

trans-1-Phenylpyrrolidine-2,5-dicarbonitrile

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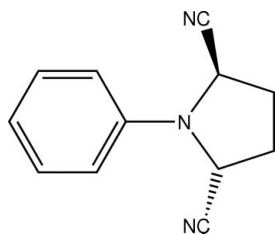
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.107; data-to-parameter ratio = 17.7.

In the title compound, $\text{C}_{12}\text{H}_{11}\text{N}_3$, the plane of the phenyl ring and the least-squares plane of the pyrrolidine ring enclose an angle of 14.30 (6)°. The intracyclic N atom features a nearly trigonal-planar coordination geometry due to π -interactions with the aromatic system. The pyrrolidine ring is present in a twist conformation for which the closest pucker descriptor is ${}^{\text{C9}}T_{\text{C8}}$. Weak intermolecular $\text{C}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\pi$ contacts occur

Related literature

For background to the synthesis, see: Han & Ofial (2009); Takahashi *et al.* (1986). For a related structure, see: Menezes *et al.* (2007). For puckering analysis, see: Cremer & Pople (1975).

**Experimental***Crystal data*

$\text{C}_{12}\text{H}_{11}\text{N}_3$
 $M_r = 197.24$
 Orthorhombic, $Pbca$
 $a = 9.1807$ (1) Å
 $b = 14.5693$ (2) Å
 $c = 15.7576$ (2) Å

$V = 2107.68$ (5) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 200$ K
 $0.33 \times 0.18 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer
 16161 measured reflections
 2413 independent reflections
 2109 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.107$
 $S = 1.06$
 2413 reflections
 136 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C1–C6 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{H6}\cdots\text{N2}^{\text{i}}$	0.95	2.70	3.5952 (17)	158
$\text{C8}-\text{H8B}\cdots\text{N2}^{\text{ii}}$	0.99	2.67	3.3777 (17)	129
$\text{C10}-\text{H10}\cdots\text{N3}^{\text{iii}}$	1.00	2.69	3.3748 (15)	126
$\text{C8}-\text{H8A}\cdots\text{Cg}^{\text{i}}$	0.99	2.74	3.6937 (13)	162
$\text{C9}-\text{H9B}\cdots\text{Cg}^{\text{iv}}$	0.99	2.88	3.5111 (13)	122

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $-x + 2, -y, -z + 1$.

Data collection: *COLLECT* (Hooft, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2285).

References

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supplementary materials

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***trans*-1-Phenylpyrrolidine-2,5-dicarbonitrile**

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Comment

Under oxidative conditions, iron salts activate C(*sp*³)-H bonds adjacent to the nitrogen atom of tertiary amines. Hence the cross-coupling reactions of a variety of tertiary amines with cyanide were enabled in the presence of *tert*-butylhydroperoxide. Performing the reaction in the presence of 4 equivalents of trimethylsilyl cyanide allowed the twofold cyanation of *N*-phenylpyrrolidine [Han *et al.* (2009)].

The asymmetric unit of (I) contains one complete molecule which is shown in Figure 1. The plane of the phenyl ring and the least-square plane of the pyrrolidine ring enclose an angle of 14.30 (6)°, which is quite similar to the angle found in a related structure of 1,2-Dichloro-4-(pyrrolidino)-5-nitrobenzene (18.69 (14)°, Menezes *et al.* (2007)).

The intracyclic nitrogen atom is nearly in the plane defined by the three carbon atoms bonded to it. The displacement of the nitrogen atom from the plane is only 0.073 (1) Å. The planarization of the nitrogen atom may be rationalized by possible π -interaction of the lone pair with the aromatic system.

The pyrrolidine ring is present in a *twist*-conformation for which the closest pucker descriptor is ^{C9}*T*_{C8} [Cremer *et al.* (1975)]. This conformation is slightly distorted towards an *envelope*-conformation *E*_{C8}. In a related structure [Menezes *et al.* (2007)], the ring is twisted along the same bond, however, in the other direction (^{C8}*T*_{C9}).

Both carbonitrile nitrogen atoms act as acceptors in very weak contacts of the type C–H⋯N. Furthermore the packing features very weak C–H⋯ π contacts with the phenyl π -system as acceptor. The packing of the title compound is shown in Figure 2.

Experimental

Under an atmosphere of dry nitrogen, a 25 ml Schlenk flask was charged with FeCl₂ (10 mol-%, 13 mg). Then *N*-phenylpyrrolidine (1.0 mmol), trimethylsilyl cyanide (4.0 mmol, 0.54 ml), and MeOH (2.0 ml) were added successively by syringe. To the mixture was added dropwise *tert*-butylhydroperoxide (2.5 mmol, 0.470 ml, 5.5 *M* solution in decane) over a period of 5 minutes. The mixture was stirred at room temperature for 24 h. Subsequently, the reaction mixture was poured into a saturated aqueous NaCl solution (20 ml) and extracted with dichloromethane (three times 20 ml). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. After column chromatography on silica gel (*n*-pentane/diethyl ether = 3:1, *v/v*), 1-phenylpyrrolidine-2,5-dicarbonitrile was isolated as a colorless solid (54%) [Han *et al.* (2009)].

