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Methyl 4-(3-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

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Key indicators

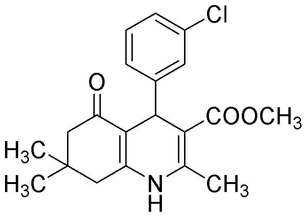
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.003 Å
R factor = 0.055
wR factor = 0.130
Data-to-parameter ratio = 17.7

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

The title compound, $C_{20}H_{22}ClNO_3$, was synthesized by the reaction of 3-chlorobenzaldehyde, 5,5-dimethyl-1,3-cyclohexanedione and methyl 2-aminocrotonate in an ionic liquid medium. The X-ray analysis reveals that the nitrogen-containing ring adopts a boat conformation and the cyclohexene ring has a half-chair conformation. Intermolecular N—H···O bonds in the structure lead to the formation of chains.

Comment

1,4-Dihydropyridines (1,4-DHPS) are well known compounds as a consequence of their pharmacological profile, *e.g.* their use as calcium channel modulators. A series of 3-chlorophenyl-1,4-dihydropyridine derivatives has been shown to produce different degrees of inhibition of parasite growth and respiration (Bossert *et al.*, 1981; Kappe *et al.*, 1997; Reinhard, *et al.*, 2003).



(I)

Room-temperature ionic liquids, especially those based on the 1-*N*-alkyl-3-methylimidazolium cation, have shown great promise as an attractive alternative to conventional solvents (Wasserscheid & Keim, 2000; Welton, 1999). They are non-volatile, recyclable, non-explosive, easy to handle and thermally robust. In many cases, the reaction products are weakly soluble in the ionic phase, so they can be easily separated by simple extraction with diethyl ether. Because of the great potential of room-temperature ionic liquids as novel reaction media for catalytic processes, much attention is currently focused on organic reactions conducted in ionic liquids. In view of this and the interest in 1,4-DHPs, the title compound, (I), was synthesized in 95% yield in a 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid at ambient temperature and its structure determined.

In (I) (Fig. 1 and Table 1), the N-containing ring of the hexahydroquinoline nucleus adopts a boat conformation. Atoms C3 and N1 deviate from the least-squares plane defined by atoms C1, C2, C4 and C5 by 0.299 (2) and 0.119 (2) Å, respectively. The cyclohexene ring has a half-chair conformation in which atom C8 deviates from the C1/C2/C6/C7/C9 plane by 0.647 (2) Å. The dihedral angle formed between the

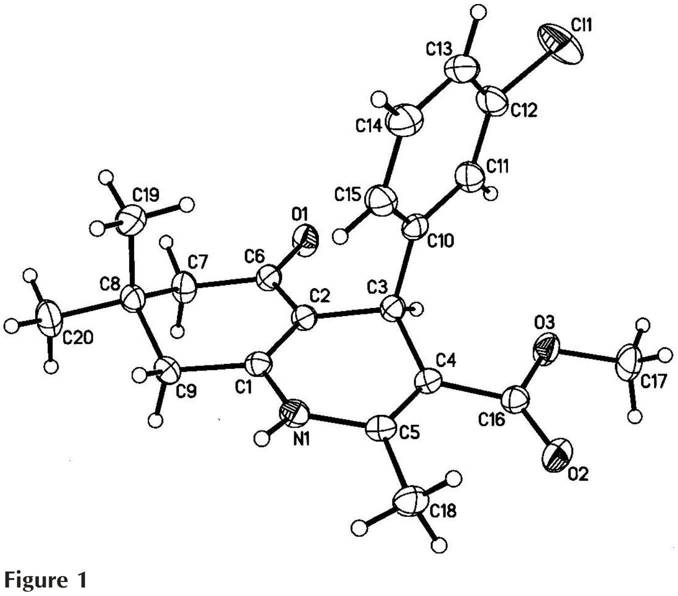


Figure 1
The molecular structure of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids.

C1/C2/C4/C5 plane and the C10–C15 benzene ring is 89.7 (2)°, indicating a perpendicular disposition.

Intermolecular N1—H1⋯O1($x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$) hydrogen bonds (Fig. 2 and Table 2) lead to the formation of polymeric chains.

