# organic compounds

# Methyl 4-[(1-methylcyclopent-3-en-1-yl)-carbonyl]benzoate

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In the title molecule, $C_{15}H_{16}O_3$, the non-H atoms of the benzoate group, the *p*-carbonyl, the attached ring C and its substituent methyl group lie on a mirror plane bisecting the five-membered ring, in which the C=C double bond is *cis* configured. Owing to symmetry considerations, the dihedral angle between the aromatic and the cyclopentyl rings is exactly 90°. There is an intermolecular C—H···O hydrogen bond, which links molecules into a one-dimensional supramolecular chain along the *c* axis in a head-to-tail fashion. These supramolecular chains, in turn, interact with each other along the *b* axis through weak $\pi$–$\pi$ contacts between neighboring aromatic rings [$Cg$···$Cg$ and interplanar distances of 3.70 (1) and 3.33 (1) Å].

## Related literature

For related literature, see: Braga *et al.* (2004); Xia *et al.* (2005, 2006); Yang *et al.* (2005).
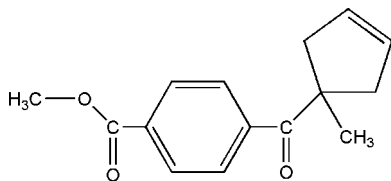


## Experimental

### Crystal data

C$_{15}$H$_{16}$O$_3$
$M_r$ = 244.28
Orthorhombic, *Pnma*
$a$ = 16.6215 (6) Å
$b$ = 6.6520 (2) Å
$c$ = 11.5581 (5) Å

$V$ = 1277.94 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 173 (2) K
0.54 × 0.12 × 0.06 mm

### Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
22416 measured reflections

1656 independent reflections
1290 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
$S$ = 1.06
1656 reflections

103 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.22 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C13—H13$A$···O1$^i$ | 0.96 | 2.45 | 3.339 (2) | 153 |

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

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2118).

## References

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**supplementary materials**

## Methyl 4-[(1-methylcyclopent-3-en-1-yl)carbonyl]benzoate

## C. Yang, W. Xia, X. Zhang, B. Li and B. Gou

### Comment

As one aspect of the green chemistry, photochemistry has attracted widespread interest and attention. During the course of our investigation on solid-state organic photochemistry (Braga *et al.*, 2004; Xia *et al.*, 2005; Xia *et al.*, 2006, Yang *et al.*, 2005), the title compound $C_{15}H_{16}O_3$ (I) was synthesized and its crystal structure is presented in this paper.

The asymmetric unit of the title compound contains sixteen non-hydrogen atoms of which two carbon lie in general position and the remaining thirteen plus two carbonyl and one ester O atoms lie onto a mirror plane (Fig. 1). Geometric parameters are in the usual ranges. The C=C double bond in the pentagonal ring is *cis* configured, and the deviation of C3 from the plane defined by C2, C1, C1[ii] and C2[ii] [symmetry code (ii) $x$, $0.5 − y$, $z$] is 0.28 (1) Å. Due to symmetry considerations, the dihedral angle between the aromatic and the cyclopentyl rings is exactly 90°. As shown in Fig. 2 and Table 1, there is an intermolecular H-bond between C13 and O1[i] [symmetry code: (i) $x$, $y$, $z − 1$] which leads to a 1-D supramolecular chain along *c*-axis in a head-to-tail fashion. These supramolecular chains, in turn, interact with each other along the *b*-axis through weak π-π contacts between neighboring aromatic rings, with *Cg···Cg* and interplanar distances of 3.70 (1) and 3.33 (1) Å (Fig. 3).

### Experimental

The preparation of the titled compound was conducted by the reaction of commercially available compounds, methyl 3-cyclopene carboxylate with LDA/MeI, reduction with LiAlH$_4$ and oxidation by pyridinium chlorochromate (PCC). After reaction with methyl 4-carboxylate phenylmagnesium bromide at −40°C, the target compound was obtained by oxidation with PCC.

