

## Synthesis, X-ray structure and N–H...O interactions in 1,3-diphenyl-urea

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**Abstract.** The synthesis, X-ray structure and role of intermolecular interactions have been studied in case of 1,3-diphenyl-urea, owing to its medicinal importance. The compound crystallizes in orthorhombic crystal system (space group,  $Pna2_1$ ) with unit cell parameters,  $a = 9.118(3)$ ,  $b = 10.558(2)$ ,  $c = 11.780(3)$  Å and  $Z = 4$ . The structure has been solved by direct methods and refined to a final  $R$ -value of 0.0316. The oxygen atom of the carbonyl group is responsible for the existence of two N–H...O intermolecular interactions.

**Keywords.** Alkaloids; X-ray structure; diffractometer; hydrogen bond.

### 1. Introduction

The substituted urea is found to possess herbicidal activities. In continuation to our on-going research on the synthesis and structure determination of nitrogen containing organic compounds (Rajnikant *et al* 2001a, b, 2002a, b, 2003, 2004) and due to the importance of this class of compounds, the synthesis and structural investigations of 1,3-diphenyl-urea have been undertaken. The title compound has been expected to be an excellent potential tyrosine phosphatase inhibitor and sickle-cell anemia treatment drug.

### 2. Experimental

A mixture of phenylisocyanate, 1.07 g (0.01 mole), aniline, 0.94 g (0.01 mole) and triethyl amine (0.5 ml) was refluxed on a water bath, then cooled and the separated solid was filtered and further recrystallized from ethanol to get the target compound, yield, 1.7 g (80%). The chemical structure assigned to the title compound as shown in figure 1 was established on the basis of some chemical studies (elemental analysis: found: C, 73.57%; H, 5.70%; N, 13.20%; O, 7.54%; spectral characteristics: IR (KBr): 3100–3300 (NH), 1670 (amide C=O)] (Deshmukh 2004).

The three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at 293(2)K.  $w/2\theta$  scan mode was employed for data collection by using  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure has been elucidated by direct methods using SHELXS97 (Sheldrick 1997a). All non-hydrogen atoms of the molecule were located from the E-map. Isotropic refinement of the structure

by least squares method using SHELXL97 (Sheldrick 1997b) was followed by anisotropic refinement of all the non-hydrogen atoms. All the hydrogen atoms were fixed stereochemically. Atomic scattering factors were taken from International Tables for Crystallography (1992, Vol. C, tables 4.2.6–8 and 6.1.1–4). Geometrical and other structural calculations were performed by using PARST (Nardelli 1995) program.

### 3. Results and discussion

The crystal data of the title compound are given in table 1. The atomic coordinates of the non-hydrogen atoms are given in table 2. The bond lengths and the bond angles are given in table 3. An ORTEP drawing of the compound with atom labeling is shown in figure 2 (Farrugia 1997).

Average bond lengths and endocyclic bond angles associated with the phenyl portions of the molecule are as expected and are in agreement with the literature values (Isik *et al* 1998). The bond lengths, C1'–N1 [1.423(4) Å] and C1''–N3 [1.416(5) Å], indicate single bond character. However, the bond lengths N1–C2 [1.342(4) Å] and N3–C2 [1.360(4) Å], are slightly shorter than the standard single C–N bond length. This shortening of bond lengths could be attributed to the position of rigid group, C2=O1, to which N1 and N3 are attached.

Ubiquitous in organic crystals is the hydrogen bond, a polar interaction which is the most effective means of recognition and attraction between molecules; so effective, that molecules with donor and acceptor groups will form hydrogen bonds without exception. There is no case where a molecule that can form hydrogen bonds does not do so in the unit cell. The crystal structure in the present case is

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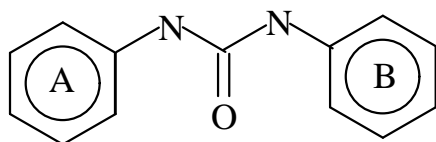
**Table 1.** Crystal data and structure refinement details.

