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ISSN 2414-3146

Ethyl 2-(4-chloro-3-methylphenoxy)acetate

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Received 25 February 2016
Accepted 11 March 2016

Edited by E. R. T. Tiekink, Sunway University, Malaysia

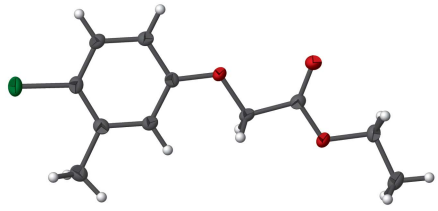
Keywords: crystal structure; phenoxy acetate; C—H···O hydrogen bonds.

CCDC reference: 1463900

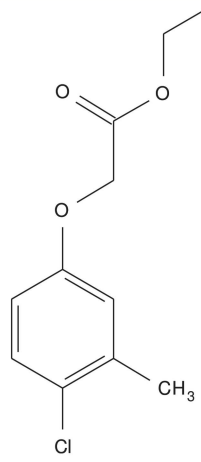
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{11}H_{13}ClO_3$, the pendant ethyl chain has an extended conformation and lies in the plane of the substituted benzene ring; the r.m.s. deviation of the 15 non-H atoms comprising the molecule is 0.002 Å. The crystal structure features inversion-related dimers linked by pairs of benzene–carbonyl C—H···O hydrogen bonds, generating $R_2^2(16)$ loops.

3D view



Chemical scheme



Structure description

Phenoxyacetates are very robust moieties towards various harsh reaction conditions. The stability is documented by numerous transformations on the aryl system without affecting the side chain (Al-Ghorbani *et al.*, 2015). This alkoxy moiety turned out to be beneficial for oxidative transformations with strong Lewis acids. Ethyl phenoxyacetate derivatives have potential antimicrobial, anticancer, antitumor, antioxidant, anti-inflammatory and plant-growth-regulation activity properties (Khanum *et al.*, 2004). These compounds are widely used as herbicides and pesticides. Ethyl phenoxyacetate analogues also show very good antiulcerogenic activity, cyclooxygenase activity and anticonvulsant activity. In view of the above, the title compound, ethyl 2-(4-chloro-3-methylphenoxy)acetate, was synthesized and we report herein its crystal structure.

The title molecule (Fig. 1) closely resembles that of ethyl 2-(2-bromophenoxy)acetate with similar geometric parameters. The pendant ethyl chain is in an extended conformation and almost lies in the plane of the substituted benzene ring, as indicated by the dihedral angle of 1.86 (2)°. The crystal structure features inversion-related dimers linked by pairs of C—H···O hydrogen bonds generating $R_2^2(16)$ loops (Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O12^{i}	0.93	2.57	3.194 (3)	125

Symmetry code: (i) $-x+2, -y+1, -z+2$.

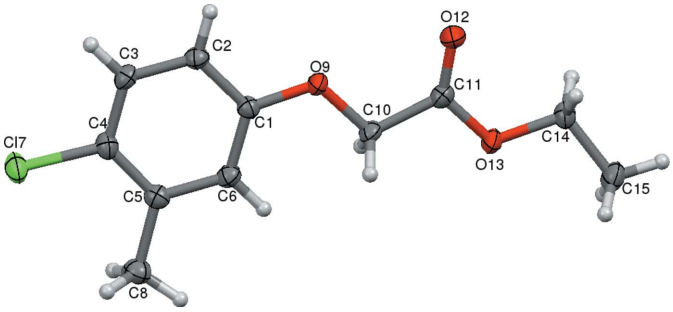


Figure 1
A view of the molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Synthesis and crystallization

