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ORIGINAL PAPER

Synthesis of Dichlorobenzamide Derivatives: Crystal Structures of 3,5-Dichloro-*N*-(2-chlorophenyl)benzamide and 3,5-Dichloro-*N*-(4-chlorophenyl)benzamide

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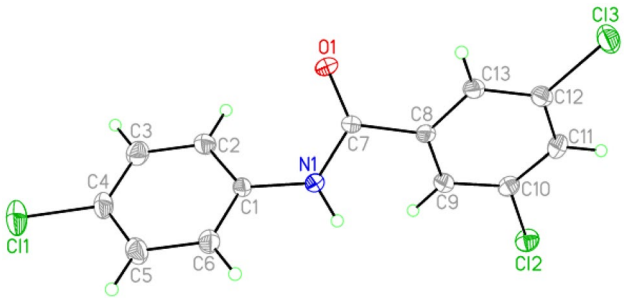
Abstract

Reactions of 3,5-dichlorobenzoyl chloride and arylamine compounds in *N*,*N*′-dimethylformamidesolution at 60 °C afforded a series of dichlorobenzamidederivatives **4**–**14** in good yields. These new compounds and accompanyingintermediates were characterized and confirmed by nuclear magneticresonance and infrared spectroscopy, of which structures of compounds **4**and **6** were established by X-ray crystallography. Compound **4** crystallizesin triclinic space group $P\bar{1}$, with $a = 5.047$ (18), $b = 10.28$ (4), $c = 13.36$ (5) Å, $\alpha = 107.59$ (5)°, $\beta = 93.55$ (5)°, $\gamma = 98.34$ (5)°, and $Z = 2$. The unit cell of **6** has a monoclinic *Pn* symmetry with the cell parameters $a = 9.581$ (3), $b = 12.217$ (4), $c = 11.072$ (3) Å, $\beta = 92.584$ (4)°, and $Z = 4$.

Graphic Abstract

A series of 3,5-dichlorobenzamide compounds were synthesized from reactions of arylamine compounds with 3,5-dichlorobenzoyl chloride, which was prepared from 3,5-dichlorobenzonitrile.



Keyword Dichlorobenzamide derivatives · Dichlorobenzoyl chloride · Arylamines · X-ray structure

Introduction

As well known, benzene nucleus is of a special structure, especially its acyl chloride compounds have various applications [1–4]. For example, 3,5-dichlorobenzoyl chloride is an important substrate in the syntheses of various benzamide derivatives. In 1991, Hitoshi Shimotori reported that isothiazole-5-carboxylic acid derivatives were treated with thionyl chloride to give carboxylic chloride, which reacted with a series of arylamines to afford isothiazole carboxamides [5]. Chlorobenzene derivatives have a lot of application ranges of physical, chemical, and biological properties. Some analogous derivatives showed their biological activity, such as antitumoral and anticonvulsive activities [6].

On the other hand, arylamines are versatile organic chemical materials, whose derivatives exhibit wide applications in the fields of medicines, industry and biology [7]. However, only two structural derivatives, such as 2,6-dichloro-*N*- (4-chlorophenyl)benzamide [8] and

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N-(2,4-dichlorophenyl)-2-nitrobenzamide [9], have been confirmed by single-crystal X-ray crystallography, showing relatively stable N−H···O hydrogen bonds. Based on these results, we are interested in reacting arylamines and 3,5-dichlorobenzoyl chloride to characterize a series of new dichlorobenzamide derivatives by way of spectroscopical methods and single crystal X-ray diffraction.

Experimental

General Procedure

All solvents were purified by routine procedures and distilled under an atmosphere of dry nitrogen before use. 3,5-Dichlorobenzonitrile, 4-chloroaniline, 3-chloroaniline, 2-chloroaniline, 2,6-diisopropylaniline, 4-iodoaniline, 3-iodoaniline, 2-iodoaniline, benzylamine, 4-nitroaniline, 2,6-disopropylaniline and 2,4,6-trimethyl-aniline were purchased from Alfa Aesar Ltd. and used directly without further purification. The infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. ^{1}H NMR spectra were recorded on a Bruker AV 400-MHz Advance NMR spectrometer. Elemental analysis were recorded by Perkin Elmer 2400 CHN elementary analyser.

