Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Carboxy-1-naphthyl acetate

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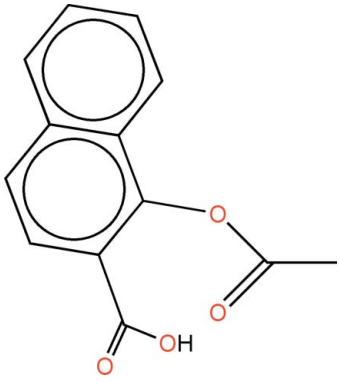
Received 9 October 2007; accepted 26 October 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.116; data-to-parameter ratio = 12.9.

In the crystal structure of the title compound, $C_{13}H_{10}O_4$, molecules are linked through centrosymmetrically related O—H···O hydrogen bonds by carboxyl pairing. Methyl H atoms of the acetoxy group are disordered over two equally occupied sites. The compound was prepared for the study of the relationship between conformation and reactivity in hydrolysis reactions of esters bearing neighboring catalytic groups.

Related literature

For related literature, see: Barros *et al.* (2001); Bergeron *et al.* (1996); Fersht & Kirby (1968); Fitzgerald & Gerkin (1993); Gu *et al.* (2001).



Experimental

Crystal data

$C_{13}H_{10}O_4$
M_r = 230.21
Triclinic, $P\overline{1}$
a = 7.569 (1) Å
b = 8.498 (1) Å
c = 8.892 (1) Å
α = 100.78 (1)°
β = 93.64 (1)°
γ = 91.56 (1)°
V = 560.27 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.50 × 0.23 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
2124 measured reflections
1987 independent reflections
1516 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
3 standard reflections
every 200 reflections
intensity decay: <1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.116
S = 1.04
1987 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O22—H22···O21^{i}	0.96	1.70	2.6517 (15)	173

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

The authors are indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Apoio à Pesquisa Científica e Tecnológica do Estado de Santa Catarina (FAPESC), Financiadora de Estudos e Projetos (FINEP) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2141).

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 doi:10.1107/S1600536807053433

supplementary materials

Acta Cryst. (2007). E**63**, o4523 [**doi:10.1107/S1600536807053433**]

2-Carboxy-1-naphthyl acetate

B. S. Souza, A. J. Bortoluzzi and F. Nome

Comment

Intramolecular carboxyl group catalysis on ester hydrolysis involves the carboxyl group acting as general base or general acid. In cases where the leaving group is activated, like 2,4-dinitro acetyl salicylic acid (Fersht & Kirby, 1968) or esters of naphthalic acid (Barros *et al.*, 2001), nucleophilic attack has been reported. General acid-base catalysis is evidently highly efficient in enzyme active sites, but in only a handful of model systems. The common feature of these efficient intramolecular model systems is the development of a strong intramolecular hydrogen bond in the product, and thus in the transition state leading to it. We are interested in the effect of the proximity and conformation of the reactive groups in ester hydrolysis catalyzed by the acid group and we have selected naphthalene rings to anchor the reactive groups, since significant effects have been reported in naphthalene derivatives. Thus, we prepared a series of naphthoic esters bearing neighboring carboxyl group in different special relationships. Here we report the structure of 1-acetoxy-2-naphthoic acid, (I).

A projection of the crystal structure of (I) is shown in Fig. 1 and the selected bond lengths and angles are given in Table 1. The acid group plane O21/C20/O22 is 3.35° less planar in relation to the mean aromatic plane than the same group in 2-naphthoic acid (Fitzgerald & Gerkin, 1993). The C1—C2—C20 and O10—C1—C10 angles are wider and narrower, respectively, than the equivalent angles in 2-naphthoic acid (Fitzgerald & Gerkin, 1993) and α-naphthyl acetate (Gu *et al.*, 2001). These results are indicative of some repulsive interaction between O22 and O10 atoms. Conversely, the dihedral angle between the aromatic mean plane C1···C10 and the ester group O10/O11/C12/C13 is 80.34 (5)°, while the equivalent angle in α-naphthyl acetate is 86.5° (Gu *et al.*, 2001). This decrease in dihedral angle could be the result of the short separation between O22 and C12, 2.860 (2) Å, which may indicate an attractive interaction, which can account for the high reactivity in solution detected in some preliminary kinetic studies.

