

3-Ferrocenyl-5-methyl-1*H*-pyrazole

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The title compound, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_9\text{N}_2)]$, has four molecules in the asymmetric unit and exists in the form of an $R_4^4(12)$ tetramer as tautomeric 3-ferrocenyl-5-methyl-1*H*-pyrazole and 5-ferrocenyl-3-methyl-1*H*-pyrazole (3:1). In a unit cell, two tetramers are linked by $\text{C}-\text{H}\cdots\pi$ hydrogen bonds involving the cyclopentadienyl rings as acceptors into a double chain in the [010] direction.

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Key indicators

Single-crystal X-ray study

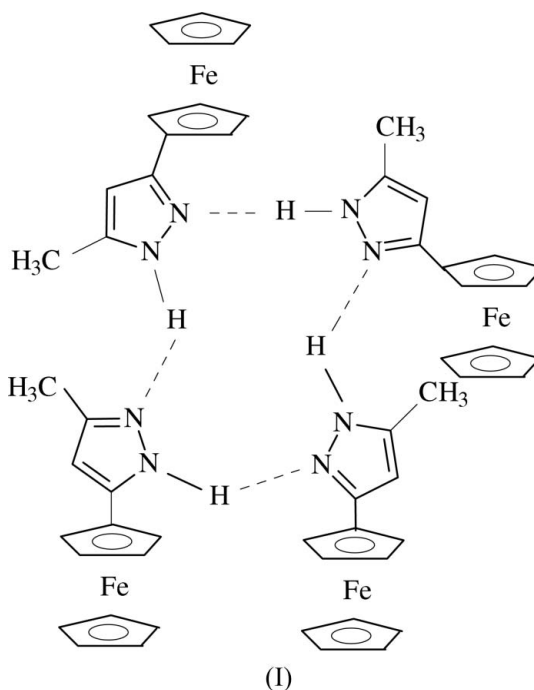
 $T = 295 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$ R factor = 0.058 wR factor = 0.152