Synthesis of 3,5-Dichlorobenzoic Acid (2)

To a solution of sodium hydroxide (2.9 g, 0.073 mol) in 10 mL of deionized water, 3,5-dichlorobenzonitrile (**1**) (5 g, 0.029 mol) was added slowly. Under stirring, the mixture was heated and refluxed for 6 h. The reaction was monitored by TLC (methanol/ethyl acetate: v/v = 1/4). After the reaction completed, the mixture was cooled to room temperature and the pH value of the solution was adjusted to 1–3 by hydrogen chloride aqueous (2 mol/L). A white solid precipitated, which was filtered under reduced pressure, washed with water, and dried to give a white powder. The filtrate was extracted with ethyl acetate. The white powder obtained in two crops was recrystallized from deionized water to obtain 3,5-dichlorobenzoic acid (**2**). Yield: 5.1 g (93%). FT-IR (KBr disc, cm^{-1}): υ(C–H) 3084, υ(O–H) 2663, υ(C=O) 1706, υ(C–C) 1570 and 1448, β(C–O–H) 1403, β(C–H) 1289 and 1237, γ(C–H) 769. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 7.90 (t, *J* = 2.0 Hz, 1H, *Ph*), 7.85 (d, *J* = 2.0 Hz, 2H, *Ph*).

Synthesis of 3,5-Dichlorobenzoyl Chloride (3)

A mixture of 3,5-dichlorobenzoic acid (5.0 g, 26 mmol) and thionyl chloride (8.2 g, 68 mmol) was heated at reflux for 2 hours. The reaction was monitored by TLC (methanol/ethyl acetate: v/v = 1/4). After the reaction completed, the mixture was cooled to room temperature and concentrated under reduced pressure to obtain 3,5-dichlorobenzoyl chloride (**3**), which may be used directly in the synthesis of the following amide derivatives.

General Synthetic Route for Dichlorobenzamide Derivatives

Under nitrogen atmosphere, to a solution of 3,5-dichlorobenzoyl chloride (50 mg, 0.24 mmol) in DMF (5 mL) at room temperature, the corresponding aryl amine in pyridine was added. The reaction was heated at 60 °C for 2 h and monitored by TLC (petroleum ether/ethyl acetate: v/v = 4/1). After the reaction completed, the mixture was cooled to room temperature. Water (20 mL) was added to the reaction mixture, a large amount of solid precipitated, which was filtered and washed with water (5 mL × 3) to obtain the crude product. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate v/v = 10/1–2/1) to obtain the corresponding pure products.

3,5-Dichloro-N-(4-chlorophenyl) benzamide (4)

White powder, yield: 68.5 mg (95%). The calculated of elemental analysis (%): C 39.93, H 1.66, N 9.32; found of elemental analysis (%): C 38.90, H 1.76, N 8.99. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.53 (s, 1H, –NH–), 7.97 (d, *J* = 1.9 Hz, 2H, *Ph*), 7.89–7.84 (m, 1H, *Ph*), 7.81–7.76 (m, 2H, *Ph*), 7.43 (d, *J* = 8.8 Hz, 2H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3280, υ(C=O) 1651, δ(N–H) 1563, υ(C–C) 1530 and 1291, β(C–H) 1096, γ(C–H) 745–873.

3,5-Dichloro-N-(3-chlorophenyl) benzamide (5)

White powder, yield: 64.2 mg (89%). The calculated of elemental analysis (%): C 39.93, H 1.66, N 9.32; found of elemental analysis (%): C 39.69, H 1.63, N 9.02. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.55 (s, 1H, –NH–), 7.97 (d, *J* = 1.9 Hz, 2H, *Ph*), 7.93 (t, *J* = 1.9 Hz, 1H, *Ph*), 7.88 (t, *J* = 1.9 Hz, 1H, *Ph*), 7.68 (d, *J* = 7.7 Hz, 1H, *Ph*), 7.40 (t, *J* = 8.1 Hz, 1H, *Ph*), 7.21–7.16 (m, 1H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ(C–H) 3078, υ(C=O) 1644, δ(N–H) 1589, υ(C–C) 1566 and 1541, β(C–H) 1310 and 1291, γ(C–H) 676–866.

3,5-Dichloro-N-(2-chlorophenyl) benzamide (6)

White powder, yield: 63.5 mg (88%). The calculated of elemental analysis (%): C 39.93, H 1.66, N 9.32; found of elemental analysis (%): C 38.77, H 1.65, N 9.27. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.36 (s, 1H, –NH–), 7.99 (d, *J* = 1.9 Hz, 2H *Ph*), 7.91 (dt, *J* = 3.8, 2.0 Hz, 1H, *Ph*), 7.56 (ddd, *J* = 9.7, 7.9, 1.6 Hz, 2H, *Ph*), 7.40 (td, *J* = 7.7, 1.5

Hz, 1H, *Ph*),7.33 (td, $J = 7.7$, 1.7 Hz, 1H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3265, υ(C=O) 1649, δ(N–H) 1587, υ(C–C) 1557 and 1527, β(C–H) 1307 and 1259, γ(C–H) 664–801.

