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1-(3-Mesityl-3-methylcyclobutyl)-2-(piperidin-1-yl)ethanone

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 20.4

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

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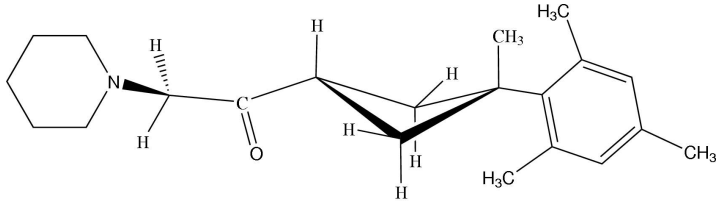
In the title compound, $C_{21}H_{31}NO$, the cyclobutane ring is puckered, with a dihedral angle of 25.74 (6)°. The mesityl and 2-*N*-piperidino-1-oxoethyl groups are in *cis* positions. The piperidine fragment adopts a chair conformation. Intermolecular C—H···O interactions involving the piperidine CH group and the keto O atom lead to the formation of dimers, and intermolecular C—H···π interactions involving the cyclobutane CH group and the benzene ring are responsible for the formation of a two-dimensional network.

Comment

3-Substituted cyclobutane carboxylic acid derivatives exhibit anti-inflammatory and antidepressant activities (Dehmlow & Schmidt, 1990), and also liquid crystal properties (Coghi *et al.*, 1976). Owing to their unique biological properties, the piperidines have been target molecules in organic synthesis (Weintraub *et al.*, 2003). In recent years, polyhydroxylated piperidine alkaloids have attracted much attention because some of them have the ability to act as selective glycosidase inhibitors (Stutz, 1999). As part of our ongoing study of cyclobutane derivatives, a crystal structure determination of the title compound, (I), has been undertaken and the results are presented here. Previously, we have reported the closely related compound 1-(3-mesityl-3-methylcyclobutyl)-2-(pyrrolidin-1-yl)ethan-1-one, (II) (Dinçer *et al.*, 2004). The main aim of the present investigation is to study the differences between the structures of (I) and (II), and also to establish the conformational features of various functional groups.



(I)

The molecular structure of (I), together with the atom-labelling scheme and the intramolecular hydrogen bonding, is shown in Fig. 1. In the crystal structure, the mesityl and 2-*N*-piperidino-1-oxoethyl groups are in *cis* positions with respect to the cyclobutane ring. The four-atom bridge is not planar, and the Φ_{CC} torsion angle (N1—C10—C11—C6) is −47.46 (13)°, which shows that the conformation about the C10—C11 bond is (−)-synclinal.

Although close to being planar, the cyclobutane ring in (I) is more puckered than that in (II), because of the steric hindrance of the substituents. The C9/C6/C7 plane forms a dihedral angle of 25.74 (6)° with the C7/C8/C9 plane [19.8 (3)°

in (II); Dinçer *et al.*, 2004]. However, when the bond lengths of the cylobutane ring in (I) are compared with those in (II), it is seen that there are no significant differences. In (I), the C═O bond distance is 1.2154 (14) Å, and this value is somewhat longer than that in (II) [1.186 (4) Å]. The C10—C11 bond distance is 1.5219 (16) Å, and this value is significantly shorter than that in (II) [1.572 (5) Å], suggesting that the attractive interaction involving the piperidine ring is greater than that for the pyrrolidine ring present in (II). The piperidine ring adopts a chair conformation, as is evident from the puckering parameters (Cremer & Pople, 1975): Q = 0.5849 (13) Å, θ = 175.48 (14)° and φ = 188.394 (13)° for the atom sequence N1/C1–C5. Atoms N1 and C3 are on opposite sides of the C1/C2/C4/C5 plane and displaced from it by 0.2656 (8) and 0.2130 (11) Å, respectively.

As a point of difference from (II), in the molecular structure, a weak intramolecular C9—H9*B*···O1 hydrogen bond (Table 2) results in the formation of a five-membered ring, which is fused with the cyclobutane ring (Fig. 1). Furthermore, weak intermolecular C—H···O interactions are also observed. Pairs of intermolecular C1—H1*A*···O1 hydrogen bonds across a centre of inversion result in the formation of dimers, generating an $R_2^2(12)$ ring. The dimers are linked to each other *via* intermolecular C9—H9···π(benzene) interactions (Fig. 2). A two-dimensional network is formed by C—H···O and C—H···π(benzene) interactions.

Experimental

A solution of 1-mesityl-1-methyl-3-(2-chloro-1-oxoethyl)cyclobutane (2.65 g, 10 mmol) and piperidine (1.70 g, 20 mmol) in absolute ethanol (50 ml) was refluxed with continuous stirring and monitoring of the course of the reaction by IR spectroscopy. After cooling to room temperature and the addition of water (200 ml), the target product (I) was precipitated, filtered off, washed with copious amounts of water and dried in air. Shiny crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution. Yield 3.04 g, 97%. M.p. 371 K. IR (ν, cm^{-1}): 1714 (C═O); ^{1}H NMR ($CDCl_3$, TMS, p.p.m.): δ 1.56 (*s*, 3H, –CH_3, on cyclobutane), 2.10–2.79 (*m*, 14H, –CH_2–, on cyclobutane plus piperidine), 2.20 (*s*, 9H, –CH_3 on aromatics), 3.09 (*s*, 2H, –CH_2– adjacent to carbonyl), 3.46 (*q*, 1H, J = 3.29 Hz, >CH–, on cyclobutane), 6.73 (*s*, 2H, aromatics).

