DOI:10.7598/cst2017.1305
ISSN:2278-3458

Chemical Science Transactions
2017, **6(1),** 35-41

RESEARCH ARTICLE

Synthesis and Crystal Structure of 2-[(4-Chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic Acid

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Received 8 July 2016 / Accepted 3 September 2016

Abstract:2-[(4-Chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic acid ($C_{17}H_{12}ClNO_4$) crystallizes in the orthorhombic space group Pbcn with unit cell parameters: a = 17.2460(13) Å, b = 9.6735(8) Å, c = 19.953(2) Å, $\alpha = \beta = \gamma = 90.00^o$ and Z=8. Direct methods were used to solve the crystal structure and refined by full matrix least squares procédures to a final R value of 0.0675 for 1294 observed reflections. The crystal structure is stabilized by N–H···O, O–H···O and C–H···O hydrogen bonds. The dimer molecule is linked through a bifurcated(acceptor) hydrogen bond (N1-H1…O4,C17-H17…O4).

Keywords: Chlorobenzoyl, Benzaldehyde, Direct methods, Hydrogen bonds, Dimer

Introduction

Acid derivatives are useful in the synthesis of heterocyclic compounds and in the present case it was possible to prepare an acid derivatives using acyl amine as a precursor. Crystal structure of some useful substituted prop-2-enoic acid exist in the literature, *viz*., (*Z*)-3-(Benzylcarbamoyl)prop-2-enoic acid[1], (*E*)-3-(4-Chlorophenyl)-2-phenylprop-2- enoic acid[2], 3-Methoxy-2-[2-({[6-(trifluoromethyl)-pyridin-2-yl]oxy}methyl)phenyl]prop-2- enoic acid[3], (2Z)-4-[(2-Hydroxyphenyl)carbamoyl]- prop-2-enoic acid[4]. Recently, amino acids and their derivatives, such as glycine ethyl ester which are non-denaturating reagents, have been

widely used in biochemical studies to increase refolding yields by decreasing aggregation and to increase protein stability[5-10]. We report herein the synthesis and crystal structure of 2-[(4-chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic acid.

Experimental

The synthetic route for 2-[(4-chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic acid (Figure 1) is presented in Scheme 1. A mixture of 4-{(*Z*)-[2-(4-chlorophenyl)-5-oxo-1,3-oxazol-4(5*H*)-ylidene]methyl}benzaldehyde (3 g 0.011 mol) was refluxed in ethanol (20 mL) containing 2 mL of sodium hydroxide (0.01 mol) for 3 hours. The solid obtained after cooling was filtered dried and recrystallized from ethanol. Single crystals were grown from methanol: dimethyl formamide (1:1) by the slow evaporation method (M.P. 492-493 K).

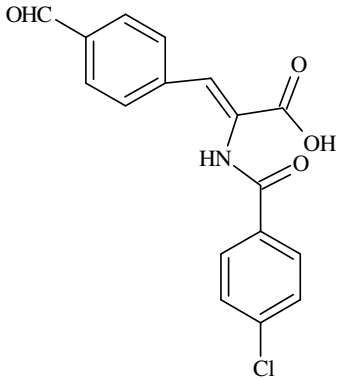
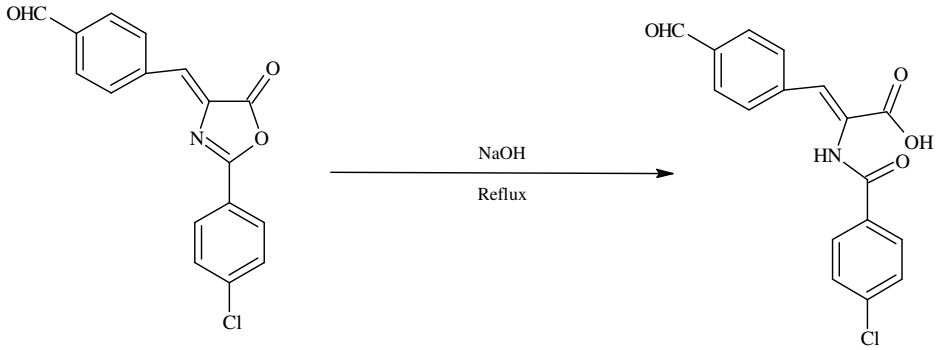


