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Ethyl (6-bromo-2-naphthyloxy)acetate

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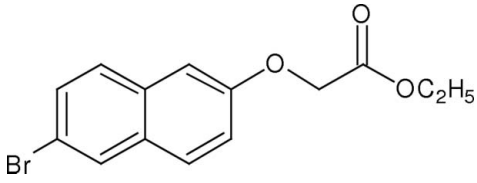
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.103; data-to-parameter ratio = 14.5.

The title compound, $C_{14}H_{13}BrO_3$, is an intermediate in the preparation of naproxen, a non-steroidal anti-inflammatory drug (NSAID). Geometric parameters are in the usual ranges. Neglecting the H atoms, the molecule comprises two planar halves, the bromonaphthyl moiety (r.m.s. deviation = 0.010 Å) and the ethoxycarbonylmethoxy moiety (r.m.s. deviation = 0.018 Å). The dihedral angle between these is 79.23 (7)°. The crystal packing is stabilized by a weak C—H···O hydrogen bond.

Related literature

For related literature, see: Bachechi *et al.* (1997); Dupont *et al.* (1996); Ravikumar *et al.* (1985); Sarojini *et al.* (2007); Sharma *et al.* (2004); Yathirajan *et al.* (2007); Ye *et al.* (2006).



Experimental

Crystal data

$C_{14}H_{13}BrO_3$
M_r = 309.15
Monoclinic, $P2_1/n$
a = 4.9979 (5) Å
b = 9.3847 (7) Å
c = 27.778 (3) Å
β = 94.857 (8)°
V = 1298.2 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.16 mm^{-1}
T = 173 (2) K
0.31 × 0.25 × 0.23 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.441, T_{max} = 0.530 (expected range = 0.402–0.483)
9302 measured reflections
2376 independent reflections
2076 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.103
S = 1.05
2376 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O3^{i}	0.99	2.52	3.499 (3)	169

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2442).

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supplementary materials

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Ethyl (6-bromo-2-naphthyloxy)acetate

B. K. Sarojini, B. Narayana, A. N. Mayekar, H. S. Yathirajan and M. Bolte

Comment

The title compound is an intermediate in the preparation of naproxen, a non-steroidal anti-inflammatory drug (NSAID) commonly used for the reduction of high to extreme pain, fever, inflammation and stiffness caused by conditions such as osteoarthritis, rheumatoid arthritis, psoriatic arthritis, gout, ankylosing spondylitis, injury. Naproxen is a member of the 2-arylpropionic acid (profen) family of NSAIDs. The structures the related compounds *viz*., naproxen (Ravikumar *et al.*, 1985), 6-methoxy-2-naphthyl acetic acid ester-glycolamide (Sharma *et al.*, 2004), 1-(5-chloro-6-methoxynaphthalen-2-yl)propan-1-one (Ye *et al.*, 2006), complex of a lisuride derivative and (S)-naproxen (Bachechi *et al.*, 1997), absolute configuration of (*R*)-1-phenylethylammonium (*S*)-2-(6-methoxy-2-naphthyl)propionate (Dupont *et al.*, 1996), *N*'-isopropylidene-6-methoxy-2-naphthohydrazide (Sarojini *et al.*, 2007), ethyl 6-methoxy-2-naphthoate (Yathirajan *et al.*, 2007) have been published. A new derivative was prepared and its crystal structure is reported.

Geometric parameters of the title compound are in the usual ranges. Neglecting the H atoms, the molecule comprises two planar halves, the bromonaphthyl moiety [r.m.s. deviation 0.010 Å] and the ethoxycarbonylmethoxy moiety [r.m.s. deviation 0.018 Å]. The dihedral angle between these moieties is 79.23 (7)°. The crystal packing is stabilized by a weak C—H···O hydrogen bond.

Experimental

A mixture of 6-bromo-2-hydroxynaphthalein (2.23 g, 0.01 mol) and ethyl chloroacetate(1.3 ml, 0.01 mol) was refluxed in acetone (50 ml) with anhydrous K_2CO_3 (2.76 g, 0.02 mol) for 5 h on a water bath. The reaction mixture was cooled to room temperature and filtered to remove the K_2CO_3 and the filtrate was concentrated over water bath to obtain the title compound. It was then recrystallized using acetonitrile [m.p.:335–338 K]. Analysis for $C_{14}H_{13}BrO_3$: Found(Calculated): C 54.31 (54.39), H 4.19% (4.24%).

Refinement

All H atoms were found in a difference map, but geometrically positioned and refined with fixed individual displacement parameters [U(H) = 1.2 U_{eq}(C) or U(H) = 1.5 U_{eq}(C_{methyl})] using a riding model with C—H ranging from 0.95Å to 0.99 Å.