3,5-Dichloro-N-(2,6-dimethylphenyl) benzamide (7)

White powder, yield: 52.2 mg (74%). The calculated of elemental analysis (%): C 61.19, H 4.42, N 4.76; found of elemental analysis (%): C 61.34, H 4.68, N 4.27. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 9.99 (s, 1H, –NH–), 8.00 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.91 (t, $J = 1.9$ Hz, 1H, *Ph*), 7.88 (t, $J = 1.9$ Hz, 1H, *Ph*), 7.86 (d, $J = 2.0$ Hz, 1H, *Ph*), 2.17 (s, 6H, –CH_3). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3427, υ(CH_3) 3074 and 2920, υ(C=O) 1652, υ(C–C) 1572 and 1521, β(C–H) 1307 and 1283, γ(C–H) 649–867.

3,5-Dichloro-N-(4-iodophenyl) benzamide (8)

White powder, yield: 83.3 mg (89%). The calculated of elemental analysis (%): C 39.77, H 2.04, N 3.57; found of elemental analysis (%): C 38.97, H 2.34, N 3.24. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.49 (s, 1H, –NH–), 7.96 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.90–7.81 (m, 1H, *Ph*), 7.81–7.68 (m, 2H, *Ph*), 7.68–7.52 (m, 2H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3448, υ(C–H) 3080 and 3059, υ_s(N–H) 2922, υ(C=O) 1653, υ(C–C) 1585, 1566, 1518 and 1487, υ(C=N) 1390, β(C–H) 1310, 1287 and 1259, γ(C–H) 688–871.

3,5-Dichloro-N-(3-iodophenyl) benzamide (9)

White powder, yield: 77.2 mg (82%). The calculated of elemental analysis (%): C 39.77, H 2.04, N 3.57; found of elemental analysis (%): C 38.09, H 2.44, N 3.56. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.45 (s, 1H, –NH–), 8.20 (s, 1H, *Ph*), 7.96 (d, $J = 1.6$ Hz, 2H, *Ph*), 7.76 (d, $J = 7.6$ Hz, 1H, *Ph*), 7.87 (d, $J = 1.7$ Hz, 1H, *Ph*), 7.48 (d, $J = 7.8$ Hz, 1H, *Ph*), 7.17 (dd, $J = 9.8$, 6.2 Hz, 1H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3452, υ_s(N–H) 3267, υ(C=O) 1643, υ(C–C) 1584, 1565 and 1541, υ(C=N) 1474, β(C–H) 1319, 1262 and 1259, γ(C–H) 678–803.

3,5-Dichloro-N-(2-iodophenyl) benzamide (10)

White powder, yield: 73.4 mg, (78%). The calculated of elemental analysis (%): C 39.77, H 2.04, N 3.57; found of elemental analysis (%): C 38.77, H 2.74, N 3.39. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.34 (s, 1H, –NH–), 8.00 (d, $J = 1.8$ Hz, 2H, *Ph*), 7.97–7.89 (m, 2H, *Ph*), 7.49–7.39 (m, 2H, *Ph*),7.12–7.06 (m, 1H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3459, υ(C=O) 1636, υ(C=N) 1303, β(C–H) 1126 and 1053, γ(C–H) 612.

3,5-Dichloro-N-benzyl benzamide (11)

White powder, yield: 47.7 mg (71%). The calculated of elemental analysis (%): C 59.98, H 3.93, N 5.00; found of elemental analysis (%): C 59.88, H 3.73, N 5.12. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 9.26 (t, $J = 5.8$ Hz, 1H, –NH–), 7.91 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.82 (t, $J = 1.9$ Hz, 1H, *Ph*), 7.35–7.30 (m, 4H, *Ph*), 7.28–7.22 (m, 1H, *Ph*), 4.47 (d, $J = 5.9$ Hz, 2H, –CH_2). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3269, υ_{as}(CH_2) 3071, υ_s(CH_2) 3065, υ(C–H) 3027, υ(C=O) 1636, υ(C–C) 1566 and 1549, β(C–H) 1288 and 1233, γ(C–H) 693–866.

3,5-Dichloro-N-(4-nitrophenyl)-benzamide (12)

Bright yellow powder, yield: 56.7 mg (76%). The calculated of elemental analysis (%): C 50.15, H 2.58, N 9.00; found of elemental analysis (%): C 51.00, H 2.63, N 9.15. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.93 (s, 1H, –NH–), 8.31–8.29 (m, 1H, *Ph*), 8.28–8.26 (m, 1H, *Ph*), 8.04 (s, 1H, *Ph*), 8.02 (d, $J = 2.1$ Hz, 1H, *Ph*), 8.00 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.91 (dd, $J = 3.9$, 1.9 Hz, 1H, *Ph*),7.85 (d, $J = 2.0$ Hz, 1H, *Ph*). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3437, υ(C–H) 3268, υ(C=O) 1634, υ(C–C) 1566 and 1542, υ_{as}(NO_2) 1506, υ_s(NO_2) 1384, β(C–H) 1328 and 1295, γ(C–H) 688–858.

