

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.095$
 $S = 1.083$
 2417 reflections
 166 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.251 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.242 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 0.04 (8)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
S1	0.94722 (7)	0.136182 (8)	0.05891 (11)	0.03939 (14)
O1	0.9504 (3)	0.19534 (3)	-0.0037 (4)	0.0662 (6)
O2	1.0364 (3)	0.20886 (4)	0.3435 (4)	0.0798 (7)
O3	1	0	-0.1333 (4)	0.0404 (4)
C1	1.0021 (3)	0.16063 (4)	0.2608 (4)	0.0397 (4)
C2	1.0612 (3)	0.14842 (4)	0.4572 (4)	0.0426 (5)
C3	1.0646 (3)	0.11879 (4)	0.4423 (4)	0.0389 (4)
C4	1.0074 (2)	0.10899 (4)	0.2350 (4)	0.0302 (4)
C5	0.9978 (4)	0.19091 (4)	0.2105 (4)	0.0501 (6)
C6	0.9571 (5)	0.22377 (5)	-0.0819 (7)	0.0847 (11)
C7	0.9994 (2)	0.08004 (3)	0.1510 (4)	0.0286 (3)
C8	1.0826 (2)	0.05803 (4)	0.2674 (3)	0.0328 (4)
C9	1.0803 (2)	0.03076 (4)	0.1847 (4)	0.0343 (4)
C10	0.9953 (2)	0.02546 (3)	-0.0218 (4)	0.0303 (4)
C11	0.9110 (2)	0.04687 (4)	-0.1404 (4)	0.0326 (4)
C12	0.9138 (2)	0.07378 (4)	-0.0547 (3)	0.0322 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S1—C1	1.720 (2)	O1—C6	1.439 (3)
S1—C4	1.7255 (19)	O2—C5	1.199 (3)
O1—C5	1.330 (4)	O3—C10	1.387 (2)
C1—S1—C4	92.05 (11)	O2—C5—C1	124.5 (2)
C5—O1—C6	116.6 (2)	O1—C5—C1	110.7 (2)
O2—C5—O1	124.9 (2)		

The H atoms of the methyl groups were placed in geometrically optimized positions and constrained to ride on their parent C atom, while all other H atoms were refined freely (x , y , z and U_{iso}); C—H distances are in the range 0.89 (2)–0.94 (2) \AA .

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1085). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1519–1522

Methyl 1-(4-chlorobenzyl)-2-oxocyclohexane-1-carboxylate and methyl (2*RS*,4*aRS*,8*aRS*)-2-(4-chlorobenzyl)-3-oxoperhydropthalene-2-carboxylate

H. SURYA PRAKASH RAO,^a S. RAJAMATHE,^a S. SHANMUGA SUNDARA RAJ,^b KANDASAMY CHINNAKALI,^b† IBRAHIM ABDUL RAZAK^b AND HOONG-KUN FUN^b

^aDepartment of Chemistry, Pondicherry University, Pondicherry 605 014, India, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my

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Abstract

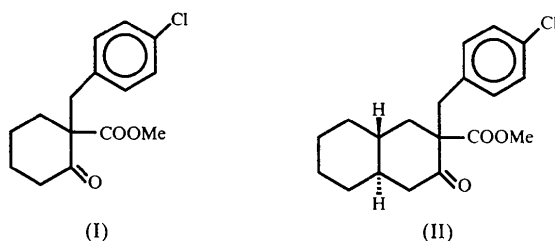
In the title compounds, methyl 1-(4-chlorobenzyl)-2-oxocyclohexane-1-carboxylate, $C_{15}H_{17}ClO_3$, (I), and methyl (2*RS*,4*aRS*,8*aRS*)-2-(4-chlorobenzyl)-3-oxoper-

† On leave from: Department of Physics, Anna University, Chennai 600 025, India.

hydronaphthalene-2-carboxylate, C₁₉H₂₃ClO₃, (II), the cyclohexane rings adopt chair conformations. In (I), the carboxylate group is attached in an axial position and in (II), it is in a biaxial position. The dihedral angles between the mean planes through the cyclohexane ring and the phenyl substituent are 48.89 (9) and 24.61 (10)^o in (I) and (II), respectively.

