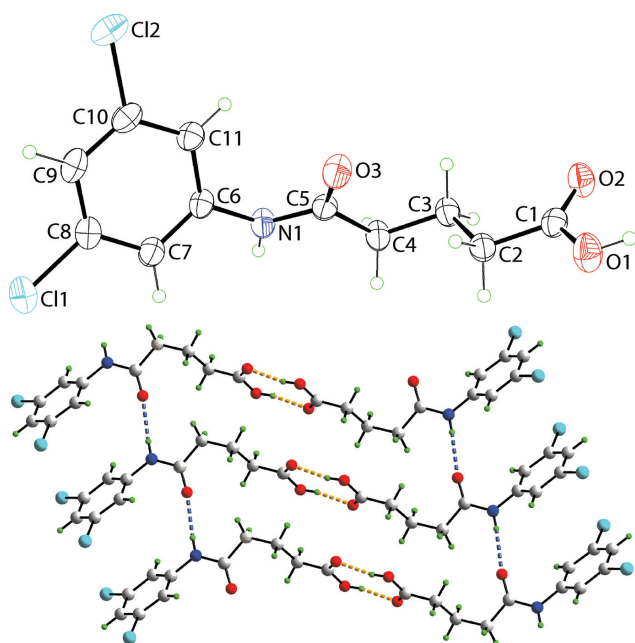


Bibi Hanifa, Muhammad Sirajuddin\*, Kong Mun Lo and Edward R.T. Tiekink\*

# Crystal structure of 4-[(3,5-dichlorophenyl)carbamoyl]butanoic acid, $C_{11}H_{11}Cl_2NO_3$



The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

Crystal:	Yellow prism
Size:	0.12 × 0.08 × 0.05 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	4.83 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	14849, 2138, 0.039
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 1891
$N(\text{param})_{\text{refined}}$ :	160
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.48564(3)	1.09295(13)	0.34310(4)	0.0735(2)
Cl2	0.66711(4)	0.35104(12)	0.55173(4)	0.06905(19)
O1	0.90134(8)	0.1446(3)	-0.03210(11)	0.0622(4)
H1O	0.9341(13)	0.044(5)	-0.049(2)	0.093*
O2	1.00358(8)	0.2343(3)	0.08242(10)	0.0561(3)
O3	0.79649(9)	0.4609(2)	0.25702(10)	0.0588(4)
N1	0.76439(9)	0.8866(3)	0.29116(11)	0.0442(3)
H1N	0.7697(12)	1.055(2)	0.2800(15)	0.053*
C1	0.93566(10)	0.2767(3)	0.04354(12)	0.0425(4)
C2	0.88343(10)	0.4812(4)	0.07677(12)	0.0444(4)
H2A	0.835531	0.392675	0.086875	0.053*
H2B	0.868459	0.614754	0.027307	0.053*
C3	0.92123(10)	0.6231(4)	0.16712(13)	0.0454(4)
H3A	0.968509	0.715060	0.156664	0.054*
H3B	0.937179	0.489456	0.216302	0.054*
C4	0.86710(11)	0.8269(3)	0.20158(14)	0.0462(4)
H4A	0.899240	0.952197	0.244318	0.055*
H4B	0.839880	0.929146	0.147572	0.055*
C5	0.80621(10)	0.7038(3)	0.25196(11)	0.0393(4)
C6	0.70292(10)	0.8267(3)	0.34117(12)	0.0403(4)
C7	0.63354(10)	0.9733(4)	0.32054(12)	0.0461(4)
H7	0.626884	1.106256	0.274058	0.055*
C8	0.57417(11)	0.9182(4)	0.37050(14)	0.0497(4)
C9	0.58288(11)	0.7261(4)	0.44066(13)	0.0520(5)
H9	0.542595	0.691507	0.473849	0.062*
C10	0.65333(11)	0.5862(4)	0.46028(12)	0.0480(4)
C11	0.71341(11)	0.6304(3)	0.41112(13)	0.0445(4)
H11	0.759929	0.530818	0.424534	0.053*

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## Abstract

$C_{11}H_{11}Cl_2NO_3$ , monoclinic,  $P2_1/c$  (no. 14),  $a = 17.2336(3)$  Å,  $b = 4.9604(1)$  Å,  $c = 14.3696(3)$  Å,  $\beta = 100.970(2)^\circ$ ,  $V = 1205.95(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0313$ ,  $wR_{\text{ref}}(F^2) = 0.0848$ ,  $T = 293(2)$  K.

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\*Corresponding authors: **Muhammad Sirajuddin**, Department of Chemistry, University of Science and Technology, Bannu, 28100, Pakistan, e-mail: m.siraj09@gmail.com; and **Edward R.T. Tiekink**, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