A mixture of 4-chloro-3-methylphenol (0.200 mol), ethyl chloroacetate (0.031 mol) and anhydrous potassium carbonate (0.037 mol) in dry acetone (50 ml) was refluxed for 12 h. The reaction mixture was cooled and the solvent was removed by distillation. The residual mass was triturated with cold water to remove potassium carbonate and extracted with ether (3 × 30 ml). The ether layer was washed successively with 10% sodium hydroxide solution (3 × 30 ml) and water (3 × 30 ml), and then dried over anhydrous sodium sulfate and evaporated, giving white crystals of ethyl 2-(4-chloro-3-methylphenoxy)acetate in good yield (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (*t*, 3H, CH_3 of ester), 2.38 (*s*, 3H, CH_3), 4.24 (*q*, 2H, CH_2 of ester), 5.01 (*s*, 2H, CH_2), 6.77–7.34 (*m*, 3H, Ar—H). IR (KBr) (ν_{max}/cm^{-1}): 1750 (ester, C═O). The mass spectrum showed molecular ion peaks at m/z = 228 [M^+] and 230 (M + 2). Analysis calculated for $C_{11}H_{13}ClO_3$: C 57.78, H 5.73, Cl 15.50%; found: C 57.63, H 5.65, Cl 15.40%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{13}ClO_3$
M_r	228.66
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	7.0296 (3), 8.3258 (4), 10.6552 (5)
α, β, γ (°)	106.031 (2), 92.977 (2), 110.489 (2)
V (Å^3)	553.75 (5)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	2.94
Crystal size (mm)	0.30 × 0.27 × 0.25
Data collection	
Diffractometer	Bruker X8 Proteum
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.472, 0.526
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5636, 1784, 1670
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.585
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.161, 1.13
No. of reflections	1784
No. of parameters	138
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.59

Computer programs: *APEX2* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008).

Acknowledgements

The authors are grateful to the Institution of Excellence, Vijnana Bhavana University of Mysore, India, for providing the single-crystal X-ray diffractometer facility. YHIM thanks the University of Hajah, Yemen, for financial support. SAK gratefully acknowledges the financial support provided by the Vision Group of Science and Technology, Government of Karnataka, under the CISEE scheme, Department of Information Technology, Biotechnology and Science and Technology, Bangalore.

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full crystallographic data

IUCrData (2016). **1**, x160416 [doi:10.1107/S2414314616004168]

Ethyl 2-(4-chloro-3-methylphenoxy)acetate

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2-Chloro-6-fluorophenyl 4-chlorobenzoate

Crystal data

$C_{11}H_{13}ClO_3$
M_r = 228.66
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.0296 (3) Å
b = 8.3258 (4) Å
c = 10.6552 (5) Å
α = 106.031 (2)°
β = 92.977 (2)°
γ = 110.489 (2)°
V = 553.75 (5) Å^3
Z = 2
$F(000)$ = 240
D_x = 1.371 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 1784 reflections
θ = 4.4–64.4°
μ = 2.94 mm^{-1}
T = 296 K
Prism, colourless
0.30 × 0.27 × 0.25 mm

