organic compounds

Methyl 4-(piperidin-1-ylcarbonyl)-benzoate

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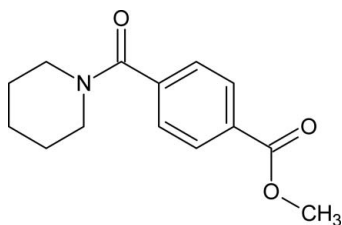Correspondence e-mail: doriguetto@unifal-mg.edu.br

In the title compound, $C_{14}H_{17}NO_3$, the piperidine ring has a chair conformation and an intramolecular C—H⋯O interaction stabilizes the molecular conformation. In the crystal, weak intermolecular C—H⋯O interactions occur.

Related literature

For Pd(0)-catalysed carbonylation of aryl halides, see: Jia & Morris (1991); Stille & Wong (1975); Magerlein, *et al.* (2001); Zhao *et al.* (2008). For procedural modifications for carbonylation reactions, see: Lagerlund & Larhed (2006). For the preparation of other piperidine derivatives, see Lima *et al.* (2002). For bond-length data, see: Allen *et al.* (1987).

Experimental

Crystal data

$C_{14}H_{17}NO_3$	$\gamma = 77.502\,(5)°$
$M_r = 247.29$	$V = 634.9\,(7)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.879\,(5)$ Å	Mo $K\alpha$ radiation
$b = 9.693\,(5)$ Å	$\mu = 0.09$ mm^{-1}
$c = 12.190\,(5)$ Å	$T = 150$ K
$\alpha = 69.684\,(5)°$	$0.05 \times 0.05 \times 0.05$ mm
$\beta = 82.535\,(5)°$	

Data collection

Oxford Diffraction Xcalibur Atlas Gemini Ultra diffractometer	2958 independent reflections
	2036 reflections with $I > 2\sigma(I)$
4958 measured reflections	$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	164 parameters
$wR(F^2) = 0.122$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
2958 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5A⋯O1	0.97	2.33	2.750 (3)	105
C14—H14B⋯O2^i	0.96	2.56	3.436 (4)	153

Symmetry code: (i) $x - 1, y, z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2043).

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supplementary materials

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Comment

There are many methods documented for the synthesis of a wide range of aromatic carboxylic acid derivatives, including benzamides. These compounds can be prepared using palladium(0)-catalyzed carbonylation of aryl halides with various nucleophiles (Zhao *et al.*, 2008; Margerlein *et al.*, 2001; Stille & Wong, 1975). The aminocarbonylation reaction of aryl halides achieved using the commercially available preligand [(^{t}Bu)$_3$PH]BF$_4$ as the key component in combination with Herrmann's palladacycle as the Pd source (Jia & Morris, 1991). In other studies procedures employing Mo(CO)$_6$ as a carbon monoxide releasing reagent, together with the use of controlled microwave irradiation as the energy source have been used to overcome the problems of introducing a gaseous reactant in small-scale high-speed protocols (Lagerlund & Larhed, 2006). In addition to other methods for obtaining derivatives of aromatic carboxylic acids, methyl 4-(piperidine-1-carbonyl)benzoate, C$_{14}$H$_{17}$N$_1$O$_3$ (I) was prepared from 4-(methoxycarbonyl)benzoic acid in excellent yield, exploring classical methodology, using thionyl chloride as the more electrophilic acid chloride, followed by treatment with piperidine in the presence of chloroform, at room temperature (Lima *et al.*, 2002). The study of this reaction showed that it could be controlled by the stoichimetric and reaction conditions, making the reaction of the piperidine with acyl chloride more favoured than with the ester group, by the use of an easy and convenient method.

In the structure of the title compound (Fig. 1) all bond lengths and angles are in agreement with literature values (Allen *et al.*, 1987). The aromatic ring and the ester are close to planar [C9–C10–C13–O3, -171.21 (12)°; C10–C13–O3–C14, 175.10 (11)°], whereas the carbonyl group is twisted out of the plane of the ring [C12–C7–C6–O1, 122.57 (15)°]. The piperidine ring has the more energetically favored boat conformation, with an intramolecular C5—H···O(carbonyl) interaction [C···O, 2.750 (3) Å] which stabilizes the molecular conformation. As expected, the supramolecular structure has no formal intermolecular hydrogen bonds (Fig. 2).

