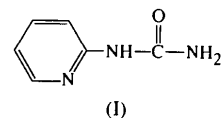Lewis, N. P. & Winfield, S. Z. (1955). *J. Am. Chem. Soc.* **77**, 3154–3157.

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(I)

N-(2-Pyridyl)urea

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Abstract

The structure of the title compound, $C_6H_7N_3O$, is built of layers stacked along the *c* axis and each layer consists of parallel zigzag ribbons of hydrogen-bonded molecules extended along the *ab* diagonals. Within the layers, the molecules are plane-to-plane coupled at distances of 3.330 (2) Å. The molecular planes from adjacent layers make an angle of 68.0 (1)°.

Comment

Recently, we have begun to examine the design and chemical and structural characterization of new non-linear optical materials based on unsymmetrical urea and thiourea derivatives with π-conjugated substituents. The polar structure of monophenylurea (Kashino & Haisa, 1977) encouraged us to examine the structure of N-(2-pyridyl)urea, (I), where the *endo*-N atom was expected to induce a non-centrosymmetric arrangement in the crystalline state. However, the crystal structure is centrosymmetric, but with interesting cyclic hydrogen-bonding bridges and molecular plane-to-plane coupling.

Bond lengths and angles in (I) fall within the expected ranges for urea and its derivatives (Blessing, 1983; Allen *et al.*, 1987). It is worth noting the chemical and geometric non-equivalence of the two ureido N—C bonds [1.379 (1) and 1.325 (2) Å for the imino and amino groups, respectively] caused by resonance effects from the π-conjugated system of the pyridyl ring. The same distance variations have been observed in the structure of monophenylurea [1.375 (10) and 1.326 (10) Å, respectively; Kashino & Haisa, 1977]. The C(pyridyl)—N2 bond distance [1.389 (2) Å] is 3σ shorter than the C(phenyl)—N distance of 1.419 (9) Å in monophenylurea and 25σ shorter than the C(methyl)—N bond length of 1.439 (2) Å in monomethylurea (Huiszoon & Tiemessen, 1976).

The molecule is planar, with the largest deviation [0.065 (1) Å] at the amino N3 atom. This corresponds well with other pyridylurea and thiourea compounds {N-(*n*-pyridyl)-N'-(4-chlorophenyl)urea, where *n* = 2, 3, 4 (Le Magueres, Ouahab, Hocquet & Fournier, 1994); N-(*n*-pyridyl)-N'-phenylurea, where *n* = 3, 4, N-(*n*-chloro-4-pyridyl)-N'-phenylurea, where *n* = 2, 3 (Yamaguchi & Shudo, 1991); tetra[1-allyl-3-(2-pyridyl)thiourea-*S*]-di-μ-chlorotetrachlorodibismuth(III) and hexa[1-allyl-3-(2-pyridyl)thiourea-*S*]bismuth(III) nitrate (Battaglia & Corradi, 1981); chloro(triphenylphosphine)[1-phenyl-3-(2-pyridyl)-2-thiourea]copper(II) and chlorobis[1-phenyl-3-(2-pyridyl)-2-thiourea]copper(II) (Ferrari, Fava, Pelizzi & Tarasconi, 1985); trichlorotris[1-phenyl-3-(2-pyridyl)-2-thiourea-*S*]bismuth(III) (Battaglia & Corradi, 1983)}. In all 2-pyridyl derivatives, the planarity of the molecule is promoted by an intramolecular *endo*-N···H—N(ureido) hydrogen bond. In (I), the geometry of this bond is N1···HN31 1.99 (2), N1···N3 2.714 (2) Å and N1···HN31—N3 135 (2)°. The 3- and 4-pyridyl compounds also retain planarity in contrast to the phenylurea and thiourea derivatives where the phenyl ring can freely rotate. Thus, the phenyl ring in monophenylurea is tilted to the urea plane by 47.4°, in 3- and 4-tolylurea by 54.4 (5) and 52.1 (4)°, respectively (Ciajolo, Lelj, Tancredi, Temussi & Tuzi, 1982), in 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea by 13.3° (Cruse, 1978), in N-(*n*-pyridyl)-N'-(4-chlorophenyl)urea, where *n* = 2, 3, 4, by 6, 3 and 11°, in N-(2,3,5,6-tetrafluoropyridyl)-N'-phenylurea by 32.1 (4)° (Yamaguchi, Matsumura, Haga & Shudo, 1992) and in N-methyl-N'-phenylurea by 30° (Brett, Rademacher & Boese, 1990). Correspondingly, the phenyl rings in the symmetrically disubstituted urea and thiourea compounds are also bent from the central plane, for example, in diphenylurea by 43.0 (2)° (Dannecker, Kopf & Rust, 1979), in bis(3,4-dichlorophenyl)urea by 16.32 and 29.53° for molecule

