Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N,*N*′-Bis(6-methyl-2-pyridyl)urea

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Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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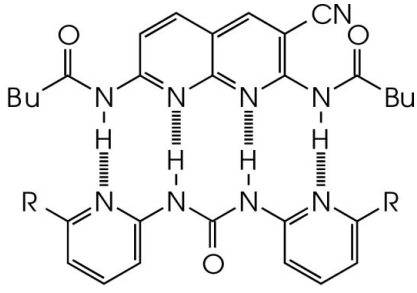
The title compound, $C_{13}H_{14}N_4O$, has been synthesized as an *ADDA* (*D*: hydrogen-bond donor; *A*: hydrogen-bond acceptor) recognition unit for quadruple hydrogen bonds. In the solid state, it crystallizes as a centrosymmetric dimer connecting one N—H group with one pyridyl N atom. Furthermore, an intramolecular hydrogen bond is formed connecting two N atoms.

Received 18 April 2001
Accepted 2 May 2001
Online 10 May 2001

Comment

Multiple hydrogen bonds attract increasing attention for the formation of host–guest complexes and for supramolecular self-assembly (Zimmerman & Corbin, 2000*a*). Therefore quadruple hydrogen-bonding patterns have been investigated and the first heterodimer based on four parallel and anti-parallel hydrogen bonds has been described (Lüning & Kühl, 1998): *DAAD*·*ADDA* (*D*: hydrogen-bond donor; *A*: hydrogen-bond acceptor). Association constants have been determined for the *DAAD* 'host' (1) and two urea 'guests' (2*a*) and (2*b*) (Clemo *et al.*, 1954; Camps, 1902; Beilsteins Handbuch der Organischen Chemie, 1979). The association constants could be calculated from Sartorius and Schneider's (1996) data if the possibility of intramolecular hydrogen bonds was taken into account. Here, we present the crystal structure of (2*a*) proving this.



(1):(2*a*) R = Me
(1):(2*b*) R = H

The title compound is a planar molecule (r.m.s. deviation of all non-H atoms 0.03 Å). As in its non-methyl relative (2*b*), an intramolecular hydrogen bond is formed between the H atom bound to the N atom of urea (N3) and the N atom (N12) of the pyridine ring bound to the urea N′. In order to allow this hydrogen bond, the urea molecule has to adopt a *Z*,*E* conformation at the two amide bonds (C2—C3 and C11—N1, respectively), resulting in an *A*,*D* hydrogen-bond pattern at the *E*-amide bond. This self recognition pattern leads to an *AD*·*DA* dimer formation in the crystal as was also observed

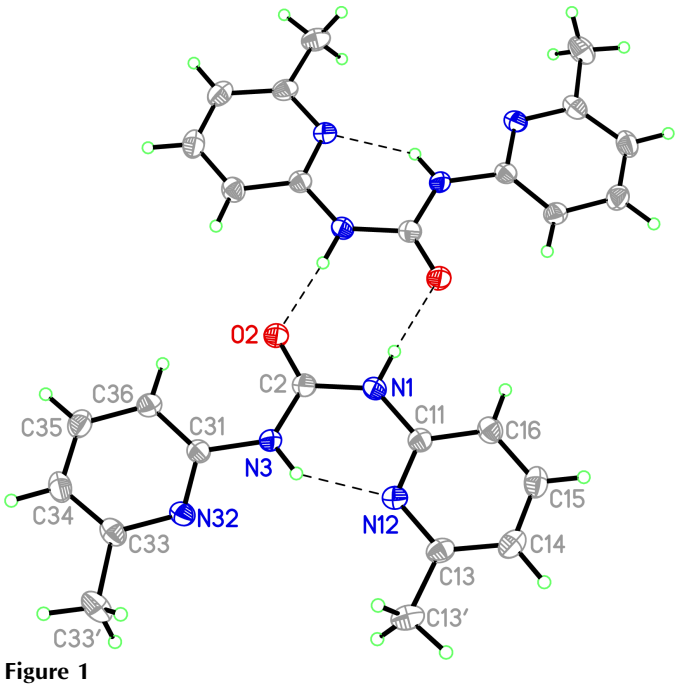


Figure 1
A perspective view of the title compound with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. Hydrogen bonds are drawn as dotted lines. The second molecule is generated applying the symmetry operator $(-x, 1-y, 1-z)$.

for (2*b*) (Zimmerman & Corbin, 2000*b*). Comparing the title compound with *N*-(4-chlorophenyl)-*N*′-(2-pyridyl)urea, *N*-(4-chlorophenyl)-*N*′-(3-pyridyl)urea, and *N*-(4-chlorophenyl)-*N*′-(4-pyridyl)urea (Le Magueres *et al.*, 1994), it can be noticed that a pyridyl-N atom in the *ortho* position is necessary for the urea moiety to adopt a *Z*,*E* conformation by hydrogen-bond formation, because only *N*-(2-pyridyl)-*N*′-(4-chlorophenyl)-urea shows this conformation, whereas the other two compounds adopt the *Z*,*Z* conformation.