Comment

The title compounds were prepared as part of studies on the effects of remote functional groups on the stereoselectivity of cyclic β -ketoester alkylations (Surya Prakash Rao *et al.*, 1994). The structures of esters (I) and (II) were confirmed by X-ray crystal structure analysis and were determined in order to elucidate the molecular conformation.



The bond lengths and angles observed in (I) and (II) are comparable with those observed in a related structure (Rajamathe *et al.*, 1999). In both structures, the $C_{sp^3}-C_{sp^2}$ bond distances involving the C2 atom are longer than the normal value of 1.507 Å (Allen *et al.*, 1987). In both molecules, the cyclohexane rings adopt chair conformations. The X-ray data shows that in the solid state, the 4-chlorobenzyl group of (I) preferentially occupies an equatorial position and the ester group occupies an axial position, as can be seen

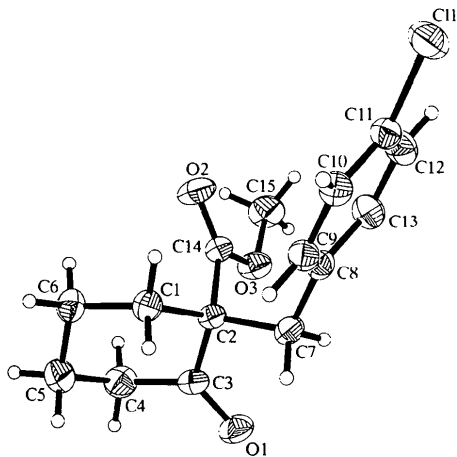


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

from the torsion angles C3—C2—C7—C8 of 177.3 (1)^o and C7—C2—C14—O3 of 74.8 (2)^o, characterizing a synclinal conformation for the C7 and O3 atoms. In the alkylated product (II), the carboxylate group is in a biaxial position, with atoms C11 and O3 in a synperiplanar conformation [C11—C2—C18—O3 28.9 (2)^o], and due to preference for axial alkylation, the 4-chlorobenzyl group is oriented towards the axial position. A C—H... π interaction is observed in (II) which involves C10 and the phenyl ring of the screw-related molecule.

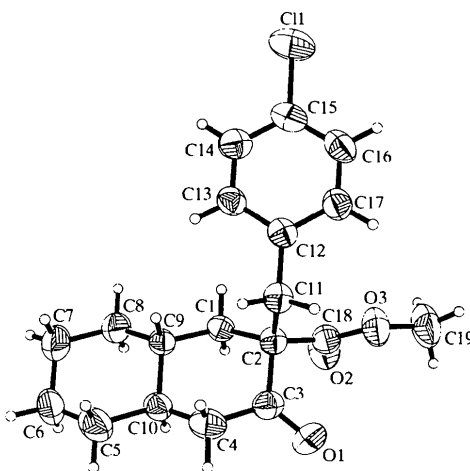


Fig. 2. The structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

For the preparation of (I), a solution of methyl 2-oxocyclohexanecarboxylate (0.047 g, 0.3 mmol) in acetone (10 ml) was added to a stirred suspension of potassium carbonate (0.297 g, 1.5 mmol) in dry acetone (15 ml) under a nitrogen atmosphere. After stirring at room temperature for 20 min, freshly distilled 4-chlorobenzyl bromide (0.308 g, 1.5 mmol) in dry acetone (15 ml) was added over a period of 10 min. The reaction mixture was stirred at room temperature for 28 h to completion (TLC), and was then filtered through a pad of celite and concentrated under reduced pressure to a volume of about 5 ml. The residue was diluted with ether (50 ml) and the ether solution was washed with water (3 \times 20 ml) and brine (15 ml). Removal of the solvent resulted in a crude product which was purified by column chromatography on silica gel (100–200 mesh) with an increasing amount of ethyl acetate in hexane (5:95 to 10:90). Pooling of the fractions obtained and removal of the solvent resulted in pure (I) in 75% yield as a colourless crystalline solid. Crystals suitable for X-ray analysis were obtained by recrystallization from an ether-hexane solvent mixture. For the preparation of (II), alkylation of methyl (4aRS,8aRS)-3-oxoperhydronaphthalene-2-carboxylate (0.105 mg, 0.5 mmol) with freshly distilled 4-chlorobenzyl bromide (0.514 mg, 2.5 mmol) in the presence of potassium carbonate (0.345 mg, 2.5 mmol) in dry acetone (65 ml) under conditions described for the earlier experiment furnished a mixture of *E* and *Z* isomeric alkylated products in 90% yield