### Refinement

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å for C$sp^2$ and 0.96 Å for methyl. $U_{iso}$(H) = xUeq(C), where $x$ = 1.2 for C$sp^2$ and 1.5 for methyl.
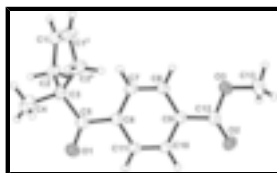
### Figures



Fig. 1. View of the title compound, with displacement ellipsoids drawn at the 50% probability level [symmetry code: (ii) $x$, $1/2 − y$, $z$].
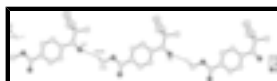


Fig. 2. The one-dimensional supramolecular chain along *c*-axis linked by intermolecular C—H···O bonds [symmetry code: (i) $x$, $y$, $z − 1$].
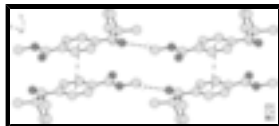
# supplementary materials



Fig. 3. A couple of neighboring chains showing the weak π-π contacts between interleaving aromatic rings linking them along the *b*-axis

## Methyl 4-[(1-methylcyclopent-3-en-1-yl)carbonyl]benzoate

*Crystal data*

| | |
|---|---|
| $C_{15}H_{16}O_3$ | $Z = 4$ |
| $M_r = 244.28$ | $F_{000} = 520$ |
| Orthorhombic, *Pnma* | $D_x = 1.270$ Mg m$^{-3}$ |
| Hall symbol: -P 2ac 2n | Mo $K\alpha$ radiation $\lambda = 0.71073$ Å |
| $a = 16.6215$ (6) Å | $\mu = 0.09$ mm$^{-1}$ |
| $b = 6.6520$ (2) Å | $T = 173$ (2) K |
| $c = 11.5581$ (5) Å | Block, colourless |
| $V = 1277.94$ (8) Å$^3$ | $0.54 \times 0.12 \times 0.06$ mm |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 1656 independent reflections |
| Radiation source: fine-focus sealed tube | 1290 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.043$ |
| Detector resolution: 10 pixels mm$^{-1}$ | $\theta_{max} = 28.0º$ |
| $T = 173(2)$ K | $\theta_{min} = 2.2º$ |
| φ and\ w scans | $h = -21 \rightarrow 21$ |
| Absorption correction: none | $k = -8 \rightarrow 8$ |
| 22416 measured reflections | $l = -15 \rightarrow 15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | H-atom parameters constrained |
| $wR(F^2) = 0.116$ | $w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.2712P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.06$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1656 reflections | $\Delta\rho_{max} = 0.27$ e Å$^{-3}$ |
| 103 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*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.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit S are based on $F^2$, conventional $R$-factors $R$ are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

