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Methyl 3-nitro-4-propoxybenzoate

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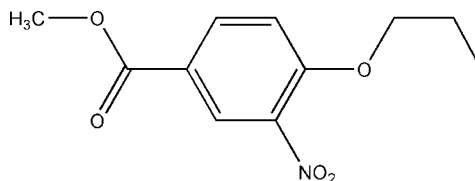
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.052; wR factor = 0.135; data-to-parameter ratio = 8.7.

In the title crystal structure, $\text{C}_{11}\text{H}_{13}\text{NO}_5$, molecules are linked through weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds to form one-dimensional chains in the c direction.

Related literature

For background information, see: Freifelder *et al.* (1958); Monguzzi *et al.* (1974). For the synthetic procedure, see: Crosby & Saffron (1976). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{13}\text{NO}_5$ $M_r = 239.22$ Orthorhombic, $P2_12_12_1$ $a = 6.9732$ (6) Å $b = 12.3149$ (11) Å $c = 13.6851$ (13) Å $V = 1175.20$ (18) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.11$ mm⁻¹ $T = 298$ (2) K $0.30 \times 0.30 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.938$, $T_{\max} = 0.969$
1368 measured reflections

1344 independent reflections
977 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
3 standard reflections every 200 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.135$
 $S = 1.07$
1344 reflections
155 parameters

1 restraint
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}1-\text{H}1\text{B}\cdots\text{O}1$	0.96	2.52	2.858 (4)	101
$\text{C}9-\text{H}9\text{A}\cdots\text{O}3^i$	0.93	2.59	3.462 (4)	156

Symmetry code: (i) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

The authors thank Dr Shan Liu and Mr Hong-Sheng Jia from Nanjing University of Technology, and the Center of Tests and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2422).

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supplementary materials

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Methyl 3-nitro-4-propoxybenzoate

S.-Y. Zhao, S.-W. Mou, S.-H. Zhao and W.-M. Qin

Comment

The title compound is an important intermediate used in the synthesis of types of local anesthetics (Freifelder *et al.*, 1958; Monguzzi *et al.*, 1974). We report its crystal structure herein.

In the molecule of the title compound (Fig. 1) the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). As shown (Fig. 2) molecules are linked into one-dimensional chains *via* weak intermolecular C—H \cdots O hydrogen bonds.

Experimental

The title compound was prepared by the literature method with a minor change (Crosby & Saffron, 1976). To a solution of methyl 3-nitro-4-hydroxybenzoate (21.3 g, 0.12 mol) and potassium carbonate (17.4 g, 0.13 mol) in 150 ml of DMF was dropwise added 1-bromopropane (13.6 ml, 0.15 mol) for 1 h, The reaction mixture was stirred at 383 K for 12 h. The reaction mixture was dropped into water (300 ml) and extracted with ethyl acetate (3 \times 100 ml). The combined ester layer was dried with sodium sulfate and evaporated, and the residue was recrystallized from ethanol and dried in vacuum at 323 K to give the title compound as white solid in 85% yield. m.p. 337–339 K (Crosby & Saffron, 1976, mp. 335–336 K), IR (KBr, cm^{-1}): ν 3052, 2977, 1720 (C=O), 1618, 1531, 1436, 1348 (NO₂), 1274. ¹H NMR(300 MHz, CDCl₃, p.p.m.): δ 1.10 (t, J = 5.6 Hz, 3H, CH₃), 1.92(m, J=5.5 Hz, J=4.9 Hz, 2H, CH₂), 3.95(s, 3H, OCH₃), 4.14 (t, J=4.8 Hz, 2H, OCH₂), 7.13 (d, J=6.6 Hz, 1H, Ph—H), 8.21 (d, J=5.0 Hz, 1H, Ph—H), 8.49(s, 1H, Ph—H).

The crystals were obtained by dissolving the title compound (0.3 g, 1.65 mmol) in ethyl acetate (50 ml) and evaporating the solvent slowly at room temperature for about 2 d.

Refinement

In the absence of significant anomalous dispersion effects Friedel pairs were merged. H atoms were positioned geometrically, with C—H = 0.93 Å (for aromatic H), 0.97 Å (for methylene H) and 0.96 Å (for methyl H), and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

Figures

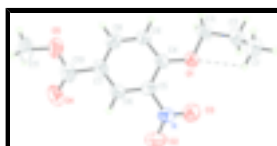


Fig. 1. The molecular structure with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. A hydrogen bond is shown as a dashed line.

