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3,5-Di-*tert*-butyl-1*H*-pyrazole-4-carbonitrile

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In the title compound, $C_{12}H_{19}N_3$, the cyano group lies in the plane of the pyrazole ring, and has a linear $C-C\equiv N$ bond angle of $179.2(1)^\circ$. The NH H atom of the pyrazole ring is disordered equally over the two ring N atoms. In the crystal, molecules are linked *via* $N-H\cdots N$ hydrogen bonds, forming inversion dimers with an $R_2^2(6)$ ring motif.

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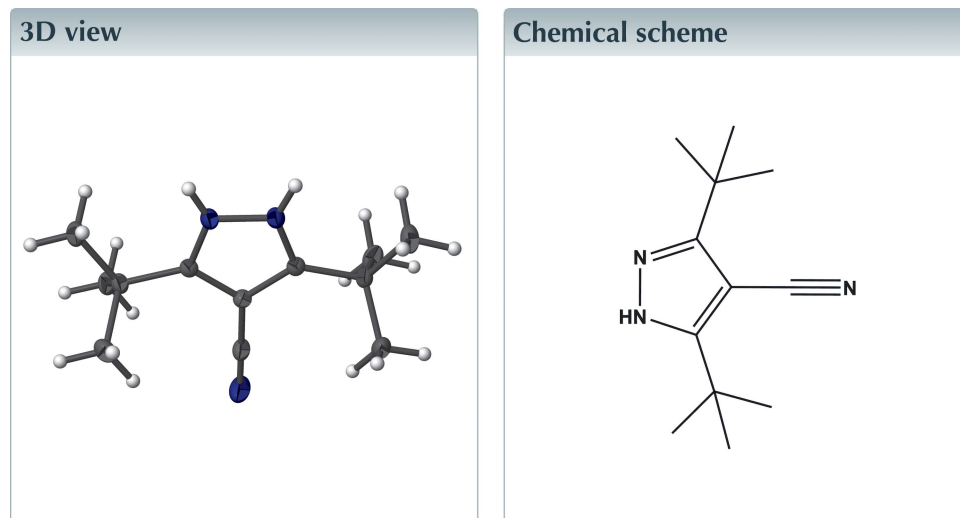
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Keywords: crystal structure; cyanopyrazole; carbonitrile; symmetrically substituted; $N-H\cdots N$ hydrogen bonds; inversion dimers.

CCDC reference: 1475402

Structural data: full structural data are available from iucrdata.iucr.org



Structure description

The title compound, represents the first symmetrically substituted 4-carbonitrile pyrazole, and was prepared as a precursor for the preparation of scorpionate ligands. In the title compound, Fig. 1, the NH H atom is disordered across the two N atoms (N2 and N3) of the pyrazole ring. The carbonitrile unit, $C2-C1\equiv N1$, lies in the plane of the pyrazole ring and deviates only slightly from linearity with a bond angle of $179.2(1)^\circ$.

In the crystal, molecules are linked by pairs of $N-H\cdots N$ hydrogen bonds, forming inversion dimers with an $R_2^2(6)$ ring motif (Fig. 2 and Table 1). There are no other significant intermolecular interactions present.

Synthesis and crystallization

Sodium hydride (0.69 g, 17.24 mmol, 60% dispersion in mineral oil) was added to 100 ml of dry toluene in an ice bath forming a suspension. Trimethylacetylacetonitrile (2.16 g, 17.24 mmol) was added to this suspension, resulting in the immediate appearance of bubbles. The mixture was stirred for 18 h before trimethylacetyl chloride (2.08 g, 17.24 mmol) was added. The reaction mixture was stirred overnight followed by three extractions using 100 ml of 0.2 M NaOH solution each time. The aqueous layers were combined and acidified with an HCl/H₂O (50/50) solution to pH1. A white precipitate appeared immediately and was extracted with three portions of 100 ml of ethyl acetate. Removal of the solvent under reduced pressure yielded 2.15 g (10.29 mmol, yield 59.67%) of the crude product, which was recrystallized from ethanol to give 4-cyano-