3,5-Dichloro-N-(2,6-diisopropylphenyl) benzamide (13)

Light pink powder, yield: 52.9 mg (63%). The calculated of elemental analysis (%): C 61.67, H 6.00, N 8.00; found of elemental analysis (%): C 61.74, H 6.05, N 7.78. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 10.00 (s, 1H, –NH–), 8.00 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.94 (s, 1H, *Ph*), 7.87 (s, 1H, *Ph*), 3.06–2.98 (m, 2H, –CH–), 1.12 (dd, $J = 6.8$ Hz, 12H, –CH_3). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3437, υ(C–H) 2977, υ(C=O) 1648, β(C–H) 1126 and 1072, γ(C–H) 603– 727.

3,5-Dichloro-N-(2,4,6-trimethylphenyl) benzamide (14)

Beige powder, yield: 57.9 mg (70%). The calculated of elemental analysis (%): C 55.71, H 4.35, N 4.06; found of elemental analysis (%): C 54.83, H 4.43, N 4.68. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 9.90 (s, 1H, : –NH–), 7.99 (d, $J = 1.9$ Hz, 2H, *Ph*), 7.89–7.85 (m, 1H, *Ph*), 6.93 (s, 2H, *Ph*), 2.25 (s, 3H, –CH_3), 2.10 (s, 6H, –CH_3). FT-IR (KBr disc, cm^{-1}): υ_{as}(N–H) 3440, υ(C–H) 2977, υ(C–H) 3027, υ(C=O) 1642, υ(C–C) 1561 and 1520, β(C–H) 1307 and 1300, γ(C–H) 707.

X-ray Crystallography

A summary of crystallographic data and experimental details for 3,5-dichloro-*N*-(4-chlorophenyl)benzamide (**4**)

and 3,5-dichloro-*N*-(2-chlorophenyl)- benzamide (**6**) are summarized in Table 1. Compound **6** crystallizes in the noncentrosymmetric space group *P*n with the Flack parameter of 0.5 and has two unique molecules in the asymmetric unit. All the intensity data of the single crystal were collected on a CCD-Bruker Smart APEX system, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The collected frames were processed with the software SAINT [10]. The data was corrected for absorption using the program SADABS [11]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [12, 13]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96 Å), C_{sp2}–H = 0.93 Å, and N–H = 0.86 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of least-squares refinement. Omit commands are used to delete the most disagreeable reflections.

Table 1 Crystallographic data and details for compounds **4** and **6**

Compound	4	6
Empirical formula	$C_{13}H_8NOCl_3$	$C_{13}H_8NOCl_3$
Formula weight	300.55	300.55
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*Pn*
a (Å)	5.047 (18)	9.581 (3)
b (Å)	10.28 (4)	12.217 (4)
c (Å)	13.36 (5)	11.072 (3)
α (°)	107.59 (5)	90
β (°)	93.55 (5)	92.584 (4)
γ (°)	98.34 (5)	90
V(Å^3)	650 (4)	647.35 (3)
Z	2	4
D_{calc} (g cm^{-3})	1.536	1.542
Temperature (K)	296 (2)	296 (2)
F (000)	304	608
μ(Mo-Kα) (mm^{-1})	0.690	0.692
Total refln	3741	3918
Independent refln	2606	2032.5
R_{int}	0.0432	0.0259
Parameters	163	163
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0733, 0.1863	0.0345, 0.0720
*R*1, *wR*2 (all data)	0.1026, 0.2184	0.0450, 0.0786
GoF[c]	0.848	0.865
Flack parameter	–	0.5

[a] $R1 = ||F_o|-|F_c||/|F_o|$

[b] $wR2 = \left[w\left(|F_o^2|-|F_c^2|\right)^2 w|F_o^2|^2\right]^{1/2}$

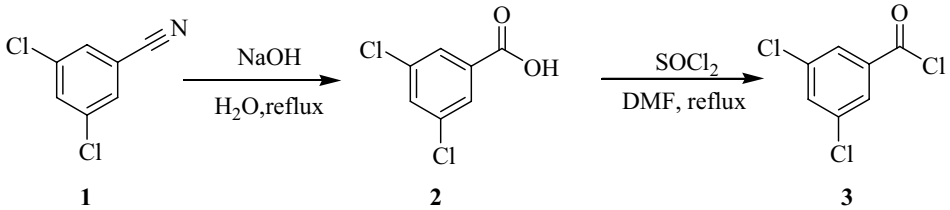
[c] $\text{GoF} = \left[w\left(|F_o|-|F_c|\right)^2 (N_{obs} - N_{param})\right]^{1/2}$

