Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 3-carboxy-5-nitrobenzoate

Ya-Ling Liu, Pei Zou,* Min-Hao Xie, Shi-Neng Luo and Yong-Jun He

Jiangsu Institute of Nuclear Medicine, Wuxi 214063, People's Republic of China
Correspondence e-mail: liuyaling158@163.com

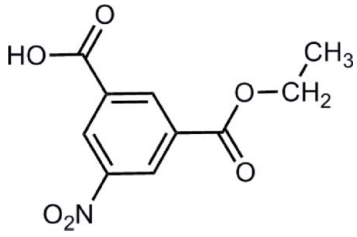
Received 9 April 2009; accepted 27 April 2009

Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.087; data-to-parameter ratio = 14.8.

In the title compound, $C_{10}H_9NO_6$, the carboxy, ethoxycarbonyl and nitro groups form dihedral angles of 3.8 (1), 4.5 (1) and 164.8 (1)°, respectively, with the mean plane of the benzene ring. In the crystal structure, molecules lying about inversion centers are linked through O—H···O hydrogen bonds. C—H···O interactions are also present.

Related literature

The title compound is an important intermediate for the preparation of iodinated X-ray contrast media, such as iotalamic acid, ioxitalamic acid, and ioxilan, which are used clinically all over the world (Morin *et al.*, 1987; Singh & Rathore, 1980; Stacul, 2001). For a related structure, see: Zou *et al.* (2009).



Experimental

Crystal data

$C_{10}H_9NO_6$
M_r = 239.18
Monoclinic, $P2_1/n$
a = 14.249 (3) Å
b = 4.6450 (9) Å
c = 16.536 (4) Å
β = 108.401 (3)°
V = 1038.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 93 K
0.40 × 0.23 × 0.23 mm

Data collection

Rigaku SPIDER diffractometer
Absorption correction: none
6542 measured reflections
2355 independent reflections
1967 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.087
S = 0.99
2355 reflections
159 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5O···O6^{i}	0.92 (3)	1.71 (3)	2.630 (2)	176.7 (17)
C6—H6···O2^{ii}	0.95	2.35	3.280 (2)	165
C9—H9A···O6^{iii}	0.98	2.56	3.354 (3)	138

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

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge financial support from the Jiangsu Institute of Nuclear Medicine.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2153).

References

Morin, J. P., Boutelet, I., Toutain, H. & Fillastre, J. P. (1987). *Pathol. Biol.* **35**, 1215–1220.
Rigaku (2004). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Singh, G. B. & Rathore, H. G. S. (1980). *Indian Drug. Pharm. Ind.* **15**, 35–38.
Stacul, F. (2001). *Eur. Radiol.* **11**, 690–697.
Zou, P., Xie, M.-H., Luo, S.-N., Liu, Y.-L. & Shen, Y.-J. (2009). *Acta Cryst.* E**65**, o335.

supplementary materials

Acta Cryst. (2009). E**65**, o1174 [**doi:10.1107/S160053680901558X**]

Ethyl 3-carboxy-5-nitrobenzoate

Y.-L. Liu, P. Zou, M.-H. Xie, S.-N. Luo and Y.-J. He

Comment

The title compound is an important intermediate for the preparation of iodinated X-ray contrast media, such as iotalamic acid, ioxitalamic acid, and ioxilan, which are used clinically all over the world (Morin *et al.*, 1987; Singh *et al.*, 1980; Stacul, 2001). We report here the crystal structure of the title compound.

The crystal data show that the bond lengths and angles in the title compound (Fig. 1) are within expected ranges and agree well with the corresponding molecular dimensions reported for a similar compound (Zou *et al.*, 2009). The carboxylic acid group (O5/C10/O6) attached at C3 and the ester group (O1/C7/O2) attached at C1 are nearly coplanar with the benzene ring (C1—C6) (dihedral angles of 3.8 (1) and 4.5 (1)°, respectively), while the nitro group (O3/N1/O4) attached at C5 forms a dihedral angle of 164.8 (1) ° with the benzene ring. In the cyrstal structure, the molecules lying about inversion centers are linked through O—H···O hydrogen bonds (Table 1).