The main feature in the crystal structure of (I) is the dimeric structure formed by intermolecular hydrogen bond. The molecules are linked through centrosymmetrically related O—H···O hydrogen bonds by carboxyl pairing (Fig. 2).

Experimental

The title compound was prepared by a procedure similar to that reported by Bergeron *et al.* (1996) for the preparation of 3-acetoxy-2-naphthoic acid. Concentrated sulfuric acid (10 drops) were added to a refluxing mixture of 1-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 pale crystals melt at 411–412 K.

Refinement

H atoms bonded to C atoms were added at calculated positions, with C—H = 0.96 (methyl CH_3) or 0.93 Å (aromatic CH), and $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for the methyl group. For the methyl group, H atoms are disordered over two positions,

by rotation about C12—C13. Both positions were idealized, with site occupancies fixed to 1/2. H atom of the acid group was found in a difference map and treated as riding on O22, with U_{iso}(H22) = 1.2U_{eq}(O22).

Figures

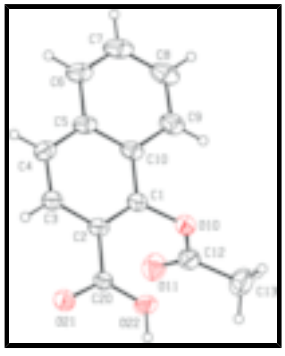

Fig. 1. The molecular structure of (I) with labeling scheme. Displacement ellipsoids are shown at the 40% probability level for non H atoms. Methyl H atoms of the acetoxy group are disordered over two positions, but a single orientation is shhown.

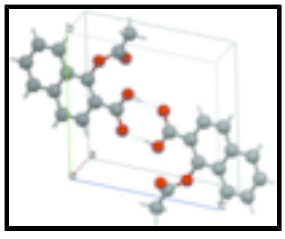

Fig. 2. Packing of (I) showing the molecules connected through hydrogen bonds and stacked along axis [010].

2-Carboxy-1-naphthyl acetate

Crystal data

$C_{13}H_{10}O_4$	$Z = 2$
$M_r = 230.21$	$F_{000} = 240$
Triclinic, $P\overline{1}$	$D_x = 1.365$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 411 K
$a = 7.569$ (1) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 8.498$ (1) Å	Cell parameters from 25 reflections
$c = 8.892$ (1) Å	$\theta = 5.4$–16.9º
$\alpha = 100.78$ (1)º	$\mu = 0.10$ mm^{-1}
$\beta = 93.64$ (1)º	$T = 293$ (2) K
$\gamma = 91.56$ (1)º	Irregular block, colourless
$V = 560.27$ (12) Å^3	0.50 × 0.23 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.010$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.1$º
Monochromator: graphite	$\theta_{min} = 2.3$º
$T = 293$(2) K	$h = -9 \rightarrow 9$