Experimental

A solution of 0.50 g of 4-(methoxycarbonyl)benzoic acid in 15 ml of chloroform, 0.30 ml of freshly distilled thionyl chloride and a catalytic amount of dimethylformamide was stirred under reflux for 1 h. After this time, the solvent was carefully evaporated at reduced pressure and a solution of 2.78 mmol of piperidine and 0.78 ml of triethylamine in 10 ml of chloroform was added. The reaction mixture was stirred for 30 min at room temperature, after which 10 ml of saturated sodium carbonate aqueous solution was added and the mixture extracted with chloroform (3x15 ml). The organic layer was separated, washed with water, rewashed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated at reduced pressure after which the compound was purified by column chromatography using Merck Silica Gel 60 (0.040–0.063 mm) and a mixture of hexane/ethyl acetate (8:2,V/V) as eluent (0.56 g, 82%). Crystals suitable for X-ray diffraction were grown from a mixture of hexane/ethyl acetate (8:2, V/V). IR (KBr, cm^{-1}): ν 1724, 1680, 1436, 1276, 1114. ^{1}H NMR (200 MHz, CDCl$_3$, p.p.m.): δ 1.27 (m, 2H), 1.70 (m, 2H), 3.33 (m, 2H), 3.74 (m, 2H), 3.95 (s, 3H), 7.47 (d, ^{3}J = 8.27 Hz), 8.09 (d, ^{3}J = 8.17). ^{13}C NMR (200 MHz, CDCl$_3$, p.p.m.): δ 24.5, 25.6, 26.5, 42.2, 51.2, 52.6, 126.7, 129.8, 130.8, 140.9, 166.4, 169.2.

supplementary materials

Refinement

The H atoms were located from the difference electron density synthesis and allowed to ride on their parent atoms, with C—H(aromatic) = 0.95 Å and C—H(aliphatic) = 0.97 Å and U_{iso}(H)= $1.5U_{eq}$ for methyl H atoms or $1.2U_{eq}$ for the remaining H atoms.
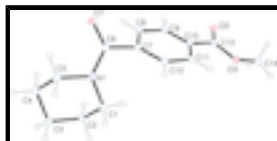
Figures

Fig. 1. The structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
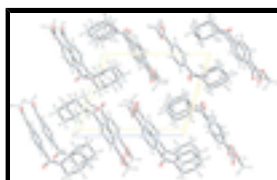
Fig. 2. The crystal packing of (I).

Methyl 4-(piperidin-1-ylcarbonyl)benzoate

Crystal data

$C_{14}H_{17}NO_3$	$Z = 2$
$M_r = 247.29$	$F(000) = 264$
Triclinic, $P\overline{1}$	$D_x = 1.294$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.879$ (5) Å	Cell parameters from 2414 reflections
$b = 9.693$ (5) Å	$\theta = 3.3$–$29.4°$
$c = 12.190$ (5) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 69.684$ (5)°	$T = 150$ K
$\beta = 82.535$ (5)°	Prism, colourless
$\gamma = 77.502$ (5)°	$0.05 \times 0.05 \times 0.05$ mm
$V = 634.9$ (7) Å^3	

Data collection

Oxford Diffraction Xcalibur Atlas Gemini Ultra diffractometer	$R_{int} = 0.033$
Detector resolution: 10.4186 pixels mm^{-1}	$\theta_{max} = 29.4°$, $\theta_{min} = 3.3°$
ω scans	$h = -7 \rightarrow 7$
4958 measured reflections	$k = -11 \rightarrow 12$
2958 independent reflections	$l = -13 \rightarrow 16$
2036 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.122$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
2958 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}
164 parameters	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O3	0.73762 (16)	0.78416 (10)	0.51830 (8)	0.0285 (2)
O2	1.10549 (18)	0.65801 (11)	0.54066 (9)	0.0377 (3)
O1	1.41852 (17)	1.30674 (12)	0.11938 (9)	0.0378 (3)
N1	1.14709 (19)	1.30851 (12)	0.00274 (9)	0.0232 (3)
C7	1.1642 (2)	1.13450 (14)	0.20582 (11)	0.0214 (3)
C11	0.8703 (2)	1.03005 (14)	0.34869 (11)	0.0220 (3)
H11	0.7179	1.0388	0.3812	0.026*
C10	1.0327 (2)	0.90031 (14)	0.39573 (11)	0.0211 (3)
C13	0.9679 (2)	0.76837 (15)	0.49291 (11)	0.0240 (3)
C4	1.3404 (3)	1.36011 (16)	−0.19405 (12)	0.0285 (3)
H4A	1.4773	1.2843	−0.167	0.034*
H4B	1.389	1.439	−0.2616	0.034*
C8	1.3275 (2)	1.00679 (15)	0.25594 (12)	0.0256 (3)
H8	1.482	1	0.2262	0.031*
C12	0.9354 (2)	1.14597 (14)	0.25349 (11)	0.0234 (3)
H12	0.8259	1.2316	0.2214	0.028*
C5	1.2352 (3)	1.42408 (15)	−0.09739 (12)	0.0281 (3)
H5A	1.3527	1.4615	−0.0725	0.034*
H5B	1.1085	1.5071	−0.1269	0.034*
C3	1.1643 (3)	1.29141 (15)	−0.22919 (12)	0.0275 (3)
H3A	1.2388	1.2434	−0.2858	0.033*
H3B	1.0372	1.3697	−0.266	0.033*
C2	1.0677 (2)	1.17679 (15)	−0.12294 (11)	0.0260 (3)
H2A	0.9453	1.1417	−0.1463	0.031*
H2B	1.1909	1.0915	−0.093	0.031*