|      | $x$          | $y$        | $z$           | $U_{iso}*/U_{eq}$ | Occ. (<1) |
| ---- | ------------ | ---------- | ------------- | ----------------- | --------- |
| C1   | 0.82779 (7)  | 0.3482 (2) | 0.16325 (12)  | 0.0432 (4)        |           |
| H1   | 0.8704       | 0.4256     | 0.1362        | 0.052*            |           |
| C2   | 0.75151 (7)  | 0.4356 (2) | 0.21171 (12)  | 0.0426 (4)        |           |
| H2A  | 0.7191       | 0.4960     | 0.1512        | 0.051*            |           |
| H2B  | 0.7631       | 0.5363     | 0.2701        | 0.051*            |           |
| C3   | 0.70802 (10) | 0.2500     | 0.26576 (15)  | 0.0365 (4)        |           |
| C4   | 0.72151 (14) | 0.2500     | 0.39724 (19)  | 0.0798 (10)       |           |
| H4A  | 0.7782       | 0.2500     | 0.4132        | 0.120*            |           |
| H4B  | 0.6974       | 0.1322     | 0.4303        | 0.120*            | 0.50      |
| H4C  | 0.6974       | 0.3678     | 0.4303        | 0.120*            | 0.50      |
| C5   | 0.61758 (10) | 0.2500     | 0.24182 (14)  | 0.0274 (4)        |           |
| C6   | 0.58474 (9)  | 0.2500     | 0.11956 (13)  | 0.0226 (3)        |           |
| C7   | 0.63221 (9)  | 0.2500     | 0.01907 (14)  | 0.0263 (4)        |           |
| H7   | 0.6880       | 0.2500     | 0.0251        | 0.032*            |           |
| C8   | 0.59613 (9)  | 0.2500     | −0.08943 (14) | 0.0265 (4)        |           |
| H8   | 0.6279       | 0.2500     | −0.1556       | 0.032*            |           |
| C9   | 0.51238 (9)  | 0.2500     | −0.09965 (13) | 0.0222 (3)        |           |
| C10  | 0.46505 (9)  | 0.2500     | −0.00022 (13) | 0.0237 (3)        |           |
| H10  | 0.4093       | 0.2500     | −0.0066       | 0.028*            |           |
| C11  | 0.50064 (9)  | 0.2500     | 0.10786 (14)  | 0.0242 (3)        |           |
| H11  | 0.4685       | 0.2500     | 0.1737        | 0.029*            |           |
| C12  | 0.47066 (10) | 0.2500     | −0.21404 (13) | 0.0255 (3)        |           |
| C13  | 0.48394 (13) | 0.2500     | −0.41695 (15) | 0.0426 (5)        |           |
| H13A | 0.5245       | 0.2500     | −0.4760       | 0.064*            |           |
| H13B | 0.4510       | 0.3678     | −0.4248       | 0.064*            | 0.50      |
| H13C | 0.4510       | 0.1322     | −0.4248       | 0.064*            | 0.50      |
| O1   | 0.56999 (7)  | 0.2500     | 0.32202 (10)  | 0.0398 (3)        |           |
| O2   | 0.39814 (7)  | 0.2500     | −0.22520 (10) | 0.0359 (3)        |           |
| O3   | 0.52206 (7)  | 0.2500     | −0.30386 (9)  | 0.0336 (3)        |           |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0253 (6) | 0.0566 (8) | 0.0478 (8) | −0.0081 (6) | −0.0026 (5) | −0.0008 (7) |
| C2 | 0.0302 (6) | 0.0424 (8) | 0.0552 (8) | −0.0084 (6) | −0.0042 (6) | −0.0145 (6) |
| C3 | 0.0266 (8) | 0.0542 (12) | 0.0287 (9) | 0.000 | −0.0049 (7) | 0.000 |
| C4 | 0.0403 (12) | 0.165 (3) | 0.0340 (11) | 0.000 | −0.0146 (9) | 0.000 |
| C5 | 0.0280 (8) | 0.0281 (8) | 0.0261 (8) | 0.000 | −0.0006 (6) | 0.000 |
| C6 | 0.0228 (7) | 0.0197 (7) | 0.0254 (7) | 0.000 | 0.0010 (6) | 0.000 |
| C7 | 0.0179 (7) | 0.0301 (8) | 0.0309 (8) | 0.000 | 0.0012 (6) | 0.000 |
| C8 | 0.0229 (7) | 0.0302 (8) | 0.0263 (8) | 0.000 | 0.0060 (6) | 0.000 |
| C9 | 0.0222 (7) | 0.0176 (7) | 0.0266 (8) | 0.000 | 0.0004 (6) | 0.000 |
| C10 | 0.0183 (7) | 0.0206 (8) | 0.0322 (8) | 0.000 | 0.0025 (6) | 0.000 |
| C11 | 0.0224 (7) | 0.0224 (8) | 0.0277 (8) | 0.000 | 0.0058 (6) | 0.000 |
| C12 | 0.0285 (8) | 0.0200 (8) | 0.0280 (8) | 0.000 | −0.0011 (6) | 0.000 |
| C13 | 0.0543 (12) | 0.0505 (12) | 0.0230 (8) | 0.000 | −0.0031 (8) | 0.000 |
| O1 | 0.0332 (7) | 0.0607 (9) | 0.0256 (6) | 0.000 | 0.0036 (5) | 0.000 |
| O2 | 0.0262 (6) | 0.0459 (8) | 0.0355 (7) | 0.000 | −0.0061 (5) | 0.000 |
| O3 | 0.0352 (7) | 0.0415 (7) | 0.0242 (6) | 0.000 | 0.0016 (5) | 0.000 |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C1[i] | 1.307 (3) | C7—C8 | 1.390 (2) |
| C1—C2 | 1.5030 (18) | C7—H7 | 0.9300 |
| C1—H1 | 0.9300 | C8—C9 | 1.397 (2) |
| C2—C3 | 1.5612 (17) | C8—H8 | 0.9300 |
| C2—H2A | 0.9700 | C9—C10 | 1.393 (2) |
| C2—H2B | 0.9700 | C9—C12 | 1.493 (2) |
| C3—C5 | 1.529 (2) | C10—C11 | 1.382 (2) |
| C3—C4 | 1.536 (3) | C10—H10 | 0.9300 |
| C3—C2[i] | 1.5612 (17) | C11—H11 | 0.9300 |
| C4—H4A | 0.9600 | C12—O2 | 1.2123 (19) |
| C4—H4B | 0.9600 | C12—O3 | 1.3444 (19) |
| C4—H4C | 0.9600 | C13—O3 | 1.453 (2) |
| C5—O1 | 1.219 (2) | C13—H13A | 0.9600 |
| C5—C6 | 1.515 (2) | C13—H13B | 0.9600 |
| C6—C7 | 1.404 (2) | C13—H13C | 0.9600 |
| C6—C11 | 1.404 (2) | | |
| | | | |
| C1[i]—C1—C2 | 112.76 (8) | C11—C6—C5 | 116.65 (13) |
| C1[i]—C1—H1 | 123.6 | C8—C7—C6 | 120.25 (13) |
| C2—C1—H1 | 123.6 | C8—C7—H7 | 119.9 |
| C1—C2—C3 | 103.51 (12) | C6—C7—H7 | 119.9 |
| C1—C2—H2A | 111.1 | C7—C8—C9 | 120.41 (14) |
| C3—C2—H2A | 111.1 | C7—C8—H8 | 119.8 |
| C1—C2—H2B | 111.1 | C9—C8—H8 | 119.8 |
| C3—C2—H2B | 111.1 | C10—C9—C8 | 119.54 (14) |
| H2A—C2—H2B | 109.0 | C10—C9—C12 | 117.93 (13) |

