organic compounds

3-Acetoxy-2-naphthoic acid

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In the title compound, $C_{13}H_{10}O_4$, an analog of acetylsalicylic acid, the naphthalene unit is twisted slightly due to *ortho* disubstitution [dihedral angle between conjugated rings system in the naphthalene unit = 2.0 (2)°]. The mean planes of the carboxylic and ester groups are almost coplanar and perpendicular, respectively, to the mean plane of the conjugated aromatic system, making dihedral angles of 8.9 (3) and 89.3 (1)°. In the crystal, molecules are paired through their carboxylic groups by the typical centrosymmetric O—H⋯O interactions with $R_2^2(8)$ hydrogen-bond motifs. In addition, several weak C—H⋯O intermolecular contacts are also observed. Finally, the molecules are stacked along crystallographic [100] and [010] directions.

Related literature

This work was undertaken as part of our study on the relationship between conformation and reactivity in the hydrolysis reactions of esters bearing neighboring catalytic groups. For the synthesis, see: Bergeron *et al.* (1996). For related structures, see: Souza *et al.* (2007); Gu *et al.* (2001); Wilson (2002). Besides electronic effects, intramolecular reactions depend on the spatial relationship of the reacting groups, see: Orth *et al.* (2010).
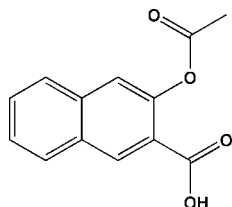
Experimental

Crystal data

$C_{13}H_{10}O_4$

M_r = 230.21

Monoclinic, $P2_1/n$
a = 10.235 (2) Å
b = 4.739 (2) Å
c = 23.0873 (16) Å
β = 101.060 (11)°
V = 1099.0 (5) Å^3

Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 K
$0.50 \times 0.33 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
1999 measured reflections
1950 independent reflections
1214 reflections with $I > 2\sigma(I)$

R_{int} = 0.026
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.204
S = 1.05
1950 reflections

155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^i	0.91	1.74	2.636 (3)	171
C7—H7⋯O4^{ii}	0.93	2.71	3.368 (5)	128
C13—H13B⋯O4^{iii}	0.96	2.52	3.435 (5)	160

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* in *CAD-4 Software*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

3-Acetoxy-2-naphthoic acid

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Comment

Besides electronic effects, intramolecular reactions depend on the spatial relationship of the reacting groups (Orth *et al.*, 2010). Subtle changes in the structure of similar compounds may lead to different relationships between nucleophilic-electrophilic centers within similar molecules, leading to different reaction mechanisms in solution. On this basis, we are currently studying the hydrolysis of a series of structurally related naphthyl esters. In a previous report (Souza *et al.*, 2007), we published the structure of 2-carboxy-1-naphthyl acetate, a naphthoic acid bearing an *ortho*-ester group. In that structure, the dihedral angle between the aromatic mean plane and the ester group is 80.34 (5)°, considerably smaller than the one observed in α-naphthyl acetate (86.50°) (Gu *et al.*, 2001), and we explained this difference in terms of an attractive interaction between the ester and the acid groups in 2-carboxy-1-naphthyl acetate. In the current work, we report the structure of 3-acetoxy-2-naphthoic acid **I** (Fig. 1), $C_{13}H_{10}O_4$, an acetylsalicylic analog. In this system the dihedral angle between acetoxy and aromatic mean planes is 89.3 (1)°, while the carboxylic acid group and naphthalene ring are almost coplanar with dihedral angle of 8.9 (3)°. Packing is controlled by carboxylic acid dimer formation, involving centrosymmetric O2–H···O1 interactions ($R^2_2(8)$ hydrogen bond pattern, Fig. 2). Several weak C–H···O intermolecular contacts are also observed. Finally, the molecules are stacked along crystallographic [100] and [010] directions (Fig. 3).

