Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 4-chloro-2′-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate

Muhammad Adeel,[a]* Peter Langer[b,c] and Alexander Villinger[b]

[a]Gomal University, Department of Chemistry, Dera Ismail Khan (KPK), Pakistan, [b]Universität Rostock, Institut für Chemie, Albert-Einstein-Strasse 3a, 18059 Rostock, Germany, and [c]Leibniz-Institut für Katalyse e.V., an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany
Correspondence e-mail: muhammad_adeel2000@yahoo.com

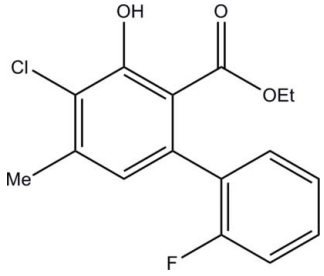
Received 18 July 2011; accepted 8 August 2011

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.047; wR factor = 0.139; data-to-parameter ratio = 19.3.

In the title compound, $C_{16}H_{14}ClFO_3$, the dihedral angle between the mean planes of the two benzene rings is 71.50 (5)°. Due to an intramolecular O—H···O hydrogen bond between the hydroxy group and the carbonyl O atom of the ethyl ester group, the ethyl ester group lies within the ring plane. The crystal structure is consolidated by intermolecular C—H···O and C—H···F interactions.

Related literature

For a related structure, see: Adeel *et al.* (2009). For synthetic procedures and the pharmacological relevance of 3-chlorosalicylates, see: Wolf *et al.* (2009).



Experimental

Crystal data

$C_{16}H_{14}ClFO_3$ M_r = 308.73
Triclinic, $P\overline{1}$
a = 8.212 (4) Å
b = 9.780 (3) Å
c = 10.156 (3) Å
α = 71.18 (3)°
β = 76.41 (2)°
γ = 71.34 (2)°
V = 723.5 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 173 K
0.31 × 0.18 × 0.08 mm

Data collection

Bruker APEXII KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.918, T_{max} = 0.978
12813 measured reflections
3773 independent reflections
2902 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.139
S = 1.07
3773 reflections
195 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7C···O1^{i}	0.98	2.59	3.473 (3)	150
C9—H9A···F^{ii}	0.99	2.40	3.320 (3)	155
O1—H1···O2	0.82 (3)	1.77 (3)	2.521 (2)	153 (3)

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Financial support from the Higher Education Commission of Pakistan (HEC) under the resource grant programme is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2433).

References

Adeel, M., Ali, I., Langer, P. & Villinger, A. (2009). *Acta Cryst.* E**65**, o2176.
Bruker (2003). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wolf, V., Adeel, M., Reim, S., Villinger, A., Fischer, C. & Langer, P. (2009). *Eur. J. Org. Chem.* **2**, 5854–5867.

supplementary materials

Acta Cryst. (2011). E**67**, o2336 [**doi:10.1107/S160053681103217X**]

Ethyl 4-chloro-2'-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate

M. Adeel, P. Langer and A. Villinger

Comment

Functionalized chloroarenes are of considerable pharmacological relevance. 3-Chlorosalicylates and related compounds are employed as pharmacological agents (Wolf *et al.*, 2009).

In the title compound (Fig. 1), the dihedral angle between the mean planes of the two benzene rings is 71.50 (5)°. The ethyllester group lies within the ring plane due to an intramolecular hydrogen bond between the hydroxyl group and the carbonyl O atom of the ehtyllester group, O1—H1···O2. The crystal structure is consolidated by weak C7—H7C···O1 and C9—H9A···F intermolecular interactions.