| | | | |
|---|---|---|---|
| C5—C3—C4 | 108.82 (15) | C8—C9—C12 | 122.53 (14) |
| C5—C3—C2 | 112.52 (9) | C11—C10—C9 | 120.27 (13) |
| C4—C3—C2 | 109.16 (10) | C11—C10—H10 | 119.9 |
| C5—C3—C2[i] | 112.52 (9) | C9—C10—H10 | 119.9 |
| C4—C3—C2[i] | 109.16 (10) | C10—C11—C6 | 120.87 (14) |
| C2—C3—C2[i] | 104.54 (14) | C10—C11—H11 | 119.6 |
| C3—C4—H4A | 109.5 | C6—C11—H11 | 119.6 |
| C3—C4—H4B | 109.5 | O2—C12—O3 | 123.34 (14) |
| H4A—C4—H4B | 109.5 | O2—C12—C9 | 123.79 (14) |
| C3—C4—H4C | 109.5 | O3—C12—C9 | 112.87 (13) |
| H4A—C4—H4C | 109.5 | O3—C13—H13A | 109.5 |
| H4B—C4—H4C | 109.5 | O3—C13—H13B | 109.5 |
| O1—C5—C6 | 118.40 (14) | H13A—C13—H13B | 109.5 |
| O1—C5—C3 | 120.05 (15) | O3—C13—H13C | 109.5 |
| C6—C5—C3 | 121.55 (14) | H13A—C13—H13C | 109.5 |
| C7—C6—C11 | 118.66 (14) | H13B—C13—H13C | 109.5 |
| C7—C6—C5 | 124.69 (13) | C12—O3—C13 | 114.69 (14) |
| | | | |
| C1[i]—C1—C2—C3 | 10.60 (11) | C5—C6—C7—C8 | 180.0 |
| C1—C2—C3—C5 | −138.49 (12) | C6—C7—C8—C9 | 0.0 |
| C1—C2—C3—C4 | 100.59 (14) | C7—C8—C9—C10 | 0.0 |
| C1—C2—C3—C2[i] | −16.10 (17) | C7—C8—C9—C12 | 180.0 |
| C4—C3—C5—O1 | 0.0 | C8—C9—C10—C11 | 0.0 |
| C2—C3—C5—O1 | −121.11 (10) | C12—C9—C10—C11 | 180.0 |
| C2[i]—C3—C5—O1 | 121.11 (10) | C9—C10—C11—C6 | 0.0 |
| C4—C3—C5—C6 | 180.0 | C7—C6—C11—C10 | 0.0 |
| C2—C3—C5—C6 | 58.89 (10) | C5—C6—C11—C10 | 180.0 |
| C2[i]—C3—C5—C6 | −58.89 (10) | C10—C9—C12—O2 | 0.0 |
| O1—C5—C6—C7 | 180.0 | C8—C9—C12—O2 | 180.0 |
| C3—C5—C6—C7 | 0.0 | C10—C9—C12—O3 | 180.0 |
| O1—C5—C6—C11 | 0.0 | C8—C9—C12—O3 | 0.0 |
| C3—C5—C6—C11 | 180.0 | O2—C12—O3—C13 | 0.0 |
| C11—C6—C7—C8 | 0.0 | C9—C12—O3—C13 | 180.0 |

Symmetry codes: (i) $x$, $−y+1/2$, $z$.


*Hydrogen-bond geometry (Å, °)*

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| C13—H13A⋯O1[ii] | 0.96 | 2.45 | 3.339 (2) | 153 |

Symmetry codes: (ii) $x, y, z−1$.

**Fig. 1**

**Fig. 2**

**Fig. 3**