Results and Discussion

As shown in Scheme 1, the key substrate 3,5-dichlorobenzoic acid (**2**) was prepared by hydrolysis of 3,5-dichlorobenzonitrile (**1**) in sodium hydroxide aqueous solution in a quantitative yield. The ^{1}H NMR spectrum of compound **2** showed the aryl protons as two groups of peaks at around 7.85 and 7.90 ppm, respectively. Treatment of 3,5-dichlorobenzoic acid with excess thionyl chloride afforded the intermediate 3,5-dichlorobenzoyl chloride (**3**), which may directly reacted with arylamines in DMF at 60 °C to give the target benzamide derivatives **4**–**14** in good yields (Scheme 2). In the ^{1}H NMR spectra of compounds **4–14**, the chemical shift in the range 2.10–4.47 ppm are attributed to the protons of the alkyl groups, the chemical shift of 7.12–7.99 ppm are ascribed to the protons on the benzene ring. The characteristic peaks of –NH– protons were observed as a singlet in the range of 9.26–13.13 ppm,. In the IR spectra of compounds **4 14**, broad bands at 3265–3452 cm^{-1} are attributed to the functional –CO–NH– stretching vibration, while the stretching vibration peak (amide I band) of C=O are in the range of 1634–1706 cm^{-1}. The bending vibration of N–H in the amide group peak (amide II band) is 1563–1589 cm^{-1} and is easily covered by the amide I band. The stretching vibration peak of the benzene ring skeleton is usually bimodal at 1487–1584 cm^{-1}. The nitro asymmetric group stretching vibration peak in compound **12** is at 1384 cm^{-1}, the in-plane bending vibration peak of C−H on the benzene ring is 1096–1310 cm^{-1}, and the out-of-plane bending vibration peak of C−H on the benzene ring is 649–873 cm^{-1} [14]. The characteristic carbonyl groups in compound **4** with 4-chlorophenyl moiety and compound **6** with 2-chlorophenyl moiety are similar to each other (1651 cm^{-1} *vs*. 1649 cm^{-1}).

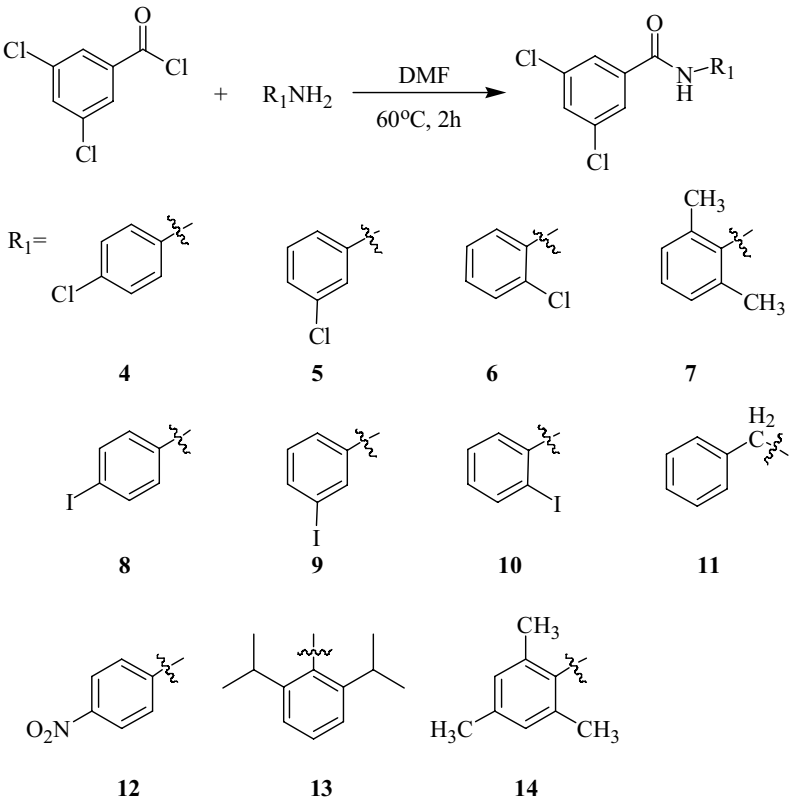
Molecular structures of compounds **4** and **6** were further confirmed by X-ray crystallography, as shown in Figs. 1 and