Empirical formula	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O
Formula weight	212.25
Temperature	293(2) K
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>
Cell dimensions	<i>a</i> = 9.118(3), <i>b</i> = 10.558(2), <i>c</i> = 11.780(3) Å
<i>Z</i> , volume, calculated density	4, 1134.0(6) Å <sup>3</sup> , 1.243 Mg/m <sup>3</sup>
Absorption coefficient	0.081 mm <sup>-1</sup>
<i>F</i> (000)	448
Crystal size	0.3 × 0.2 × 0.2 mm
<i>q</i> <sub>max</sub>	24.96°
Radiation, wavelength	MoK <sub>α</sub> , <i>λ</i> = 0.71073 Å
<i>q</i> range for data collection	2.59 to 24.96°
Index ranges	0 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 13
Reflections collected/unique	1048/1048 [ <i>R</i> (int) = 0.000]
Largest diff. peak and hole	0.124 < Δ <i>r</i> < -0.129 e Å <sup>-3</sup>
No. of parameters	195
Final <i>R</i> indices [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )]	<i>R</i> <sub>1</sub> = 0.0316, <i>wR</i> <sub>2</sub> = 0.0697
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.044
Measurement	ENRAF-NONIUS Detector Program
Program system	ENRAF-NONIUS Program
Structure determination	SHELXS97
Structure drawing	ORTEP III
Refinement	SHELXL97

**Table 2.** Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>) with e.s.d's in parentheses, for the non-hydrogen atoms.

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> <sub>eq</sub> <sup>*</sup>
N1	0.0894(3)	0.2830(3)	0.2435(2)	0.049(1)
N3	0.0923(3)	0.2014(3)	0.4221(2)	0.049(1)
C2	0.0111(3)	0.2350(3)	0.3300(3)	0.044(1)
O1	-0.1234(2)	0.2231(2)	0.3278(2)	0.059(1)
C1'	0.0334(3)	0.3255(3)	0.1374(3)	0.048(1)
C2'	0.0905(4)	0.4339(3)	0.0911(3)	0.064(1)
C3'	0.0445(5)	0.4756(4)	-0.0130(4)	0.083(1)
C4'	-0.0612(5)	0.4087(5)	-0.0707(4)	0.087(1)
C5'	-0.1213(4)	0.3011(4)	-0.0242(3)	0.073(1)
C6'	-0.0734(3)	0.2574(4)	0.0801(3)	0.055(1)
C1''	0.0348(3)	0.1557(3)	0.5260(3)	0.046(1)
C2''	0.1034(3)	0.1915(3)	0.6258(3)	0.063(1)
C3''	0.0518(5)	0.1476(4)	0.7289(3)	0.076(1)
C4''	-0.0670(4)	0.0693(4)	0.7345(3)	0.070(1)
C5''	-0.1327(4)	0.0327(3)	0.6362(3)	0.065(1)
C6''	-0.0832(3)	0.0740(3)	0.5319(3)	0.054(1)

$$U_{eq}^* = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i, a_j).$$

**Figure 1.** Chemical structure of 1,3-diphenyl-urea.

stabilized by two intermolecular N1–NH1...O1 and N3–NH3...O1 hydrogen bonded interactions where N1 and N3 act as proton donors and O1 is the bifurcated acceptor

(figure 3). Geometry of interactions (e.s.d's are given in parentheses) is presented below:

