

2,4-Dichloro-6-nitrobenzoic acid

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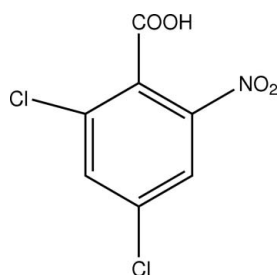
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 12.9.

The title compound, $\text{C}_7\text{H}_3\text{Cl}_2\text{NO}_4$, was prepared by the reaction of 2,4-dichloro-6-nitrotoluene with 20% HNO_3 solution at 430 K. The carboxyl and nitro groups are twisted by 82.82 (12) and 11.9 (2)°, respectively, with respect to the benzene ring. The crystal structure is stabilized by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding between carboxyl groups and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding between the nitro group and the benzene ring of an adjacent molecule.

Related literature

For general background, see: Jacobson (1997); Langer *et al.* (2006); Li & Zhu (2007).



Experimental

Crystal data

 $\text{C}_7\text{H}_3\text{Cl}_2\text{NO}_4$
 $M_r = 236.00$

 Triclinic, $P\bar{1}$
 $a = 4.6930$ (7) Å

 $b = 7.5590$ (11) Å
 $c = 13.0721$ (19) Å
 $\alpha = 97.120$ (2)°
 $\beta = 95.267$ (2)°
 $\gamma = 100.631$ (2)°
 $V = 449.11$ (11) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.71$ mm⁻¹
 $T = 295$ (2) K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.765$, $T_{\max} = 0.872$

 2415 measured reflections
 1641 independent reflections
 1457 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.011$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.086$
 $S = 1.06$
 1641 reflections

 127 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4A}\cdots\text{O3}^{\text{i}}$	0.90	1.77	2.664 (2)	173
$\text{C3}-\text{H5}\cdots\text{O2}^{\text{ii}}$	0.93	2.56	3.453 (2)	160

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2399).

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supplementary materials

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Comment

Ortho-nitro aromatic acids have been used as intermediates of dyes, pharmaceuticals and agrochemicals (Jacobson, 1997; Langer *et al.*, 2006). The title compound is an important chemical intermediates of a kind of synthetic dyes, pharmaceuticals (Li & Zhu, 2007). Its crystal structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The molecule displays a non-planar structure. The carboxyl and nitro groups are twisted with respect to the benzene ring by 82.82 (12) and 11.9 (2)°, respectively. Within the carboxyl group, the O3—C7 bond distance is appreciably shorter than the O4—C7 bond distance (Table 1). The crystal structure is stabilized by O—H···O hydrogen bonding between carboxyl groups and weak C—H···O hydrogen bonding between nitro group and benzene ring of adjacent molecules (Table 2).

Experimental

The title compound was prepared by a reaction of 2-nitro-4,6-dichlorotoluene (1 mmol) with 20% HNO₃ solution (15 ml) in an autoclave at 430 K for 20 h. Single crystals suitable for X-ray data collection were obtained by recrystallization from a methanol solution.

Refinement

Carboxyl H atom was located in a difference Fourier map and refined as riding in as-found relative position with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

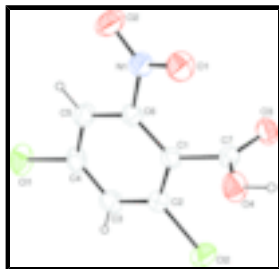


Fig. 1. The molecular structure of the title compound with 40% probability displacement ellipsoids.

2,4-Dichloro-6-nitrobenzoic acid

Crystal data

$C_7H_3Cl_2NO_4$

$M_r = 236.00$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 4.6930$ (7) Å

$b = 7.5590$ (11) Å

$c = 13.0721$ (19) Å

$\alpha = 97.120$ (2)°

$\beta = 95.267$ (2)°

$\gamma = 100.631$ (2)°

$V = 449.11$ (11) Å³

$Z = 2$

$F_{000} = 236$

$D_x = 1.745$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2069 reflections

$\theta = 2.8$ – 27.5 °

$\mu = 0.71$ mm⁻¹

$T = 295$ (2) K

Prism, colorless

$0.40 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295$ (2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2002)