ω–2θ scans	$k = -9 \rightarrow 10$
Absorption correction: none	$l = -10 \rightarrow 0$
2124 measured reflections	3 standard reflections
1987 independent reflections	every 200 reflections
1516 reflections with $I > 2\sigma(I)$	intensity decay: <1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.0777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1987 reflections	$\Delta\rho_{max} = 0.14$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.20498 (18)	0.67195 (18)	0.10960 (16)	0.0424 (4)	
C2	0.17587 (18)	0.53133 (18)	0.16112 (16)	0.0416 (4)	
C3	0.21410 (19)	0.38603 (19)	0.06528 (17)	0.0468 (4)	
H3	0.1957	0.2900	0.0988	0.056*	
C4	0.2771 (2)	0.3831 (2)	−0.07489 (18)	0.0506 (4)	
H4	0.3015	0.2856	−0.1354	0.061*	
C5	0.30595 (19)	0.5267 (2)	−0.12959 (16)	0.0487 (4)	
C6	0.3692 (2)	0.5273 (2)	−0.27633 (19)	0.0608 (5)	
H6	0.3939	0.4311	−0.3389	0.073*	
C7	0.3940 (2)	0.6671 (3)	−0.3258 (2)	0.0724 (6)	
H7	0.4348	0.6657	−0.4225	0.087*	
C8	0.3592 (3)	0.8128 (3)	−0.2338 (2)	0.0742 (6)	
H8	0.3779	0.9077	−0.2694	0.089*	
C9	0.2978 (2)	0.8182 (2)	−0.0910 (2)	0.0628 (5)	
H9	0.2746	0.9161	−0.0305	0.075*	
C10	0.26988 (18)	0.6744 (2)	−0.03603 (17)	0.0474 (4)	
C12	0.2811 (2)	0.88957 (19)	0.31165 (19)	0.0527 (4)	
C13	0.2144 (3)	1.0414 (2)	0.3956 (2)	0.0781 (6)	
H13A	0.0997	1.0594	0.3510	0.117*	0.50
H13B	0.2948	1.1287	0.3889	0.117*	0.50
H13C	0.2056	1.0343	0.5014	0.117*	0.50
H13D	0.3004	1.0889	0.4765	0.117*	0.50
H13E	0.1053	1.0195	0.4386	0.117*	0.50
H13F	0.1945	1.1140	0.3261	0.117*	0.50
C20	0.10309 (18)	0.52309 (17)	0.31152 (16)	0.0417 (4)	

O10	0.16270 (14)	0.81991 (12)	0.19450 (12)	0.0508 (3)
O11	0.41900 (17)	0.83269 (15)	0.33735 (15)	0.0704 (4)
O21	0.08911 (17)	0.38850 (14)	0.34850 (13)	0.0639 (4)
O22	0.05509 (16)	0.65000 (13)	0.39605 (12)	0.0582 (3)
H22	−0.0060	0.6349	0.4841	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0409 (8)	0.0493 (9)	0.0383 (8)	0.0025 (6)	0.0031 (6)	0.0115 (6)
C2	0.0386 (7)	0.0520 (9)	0.0357 (8)	0.0020 (6)	0.0031 (6)	0.0123 (6)
C3	0.0476 (8)	0.0509 (9)	0.0428 (8)	0.0028 (7)	0.0044 (7)	0.0104 (7)
C4	0.0481 (8)	0.0589 (10)	0.0429 (8)	0.0056 (7)	0.0060 (7)	0.0035 (7)
C5	0.0371 (8)	0.0728 (11)	0.0366 (8)	0.0017 (7)	0.0036 (6)	0.0108 (7)
C6	0.0526 (9)	0.0897 (13)	0.0420 (9)	0.0040 (9)	0.0106 (7)	0.0144 (9)
C7	0.0659 (11)	0.1106 (17)	0.0469 (10)	−0.0015 (11)	0.0157 (8)	0.0273 (11)
C8	0.0765 (13)	0.0933 (15)	0.0648 (12)	−0.0064 (11)	0.0155 (10)	0.0435 (11)
C9	0.0688 (11)	0.0692 (12)	0.0566 (10)	−0.0013 (9)	0.0127 (8)	0.0258 (9)
C10	0.0405 (8)	0.0636 (10)	0.0419 (8)	−0.0009 (7)	0.0042 (6)	0.0197 (7)
C12	0.0637 (10)	0.0455 (9)	0.0511 (9)	−0.0050 (8)	0.0121 (8)	0.0134 (7)
C13	0.0923 (15)	0.0567 (11)	0.0830 (14)	0.0045 (10)	0.0197 (11)	0.0024 (10)
C20	0.0432 (8)	0.0456 (8)	0.0383 (8)	0.0042 (6)	0.0054 (6)	0.0122 (6)
O10	0.0589 (7)	0.0492 (6)	0.0480 (6)	0.0071 (5)	0.0091 (5)	0.0162 (5)
O11	0.0671 (8)	0.0618 (8)	0.0761 (9)	0.0029 (6)	−0.0066 (7)	0.0011 (6)
O21	0.0883 (9)	0.0547 (7)	0.0583 (7)	0.0167 (6)	0.0303 (6)	0.0254 (6)
O22	0.0801 (8)	0.0535 (7)	0.0442 (6)	0.0015 (6)	0.0240 (6)	0.0115 (5)