A, and 29.73 and 39.67° for molecule *B* (Stanković & Andreetti, 1978), in bis(3-nitrophenyl)urea and its adducts within the 2.3–19.1° range (Etter, Urbanczyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990), and in diphenylthiourea by 104.8 (1)° (Ramnathan *et al.*, 1995).

The *ortho* position of the *endo*-N atom confers conformational flexibility around the N2—C2 single bond in addition to that arising from the N2—C1 single bond. Hence, the overall conformation can be described as being *s-trans-s-cis* (or anticlinal–synclinal). The same conformation is adopted by *N*-(2-pyridyl)-*N'*-(4-chlorophenyl)urea but the corresponding 3- and 4-pyridyl derivatives are stabilized in the opposite *s-cis* conformation with respect to the carbonyl bond.

The close disposition of the carbonyl O and imino H atoms in (I) leads to dimerization of the molecules through the formation of eight-membered centrosymmetric hydrogen-bonded rings similar to those found in the structures of the carboxylic acids. The corresponding geometric parameters are as follows: $O1 \cdots HN21(\frac{1}{2} - x, \frac{3}{2} - y, -z)$ 1.98 (2), $O1 \cdots N2$ 2.878 (1) Å and $O1 \cdots HN21$—N2 176 (2)°. Similar dimers have been found in the structures of 2-pyridyl-(4-chlorophenyl)urea, -(4-chlorophenyl)-(2,6-difluorobenzoyl)urea, 1,3-diethyl- and 1,3-diisopropylthiourea (Ramnathan *et al.*, 1995) and 1,3-bis(2-chlorophenyl)thiourea (Ramnathan *et al.*, 1996). The availability of a *cisoid* H atom from the unsubstituted amino group in (I) favours the formation of an additional hydrogen-bonded ring with the following geometry: $O1 \cdots HN32(1 - x, 1 - y, -z)$ 2.02 (2), $O1 \cdots N3$

2.941 (1) Å and $O1 \cdots HN32$—N3 178 (2)°. This type of hydrogen bonding leads to the extension of parallel zigzag ribbons of molecules along the *ab* diagonals. The ribbons are stacked in an alternating manner in layers along the *c* axis (Fig. 1). Within the layer the molecules are additionally plane-to-plane stacked in parallel centrosymmetric dimers and the distance between the molecular mean planes is 3.330 (2) Å. This separation is comparable with the distances within the TCNQ organic conductors (Wheland, 1976; Govers, 1981). Similar coupling has been found in some other planar urea derivatives (Uchida, Ohashi, Sasada, Kaneko & Endo, 1984; Ohashi, Uchida, Sasada, Kinoshita & Endo, 1984; Uchida, Ohashi, Sasada, Moriya & Endo, 1984).

The cohesion of the layers occurs through van der Waals interactions, mainly between the pyridyl atoms. The planes of the molecules from adjacent layers make an angle of 68.0 (1)°.

Experimental

The title compound was synthesized by transamidation of urea with 2-aminopyridine. The procedure was developed on the basis of the results obtained by Gertscuk & Tayts (1950). 2-Aminopyridine (4.76 g, 5 × 10^{-2} mol) and 3.0 g (5 × 10^{-2} mol) urea were heated at 423 K for 5 h. The reaction was controlled by ammonia liberation. The mixture was then cooled and the raw product was recrystallized from ethanol. The yield was 85%. A single crystal was obtained from ethanol solution.

