Methyl (*E*,*E*)-{2-[({[1,3-dimethyl-5-(2-fluorophenoxy)-1*H*-pyrazol-4-ylmethylene]amino}oxy)methyl]phenyl}-2-(methoxyimino)acetate

Yan Li,[a]* Xiang-Ping Yang,[a] Hong-Quan Zhang,[a] Xiang-Gao Meng[b] and Zhao-Jie Liu[b]

[a]Key Laboratory of Synthesis and Application of Organic Functional Molecules of the Education Ministry, Hubei University, Wuhan, Hubei 430062, People's Republic of China, and [b]Key Laboratory of Pesticides and Chemical Biology of the Education Ministry, Central China Normal University, Wuhan, Hubei 430079, People's Republic of China

Correspondence e-mail: liyanok@hotmail.com

The molecule of the title compound, $C_{23}H_{23}FN_4O_5$, assumes an overall U-shaped conformation and exhibits orientational disorder. The crystal packing is stabilized by intra- and intermolecular C—H⋯O hydrogen bonds.

Comment

The title compound, (I), belongs to the class of the strobilurin fungicides, which represents one of the most significant classes of agricultural fungicides. These compounds inhibit mitochondrial respiration by blocking electron transfer at the Qo-site of the cytochrome bc1 enzyme complex (Sauter *et al.*, 1999; Zakharychev & Kovalenko, 1998). Preliminary bioassays indicate that (I) shows a broad spectrum of fungicidal activity. The present structure determination of (I) was carried out in order to obtain information on the stereochemistry of the molecule.


(I)
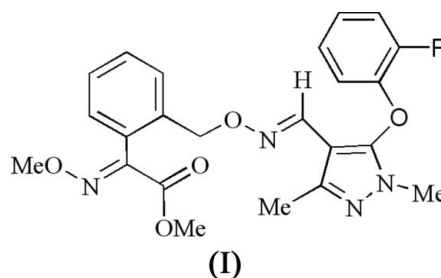
The molecule of (I) displays a U-shaped conformation (Fig. 1), the dihedral angles formed by the benzene rings C1–C6 and C14–C19 with the central N1/N2/C7/C8/C9/C12/N3/O2/C13 unit being 80.88 (7) and 87.91 (8)°, respectively. As observed in 4-cinnamoyl-1,3-dimethylpyrazol-5-one (Guard & Steel, 1994) and 4-(5-hydroxy-1,3-dimethyl-4-pyrazolylmethylene)-1,3-dimethyl-2-pyrazolin-5-one (Drück & Littke, 1980), the N1—C7 single bond is significantly shorter than the N1—N2 single bond (Table 1). The torsion angles C22—C20—N4—O3 and C8—C12—N3—O2 are 177.8 (6) and 179.0 (2)°, respectively, indicating that both the C=N double bonds adopt an E configuration. Compound (I) exhibits orientational disorder, such that the methoxyimino and carboxylate groups are exchanged.

The crystal structure of (I) is stabilized by intra- and intermolecular C—H⋯O hydrogen interactions (Table 2, Fig. 2).

