Methyl 1,6-dimethyl-4-(3-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

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The dihydropyrimidine ring of the title compound, $C_{14}H_{15}N_3O_5$, assumes a boat conformation. The stability of the solid-state structure is enhanced by π–π stacking interactions and hydrogen-bonding interactions, linking the molecules into an extended three-dimensional network.

Comment

In the past decade, dihydropyrimidinones have attracted considerable interest due to their therapeutic and pharmacological activities (Kappe, 1993). Some of them have also emerged as the integral backbones of several calcium-channel blockers, antihypertensive agents and neuropeptide Y (NPY) antagonists (Atwal *et al.*, 1990; Rovnyak *et al.*, 1995). The synthesis of this kind of heterocyclic compound has therefore gained great importance. A simple, efficient and practical procedure for obtaining dihydropyrimidinones has recently been reported by our laboratory (Su *et al.*, 2005).

(I)
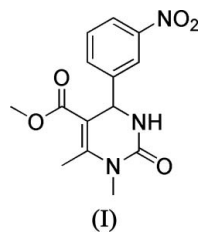
In the title compound, (I) (Fig. 1), the six-membered dihydropyrimidine ring assumes a boat conformation, with puckering parameters $Q = 0.429$ (3), $\theta = 75.6$ (4)° and $\varphi = 6.2$ (4)° (Cremer & Pople, 1975). The molecular conformation is stabilized by intramolecular C—H⋯O bonds (Table 2).

In the crystal structure, the benzene rings of centrosymmetrically related molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ overlap with a distance of 3.597 (5) Å between their centroids, indicating the existence of π–π stacking interactions. In addition, one strong N—H⋯O and two weak C—H⋯O intermolecular hydrogen bonds (Table 2) link the molecules into an extended three-dimensional network (Fig. 2).

Experimental

A mixture of 3-nitrobenzaldehyde (5 mmol), methyl 3-oxobutanoate (5 mmol), urea (7.5 mmol) and strontium trifluoromethanesulfonate (0.05 mmol) was heated at 343 K with stirring for 4 h. After cooling, the reaction mixture was poured into cold water and stirred for 5 min. The precipitate was suction filtered, washed with cold water, filtered and recrystallized from ethanol to afford the pure product (m.p. 461–

463 K). Single crystals suitable for X-ray data collection were obtained by slow evaporation of an ethanol solution. ^{1}H NMR (DMSO-d_6): δ 8.19–8.11 (*m*, 2H), 8.07 (*s*, 1H), 7.67–7.61 (*m*, 2H), 5.30 (*d*, 1H, *J* = 4.4 Hz), 3.59 (*s*, 3H), 3.11 (*s*, 3H), 2.99 (*s*, 3H). ^{13}C NMR (DMSO-d_6): δ 165.8, 157.5, 152.7, 147.6, 145.5, 132.9, 129.6, 122.4, 120.5, 101.0, 58.8, 51.6, 29.8, 16.1.

Crystal data

$C_{14}H_{15}N_3O_5$	$D_x = 1.448$ Mg m^{-3}
$M_r = 305.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2134
$a = 7.5489$ (7) Å	reflections
$b = 19.616$ (2) Å	$\theta = 2.5$–24.2°
$c = 9.5165$ (9) Å	$\mu = 0.11$ mm^{-1}
$\beta = 96.537$ (2)°	$T = 298$ (2) K
$V = 1400.0$ (2) Å^3	Block, colourless
$Z = 4$	$0.25 \times 0.16 \times 0.09$ mm