The title compound (50 mg) was dissolved in 2 ml of a mixture of dichloromethane/*n*-pentane/ethyl ether mixture (2/1/1, *v/v/v*). The solvent was allowed to evaporate slowly at room temperature. The thus formed crystals were suitable for X-ray analysis. mp 149–151 °C ([Takahashi *et al.* (1986)], mp 161.5–163 °C (from ethanol)).

Refinement

All H atoms were found in difference maps. The H atoms were positioned geometrically (bond distances for phenyl-CH: 0.95 Å, for aliphatic CH: 1.00 Å, for aliphatic CH₂: 0.99 Å) and treated as riding on their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Figures

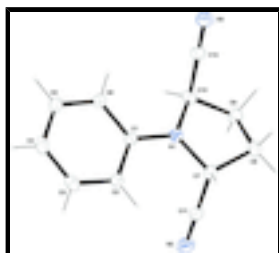


Fig. 1. The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.

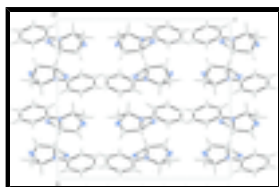


Fig. 2. The packing of the title compound viewed along [-100].

trans-1-Phenylpyrrolidine-2,5-dicarbonitrile

Crystal data

C₁₂H₁₁N₃

$M_r = 197.24$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 9.1807(1) \text{ \AA}$

$b = 14.5693(2) \text{ \AA}$

$c = 15.7576(2) \text{ \AA}$

$V = 2107.68(5) \text{ \AA}^3$

$Z = 8$

$F(000) = 832$

$D_x = 1.243(1) \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9019 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 0.08 \text{ mm}^{-1}$

$T = 200 \text{ K}$

Block, colourless

$0.33 \times 0.18 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: rotating anode

MONTEL, graded multilayered X-ray optics

Detector resolution: 9 pixels mm^{-1}

CCD; rotation images; thick slices, ϕ/ω -scan

16161 measured reflections

2413 independent reflections

2109 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.4^\circ$

$h = -11 \rightarrow 11$

$k = -18 \rightarrow 18$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.5393P]$
2413 reflections	where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.91889 (10)	0.12762 (7)	0.48710 (6)	0.0339 (2)
N2	0.63244 (13)	0.15665 (9)	0.34906 (8)	0.0515 (3)
N3	1.27530 (11)	0.14135 (8)	0.55151 (7)	0.0460 (3)
C1	0.84192 (11)	0.11277 (7)	0.56211 (6)	0.0289 (2)
C2	0.71584 (12)	0.05831 (8)	0.56245 (7)	0.0331 (3)
H2	0.6806	0.0329	0.5109	0.040*
C3	0.64254 (13)	0.04149 (8)	0.63784 (8)	0.0395 (3)
H3	0.5569	0.0049	0.6373	0.047*
C4	0.69229 (13)	0.07717 (9)	0.71358 (8)	0.0414 (3)
H4	0.6423	0.0647	0.7651	0.050*
C5	0.81566 (13)	0.13119 (9)	0.71352 (7)	0.0393 (3)
H5	0.8501	0.1561	0.7655	0.047*
C6	0.89031 (12)	0.14984 (8)	0.63898 (7)	0.0338 (3)
H6	0.9744	0.1878	0.6401	0.041*
C7	0.87833 (12)	0.08771 (7)	0.40605 (6)	0.0313 (2)
H7	0.8707	0.0195	0.4112	0.038*
C8	1.00567 (13)	0.11327 (8)	0.34813 (7)	0.0385 (3)
H8A	1.0857	0.0680	0.3527	0.046*