C6	1.2522 (2)	1.25752 (15)	0.10503 (12)	0.0233 (3)
C9	1.2617 (2)	0.89002 (15)	0.34957 (12)	0.0259 (3)
H9	1.3711	0.8044	0.3817	0.031*
C1	0.9701 (2)	1.24338 (16)	−0.02665 (12)	0.0258 (3)
H1A	0.8338	1.3201	−0.0527	0.031*
H1B	0.9226	1.1659	0.0424	0.031*
C14	0.6585 (3)	0.65522 (17)	0.60534 (13)	0.0328 (3)
H14A	0.7227	0.5674	0.5842	0.049*
H14B	0.4912	0.6707	0.6088	0.049*
H14C	0.7094	0.6423	0.6806	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0247 (5)	0.0288 (5)	0.0255 (5)	−0.0082 (4)	0.0020 (4)	−0.0002 (4)
O2	0.0287 (6)	0.0328 (6)	0.0408 (6)	−0.0048 (5)	−0.0073 (5)	0.0027 (5)
O1	0.0341 (6)	0.0479 (6)	0.0359 (6)	−0.0257 (5)	−0.0023 (5)	−0.0085 (5)
N1	0.0275 (6)	0.0235 (6)	0.0219 (6)	−0.0127 (5)	0.0033 (4)	−0.0085 (5)
C7	0.0230 (7)	0.0256 (6)	0.0204 (7)	−0.0095 (5)	0.0002 (5)	−0.0110 (5)
C11	0.0180 (7)	0.0274 (7)	0.0226 (7)	−0.0067 (5)	0.0020 (5)	−0.0102 (6)
C10	0.0228 (7)	0.0254 (7)	0.0184 (6)	−0.0077 (5)	−0.0025 (5)	−0.0088 (5)
C13	0.0234 (7)	0.0286 (7)	0.0215 (7)	−0.0067 (6)	−0.0033 (5)	−0.0083 (6)
C4	0.0320 (8)	0.0276 (7)	0.0240 (7)	−0.0118 (6)	0.0052 (6)	−0.0050 (6)
C8	0.0175 (7)	0.0344 (7)	0.0260 (7)	−0.0073 (6)	0.0012 (5)	−0.0108 (6)
C12	0.0216 (7)	0.0233 (7)	0.0260 (7)	−0.0030 (5)	−0.0020 (5)	−0.0095 (6)
C5	0.0356 (8)	0.0213 (7)	0.0279 (7)	−0.0126 (6)	0.0033 (6)	−0.0064 (6)
C3	0.0311 (8)	0.0294 (7)	0.0221 (7)	−0.0055 (6)	−0.0010 (5)	−0.0090 (6)
C2	0.0286 (8)	0.0279 (7)	0.0251 (7)	−0.0089 (6)	−0.0044 (6)	−0.0099 (6)
C6	0.0214 (7)	0.0252 (7)	0.0259 (7)	−0.0077 (5)	0.0034 (5)	−0.0113 (6)
C9	0.0221 (7)	0.0291 (7)	0.0257 (7)	−0.0020 (6)	−0.0053 (5)	−0.0083 (6)
C1	0.0235 (7)	0.0308 (7)	0.0250 (7)	−0.0103 (6)	−0.0004 (5)	−0.0087 (6)
C14	0.0298 (8)	0.0348 (8)	0.0278 (8)	−0.0132 (6)	0.0000 (6)	0.0008 (6)

Geometric parameters (Å, °)

O3—C13	1.337 (2)	C4—H4B	0.97
O3—C14	1.4514 (17)	C8—C9	1.3826 (19)
O2—C13	1.2054 (17)	C8—H8	0.93
O1—C6	1.2320 (18)	C12—H12	0.93
N1—C6	1.3496 (18)	C5—H5A	0.97
N1—C1	1.4655 (19)	C5—H5B	0.97
N1—C5	1.4664 (17)	C3—C2	1.5223 (19)
C7—C12	1.391 (2)	C3—H3A	0.97
C7—C8	1.393 (2)	C3—H3B	0.97
C7—C6	1.5113 (18)	C2—C1	1.5213 (19)
C11—C12	1.3861 (18)	C2—H2A	0.97
C11—C10	1.3942 (19)	C2—H2B	0.97
C11—H11	0.93	C9—H9	0.93
C10—C9	1.387 (2)	C1—H1A	0.97