Figure 1. Chemical structure of 2-[(4-chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic acid



Scheme 1. Synthesis of 2-[(4-chlorobenzoyl)amino]-3-(4-formylphenyl)prop-2-enoic acid

Crystal structure determination

A well defined crystal of dimensions 0.30x0.20x0.20 mm^3 was used for data collection on X'calibur CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). X-ray intensity data of 8359 reflections were collected at 293(2) K and out of these reflections 3266 were found unique. The intensities were measured by ω scan mode for θ ranges 3.77° to 26.00°. 1294 reflections were treated as observed using (I>2σ (I)) as criterion. Data was corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using SHELXS97[11]. All non-hydrogen atoms of

the molecule were located from the best E-map. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with O-H= 0.82 Å, N-H= 0.86 Å, C-H= 0.93-0.97Å and U_{iso}= 1.2 U_{eq}(C), except for the methyl groups where U_{iso}(H) = 1.5U_{eq}(C). The final refinement cycles converged to an R- factor of 0.0657 (wR(F2) = 0.1962) for the 1268 observed reflections. Residual electron densities ranges from -0.375 to 0.291eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography. Geometrical calculations of the molecule was done using the WinGX[12], PARST[13] and PLATON[14] softwares.

Crystallographic information has been deposited to Cambridge crystallographic data centre with CCDC number 1495218. This data can be obtained free of charge at Cambridge crystallographic data centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The molecular structure with atomic labelling is shown in Figure 2 (ORTEP)[15]. The molecule consists of one formylphenyl and one chlorobenzoyl ring. The crystallographic and refinement data of the crystal is given in Table 1. Some selected bond distances, bond angles and torsion angle values are given in Table 2. The structural parameters, including bond distances and bond angles show a normal geometry[16]. The double bonds C10=O2 [=1.237(5)Å] and C11=O4 [=1.233(4)Å] agree with the corresponding distances in structures containing similar systems. The formylphenyl and chlorobenzoyl rings are *planar* and are inclined at an angle of 40.25(2)° with respect to each other. The prop-2-enoic acid and the formylphenyl ring are rigid with torsion angle (C5-C8-C9-C10) of 173.5(4)°. The chlorobenzoyl and amino group are also rigid having torsion angle (N1-C11-C12-C13) of 169.6(4)°. The atoms of formylphenyl ring and chlorobenzoyl ring are almost planar with maximum deviation of -0.016(5)Å observed for C2 atom and 0.0078(5)Å corresponding to C14 atom for respective rings. The conformations of the N-H and C=O bonds are *anti* with respect to each other.

Examination of non- bonding contacts in the molecular packing (Figure 3) reveals the presence of C8-H8…O3 and C4-H4…N1 intramolecular hydrogen bonds resulting in the formation of S(5) and S(6) graph-set motifs (Figure 2). In the crystal structure, adjacent molecules are interconnected through bifurcated(acceptor) N1-H1…O4 and C17-H17…O4 hydrogen bonds resulting in the formation of ring motif $R_2^1(7)$ shown in Figure 4. The O3-H8…O2 and O2-H8…O3 inter molecular hydrogen bonds results in the formation of a dimer with ring motif $R_2^2(8)$ (Figure 4). Details of intra/intermolecular hydrogen bonds are given in Table 3.

