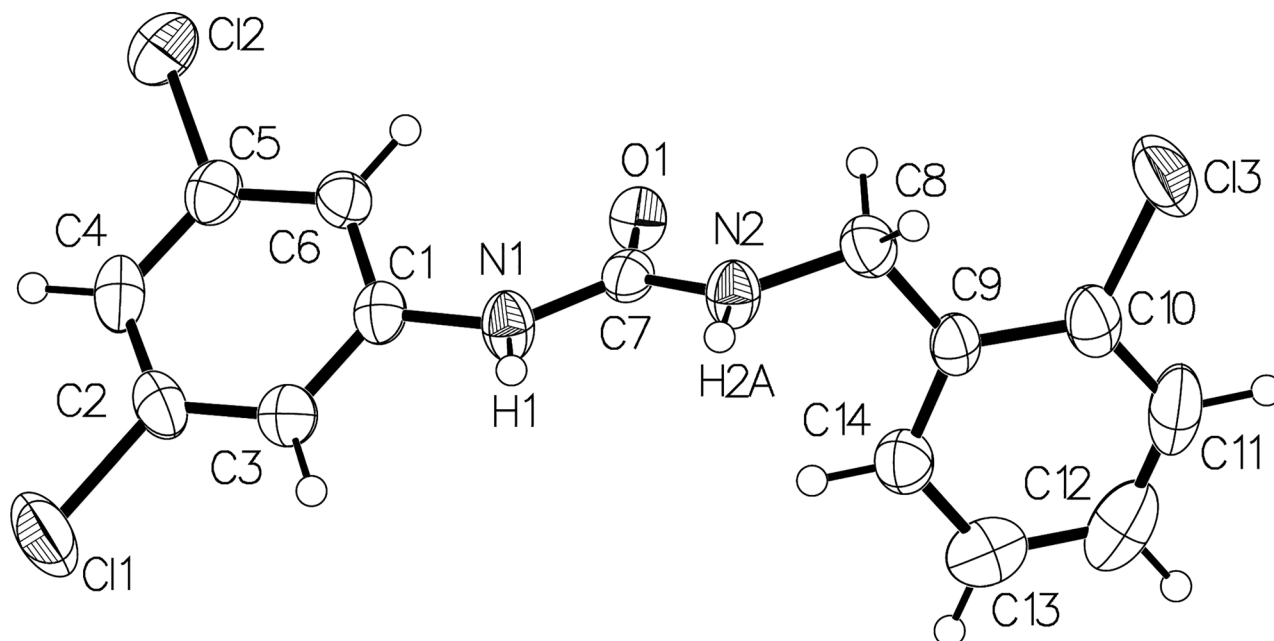


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The crystal structure of 1-(2-chlorobenzyl)-3-(3,5-dichlorophenyl)urea, $C_{14}H_{11}Cl_3N_2O$



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Abstract

$C_{14}H_{11}Cl_3N_2O$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.3600(4)$ Å, $b = 12.0085(8)$ Å, $c = 14.3665(6)$ Å, $V = 1442.27(13)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0460$, $wR_{ref}(F^2) = 0.0944$, $T = 293$ K.

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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:	Colourless block
Size:	0.26 × 0.22 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.63 mm ⁻¹
Diffraction, scan mode:	φ and ω
θ_{max} , completeness:	29.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	4927, 3047, 0.022
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2492
$N(param)_{refined}$:	181
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [3]

Source of materials

In a typical process, 1,3-dichloro-5-isocyanatobenzene (188 mg, 1 mmol) was dissolved in 10 mL dichloromethane under vigorous stirring for 20 min. Then, 2-chlorobenzylamine (142 mg, 1 mmol) was added to the resultant mixture, which was further stirred for 24 h at room temperature. After the natural volatilization of the dichloromethane solvent, the white powder product of the title compound was obtained. Fifty milligram of the obtained white powder product was dissolved in 5 mL ethanol/trichloromethane (v/v = 1:1) followed by a 5 min ultrasonic dispersion at room temperature. Subsequently, after slow volatilization of partial solvent at