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H8B	0.9742	0.1176	0.2882	0.046*
C9	1.05183 (14)	0.20663 (8)	0.38243 (8)	0.0405 (3)
H9A	0.9888	0.2561	0.3598	0.049*
H9B	1.1544	0.2202	0.3676	0.049*
C10	1.03301 (11)	0.19671 (7)	0.47859 (7)	0.0326 (3)
H10	1.0003	0.2562	0.5038	0.039*
C11	0.73934 (13)	0.12635 (8)	0.37363 (7)	0.0349 (3)
C12	1.16995 (12)	0.16549 (7)	0.51982 (7)	0.0342 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0323 (5)	0.0433 (5)	0.0262 (5)	-0.0116 (4)	0.0000 (4)	0.0001 (4)
N2	0.0473 (7)	0.0588 (7)	0.0483 (6)	0.0060 (5)	-0.0134 (5)	-0.0106 (5)
N3	0.0382 (6)	0.0456 (6)	0.0542 (7)	-0.0001 (5)	-0.0083 (5)	-0.0055 (5)
C1	0.0275 (5)	0.0320 (5)	0.0270 (5)	0.0013 (4)	-0.0005 (4)	0.0025 (4)
C2	0.0315 (6)	0.0356 (6)	0.0321 (5)	-0.0039 (4)	0.0000 (4)	-0.0001 (4)
C3	0.0342 (6)	0.0412 (6)	0.0432 (6)	-0.0030 (5)	0.0068 (5)	0.0056 (5)
C4	0.0421 (7)	0.0493 (7)	0.0327 (6)	0.0067 (5)	0.0094 (5)	0.0067 (5)
C5	0.0426 (7)	0.0476 (6)	0.0277 (5)	0.0067 (5)	-0.0022 (5)	-0.0020 (5)
C6	0.0311 (6)	0.0391 (6)	0.0311 (6)	0.0004 (4)	-0.0027 (4)	-0.0014 (4)
C7	0.0351 (6)	0.0322 (5)	0.0267 (5)	-0.0007 (4)	0.0003 (4)	0.0000 (4)
C8	0.0388 (6)	0.0453 (7)	0.0315 (6)	0.0038 (5)	0.0070 (5)	0.0045 (5)
C9	0.0384 (6)	0.0427 (6)	0.0405 (6)	-0.0041 (5)	0.0031 (5)	0.0128 (5)
C10	0.0290 (5)	0.0310 (5)	0.0379 (6)	-0.0032 (4)	0.0005 (4)	0.0036 (4)
C11	0.0387 (6)	0.0369 (6)	0.0289 (5)	-0.0030 (5)	-0.0031 (5)	-0.0057 (4)
C12	0.0328 (6)	0.0312 (5)	0.0388 (6)	-0.0052 (4)	0.0003 (5)	-0.0022 (4)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.3939 (13)	C5—H5	0.9500
N1—C7	1.4519 (14)	C6—H6	0.9500
N1—C10	1.4591 (13)	C7—C11	1.4853 (16)
N2—C11	1.1437 (16)	C7—C8	1.5291 (15)
N3—C12	1.1438 (16)	C7—H7	1.0000
C1—C6	1.3987 (15)	C8—C9	1.5238 (17)
C1—C2	1.4034 (15)	C8—H8A	0.9900
C2—C3	1.3873 (15)	C8—H8B	0.9900
C2—H2	0.9500	C9—C10	1.5320 (16)
C3—C4	1.3796 (18)	C9—H9A	0.9900
C3—H3	0.9500	C9—H9B	0.9900
C4—C5	1.3791 (18)	C10—C12	1.4864 (15)
C4—H4	0.9500	C10—H10	1.0000
C5—C6	1.3868 (16)		
C1—N1—C7	123.63 (9)	N1—C7—H7	110.2
C1—N1—C10	123.29 (9)	C11—C7—H7	110.2
C7—N1—C10	112.31 (8)	C8—C7—H7	110.2
N1—C1—C6	120.89 (10)	C9—C8—C7	102.62 (9)

N1—C1—C2	120.60 (9)	C9—C8—H8A	111.2
C6—C1—C2	118.49 (10)	C7—C8—H8A	111.2
C3—C2—C1	120.22 (10)	C9—C8—H8B	111.2
C3—C2—H2	119.9	C7—C8—H8B	111.2
C1—C2—H2	119.9	H8A—C8—H8B	109.2
C4—C3—C2	120.91 (11)	C8—C9—C10	103.60 (9)
C4—C3—H3	119.5	C8—C9—H9A	111.0
C2—C3—H3	119.5	C10—C9—H9A	111.0
C5—C4—C3	119.10 (11)	C8—C9—H9B	111.0
C5—C4—H4	120.5	C10—C9—H9B	111.0
C3—C4—H4	120.5	H9A—C9—H9B	109.0
C4—C5—C6	121.22 (11)	N1—C10—C12	110.86 (9)
C4—C5—H5	119.4	N1—C10—C9	103.71 (9)
C6—C5—H5	119.4	C12—C10—C9	111.46 (9)
C5—C6—C1	120.06 (11)	N1—C10—H10	110.2
C5—C6—H6	120.0	C12—C10—H10	110.2
C1—C6—H6	120.0	C9—C10—H10	110.2
N1—C7—C11	111.78 (9)	N2—C11—C7	179.49 (13)
N1—C7—C8	103.38 (9)	N3—C12—C10	179.91 (15)
C11—C7—C8	111.05 (9)		
C7—N1—C1—C6	177.08 (10)	C10—N1—C7—C11	-102.29 (11)
C10—N1—C1—C6	-13.76 (16)	C1—N1—C7—C8	-172.55 (10)
C7—N1—C1—C2	-1.36 (16)	C10—N1—C7—C8	17.22 (12)
C10—N1—C1—C2	167.81 (10)	N1—C7—C8—C9	-33.54 (11)
N1—C1—C2—C3	177.94 (10)	C11—C7—C8—C9	86.48 (11)
C6—C1—C2—C3	-0.53 (16)	C7—C8—C9—C10	37.66 (11)
C1—C2—C3—C4	-0.45 (18)	C1—N1—C10—C12	76.32 (13)
C2—C3—C4—C5	0.83 (18)	C7—N1—C10—C12	-113.42 (10)
C3—C4—C5—C6	-0.22 (18)	C1—N1—C10—C9	-163.96 (10)
C4—C5—C6—C1	-0.78 (18)	C7—N1—C10—C9	6.30 (12)
N1—C1—C6—C5	-177.33 (10)	C8—C9—C10—N1	-27.35 (12)
C2—C1—C6—C5	1.14 (16)	C8—C9—C10—C12	91.97 (11)
C1—N1—C7—C11	67.93 (13)		