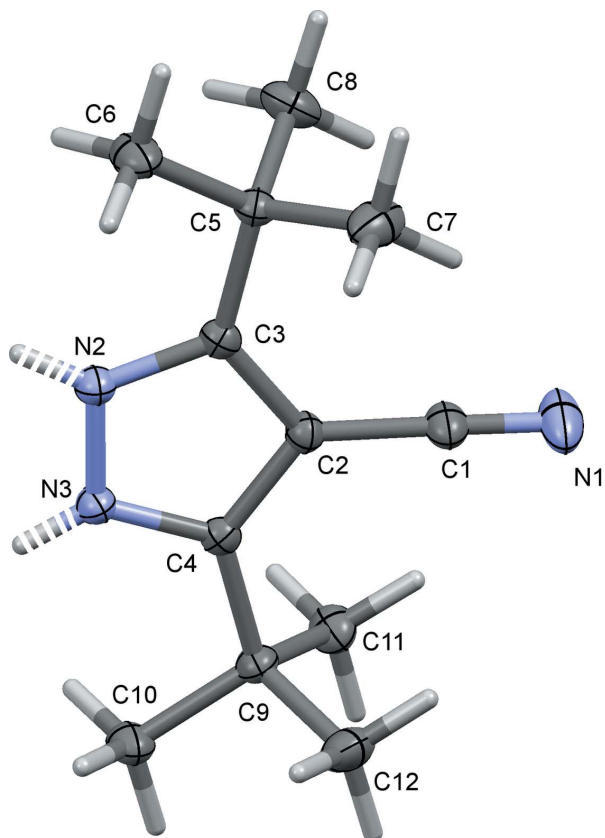


Figure 1
A view of the molecular structure of the title compound, showing the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. The two positions of the disordered NH H atoms are shown, with hashed bonds.

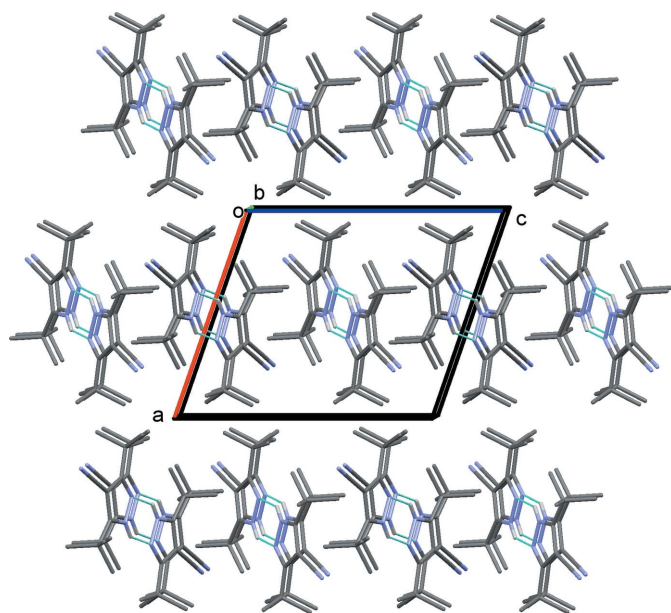


Figure 2
A view along the *b* axis of the crystal packing of the title compound. The N–H...N hydrogen bonds are shown as dashed lines. Only one disordered NH H atom is shown and all C-bound H atoms have been omitted for clarity.

