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

In the title molecule, C₉H₇N₃O₆, all bond lengths and angles are normal. The crystal packing shows intermolecular C—H···O hydrogen bonds, with H···O distances of 2.299 (16) and 2.374 (15) Å, which link the molecules into ribbons.

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 [C₅—C₄—C₈—O₆ = −115.07 (13)°; C₄—C₅—C₆—O₄ = 19.57 (17)] and to allow some degree of coplanarity between the azole and the olefinic planes [C₅—C₄—N₃—C₃ = 161.05 (11)°; C₅—C₄—N₃—C₂ = −15.99 (17)]. In accordance with the cases of non-sterically constrained carboxylic esters (Kulbida et al., 1995; Macoás et al., 2001; Lopes et al., 2002) the methyl ester substituent adopts the cis (C—O) configuration.

The intermolecular C—H···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 \(E\) stereochirality. Crystals suitable for an X-ray study were obtained by recrystallization from hexane (m.p. 375–377 K).

Crystal data

\(\text{C}_9\text{H}_9\text{N}_3\text{O}_6\)  

\(M_r = 255.19\)  

Triclinic, \(\text{P}1\)  

\(a = 4.7704 (1) \text{ Å}\)  

\(b = 10.5020 (1) \text{ Å}\)  

\(c = 11.2873 (1) \text{ Å}\)  

\(\alpha = 104.931 (1)^\circ\)  

\(\beta = 96.330 (1)^\circ\)  

\(\gamma = 100.034 (1)^\circ\)  

\(V = 530.83 (1) \text{ Å}^3\)  

\(Z = 2\)  

\(\mu = 1.19 \text{ mm}^{-1}\)  

\(T = 100 (2) \text{ K}\)  

\(\rho_{\text{calc}} = 1.19 \text{ mm}^{-1}\)  

\(\rho_{\text{max}} = 0.35 \times 0.30 \times 0.12 \text{ mm}\)

Data collection

Bruker SMART CCD area-detector diffractometer  

Absorption correction: multi-scan  

\(SADABS\) (Sheldrick, 1997)  

\(\Delta \rho_{\text{max}} = 0.22 \text{ e Å}^{-3}\)  

\(\Delta \rho_{\text{min}} = -0.20 \text{ e Å}^{-3}\)

Refinement

\(R[F^2 > 2\sigma(F^2)] = 0.028\)  

\(wR(F^2) = 0.079\)  

\(S = 1.03\)  

1846 reflections  

200 parameters

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

Table 1

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

\[
\begin{array}{ccccc}
D & \cdots & H & \cdots & A \\
C2 & -H2 & -O1i & 0.937 (16) & 2.299 (16) & 3.2298 (15) & 172.7 (13) \\
C3 & -H3 & -O6ii & 0.944 (15) & 2.374 (15) & 3.2440 (15) & 152.9 (13) \\
\end{array}
\]

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

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References


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.

Sheldrick, G. M. 1997. \(\text{SHELXS97}\) and \(\text{SHELXL97}\). University of Göttingen, Germany.  