Data collection

Bruker X8 Proteum diffractometer
Radiation source: Bruker MicroStar microfocus rotating anode
Helios multilayer optics monochromator
Detector resolution: 18.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.472, T_{max} = 0.526
5636 measured reflections
1784 independent reflections
1670 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 64.4°, θ_{min} = 4.4°
h = −7→8
k = −9→9
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.161
S = 1.13
1784 reflections
138 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
$w = 1/[\sigma^2(F_o^2) + (0.1056P)^2 + 0.2726P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl7	1.37595 (9)	0.87199 (8)	0.58887 (6)	0.0312 (2)
O9	0.7485 (2)	0.4639 (2)	0.84725 (15)	0.0224 (5)
O12	0.4792 (3)	0.2730 (3)	0.97377 (17)	0.0284 (6)
O13	0.2155 (2)	0.2149 (2)	0.81678 (15)	0.0241 (5)
C1	0.8857 (4)	0.5586 (3)	0.7817 (2)	0.0198 (7)
C2	1.0925 (4)	0.6208 (3)	0.8362 (2)	0.0215 (7)
C3	1.2409 (4)	0.7181 (3)	0.7765 (2)	0.0222 (7)
C4	1.1822 (4)	0.7507 (3)	0.6622 (2)	0.0227 (7)
C5	0.9776 (4)	0.6918 (3)	0.6062 (2)	0.0218 (7)
C6	0.8291 (4)	0.5936 (3)	0.6680 (2)	0.0215 (7)
C8	0.9113 (4)	0.7284 (4)	0.4843 (2)	0.0283 (8)
C10	0.5383 (3)	0.3888 (3)	0.7888 (2)	0.0218 (7)
C11	0.4128 (4)	0.2861 (3)	0.8724 (2)	0.0207 (7)
C14	0.0719 (4)	0.1132 (3)	0.8866 (2)	0.0242 (7)
C15	−0.1422 (4)	0.0697 (4)	0.8207 (3)	0.0300 (8)
H2	1.13040	0.59710	0.91210	0.0260*
H3	1.37950	0.76150	0.81250	0.0270*
H6	0.69040	0.55110	0.63240	0.0260*
H8A	0.97420	0.85530	0.49600	0.0420*
H8B	0.76420	0.69110	0.46950	0.0420*
H8C	0.95310	0.66220	0.40940	0.0420*
H10A	0.52010	0.30820	0.69990	0.0260*
H10B	0.49260	0.48430	0.78320	0.0260*
H14A	0.09320	0.18430	0.97890	0.0290*
H14B	0.09280	0.00280	0.88250	0.0290*
H15A	−0.16000	0.17970	0.82350	0.0450*
H15B	−0.24060	0.00510	0.86630	0.0450*
H15C	−0.16280	−0.00370	0.73020	0.0450*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl7	0.0252 (4)	0.0335 (4)	0.0300 (4)	0.0018 (3)	0.0071 (3)	0.0141 (3)
O9	0.0139 (9)	0.0291 (10)	0.0229 (9)	0.0039 (7)	0.0014 (6)	0.0119 (7)
O12	0.0211 (9)	0.0383 (11)	0.0277 (9)	0.0088 (8)	0.0014 (7)	0.0168 (8)
O13	0.0145 (8)	0.0308 (10)	0.0240 (9)	0.0031 (7)	0.0019 (7)	0.0115 (7)
C1	0.0199 (12)	0.0193 (12)	0.0197 (12)	0.0064 (10)	0.0035 (9)	0.0066 (9)
C2	0.0205 (12)	0.0233 (12)	0.0189 (11)	0.0073 (10)	0.0007 (9)	0.0058 (9)
C3	0.0168 (11)	0.0232 (13)	0.0230 (12)	0.0058 (10)	0.0008 (9)	0.0047 (9)

C4	0.0216 (13)	0.0215 (12)	0.0217 (12)	0.0047 (10)	0.0051 (10)	0.0059 (10)
C5	0.0249 (12)	0.0200 (12)	0.0193 (12)	0.0081 (10)	0.0024 (9)	0.0050 (9)
C6	0.0188 (12)	0.0217 (12)	0.0218 (12)	0.0065 (10)	0.0003 (9)	0.0054 (10)
C8	0.0301 (14)	0.0304 (14)	0.0244 (13)	0.0097 (11)	0.0027 (10)	0.0113 (10)
C10	0.0150 (12)	0.0276 (13)	0.0201 (11)	0.0058 (10)	−0.0004 (9)	0.0072 (10)
C11	0.0179 (12)	0.0219 (12)	0.0213 (12)	0.0080 (10)	0.0026 (9)	0.0049 (10)
C14	0.0205 (12)	0.0252 (13)	0.0257 (12)	0.0056 (10)	0.0074 (9)	0.0097 (10)
C15	0.0190 (12)	0.0301 (14)	0.0370 (14)	0.0051 (11)	0.0048 (10)	0.0101 (11)

Geometric parameters (Å, º)