Scheme 1 Synthesis of 3,5-dichlorobenzoyl chloride



1 **2** **3**

Scheme 2 Synthesis of 3,5-dichlorobenzamide derivatives



2, respectively. Selected bond lengths and angles are given in Tables 2 and 3 accordingly, while the hydrogen-bond characteristics and geometric parameters for the two compounds are listed in Table 4. The C–O bond lengths are 1.225(5) Å in compound **4**, 1.220(3) and 1.230(4) Å in compound **6**, an indication of the carbon-oxygen double-bond character [8]. In compound **4**, the N(1)–C(7) and N(1)–C(1) bond lengths are 1.345(6) and 1.419(6) Å, respectively, while in compound **6**, the N–C bond lengths are in the range of 1.343(4) and 1.430(4) Å, inferring they are partial double bonds. The dihedral angle between the benzene rings is 79.3(2)° for compound **4**, much larger than those of 11.2(2)° and 12.3(2)° for compound **6**, suggestive of the chloro substituent at different positions having effect on parameters of the dihedral angles. The C−N−C−C torsion angles are − 169.2(4)° for compound **4**, − 176.0(2)° and − 178.6(2)° for compound **6**, which are compared to those in 2,6-dichloro-*N*-(4-chlorophenyl)benzamide (172.6(3)°) [8] and *N*-(4-chlorophenyl)-4-nitrobenzamide (− 179.7(1)°) [15].

Packing views of compounds **4** and **6** are shown in Figs. 1b and 2b, respectively. Crystal packing in molecules **4** and **6** are governed by the intermolecular N–H···O hydrogen-bonding interactions (see Table 4). The N···O hydrogen bonds in compounds **4** (2.908 (10) Å) and **6** (2.940 (3) and 2.974 (3) Å) agree well to those in related compounds of 2,6-dichloro-*N*-(4-chlorophenyl)benzamide (2.828 (4) Å) [8] and *N*-(4-chlorophenyl)-4-nitrobenzamide (3.1312 (17) Å) [15]. The bond angle of N–H···O in molecule **4** is 163.7°, similar to those in compound **6** (163.1° and 165.5°), and compared to those in compounds *N*-(4-chlorophenyl)-4-nitrobenzamide (159°) [15] and 2,6-dichloro-*N*-(4-chlorophenyl)-benzamide (176°) [8]. The intermolecular Cl···Cl separations of 3.429 Å in compound **4** and 3.568 Å in compound **6** are similar to the Cl···Cl contact in methyl *N*-(4-chlorophenyl)-*N'*-cyanocarbamimidothioate (3.581 Å) [16]. The intermolecular C−H···Cl (C···Cl *ca*. 2.89 Å) hydrogen bonds in compounds **4** and **6** also contribute to the stabilization of their crystal structures. Moreover, H-pi interactions (3.70 Å) of the phenyl groups exist in compound **4**. The slightly offset face-to-face pi stacking interactions between the two molecules are observed in the compound **6** with a centroid-centroid distance of adjacent phenyl rings of 3.66 A.

In summary, we have synthesized a series of dichlorobenzamide derivatives by the reaction of 3,5-dichlorobenzoyl chloride with arylamines in good yields. Two compounds were further characterized by X-ray crystallography, displaying the solid states being of *trans*-isomerism characteristic of the −NH−CO− groups [8, 15]. Different dihedral angles between the benzene rings were observed for compounds **4** (79.3(2)°) and **6** (11.2(2)° and 12.3(2)°), possibly due to the presence of 4-chloro and 2-chloro substituent on benzene ring. Short halogen–halogen interactions have been studied, showing the intermolecular Cl···Cl distances being of