Experimental

Experimental: The title compound was prepared according to a previously published procedure (Wolf *et al.* 2009). To a CH_2Cl_2 (6 ml) solution of 1-(2-fluoro-phenyl)-3-trimethylsilanyloxy-but-2-en-1-one (720 mg, 2.8 mmol) and 4-chloro-1-ethoxy-1,3-bis-trimethylsilanyloxy-buta-1,3-diene (970 mg, 3.1 mmol) was added $TiCl_4$ (0.34 ml, 3.1 mmol) at 195 K under argon atmosphere. The solution was allowed to warm to ambient temperature within 20 hrs. To the solution was added a saturated solution of $NaHCO_3$ (15 mL). The organic and the aqueous layers were separated and the latter was extracted with diethyl ether (3 × 20 ml). The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, EtOAc / n-heptane = 1:4). The title compound was isolated as a colorless crystalline solid. Yield: 390 mg, 45%. Mp. = 352 K. Crystallization from a saturated dichloromethane/methanol (9:1) solution at ambient temperature gave colorless crystals.

Refinement

The H atom bonded to O1 was located from a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 (methyl groups) or 0.95 Å (aryl CH) and with U_{iso}(H) = 1.5 times U_{eq}(C) (methyl groups) or with U_{iso}(H) = 1.2 times U_{eq}(C) (aryl CH). Torsion angles of all methyl groups were allowed to refine.

Figures

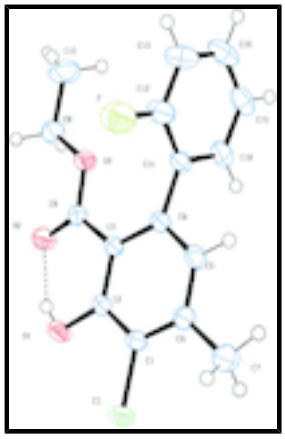


Fig. 1. Molecular structure of the title compound drawn with thermal elliposids at the 50% probability level.

Ethyl 4-chloro-2'-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate

Crystal data

$C_{16}H_{14}ClFO_3$	$Z = 2$
$M_r = 308.73$	$F(000) = 320$
Triclinic, $P\overline{1}$	$D_x = 1.417$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 342 K
$a = 8.212$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.780$ (3) Å	Cell parameters from 12813 reflections
$c = 10.156$ (3) Å	$\theta = 0.9$–$1.0°$
$\alpha = 71.18$ (3)°	$\mu = 0.28$ mm^{-1}
$\beta = 76.41$ (2)°	$T = 173$ K
$\gamma = 71.34$ (2)°	Block, colourless
$V = 723.5$ (5) Å^3	0.31 × 0.18 × 0.08 mm

Data collection

Bruker APEXII KappaCCD diffractometer	3773 independent reflections
Radiation source: fine-focus sealed tube	2902 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$
ω scans	$\theta_{max} = 29.0°$, $\theta_{min} = 4.6°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$h = -11 \rightarrow 11$
$T_{min} = 0.918$, $T_{max} = 0.978$	$k = -10 \rightarrow 13$
12813 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.139$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.1732P]$ where $P = (F_o^2 + 2F_c^2)/3$
3773 reflections	$(\Delta/\sigma)_{max} < 0.001$
195 parameters	$\Delta\rho_{max} = 0.87$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Experimental. Yield: 390 mg, 45%. Mp. = 352(???) K ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75 (t,3*H*, J = 6.5 Hz, CH_3) 2.34 (s, 3H, CH_3), 3.96 (q, 2H, J = 7.0 Hz,OCH_2),6.60 (s, 1H, ArH), 6.91–6.98 (m, 1H, ArH), 7.06–7.11 (m, 2H, ArH), 7.22 (m, 1H, ArH), 11.53 (s, 1 H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.0 (CH3), 20.7 (CH3), 61.5 (OCH_2), 111.0 (C), 114.4, 114.8 (CH), 122.3 (C), 123.7, 124.4, 129.0 (CH), 135.4, 142.9, 142.4, 157.7, 161.0 (C), 170.5 (C=O). IR (ATR, cm $^{-1}$): \~ν = 3040 (w), 2979 (*m*), 1657 (*m*), 1604 (*m*), 1495 (*m*), 1440 (*m*), 1374 (*s*), 1260 (*s*), 1215 (*s*), 759 (*s*). GC—MS (EI, 70 eV): m/*z* (%): 310 (M^+, ^{37}Cl, 8), 308 (M^+, 24), 262 (100), 234 (12), 199 (11), 170 (24). HRMS (EI, 70 eV): calcd for $C_{116}H_{14}ClFO_3$ [*M*, ^{35}Cl]: 308.06100; found 308.060555.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
Cl	−0.02886 (6)	0.86275 (5)	0.43812 (5)	0.03926 (16)
F	0.3361 (2)	0.44171 (16)	−0.01240 (13)	0.0725 (5)
O1	−0.18805 (15)	0.68979 (15)	0.35763 (15)	0.0384 (3)
H1	−0.225 (3)	0.630 (3)	0.341 (3)	0.058*
O2	−0.19906 (16)	0.46568 (15)	0.29190 (16)	0.0422 (3)
O3	0.04108 (15)	0.32871 (13)	0.19277 (14)	0.0341 (3)
C1	0.0830 (2)	0.71258 (18)	0.36909 (17)	0.0280 (3)
C2	−0.0136 (2)	0.63762 (17)	0.33593 (17)	0.0265 (3)
C3	0.07182 (19)	0.51135 (17)	0.28378 (16)	0.0247 (3)
C4	0.2551 (2)	0.46328 (17)	0.26719 (16)	0.0253 (3)
C5	0.3454 (2)	0.54158 (19)	0.30155 (18)	0.0307 (4)
H5	0.4687	0.5086	0.2899	0.037*
C6	0.2626 (2)	0.66689 (19)	0.35253 (19)	0.0313 (4)
C7	0.3663 (3)	0.7464 (3)	0.3907 (3)	0.0478 (5)