Experimental

5-Nitroisophthalic acid (2.1 g, 0.01 mol) was dissolved in 1.5 M ethanolic hydrochloric acid solution (7.5 ml) at 323 K. The mixture was stirred at 323 K for 6 hr. Then sodium chloride (1.8 g, 0.03 mol) in water (20 ml) was added. An oily liquid separated and crystallized on cooling. The precipitate was suction filtered and washed with water until neutral. The solid was suspended in sodium bicarbonate (1.0 g, 0.01 mol) in water (10 ml) and the undissolved diester was filtered off. The filtrate was acidified with 1 M hydrochloric acid to a pH of 4. The precipitate was filtered and washed with cold water. The crude product was purified by recrystallization from ethanol (yield: 41%). Single crystals were grown by slow evaporation of a ethanol/water(*v*/*v* 1:1) solution: colourless prismatic crystals were formed after several days.

Refinement

All the H atoms could have been discerned in the difference electron density maps. With the exception of the hydrogen belonging to the hydroxyl group of the carboxyl the H atoms were situated into the idealized positions and refined in riding motion approximation. The hydroxyl hydrogen was refined freely. The used constraints: C_{aryl}—H = 0.95 Å, C_{methyl}—H = 0.98 Å and $C_{methylene}$—H = 0.99 Å, U_{iso}(H) = 1.2U_{eq}(C).

Figures

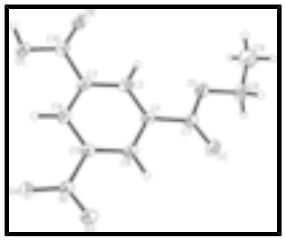


Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

Ethyl 3-carboxy-5-nitrobenzoate

Crystal data

$C_{10}H_9NO_6$	$F_{000} = 496$
$M_r = 239.18$	$D_x = 1.530$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 3010 reflections
$a = 14.249$ (3) Å	$\theta = 3.0$–27.5º
$b = 4.6450$ (9) Å	$\mu = 0.13$ mm^{-1}
$c = 16.536$ (4) Å	$T = 93$ K
$\beta = 108.401$ (3)º	Prism, colorless
$V = 1038.5$ (4) Å^3	0.40 × 0.23 × 0.23 mm
$Z = 4$	

Data collection

Rigaku SPIDER diffractometer	1967 reflections with $I > 2\sigma(I)$
Radiation source: Rotating Anode	$R_{int} = 0.024$
Monochromator: graphite	$\theta_{max} = 27.5$º
$T = 93$ K	$\theta_{min} = 3.0$º
ω scans	$h = -18\rightarrow16$
Absorption correction: none	$k = -5\rightarrow5$
6542 measured reflections	$l = -21\rightarrow20$
2355 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.9P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$

2355 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
159 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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}
O1	0.13780 (9)	0.1168 (3)	0.34968 (7)	0.0298 (3)
O2	0.03728 (8)	0.0126 (3)	0.42538 (7)	0.0276 (3)
O3	0.08919 (8)	0.5402 (3)	0.69486 (7)	0.0264 (3)
O4	0.18028 (8)	0.9233 (3)	0.71824 (7)	0.0254 (3)
O5	0.42632 (9)	1.0386 (3)	0.57257 (8)	0.0295 (3)
O6	0.41511 (9)	0.7677 (3)	0.45857 (8)	0.0372 (3)
N1	0.14799 (9)	0.7034 (3)	0.67837 (8)	0.0204 (3)
C1	0.16237 (11)	0.3639 (3)	0.47870 (9)	0.0191 (3)
C2	0.24472 (11)	0.5011 (4)	0.46934 (10)	0.0212 (3)
H2	0.2662	0.4570	0.4219	0.025*
C3	0.29609 (11)	0.7032 (4)	0.52916 (10)	0.0207 (3)
C4	0.26459 (11)	0.7719 (3)	0.59811 (10)	0.0202 (3)
H4	0.2985	0.9114	0.6389	0.024*
C5	0.18231 (11)	0.6311 (3)	0.60566 (9)	0.0186 (3)
C6	0.13113 (11)	0.4266 (3)	0.54859 (9)	0.0188 (3)