Geometric parameters (Å, °)

C1—C2	1.375 (2)	C8—H8	0.9300
C1—O10	1.3967 (18)	C9—C10	1.413 (2)
C1—C10	1.417 (2)	C9—H9	0.9300
C2—C3	1.411 (2)	C12—O11	1.189 (2)
C2—C20	1.491 (2)	C12—O10	1.364 (2)
C3—C4	1.359 (2)	C12—C13	1.483 (2)
C3—H3	0.9300	C13—H13A	0.9600
C4—C5	1.412 (2)	C13—H13B	0.9600
C4—H4	0.9300	C13—H13C	0.9600
C5—C10	1.414 (2)	C13—H13D	0.9600
C5—C6	1.419 (2)	C13—H13E	0.9600
C6—C7	1.354 (3)	C13—H13F	0.9600
C6—H6	0.9300	C20—O21	1.2514 (17)
C7—C8	1.392 (3)	C20—O22	1.2700 (18)
C7—H7	0.9300	O22—H22	0.9613
C8—C9	1.373 (3)		
C2—C1—O10	121.68 (12)	O11—C12—O10	122.40 (15)
C2—C1—C10	122.05 (14)	O11—C12—C13	126.65 (17)
O10—C1—C10	116.18 (13)	O10—C12—C13	110.95 (16)

C1—C2—C3	118.25 (13)	C12—C13—H13A	109.5
C1—C2—C20	123.76 (13)	C12—C13—H13B	109.5
C3—C2—C20	117.98 (13)	H13A—C13—H13B	109.5
C4—C3—C2	121.56 (15)	C12—C13—H13C	109.5
C4—C3—H3	119.2	H13A—C13—H13C	109.5
C2—C3—H3	119.2	H13B—C13—H13C	109.5
C3—C4—C5	120.68 (15)	C12—C13—H13D	109.5
C3—C4—H4	119.7	H13A—C13—H13D	141.1
C5—C4—H4	119.7	H13B—C13—H13D	56.3
C4—C5—C10	119.17 (13)	H13C—C13—H13D	56.3
C4—C5—C6	121.96 (16)	C12—C13—H13E	109.5
C10—C5—C6	118.86 (16)	H13A—C13—H13E	56.3
C7—C6—C5	120.44 (18)	H13B—C13—H13E	141.1
C7—C6—H6	119.8	H13C—C13—H13E	56.3
C5—C6—H6	119.8	H13D—C13—H13E	109.5
C6—C7—C8	120.88 (17)	C12—C13—H13F	109.5
C6—C7—H7	119.6	H13A—C13—H13F	56.3
C8—C7—H7	119.6	H13B—C13—H13F	56.3
C9—C8—C7	120.75 (18)	H13C—C13—H13F	141.1
C9—C8—H8	119.6	H13D—C13—H13F	109.5
C7—C8—H8	119.6	H13E—C13—H13F	109.5
C8—C9—C10	119.83 (18)	O21—C20—O22	122.29 (13)
C8—C9—H9	120.1	O21—C20—C2	117.85 (13)
C10—C9—H9	120.1	O22—C20—C2	119.85 (13)
C9—C10—C5	119.24 (14)	C12—O10—C1	117.11 (12)
C9—C10—C1	122.48 (16)	C20—O22—H22	115.8
C5—C10—C1	118.28 (14)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—H22···O21^{i}	0.96	1.70	2.6517 (15)	173