Hydrogen-bond geometry (\AA , $^\circ$)

Cg is the centroid of the C1—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots N2 ⁱ	0.95	2.70	3.5952 (17)	158
C8—H8B \cdots N2 ⁱⁱ	0.99	2.67	3.3777 (17)	129
C10—H10 \cdots N3 ⁱⁱⁱ	1.00	2.69	3.3748 (15)	126
C8—H8A \cdots Cg ⁱ	0.99	2.74	3.6937 (13)	162
C9—H9B \cdots Cg ^{iv}	0.99	2.88	3.5111 (13)	122

Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $x+1/2, y, -z+1/2$; (iii) $x-1/2, -y+1/2, -z+1$; (iv) $-x+2, -y, -z+1$.

Fig. 1

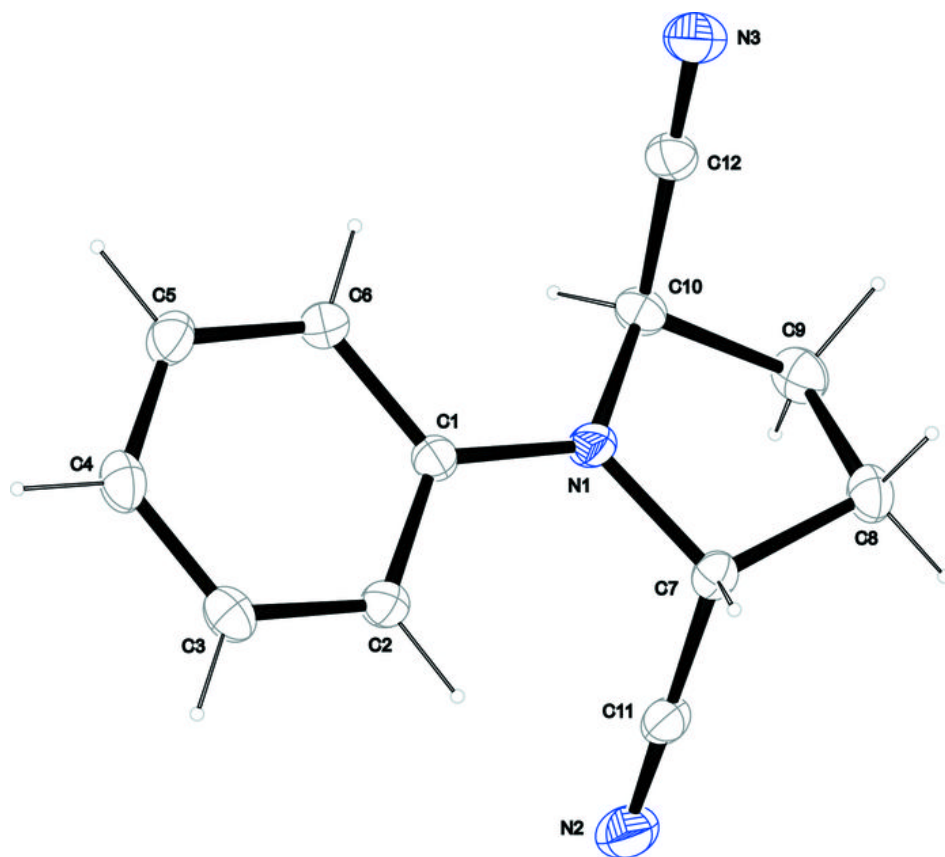


Fig. 2

