

***N*-*tert*-Butyl-*N'*-(5,7-dimethyl-1,8-naphthyridin-2-yl)urea**Ulrich Lüning,^a Christine Kühl^a and Michael Bolte^{b*}^aInstitut für Organische Chemie, Universität Kiel, Olshausenstraße 40, 24098 Kiel, Germany, and ^bInstitut für Organische Chemie, J. W. Goethe-Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany
Correspondence e-mail: bolte@chemie.uni-frankfurt.de

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The title compound, C₁₅H₂₀N₄O, has been synthesized as an *AADD* recognition unit for quadruple hydrogen bonds. All non-H atoms of the molecule apart from two methyl groups of the *tert*-butyl group lie in a common plane. An intramolecular hydrogen bond is formed connecting two N atoms. In the solid state, the title compound crystallizes as a centrosymmetric dimer connected by N—H...O=C interactions with an N...O distance of 2.824 (2) Å.

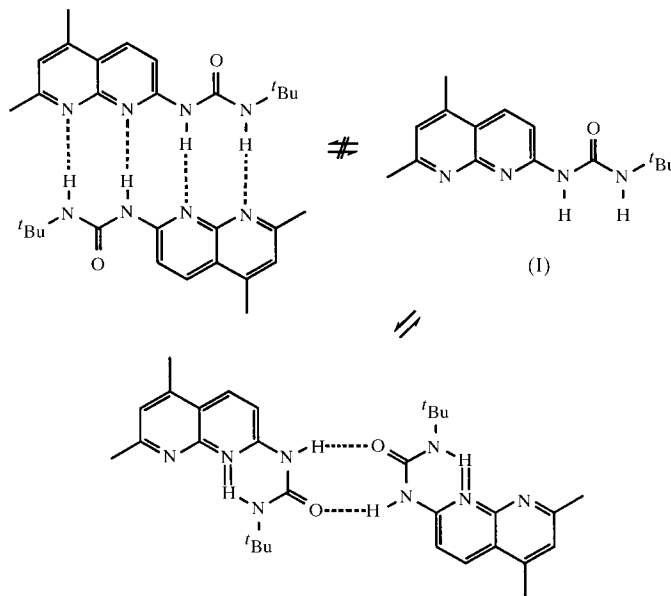
Comment

Multiple hydrogen bonds are attracting increasing attention for the formation of host–guest complexes and for supramolecular self-assembly (Zimmerman & Corbin, 2000). Therefore, quadruple hydrogen-bonding patterns based on four parallel and antiparallel hydrogen bonds have been investigated. While a non-self-complementary pattern like *DAAD-ADDA* (*D* is hydrogen-bond donor and *A* is hydrogen-bond acceptor; Lüning & Kühl, 1998) can be used for molecular recognition, the two conceivable self-complementary patterns of a four hydrogen-bond system, *AADD* or *ADAD*, may form dimers. This has been exploited by Sijbesma *et al.* (1997) and Beijer *et al.* (1998) to construct new types of polymers. We present here a naphthyridyl urea, (I), designed for self-complexation. It was synthesized from 7-amino-2,4-dimethyl-1,8-naphthyridine (Gorecki & Hawes, 1977) by addition to *tert*-butyl isocyanate in 87% yield.

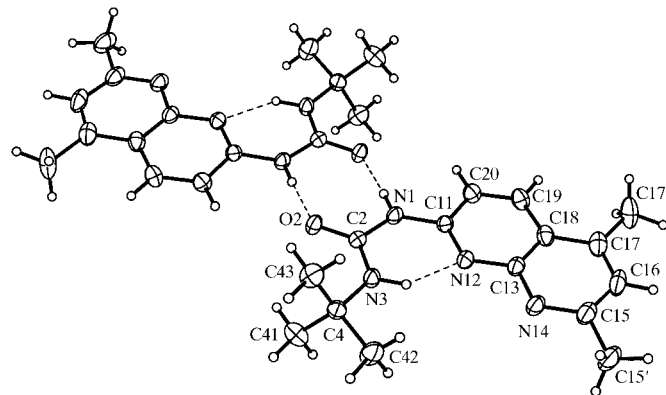
Meijer's *AADD* systems (Sijbesma *et al.*, 1997; Beijer *et al.*, 1998) possess a linear orientation of the hydrogen bonds, leading to dimers held together by four parallel and antiparallel hydrogen bonds. Such a linear dimer of (I) could only be formed if the urea exists in a *Z,Z* conformation. However, the naphthyridyl urea (I) first forms an intramolecular hydrogen bond between the H atom of the *tert*-butyl-amino NH group and atom N1 of the naphthyridyl ring, which leads to a *Z,E* conformer. This was proven by X-ray analysis (see Fig. 1). Bond lengths and angles of (I) are in the usual

ranges. The molecule is essentially planar, except for two methyl groups of the *tert*-butyl group (r.m.s. deviation 0.05 Å).

The twist from a *Z* to an *E* amide bond presents a hydrogen-bond donor *D* and a hydrogen-bond acceptor *A* on the surface of (I). Thus, self-recognition (*AD·DA*) forms a dimer which also contains four hydrogen bonds. However, two of these are



intramolecular and only two are intermolecular. The dimerization of ureas which are substituted by N-heterocycles in an *AD·DA* fashion has already been observed for pyridyl ureas (Bolte *et al.*, 2001; Corbin & Zimmerman, 2000). The driving force for dimer formation by only two hydrogen bonds accompanied by two intramolecular hydrogen bonds is possibly steric consideration: the 7-methyl group and the *tert*-butyl group are in closer contact in the strictly intermolecular dimer than in the *E,Z* form. The new *N*-substituted naphthyridine (I) is also an interesting ligand for the complexation of two metal atoms in close proximity. Mintert & Sheldrick (1996) have reported complexes of related 2-amino- or 2-oxo-substituted naphthyridines containing Mo–Mo moieties.