Cl7—C4	1.752 (3)	C14—C15	1.503 (4)
O9—C1	1.372 (3)	C2—H2	0.9300
O9—C10	1.416 (3)	C3—H3	0.9300
O12—C11	1.202 (3)	C6—H6	0.9300
O13—C11	1.331 (3)	C8—H8A	0.9600
O13—C14	1.455 (3)	C8—H8B	0.9600
C1—C2	1.392 (4)	C8—H8C	0.9600
C1—C6	1.392 (3)	C10—H10A	0.9700
C2—C3	1.382 (4)	C10—H10B	0.9700
C3—C4	1.391 (3)	C14—H14A	0.9700
C4—C5	1.386 (4)	C14—H14B	0.9700
C5—C6	1.401 (4)	C15—H15A	0.9600
C5—C8	1.501 (3)	C15—H15B	0.9600
C10—C11	1.509 (3)	C15—H15C	0.9600
C1—O9—C10	116.67 (18)	C5—C6—H6	119.00
C11—O13—C14	115.92 (18)	C5—C8—H8A	109.00
O9—C1—C2	115.63 (19)	C5—C8—H8B	109.00
O9—C1—C6	124.1 (2)	C5—C8—H8C	109.00
C2—C1—C6	120.3 (2)	H8A—C8—H8B	109.00
C1—C2—C3	119.3 (2)	H8A—C8—H8C	109.00
C2—C3—C4	119.8 (3)	H8B—C8—H8C	109.00
Cl7—C4—C3	118.1 (2)	O9—C10—H10A	110.00
Cl7—C4—C5	119.66 (17)	O9—C10—H10B	110.00
C3—C4—C5	122.3 (2)	C11—C10—H10A	110.00
C4—C5—C6	117.3 (2)	C11—C10—H10B	110.00
C4—C5—C8	123.0 (2)	H10A—C10—H10B	108.00
C6—C5—C8	119.7 (2)	O13—C14—H14A	110.00
C1—C6—C5	121.1 (3)	O13—C14—H14B	110.00
O9—C10—C11	108.97 (18)	C15—C14—H14A	110.00
O12—C11—O13	125.5 (2)	C15—C14—H14B	110.00
O12—C11—C10	125.7 (3)	H14A—C14—H14B	108.00
O13—C11—C10	108.80 (18)	C14—C15—H15A	109.00
O13—C14—C15	107.6 (2)	C14—C15—H15B	109.00
C1—C2—H2	120.00	C14—C15—H15C	109.00
C3—C2—H2	120.00	H15A—C15—H15B	109.00
C2—C3—H3	120.00	H15A—C15—H15C	110.00

C4—C3—H3	120.00	H15B—C15—H15C	109.00
C1—C6—H6	119.00		
C10—O9—C1—C2	−175.9 (2)	C2—C3—C4—Cl7	−179.15 (19)
C10—O9—C1—C6	4.2 (3)	C2—C3—C4—C5	1.3 (4)
C1—O9—C10—C11	178.42 (19)	Cl7—C4—C5—C8	−0.6 (3)
C14—O13—C11—O12	−0.1 (4)	Cl7—C4—C5—C6	179.27 (18)
C14—O13—C11—C10	−179.00 (18)	C3—C4—C5—C8	178.9 (2)
C11—O13—C14—C15	171.3 (2)	C3—C4—C5—C6	−1.2 (4)
C2—C1—C6—C5	−0.1 (4)	C8—C5—C6—C1	−179.5 (2)
O9—C1—C2—C3	−179.8 (2)	C4—C5—C6—C1	0.6 (4)
O9—C1—C6—C5	179.8 (2)	O9—C10—C11—O12	1.5 (3)
C6—C1—C2—C3	0.2 (4)	O9—C10—C11—O13	−179.67 (18)
C1—C2—C3—C4	−0.8 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O12^{i}	0.93	2.57	3.194 (3)	125

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+2.