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2...N3 ⁱ	0.86 (3)	2.23 (3)	2.9232 (14)	138 (2)
N3–H3...N2 ⁱ	0.85 (3)	2.19 (3)	2.9232 (14)	144 (2)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₉ N ₃
<i>M</i> _r	205.30
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.5993 (3), 9.7641 (3), 12.4435 (4)
β (°)	109.065 (1)
<i>V</i> (Å ³)	1217.17 (6)
<i>Z</i>	4
Radiation type	Cu Kα
μ (mm ⁻¹)	0.53
Crystal size (mm)	0.15 × 0.10 × 0.09
Data collection	
Diffractometer	Bruker D8 Platinum135
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T</i> _{min} , <i>T</i> _{max}	0.211, 0.320
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11126, 2183, 2037
<i>R</i> _{int}	0.040
(sin θ/λ) _{max} (Å ⁻¹)	0.602
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.096, 1.05
No. of reflections	2183
No. of parameters	150
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.21, -0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

2,2,6,6-tetramethyl-3,5-heptanedione (1.07 g, 5.12 mmol, 29.70%). This diketone compound was then reacted with hydrazine monohydrate (0.26 g, 5.12 mmol) in 100 ml of methanol and stirred overnight. The solvent was removed under reduced pressure to yield the crude product of the title compound as a white solid (0.93 g, 4.54 mmol, 26.31%). X-ray quality crystals were obtained by slow evaporation of a solution in ethanol at room temperature (0.66 g, 3.22 mmol, 18.67%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH H atom was located in a difference Fourier map and found to be disordered equally across the two N atoms (N2 and N3) of the pyrazole ring. These two H atoms (H2 and H3) were freely refined with an occupancy of 0.5 each.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160673 [doi:10.1107/S2414314616006738]

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3,5-Di-*tert*-butyl-1*H*-pyrazole-4-carbonitrile*Crystal data*

$C_{12}H_{19}N_3$

$M_r = 205.30$

Monoclinic, $P2_1/c$

$a = 10.5993$ (3) Å

$b = 9.7641$ (3) Å

$c = 12.4435$ (4) Å

$\beta = 109.065$ (1)°

$V = 1217.17$ (6) Å³

$Z = 4$

$F(000) = 448$

$D_x = 1.120$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 7895 reflections

$\theta = 4.4$ – 68.3 °

$\mu = 0.53$ mm⁻¹

$T = 100$ K

Block, colourless

$0.15 \times 0.10 \times 0.09$ mm

Data collection

Bruker D8 Platinum135

diffractometer

Radiation source: Micro Focus Rotating Anode,

Bruker FR-591

Multilayer Mirrors monochromator

Detector resolution: 7.9 pixels mm⁻¹

ω and ϕ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2016)

$T_{\min} = 0.211$, $T_{\max} = 0.320$

11126 measured reflections

2183 independent reflections

2037 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 68.2$ °, $\theta_{\min} = 4.4$ °

$h = -10 \rightarrow 12$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.096$

$S = 1.05$

2183 reflections

150 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.4223P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.19$ e Å⁻³