Data collection

Bruker SMART APEX area-detector diffractometer	2519 independent reflections
	2190 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan	$\theta_{max} = 25.2°$
(*SADABS*; Bruker, 2002)	$h = -9 \rightarrow 7$
$T_{min} = 0.972$, $T_{max} = 0.983$	$k = -23 \rightarrow 21$
7410 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.087$	$+ 1.3461P]$
$wR(F^2) = 0.168$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.28$	$(\Delta/\sigma)_{max} < 0.001$
2519 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
202 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.228 (4)	N1—C2	1.448 (4)
O2—C7	1.341 (4)	N2—C1	1.391 (4)
O2—C8	1.437 (4)	N2—C4	1.405 (4)
O3—C7	1.194 (4)	N2—C5	1.464 (4)
O4—N3	1.205 (4)	N3—C13	1.476 (5)
O5—N3	1.213 (4)	C2—C3	1.520 (4)
N1—C1	1.338 (4)	C2—C9	1.528 (4)
C7—O2—C8	117.0 (3)	C4—N2—C5	121.1 (3)
C1—N1—C2	121.8 (3)	O4—N3—O5	123.1 (4)
C1—N2—C4	120.8 (3)	O4—N3—C13	118.4 (3)
C1—N2—C5	115.8 (3)	O5—N3—C13	118.5 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H2$\cdots$O2	0.98	2.24	2.693 (4)	107
C6—H6$C\cdots$O3	0.96	2.15	2.897 (5)	133
N1—H1$\cdots$O1^i	0.86	2.07	2.901 (3)	162
C5—H5$C\cdots$O1^{ii}	0.96	2.60	3.398 (5)	141
C8—H8$A\cdots$O4^{iii}	0.96	2.52	3.413 (6)	155

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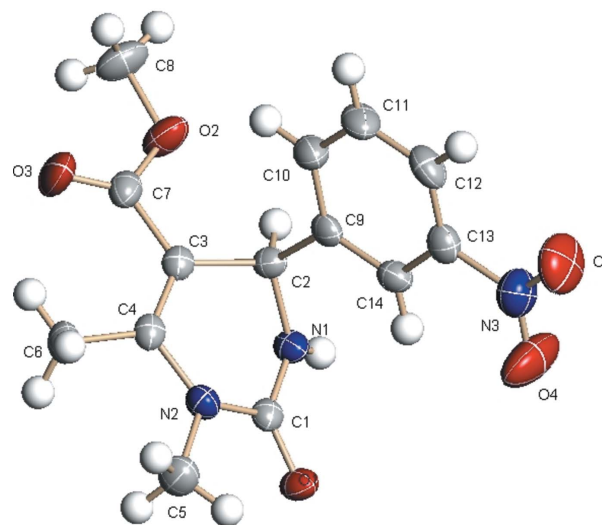

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.
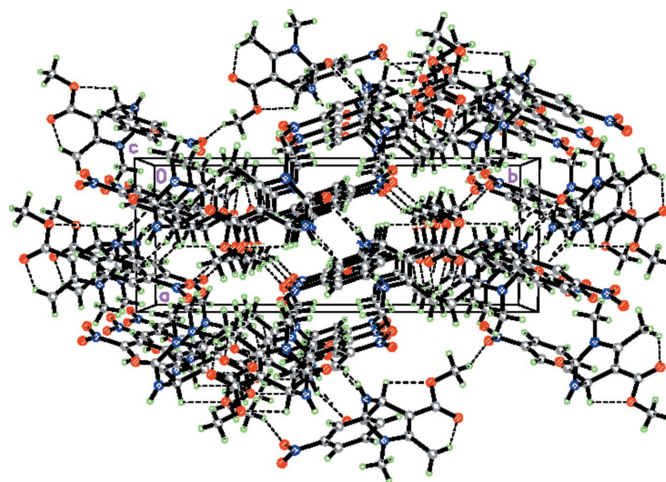

Figure 2
The crystal packing of (I), showing intra- and intermolecular hydrogen-bonding interactions as dashed lines.

All H atoms were positioned geometrically and allowed to ride on their parent atoms (C—H = 0.93, 0.96 and 0.98 Å for aromatic, methyl and methine H atoms, respectively, and N—H = 0.86 Å), with U_{iso}(H) = $1.2U_{eq}$(C,N) or $1.5U_{eq}$(methyl C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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, 2002); software used to prepare material for publication: *SHELXL97*.

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