

N-(4-Biphenyl)urea

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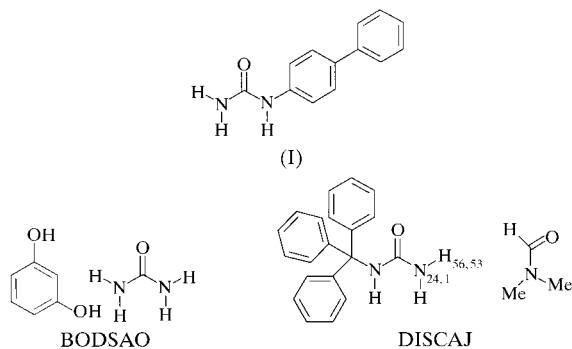
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In the crystal structure of the title compound, C₁₃H₁₂N₂O, N—H(*anti*)···O hydrogen bonds produce the so-called urea α -network and the N—H(*syn*) donor forms an unconventional N—H··· π hydrogen bond.

Comment

The packing motifs of substituted ureas have been studied in the context of crystal engineering, supramolecular synthesis and polymorphism (Coe *et al.*, 1997; Hollingsworth *et al.*, 1994; Kane *et al.*, 1995). Phenylurea (Kashino & Haisa, 1977; space group *P2*₁) contains the one-dimensional α -network, which in turn is linked to form two-dimensional β -sheets through N—H···O hydrogen bonds. Given that a biphenyl group tends to induce non-centrosymmetry in crystal packing (Sarma *et al.*, 1997; Swift & Ward, 2000), we have now determined the crystal structure of *N*-(4-biphenyl)urea, (I). Although the structure of (I) is centrosymmetric (*Pbca*) and hence of no utility for second harmonic generation, the existence of an unconventional N—H··· π hydrogen bond (π refers to the C7–C12 phenyl-ring centroid) deserves discussion. Weak N—H··· π -type hydrogen bonding (Desiraju & Steiner, 1999) in small molecule (Malone *et al.*, 1997) and protein (Steiner & Koellner, 2001) crystal structures has received recent attention.



The biphenyl moiety is twisted by an angle of 45.41 (17)^o about the C—C bond (Fig. 1). Molecules of (I) are connected by N—H(*anti*)···O hydrogen bonds along [100]. The biphenyl groups interdigitate between α -networks, with the phenyl

rings involved in edge-to-face herring-bone packing. The N—H(*syn*) group forms an N—H··· π interaction with the phenyl ring of a screw-axis-related molecule (Fig. 2). Malone *et al.* (1997) have classified N—H··· π hydrogen bonds into six categories depending on the approach geometry of the N—H vector to different regions of the phenyl ring. In this nomenclature, the N—H··· π interaction in (I) is of type II; $d_{\pi\cdots H} = 2.57$ Å, $\alpha = 169.0^{\circ}$, angle of H··· π vector with the plane of the phenyl ring (θ) = 76.8^o, offset distance of H atom from the centroid of the phenyl ring (d) = 0.58 Å. Type II N—H··· π geometry is present in about 10% of crystal structures (Malone *et al.*, 1997).

A search of the Cambridge Structural Database (version 5.20, 224 400 entries, October 2000 update; Allen & Kennard, 1993) for N—H··· π contacts in monosubstituted urea structures in the ranges $1.8 < \text{H}\cdots\pi < 3.0$ Å and $120 < \text{N—H}\cdots\pi < 180^{\circ}$ furnished two hits (BODSAO: Pickering & Small, 1982; DISCAJ: Goldberg *et al.*, 1985); the corresponding structures are shown in the Scheme. The crystal structure of the *N,N*-dimethylformamide solvate of triphenylmethyl urea (DISCAJ, space group *Cc*) has two N—H··· π contacts (N24—H56··· π 2.69 Å and 166.4^o; N1—H53··· π 2.63 Å and 171.8^o). This study shows that correspondence between molecular and crystal structures (Desiraju, 1999) can be difficult to establish