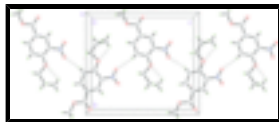


Fig. 2. The packing of the title compound showing hydrogen bonds as dashed lines.

Methyl 3-nitro-4-propoxybenzoate

Crystal data

$C_{11}H_{13}NO_5$

$M_r = 239.22$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 6.9732$ (6) Å

$b = 12.3149$ (11) Å

$c = 13.6851$ (13) Å

$V = 1175.20$ (18) Å³

$Z = 4$

$F_{000} = 504$

$D_x = 1.352$ Mg m⁻³

Melting point: 333 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10\text{--}13^\circ$

$\mu = 0.11$ mm⁻¹

$T = 298$ (2) K

Plate, colorless

$0.30 \times 0.30 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.938$, $T_{\max} = 0.969$

1368 measured reflections

1344 independent reflections

977 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 25.9^\circ$

$\theta_{\min} = 2.2^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 16$

3 standard reflections

every 200 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.135$

$S = 1.07$

1344 reflections

155 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.25$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Extinction correction: SHELXL97,

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.026 (5)

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7410 (4)	-0.02317 (14)	0.42026 (13)	0.0528 (6)
O2	0.8326 (5)	0.2167 (2)	0.23616 (17)	0.0841 (10)
O3	0.6856 (5)	0.0646 (2)	0.24957 (17)	0.0860 (10)
O4	0.7253 (6)	0.48616 (18)	0.4980 (2)	0.0833 (9)
O5	0.6959 (4)	0.41751 (17)	0.64755 (19)	0.0728 (8)
N	0.7515 (5)	0.1465 (2)	0.28476 (18)	0.0561 (8)
C1	0.6287 (8)	-0.2330 (3)	0.3518 (3)	0.0867 (14)
H1A	0.6609	-0.2982	0.3169	0.130*
H1B	0.6313	-0.1724	0.3078	0.130*
H1C	0.5026	-0.2401	0.3793	0.130*
C2	0.7691 (7)	-0.2153 (2)	0.4310 (3)	0.0720 (11)
H2A	0.8967	-0.2127	0.4029	0.086*
H2B	0.7646	-0.2767	0.4754	0.086*
C3	0.7354 (7)	-0.1120 (2)	0.4890 (2)	0.0590 (10)
H3A	0.6117	-0.1147	0.5214	0.071*
H3B	0.8342	-0.1031	0.5382	0.071*
C4	0.7267 (5)	0.0781 (2)	0.4549 (2)	0.0415 (7)
C5	0.7335 (5)	0.1646 (2)	0.3898 (2)	0.0426 (7)
C6	0.7278 (5)	0.2716 (2)	0.4213 (2)	0.0453 (8)
H6A	0.7349	0.3278	0.3760	0.054*
C7	0.7119 (5)	0.2947 (2)	0.5191 (2)	0.0460 (7)
C8	0.7027 (5)	0.2091 (2)	0.5844 (2)	0.0495 (8)
H8A	0.6913	0.2237	0.6509	0.059*
C9	0.7099 (5)	0.1033 (2)	0.5538 (2)	0.0481 (8)
H9A	0.7035	0.0475	0.5996	0.058*
C10	0.7133 (5)	0.4097 (2)	0.5509 (3)	0.0560 (9)
C11	0.7040 (8)	0.5248 (3)	0.6906 (3)	0.0902 (15)

