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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.049
 wR factor = 0.139
 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>.

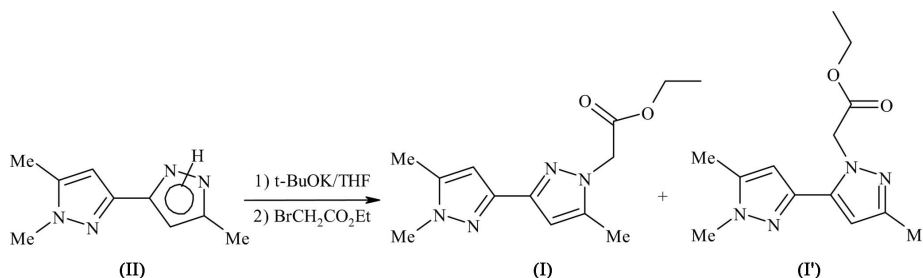
Ethyl 2-(5,1',5'-trimethyl-3,3'-bi-1H-pyrazol-1-yl)acetate

In the title compound, $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_2$, the dihedral angle between the two planar pyrazole rings is $2.20 (9)^\circ$; the relative orientation of the rings is also characterized by a C—C—C—C torsion angle of $179.07 (16)^\circ$.

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Comment

Bipyrazoles are a class of pyrazolyl compounds which are of considerable interest because of their biological properties. Many bipyrazolyl derivatives are useful either as anti-inflammatory (El-Khawass *et al.*, 1990) or cytotoxic agents (Cuadro *et al.*, 1985). They may find applications as insecticides (Tsuboi *et al.*, 1994), herbicides (Hartfiel *et al.*, 1993) or fungicides (Nayak & Mitra, 1980) as well as in the photographic and paint industries (Pfeiffer & Bulka, 1991).



In order to evaluate its biological activity and use as an intermediate for the construction of functionalized pyrazole derivatives, we have prepared the new title 3,3'-bipyrazole, (I), by *N*-alkylation of 2,3,3'-trimethyl-5,5'-bipyrazole (II) (Touzani, 2001) with ethyl bromoacetate in the presence of potassium *tert*-butoxide as a base (see *Experimental*).

2,3,3'-Trimethyl-5,5'-bipyrazole, (II), is an ambident nucleophile, so the nucleophilic centre is not specifically localized at one N atom. Indeed, both N atoms of the pyrazole ring can be alkylated, providing a mixture of two regioisomers, *viz.* (I) and (I') (see scheme). To confirm the position at which the ethoxycarbonyl group is bonded to the pyrazole rings and to obtain some information about the geometry of the molecule in the solid state, the reaction product, (I), was characterized by X-ray analysis (Fig. 1 and Table 1).

The C2—C3 and C8—C9 bond lengths are close to that observed for the methyl group in 1-(*p*-nitrophenyl)-3-methyl-4-bromopyrazole (Lapasset & Falgueirettes, 1972). The N1—N2 and N3—N4 distances agree well with bond lengths reported in related compounds [*e.g.* 1.385 (4) Å; Krishna *et al.*, 1999]. The pyrazole rings are nearly planar, the maximum deviations from their mean planes being 0.010 (4) Å for atom N4 and 0.006 (4) Å for atom C2. With a small dihedral angle of $2.20 (9)^\circ$, the two heterocycles are nearly coplanar and their N

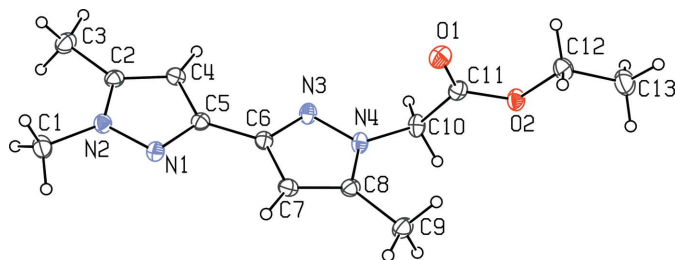


Figure 1

Representation of the molecule of (I), with displacement ellipsoids for non-H atoms drawn at the 30% probability level.

