Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 4-oxo-2,6-diphenyl-4-piperidine-3-carboxylate

M. Subha Nandhini,[a] V. Vijayakumar,[b] A. Mostad,[c] M. Sundaravadivelu[b] and S. Natarajan[a]*

[a]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India, [b]Department of Chemistry, Gandhigram Rural Institute (Deemed University), Gandhigram 624 302, India, and [c]Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo 3, Norway.

Correspondence e-mail: s_natarajan50@yahoo.com

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.068
wR factor = 0.183
Data-to-parameter ratio = 18.4

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

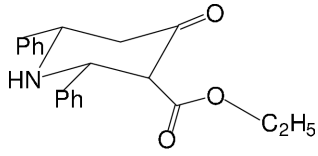
© 2003 International Union of Crystallography
Printed in Great Britain – all rights reserved

Received 23 September 2003
Accepted 1 October 2003
Online 7 October 2003

The asymmetric unit of the title compound, $C_{20}H_{21}NO_3$, contains two crystallographically independent molecules, approximately related by a local twofold axis. These two molecules differ from each other in the orientation of the ethyl group. In both molecules, the piperidone ring adopts a slightly distorted chair conformation, with the phenyl rings and carbethoxy group attached equatorially. The crystal packing is characterized by C—H···π and C—H···O interactions.

Comment

Nitrogen heterocycles, in particular piperidone alkaloids, occur in both plants and animals and some of them possess a variety of biological activity, including cytotoxic and anticancer properties (Dimmock *et al.*, 1990; Mutus *et al.*, 1989). The 2,6-disubstituted 4-piperidones have various pharmacological activities. A series of investigations on the synthesis, NMR and crystal structure elucidation of piperidine derivatives is being carried out in our laboratory. Recently, the crystal structure of 2,6-bis(4-methylphenyl)-3-phenylpiperidin-4-one was elucidated in our laboratory (Subha Nandhini *et al.*, 2003). We report here the structure of ethyl 4-oxo-2,6-diphenyl-4-piperidine-3-carboxylate, (I).



Ph = C_6H_5

(I)

The asymmetric unit of (I) consists of two crystallographically independent molecules (*A* and *B*), approximately related by a local twofold axis (Fig. 1). These two molecules differ from each other in the orientation of the ethyl group. In both molecules, the piperidone ring has a slightly distorted chair conformation, which may be due to the presence of the bulky aryl groups at C2, C6 and carbethoxy group at C3. The phenyl rings and carbethoxy group are oriented equatorially with respect to the piperidone ring. The conformations of the molecules seem to be similar to those observed in related structures reported by Subha Nandhini *et al.* (2003), Nilofar Nissa *et al.* (2001), Sekar *et al.* (1990, 1993), Singh *et al.* (1990) and Zongchao *et al.* (1988).

The bond length of C2—C3 is slightly greater than that of C5—C6 (Table 1); this may be to minimize the steric effect of the phenyl (at C2 and C6) and carbethoxy (at C3) substituents.

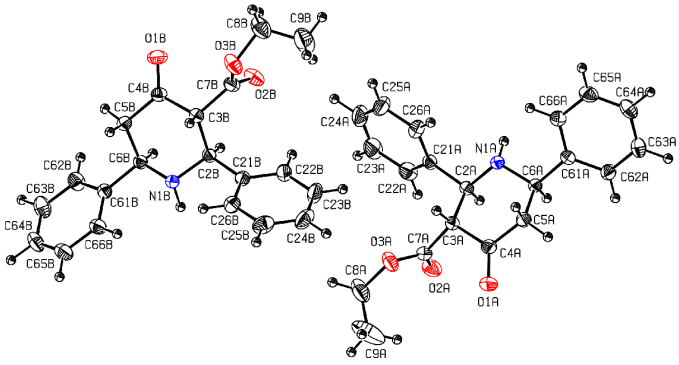


Figure 1
The structure of the asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