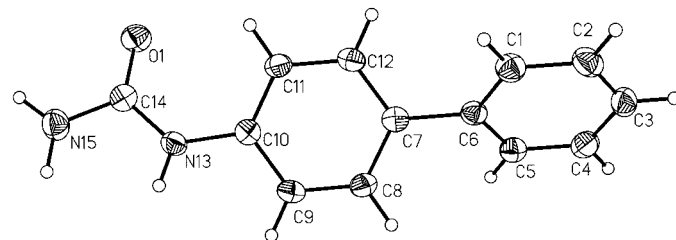


Figure 1
ORTEPII (Johnson, 1976) diagram and atom-numbering scheme for (I); displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

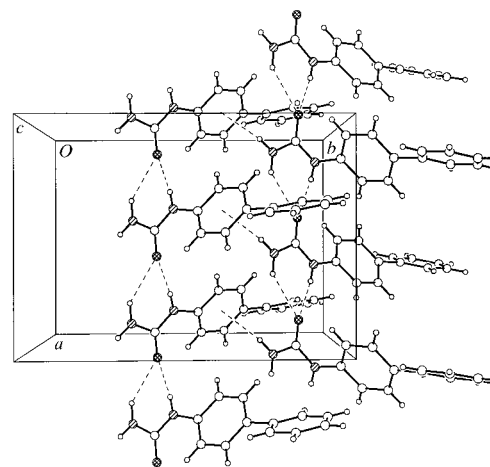


Figure 2
Packing diagram of (I) showing the N—H(*anti*)···O hydrogen-bonded α -network along [100] and the N—H(*syn*)··· π interaction. Interdigitation of biphenyl groups is not shown for clarity.

even for simple molecules with robust hydrogen-bonding supramolecular synthons.

Experimental

Compound (I) was prepared according to Vogel (1991). 4-Aminobiphenyl (507 mg, 3 mmol) was dissolved in glacial acetic acid (4.5 ml) and hot water (7 ml). Sodium cyanate (195 mg, 3 mmol) dissolved in hot water (5 ml) was added dropwise with stirring. After precipitation of 4-biphenylurea, the reaction mixture was cooled in an ice bath, filtered and dried (98%). The product was recrystallized from ethyl acetate (m.p. 446–448 K).

Crystal data

$C_{13}H_{12}N_2O$	$D_m = 1.293 \text{ Mg m}^{-3}$
$M_r = 212.25$	Mo $K\alpha$ radiation
Orthorhombic, $Pbca$	Cell parameters from 14801 reflections
$a = 9.3700$ (4) Å	$\theta = 2.9\text{--}27.5^\circ$
$b = 13.0330$ (5) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 17.5210$ (6) Å	$T = 123$ (2) K
$V = 2139.7$ (1) Å ³	Prism, colourless
$Z = 8$	$0.34 \times 0.30 \times 0.23 \text{ mm}$
$D_x = 1.318 \text{ Mg m}^{-3}$	

Data collection

Nonius Kappa-CCD diffractometer	$R_{\text{int}} = 0.029$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
10130 measured reflections	$h = -12 \rightarrow 9$
2436 independent reflections	$k = -13 \rightarrow 16$
1964 reflections with $I > 2\sigma(I)$	$l = -22 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0490P)^2 + 0.7752P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{\text{max}} = 0.029$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
2436 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
157 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Hydrogen-bonding geometry (Å, °).

π is the centroid of the C7–C12 phenyl ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N13–H13A \cdots O1 ⁱ	0.855 (16)	1.982 (16)	2.8320 (16)	172.8 (14)
N15–H15B \cdots O1 ⁱ	0.959 (19)	2.464 (18)	3.2615 (18)	140.5 (14)
N15–H15A \cdots π^{ii}	0.95	2.57	3.50	169

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms of phenyl groups were fixed (riding on their C atoms) and H atoms bonded to nitrogen were refined isotropically.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL93 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976) and PLUTON (Spek, 1992); software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1458). Services for accessing these data are described at the back of the journal.

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