Figures

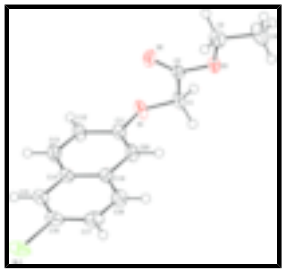

Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

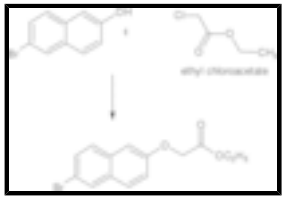

Fig. 2. The formation of the title compound.

Ethyl (6-bromo-2-naphthyloxy)acetate

Crystal data

$C_{14}H_{13}BrO_3$	F_{000} = 624
M_r = 309.15	D_x = 1.582 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 9086 reflections
a = 4.9979 (5) Å	θ = 2.7–25.7º
b = 9.3847 (7) Å	μ = 3.16 mm^{-1}
c = 27.778 (3) Å	T = 173 (2) K
β = 94.857 (8)º	Block, colourless
V = 1298.2 (2) Å^3	0.31 × 0.25 × 0.23 mm
Z = 4	

Data collection

Stoe IPDSII two-circle diffractometer	2376 independent reflections
Radiation source: fine-focus sealed tube	2076 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.063
T = 173(2) K	θ_{max} = 25.4º
ω scans	θ_{min} = 2.6º
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	h = −6→6
T_{min} = 0.441, T_{max} = 0.530	k = −11→10
9302 measured reflections	l = −33→29

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.103$

$S = 1.05$

2376 reflections

164 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.6519P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.58$ e Å^{-3}

$\Delta\rho_{min} = -0.86$ e Å^{-3}

Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0201 (18)

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 $F^2 > 2$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}
Br1	0.71291 (7)	0.13541 (4)	0.159251 (11)	0.04132 (18)
O1	0.3202 (4)	0.2554 (2)	0.43981 (7)	0.0302 (5)
O2	0.5705 (4)	0.5159 (2)	0.43859 (8)	0.0329 (5)
O3	0.1838 (4)	0.62828 (18)	0.44924 (8)	0.0245 (4)
C1	0.1656 (6)	0.3806 (3)	0.44683 (11)	0.0258 (6)
H1A	0.0923	0.3760	0.4788	0.031*
H1B	0.0125	0.3849	0.4218	0.031*
C2	0.3349 (5)	0.5135 (3)	0.44403 (9)	0.0212 (6)
C3	0.3183 (6)	0.7654 (3)	0.44642 (12)	0.0318 (7)
H3A	0.3878	0.7775	0.4143	0.038*
H3B	0.4708	0.7719	0.4715	0.038*
C4	0.1136 (8)	0.8775 (3)	0.45435 (16)	0.0451 (9)
H4A	0.1958	0.9720	0.4525	0.068*
H4B	0.0475	0.8646	0.4863	0.068*
H4C	−0.0365	0.8694	0.4294	0.068*
C11	0.3974 (5)	0.2311 (3)	0.39419 (10)	0.0242 (6)

