organic papers

N,N'-Bis(4-bromophenyl)urea

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The crystal structure of the title compound, $C_{13}H_{10}Br_2N_2O$, has been determined by X-ray analysis. The molecule has a twofold axis coincident with the C=O bond. In the crystal structure, the molecules are linked into columns along the b axis by bifurcated intermolecular N—H···O hydrogen bonds and π–π interactions. The columns are connected by strong intermolecular π–π interactions, forming T-shaped dimers.

Comment

Biological activity is closely related to structure, and urea derivatives exhibit a wide range of biological activities; in particular, their herbicidal ability is excellent (Ye *et al.*, 2003). The crystal structures of N,N'-diphenylurea and thiourea derivatives have revealed many interesting structural phenomena, including intermolecular hydrogen bonds (Wang *et al.*, 2001; Ramnathan *et al.*, 1995; Wamhoff *et al.*, 1994; Dannecker & Kopf, 1979) and π–π interactions between phenyl groups. In the light of these findings, and as part of our work on the synthesis, biological activity (Zhang *et al.*, 2001) and coordination behavior of thiourea and urea derivatives (Zhang *et al.*, 2003), we report here the synthesis and crystal structure of the title compound, (I).

(I)
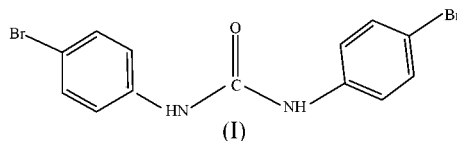
The bond lengths and angles in (I) are unexceptional. The molecule lies on a crystallographic twofold axis, coincident with the C1=O1 bond, as shown in Fig. 1. Thus the two 4-bromophenyl groups adopt a *syn–syn* conformation with respect to the urea moiety. The O1—C1—N1—C2 torsion angle is $-1.6\ (5)°$. This *syn–syn* conformation of the urea fragment facilitates the formation of bifurcated intermolecular N1—H1···O1$(x, y + 1, z)$ hydrogen bonds (Fig. 2). The N···O
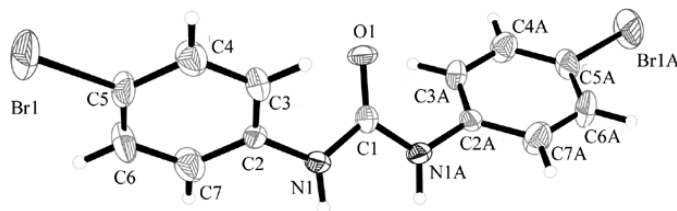

Figure 1
A view of the title compound, showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (A) $x, -y, -z$.]
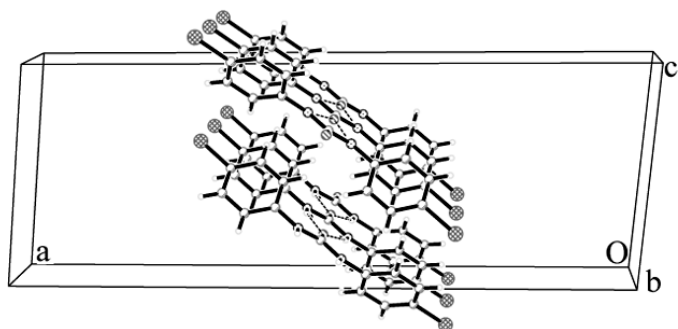
Figure 2
A view of the molecular arrangement and intermolecular interactions in the crystal structure.

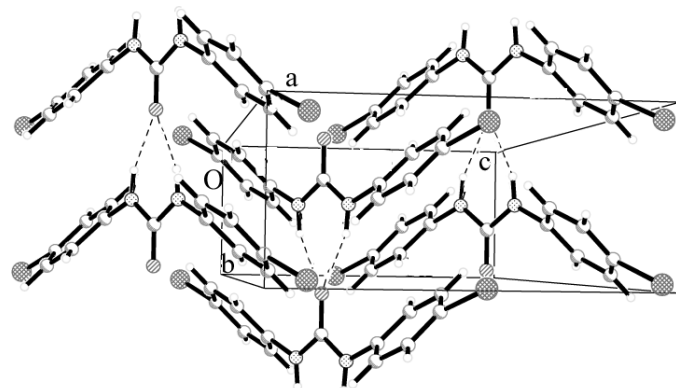**Figure 3**
A view of the T-shaped dimers formed by the intermolecular π–π interactions that connect molecular columns.

distance is 2.054 (3) Å and the N—H···O angle is 154°. As a result, the molecules are linked into columns along the *b* axis.

There are two kinds of π–π interactions between the benzene rings in the crystal structure. On the one hand, Fig. 3 illustrates the parallel packing of the benzene rings, resulting in the formation of a column along the *b* axis. The distance between the centers of the two benzene rings is 4.551 Å. According to recent calculations (Tsuzuki *et al.*, 2002), phenyl intermolecular π–π interaction energies of parallel rings are very significant in the range 3.5–4.5 Å and are at a maximum when the distance between the centers of the phenyl rings is 3.8 Å. On the other hand, we find another kind of π–π interaction between adjacent columns. According to Tsuzuki *et al.* (2002), the phenyl intermolecular π–π interaction energies of T-shaped dimers, where the phenyl rings are perpendicular to each other, are at a maximum when the distance between the centers of the phenyl rings is 5.2 Å. The dihedral angle between the C2–C7 benzene ring and the C2′–C7′ benzene ring of an adjacent molecule at $(x + \frac{1}{2}, y + \frac{3}{2}, z)$ is 87.1 (2)°, and the distance between their centers is 5.384 Å. Thus they form T-shaped dimers and should have strong intermolecular π–π interaction energies. Furthermore, the dihedral angle between the benzene ring and the plane of the urea moiety (N1/C1/O1/N1A) is 50.7 (2)°, and that between the two benzene rings is 87.1 (2)°.

Experimental

The title compound was synthesized by refluxing an ethanol−DMF (dimethylformamide) solution of 4-bromophenylamine (10 mmol) and 4-bromophenyl isocyanate (10 mmol) for 0.5 h. Colorless single crystals were obtained by slow evaporation of an ethanol−DMF solution of the compound over about one week.

Crystal data

$C_{13}H_{10}Br_2N_2O$	$D_x = 1.968$ Mg m^{-3}
$M_r = 370.05$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 624
$a = 27.701$ (12) Å	reflections
$b = 4.551$ (2) Å	$\theta = 3.0$–$25.9°$
$c = 9.953$ (4) Å	$\mu = 6.48$ mm^{-1}
$\beta = 95.418$ (7)°	$T = 293$ (2) K
$V = 1249.1$ (9) Å^3	Block, colorless
$Z = 4$	$0.30 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1272 independent reflections
	892 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.047$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$\theta_{max} = 26.3°$
	$h = -34 \rightarrow 34$
$T_{min} = 0.175$, $T_{max} = 0.355$	$k = -4 \rightarrow 5$
3676 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.7328P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
1272 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.60$ e Å^{-3}
H-atom parameters constrained	

All H atoms were positioned geometrically and refined as riding, with N—H = 0.86 Å and C—H = 0.93 Å; U_{iso}(H) values were set equal to 1.2U_{eq}(N) and 1.5U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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