Experimental

A 50 ml round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet was charged with 5-(2-fluorophenoxy)-1,3-dimethyl-1*H*-pyrazole-4-carbaldehyde (0.73 g, 3.1 mmol) and methyl (*E*)-α-methoxyimino-2-(aminooxymethyl)-phenylacetate (0.83 g,
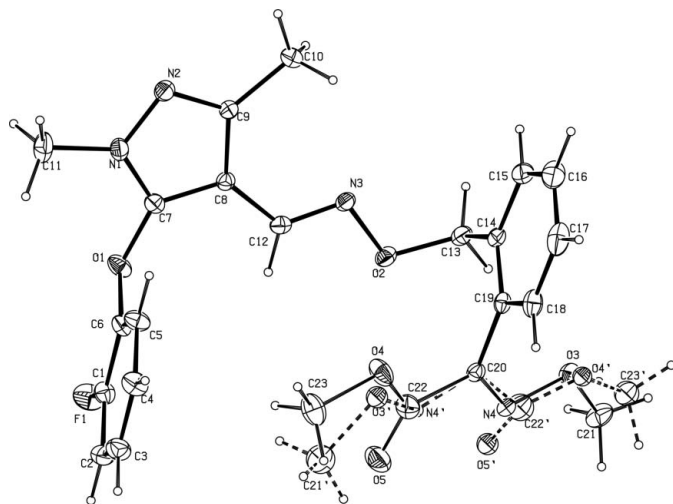
Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown.
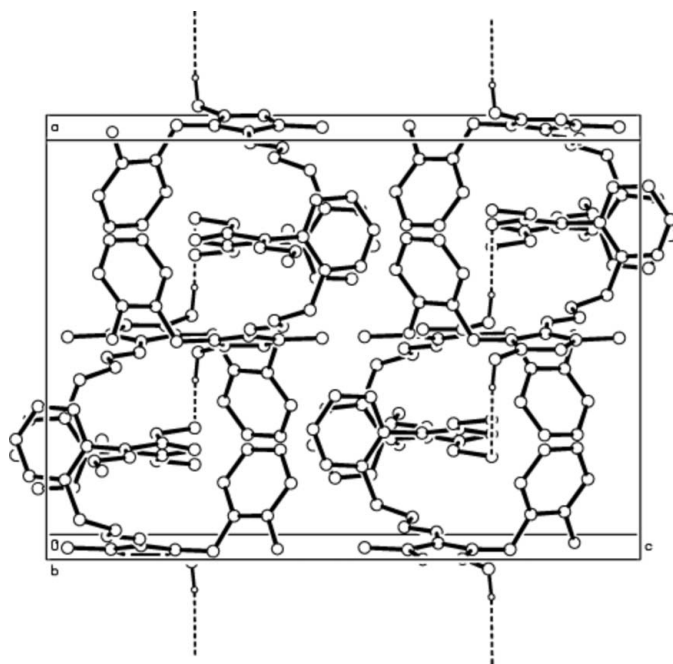
Figure 2
The molecular packing of (I), viewed approximately along the *b* axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

3.5 mmol). The mixture was dissolved in anhydrous methanol (20 ml), and one drop of glacial acetic acid was added as catalyst. The flask was stirred at ambient temperature overnight, then poured into water (100 ml) and extracted with diethyl ether (3 × 100 ml). The combined ether extracts were washed with water (2 × 100 ml) and brine (100 ml), dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated to afford an oil which was chromatographed on silica gel with ethyl acetate and hexane. Each fraction was monitored by thin-layer chromatography. The pure fractions were combined and crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent.

Crystal data

$C_{23}H_{23}FN_4O_5$	$Z = 8$
$M_r = 454.45$	$D_x = 1.294$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation
$a = 14.2781$ (10) Å	$\mu = 0.10$ mm^{-1}
$b = 16.1865$ (12) Å	$T = 292$ (2) K
$c = 20.1828$ (15) Å	Block, colourless
$V = 4664.5$ (6) Å^3	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4578 independent reflections
	2596 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.062$
Absorption correction: none	$\theta_{max} = 26.0°$
24306 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$+ 0.6674P]$
$wR(F^2) = 0.172$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
4578 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
332 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C7—N1	1.339 (4)	N3—O2	1.422 (3)
N2—N1	1.360 (3)	O3—N4	1.362 (5)
C9—C8	1.413 (3)		
C8—C12—N3—O2	−179.0 (2)	C22—C20—N4—O3	−177.8 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C13—H13$B\cdots$O3	0.97	2.51	3.192 (9)	127
C11—H11$B\cdots$O5^i	0.96	2.52	3.470 (5)	169
C5—H5$\cdots$O5^{ii}	0.93	2.52	3.154 (5)	126

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$.

The methoxyimino and carboxylate groups are disordered over two positions related by a pseudo-twofold axis. The occupancies were initially refined and finally fixed at 0.83 and 0.17. The non-H atoms of the minor component were refined isotropically. All H atoms were positioned geometrically, with C—H = 0.93–0.97 Å, and refined as riding, with $U_{iso} = 1.2U_{eq}$(C), or $1.5U_{eq}$(C) for methyl H atoms.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

References

Bruker (2003). *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Drück, U. & Littke, W. (1980). *Acta Cryst.* B**36**, 3002–3007.

Guard, J. A. M. & Steel, P. J. (1994). *Aust. J. Chem.* **47**, 1453–1459.

Sauter, H., Steglich, W. & Anke, T. (1999). *Angew. Chem. Int. Ed.* **38**, 1328–1349.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Zakharychev, V. V. & Kovalenko, L. V. (1998). *Russ. Chem. Rev.* **67**, 535–544.