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

Fig. 1

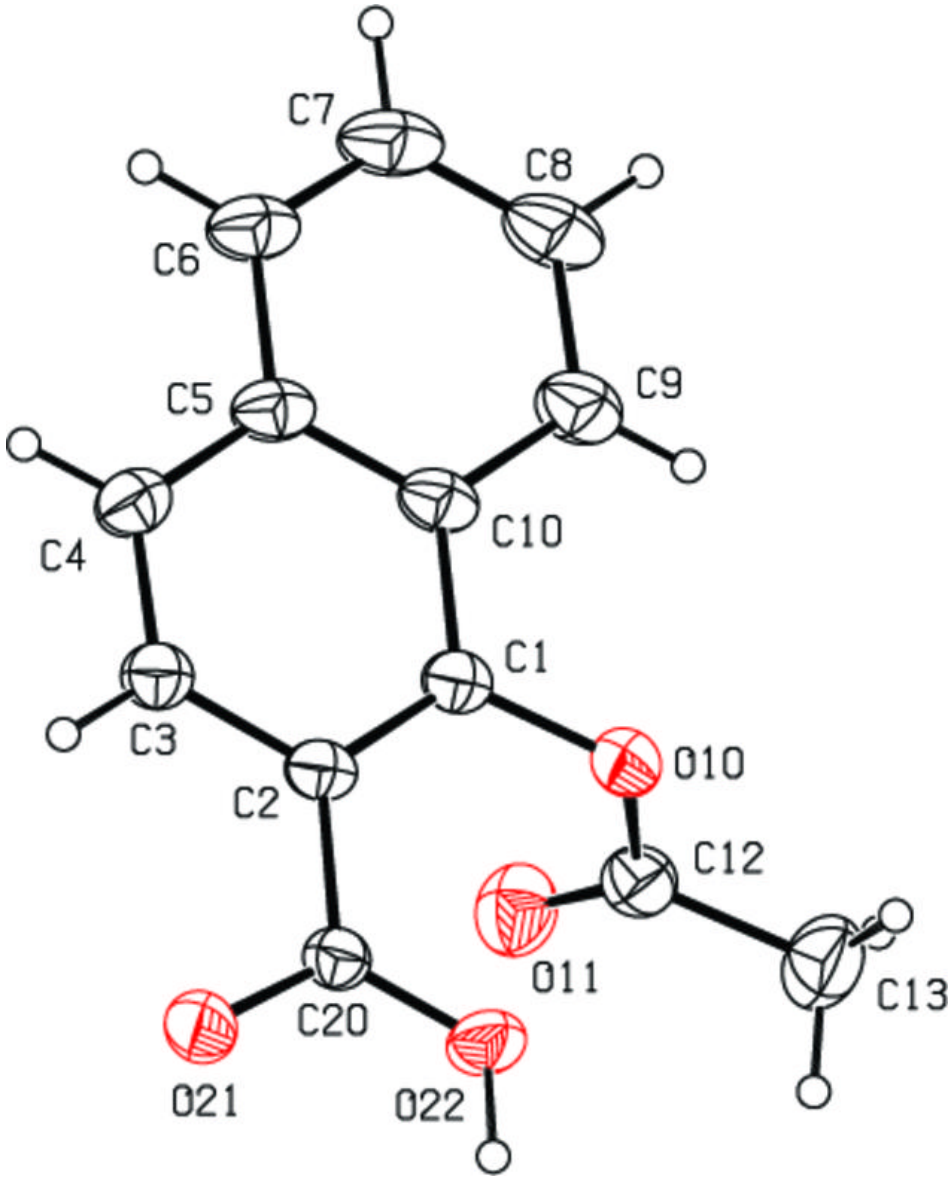

Fig. 2