Experimental

The title compound was prepared by following the procedure reported by Bergeron *et al.*, (1996). Concentrated sulfuric acid (10 drops) was added to a refluxing mixture of 3-hydroxy-2-naphthoic acid (3.50 g, 18.6 mmol) in acetic anhydride (8 ml, 89.7 mmol). The mixture was kept under reflux for 10 additional minutes and, after cooling to room temperature, the pale solid was filtered off and recrystallized in aqueous ethanol. The 10 mg of the prepared 3-acetoxy-2-naphthoic acid were dissolved in 5 ml of dry $CHCl_3$ in a 10 ml glass vial and the flask was kept in a saturated petroleum ether (313-333 K) atmosphere at 293 K, giving the title compound as pale yellow crystals that melt at 458-459 K.

Refinement

All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed at their idealized positions with distances of 0.93Å for C–H_{Ar} and 0.96Å for CH_3 group. Their $U_{iso}H$ were fixed at 1.2 and 1.5 times $U_{eq}C$ of the preceding atom for aromatic and methyl group, respectively. The hydrogen atom of the acid group was located from the Fourier difference map and treated using a riding model with $U_{iso}H = 1.2U_{eq}O$.
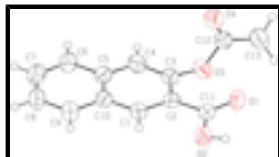
supplementary materials

Figures

Fig. 1. The molecular structure of the title compound with the atom labeling scheme. Displacement ellipsoids are shown at the 40% probability level. H atoms are presented as a small spheres of arbitrary radius.
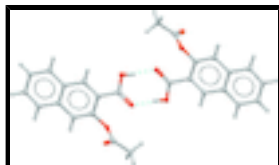

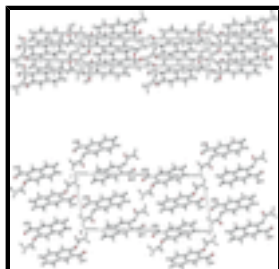Fig. 2. Molecules paired by centrosymmetric $R^2_2(8)$ hydrogen bonds.

Fig. 3. Molecules of **I** stacked along [100] direction (top) and along [010] direction (bottom).