Experimental

The title compound was synthesized according to Clemo *et al.* (1954): Under nitrogen, 2-(ethoxycarbonylamino)-6-methylpyridine (900 mg, 5.00 mmol) and 2-amino-6-methylpyridine (1.10 g, 10.2 mmol) were dissolved in 30 ml of dry pyridine and were heated at reflux for 7 d. After evaporation of the solvent *in vacuo*, the residue was recrystallized from ethanol, from toluene/ethanol (1:1) and then from toluene, giving 407 mg (57%), [Clemo *et al.* (1954): 11%] of colourless needles, m.p. 459–460 K. IR (KBr): $\tilde{\nu}$ = 3439, 3222, 3065 cm^{-1} (NH), 3002 (aliphatic CH), 1702 (C═O), 1605, 1576, 1518 (aromatic), 1564 (NH), 1458 (CH). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.55 (*s*, 6H, CH_3), 6.83 (*d*, *J* = 7.7 Hz, 2H, ArH), 7.2–7.5 (*br s*, 2H, ArH), 7.56 (dd, *J* = 7.7 Hz, *J* = 7.9 Hz, 2H, ArH), 9.0–13.0 (*br s*, 2H, NH). MS (EI, 70 eV): *m*/*z* (%) = 242 (9), 135 (28), 108 (100). MS (CI/isobutane): *m*/*z* (%) = 243 (100). The predecessor of the title compound, 2-(ethoxycarbonylamino)-6-methylpyridine, was synthesized as described by Katritzky (1956). Under nitrogen, ethyl chloroformiate (2.17 g, 20.0 mmol) was added dropwise to a solution of 2-amino-6-methylpyridine (2.16 g, 20.0 mmol) in 10 ml of dry pyridine. After 15 h at 278 K, the reaction mixture was hydrolyzed with 30 ml of ice water. The solid was filtered off and recrystallized from ethanol/toluene (1:3), giving 1.59 g (44%) [Katritzky (1956): 30%] of a colourless solid, m.p. 328–329 K. IR (KBr): $\tilde{\nu}$ = 3192 cm^{-1} (NH), 2980 (aliphatic CH), 1724 (C═O), 1605, 1583 (aromatic), 1537 (NH), 1461 (CH), 1220, 1084 (CO). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25 (*t*, *J* = 7.0 Hz, 3H, CH_3), 2.38 (*s*, 3 H, CH_3), 4.25 (*q*, *J* = 7.0 Hz, 2H, CH_2), 6.75 (*d*, *J* = 7.0 Hz, 1H, ArH), 7.45 (*t*, *J* = 7.0 Hz, 1H, ArH), 7.75 (*d*, *J* = 7.0 Hz, 1H, ArH), 8.10 (*br s*, 2 H, NH_2). MS (EI, 70 eV): *m*/*z* (%) = 180 (90), 135 (31), 121 (26), 108 (100), 92 (35). MS (CI/isobutane): *m*/*z* (%) = 181 (100).

Crystal data

$C_{13}H_{14}N_4O$
M_r = 242.28
Monoclinic, $P2_1/c$
a = 7.1142 (2) Å
b = 11.0127 (3) Å
c = 16.4630 (4) Å
β = 90.078 (1)°
V = 1289.82 (6) Å^3
Z = 4
D_x = 1.248 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6371 reflections
θ = 1.0–25.0°
μ = 0.08 mm^{-1}
T = 133 K
Block, colourless
0.50 × 0.30 × 0.20 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)'
T_{min} = 0.960, T_{max} = 0.984
23 905 measured reflections
2629 independent reflections
2240 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.3°
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$
831 standard reflections
frequency: 900 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 1.09
2629 reflections
173 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.3616P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.920 (17)	1.928 (17)	2.8468 (13)	177.0 (15)
N3—H3···N12	0.879 (16)	1.948 (16)	2.6757 (14)	139.3 (13)

Symmetry code: (i) $-x, 1-y, 1-z$.

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.5U_{eq}(C_{methyl}) or 1.2U_{eq}(C)] using a riding model with C—H(aromatic) = 0.95 or C—H(methyl) = 0.98 Å. The methyl group was allowed to rotate about its local threefold axis. The H atoms bonded to N were refined isotropically.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1991).

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