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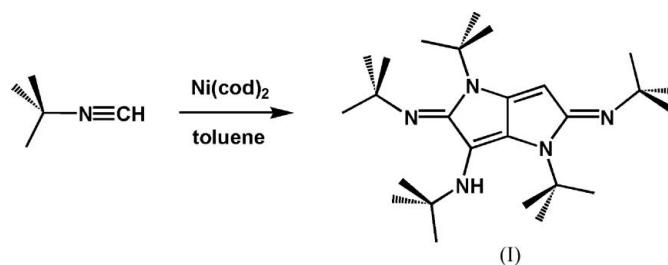
Key indicators

Single-crystal X-ray study
 $T = 183\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.057
 wR factor = 0.137
Data-to-parameter ratio = 20.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,4,*N*-Tri-*tert*-butyl-2,5-bis-*tert*-butylimino-1,2,4,5-
tetrahydropyrrolo[3,2-*b*]pyrrole-3-amineThe title compound, $\text{C}_{26}\text{H}_{47}\text{N}_5$, is the first unsymmetrically substituted tetrahydropyrrolo[3,2-*b*]pyrrole derivative to be structurally characterized. The bicyclic ring system with two exocyclic imine functions and one amino group is formed by the oligomerization of five *tert*-butyl isocyanide groups.

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Comment

The reaction of metal carbonyls and *tert*-butyl isocyanide leads to metal(II) complexes with a mixed isocyanide–cyanide ligand environment [$\text{Ru}_3(\text{CO})_{12}$: Dönnecke & Imhof, 2003; Imhof & Halbauer, 2006; $\text{Fe}_2(\text{CO})_9$: Halbauer, Dönnecke *et al.*, 2006; $\text{Mn}_2(\text{CO})_{10}$: Halbauer, Görls *et al.*, 2006] which were used for the construction of coordination polymers (Halbauer, Leibelng & Imhof, 2006). In the reaction of $\text{Mn}_2(\text{CO})_{10}$, we observed the formation of the organic side-product *N,N'*-di-*tert*-butyl-3,5-bis-*t*-butylimino-4-phenylcyclopent-1-ene-1,2-diamine formed from four isocyanide molecules together with an additional CH(Ph) group originating from the solvent toluene.Starting from $\text{Ni}(\text{cod})_2$ (cod is cyclooctadiene) as an Ni^0 precursor we obtained crystals of another organic side product, (I), in addition to the expected coordination compounds, with a mixed cyanide–isocyanide ligand environment. The molecular structure of the title compound is depicted in Fig. 1. The bond lengths in the bicyclic ring system clearly show a bonding situation with localized single (C1–C6, C3–C4) and double bonds (C2=C3, C5=C6). The C–N bond lengths in the pyrrolo[3,2-*b*]pyrrole system are also in a range typical for single bonds. Nevertheless, the bond lengths of atoms N2 and N5 with the bridgehead atoms C2 and C5 are shorter than the bonds with the imine atoms C1 and C4. The C=N bonds of C1 and C4 with the exocyclic imine N atoms are clearly double bonds. Corresponding to the bonding situation the bicyclic system is almost perfectly planar with deviations from planarity of less than 0.014 Å.

A Cambridge Structural Database (Version 5.26; Allen, 2002) search found only three closely related compounds. One

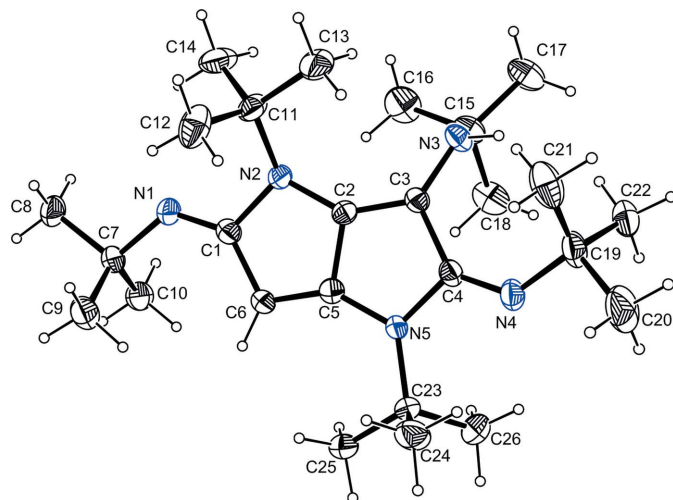


Figure 1

The molecular structure of $C_{26}H_{47}N_5$ with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