3-Acetoxy-2-naphthoic acid

Crystal data

$C_{13}H_{10}O_4$	$F(000) = 480$
$M_r = 230.21$	$D_x = 1.391$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
$a = 10.235$ (2) Å	$\theta = 6.5–18.5°$
$b = 4.739$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 23.0873$ (16) Å	$T = 295$ K
$\beta = 101.060$ (11)°	Block, pale yellow
$V = 1099.0$ (5) Å^3	$0.50 \times 0.33 \times 0.10$ mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.026$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.1°$, $\theta_{min} = 1.8°$
graphite	$h = -11 \rightarrow 12$
ω–2θ scans	$k = -5 \rightarrow 0$
1999 measured reflections	$l = -27 \rightarrow 0$
1950 independent reflections	3 standard reflections every 200 reflections
1214 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.063$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.204$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o{}^2) + (0.1252P)^2 + 0.1035P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
1950 reflections	$(\Delta/\sigma)_{max} < 0.001$
155 parameters	$\Delta\rho_{max} = 0.26$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.5573 (3)	0.3368 (7)	0.18259 (12)	0.0566 (8)
H1	0.6184	0.4763	0.1779	0.068*
C2	0.4810 (3)	0.2182 (6)	0.13351 (12)	0.0518 (7)
C3	0.3930 (3)	−0.0003 (6)	0.14168 (12)	0.0540 (8)
C4	0.3780 (3)	−0.0817 (7)	0.19648 (14)	0.0632 (9)
H4	0.3170	−0.2222	0.2006	0.076*
C5	0.4544 (3)	0.0454 (7)	0.24728 (13)	0.0599 (8)
C6	0.4428 (3)	−0.0331 (9)	0.30541 (14)	0.0737 (10)
H6	0.3804	−0.1680	0.3110	0.088*
C7	0.5213 (4)	0.0861 (9)	0.35239 (15)	0.0806 (11)
H7	0.5127	0.0308	0.3901	0.097*
C8	0.6136 (4)	0.2872 (9)	0.34600 (14)	0.0815 (11)
H8	0.6669	0.3659	0.3792	0.098*
C9	0.6278 (3)	0.3735 (8)	0.29060 (13)	0.0736 (10)
H9	0.6906	0.5097	0.2863	0.088*
C10	0.5463 (3)	0.2538 (7)	0.24028 (12)	0.0564 (8)
C11	0.4918 (3)	0.3266 (7)	0.07423 (12)	0.0543 (7)
C12	0.2108 (3)	−0.0557 (7)	0.06310 (13)	0.0583 (8)
C13	0.1651 (3)	−0.2253 (8)	0.00866 (15)	0.0770 (10)
H13A	0.0772	−0.1662	−0.0098	0.115*
H13B	0.1635	−0.4215	0.0188	0.115*
H13C	0.2250	−0.1974	−0.0181	0.115*
O1	0.4153 (2)	0.2552 (5)	0.02898 (9)	0.0680 (7)
O2	0.5866 (2)	0.5076 (6)	0.07447 (9)	0.0768 (8)
H2	0.5764	0.5907	0.0385	0.092*
O3	0.32733 (19)	−0.1555 (4)	0.09356 (9)	0.0623 (6)
O4	0.1549 (2)	0.1389 (6)	0.07911 (10)	0.0802 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0497 (15)	0.073 (2)	0.0460 (16)	0.0003 (15)	0.0077 (12)	0.0016 (14)
C2	0.0447 (14)	0.0656 (18)	0.0458 (15)	0.0087 (13)	0.0105 (12)	0.0041 (13)
C3	0.0466 (15)	0.0625 (18)	0.0508 (16)	0.0069 (14)	0.0043 (12)	0.0017 (14)
C4	0.0547 (17)	0.071 (2)	0.0629 (19)	−0.0013 (15)	0.0080 (14)	0.0167 (16)
C5	0.0536 (17)	0.073 (2)	0.0530 (17)	0.0156 (16)	0.0112 (13)	0.0124 (15)
C6	0.073 (2)	0.096 (3)	0.0540 (19)	0.0135 (19)	0.0171 (16)	0.0212 (18)
C7	0.089 (2)	0.105 (3)	0.050 (2)	0.029 (2)	0.0195 (18)	0.0172 (19)
C8	0.089 (2)	0.109 (3)	0.0429 (18)	0.021 (2)	0.0032 (16)	−0.0017 (18)
C9	0.071 (2)	0.097 (3)	0.0500 (18)	0.0015 (19)	0.0058 (15)	−0.0016 (17)
C10	0.0523 (16)	0.070 (2)	0.0465 (16)	0.0156 (15)	0.0082 (13)	0.0037 (14)
C11	0.0464 (15)	0.0720 (19)	0.0457 (16)	0.0021 (15)	0.0116 (12)	−0.0024 (14)
C12	0.0507 (16)	0.067 (2)	0.0567 (17)	0.0070 (15)	0.0100 (13)	0.0112 (16)
C13	0.069 (2)	0.092 (3)	0.064 (2)	0.0046 (19)	−0.0036 (15)	−0.0056 (18)
O1	0.0652 (13)	0.0970 (16)	0.0415 (11)	−0.0110 (12)	0.0096 (9)	−0.0044 (11)
O2	0.0623 (13)	0.120 (2)	0.0481 (12)	−0.0266 (14)	0.0093 (9)	0.0100 (12)
O3	0.0549 (12)	0.0653 (13)	0.0612 (13)	0.0042 (10)	−0.0029 (9)	0.0011 (10)
O4	0.0618 (13)	0.1063 (19)	0.0698 (15)	0.0223 (14)	0.0057 (11)	−0.0064 (13)

Geometric parameters (Å, °)