Experimental

The title compound, (I), was prepared by the reaction of 3-chlorobenzaldehyde (0.28 g, 2 mmol), dimedone (0.28 g, 2 mmol) and methyl 2-amino-crotonate (0.23 g, 2 mmol) in the presence of a 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid (2 ml) held at 353 K for 5 min (yield 95%, m.p. 481–483 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an EtOH solution of the compound. Analysis calculated: C 66.75, H 6.16, N 3.89%; found: C 66.64, H 6.04, N 4.09%. ^{1}H NMR (CDCl$_3$): 0.98 (*s*, 3H, CH$_3$), 1.08 (*s*, 3H, CH$_3$), 2.40 (*s*, 3H, CH$_3$), 3.63 (*s*, 3H, CH$_3$), 2.15–2.33 (*m*, 4H, 2CH$_2$), 5.06 (*s*, 1H, CH), 6.03 (*s*, 1H, NH), 7.07–7.36 (*m*, 4H, ArH); IR (cm^{-1}): 3279 (N—H), 3076 (Ar—H), 2962, 2850 (C—H), 1710, 1608 (C=O).

Crystal data

$C_{20}H_{22}ClNO_3$
$M_r = 359.84$
Monoclinic, $P2_1/n$
$a = 9.2293$ (17) Å
$b = 16.506$ (3) Å
$c = 12.354$ (2) Å
$\beta = 107.286$ (4)°
$V = 1797.0$ (5) Å^3
$Z = 4$
$D_x = 1.330$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7337 reflections
$\theta = 3.0$–27.5°
$\mu = 0.23$ mm^{-1}
$T = 193$ (2) K
Block, light yellow
0.42 × 0.30 × 0.19 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.909$, $T_{\max} = 0.957$
19 907 measured reflections
4094 independent reflections
3542 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 21$
$l = -15 \rightarrow 15$

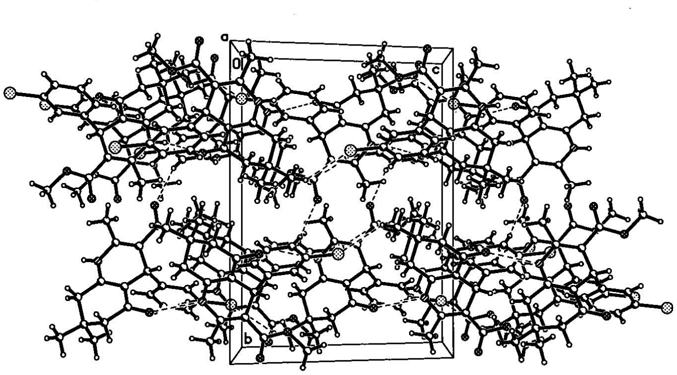


Figure 2
A molecular packing diagram for (I). Dashed lines indicate hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.130$
$S = 1.13$
4094 reflections
231 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.8384P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C6	1.236 (2)	C1—C9	1.500 (2)
N1—C1	1.366 (2)	C2—C6	1.444 (2)
N1—C5	1.391 (2)	C2—C3	1.513 (2)
C1—C2	1.359 (2)	C4—C5	1.352 (2)
C1—N1—C5	122.47 (14)	C1—C2—C3	121.01 (15)
C2—C1—N1	120.22 (15)	C2—C3—C4	109.98 (13)
C2—C1—C9	123.69 (15)	C5—C4—C3	121.28 (15)
C1—C2—C6	119.94 (15)	C4—C5—N1	119.29 (15)
C5—N1—C1—C2	−12.4 (2)	C1—C2—C6—C7	−0.7 (2)
C9—C1—C2—C6	−4.2 (3)	C2—C6—C7—C8	31.2 (2)
N1—C1—C2—C3	−6.6 (2)	C6—C7—C8—C9	−53.7 (2)
C2—C3—C4—C5	−24.2 (2)	C7—C8—C9—C1	48.2 (2)
C1—N1—C5—C4	11.3 (2)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1$^{\rm i}$	0.88	2.07	2.8841 (19)	154
C20—H20A⋯Cl1$^{\rm ii}$	0.98	2.81	3.511 (2)	129
C13—H13⋯O2$^{\rm iii}$	0.95	2.39	3.260 (2)	152

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

The H atoms were positioned geometrically and refined in the riding-model approximation, with C—H distances of 0.95 Å for aromatic, 1.00 Å for methine, 0.98 Å for methyl and 0.99 Å for methylene H atoms, and N—H = 0.88 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N), except for the methyl H atoms, for which $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C).

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

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molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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