C10—C13	1.4918 (19)	C1—H1B	0.97
C4—C5	1.5191 (19)	C14—H14A	0.96
C4—C3	1.520 (2)	C14—H14B	0.96
C4—H4A	0.97	C14—H14C	0.96
C13—O3—C14	115.47 (10)	C4—C5—H5B	109.6
C6—N1—C1	125.92 (11)	H5A—C5—H5B	108.1
C6—N1—C5	119.70 (12)	C4—C3—C2	110.94 (12)
C1—N1—C5	113.67 (11)	C4—C3—H3A	109.5
C12—C7—C8	119.40 (12)	C2—C3—H3A	109.5
C12—C7—C6	123.66 (11)	C4—C3—H3B	109.5
C8—C7—C6	116.86 (12)	C2—C3—H3B	109.5
C12—C11—C10	120.13 (12)	H3A—C3—H3B	108
C12—C11—H11	119.9	C1—C2—C3	111.32 (11)
C10—C11—H11	119.9	C1—C2—H2A	109.4
C9—C10—C11	119.69 (12)	C3—C2—H2A	109.4
C9—C10—C13	118.03 (11)	C1—C2—H2B	109.4
C11—C10—C13	122.26 (12)	C3—C2—H2B	109.4
O2—C13—O3	123.63 (13)	H2A—C2—H2B	108
O2—C13—C10	124.22 (13)	O1—C6—N1	122.56 (12)
O3—C13—C10	112.10 (11)	O1—C6—C7	118.58 (12)
C5—C4—C3	110.68 (12)	N1—C6—C7	118.86 (12)
C5—C4—H4A	109.5	C8—C9—C10	120.14 (12)
C3—C4—H4A	109.5	C8—C9—H9	119.9
C5—C4—H4B	109.5	C10—C9—H9	119.9
C3—C4—H4B	109.5	N1—C1—C2	110.13 (12)
H4A—C4—H4B	108.1	N1—C1—H1A	109.6
C9—C8—C7	120.44 (13)	C2—C1—H1A	109.6
C9—C8—H8	119.8	N1—C1—H1B	109.6
C7—C8—H8	119.8	C2—C1—H1B	109.6
C11—C12—C7	120.15 (12)	H1A—C1—H1B	108.1
C11—C12—H12	119.9	O3—C14—H14A	109.5
C7—C12—H12	119.9	O3—C14—H14B	109.5
N1—C5—C4	110.27 (11)	H14A—C14—H14B	109.5
N1—C5—H5A	109.6	O3—C14—H14C	109.5
C4—C5—H5A	109.6	H14A—C14—H14C	109.5
N1—C5—H5B	109.6	H14B—C14—H14C	109.5
C12—C11—C10—C9	2.35 (19)	C5—C4—C3—C2	−54.04 (15)
C12—C11—C10—C13	−175.86 (12)	C4—C3—C2—C1	53.59 (15)
C14—O3—C13—O2	−2.60 (19)	C1—N1—C6—O1	171.43 (13)
C14—O3—C13—C10	175.10 (11)	C5—N1—C6—O1	1.71 (19)
C9—C10—C13—O2	6.5 (2)	C1—N1—C6—C7	−8.12 (19)
C11—C10—C13—O2	−175.28 (13)	C5—N1—C6—C7	−177.84 (11)
C9—C10—C13—O3	−171.20 (11)	C12—C7—C6—O1	122.57 (15)
C11—C10—C13—O3	7.03 (18)	C8—C7—C6—O1	−54.07 (17)
C12—C7—C8—C9	2.31 (19)	C12—C7—C6—N1	−57.86 (18)
C6—C7—C8—C9	179.10 (12)	C8—C7—C6—N1	125.50 (14)
C10—C11—C12—C7	−1.17 (19)	C7—C8—C9—C10	−1.1 (2)
C8—C7—C12—C11	−1.15 (19)	C11—C10—C9—C8	−1.19 (19)

C6—C7—C12—C11	−177.71 (12)	C13—C10—C9—C8	177.09 (12)
C6—N1—C5—C4	112.46 (14)	C6—N1—C1—C2	−112.70 (14)
C1—N1—C5—C4	−58.47 (15)	C5—N1—C1—C2	57.56 (15)
C3—C4—C5—N1	55.55 (15)	C3—C2—C1—N1	−54.21 (15)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···O1	0.97	2.33	2.750 (3)	105
C14—H14B···O2[i]	0.96	2.56	3.436 (4)	153

Symmetry codes: (i) $x-1, y, z$.

Fig. 1

Fig. 2