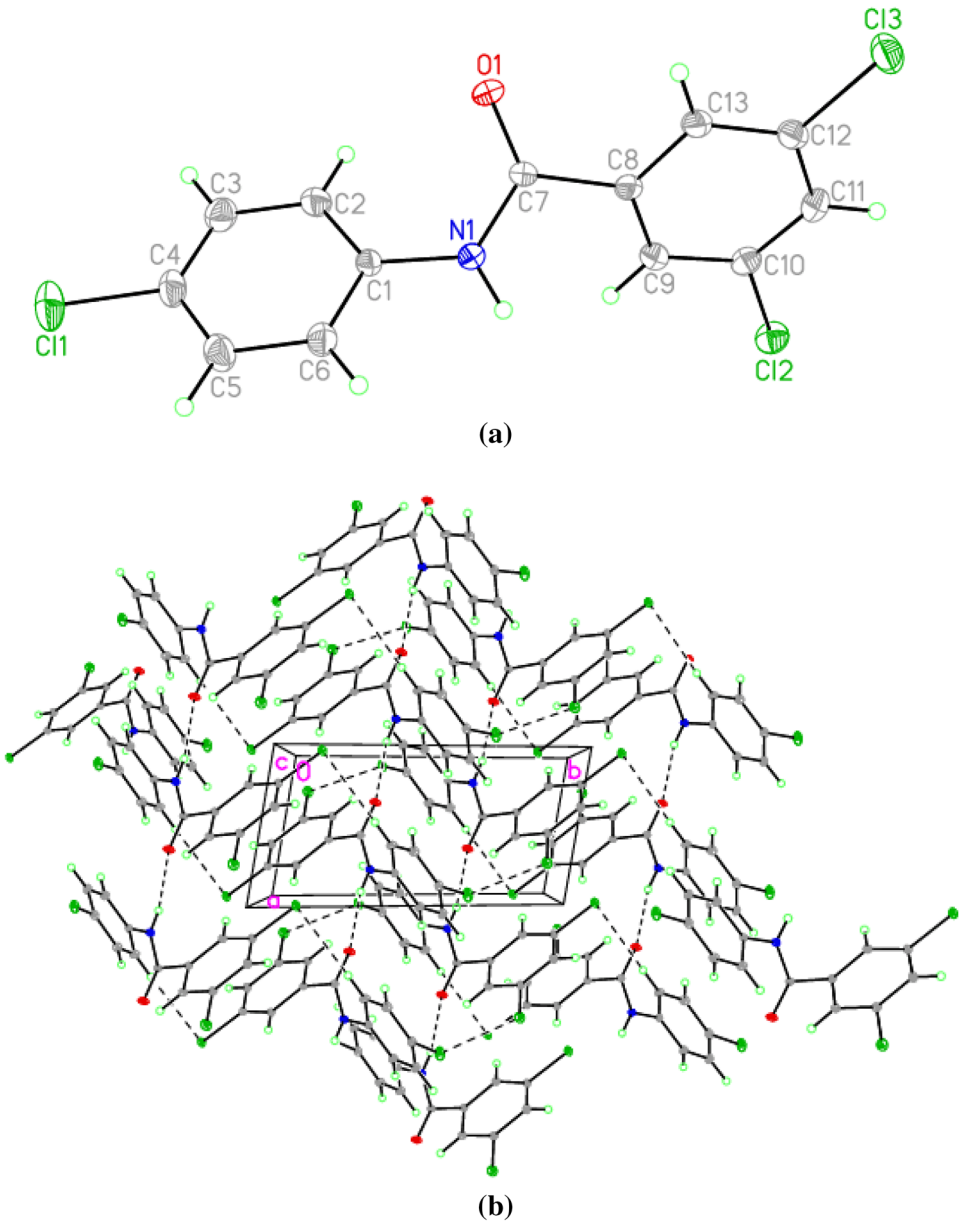
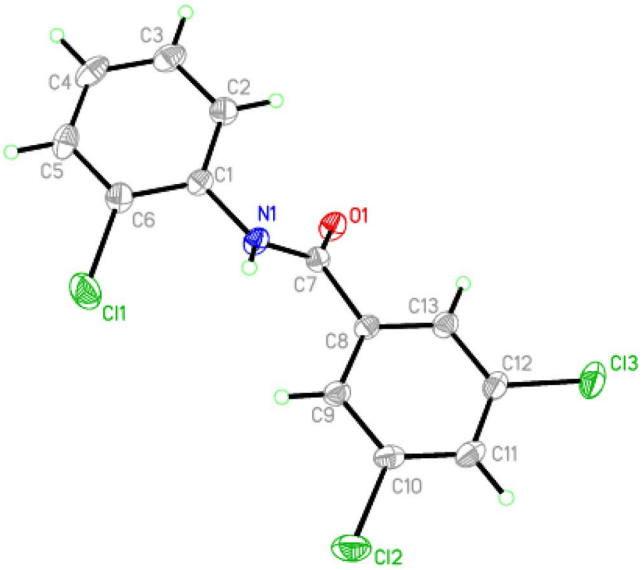


Fig. 1 **a** Structure of 3,5-dichloro-*N*-(4-chlorophenyl) benzamide (**4**), showing the atom-labelling scheme of one molecule in the asymmetric unit. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii. **b** The crystal structure of **4**, viewed along the *c* axis. Dashed lines indicate N–H···O, C–H···Cl hydrogen bonds and Cl···Cl short contacts