H7A	0.3351	0.7412	0.4911	0.072*
H7B	0.3410	0.8515	0.3355	0.072*
H7C	0.4905	0.6983	0.3704	0.072*
C8	−0.0406 (2)	0.43450 (18)	0.25693 (18)	0.0284 (3)
C9	−0.0649 (3)	0.2461 (2)	0.1702 (2)	0.0431 (5)
H9A	−0.1626	0.3160	0.1207	0.052*
H9B	−0.1129	0.1862	0.2612	0.052*
C10	0.0523 (3)	0.1462 (3)	0.0828 (3)	0.0612 (7)
H10A	0.1556	0.0866	0.1276	0.092*
H10B	0.0874	0.2072	−0.0110	0.092*
H10C	−0.0092	0.0792	0.0744	0.092*
C11	0.3638 (2)	0.32652 (18)	0.22316 (18)	0.0280 (3)
C12	0.4056 (3)	0.3214 (2)	0.0855 (2)	0.0422 (4)
C13	0.5149 (3)	0.1975 (3)	0.0445 (2)	0.0536 (6)
H13	0.5400	0.1975	−0.0517	0.064*
C14	0.5866 (3)	0.0741 (2)	0.1454 (3)	0.0487 (5)
H14	0.6625	−0.0120	0.1188	0.058*
C15	0.5496 (2)	0.0742 (2)	0.2836 (2)	0.0428 (5)
H15	0.5994	−0.0118	0.3529	0.051*
C16	0.4392 (2)	0.19994 (19)	0.3228 (2)	0.0350 (4)
H16	0.4147	0.1996	0.4191	0.042*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0353 (2)	0.0323 (2)	0.0569 (3)	−0.00351 (17)	−0.00615 (19)	−0.0267 (2)
F	0.0975 (11)	0.0589 (8)	0.0352 (7)	0.0110 (8)	−0.0107 (7)	−0.0092 (6)
O1	0.0198 (6)	0.0397 (7)	0.0629 (9)	−0.0002 (5)	−0.0055 (5)	−0.0315 (7)
O2	0.0243 (6)	0.0488 (8)	0.0664 (9)	−0.0072 (5)	−0.0058 (6)	−0.0358 (7)
O3	0.0293 (6)	0.0323 (6)	0.0484 (7)	−0.0034 (5)	−0.0091 (5)	−0.0233 (5)
C1	0.0259 (8)	0.0253 (7)	0.0348 (8)	−0.0036 (6)	−0.0039 (6)	−0.0141 (6)
C2	0.0217 (7)	0.0263 (7)	0.0319 (8)	−0.0022 (6)	−0.0055 (6)	−0.0115 (6)
C3	0.0217 (7)	0.0241 (7)	0.0295 (8)	−0.0038 (6)	−0.0048 (6)	−0.0102 (6)
C4	0.0232 (7)	0.0240 (7)	0.0260 (7)	−0.0028 (6)	−0.0027 (6)	−0.0072 (6)
C5	0.0198 (7)	0.0328 (8)	0.0405 (9)	−0.0054 (6)	−0.0026 (6)	−0.0142 (7)
C6	0.0266 (8)	0.0323 (8)	0.0392 (9)	−0.0094 (7)	−0.0041 (7)	−0.0140 (7)
C7	0.0310 (9)	0.0527 (12)	0.0750 (14)	−0.0154 (9)	−0.0031 (9)	−0.0364 (11)
C8	0.0269 (8)	0.0276 (8)	0.0335 (8)	−0.0031 (6)	−0.0085 (6)	−0.0130 (6)
C9	0.0378 (10)	0.0391 (10)	0.0661 (13)	−0.0065 (8)	−0.0155 (9)	−0.0304 (10)
C10	0.0624 (15)	0.0610 (15)	0.0806 (17)	−0.0138 (12)	−0.0091 (13)	−0.0497 (14)
C11	0.0201 (7)	0.0268 (8)	0.0371 (9)	−0.0038 (6)	−0.0011 (6)	−0.0130 (7)
C12	0.0457 (11)	0.0361 (10)	0.0382 (10)	−0.0026 (8)	0.0002 (8)	−0.0139 (8)
C13	0.0567 (13)	0.0537 (13)	0.0479 (12)	−0.0089 (10)	0.0120 (10)	−0.0298 (10)
C14	0.0357 (10)	0.0320 (10)	0.0755 (15)	−0.0042 (8)	0.0070 (10)	−0.0262 (10)
C15	0.0321 (9)	0.0269 (9)	0.0646 (13)	−0.0034 (7)	−0.0078 (9)	−0.0098 (8)
C16	0.0255 (8)	0.0288 (8)	0.0503 (10)	−0.0058 (6)	−0.0062 (7)	−0.0109 (7)

