

4-{3,5-Dimethyl-4-[(*E*)-(4-methylphenyl)diazenyl]-1*H*-pyrazol-1-yl}benzonitrile

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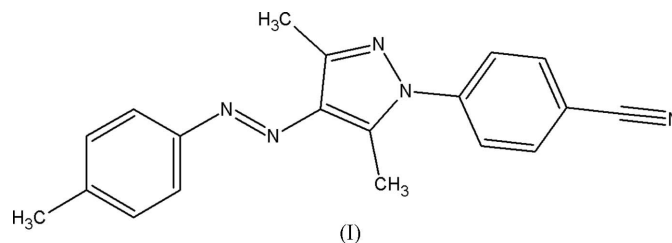
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ (C–C) = 0.004 Å
R factor = 0.072
wR factor = 0.141
Data-to-parameter ratio = 15.1

Molecules in the title compound, C₁₉H₁₇N₅, are linked into chains *via* weak C–H··· π (cyano) interactions, and these chains are linked *via* C–H··· π (arene) interactions to form a three-dimensional structure of parallel sheets.

Comment

Pyrazole nuclei have long attracted pharmacological interest as anti-anxiety (Haufel & Breitmaier, 1974; Wustrow *et al.*, 1998), antipyretic, analgesic and anti-inflammatory drugs (Eid *et al.*, 1978; Menozzi *et al.*, 1997; Penning *et al.*, 1997). In addition, they show antimicrobial (Habit & Tawil, 1981; Pathak & Bahel, 1980; Devi *et al.*, 1983; Daidone *et al.*, 1998; El-Emary & Bakhite, 1999) and antiparasitic activities in the *N*-heterocyclic series (Rathelot *et al.*, 1995; Tedlaouti *et al.*, 1990; Tedlaouti *et al.*, 1991). Compounds from a family of pyrazole-related derivatives have been described as potent PDE4B or PDE4D inhibitors (Card *et al.*, 2005). Pyrazole compounds have been used for some time as ligands in transition metal complexes, since the heterocyclic nucleus may coordinate the metal directly *via* one or both vicinal N atoms; some of these compounds present catalytic activity (Rojas *et al.*, 2004). Moreover, it is known that the metal may be bound to several pyrazole nuclei, to yield polypyrazole systems linked to the heteroatoms and/or C atoms (Duprez & Heumann, 2004). We present here the crystal structure of the title compound, (I).



The molecular structure of compound (I) is shown in Fig. 1. Bond lengths (Table 1) are in good agreement with reference values (Allen *et al.*, 1987). The dihedral angle between the mean planes formed by the C1–C6 and C13–C18 benzene rings is 50.15 (14)°, while that between the mean planes of the pyrazole and C1–C6 rings is 30.50 (16)°. The pyrazole ring is essentially coplanar (r.m.s. deviation = 0.03 Å for all atoms). On the other hand, the widening of the exocyclic C4–N2–C11 angle [131.0 (3)°] may be due to the steric interaction between atoms H5 and H12C (H···H = 2.35 Å).

There are no conventional intermolecular hydrogen bonds in (I) and the entire supramolecular structure is constructed

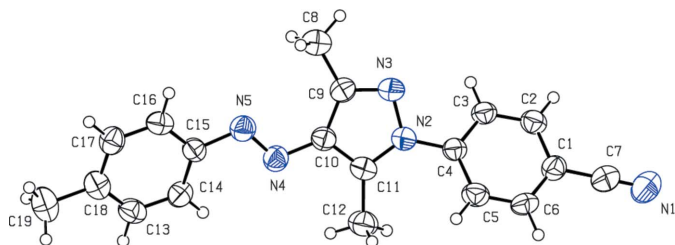


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and showing the atom-labelling scheme.

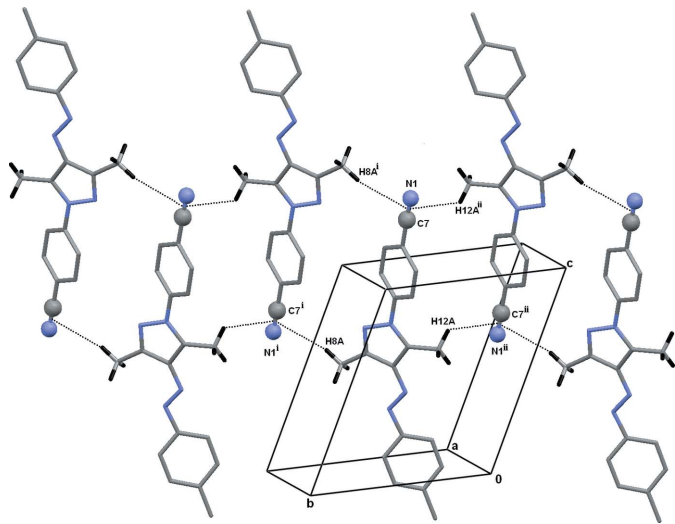


Figure 2
Part of the crystal structure, showing the formation of chains along [110], which are formed by C–H... π (cyano) interactions (dotted lines). H atoms not involved in these interactions have been omitted. [Symmetry codes: (i) $2-x, 2-y, 2-z$; (ii) $1-x, 1-y, 2-z$].

