organic compounds

Methyl 4-nitrobenzoate

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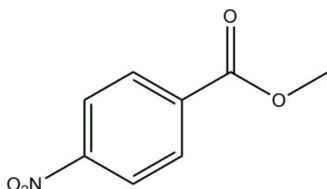Correspondence e-mail: haijiaoyiya@sina.com

In the molecule of the title compound, $C_8H_7NO_4$, the nitro group is approximately coplanar with the benzene ring [dihedral angle = 0.6 (1)°], while the dihedral angle between the methoxycarbonyl group and the benzene ring is 8.8 (1)°. In the crystal structure, weak intermolecular aromatic C—H···$O_{carboxyl}$ and C—H···O_{nitro} hydrogen-bonding interactions are present.

Related literature

For related literature on benzoates, see: Zhang (1992); Zhang *et al.* (1990); Zhang *et al.* (1995).

Experimental

Crystal data

$C_8H_7NO_4$	$c = 7.193$ (3) Å
$M_r = 181.15$	$\beta = 116.292$ (4)°
Monoclinic, $P2_1/c$	$V = 783.6$ (5) Å^3
$a = 7.109$ (3) Å	$Z = 4$
$b = 17.092$ (6) Å	Mo $K\alpha$ radiation
	$\mu = 0.13$ mm^{-1}
	$T = 93$ K
	$0.43 \times 0.40 \times 0.10$ mm

Data collection

Rigaku SPIDER CCD-detector diffractometer	6176 measured reflections
Absorption correction: ψ scan (North *et al.*, 1968)	1787 independent reflections
$T_{min} = 0.948$, $T_{max} = 0.988$	1445 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	119 parameters
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
1787 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2^i	0.95	2.59	3.384 (2)	141
C5—H5···O4^{ii}	0.95	2.58	3.378 (2)	142

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$.

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*.

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supplementary materials

Methyl 4-nitrobenzoate

H. Wu, M.-H. Xie, P. Zou, Y.-L. Liu and Y.-J. He

Comment

Benzoates are important intermediates in the chemistry of pigments and pharmaceuticals, which are used worldwide (Zhang, 1992; Zhang *et al.*, 1990; Zhang *et al.*, 1995). We report here the crystal structure of methyl 4-nitrobenzoate, $C_8H_7NO_4$ (I). In the structure of the title compound (Fig. 1) the bond lengths and angles are within expected ranges. The nitro substituent group is nearly coplanar with the benzene ring [dihedral angle, 0.6 (1)°], while the methoxycarbonyl group forms a dihedral angle of 8.8 (1)° with the benzene ring. In the crystal structure, adjacent molecules are linked by weak intermolecular aromatic C—H···$O_{carboxyl}$ and O_{nitro} hydrogen bonds (Table 1).

Experimental

4-Nitrobenzoic acid (5.0 g, 30 mmol) was dissolved in hot methanol (10 ml), then six drops of concentrated sulfuric acid were added. The mixture was stirred at 353 K for 4 h, poured into ice water and stirred for 3 min. After filtering, washing with water and drying in vacuum, a white powder was then obtained (yield: 73%). The crude product was purified by recrystallization from methanol (yield: 51%). Colourless plate-shaped crystals [m.p. 369 (2) K] were obtained after several days, by slow evaporation of a 1:1 (*v*/*v*) methanol-water solution. .

Refinement

Positional parameters of all H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with C_{aryl}—H = 0.95 Å, and C_{methyl}—H = 0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$

Figures
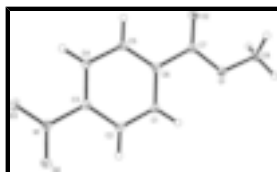

Fig. 1. Atom numbering scheme for the title compound (I) with the displacement ellipsoids drawn at the 30% probability level.