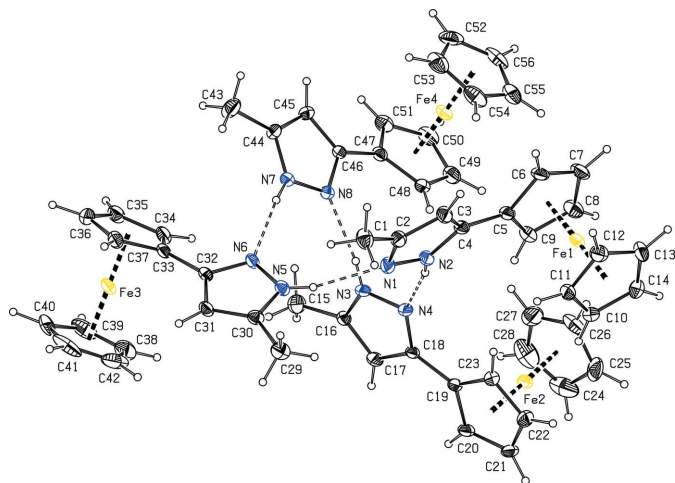
Data-to-parameter ratio = 15.2

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

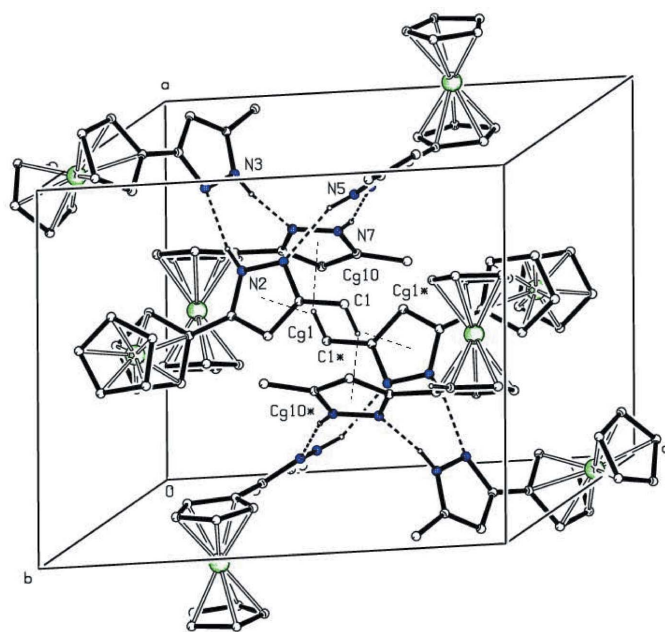
Comment

Pyrazole compounds have important applications in coordination chemistry (Chakrabarty *et al.*, 2004; Davies *et al.*, 2005; Hardie *et al.*, 2004; Michaud *et al.*, 2005), supramolecular chemistry (Miranda *et al.*, 2005) and organometallic chemistry (Esquiú *et al.*, 2001; Reger *et al.*, 1996). They have proven to be useful as potential anti-inflammatory agents (Bruno *et al.*, 1993), cytotoxic agents (Cuadro *et al.*, 1985), insecticides (Tsuboi *et al.*, 1994), herbicides (Hartfiel *et al.*, 1993) and fungicides (Desbordes *et al.*, 1994). We have therefore initiated a systematic study on organometallic pyrazoles. The title compound, (I), was synthesized as an intermediate for *N*-acyl organometallic pyrazoles (Shi, Sui & Zhu, 2006; Shi, Zhu & Sui, 2006) and its crystal structure has been determined (Fig. 1).




Figure 1

The asymmetric unit of (I), showing the formation of a tetramer linked by N—H···N hydrogen bonds. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines.


Figure 2

Part of the crystal structure of (I), showing two tetramers linked by C—H··· π (arene) hydrogen bonds. For clarity, H atoms not involved in the motif shown have been omitted. Cg1 is the centroid of the N1—C4 ring and Cg10 is the centroid of the N7—C46 ring. Cg1* and Cg10* are at the symmetry position (1 - x, 1 - y, 1 - z).

(Ic) and (Id)], which belong to tautomeric 5-ferrocenyl-3-methyl-1*H*-pyrazole and 3-ferrocenyl-5-methyl-1*H*-pyrazole (1:3), exist in the asymmetric unit of (I) whereas its analog (II), 3-methyl-5-phenyl-1*H*-pyrazole, crystallizes in the centrosymmetric space group *C2/c* with *Z* = 16 and the asymmetric unit contains two molecules [(IIa) and (IIb)]; Maslen *et al.*, 1974].

The bond lengths in the pyrazole ring in each of (I) are very close to those in each of (II) except that the N—N bond length

in each of (I) is slightly shorter than that in each of (II) [Table 1; (IIa) 1.367 (5) Å and (IIb) 1.363 (5) Å]. As in (II), each pyrazole ring in (I) exhibits electron delocalization (Shi *et al.*, 2005). However, the dihedral angle between the pyrazole ring and the corresponding substituted cyclopentadienyl ring or phenyl ring is different. The dihedral angle is 12.9 (3)° for (Ia), 2.4 (3)° for (Ib), 32.0 (3)° for (Ic) and 25.8 (3)° for (Id); the corresponding value is 21.61° for (IIa) and 18.06° for (IIb). Furthermore, the bond linking the pyrazole ring and the corresponding substituted cyclopentadienyl ring in each of (I) is in the range 1.453 (6)–1.462 (6) Å, suggesting that the pyrazole ring and the corresponding substituted cyclopentadienyl ring are conjugated, while the bond linking the pyrazole ring and the benzene ring is 1.474 (7) Å for (IIa) and 1.457 (6) Å for (IIb), indicating that the pyrazole ring and the benzene ring in (IIb) are conjugated.

As in (II), the title compound exists in the form of a tetramer (Fig. 2). Each of four molecules in (I) in the asymmetric unit acts as both a donor and an acceptor of hydrogen bonds, generating an $R_4^4(12)$ tetramer by N—H···N hydrogen bonds (Table 2). The tetramer is linked by C—H··· π hydrogen bonds involving the cyclopentadienyl rings as acceptors into a [010] chain. Two chains of this type pass through each unit cell and are also linked by C—H··· π hydrogen bonds in which the pyrazoles act as acceptors, thus leading to a [010] double chain (Fig. 2).