C12	0.6027 (6)	0.1268 (3)	0.39287 (12)	0.0294 (6)
H12	0.6735	0.0822	0.4219	0.035*
C13	0.6977 (6)	0.0911 (3)	0.35017 (11)	0.0311 (6)
H13	0.8353	0.0214	0.3497	0.037*
C14	0.5957 (6)	0.1557 (3)	0.30589 (11)	0.0252 (6)
C15	0.6936 (6)	0.1211 (3)	0.26118 (12)	0.0302 (7)
H15	0.8344	0.0536	0.2598	0.036*
C16	0.5853 (6)	0.1848 (3)	0.21983 (11)	0.0307 (6)
C17	0.3772 (6)	0.2856 (3)	0.22061 (11)	0.0342 (7)
H17	0.3024	0.3276	0.1914	0.041*
C18	0.2840 (6)	0.3222 (3)	0.26353 (12)	0.0337 (7)
H18	0.1456	0.3915	0.2641	0.040*
C19	0.3897 (5)	0.2589 (3)	0.30763 (10)	0.0248 (6)
C20	0.2940 (5)	0.2957 (3)	0.35258 (11)	0.0275 (6)
H20	0.1573	0.3656	0.3538	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0533 (3)	0.0473 (3)	0.0245 (2)	−0.01467 (14)	0.01019 (15)	−0.00939 (13)
O1	0.0420 (11)	0.0227 (10)	0.0276 (11)	0.0120 (8)	0.0127 (9)	0.0034 (8)
O2	0.0215 (11)	0.0365 (11)	0.0417 (13)	0.0050 (8)	0.0074 (9)	−0.0026 (10)
O3	0.0249 (9)	0.0192 (10)	0.0301 (11)	0.0044 (7)	0.0067 (8)	0.0016 (7)
C1	0.0304 (14)	0.0196 (13)	0.0291 (16)	0.0055 (10)	0.0115 (12)	0.0004 (11)
C2	0.0255 (14)	0.0241 (13)	0.0143 (13)	0.0055 (10)	0.0030 (10)	0.0011 (10)
C3	0.0334 (15)	0.0244 (14)	0.0387 (18)	−0.0039 (11)	0.0093 (13)	0.0006 (13)
C4	0.059 (2)	0.0210 (15)	0.058 (2)	0.0044 (14)	0.0215 (19)	0.0020 (14)
C11	0.0295 (13)	0.0185 (12)	0.0253 (15)	0.0024 (10)	0.0071 (11)	−0.0008 (11)
C12	0.0351 (15)	0.0256 (14)	0.0280 (16)	0.0111 (11)	0.0059 (12)	0.0043 (11)
C13	0.0352 (15)	0.0304 (15)	0.0283 (16)	0.0129 (12)	0.0051 (12)	0.0014 (13)
C14	0.0295 (14)	0.0205 (13)	0.0256 (15)	−0.0016 (10)	0.0031 (11)	−0.0039 (11)
C15	0.0352 (15)	0.0261 (15)	0.0297 (16)	−0.0005 (11)	0.0057 (13)	−0.0044 (12)
C16	0.0373 (15)	0.0307 (15)	0.0246 (15)	−0.0110 (12)	0.0058 (12)	−0.0053 (13)
C17	0.0412 (16)	0.0340 (16)	0.0265 (16)	−0.0065 (13)	−0.0021 (13)	0.0047 (13)
C18	0.0365 (16)	0.0328 (16)	0.0316 (17)	0.0061 (13)	0.0012 (12)	0.0032 (14)
C19	0.0272 (13)	0.0194 (13)	0.0279 (15)	−0.0003 (10)	0.0019 (11)	−0.0003 (11)
C20	0.0291 (14)	0.0227 (14)	0.0312 (16)	0.0089 (11)	0.0056 (11)	0.0021 (12)

Geometric parameters (Å, °)

Br1—C16	1.907 (3)	C11—C12	1.421 (4)
O1—C11	1.374 (3)	C12—C13	1.357 (4)
O1—C1	1.428 (3)	C12—H12	0.9500
O2—C2	1.200 (3)	C13—C14	1.426 (4)
O3—C2	1.330 (3)	C13—H13	0.9500
O3—C3	1.457 (3)	C14—C15	1.411 (4)
C1—C2	1.513 (4)	C14—C19	1.417 (4)
C1—H1A	0.9900	C15—C16	1.366 (4)
C1—H1B	0.9900	C15—H15	0.9500

C3—C4	1.497 (4)	C16—C17	1.407 (5)
C3—H3A	0.9900	C17—C18	1.360 (5)
C3—H3B	0.9900	C17—H17	0.9500
C4—H4A	0.9800	C18—C19	1.423 (4)
C4—H4B	0.9800	C18—H18	0.9500
C4—H4C	0.9800	C19—C20	1.417 (4)
C11—C20	1.367 (4)	C20—H20	0.9500
C11—O1—C1	117.4 (2)	C13—C12—H12	120.0
C2—O3—C3	116.1 (2)	C11—C12—H12	120.0
O1—C1—C2	111.1 (2)	C12—C13—C14	121.5 (3)
O1—C1—H1A	109.4	C12—C13—H13	119.2
C2—C1—H1A	109.4	C14—C13—H13	119.2
O1—C1—H1B	109.4	C15—C14—C19	119.6 (3)
C2—C1—H1B	109.4	C15—C14—C13	122.4 (3)
H1A—C1—H1B	108.0	C19—C14—C13	118.0 (3)
O2—C2—O3	124.8 (3)	C16—C15—C14	119.8 (3)
O2—C2—C1	125.5 (2)	C16—C15—H15	120.1
O3—C2—C1	109.7 (2)	C14—C15—H15	120.1
O3—C3—C4	106.8 (2)	C15—C16—C17	121.5 (3)
O3—C3—H3A	110.4	C15—C16—Br1	119.8 (2)
C4—C3—H3A	110.4	C17—C16—Br1	118.7 (2)
O3—C3—H3B	110.4	C18—C17—C16	119.5 (3)
C4—C3—H3B	110.4	C18—C17—H17	120.3
H3A—C3—H3B	108.6	C16—C17—H17	120.3
C3—C4—H4A	109.5	C17—C18—C19	121.3 (3)
C3—C4—H4B	109.5	C17—C18—H18	119.4
H4A—C4—H4B	109.5	C19—C18—H18	119.4
C3—C4—H4C	109.5	C20—C19—C14	119.8 (3)
H4A—C4—H4C	109.5	C20—C19—C18	121.9 (3)
H4B—C4—H4C	109.5	C14—C19—C18	118.3 (3)
C20—C11—O1	126.2 (2)	C11—C20—C19	120.3 (2)
C20—C11—C12	120.4 (3)	C11—C20—H20	119.8
O1—C11—C12	113.4 (3)	C19—C20—H20	119.8
C13—C12—C11	120.0 (3)		
C11—O1—C1—C2	−70.4 (3)	C14—C15—C16—C17	0.2 (4)
C3—O3—C2—O2	2.1 (4)	C14—C15—C16—Br1	−178.8 (2)
C3—O3—C2—C1	−178.9 (2)	C15—C16—C17—C18	1.0 (5)
O1—C1—C2—O2	−2.8 (4)	Br1—C16—C17—C18	−179.9 (2)
O1—C1—C2—O3	178.1 (2)	C16—C17—C18—C19	−1.1 (5)
C2—O3—C3—C4	−178.7 (3)	C15—C14—C19—C20	−178.9 (3)
C1—O1—C11—C20	−15.6 (4)	C13—C14—C19—C20	0.7 (4)
C1—O1—C11—C12	165.1 (2)	C15—C14—C19—C18	1.3 (4)
C20—C11—C12—C13	0.2 (5)	C13—C14—C19—C18	−179.0 (3)
O1—C11—C12—C13	179.5 (3)	C17—C18—C19—C20	−179.8 (3)
C11—C12—C13—C14	−0.2 (5)	C17—C18—C19—C14	−0.1 (4)
C12—C13—C14—C15	179.3 (3)	O1—C11—C20—C19	−179.0 (3)
C12—C13—C14—C19	−0.3 (4)	C12—C11—C20—C19	0.3 (4)
C19—C14—C15—C16	−1.4 (4)	C14—C19—C20—C11	−0.7 (4)