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.75868 (11)	0.50824 (12)	0.79507 (11)	0.0384 (3)	
N2	0.49278 (10)	0.84937 (10)	0.55771 (8)	0.0189 (2)	
H2	0.425 (3)	0.897 (3)	0.520 (2)	0.020 (6)*	0.5
N3	0.61616 (9)	0.90020 (10)	0.56683 (8)	0.0182 (2)	
H3	0.622 (2)	0.975 (3)	0.534 (2)	0.013 (6)*	0.5
C1	0.70672 (11)	0.59805 (12)	0.73785 (10)	0.0238 (3)	
C2	0.64420 (11)	0.70939 (11)	0.66689 (9)	0.0172 (2)	
C3	0.50608 (11)	0.73346 (11)	0.61695 (9)	0.0165 (2)	
C4	0.70997 (11)	0.81784 (11)	0.63223 (9)	0.0160 (2)	
C5	0.38860 (11)	0.65176 (11)	0.62665 (9)	0.0179 (3)	
C6	0.25914 (12)	0.70092 (14)	0.53837 (11)	0.0289 (3)	
H6A	0.2429	0.7966	0.5537	0.043*	
H6B	0.1847	0.6441	0.5426	0.043*	
H6C	0.2668	0.6936	0.4622	0.043*	
C7	0.40648 (13)	0.49897 (13)	0.60832 (12)	0.0313 (3)	
H7A	0.4089	0.4842	0.5311	0.047*	
H7B	0.3317	0.4478	0.6185	0.047*	
H7C	0.4903	0.4671	0.6636	0.047*	
C8	0.38019 (13)	0.67309 (13)	0.74628 (10)	0.0283 (3)	
H8A	0.4647	0.6455	0.8031	0.043*	
H8B	0.3074	0.6174	0.7553	0.043*	
H8C	0.3631	0.7700	0.7569	0.043*	
C9	0.85791 (11)	0.84303 (11)	0.65776 (9)	0.0188 (3)	
C10	0.88128 (12)	0.97784 (13)	0.60457 (10)	0.0251 (3)	
H10A	0.8377	0.9740	0.5220	0.038*	
H10B	0.9773	0.9923	0.6217	0.038*	
H10C	0.8437	1.0537	0.6360	0.038*	
C11	0.92803 (12)	0.84933 (12)	0.78699 (10)	0.0248 (3)	
H11A	0.8899	0.9241	0.8191	0.037*	
H11B	1.0236	0.8656	0.8030	0.037*	
H11C	0.9153	0.7623	0.8214	0.037*	
C12	0.91653 (12)	0.72457 (13)	0.60780 (11)	0.0295 (3)	
H12A	0.9014	0.6379	0.6414	0.044*	
H12B	1.0126	0.7389	0.6249	0.044*	
H12C	0.8729	0.7214	0.5252	0.044*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0241 (6)	0.0312 (6)	0.0507 (7)	-0.0030 (5)	-0.0004 (5)	0.0191 (5)
N2	0.0160 (5)	0.0200 (5)	0.0209 (5)	-0.0003 (4)	0.0062 (4)	0.0026 (4)
N3	0.0150 (5)	0.0202 (5)	0.0191 (5)	0.0002 (4)	0.0052 (4)	0.0033 (4)
C1	0.0171 (6)	0.0230 (6)	0.0285 (6)	-0.0030 (4)	0.0036 (5)	0.0048 (5)
C2	0.0168 (6)	0.0171 (5)	0.0168 (5)	0.0005 (4)	0.0042 (4)	0.0015 (4)
C3	0.0174 (6)	0.0170 (5)	0.0150 (5)	-0.0010 (4)	0.0052 (4)	-0.0010 (4)

C4	0.0160 (6)	0.0173 (5)	0.0144 (5)	0.0004 (4)	0.0047 (4)	-0.0010 (4)
C5	0.0158 (6)	0.0182 (6)	0.0202 (6)	-0.0019 (4)	0.0065 (4)	0.0005 (4)
C6	0.0171 (6)	0.0366 (7)	0.0307 (7)	-0.0043 (5)	0.0047 (5)	0.0086 (5)
C7	0.0244 (7)	0.0213 (6)	0.0510 (8)	-0.0056 (5)	0.0161 (6)	-0.0072 (5)
C8	0.0332 (7)	0.0303 (7)	0.0258 (6)	-0.0101 (5)	0.0153 (5)	-0.0012 (5)
C9	0.0139 (5)	0.0209 (6)	0.0212 (6)	0.0002 (4)	0.0050 (4)	0.0016 (4)
C10	0.0179 (6)	0.0279 (6)	0.0294 (6)	-0.0025 (4)	0.0074 (5)	0.0059 (5)
C11	0.0184 (6)	0.0280 (6)	0.0240 (6)	-0.0025 (5)	0.0015 (5)	0.0027 (5)
C12	0.0220 (6)	0.0307 (7)	0.0388 (7)	0.0029 (5)	0.0142 (5)	-0.0035 (5)

Geometric parameters (Å, °)