Crystal data

$C_{21}H_{31}NO$
M_r = 313.47
Monoclinic, $P2_1/n$
a = 13.3063 (7) Å
b = 9.8112 (3) Å
c = 13.9186 (7) Å
β = 91.702 (4)°
V = 1816.28 (14) Å^3
Z = 4
D_x = 1.146 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 333 reflections
θ = 2.1–28.0°
μ = 0.07 mm^{-1}
T = 100 K
Prism, light yellow
0.46 × 0.32 × 0.20 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.666, T_{max} = 0.948
30 598 measured reflections
4334 independent reflections
3647 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 28.0°
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$

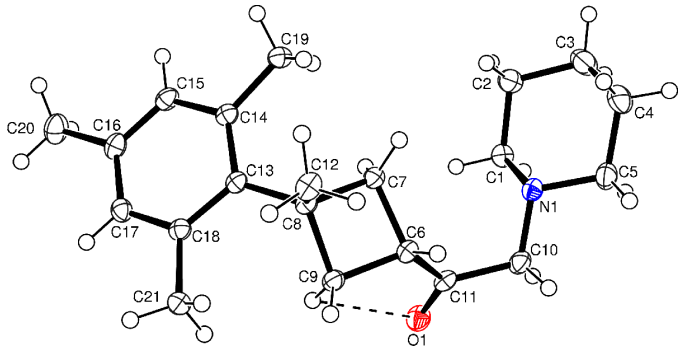


Figure 1
An *ORTEP-3* (Farrugia, 1997) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular C—H···O hydrogen bond is represented by a dashed line.

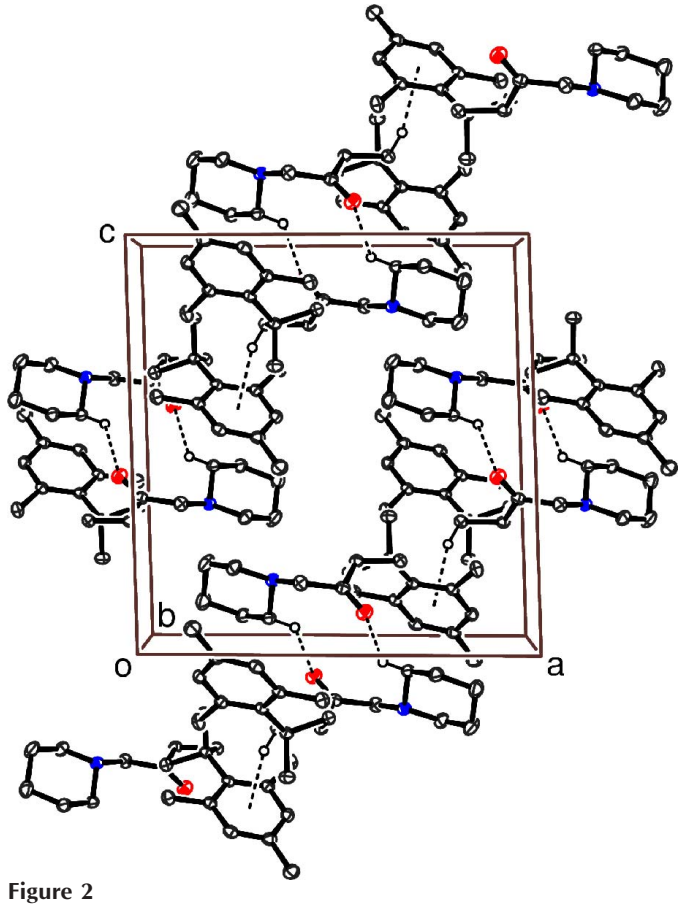


Figure 2
A projection of the crystal structure of (I) along the b axis. Dashed lines show the C—H···O and C—H···π(benzene) intermolecular interactions. H atoms have been omitted unless they are involved in hydrogen bonding.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.112
S = 1.04
4334 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.587P]$ where P 97 = $(F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0109 (17)

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.2154 (14)	C6—C7	1.5560 (15)
N1—C10	1.4549 (15)	C7—C8	1.5639 (15)
N1—C5	1.4657 (15)	C8—C13	1.5250 (15)
N1—C1	1.4702 (14)	C8—C12	1.5344 (15)
C6—C11	1.5064 (15)	C8—C9	1.5642 (15)
C6—C9	1.5322 (15)	C10—C11	1.5219 (16)
C10—N1—C5	110.48 (9)	C6—C7—C8	89.27 (8)
C10—N1—C1	109.71 (9)	C7—C8—C9	86.63 (8)
C5—N1—C1	109.40 (9)	C6—C9—C8	90.13 (8)
C9—C6—C7	88.03 (8)	N1—C10—C11	112.49 (9)
C5—N1—C10—C11	168.37 (9)	C9—C6—C11—C10	−169.43 (9)
C1—N1—C10—C11	−70.94 (12)	C7—C6—C11—C10	86.74 (12)
C9—C6—C11—O1	8.08 (16)	N1—C10—C11—O1	134.98 (11)
C7—C6—C11—O1	−95.75 (14)	N1—C10—C11—C6	−47.46 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*B*···O1	0.97	2.57	2.8903 (14)	100
C1—H1*A*···O1^{i}	0.97	2.65	3.3508 (15)	130
C9—H9*A*···*Cg*1^{ii}	0.97	2.61	3.5435 (14)	160

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

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.98, 0.97, 0.96 and 0.93 Å for CH, CH_2, CH_3 and CH(aromatic), respectively. The displacement parameters of the H atoms were constrained as $U_{iso}(H) = 1.2U_{eq}(C)$ ($1.5U_{eq}$ for methyl groups>.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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