)	1.250(15)	C(3)-C(4)	1.378(16)
N(1)-N(2)	1.271(14)	C(4)-C(5)	1.323(19)
N(1)-C(4)	1.378(14)	C(5)-C(6)	1.379(18)
N(2)-C(7)	1.317(14)	C(7)-C(8)	1.502(15)
		C(7)-C(9)	1.439(18)
		C(9)-C(10)	1.501(16)
N(2)-C(7)-C(8)	123.9(11)	C(1)-C(6)-C(5)	120.6(12)
N(2)-N(1)-C(4)	119.5(9)	N(2)-C(7)-C(8)	123.9(11)
N(1)-N(2)-C(7)	124.1(9)	N(2)-C(7)-C(9)	117.6(10)
Br-C(1)-C(2)	123.6(9)	C(8)-C(7)-C(9)	118.5(9)
Br-C(1)-C(6)	118.1(9)	O(1)-C(8)-O(2)	122.7(10)
C(2)-C(1)-C(6)	118.2(11)	O(1)-C(8)-C(7)	119.3(10)
C(1)-C(2)-C(3)	122.3(11)	O(2)-C(8)-C(7)	117.9(10)
C(2)-C(3)-C(4)	120.3(12)	O(3)-C(9)-C(7)	121.9(10)
N(1)-C(4)-C(3)	122.9(11)	O(3)-C(9)-C(10)	119.5(12)
N(1)-C(4)-C(5)	118.9(10)	C(7)-C(9)-C(10)	118.6(11)
C(3)-C(4)-C(5)	118.1(11)	C(4)-C(5)-C(6)	120.4(12)

The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme is shown in Figure 2.



The phenyl ring exhibits usual geometry in terms of bond distances and angles. The torsion angle N(1)-N(2)-C(7)-C(8) is 1.0(6)° and N(1)-N(2)-C(7)-C(9) is 179(13)° which fixes the conformation around -N=C < and confirms that the molecule is the first space isomer Fig 1(a) in which the carbonyl oxygen atom of the carboxyl group links with the -NH through intra-molecular hydrogen bond N—H...O(1) of 2.568 Å and with H...O(1) 2.08 Å.

There is another intra-molecular H- bond O(2)—H...O(3) of 2.543 Å. and with H...O(3) is 1.754 Å. The Br—C(1) bond is 1.897(11) Å. The bond C(8)—O(2) is 1.306(14) and bond C(8)—O(1) is 1.232(15) Å. Therefore O(2) is the single bonded OH group and atom O(1) is the double bonded carbonyl oxygen atom of the carboxyl group.

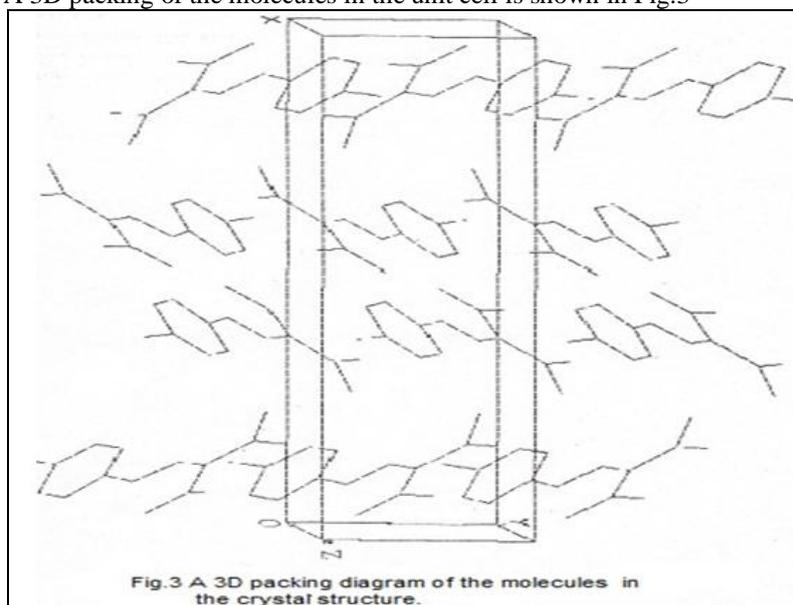
The phenyl ring is nearly planar with maximum deviation of -0.021 Å for atom C(2).

The least square plane through the atoms C(4), N(1), N(2), C(7), C(8), C(9) is also planar with maximum deviation of 0.012 Å for atom C(9). The plane of the carboxyl group is rotated out of these planes by 8.0° and 2.8° respectively.

There is no inter-molecular hydrogen bonds in the structure. All inter-molecular contacts are of vander Waal's type greater than 3.2 Å. excepts for the following contacts:

- O(2)... ..O(2 at -x,-y,1-z) 2.853 Å
- O(2)... ..O(2 at -x, 1-y,1-z) 3.0853 Å

A 3D packing of the molecules in the unit cell is shown in Fig.3



IV. Conclusions

1. The X-ray structural studies confirms the existence of space isomer [Fig. 1(a)] as the isomer angles fix the conformation around the -N=C bond.
2. The crystallographic result from the above study shall help chemists in defining with the isomeric forms of similar looking structures.
3. The intra molecular bonds N(1)-H(1)-O(1) and O(2)-H(2)-O(3) give rise to the formation of two virtual six-membered rings, thus making the entire structure look like a three ring structure.

Data collection: CAD-4 EXPRESS (Enraf±Nonius, 1994);
Cell refinement: CAD-4 EXPRESS; data reduction: MolEN (Fair, 1990);
program(s) used to solve structure: SHELXS97 (Sheldrick, 1997);
program(s) used to refine structure: SHELXL97 (Sheldrick, 1997);
molecular graphics: ORTEP-3 (Farrugia, 1997);
software used to prepare material for publication: SHELXL97.

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