Experimental

An ethanol solution (20 ml) of ferrocenylacetone and hydrated hydrazine (1:1) was stirred for 7 h under N_2 . The resulting residue was collected and air-dried to afford the yellow title compound (yield 92%; m.p. 441.15–442.15 K). Analysis calculated for $C_{14}H_{14}FeN_2$: C 63.19, H 5.30, N 10.53%; found: C 62.97, H 5.18, N 10.83%. IR (KBr): 3179 (*vs*, NH), 3081 (*vs*, CH), 1587 (*s*, C=N), 1290 (*m*, C—N) cm^{-1} . UV (λ_{max} , in DMF): 275.00 (B band), 361.00 (*R* band), 455.50 (*d-d* band) nm. 1H NMR (600 MHz, $CDCl_3$): δ 9.946 (1 H, *s*, NH), 6.089 (1H, *s*, CH), 4.591, 4.267 (2H, *s*, 2H, 2 *s*, C_5H_4), 4.079 (5H, *s*, C_5H_5), 2.317 (3H, *s*, CH_3).

Crystal data

[Fe(C_5H_5)($C_9H_9N_2$)]
 M_r = 266.12
 Triclinic, $P\bar{1}$
 a = 11.533 (2) Å
 b = 13.375 (3) Å
 c = 17.109 (3) Å
 α = 70.99 (3)°
 β = 78.50 (3)°
 γ = 86.16 (3)°

V = 2445.1 (10) Å³
 Z = 8
 D_x = 1.446 Mg m⁻³
 Mo $K\alpha$ radiation
 μ = 1.21 mm⁻¹
 T = 295 K
 Prism, orange–yellow
 0.40 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 T_{min} = 0.743, T_{max} = 0.882
 10086 measured reflections

9581 independent reflections
 6355 reflections with $I > 2\sigma(I)$
 R_{int} = 0.031
 θ_{max} = 26.0°
 3 standard reflections
 every 200 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.152$
 $S = 1.04$
 9581 reflections
 629 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.8041P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (Å).

N1—N2	1.362 (5)	N5—N6	1.355 (5)
N1—C2	1.331 (6)	N5—C30	1.346 (6)
N2—C4	1.357 (5)	N6—C32	1.341 (5)
C1—C2	1.493 (7)	C29—C30	1.487 (6)
C2—C3	1.401 (6)	C30—C31	1.369 (6)
C3—C4	1.372 (6)	C31—C32	1.394 (6)
C4—C5	1.453 (6)	C32—C33	1.462 (6)
N3—N4	1.350 (5)	N7—N8	1.347 (5)
N3—C16	1.325 (6)	N7—C44	1.349 (5)
N4—C18	1.339 (5)	N8—C46	1.345 (5)
C15—C16	1.491 (6)	C43—C44	1.496 (6)
C16—C17	1.380 (6)	C44—C45	1.370 (6)
C17—C18	1.391 (6)	C45—C46	1.394 (6)
C18—C19	1.462 (6)	C46—C47	1.458 (6)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2N \cdots N4	0.84 (5)	2.07 (5)	2.896 (5)	168 (5)
N3—H3N \cdots N8	0.85 (7)	1.99 (7)	2.812 (6)	165 (7)
N5—H5N \cdots N1	0.83 (7)	2.11 (7)	2.900 (5)	160 (7)
N7—H7N \cdots N6	0.88 (7)	2.06 (6)	2.915 (5)	166 (6)
C1—H1B \cdots Cg1 ⁱ	0.96	3.00	3.554 (6)	118
C1—H1B \cdots Cg10 ⁱ	0.96	2.98	3.496 (6)	115
C51—H51 \cdots Cg3 ⁱⁱ	0.93	2.86	3.674 (6)	146

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y - 1, z$. Cg1 is the centroid of the N1—C4 ring, Cg3 is the centroid of the C10—C14 ring and Cg10 is the centroid of the N7—C46 ring.

Four H atoms bonded to N atoms were located in difference maps and refined isotropically, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. All other H atoms were placed at geometrically idealized positions, with C—H = 0.93–0.98 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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