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Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}—\text{C}) = 0.002\text{ Å}$
 R factor = 0.028
 wR factor = 0.079
Data-to-parameter ratio = 9.2

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

Dimethyl (2*E*)-2-(4-nitro-1*H*-imidazol-1-yl)-but-2-enedioate

In the title molecule, $\text{C}_9\text{H}_9\text{N}_3\text{O}_6$, all bond lengths and angles are normal. The crystal packing shows intermolecular $\text{C}—\text{H} \cdots \text{O}$ hydrogen bonds, with $\text{H} \cdots \text{O}$ distances of 2.299 (16) and 2.374 (15) Å, which link the molecules into ribbons.

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Comment

Hypoxia has been known for a long time to be an important physiological parameter in tumor development (Williams *et al.*, 2005). In recent years, several nitroimidazoles have been described to measure hypoxia in tumors using invasive or even non-invasive methods (Menon & Fraker, 2005; Gallez *et al.*, 2004; Urtasun *et al.*, 1996; Groshar *et al.*, 1993; Koh *et al.*, 1992). In order to prepare the first nitroimidazolyl succinic esters or their diacids as hypoxia probes for proton magnetic resonance spectroscopic imaging (^1H MRSI), we reported an experimental and theoretical study of the addition reaction of the 2- and 4(5)-nitroimidazoles to electrophiles such as ethyl fumarate or dimethylacetylene dicarboxylate (Pacheco-Torres *et al.*, 2006). In the latter case, 4-nitroimidazole derivatives were obtained as a mixture of *Z* and *E* isomers, and the title compound, (I), was isolated as a white solid. Here we report its crystal structure.

In (I) (Fig. 1), all bond lengths and angles are normal (Allen *et al.*, 1987). The molecule shows a distorted *trans*–*cis* arrangement where one ester group deviates markedly from planarity to avoid short non-bonded interactions with the second carboxylic unit [$\text{C5}—\text{C4}—\text{C8}—\text{O6} = -115.07(13)^\circ$; $\text{C4}—\text{C5}—\text{C6}—\text{O4} = 19.57(17)^\circ$] and to allow some degree of coplanarity between theazole and the olefinic planes [$\text{C5}—\text{C4}—\text{N3}—\text{C3} = 161.05(11)^\circ$; $\text{C5}—\text{C4}—\text{N3}—\text{C2} = -15.99(17)^\circ$]. In accordance with the cases of non-sterically constrained carboxylic esters (Kulbida *et al.*, 1995; Macôas *et al.*, 2001; Lopes *et al.*, 2002) the methyl ester substituent adopts the *cis* ($\text{C}—\text{O}$) configuration.

The intermolecular $\text{C}—\text{H} \cdots \text{O}$ hydrogen bonds (Table 1) link the molecules into ribbons (Fig. 2). The crystal packing (Fig. 2) is further stabilized by van der Waals forces.

Experimental

The synthesis of (I) has been recently reported by us (Pacheco-Torres *et al.*, 2006). This compound has been prepared by nucleophilic

addition of 4(5)-nitroimidazole to acetylenedicarboxylate dimethyl ester in acetonitrile giving the corresponding *Z-E* isomer mixture. Compound (I) shows *E* stereochemistry. Crystals suitable for an X-ray study were obtained by recrystallization from hexane (m.p. 375–377 K).

Crystal data

$C_9H_9N_3O_6$	$\gamma = 100.034 (1)^\circ$
$M_r = 255.19$	$V = 530.83 (1) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.7704 (1) \text{ \AA}$	Cu $K\alpha$ radiation
$b = 10.5020 (1) \text{ \AA}$	$\mu = 1.19 \text{ mm}^{-1}$
$c = 11.2873 (1) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 104.931 (1)^\circ$	$0.35 \times 0.30 \times 0.12 \text{ mm}$
$\beta = 96.330 (1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	4928 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	1846 independent reflections
$T_{\min} = 0.692$, $T_{\max} = 0.867$	1752 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	200 parameters
$wR(F^2) = 0.079$	All H-atom parameters refined
$S = 1.03$	$\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
1846 reflections	$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots O1^i$	0.937 (16)	2.299 (16)	3.2298 (15)	172.7 (13)
$C3-H3\cdots O6^{ii}$	0.944 (15)	2.374 (15)	3.2440 (15)	152.9 (13)

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

All H atoms were located in a difference map and were isotropically refined [$C-H = 0.937 (19)$ – $0.986 (15) \text{ \AA}$].

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT*.

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Figure 1

The molecular structure of (I), showing the atomic labeling and displacement ellipsoids at the 50% probability level. H atoms are drawn as small circles of arbitrary radius.

Figure 2

A portion of the crystal packing viewed down the *a* axis. Dashed lines denote hydrogen bonds.

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