(0.186 g). The ^1H NMR spectrum indicated the *E:Z* isomer ratio to be 95:5. The individual isomers were separated by column chromatography on silica gel (100–200 mesh) with a hexane–ethyl acetate solvent mixture (90:10). The alkylated product (II) was obtained as a colourless crystalline solid which was further recrystallized from an ether–hexane solvent mixture to obtain crystals suitable for X-ray analysis.

Compound (I)*Crystal data* $\text{C}_{15}\text{H}_{17}\text{ClO}_3$ $M_r = 280.74$

Monoclinic

 $P2_1/c$ $a = 7.6230$ (1) Å $b = 9.9780$ (1) Å $c = 19.1161$ (1) Å $\beta = 99.730$ (1)° $V = 1433.10$ (2) Å³ $Z = 4$ $D_x = 1.301$ Mg m⁻³ D_m not measured*Data collection*

Siemens SMART CCD area-detector diffractometer

 ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

 $T_{\min} = 0.89$, $T_{\max} = 0.94$

9555 measured reflections

3530 independent reflections

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.119$ $S = 1.01$

3530 reflections

173 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.3300P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (Å, °) for (I)

C11–C11	1.750 (2)	O3–C14	1.337 (2)
O1–C3	1.205 (2)	O3–C15	1.450 (2)
O2–C14	1.190 (2)		
C14–O3–C15	116.5 (1)	O2–C14–C2	126.0 (2)
O2–C14–O3	123.6 (2)		
C1–C2–C7–C8	–61.9 (2)	C1–C2–C14–O3	–163.2 (1)
C3–C2–C7–C8	177.3 (1)	C3–C2–C14–O3	–44.0 (2)
C15–O3–C14–C2	–176.9 (2)		

Compound (II)*Crystal data* $\text{C}_{19}\text{H}_{23}\text{ClO}_3$ $M_r = 334.82$ Mo $K\alpha$ radiation $\lambda = 0.71073$ Å

Cell parameters from 5247

reflections

 $\theta = 2.16$ – 28.29 ° $\mu = 0.268$ mm⁻¹ $T = 293$ (2) K

Parallelepiped

 $0.46 \times 0.38 \times 0.22$ mm

Colourless

Monoclinic

 $P2_1/n$ $a = 11.7762$ (3) Å $b = 11.8495$ (4) Å $c = 13.0464$ (4) Å $\beta = 102.905$ (1)° $V = 1774.54$ (9) Å³ $Z = 4$ $D_x = 1.253$ Mg m⁻³ D_m not measured*Data collection*

Siemens SMART CCD area-detector diffractometer

 ω scans

Absorption correction:

multi-scan (empirical

using SADABS; Sheldrick,

1996)

 $T_{\min} = 0.93$, $T_{\max} = 0.97$

Cell parameters from 4448 reflections

 $\theta = 2.11$ – 28.17 ° $\mu = 0.227$ mm⁻¹ $T = 293$ (2) K

Parallelepiped

 $0.34 \times 0.16 \times 0.14$ mm

Colourless

11 499 measured reflections
4316 independent reflections
2436 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.043$ $\theta_{\text{max}} = 28.17$ ° $h = -15 \rightarrow 15$ $k = 0 \rightarrow 15$ $l = 0 \rightarrow 17$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.054$ $wR(F^2) = 0.139$ $S = 1.008$

4316 reflections

209 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.3434P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 2. Selected geometric parameters (Å, °) for (II)