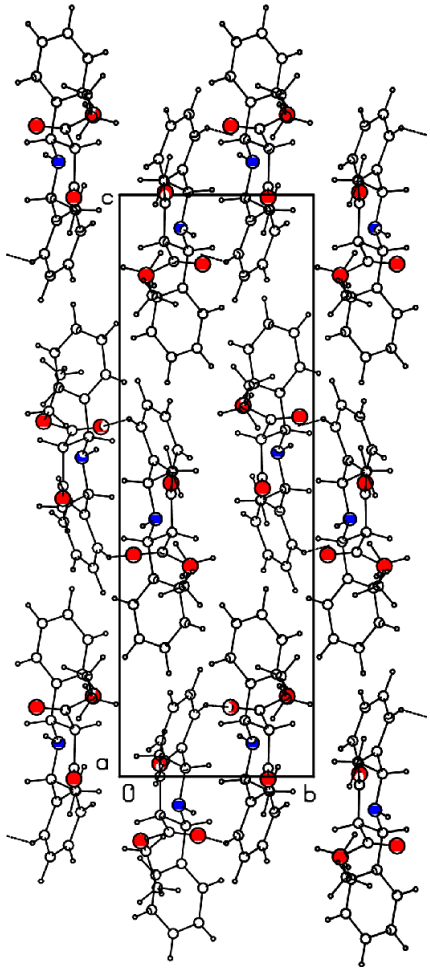


Figure 2
A packing diagram for (I), viewed down the *a* axis.

The bond length C6—C61 deviates slightly and C2—C21 agrees with the overall distances of Csp^2—Csp^3 bond [1.513 (4) Å; Allen *et al.*, 1987]. The endocyclic angles C26—C21—C22 and C66—C61—C62 (Table 1) are slightly smaller than the average value of 120°, as observed in related structures (Subha Nandhini *et al.*, 2003; Nilofar Nissa *et al.*, 2001; Singh *et al.*, 1990; Eswaramoorthy, 1992). This may be due to conjugation.

The molecules aggregate as alternate columns of inversion-related molecules along the *b* axis. Apart from the C—H···O and C—H···π interactions listed in Table 2, there are no other notable intermolecular interactions. The N-bound H atoms, H1*A* and H1*B*, are not involved in any hydrogen bonds.

Experimental

A mixture of benzaldehyde (21.2 ml), ethyl acetate (13.0 ml) and ammonium acetate (7.7 g) was heated gently until the colour of the solution changed to orange. The solution was stored at room temperature for 24 h. Dry ether (50 ml) and concentrated HCl (2–5 ml) were added and the mixture was stirred. The precipitate formed was filtered off using a Buchner funnel and washed with a 1:1 ethanol–ether mixture. The hydrochloride salt was suspended in acetone and neutralized with (aqueous) ammonia solution. Water was added and the substance was filtered through a Buchner funnel and dried using a pistol drier (yield: 90%).

Crystal data

$C_{20}H_{21}NO_3$
M_r = 323.39
Monoclinic, $P2_1/c$
a = 20.261 (4) Å
b = 7.5561 (15) Å
c = 23.034 (5) Å
β = 100.11 (3)°
V = 3471.6 (12) Å^3
Z = 8
D_x = 1.237 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 2.5–23°
μ = 0.08 mm^{-1}
T = 150 (2) K
Block, colourless
0.44 × 0.30 × 0.24 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.97, T_{max} = 0.98
31988 measured reflections
8517 independent reflections
6735 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 28.3°
$h = -26 \rightarrow 26$
$k = -10 \rightarrow 9$
$l = -29 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.183
S = 1.10
8517 reflections
463 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 3.4759P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C4*A*	1.213 (2)	O1*B*—C4*B*	1.210 (2)
O2*A*—C7*A*	1.205 (3)	O2*B*—C7*B*	1.206 (3)
O3*A*—C7*A*	1.334 (2)	O3*B*—C7*B*	1.344 (2)
O3*A*—C8*A*	1.465 (3)	O3*B*—C8*B*	1.481 (3)
N1*A*—C6*A*	1.468 (2)	N1*B*—C6*B*	1.469 (2)
N1*A*—C2*A*	1.469 (2)	N1*B*—C2*B*	1.470 (2)
C2*A*—C21*A*	1.514 (2)	C2*B*—C21*B*	1.518 (3)
C2*A*—C3*A*	1.554 (2)	C2*B*—C3*B*	1.553 (2)
C5*A*—C6*A*	1.541 (2)	C5*B*—C6*B*	1.541 (3)
C6*A*—C61*A*	1.520 (2)	C6*B*—C61*B*	1.521 (2)
C66*A*—C61*A*—C62*A*	118.99 (17)	C66*B*—C61*B*—C62*B*	118.93 (18)
C22*B*—C21*B*—C26*B*	118.89 (19)	C26*A*—C21*A*—C22*A*	118.83 (19)
C7*A*—O3*A*—C8*A*—C9*A*	94.7 (3)	C7*B*—O3*B*—C8*B*—C9*B*	−81.2 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C6A—H6A···O2B^{i}	0.98	2.69	3.332 (2)	124
C6B—H6B···O2A^{ii}	0.98	2.83	3.479 (2)	124
C62A—H62A···O2B^{i}	0.93	2.48	3.324 (3)	153
C62B—H62B···O2A^{ii}	0.95	2.60	3.474 (3)	154
C65A—H65A···O1B^{iii}	0.93	2.63	3.380 (3)	138
C65B—H65B···O1A^{iv}	0.97	2.64	3.421 (3)	138
N1A—H1A···$Cg3^{v}$	0.90 (3)	2.78 (2)	3.586 (2)	151 (2)
N1B—H1B···$Cg4^{vi}$	0.95 (2)	2.80 (2)	3.677 (2)	155 (2)
C9A—H9A3···$Cg4^{vii}$	0.96	3.04	3.911 (4)	151
C8B—H8B1···$Cg3^{viii}$	0.97	3.21	4.159 (2)	167
C23A—H23A···$Cg2^{ix}$	0.99	3.17	3.906 (3)	133
C23B—H23B···$Cg1$	0.94	3.10	3.848 (3)	139
C63B—H63B···$Cg2^{vi}$	1.04	3.37	3.928 (3)	115