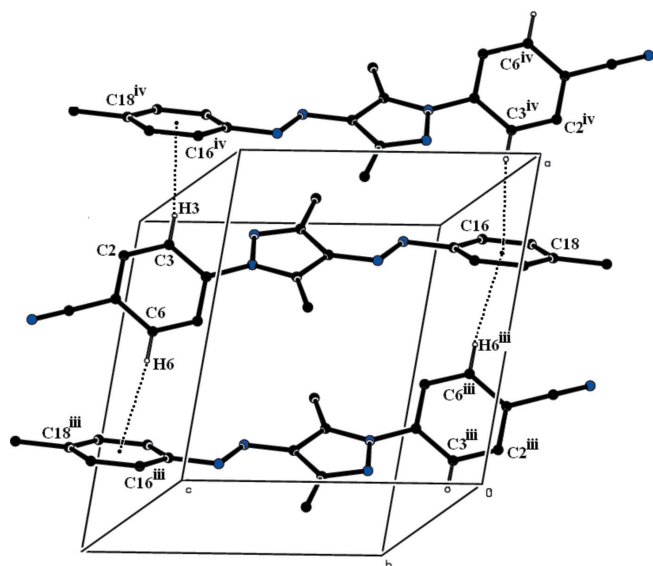


Figure 3
Detail of the two C–H... π (phenyl) interactions which form sheets parallel to the $(2\bar{2}1)$ plane. The dotted lines represent the vectors between H atoms and the ring centroids. [Symmetry codes: (iii) $1-x, 1-y, 1-z$; (iv) $2-x, 1-y, 1-z$].

only by weak interactions. Chains along the [110] direction are formed *via* C–H... π (cyano) interactions (Table 2 and Fig. 2).

Although no reliable example of a C–H... π (cyano) hydrogen bond has been reported in the literature, that reported here can be classified as intermediate between normal C–H...N and C–H... π (cyano) (C–H perpendicular to C \equiv N) hydrogen bonds (Desiraju & Steiner, 1999). The structure is further stabilized *via* two C–H... π (arene) interactions (Malone *et al.*, 1997), which connect the chains into sheets parallel to $(2\bar{2}1)$ (Table 3 and Fig. 3).

Experimental

A mixture of 2,3,4-pentanetrione 3-[(4-methylphenyl)hydrazone] (0.005 mol), 4-hydrazinobenzonitrile (0.005 mol) and glacial acetic acid (2 ml) in ethanol (25 ml) was stirred and heated under reflux for 18 h. After cooling to room temperature, water (30 ml) was added, precipitating an abundant quantity of orange solid. The product was washed twice with water and dried under vacuum at 313 K. The crude compound was recrystallized by diffusion of methanol over a mixture of the compound dissolved in tetrahydrofuran–methanol (1:1).

Crystal data

$C_{19}H_{17}N_5$	$V = 818.9 (3) \text{ \AA}^3$
$M_r = 315.38$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.279 \text{ Mg m}^{-3}$
$a = 9.3464 (18) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.4021 (18) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 10.422 (2) \text{ \AA}$	$T = 273 \text{ K}$
$\alpha = 108.580 (3)^\circ$	Plate, orange
$\beta = 98.301 (4)^\circ$	$0.45 \times 0.13 \times 0.06 \text{ mm}$
$\gamma = 103.722 (4)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3312 independent reflections
φ and ω scans	1932 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.046$
6660 measured reflections	$\theta_{\text{max}} = 26.4^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2]$
$wR(F^2) = 0.141$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} = 0.011$
3312 reflections	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
220 parameters	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1–C7	1.139 (5)	C9–C10	1.414 (4)
N4–N5	1.252 (3)	C10–C11	1.366 (4)
N2–N3	1.383 (4)	N2–C11	1.350 (4)
N3–C9	1.316 (3)		
H8A...N1 ⁱ	2.79	H12A...N1 ⁱⁱ	2.93
C4–N2–C11	131.0 (3)	C8–C9–C10	129.6 (3)
N1–C7–C1	179.1 (4)		
C11–N2–C4–C5	−33.7 (5)	N4–N5–C15–C14	−17.4 (4)
C10–N4–N5–C15	179.2 (2)		

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

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C13–C18 benzene ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C6-H6 \cdots Cg1^{iii}$	0.93	2.82	3.533 (3)	135
$C3-H3 \cdots Cg1^{iv}$	0.93	2.79	3.464 (3)	131

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

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with aromatic C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and methyl C–H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PLATON* (Spek, 2003) and *MERCURY* (Macrae *et al.*, 2006).

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