C11–C15	1.751 (2)	O3–C19	1.451 (3)
O1–C3	1.210 (3)	C2–C18	1.530 (3)
O2–C18	1.202 (2)	C2–C3	1.549 (3)
O3–C18	1.337 (3)		
C18–O3–C19	116.1 (2)	O2–C18–C2	124.1 (2)
O2–C18–O3	123.0 (2)	O3–C18–C2	112.9 (2)
C1–C2–C11–C12	–59.7 (2)	C1–C2–C18–O3	155.0 (2)
C3–C2–C11–C12	–179.1 (2)	C3–C2–C18–O3	–88.5 (2)
C19–O3–C18–C2	178.9 (2)		

Table 3. Hydrogen-bonding geometry (Å, °) for (II)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C10–H10A $\cdots\pi$ (Ph')	0.98	2.64	3.613 (3)	172

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$.

For both compounds, data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structures: SHELXTL (Sheldrick, 1997); program(s) used to refine structures: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1299). Services for accessing these data are described at the back of the journal.

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Intramolecular N—H···π(phenyl) and intermolecular C—H···π(phenyl) interactions in 5-amino-4-(4-methoxyphenyl)-2-phenyl-7-piperidino-1,6-naphthyridine-8-carbonitrile–benzene (2/1)

R. THIRUMURUGAN,^a S. SHANMUGA SUNDARA RAJ,^b
G. SHANMUGAM,^a HOONG-KUN FUN,^b V. RAGHUKUMAR^c
AND V. T. RAMAKRISHNAN^c

^aDepartment of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^cDepartment of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India. E-mail: rptm@cyberspace.org

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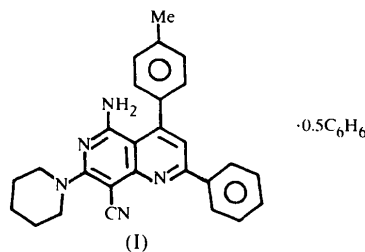
Abstract

The structure of the title compound, C₂₇H₂₅N₅O·0.5C₆H₆, has been determined from X-ray diffraction data. The compound crystallizes from benzene in the

triclinic system, space group *P* $\bar{1}$, with two molecules in the asymmetric unit. The naphthyridine ring system is almost planar and the six-membered piperidine ring adopts a chair conformation. Intramolecular N—H···π interactions are observed in the system with an N···π(phenyl centroid) distance of 3.619 (3) Å, and C—H···π interactions between the naphthyridine molecule and the solvent are also observed.

Comment

A number of 1,6-naphthyridine derivatives have been found to possess anti-inflammatory, anticonvulsant and insecticidal activities, and their physiological activity has been studied (Damon & Nadelson, 1981, 1982; Takeuchi & Hamada, 1976). They exhibit unique photophysical, photochemical and optical properties due to the charge-transfer interaction between the donor and acceptor substituents. They can behave as non-linear optical materials, which have various applications in the field of telecommunications (Murugan, 1997). The piperidine ring substituted at the seventh position of the 1,6-naphthyridine ring leads to pharmacological activity and is essential in the molecular structure of some important drugs (Lu *et al.*, 1991). However, few structural data have been reported for these compounds (Balogh *et al.*, 1986). For these reasons, the title compound, (I), was synthesized and its structure has been determined.



All the aromatic rings are planar with normal geometry and the piperidine ring, *C*, adopts a chair conformation. In molecule *A*, rings *C*, *D* and *E* make dihedral angles of 52.3 (1), 10.3 (1) and 63.8 (1)°, respectively, with the naphthyridine system (rings *A* and *B*), whereas in molecule *B*, these angles are 29.2 (5), 22.5 (6) and 80.0 (5)°, respectively. A *ZORTEP* (Zsolnai, 1997) plot of the two molecules in the asymmetric unit is shown in Fig. 1; the benzene solvent molecule, which is essentially planar and possesses usual geometry, has been omitted for clarity.

Amino N—H···π(phenyl) interactions have recently been theoretically postulated in model systems and experimentally described in globular proteins. It has also been suggested that such interactions may provide stability, contribute to the folding process and/or have a functional role in proteins (Levitt & Perutz, 1988). In