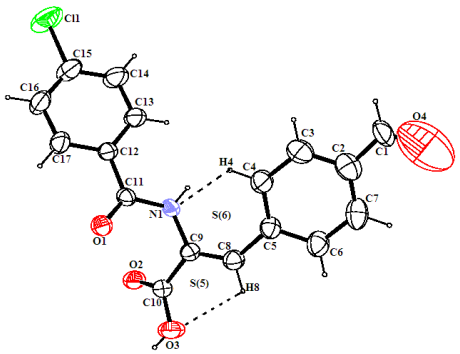


Figure 2. ORTEP view of the molecules with displacement ellipsoids drawn at 40% probability level H atoms are shown as small spheres of arbitrary radii

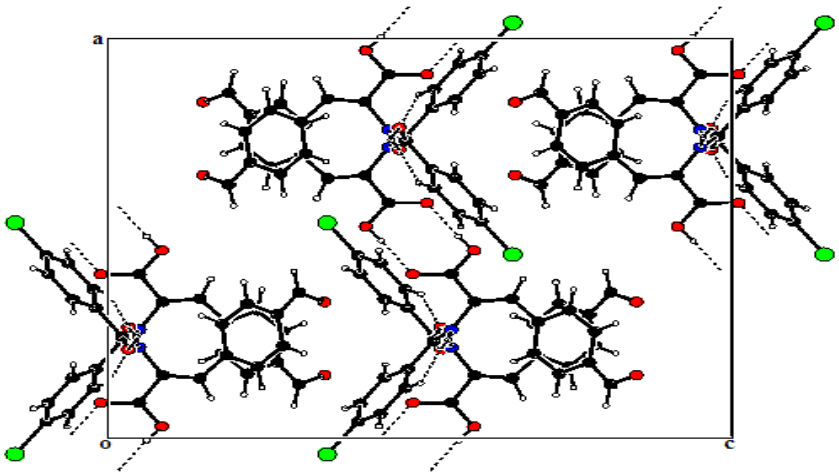


Figure 4. Packing viewed down the *b-axis*.

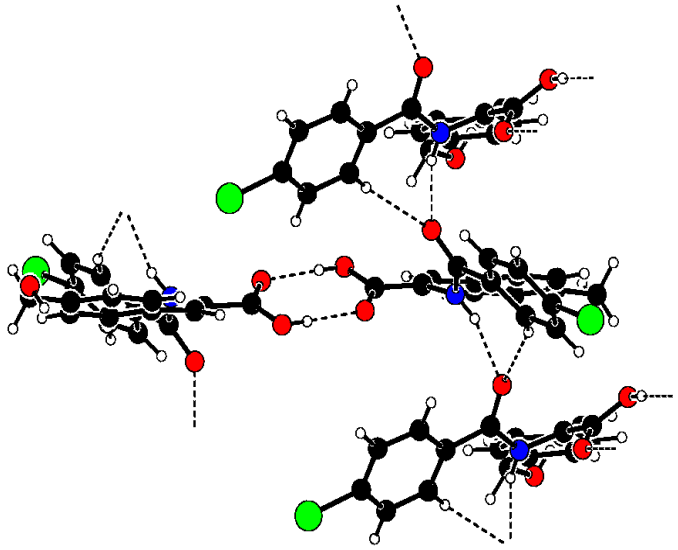


Figure 4. View of bifurcated(acceptor) hydrogen bond, $R_2^1(7)$ and $R_2^2(8)$ ring motif down the *z- axis*

Table 1. Crystal and experimental data for $C_{17}H_{12}ClNO_4$

CCDC No.	1495218
Crystal size	0.30x0.20x0.20 mm
Empirical formula	$C_{17}\ H_{12}\ ClNO_4$
Formula weight	329.73
Radiation, Wavelength	Mo*K*α, 0.71073
Unit cell dimensions	a = 17.2460(13) Å,
	b = 9.6735(8) Å,

Contd.....