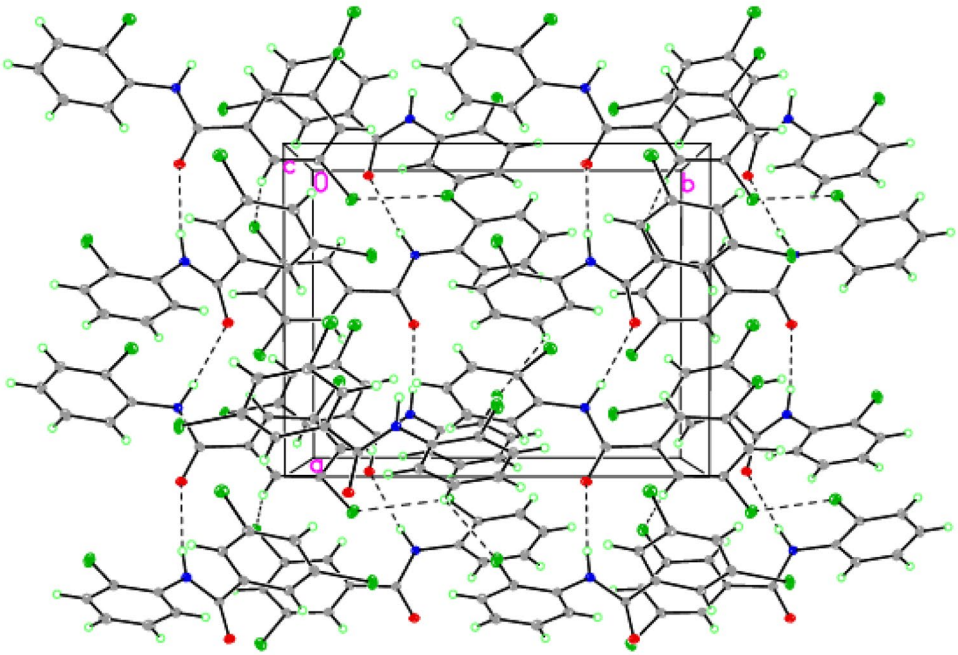
3.429 Å in compound **4** and 3.568 Å in compound **6**, similar to the Cl···Cl contact in related compound methyl *N*-(4-chlorophenyl)-*N*′-cyanocarbamimidothioate (3.581 Å) [16]. Classical C−H···Cl hydrogen bonds in compounds **4** and **6** also contribute to the stabilization of their crystal structures.

Supplementary material

Crystallographic data for 3,5-dichloro-*N*-(4-chlorophenyl) benzamide (**4**) and 3,5-dichloro-*N*-(2-chlorophenyl)benzamide (**6**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1948596 and 1948597, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].



(a)



(b)

Fig. 2 **a** Structure of3,5-dichloro-*N*-(2-chlorophenyl) benzamide(**6**), showing the atom-labelling scheme of onemolecule in the asymmetric unit. Displacementellipsoids are drawn at 50% probability level and H atoms are shown as smallspheres of arbitrary radii. **b** The crystalstructure of **6**, viewed along the *c* axis. Dash-edlines indicate N–H···O,C–H···Cl hydrogen bonds and Cl···Cl short contacts

Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

O(1)–C(7)	1.225 (5)	Cl(1)–C(4)	1.748 (7)
N(1)–C(7)	1.345 (6)	Cl(2)–C(10)	1.757 (6)
N(1)–C(1)	1.419 (6)	Cl(3)–C(12)	1.731 (6)
C(7)–C(8)	1.509 (6)		
C(1)–N(1)–C(7)	125.6 (3)	O(1)–C(7)–C(8)	121.3 (3)
O(1)–C(7)–N(1)	123.7 (4)	N(1)–C(7)–C(8)	115.0 (3)

Table 3 Selected bond lengths (Å) and angles (°) for compound **6**

O(1)–C(7)	1.230 (4)	Cl(1)–C(6)	1.733 (4)
N(1)–C(1)	1.430 (4)	Cl(2)–C(10)	1.742 (4)
N(1)–C(7)	1.343 (5)	Cl(3)–C(12)	1.731 (6)
C(7)–C(8)	1.499 (5)		
C(1)–N(1)–C(7)	123.9 (3)	O(1)–C(7)–C(8)	120.6 (3)
O(1)–C(7)–N(1)	124.5 (3)	N(1)–C(7)–C(8)	114.9 (3)

Table 4 Hydrogen-bonding system for compounds **4**, **6**

Compound	D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (deg)
4	N(1)–H(1)···O(2)^{i}	0.86	2.07	2.908(10)	163.7
6	N(1)–H(1)···O(2)^{ii}	0.86	2.11	2.940(3)	163.1
	N(2)–H(2)···O(1)	0.86	2.13	2.974(3)	165.5

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$

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