H6	0.0759	0.3304	0.5566	0.023*
C7	0.10519 (11)	0.1465 (4)	0.41636 (9)	0.0207 (3)
C8	0.08258 (14)	−0.0899 (5)	0.28589 (11)	0.0362 (5)
H8A	0.0140	−0.0217	0.2590	0.043*
H8B	0.0802	−0.2788	0.3129	0.043*
C9	0.13330 (17)	−0.1176 (6)	0.22150 (14)	0.0530 (6)
H9A	0.1328	0.0686	0.1935	0.064*
H9B	0.0991	−0.2611	0.1789	0.064*
H9C	0.2018	−0.1787	0.2491	0.064*
C10	0.38474 (12)	0.8391 (4)	0.51701 (10)	0.0242 (4)
H5O	0.4809 (18)	1.103 (5)	0.5597 (14)	0.064 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0321 (6)	0.0351 (7)	0.0270 (6)	−0.0129 (6)	0.0161 (5)	−0.0098 (5)
O2	0.0262 (6)	0.0316 (7)	0.0261 (6)	−0.0117 (5)	0.0098 (5)	−0.0031 (5)
O3	0.0269 (6)	0.0273 (7)	0.0288 (6)	−0.0054 (5)	0.0143 (5)	0.0005 (5)
O4	0.0235 (6)	0.0245 (6)	0.0282 (6)	−0.0031 (5)	0.0080 (5)	−0.0077 (5)
O5	0.0227 (6)	0.0336 (7)	0.0357 (7)	−0.0122 (5)	0.0140 (5)	−0.0083 (6)
O6	0.0312 (7)	0.0485 (9)	0.0394 (7)	−0.0200 (6)	0.0218 (6)	−0.0161 (6)
N1	0.0171 (6)	0.0220 (7)	0.0220 (6)	0.0000 (5)	0.0057 (5)	0.0014 (6)
C1	0.0181 (7)	0.0184 (8)	0.0202 (7)	−0.0002 (6)	0.0052 (6)	0.0026 (6)
C2	0.0193 (7)	0.0234 (9)	0.0219 (7)	−0.0006 (6)	0.0079 (6)	0.0019 (7)
C3	0.0158 (7)	0.0212 (8)	0.0248 (7)	−0.0020 (6)	0.0060 (6)	0.0030 (7)
C4	0.0171 (7)	0.0189 (8)	0.0229 (7)	−0.0010 (6)	0.0040 (6)	0.0014 (6)
C5	0.0176 (7)	0.0194 (8)	0.0191 (7)	0.0018 (6)	0.0062 (6)	0.0032 (6)
C6	0.0155 (7)	0.0188 (8)	0.0219 (7)	−0.0003 (6)	0.0056 (6)	0.0051 (6)
C7	0.0200 (7)	0.0217 (9)	0.0209 (7)	−0.0010 (6)	0.0074 (6)	0.0024 (6)
C8	0.0397 (10)	0.0404 (12)	0.0311 (9)	−0.0145 (9)	0.0147 (8)	−0.0134 (8)
C9	0.0542 (14)	0.0675 (17)	0.0422 (12)	−0.0140 (12)	0.0224 (10)	−0.0208 (11)
C10	0.0197 (8)	0.0254 (9)	0.0272 (8)	−0.0044 (7)	0.0070 (6)	−0.0007 (7)

Geometric parameters (Å, °)

