tert-Butyl (2-phenyl-1,2-dihydro-1-naphthyl)-carbamate

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Key indicators

Single-crystal X-ray study

$T = 150$ K

Mean σ(C–C) = 0.002 Å

R factor = 0.045

wR factor = 0.126

Data-to-parameter ratio = 17.9

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

In the title molecule, $C_{21}H_{23}NO_2$, the phenyl ring and the fused benzene ring of the naphthyl system form a dihedral angle of 64.22 (5) Å. The cyclohexene ring is in a half-chair conformation. In the crystal structure, molecules are linked into one-dimensional chains in the b-axis direction *via* intermolecular N—H⋯O [N⋯O = 3.3517 (15) Å] hydrogen bonds.

Comment

The addition of carbon-based nucleophiles to activated alkenes represents one of the fundamental methods for the controlled construction of carbon–carbon bonds in organic synthesis. To this end, we have reported that heterobicyclic alkenes are effective substrates for metal-catalysed ring-opening reactions with a variety of nucleophiles (for a review, see Lautens, Fagnou & Hiebert, 2003). One example of such a reaction is the Pd^{II}-catalysed ring-opening addition of boronic acids to heterobicyclic alkenes (Lautens & Dockendorff, 2003). This reaction is particularly useful for the synthesis of 1-aminotetralin scaffolds *via* the ring-opening of azabicyclic alkenes such as (1). Here, we report the crystal structure of the title dihydronaphthalene, (2), derived from the Pd^{II}-catalysed ring-opening of the azabicycle, (1), with phenylboronic acid.

DPPP = bis-1,3-diphenylphosphinopropane

Boc = t-butoxycarbonyl
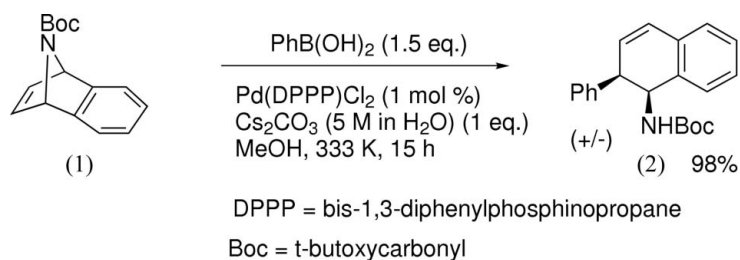
The title molecule is shown in Fig. 1. All bond lengths and angles are within the expected ranges (Allen *et al.*, 1987). The benzene ring of the naphthalen-1-yl system (C2–C7) and the phenyl ring (C11–C16) form a dihedral angle of 64.22 (5)°. In the cyclohexene ring, atoms C2, C7, C8 and C9 form a plane with an r.m.s. deviation 0.023 Å, while atoms C1 and C10 are −0.225 (3) and 0.203 (3) Å from this plane, respectively. Conformational analysis of that ring (Duax *et al.*, 1976) shows that the conformation is a half-chair, with a local pseudo-twofold axis running through the midpoints of the C7—C8 and C1—C10 bonds.

In the crystal structure, molecules related by unit-cell translations are linked *via* intermolecular N—H⋯O hydrogen bonds to form extended $C4$ chains (Bernstein *et al.*, 1995) in the b-axis direction (Table 1 and Fig. 1).

Experimental

The azabicycle (1) (5 g, 20.55 mmol), phenylboronic acid (3.76 g, 30.84 mmol), and dichlorobis(1,3-diphenylphosphinopropane)-palladium(II) (0.121 g, 0.205 mmol, 0.01 eq.) were added to a 250 ml round-bottomed flask with a stir bar. The flask was sealed with a septum and evacuated/flushed with nitrogen three times. Methanol (75 ml) was added by syringe, followed by a saturated aqueous solution of Cs_2CO_3 ($5M$, 4.1 ml, 1 eq.). The flask was placed in an oil bath at 333 K and heated for 1.5 h, after which time NMR analysis indicated that reaction was complete. The reaction mixture was adsorbed onto a minimum amount of silica gel and purified by flash column chromatography (4" × 6" silica gel, eluted with 2–10% EtOAc/hexanes) (yield 98%). X-ray quality crystals were obtained from an analogous reaction on a smaller scale. The crude reaction mixture, still as a solution in methanol, was stored in a sealed flask in a 258 K freezer for an extended period, after which time crystallization occurred.

Crystal data

$C_{21}H_{23}NO_2$	$D_x = 1.224$ Mg m^{-3}
$M_r = 321.40$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 12640
$a = 29.4222$ (10) Å	reflections
$b = 5.4655$ (1) Å	$\theta = 3.2–27.5°$
$c = 21.7842$ (7) Å	$\mu = 0.08$ mm^{-1}
$\beta = 95.4570$ (13)°	$T = 150$ (1) K
$V = 3487.18$ (18) Å^3	Needle, colourless
$Z = 8$	$0.46 \times 0.22 \times 0.18$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer	3901 independent reflections
φ scans, and ω scans with κ offsets	2869 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$R_{int} = 0.042$
	$\theta_{max} = 27.5°$
$T_{min} = 0.824$, $T_{max} = 0.991$	$h = -38 \rightarrow 37$
12640 measured reflections	$k = -6 \rightarrow 7$
	$l = -25 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 1.1855P]$
$wR(F^2) = 0.126$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
3901 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
218 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXTL/ PC* (Sheldrick, 2001)
	Extinction coefficient: 0.0085 (13)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A$\cdots$O1^i	0.88	2.48	3.3517 (15)	169

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

H atoms were positioned geometrically, with C—H distances ranging from 0.95 to 1.00 Å and an N—H distance of 0.88 Å. They were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2001); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.
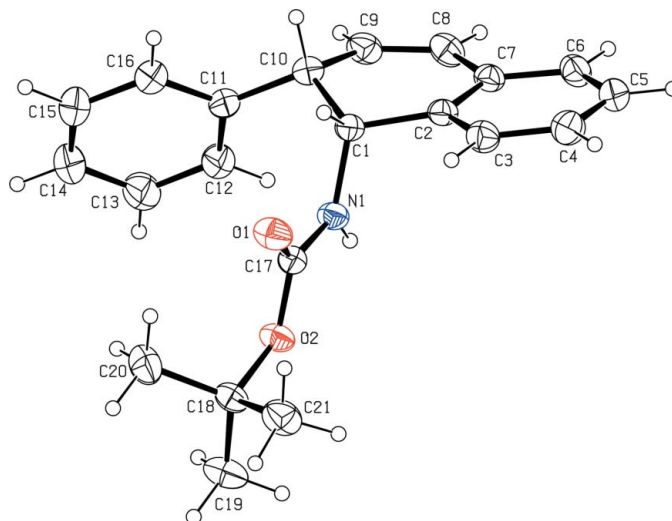

Figure 1
View of (2), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms).
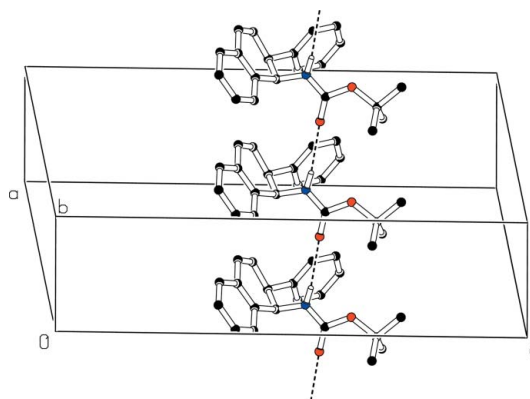

Figure 2
A partial packing plot (Spek, 2003) of (2), showing hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

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