Geometric parameters (Å, °)

Cl—C1	1.7294 (17)	C7—H7B	0.9800
F—C12	1.334 (2)	C7—H7C	0.9800
O1—C2	1.348 (2)	C9—C10	1.492 (3)
O1—H1	0.82 (3)	C9—H9A	0.9900
O2—C8	1.229 (2)	C9—H9B	0.9900
O3—C8	1.315 (2)	C10—H10A	0.9800
O3—C9	1.458 (2)	C10—H10B	0.9800
C1—C6	1.384 (2)	C10—H10C	0.9800
C1—C2	1.392 (2)	C11—C12	1.372 (3)
C2—C3	1.411 (2)	C11—C16	1.392 (3)
C3—C4	1.412 (2)	C12—C13	1.379 (3)
C3—C8	1.479 (2)	C13—C14	1.372 (3)
C4—C5	1.384 (2)	C13—H13	0.9500
C4—C11	1.490 (2)	C14—C15	1.365 (3)
C5—C6	1.394 (2)	C14—H14	0.9500
C5—H5	0.9500	C15—C16	1.388 (3)
C6—C7	1.501 (2)	C15—H15	0.9500
C7—H7A	0.9800	C16—H16	0.9500
C2—O1—H1	105.4 (18)	O3—C9—H9A	110.5
C8—O3—C9	116.61 (14)	C10—C9—H9A	110.5
C6—C1—C2	121.84 (15)	O3—C9—H9B	110.5
C6—C1—Cl	120.26 (13)	C10—C9—H9B	110.5
C2—C1—Cl	117.86 (12)	H9A—C9—H9B	108.7
O1—C2—C1	117.25 (14)	C9—C10—H10A	109.5
O1—C2—C3	122.85 (15)	C9—C10—H10B	109.5
C1—C2—C3	119.89 (14)	H10A—C10—H10B	109.5
C2—C3—C4	118.74 (14)	C9—C10—H10C	109.5
C2—C3—C8	116.40 (14)	H10A—C10—H10C	109.5
C4—C3—C8	124.79 (14)	H10B—C10—H10C	109.5
C5—C4—C3	119.21 (14)	C12—C11—C16	116.99 (16)
C5—C4—C11	115.36 (14)	C12—C11—C4	123.15 (16)
C3—C4—C11	125.31 (14)	C16—C11—C4	119.67 (15)
C4—C5—C6	122.64 (15)	F—C12—C11	118.25 (17)
C4—C5—H5	118.7	F—C12—C13	118.85 (19)
C6—C5—H5	118.7	C11—C12—C13	122.90 (19)
C1—C6—C5	117.68 (15)	C14—C13—C12	118.7 (2)
C1—C6—C7	121.70 (16)	C14—C13—H13	120.6
C5—C6—C7	120.60 (16)	C12—C13—H13	120.6
C6—C7—H7A	109.5	C15—C14—C13	120.53 (18)
C6—C7—H7B	109.5	C15—C14—H14	119.7
H7A—C7—H7B	109.5	C13—C14—H14	119.7
C6—C7—H7C	109.5	C14—C15—C16	119.91 (19)
H7A—C7—H7C	109.5	C14—C15—H15	120.0
H7B—C7—H7C	109.5	C16—C15—H15	120.0
O2—C8—O3	121.77 (15)	C15—C16—C11	120.95 (19)
O2—C8—C3	123.07 (15)	C15—C16—H16	119.5