Methyl 4-nitrobenzoate

Crystal data

$C_8H_7NO_4$	$F_{000} = 376$
$M_r = 181.15$	$D_x = 1.536$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 369(2) K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

supplementary materials

$a = 7.109\ (3)$ Å

$b = 17.092\ (6)$ Å

$c = 7.193\ (3)$ Å

$\beta = 116.292\ (4)°$

$V = 783.6\ (5)$ Å^3

$Z = 4$

Cell parameters from 2257 reflections

$\theta = 3.2–27.4°$

$\mu = 0.13$ mm^{-1}

$T = 93$ K

Plate, colorless

$0.43 \times 0.40 \times 0.10$ mm

Data collection

Rigaku SPIDER CCD-detector diffractometer

Radiation source: rotating anode

Monochromator: graphite

$T = 93$ K

ω scans

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

$T_{min} = 0.948$, $T_{max} = 0.988$

6176 measured reflections

1787 independent reflections

1445 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$

$\theta_{max} = 27.5°$

$\theta_{min} = 3.2°$

$h = -9 \rightarrow 9$

$k = -20 \rightarrow 22$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.080$

$S = 1.00$

1787 reflections

119 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

$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.336P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.31$ e Å^{-3}

$\Delta\rho_{min} = -0.18$ e Å^{-3}

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	0.35100 (15)	0.66883 (5)	0.67509 (14)	0.0205 (2)
O2	0.30933 (15)	0.59510 (5)	0.91414 (14)	0.0216 (2)
O3	0.14128 (16)	0.28185 (5)	0.23700 (16)	0.0265 (2)
O4	0.14076 (17)	0.36321 (6)	0.00524 (15)	0.0275 (2)
N1	0.15702 (17)	0.34819 (6)	0.17881 (17)	0.0185 (2)
C1	0.25319 (19)	0.54972 (7)	0.39808 (19)	0.0155 (3)
H1	0.2638	0.6016	0.3563	0.019*
C2	0.21513 (19)	0.48826 (7)	0.2601 (2)	0.0160 (3)
H2	0.2007	0.4971	0.1240	0.019*
C3	0.19872 (19)	0.41347 (7)	0.3264 (2)	0.0155 (3)
C4	0.21927 (19)	0.39748 (7)	0.5240 (2)	0.0167 (3)
H4	0.2065	0.3456	0.5643	0.020*
C5	0.25907 (19)	0.45958 (7)	0.6606 (2)	0.0160 (3)
H5	0.2749	0.4503	0.7970	0.019*
C6	0.27592 (18)	0.53560 (7)	0.59852 (19)	0.0149 (3)
C7	0.31372 (19)	0.60132 (7)	0.7484 (2)	0.0162 (3)
C8	0.3760 (2)	0.73724 (8)	0.8036 (2)	0.0239 (3)
H8A	0.2532	0.7425	0.8310	0.029*
H8B	0.3890	0.7840	0.7313	0.029*
H8C	0.5025	0.7314	0.9351	0.029*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0302 (5)	0.0155 (5)	0.0190 (5)	−0.0039 (4)	0.0139 (4)	−0.0029 (4)
O2	0.0259 (5)	0.0241 (5)	0.0167 (5)	−0.0026 (4)	0.0111 (4)	−0.0005 (4)
O3	0.0390 (6)	0.0150 (5)	0.0290 (6)	−0.0025 (4)	0.0182 (5)	0.0006 (4)
O4	0.0437 (6)	0.0225 (5)	0.0202 (5)	−0.0009 (5)	0.0177 (5)	−0.0016 (4)
N1	0.0196 (5)	0.0163 (5)	0.0211 (6)	0.0005 (4)	0.0102 (5)	0.0002 (4)
C1	0.0151 (6)	0.0144 (6)	0.0172 (7)	−0.0002 (5)	0.0075 (5)	0.0022 (5)
C2	0.0152 (6)	0.0189 (6)	0.0142 (6)	0.0007 (5)	0.0067 (5)	0.0024 (5)
C3	0.0132 (6)	0.0160 (6)	0.0172 (6)	0.0011 (5)	0.0066 (5)	−0.0008 (5)
C4	0.0152 (6)	0.0153 (6)	0.0204 (7)	0.0008 (5)	0.0088 (5)	0.0033 (5)
C5	0.0143 (6)	0.0196 (6)	0.0150 (6)	0.0012 (5)	0.0071 (5)	0.0036 (5)
C6	0.0115 (5)	0.0175 (6)	0.0152 (6)	0.0003 (5)	0.0055 (5)	−0.0002 (5)
C7	0.0134 (6)	0.0181 (6)	0.0162 (6)	0.0005 (5)	0.0059 (5)	0.0017 (5)
C8	0.0339 (8)	0.0176 (6)	0.0243 (7)	−0.0055 (6)	0.0167 (6)	−0.0060 (5)