atoms are in opposite positions, limiting steric hindrance. Although the C7–C6–C5–C4 torsion angle of 179.07 (16)^o is very close to that observed in 3,3'-bipyrazole, 180^o (Monge *et al.*, 1994), it is very far from values found for other C–C-linked bipyrazoles, *e.g.* 107.0 (6)^o in 3,3'-dichloro-4,4'-bis-(methoxycarbonyl)-1,1'-dimethyl-5,5'-bipyrazolyl (Murakami & Yamamoto 1999), in which steric strain is responsible for the very different molecular conformation. In the case of (I), the other torsion angles in Table 1 reflect the low steric strain occurring at the pyrazole rings, not only between the two methyl groups, but also between the methyl and ethoxy-carbonyl groups in the second ring.

Experimental

A mixture of (II) (1 g, 5.68 mmol) and potassium *tert*-butoxide (0.85 g, 7.59 mmol) in anhydrous tetrahydrofuran (THF, 75 ml) was refluxed for 30 min. After cooling to 273 K, a solution of ethyl bromoacetate (1.3 g, 7.78 mmol) in THF (25 ml) was added slowly. The reaction mixture was stirred for 5 h at 298 K, then filtered, and the solvent evaporated to dryness. The resulting residue was purified on alumina using dichloromethane as eluant to give 0.71 g of (I) as a white solid (yield 48%). This solid was dissolved in the minimum amount of THF and allowed to stand at 298 K. Clear colourless crystals formed after a few days; these were filtered off and dried in air.

Crystal data

C ₁₃ H ₁₈ N ₄ O ₂	Z = 2
M _r = 262.31	D _x = 1.288 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
a = 7.616 (1) Å	Cell parameters from 9864 reflections
b = 9.733 (2) Å	θ = 3.2–26.1 ^o
c = 9.902 (2) Å	μ = 0.09 mm ⁻¹
α = 73.55 (2) ^o	T = 173 (2) K
β = 77.89 (1) ^o	Parallelepiped, colourless
γ = 76.57 (2) ^o	0.26 × 0.23 × 0.16 mm
V = 676.5 (2) Å ³	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	2000 reflections with I > 2σ(I)
ω scans	R _{int} = 0.087
Absorption correction: none	θ _{max} = 26.1 ^o
9864 measured reflections	h = -9 → 9
2670 independent reflections	k = -12 → 12
	l = -12 → 12

Refinement

Refinement on F²
 R[F² > 2σ(F²)] = 0.049
 wR(F²) = 0.139
 S = 1.10
 2670 reflections
 176 parameters

H-atom parameters constrained
 w = 1/[σ²(F_o²) + (0.0708P)²]
 where P = (F_o² + 2F_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.22 e Å⁻³
 Δρ_{min} = -0.24 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N3–N4	1.363 (2)	C8–C7	1.369 (2)
N4–C8	1.364 (2)	C8–C9	1.492 (2)
N3–C6	1.346 (2)	C6–C7	1.409 (2)
N2–C2	1.354 (2)	C2–C3	1.492 (2)
N1–N2	1.3597 (19)	C2–C4	1.374 (2)
N2–C1	1.453 (2)	C4–C5	1.409 (2)
N1–C5	1.348 (2)	C5–C6	1.460 (2)
N3–N4–C8	112.39 (14)	N3–C6–C7	111.02 (16)
C6–N3–N4	104.33 (14)	N2–C2–C4	106.42 (15)
C2–N2–N1	112.60 (14)	N1–C5–C4	110.57 (15)
C5–N1–N2	104.58 (14)	C8–C7–C6	105.83 (15)
N4–C8–C7	106.43 (15)	C2–C4–C5	105.83 (15)
C10–N4–C8–C9	-2.9 (3)	C7–C6–C5–C4	179.07 (16)
C1–N2–C2–C3	2.9 (3)		

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The constrained C–H distances and isotropic displacement parameters were as follows: C–H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups; C–H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene groups; C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic CH groups.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.075; Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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