**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 by applying the symmetry operator ($2 - x, 1 - y, 1 - z$).

Experimental

Under nitrogen, 7-amino-2,4-dimethyl-1,8-naphthyridine (Gorecki & Hawes, 1977) (866 mg, 5.01 mmol) was dissolved in dry toluene (50 ml), and *tert*-butyl isocyanate (500 mg, 5.05 mmol) was added; the mixture was heated to reflux for 2 h. After cooling to room temperature, the solid was filtered off, washed with toluene and dried. Recrystallization from ethanol, toluene/ethanol (10:1) and then toluene gave 1.19 g (87%) of a colourless solid; m.p. 513 K. IR (KBr, cm^{-1}): $\bar{\nu}$ 3360, 3187, 3119, 3042 (N—H), 2968 (aliphatic C—H), 1682 (C=O), 1601, 1523 (aromatic), 1566 (N—H), 1401 (*tert*-butyl, C—H); ^1H NMR (200 MHz, CDCl_3): δ 1.54 [s, 9H, $\text{C}(\text{CH}_3)_3$], 2.61 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 7.05 (s, 1H, ArH), 7.46 (d, $J = 8.9$ Hz, 1H, ArH), 8.18 (d, $J = 8.9$ Hz, 1H, ArH), 9.59 (br s, 1H, NH), 10.08 (br s, 1H, NH); MS (EI, 70 eV): m/z (%) = 272 (3), 257 (16), 200 (57), 173 (100); MS (CI/isobutane): m/z (%) = 273 (100). Analysis calculated for $\text{C}_{15}\text{H}_{20}\text{N}_4\text{O}$ (272.4): C 66.15, H 7.40, N 20.57%; found C 66.04, H 7.42, N 20.48%.

Crystal data

$\text{C}_{15}\text{H}_{20}\text{N}_4\text{O}$ $D_x = 1.154 \text{ Mg m}^{-3}$
 $M_r = 272.35$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/c$ Cell parameters from 5891 reflections
 $a = 12.7129$ (2) Å $\theta = 1-25^\circ$
 $b = 11.2067$ (1) Å $\mu = 0.08 \text{ mm}^{-1}$
 $c = 11.6822$ (2) Å $T = 140$ (2) K
 $\beta = 109.578$ (1)° Block, colourless
 $V = 1568.14$ (4) Å³ $0.40 \times 0.20 \times 0.08 \text{ mm}$
 $Z = 4$

Data collection

Siemens CCD three-circle diffractometer $R_{\text{int}} = 0.051$
 ω scans $\theta_{\text{max}} = 26.4^\circ$
 Absorption correction: empirical $h = -15 \rightarrow 15$
 (*SADABS*; Sheldrick, 1996) $k = -13 \rightarrow 13$
 $T_{\text{min}} = 0.970$, $T_{\text{max}} = 0.994$ $l = -13 \rightarrow 14$
 10199 measured reflections 512 standard reflections
 3174 independent reflections frequency: 900 min
 2135 reflections with $I > 2\sigma(I)$ intensity decay: none

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.4824P]$
 $R[F^2 > 2\sigma(F^2)] = 0.050$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.136$ $(\Delta/\sigma)_{\text{max}} = 0.02$
 $S = 1.02$ $\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
 3174 reflections $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
 192 parameters Extinction correction: *SHELXL97*
 H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.014 (2)

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}$ for methyl H atoms or $1.2U_{\text{eq}}$ for all other H atoms] using a riding model, with C—H(aromatic) = 0.95 Å and C—H(methyl) 0.98 Å. The methyl groups attached to the aromatic system were allowed to rotate about their local threefold axis. The H atoms bound to N atoms were refined isotropically.

Table 1

Selected geometric parameters (Å, °).

N1—C11	1.391 (2)	C11—N12	1.322 (2)
N1—C2	1.400 (2)	N12—C13	1.374 (2)
C2—O2	1.249 (2)	C13—N14	1.367 (2)
C2—N3	1.337 (2)	N14—C15	1.336 (2)
N3—C4	1.483 (2)		
C11—N1—C2	129.94 (16)	C2—N3—C4	125.23 (15)
O2—C2—N3	124.82 (16)	C11—N12—C13	118.95 (16)
O2—C2—N1	118.28 (15)	C15—N14—C13	117.08 (18)
N3—C2—N1	116.90 (15)		
C11—N1—C2—O2	179.46 (17)	N1—C2—N3—C4	178.18 (16)
C11—N1—C2—N3	−0.3 (3)	C2—N1—C11—N12	−0.2 (3)
O2—C2—N3—C4	−1.6 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O2 ⁱ	0.90 (2)	1.93 (2)	2.824 (2)	175.7 (19)
N3—H3 \cdots N12	0.91 (2)	1.91 (2)	2.676 (2)	141 (2)

Symmetry code: (i) 2 − x, 1 − y, 1 − z.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1059). Services for accessing these data are described at the back of the journal.

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