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Ethyl 3-methyl-5-nitro-1*H*-imidazole-2-carboxylate

Hai-Qiang Wu,[a] Lin-Kun An,[b] Zhi-Shu Huang,[b] Lian-Quan Gu,[b] Sharifuddin M. Zain[c] and Seik Weng Ng[c]*

[a]School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, [b]School of Pharmaceutical Sciences, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and [c]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.124
Data-to-parameter ratio = 11.0

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

The title compound, $C_7H_9N_3O_4$, exists as a planar molecule whose carboxyethyl fragment is disordered across a crystallographic mirror plane. The fragment is twisted by 15.1 (1)° with respect to the plane.

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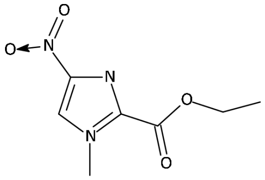
Comment

Ethyl 3-methyl-5-nitro-1*H*-imidazole-2-carboxylate (Fig. 1), (I), is a reagent that is used for the synthesis of the analogs of netropsin and distamycin, which represent a class of extremely potent *anti*-cancer compounds having an imidazole unit in the molecular structure (Baraldi *et al.*, 2003; Bhattacharya & Thomas, 2000; Dwyer *et al.*, 1992; Grehn *et al.*, 1990; Krowicki & Lown, 1987; Xue *et al.*, 1995; Zaffaroni *et al.*, 2002). The present report deals with the structure determination of another reagent that is used in the synthesis of a class of psychoactive drugs (Wu *et al.*, 2004).



(I)

The molecule of the title compound, (I), is flat in the imidazole portion (as required by crystallographic mirror-plane symmetry), but the carboxethyl group is twisted by 15.0 (1)°. An understanding of the twist is derived from the potential energy surface of the carboxyethyl group rotation, which exhibits double minima at dihedral angles of 50° (total energy −2196.1 kcal mol^{-1}) and −40° (total energy −2196.2 kcal mol^{-1}). This barrier (0.61 kcal mol^{-1}), being of the order of kT (0.59 kcal mol^{-1}) only, is in good agreement

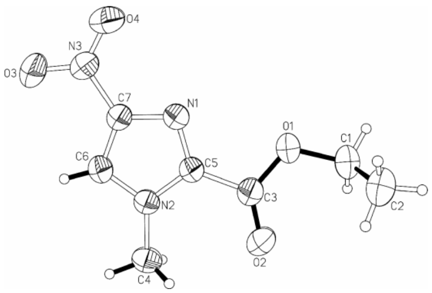


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsods drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. The carboxyethyl unit that is disordered across the mirror plane is drawn with a slightly different shading for the ellipsoids.

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with the twist found in the X-ray structure, whose molecules are stacked such that the steric interaction between adjacent carboxyethyl groups is minimized (Fig. 2).

Experimental

The title compound, (I), was synthesized using a published procedure (Baird & Dervan, 1996, 1997) and crystals were obtained by recrystallization from diethyl ether. The structure from the X-ray measurements was used for the calculation of the potential energy surface at the *PM*3 level using *HyperChem* (Hypercube Inc., 2000).

Crystal data

$C_7H_9N_3O_4$
$M_r = 199.17$
Orthorhombic, *Pnma*
$a = 8.940\ (1)$ Å
$b = 6.768\ (1)$ Å
$c = 15.028\ (2)$ Å
$V = 909.2\ (2)$ Å^3
$Z = 4$
$D_x = 1.455$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 861 reflections
$\theta = 2.7$–27.1°
$\mu = 0.12$ mm^{-1}
$T = 298\ (2)$ K
Block, colorless
$0.50 \times 0.33 \times 0.21$ mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: none
11054 measured reflections
1089 independent reflections

954 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 27.1^\circ$
$h = -10 \rightarrow 11$
$k = -7 \rightarrow 8$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.124$
$S = 1.02$
1089 reflections
99 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.1466P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.453 (3)	N2—C4	1.469 (2)
O1—C3	1.355 (2)	N2—C6	1.342 (2)
O2—C3	1.203 (4)	N2—C5	1.367 (2)
O3—N3	1.223 (2)	N3—C7	1.432 (2)
O4—N3	1.203 (2)	C1—C2	1.464 (4)
N1—C5	1.312 (2)	C3—C5	1.475 (2)
N1—C7	1.343 (2)	C6—C7	1.363 (2)
C1—O1—C3	117.6 (2)	O1—C3—C5	110.4 (2)
C5—N1—C7	103.5 (1)	O2—C3—C5	122.8 (2)
C4—N2—C5	128.5 (2)	N1—C5—N2	112.2 (1)
C4—N2—C6	124.7 (2)	N1—C5—C3	125.2 (2)
C5—N2—C6	106.8 (1)	N2—C5—C3	122.6 (2)
O4—N3—O3	124.1 (2)	N2—C6—C7	104.8 (1)
O3—N3—C7	117.0 (2)	N1—C7—C6	112.7 (1)
O4—N3—C7	119.0 (2)	N1—C7—N3	121.3 (1)
O1—C1—C2	112.7 (2)	N3—C7—C6	126.1 (2)
O2—C3—O1	126.6 (2)		

The carboxyethyl group is disordered across a mirror plane. No bond restraints were necessary. Atom C3 is common to both disorder components, so the disorder corresponds to a rotation around the bond joining the five-membered ring to the carboxyethyl substituent. The H atoms were placed at calculated positions in the riding-model approximation (C—H = 0.93 Å for the ring H atoms, 0.96 Å for the methyl H atoms and 0.97 Å for the methylene H atoms). The H atoms of the methyl groups were rotated to fit the observed electron density. The H atoms of the 3-methyl group are also disordered across the mirror plane. For the methyl groups, $U_{\rm iso} = 1.5U_{\rm eq}$(parent atom); for all other atoms, $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom).

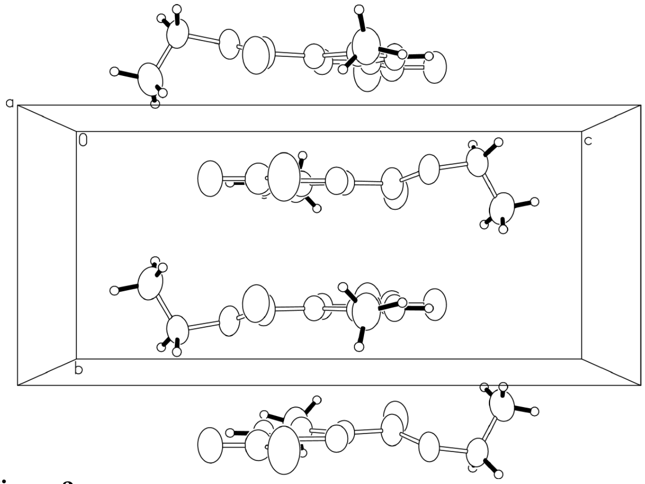

Figure 2
*ORTEP*II (Johnson, 1976) plot, showing the stacking of the molecules of (I) in the unit cell. The choice of disorder component for the carboxyethyl substituent is arbitrary for each molecule.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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