O3—C8—C3	115.17 (14)	C11—C16—H16	119.5
O3—C9—C10	106.34 (17)		
C6—C1—C2—O1	179.12 (16)	C9—O3—C8—C3	177.37 (15)
Cl—C1—C2—O1	1.3 (2)	C2—C3—C8—O2	−8.1 (2)
C6—C1—C2—C3	0.0 (3)	C4—C3—C8—O2	168.84 (16)
Cl—C1—C2—C3	−177.88 (12)	C2—C3—C8—O3	172.18 (14)
O1—C2—C3—C4	−178.74 (15)	C4—C3—C8—O3	−10.9 (2)
C1—C2—C3—C4	0.4 (2)	C8—O3—C9—C10	173.83 (17)
O1—C2—C3—C8	−1.6 (2)	C5—C4—C11—C12	−102.9 (2)
C1—C2—C3—C8	177.49 (14)	C3—C4—C11—C12	81.1 (2)
C2—C3—C4—C5	−0.4 (2)	C5—C4—C11—C16	72.0 (2)
C8—C3—C4—C5	−177.26 (15)	C3—C4—C11—C16	−104.1 (2)
C2—C3—C4—C11	175.50 (15)	C16—C11—C12—F	−179.55 (18)
C8—C3—C4—C11	−1.4 (3)	C4—C11—C12—F	−4.6 (3)
C3—C4—C5—C6	0.1 (3)	C16—C11—C12—C13	1.0 (3)
C11—C4—C5—C6	−176.19 (15)	C4—C11—C12—C13	175.94 (19)
C2—C1—C6—C5	−0.3 (3)	F—C12—C13—C14	179.8 (2)
Cl—C1—C6—C5	177.53 (13)	C11—C12—C13—C14	−0.7 (4)
C2—C1—C6—C7	−178.94 (18)	C12—C13—C14—C15	0.3 (3)
Cl—C1—C6—C7	−1.2 (3)	C13—C14—C15—C16	−0.2 (3)
C4—C5—C6—C1	0.2 (3)	C14—C15—C16—C11	0.5 (3)
C4—C5—C6—C7	178.92 (18)	C12—C11—C16—C15	−0.9 (3)
C9—O3—C8—O2	−2.4 (3)	C4—C11—C16—C15	−176.02 (16)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7C···O1^{i}	0.98	2.59	3.473 (3)	150
C9—H9A···F^{ii}	0.99	2.40	3.320 (3)	155
O1—H1···O2	0.82 (3)	1.77 (3)	2.521 (2)	153 (3)

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*, −*y*+1, −*z*.

Fig. 1