supplementary materials

H11A	0.6882	0.5192	0.7601	0.135*
H11B	0.6032	0.5689	0.6639	0.135*
H11C	0.8258	0.5574	0.6763	0.135*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0797 (16)	0.0365 (10)	0.0424 (11)	0.0023 (13)	-0.0004 (13)	0.0020 (8)
O2	0.114 (2)	0.0872 (18)	0.0510 (13)	-0.0132 (18)	0.0124 (15)	0.0191 (14)
O3	0.153 (3)	0.0613 (15)	0.0436 (12)	-0.0093 (18)	-0.0063 (18)	-0.0039 (11)
O4	0.107 (2)	0.0401 (12)	0.1029 (19)	0.0009 (16)	0.012 (2)	0.0036 (13)
O5	0.095 (2)	0.0493 (13)	0.0745 (15)	-0.0003 (14)	-0.0025 (16)	-0.0210 (11)
N	0.075 (2)	0.0526 (14)	0.0406 (13)	0.0031 (18)	0.0026 (15)	0.0096 (12)
C1	0.131 (4)	0.063 (2)	0.066 (2)	-0.013 (3)	0.009 (3)	-0.011 (2)
C2	0.099 (3)	0.0386 (15)	0.078 (2)	-0.001 (2)	0.004 (3)	0.0033 (16)
C3	0.089 (3)	0.0378 (14)	0.0498 (16)	-0.001 (2)	-0.009 (2)	0.0105 (13)
C4	0.0474 (18)	0.0334 (14)	0.0438 (15)	-0.0011 (14)	-0.0009 (15)	0.0013 (11)
C5	0.0455 (18)	0.0458 (14)	0.0364 (13)	0.0001 (15)	-0.0004 (14)	0.0035 (12)
C6	0.0466 (18)	0.0409 (14)	0.0483 (16)	0.0018 (16)	0.0038 (16)	0.0094 (12)
C7	0.0416 (17)	0.0391 (15)	0.0572 (17)	-0.0008 (15)	-0.0002 (15)	0.0006 (13)
C8	0.055 (2)	0.0515 (17)	0.0417 (15)	0.0008 (17)	-0.0003 (16)	-0.0044 (13)
C9	0.062 (2)	0.0403 (14)	0.0421 (15)	-0.0012 (17)	0.0032 (16)	0.0073 (13)
C10	0.048 (2)	0.0415 (17)	0.078 (2)	-0.0022 (17)	-0.0007 (19)	-0.0087 (17)
C11	0.112 (4)	0.056 (2)	0.103 (3)	0.000 (3)	-0.018 (3)	-0.039 (2)

Geometric parameters (\AA , $^\circ$)

O1—C4	1.337 (3)	C3—H3A	0.9700
O1—C3	1.443 (3)	C3—H3B	0.9700
O2—N	1.229 (3)	C4—C5	1.390 (4)
O3—N	1.209 (3)	C4—C9	1.394 (4)
O4—C10	1.190 (4)	C5—C6	1.386 (4)
O5—C10	1.332 (4)	C6—C7	1.374 (4)
O5—C11	1.447 (4)	C6—H6A	0.9300
N—C5	1.460 (4)	C7—C8	1.384 (4)
C1—C2	1.477 (6)	C7—C10	1.482 (4)
C1—H1A	0.9600	C8—C9	1.370 (4)
C1—H1B	0.9600	C8—H8A	0.9300
C1—H1C	0.9600	C9—H9A	0.9300
C2—C3	1.518 (4)	C11—H11A	0.9600
C2—H2A	0.9700	C11—H11B	0.9600
C2—H2B	0.9700	C11—H11C	0.9600
C4—O1—C3	118.3 (2)	C5—C4—C9	117.0 (2)
C10—O5—C11	117.8 (3)	C6—C5—C4	121.9 (3)
O3—N—O2	123.1 (3)	C6—C5—N	117.0 (2)
O3—N—C5	119.1 (3)	C4—C5—N	121.1 (2)
O2—N—C5	117.7 (3)	C7—C6—C5	120.1 (3)
C2—C1—H1A	109.5	C7—C6—H6A	119.9