of them is constructed of six isocyanide groups which are coupled at a palladium center. The difference from the title compound is that there is a second amine function at the C-4 position of the heterocycle, making the compound perfectly symmetric (Tanase *et al.*, 1992, 1996). If the same reaction is performed under a CO atmosphere one of the imine functions is replaced by a carbonyl group (Tanase *et al.*, 1996). Compounds with two carbonyl functions at the C-2 and C-5 positions of the heterocycle may be produced by a one-pot reaction from bis-imidoyl chlorides of oxalic acid and mono-anions of acetic acid ester derivatives (Wuckelt *et al.*, 1997). The title compound is the first unsymmetrically substituted pyrrolo[3,2-*b*]pyrrole derivative that has been structurally characterized.

Experimental

In a stainless steel autoclave a 106 mg (0.386 mmol) sample of $Ni(cod)_2$ dissolved in 4 ml of anhydrous toluene was treated with 0.39 ml (3.473 mmol) of *tert*-butyl isocyanide. The solution was heated to 400 K for 24 h. After the autoclave had been cooled to room temperature, the solution was transferred to a Schlenk tube and volatile material was removed *in vacuo*. The residue was washed with chloroform and anhydrous light petroleum (b.p. 313–333 K). Column chromatography using acetone and methanol (1:1) as eluants separated four fractions. The fourth fraction was recrystallized from methanol to produce single crystals of the title compound.

Crystal data

$C_{26}H_{47}N_5$
 $M_r = 429.69$
 Monoclinic, $P2_1/n$
 $a = 11.5558$ (4) Å
 $b = 17.9911$ (9) Å
 $c = 12.9268$ (6) Å
 $\beta = 93.201$ (3)°
 $V = 2683.3$ (2) Å³

$Z = 4$
 $D_x = 1.064$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.06$ mm⁻¹
 $T = 183$ (2) K
 Prism, colorless
 $0.04 \times 0.04 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: none
 17978 measured reflections

6112 independent reflections
 3452 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.078$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.137$
 $S = 1.01$
 6112 reflections
 298 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.3727P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$
 $\Delta\rho_{max} = 0.21$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N2—C2	1.390 (2)	N3—C3	1.417 (2)
N2—C1	1.445 (2)	C4—C3	1.502 (2)
N1—C1	1.270 (2)	C5—C6	1.354 (2)
N5—C5	1.378 (2)	C5—C2	1.458 (2)
N5—C4	1.442 (2)	C2—C3	1.355 (2)
N4—C4	1.268 (2)	C1—C6	1.466 (2)
C2—N2—C1	106.96 (13)	C3—C2—C5	109.21 (14)
C5—N5—C4	107.19 (13)	N2—C2—C5	108.79 (14)
N4—C4—N5	118.47 (16)	C2—C3—N3	130.17 (16)
N4—C4—C3	135.25 (17)	C2—C3—C4	105.74 (15)
N5—C4—C3	106.20 (13)	N3—C3—C4	123.37 (14)
C6—C5—N5	142.05 (17)	N1—C1—N2	118.54 (15)
C6—C5—C2	108.76 (15)	N1—C1—C6	134.26 (17)
N5—C5—C2	108.87 (14)	N2—C1—C6	107.19 (14)
C3—C2—N2	141.27 (17)		

All H atoms attached to C atoms were positioned geometrically and treated as riding with C—H = 0.93 Å (CH) and 0.96 Å (CH₃), and with $U_{iso}(H) = 1.2U_{eq}(C)$ (for CH) or $U_{iso}(H) = 1.5U_{eq}(C)$ (for CH₃). The H atom attached to nitrogen was located in a difference Fourier map and included in the subsequent refinement using restraints [N—H = 0.86 (1) Å] with $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: XP (Siemens, 1990).

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