Crystal data

$C_6H_7N_3O$	Mo $K\alpha$ radiation
$M_r = 137.14$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 22
$C2/c$	reflections
$a = 13.339\,(4)$ Å	$\theta = 19.96$–$21.90°$
$b = 5.480\,(2)$ Å	$\mu = 0.09$ mm^{-1}
$c = 18.208\,(5)$ Å	$T = 292$ K
$\beta = 93.73\,(2)°$	Prismatic
$V = 1328\,(1)$ Å^3	$0.396 \times 0.330 \times 0.231$ mm
$Z = 8$	Pale yellow
$D_x = 1.371$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.037$
diffractometer	$\theta_{max} = 28.0°$
ω/θ scans	$h = 0 \rightarrow 17$
Absorption correction: none	$k = -7 \rightarrow 7$
3340 measured reflections	$l = -24 \rightarrow 24$
1768 independent reflections	3 standard reflections
1097 reflections with	frequency: 120 min
$I > 2\sigma(I)$	intensity decay: none

Refinement

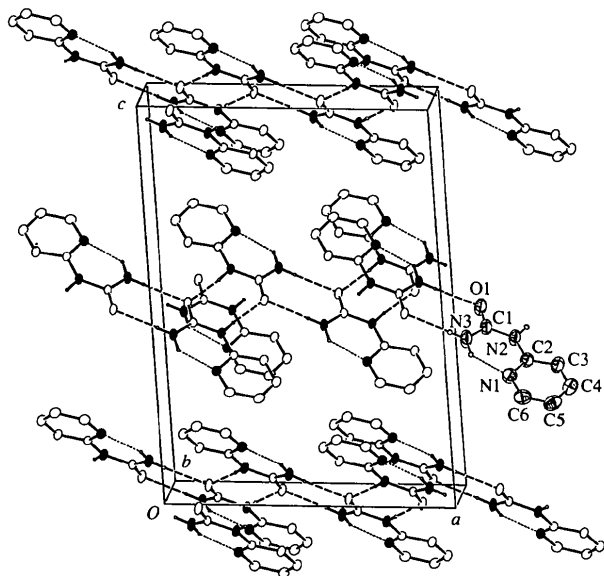|	
Refinement on F	$(\Delta/\sigma)_{max} = 0.013$
$R = 0.039$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$wR = 0.053$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
$S = 1.028$	Extinction correction: none

Fig. 1. A view of the structure along the *b* axis with the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level. Full circles denote N atoms. The intra- and intermolecular hydrogen bonds are shown as dotted and dashed lines, respectively, and ureido H atoms as spheres of arbitrary radii.

1189 reflections
112 parameters
H-atom positional
parameters refined
$w = 1/[\sigma^2(F) + (0.039F)^2]$

Scattering factors as coded in
SDP/PDP User's Guide
(Enraf–Nonius, 1985)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.242 (2)	N3—C1	1.325 (2)
N1—C2	1.332 (2)	C2—C3	1.400 (2)
N1—C6	1.347 (2)	C3—C4	1.367 (2)
N2—C1	1.379 (1)	C4—C5	1.381 (2)
N2—C2	1.389 (2)	C5—C6	1.374 (2)
C2—N1—C6	117.3 (1)	N1—C2—C3	122.4 (1)
C1—N2—C2	130.4 (1)	N2—C2—C3	117.7 (1)
O1—C1—N2	118.2 (1)	C2—C3—C4	118.8 (1)
O1—C1—N3	123.4 (1)	C3—C4—C5	119.6 (1)
N2—C1—N3	118.4 (1)	C4—C5—C6	118.0 (1)
N1—C2—N2	119.9 (1)	N1—C6—C5	123.8 (1)

H atoms were initially located from difference Fourier maps; their coordinates were refined but they were assigned a common $U_{iso} = 0.0506$ Å^2.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP User's Guide* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP User's Guide*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, unpublished).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1272). Services for accessing these data are described at the back of the journal.

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4-(3-Phenanthryl)butanoic Acid

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Abstract

The title compound, C$_{18}$H$_{16}$O$_2$, crystallized in the centrosymmetric space group $P2_1/a$. The single type of carboxylic hydrogen bond forms cyclic dimers about centers of symmetry. The carboxylic H atom is ordered as are the carboxylic O atoms. This structure comprises double layers of aromatic rings in a herring-bone array separated by double layers of hydrogen-bonded aliphatic strings and is a very close analog of the structures of 4-(2-naphthyl)butanoic acid and other terminally aryl-substituted *n*-aliphatic carboxylic acids.

Comment

This study of 4-(3-phenanthryl)butanoic acid, (I), is one of a series of studies of hydrogen bonding in carboxylic acids. It follows a recent report on the related acid,