C2—C1—H1B	109.5	C5—C6—H6A	119.9
H1A—C1—H1B	109.5	C6—C7—C8	118.4 (3)
C2—C1—H1C	109.5	C6—C7—C10	118.9 (3)
H1A—C1—H1C	109.5	C8—C7—C10	122.7 (3)
H1B—C1—H1C	109.5	C9—C8—C7	121.7 (3)
C1—C2—C3	113.9 (4)	C9—C8—H8A	119.1
C1—C2—H2A	108.8	C7—C8—H8A	119.1
C3—C2—H2A	108.8	C8—C9—C4	120.8 (3)
C1—C2—H2B	108.8	C8—C9—H9A	119.6
C3—C2—H2B	108.8	C4—C9—H9A	119.6
H2A—C2—H2B	107.7	O4—C10—O5	123.6 (3)
O1—C3—C2	106.9 (2)	O4—C10—C7	125.3 (3)
O1—C3—H3A	110.3	O5—C10—C7	111.1 (3)
C2—C3—H3A	110.3	O5—C11—H11A	109.5
O1—C3—H3B	110.3	O5—C11—H11B	109.5
C2—C3—H3B	110.3	H11A—C11—H11B	109.5
H3A—C3—H3B	108.6	O5—C11—H11C	109.5
O1—C4—C5	119.1 (2)	H11A—C11—H11C	109.5
O1—C4—C9	123.9 (2)	H11B—C11—H11C	109.5
C4—O1—C3—C2	-175.9 (3)	C5—C6—C7—C8	0.3 (5)
C1—C2—C3—O1	-57.8 (5)	C5—C6—C7—C10	177.8 (3)
C3—O1—C4—C5	179.5 (3)	C6—C7—C8—C9	0.3 (5)
C3—O1—C4—C9	1.2 (5)	C10—C7—C8—C9	-177.1 (4)
O1—C4—C5—C6	-177.1 (3)	C7—C8—C9—C4	-0.1 (6)
C9—C4—C5—C6	1.3 (5)	O1—C4—C9—C8	177.6 (3)
O1—C4—C5—N	1.4 (5)	C5—C4—C9—C8	-0.7 (6)
C9—C4—C5—N	179.8 (3)	C11—O5—C10—O4	-3.9 (7)
O3—N—C5—C6	-151.7 (3)	C11—O5—C10—C7	177.1 (3)
O2—N—C5—C6	27.8 (5)	C6—C7—C10—O4	0.9 (6)
O3—N—C5—C4	29.7 (5)	C8—C7—C10—O4	178.3 (4)
O2—N—C5—C4	-150.8 (3)	C6—C7—C10—O5	179.8 (3)
C4—C5—C6—C7	-1.1 (5)	C8—C7—C10—O5	-2.8 (5)
N—C5—C6—C7	-179.7 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1B...O1	0.96	2.52	2.858 (4)	101
C9—H9A...O3 ⁱ	0.93	2.59	3.462 (4)	156

Symmetry codes: (i) $-x+3/2, -y, z+1/2$.

Fig. 1

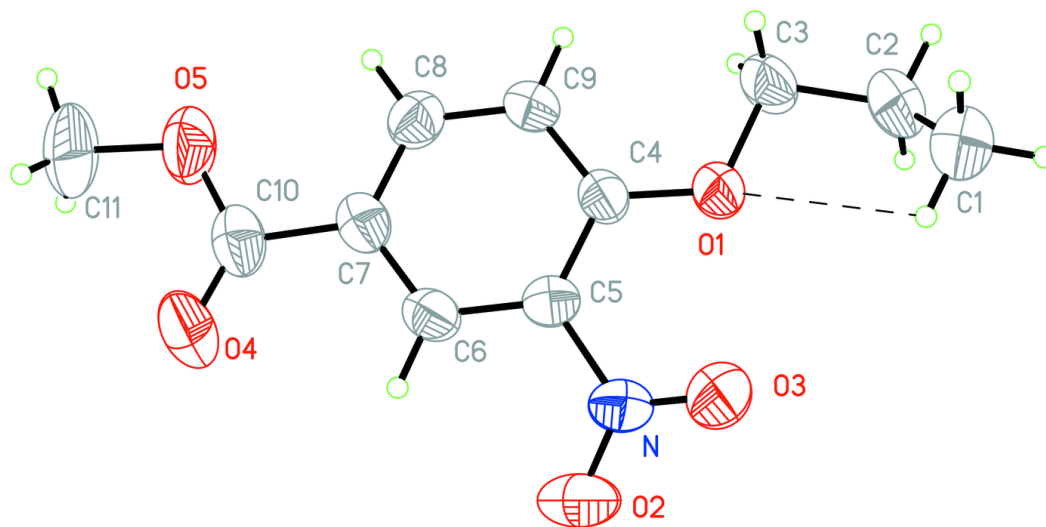


Fig. 2