O1—C7	1.3320 (19)	C2—H2	0.9500
O1—C8	1.460 (2)	C3—C4	1.388 (2)
O2—C7	1.1986 (19)	C3—C10	1.481 (2)
O3—N1	1.2230 (17)	C4—C5	1.382 (2)
O4—N1	1.2242 (17)	C4—H4	0.9500
O5—C10	1.308 (2)	C5—C6	1.375 (2)
O5—H5O	0.92 (3)	C6—H6	0.9500
O6—C10	1.223 (2)	C8—C9	1.469 (3)
N1—C5	1.4726 (19)	C8—H8A	0.9900
C1—C2	1.386 (2)	C8—H8B	0.9900
C1—C6	1.394 (2)	C9—H9A	0.9800
C1—C7	1.488 (2)	C9—H9B	0.9800
C2—C3	1.392 (2)	C9—H9C	0.9800

C7—O1—C8	114.65 (13)	C5—C6—H6	120.8
C10—O5—H5O	107.3 (15)	C1—C6—H6	120.8
O3—N1—O4	124.39 (13)	O2—C7—O1	123.74 (15)
O3—N1—C5	117.92 (13)	O2—C7—C1	123.56 (14)
O4—N1—C5	117.69 (13)	O1—C7—C1	112.70 (13)
C2—C1—C6	119.97 (14)	O1—C8—C9	107.75 (16)
C2—C1—C7	122.15 (14)	O1—C8—H8A	110.2
C6—C1—C7	117.88 (14)	C9—C8—H8A	110.2
C1—C2—C3	120.29 (14)	O1—C8—H8B	110.2
C1—C2—H2	119.9	C9—C8—H8B	110.2
C3—C2—H2	119.9	H8A—C8—H8B	108.5
C4—C3—C2	120.32 (14)	C8—C9—H9A	109.5
C4—C3—C10	121.61 (14)	C8—C9—H9B	109.5
C2—C3—C10	118.07 (14)	H9A—C9—H9B	109.5
C5—C4—C3	117.97 (14)	C8—C9—H9C	109.5
C5—C4—H4	121.0	H9A—C9—H9C	109.5
C3—C4—H4	121.0	H9B—C9—H9C	109.5
C6—C5—C4	123.11 (14)	O6—C10—O5	123.54 (15)
C6—C5—N1	118.49 (13)	O6—C10—C3	121.42 (15)
C4—C5—N1	118.40 (14)	O5—C10—C3	115.04 (14)
C5—C6—C1	118.31 (14)		
C6—C1—C2—C3	−0.5 (2)	C2—C1—C6—C5	1.7 (2)
C7—C1—C2—C3	179.98 (14)	C7—C1—C6—C5	−178.76 (13)
C1—C2—C3—C4	−0.8 (2)	C8—O1—C7—O2	1.3 (2)
C1—C2—C3—C10	178.79 (14)	C8—O1—C7—C1	−178.77 (14)
C2—C3—C4—C5	0.9 (2)	C2—C1—C7—O2	175.54 (15)
C10—C3—C4—C5	−178.73 (14)	C6—C1—C7—O2	−4.0 (2)
C3—C4—C5—C6	0.4 (2)	C2—C1—C7—O1	−4.3 (2)
C3—C4—C5—N1	−179.71 (13)	C6—C1—C7—O1	176.11 (14)
O3—N1—C5—C6	14.8 (2)	C7—O1—C8—C9	−174.64 (17)
O4—N1—C5—C6	−165.20 (13)	C4—C3—C10—O6	176.32 (16)
O3—N1—C5—C4	−165.12 (14)	C2—C3—C10—O6	−3.3 (2)
O4—N1—C5—C4	14.9 (2)	C4—C3—C10—O5	−4.1 (2)
C4—C5—C6—C1	−1.7 (2)	C2—C3—C10—O5	176.29 (14)
N1—C5—C6—C1	178.44 (13)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5O···O6^{i}	0.92 (3)	1.71 (3)	2.630 (2)	176.7 (17)
C6—H6···O2^{ii}	0.95	2.35	3.280 (2)	165
C9—H9A···O6^{iii}	0.98	2.56	3.354 (3)	138

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

Fig. 1