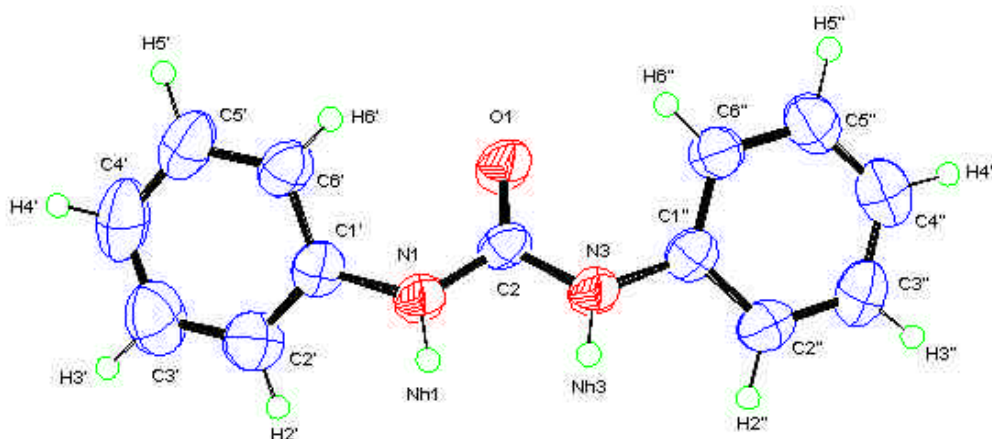
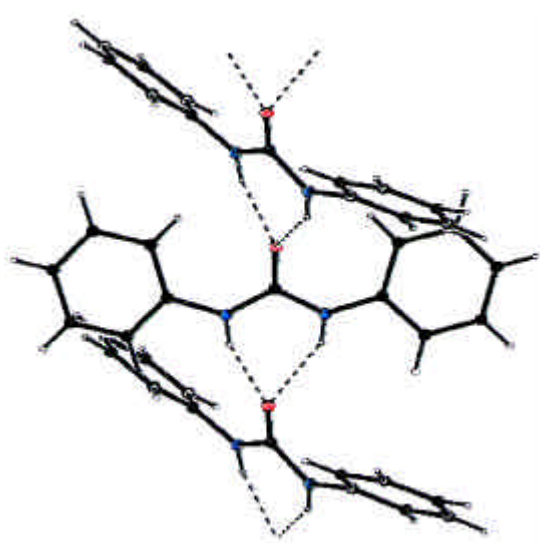
X–H...A	D[X...A(Å)]	<i>d</i> [H...A(Å)]	<i>q</i> [X–H...A(°)]
N1–NH1...O1 <sup>(i)</sup>	2.800	1.943	159.27
N3–NH3...O1 <sup>(ii)</sup>	2.930	2.154	149.95

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

Using the distance, *d* [H...A(Å)] and angle, *q* [X–H...A(°)] cut-off criterion as proposed by Steiner and Desiraju

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

N(1)–C(2)	1.342(5)	N(1)–C(1')	1.426(5)
N(3)–C(2)	1.363(5)	N(3)–C(1'')	1.414(5)
C(2)–O(1)	1.233(3)	C(1')–C(2')	1.371(5)
C(1')–C(6')	1.385(5)	C(2')–C(3')	1.366(6)
C(3')–C(4')	1.383(7)	C(4')–C(5')	1.370(7)
C(5')–C(6')	1.378(5)	C(1'')–C(6'')	1.379(4)
C(1'')–C(2'')	1.386(5)	C(2'')–C(3'')	1.384(6)
C(3'')–C(4'')	1.367(6)	C(4'')–C(5'')	1.365(6)
C(5'')–C(6'')	1.381(5)		
C(2)–N(1)–C(1')	126.3(3)	C(2)–N(3)–C(1'')	125.2(3)
O(1)–C(2)–N(1)	123.6(5)	O(1)–C(2)–N(3)	122.0(5)
N(1)–C(2)–N(3)	114.4(2)	C(2')–C(1')–C(6')	120.1(4)
C(2')–C(1')–N(1)	118.6(3)	C(6')–C(1')–N(1)	121.2(3)
C(3')–C(2')–C(1')	121.0(5)	C(2')–C(3')–C(4')	118.9(5)
C(5')–C(4')–C(3')	120.7(4)	C(4')–C(5')–C(6')	120.2(5)
C(5')–C(6')–C(1')	119.0(4)	C(6'')–C(1'')–C(2'')	118.8(3)
C(6'')–C(1'')–N(3)	122.9(3)	C(2'')–C(1'')–N(3)	118.3(3)
C(3'')–C(2'')–C(1'')	119.9(3)	C(4'')–C(3'')–C(2'')	121.2(4)
C(5'')–C(4'')–C(3'')	118.7(4)	C(4'')–C(5'')–C(6'')	121.3(4)
C(1'')–C(6'')–C(5'')	120.1(4)		

**Figure 2.** ORTEP view of 1,3-diphenyl-urea drawn at 50% probability level with atomic numbering scheme.**Figure 3.** Hydrogen-bonding network of 1,3-diphenyl-urea.

(1999), it has been found that the crystal structure is stabilized by strong intermolecular interactions.

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