N1—C1	1.1502 (16)	C7—H7B	0.9800
N2—H2	0.86 (3)	C7—H7C	0.9800
N2—N3	1.3683 (13)	C8—H8A	0.9800
N2—C3	1.3328 (14)	C8—H8B	0.9800
N3—H3	0.85 (3)	C8—H8C	0.9800
N3—C4	1.3301 (14)	C9—C10	1.5295 (16)
C1—C2	1.4207 (16)	C9—C11	1.5366 (16)
C2—C3	1.4107 (15)	C9—C12	1.5372 (16)
C2—C4	1.4107 (15)	C10—H10A	0.9800
C3—C5	1.5165 (15)	C10—H10B	0.9800
C4—C9	1.5148 (15)	C10—H10C	0.9800
C5—C6	1.5281 (16)	C11—H11A	0.9800
C5—C7	1.5303 (16)	C11—H11B	0.9800
C5—C8	1.5343 (15)	C11—H11C	0.9800
C6—H6A	0.9800	C12—H12A	0.9800
C6—H6B	0.9800	C12—H12B	0.9800
C6—H6C	0.9800	C12—H12C	0.9800
C7—H7A	0.9800		
N3—N2—H2	117.6 (18)	H7A—C7—H7C	109.5
C3—N2—H2	132.6 (18)	H7B—C7—H7C	109.5
C3—N2—N3	109.67 (9)	C5—C8—H8A	109.5
N2—N3—H3	119.1 (17)	C5—C8—H8B	109.5
C4—N3—N2	109.55 (9)	C5—C8—H8C	109.5
C4—N3—H3	131.3 (17)	H8A—C8—H8B	109.5
N1—C1—C2	179.21 (13)	H8A—C8—H8C	109.5
C3—C2—C1	127.41 (10)	H8B—C8—H8C	109.5
C4—C2—C1	125.99 (10)	C4—C9—C10	110.60 (9)
C4—C2—C3	106.60 (9)	C4—C9—C11	109.86 (9)
N2—C3—C2	106.99 (9)	C4—C9—C12	108.69 (9)
N2—C3—C5	123.33 (10)	C10—C9—C11	109.09 (9)
C2—C3—C5	129.66 (10)	C10—C9—C12	109.18 (10)
N3—C4—C2	107.19 (10)	C11—C9—C12	109.40 (9)
N3—C4—C9	123.09 (10)	C9—C10—H10A	109.5
C2—C4—C9	129.71 (10)	C9—C10—H10B	109.5
C3—C5—C6	110.21 (9)	C9—C10—H10C	109.5

C3—C5—C7	110.86 (9)	H10A—C10—H10B	109.5
C3—C5—C8	108.38 (9)	H10A—C10—H10C	109.5
C6—C5—C7	108.96 (10)	H10B—C10—H10C	109.5
C6—C5—C8	109.37 (10)	C9—C11—H11A	109.5
C7—C5—C8	109.04 (10)	C9—C11—H11B	109.5
C5—C6—H6A	109.5	C9—C11—H11C	109.5
C5—C6—H6B	109.5	H11A—C11—H11B	109.5
C5—C6—H6C	109.5	H11A—C11—H11C	109.5
H6A—C6—H6B	109.5	H11B—C11—H11C	109.5
H6A—C6—H6C	109.5	C9—C12—H12A	109.5
H6B—C6—H6C	109.5	C9—C12—H12B	109.5
C5—C7—H7A	109.5	C9—C12—H12C	109.5
C5—C7—H7B	109.5	H12A—C12—H12B	109.5
C5—C7—H7C	109.5	H12A—C12—H12C	109.5
H7A—C7—H7B	109.5	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2 \cdots N3 ⁱ	0.86 (3)	2.23 (3)	2.9232 (14)	138 (2)
N3—H3 \cdots N2 ⁱ	0.85 (3)	2.19 (3)	2.9232 (14)	144 (2)

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