	c = 19.953(2) Å,
	$\alpha = \beta = \gamma = 90^{o}$
Crystal system	orthorhombic
Space group	Pbcn
Unit cell volume	3328.7(5) $Å^3$
No. of molecules per unit cell, Z	8
Temperature	293(2)
Absorption coefficient	0.248 mm^{-1}
F(000)	1360
Scan mode	ω scan
θrange for entire data collection	3.77< θ<26.00
Range of indices	$-20 \leq h \leq 20$
	$-11 \leq k \leq 7$
	$-15 \leq l \leq 23$
Reflections collected / unique	7713 /2921
Reflections observed (I > 2σ(I))	1294
Rint	0.0517
Rsigma	0.0855
No. of parameters refined	209
Final R	0.0675
wR(F2)	0.1962
Goodness-of-fit	0.955
$(\Delta/\sigma)_{max}$	0.002
Final residual electron density	-0.375 to 0.291 $eÅ^{-3}$

Table 2. Some selected bond distances, bond angles and torsion angles

Bond Distances(Å)		Bond Distances(Å)	
C1-O1	1.178(12)	O3-C10	1.290(4)
C1-C2	1.351(7)	C11-C12	1.474(5)
C5-C8	1.457(5)	C9-C10	1.486(5)
C8-C9	1.332(5)	N1-C11	1.348(4)
O4-C11	1.233(7)	O2-C10	1.237(5)
N1-H1	0.8600	O3-H9	0.8200

Bond Angles(°)		Bond Angles(°)	
C1-C2-C3	115.6(6)	O4-C11-C12	122.0(3)
C6-C5-C8	117.1(4)	C13-C12-C11	118.8(4)
C5-C8-C9	130.4(4)	C17-C12-C11	124.2(4)
C8-C9-C10	120.9(4)	C11-N1-C9	122.3(3)
O2-C10-C9	120.8(4)	O4-C11-N1	118.8(3)
O3-C10-C9	116.1(4)	C14-C15-CL1	120.7(4)
N1-C11-C12	119.2(3)	C12-C17-C16	121.1(4)
O2-C10-O3	123.0(4)	N1-C9-C10	114.4(3)
C5-C6-C7	120.5(5)		
O4-C11-N1	118.8(3)		

Torsion Angle(°)		Torsion Angle(°)	
C9-C8-C5-C4	17.1(7)	O4-C11-C12-C13	-11.7(6)
O2-C10-C9-C8	-151.9(4)	C11-N1-C9-C8	-132.6(4)
O2-C10-C9-N1	19.1(5)	O4-C11-C12-C13	-11.7(6)
O3-C10-C9-C8	26.1(5)	N1-C11-C12-C17	-10.5(6)
C11-N1-C9-C8	-132.6(4)	C11-N1-C9-C10	56.7(4)

Table 3. Hydrogen bonding geometry (e.s.d.'s in parentheses)

D–H…A	D–H(Å)	H…A(Å)	D…A(Å)	D–H…A(°)
C4-H4…N1	0.93	2.48	3.053(5)	120
C8-H8…O3	0.93	2.42	2.788(5)	104
O3-H9…O2 [i]	0.82	1.82	2.639(4)	174
N1-H1…O4 [ii]	0.86	1.98	2.805(4)	162
C17-H17…O4 [ii]	0.93	2.41	3.269(5)	154

Symmetry code: (i) 1-x, 1-y,-z (ii) 1/2-x,-1/2+y, z.

Conclusion

Facile and efficient synthesis of the compound was achieved when 4-{(*Z*)-[2-(4-chlorophenyl)-5-oxo-1,3-oxazol-4(5*H*)-ylidene]methyl}benzaldehyde was refluxed in ethanol sodium hydroxide. Then single crystals were grown from methanol: dimethyl formamide (1:1) by the slow evaporation method. The molecular and crystal structure of the given compound was determined using single crystal x-ray diffraction data collected at 293(2) K. The molecules are assembled in three dimensional network and the intermolecular interactions (N–H...O, O-H...O and C–H···O) play a crucial part in it.

Acknowledgment

RK is thankful to DST, New Delhi for funding research project under research project no: EMR/2014/000467.

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