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.4442 (4)	0.6117 (3)	0.3845 (2)	0.0315 (8)
C2	0.4787 (4)	0.6263 (3)	0.2910 (3)	0.0361 (9)
H2	0.540130	0.686415	0.271430	0.043*
C3	0.4210 (4)	0.5507 (4)	0.2276 (2)	0.0398 (9)
C4	0.3314 (4)	0.4589 (3)	0.2538 (3)	0.0424 (9)
H4	0.292799	0.408309	0.210297	0.051*
C5	0.3021 (4)	0.4463 (3)	0.3477 (2)	0.0365 (8)
C6	0.3555 (4)	0.5210 (3)	0.4139 (2)	0.0345 (8)
H6	0.332361	0.510622	0.476584	0.041*
C7	0.4461 (4)	0.7219 (3)	0.5305 (2)	0.0292 (8)
C8	0.4978 (4)	0.8333 (3)	0.6707 (2)	0.0377 (9)
H8A	0.595255	0.845309	0.705951	0.045*
H8B	0.435791	0.777121	0.703027	0.045*
C9	0.4038 (4)	0.9400 (3)	0.6695 (2)	0.0326 (8)
C10	0.3756 (4)	0.9994 (4)	0.7512 (3)	0.0450 (10)
C11	0.2898 (5)	1.0976 (4)	0.7520 (4)	0.0615 (13)
H11	0.271136	1.134634	0.807874	0.074*
C12	0.2324 (5)	1.1403 (4)	0.6703 (4)	0.0656 (14)
H12	0.176199	1.207092	0.670272	0.079*
C13	0.2578 (5)	1.0847 (4)	0.5885 (3)	0.0574 (12)
H13	0.218513	1.113586	0.533000	0.069*
C14	0.3423 (4)	0.9849 (3)	0.5884 (3)	0.0408 (9)
H14	0.357759	0.947533	0.532476	0.049*
Cl1	0.46236 (15)	0.56963 (12)	0.11033 (7)	0.0693 (4)
Cl2	0.19757 (14)	0.32855 (9)	0.38288 (8)	0.0596 (3)
Cl3	0.45331 (16)	0.94840 (12)	0.85574 (7)	0.0698 (4)
N1	0.5093 (3)	0.6892 (3)	0.4472 (2)	0.0370 (8)
H1	0.598534	0.719357	0.431414	0.044*
N2	0.5402 (3)	0.7909 (2)	0.5797 (2)	0.0369 (7)
H2A	0.630185	0.810793	0.555855	0.044*
O1	0.3121 (2)	0.6907 (2)	0.55759 (16)	0.0337 (6)

room temperature, colorless single-crystal products were obtained.

Experimental details

The structure was solved with the ShelXT [2] program and refined with the ShelXL [3] software package in Olex2 [4]. All hydrogen atoms were placed in idealized positions and refined as riding atoms. Their U_{iso} values were set to $1.2 U_{eq}$ of the parent atoms.

Comment

The urea derivatives frequently crystallize into structures through the self-assembly of intermolecular hydrogen bonds between urea groups, which is a crucial crystal design

element [5]. Additionally, diphenylurea has conformational polymorphism because of the low rotation energy around the central amide bond. On the one hand, the one-dimensional chains were formed via self-assembly of N–H...O hydrogen bonds in the diphenylurea derivative structures. For instance, 1,3-diphenylurea [6] and 1,3-bis (m-X-phenyl) urea [7], where X = chlorine, bromine, iodine, or methyl, exhibited one-dimensional urea chains. On the other hand, some intermolecular hydrogen bonds were observed in 1,3-bis (m-nitrophenyl) urea [8, 9], leading to various polymorphs and hydrates. Due to the vital application prospect in drug development and the interesting crystal structures, there are many crystal structures of diphenylurea derivatives reported [10–16].

Three Cl atoms replaced three H atoms in the two phenyl groups of the title compound (see the figure). The bond length of these three C–Cl bonds is 1.747 (5) Å of the C10–Cl3 bond, 1.737 (4) Å of the C5–Cl2 bond, and 1.735 (4) Å of C3–Cl1 bond, respectively. The dihedral angles of C13–C11–C10–Cl3, C2–C6–C5–Cl2, and C1–C4–C3–Cl1 are 178.6 (3)°, 177.2 (3)°, and 179.9 (4)° respectively, which are all close to 180°, indicating these Cl groups are almost in the same plane of the corresponding phenyl group. These parameters agree with the literature [17, 18]. The dihedral angle of the chlorophenyl plane and the urea group plane is 88.8°, and the dihedral angle of the dichlorophenyl plane and the urea group plane is 32.5°. These torsions of these two phenyl groups are more evident than that of 1,3-diphenylurea without Cl substitute with dihedral angles of 37.1° and 43.8° [19].

The hydrogen bonds N1–H1...O1 and N2–H2A...O1 connect molecules forming a chain structure. The bond angles of N1–H1...O1 and N2–H2A...O1 are 159.7(3)° and 152.3(2)°, and the bond length are 2.093 (2) and 2.229 (3) Å, respectively. Compared with the hydrogen bond of diphenylurea, bond angles of 157(3)° and 148(3)°, bond lengths of 1.954 (19) Å and 2.12(2) Å, the hydrogen bonds of the title compound are little longer, indicating that the hydrogen bonds between urea groups may be weakened after chlorine substitution.

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