**Bibi Hanifa**: Department of Chemistry, University of Science and Technology, Bannu, 28100, Pakistan

**Kong Mun Lo**: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

### Source of material

3,5-Dichloroaniline (Sigma-Aldrich; 0.51 mL, 5 mmol) and glutaric anhydride (Sigma-Aldrich; 0.57 g, 5 mmol) were dissolved separately in about 10–15 mL analytical grade toluene. The two solutions were then slowly mixed and stirred at room temperature until the appearance of a brown precipitate. This was washed with a minimum amount of toluene (to remove any unreacted reactants) and then with water (to remove any glutaric acid formed during the reaction). The desired compound was air-dried and recrystallised in an ethanol:acetone mixture (1:1) to form yellow crystals. Yield: 80%. **M. pt.** (Gallenkamp (UK) electrothermal melting point apparatus): 401–403 K. **FTIR** (FTIR Spectrometer Model Thermo Nicolet iS50; cm<sup>-1</sup>): 3347 ν(NH); 3296 ν(OH); 1694 ν(amide C=O); 1536 ν(CO<sub>asym</sub>); 1307 ν(CO<sub>sym</sub>). **<sup>1</sup>H NMR** (Bruker Advanced Digital 500 MHz NMR spectrometer, chemical shifts relative to Me<sub>4</sub>Si, CDCl<sub>3</sub> solution at 298 K; numbering as per the figure; δ in ppm): δ 11.12 (1H, OH), 9.53 (1H, NH), 7.28 (2H, H7, H11), 6.63 (1H, H9), 2.07 (2H, H2), 2.00 (2H, H4) 1.60 (2H, H3). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 174.6 (C1), 33.1 (C2), 20.3 (C3), 35.8 (C4), 171.5 (C5), 141.1 (C6), 117.4 (C7, C11), 134.3 (C8, C10), 122.5 (C9).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$ . The O- and N-bound H atoms were refined with O–H = 0.82 ± 0.01 Å and N–H = 0.86 ± 0.01 Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$  or  $1.2U_{eq}(N)$ .

### Comment

For a rather simple formulation, it is surprising that 4-[(aryl)carbamoyl]butanoic acids, i.e. molecules of the general formula ArN(H)C(=O)(CH<sub>2</sub>)<sub>3</sub>C(=O)OH, are not well studied, at least by crystallographic methods. The title compound with Ar = 3,5-dichlorophenyl, (I), complements only three known crystal structures, namely 4-((methylsulfonyl)amino)-3-phenoxyphenyl [5], (II), and the very recently reported species with Ar = 4-methoxy-2-nitrophenyl [6] and 2-methoxyphenyl [7], hereafter (III) and (IV), respectively. An emerging interesting feature of these structures is the conformational flexibility in the side-chain. Over and above structural investigations, these molecules have been reported to exhibit biological potential against leishmaniasis and cancerous cells [8] as do some of their organotin derivatives [9]. Herein, in continuation of structural studies in this area, the crystal and molecular structures of (I) are described.

The molecular structure of (I) is shown in the figure (35% probability displacement ellipsoids). There are significant differences in the C–O bond lengths in the carboxylic acid

residue [C1–O1, O2 = 1.310(2) and 1.216(2) Å] which confirm protonation at the O1 atom. The molecule is highly twisted as evidenced in the sequence of C1–C2–C3–C4 [–178.81(14)°], C2–C3–C4–C5 [78.5(2)°], C3–C4–C5–N1 [173.14(16)°] and C4–C5–N1–C6 [178.97(16)°] torsion angles, respectively, pointing to a major twist about the C3–C4 bond. By contrast, the carboxylic acid group is co-planar with the terminal residue with the O1–C1–C2–C3 torsion angle being 176.77(15)°. Complementing the twist about the C3–C4 bond, is a second twist in the molecule involving the aryl group as seen in the C5–N1–C6–C7 torsion angle of –133.95(18)°. The highly twisted conformation for (I) matches that seen in (II) [5] and one of two independent molecules of (IV) [7]. Decidedly more planar conformations are noted for the other molecules [6, 7].

In the crystal, significant hydrogen bonding is observed. Most notably is the formation of an eight-membered {···OCOH}<sub>2</sub> homosynthon resulting from hydroxy-O–H···O(carbonyl) hydrogen bonding [O1–H1o···O2<sup>i</sup>: H1o···O2<sup>i</sup> = 1.87(2) Å, O1···O2<sup>i</sup> = 2.682(2) Å with angle at H1o = 170(2)° for symmetry operation (i) 2 – x, –y, –z]. The dimeric aggregates are linked into a supramolecular tape via amide-N–H···O(amide) [N1–H1n···O3<sup>ii</sup>: H1n···O3<sup>ii</sup> = 2.106(11) Å, N1···O3<sup>ii</sup> = 2.9606(18) Å with angle at H1n = 173.6(19)° for (ii) x, 1 + y, z] hydrogen bonding as shown in the lower view of the figure. The tapes are orientated along the *b*-axis and are connected into a supramolecular layer in the *bc*-plane by phenyl-C–H···O(hydroxyl) [C11–H11···O1<sup>iii</sup>: H11···O1<sup>iii</sup> = 2.55 Å, C11···O1<sup>iii</sup> = 3.466(2) Å with angle at H11 = 168° for (iii) x, 1/2 – y, 1/2 + z] and side-on Cl···π(phenyl) [C10–Cl2···Cg(C6–C11)<sup>iv</sup>: Cl2···Cg(C6–C11)<sup>iv</sup> = 3.6433(9) Å with angle at Cl2 = 93.54(7)° for (iv) x, –1 + y, z] interactions. The connections between layers along the *c*-axis are also of the type side-on Cl···π(phenyl) [C8–Cl1···Cg(C6–C11)<sup>v</sup>: Cl1···Cg(C6–C11)<sup>v</sup> = 3.7710(9) Å with angle at Cl1 = 131.87(7)° for (v) 1 – x, 1/2 + y, 1/2 – z].

Complementing the above analysis was the calculation of the Hirshfeld surface and the two-dimensional fingerprint plots using Crystal Explorer 17 [10] and literature procedures [11]. The fingerprint plot for the H···O/O···H reveals distinctive features due to the hydrogen bonds formed in the crystal and all H···O/O···H contacts contribute 23.0% to the overall surface. Reflecting the influence of the Cl atoms on the molecular packing, H···C/Cl···H and Cl···C/C···Cl contacts account for 22.7 and 10.8% of all contacts; Cl···Cl contacts account for 2.9% of the surface contacts but, at distances greater than van der Waals separations. The dominant contribution to the surface comes from H···H contacts, i.e. 26.1%, with an important contribution from H···C/C···C contacts [8.0%].

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