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $1-x, -y, 1-z$; (vi) $-x, 1-y, -z$; (vii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (viii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ix) $x, y-1, z$. $Cg1$, $Cg2$, $Cg3$ and $Cg4$ denote centroids of rings C21A—C26A, C21B—C26B, C61A—C66A and C61B—C66B, respectively.

Atoms H1A and H1B were found in a difference Fourier map and their positional and isotropic displacement parameters were refined. The remaining H atoms were placed in calculated positions and allowed to ride on their parent C atoms, with the U_{iso} values set to $1.5U_{eq}$(parent atom) for the methyl H atoms and $1.2U_{eq}$(parent atom) for the other H atoms. For the aromatic H atoms, the C—H distances were allowed to refine freely and for other C-bound H atoms the C—H distances were fixed in the range 0.96–0.98 Å. A rotating-group model was used for the methyl groups. The highest difference peak is almost twice the absolute value of the deepest hole. The highest peaks were observed close to carbethoxy groups, suggesting disorder, but no reasonable disorder model was found.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

MSN and SN thank the UGC for the Special Assistance Programme.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Bruker (1998). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SMART-NT* and *SAINT-NT*. Versions. 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.

Dimmock, J. R., Arora, V. K., Wonko, S. L., Hamon, N. W., Quail, J. W., Jia, Z., Warrington, R. C., Fang, W. D. & Lee, J. S. (1990). *Drug Des. Deliv*. **6**, 183–194.

Eswaramoorthy, S. (1992). PhD Thesis, University of Madras, Chennai, India.

Mutus, B., Wagner, J. D., Talpas, C. J., Dimmock, J. R., Phillips, O. A. & Reid, R. S. (1989). *Anal. Biochem.* pp. 237–243.

Nilofar Nissa, M., Velmurugan, D., Narasimhan, S., Rajagopal, V. & *Kim*, M.-J. (2001). *Acta Cryst.* E**57**, o996–o998.

Sekar, K., Parthasarathy, S. & Radhakrishnan, T. R. (1990). *Acta Cryst.* C**46**, 1153–1155.

Sekar, K., Parthasarathy, S. & Radhakrishnan, T. R. (1993). *Acta Cryst.* C**49**, 93–95.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Singh, P., Levine, S. G. & Kasdore, K. (1990). *Acta Cryst.* C**46**, 2469–2470.

Spek, A. L. (1999). *PLATON*. Utrecht University, The Netherlands.

Subha Nandhini, M., Srinivasan, M., Krishnakumar, R. V., Mostad, A., Perumal, S., Selvaraj, S. & Natarjan, S. (2003). *Acta Cryst.* E**59**, o1538–o1540.

Zongchao, J., Wilson, Q. J., Arora, V. K. & Dimmock, J. R. (1988). *Acta Cryst.* C**44**, 2114–2117.