C1—C2	1.368 (4)	C7—H7	0.9300
C1—C10	1.414 (4)	C8—C9	1.377 (5)
C1—H1	0.9300	C8—H8	0.9300
C2—C3	1.409 (4)	C9—C10	1.412 (4)
C2—C11	1.486 (4)	C9—H9	0.9300
C3—C4	1.359 (4)	C11—O1	1.227 (3)
C3—O3	1.393 (3)	C11—O2	1.295 (3)
C4—C5	1.413 (4)	C12—O4	1.181 (4)
C4—H4	0.9300	C12—O3	1.349 (3)
C5—C10	1.395 (4)	C12—C13	1.490 (4)
C5—C6	1.419 (4)	C13—H13A	0.9600
C6—C7	1.344 (5)	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—C8	1.370 (5)	O2—H2	0.9071
C2—C1—C10	122.0 (3)	C7—C8—H8	119.9
C2—C1—H1	119.0	C9—C8—H8	119.9
C10—C1—H1	119.0	C8—C9—C10	119.6 (4)
C1—C2—C3	118.0 (3)	C8—C9—H9	120.2
C1—C2—C11	119.3 (3)	C10—C9—H9	120.2
C3—C2—C11	122.7 (3)	C5—C10—C9	119.6 (3)
C4—C3—O3	118.0 (3)	C5—C10—C1	118.9 (3)
C4—C3—C2	121.5 (3)	C9—C10—C1	121.5 (3)
O3—C3—C2	120.3 (2)	O1—C11—O2	122.8 (3)
C3—C4—C5	120.6 (3)	O1—C11—C2	122.8 (3)

C3—C4—H4	119.7	O2—C11—C2	114.4 (2)
C5—C4—H4	119.7	O4—C12—O3	122.9 (3)
C10—C5—C4	118.9 (3)	O4—C12—C13	126.3 (3)
C10—C5—C6	118.4 (3)	O3—C12—C13	110.7 (3)
C4—C5—C6	122.7 (3)	C12—C13—H13A	109.5
C7—C6—C5	120.5 (4)	C12—C13—H13B	109.5
C7—C6—H6	119.8	H13A—C13—H13B	109.5
C5—C6—H6	119.8	C12—C13—H13C	109.5
C6—C7—C8	121.6 (3)	H13A—C13—H13C	109.5
C6—C7—H7	119.2	H13B—C13—H13C	109.5
C8—C7—H7	119.2	C11—O2—H2	109.2
C7—C8—C9	120.3 (3)	C12—O3—C3	118.3 (2)
C10—C1—C2—C3	−2.4 (4)	C6—C5—C10—C9	2.1 (4)
C10—C1—C2—C11	176.4 (3)	C4—C5—C10—C1	1.8 (4)
C1—C2—C3—C4	3.6 (4)	C6—C5—C10—C1	−179.1 (3)
C11—C2—C3—C4	−175.2 (3)	C8—C9—C10—C5	−1.3 (5)
C1—C2—C3—O3	−170.7 (2)	C8—C9—C10—C1	179.8 (3)
C11—C2—C3—O3	10.5 (4)	C2—C1—C10—C5	−0.3 (4)
O3—C3—C4—C5	172.3 (2)	C2—C1—C10—C9	178.6 (3)
C2—C3—C4—C5	−2.1 (5)	C1—C2—C11—O1	−170.7 (3)
C3—C4—C5—C10	−0.6 (5)	C3—C2—C11—O1	8.0 (5)
C3—C4—C5—C6	−179.7 (3)	C1—C2—C11—O2	7.7 (4)
C10—C5—C6—C7	−1.7 (5)	C3—C2—C11—O2	−173.5 (2)
C4—C5—C6—C7	177.4 (3)	O4—C12—O3—C3	−8.7 (4)
C5—C6—C7—C8	0.5 (6)	C13—C12—O3—C3	171.9 (3)
C6—C7—C8—C9	0.3 (6)	C4—C3—O3—C12	98.6 (3)
C7—C8—C9—C10	0.1 (5)	C2—C3—O3—C12	−86.8 (3)
C4—C5—C10—C9	−177.1 (3)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1[i]	0.91	1.74	2.636 (3)	171
C7—H7···O4[ii]	0.93	2.71	3.368 (5)	128
C13—H13B···O4[iii]	0.96	2.52	3.435 (5)	160

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) *x*, *y*−1, *z*.

Fig. 1

Fig. 2

Fig. 3