Geometric parameters (Å, °)

O1—C7	1.3429 (15)	C2—H2	0.9500
O1—C8	1.4517 (15)	C3—C4	1.3901 (18)
O2—C7	1.2111 (16)	C4—C5	1.3880 (18)
O3—N1	1.2308 (14)	C4—H4	0.9500
O4—N1	1.2290 (15)	C5—C6	1.3962 (18)

N1—C3	1.4770 (16)	C5—H5	0.9500
C1—C2	1.3872 (18)	C6—C7	1.4965 (18)
C1—C6	1.3988 (18)	C8—H8A	0.9800
C1—H1	0.9500	C8—H8B	0.9800
C2—C3	1.3873 (17)	C8—H8C	0.9800
C7—O1—C8	115.59 (10)	C4—C5—C6	120.30 (12)
O4—N1—O3	123.79 (11)	C4—C5—H5	119.8
O4—N1—C3	118.11 (10)	C6—C5—H5	119.8
O3—N1—C3	118.10 (11)	C5—C6—C1	120.22 (12)
C2—C1—C6	120.25 (12)	C5—C6—C7	118.78 (11)
C2—C1—H1	119.9	C1—C6—C7	120.98 (11)
C6—C1—H1	119.9	O2—C7—O1	123.89 (12)
C1—C2—C3	118.10 (12)	O2—C7—C6	124.65 (11)
C1—C2—H2	121.0	O1—C7—C6	111.46 (11)
C3—C2—H2	121.0	O1—C8—H8A	109.5
C2—C3—C4	123.11 (12)	O1—C8—H8B	109.5
C2—C3—N1	118.00 (11)	H8A—C8—H8B	109.5
C4—C3—N1	118.89 (11)	O1—C8—H8C	109.5
C5—C4—C3	118.01 (12)	H8A—C8—H8C	109.5
C5—C4—H4	121.0	H8B—C8—H8C	109.5
C3—C4—H4	121.0		
C6—C1—C2—C3	0.59 (18)	C4—C5—C6—C1	−0.12 (18)
C1—C2—C3—C4	−0.22 (18)	C4—C5—C6—C7	178.53 (11)
C1—C2—C3—N1	179.66 (11)	C2—C1—C6—C5	−0.43 (18)
O4—N1—C3—C2	0.62 (17)	C2—C1—C6—C7	−179.05 (11)
O3—N1—C3—C2	−179.62 (11)	C8—O1—C7—O2	−3.17 (18)
O4—N1—C3—C4	−179.49 (12)	C8—O1—C7—C6	176.11 (10)
O3—N1—C3—C4	0.27 (17)	C5—C6—C7—O2	−8.15 (19)
C2—C3—C4—C5	−0.31 (18)	C1—C6—C7—O2	170.48 (12)
N1—C3—C4—C5	179.80 (11)	C5—C6—C7—O1	172.58 (11)
C3—C4—C5—C6	0.48 (18)	C1—C6—C7—O1	−8.78 (16)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1⋯O1	0.95	2.39	2.7149 (19)	100
C2—H2⋯O2[i]	0.95	2.59	3.384 (2)	141
C5—H5⋯O4[ii]	0.95	2.58	3.378 (2)	142

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

Fig. 1