C13—C14—C15—C16	179.0 (3)	C18—C19—C20—C11	179.0 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1A···O3^{i}	0.99	2.52	3.499 (3)	169

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

Fig. 1

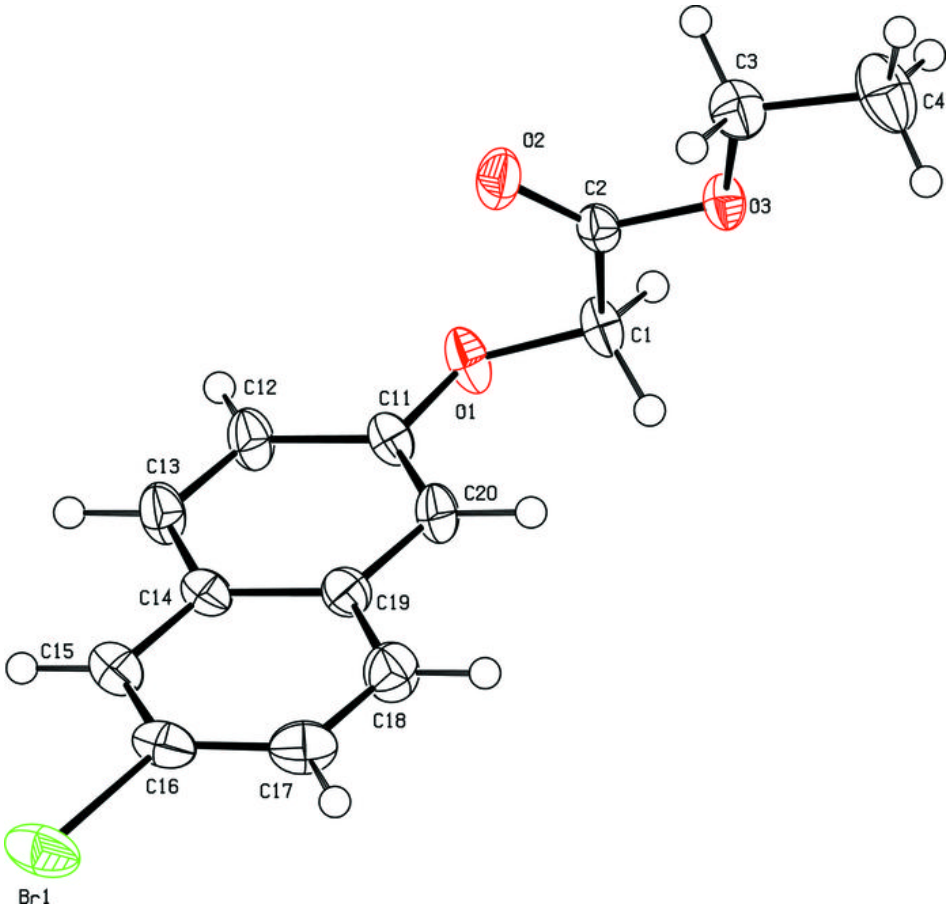

Fig. 2