$T_{\min} = 0.765$, $T_{\max} = 0.872$

2415 measured reflections

1641 independent reflections

1457 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.011$

$\theta_{\max} = 25.5$ °

$\theta_{\min} = 2.8$ °

$h = -5 \rightarrow 5$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.087$

$S = 1.06$

1641 reflections

127 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

$$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.1228P]$$

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

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

$\Delta\rho_{\max} = 0.22$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ 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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.66419 (15)	0.23838 (7)	0.04930 (4)	0.0620 (2)
Cl2	0.19170 (13)	0.45919 (8)	0.38873 (4)	0.0611 (2)
N1	0.8796 (4)	0.9077 (2)	0.20929 (13)	0.0425 (4)
O1	0.8119 (3)	1.03193 (18)	0.26405 (12)	0.0542 (4)
O2	1.0647 (4)	0.9276 (2)	0.15015 (13)	0.0651 (5)
O3	0.7264 (3)	0.86356 (19)	0.45830 (10)	0.0456 (3)
O4	0.3076 (3)	0.9004 (2)	0.37628 (11)	0.0540 (4)
H4A	0.2886	0.9850	0.4282	0.081*
C1	0.5569 (4)	0.6891 (2)	0.29482 (13)	0.0335 (4)
C2	0.4126 (4)	0.5107 (3)	0.29348 (14)	0.0388 (4)
C3	0.4410 (4)	0.3708 (2)	0.21800 (15)	0.0428 (5)
H5	0.3413	0.2525	0.2182	0.051*
C4	0.6193 (4)	0.4107 (3)	0.14305 (15)	0.0413 (4)
C5	0.7657 (4)	0.5858 (3)	0.14027 (15)	0.0410 (4)
H3	0.8852	0.6117	0.0889	0.049*
C6	0.7292 (4)	0.7212 (2)	0.21587 (14)	0.0346 (4)
C7	0.5340 (4)	0.8318 (2)	0.38368 (14)	0.0352 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0958 (5)	0.0399 (3)	0.0486 (3)	0.0164 (3)	0.0174 (3)	-0.0113 (2)
Cl2	0.0633 (4)	0.0609 (4)	0.0532 (3)	-0.0092 (3)	0.0264 (3)	0.0033 (3)
N1	0.0503 (9)	0.0346 (8)	0.0403 (9)	0.0024 (7)	0.0099 (7)	0.0021 (7)
O1	0.0708 (10)	0.0309 (7)	0.0605 (9)	0.0096 (6)	0.0189 (7)	-0.0021 (6)
O2	0.0816 (11)	0.0478 (9)	0.0627 (10)	-0.0061 (8)	0.0389 (9)	0.0017 (7)
O3	0.0431 (7)	0.0502 (8)	0.0388 (7)	0.0098 (6)	-0.0012 (6)	-0.0080 (6)
O4	0.0438 (8)	0.0655 (10)	0.0506 (8)	0.0230 (7)	0.0038 (6)	-0.0162 (7)
C1	0.0319 (9)	0.0341 (9)	0.0326 (9)	0.0062 (7)	0.0029 (7)	-0.0017 (7)
C2	0.0370 (10)	0.0418 (10)	0.0349 (9)	0.0026 (8)	0.0064 (8)	0.0013 (8)
C3	0.0490 (11)	0.0306 (9)	0.0442 (11)	0.0003 (8)	0.0042 (9)	0.0003 (8)
C4	0.0531 (11)	0.0346 (10)	0.0347 (10)	0.0106 (8)	0.0054 (8)	-0.0047 (7)

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C5	0.0496 (11)	0.0385 (10)	0.0354 (10)	0.0088 (8)	0.0131 (8)	0.0008 (8)
C6	0.0388 (9)	0.0301 (9)	0.0330 (9)	0.0040 (7)	0.0056 (7)	0.0007 (7)
C7	0.0327 (9)	0.0372 (10)	0.0341 (9)	0.0048 (7)	0.0077 (7)	-0.0009 (7)

Geometric parameters (Å, °)

C11—C4	1.7309 (18)	C1—C2	1.390 (3)
C12—C2	1.7277 (19)	C1—C7	1.510 (2)
N1—O2	1.216 (2)	C2—C3	1.388 (3)
N1—O1	1.217 (2)	C3—C4	1.372 (3)
N1—C6	1.472 (2)	C3—H5	0.9300
O3—C7	1.235 (2)	C4—C5	1.381 (3)
O4—C7	1.266 (2)	C5—C6	1.377 (2)
O4—H4A	0.8961	C5—H3	0.9300
C1—C6	1.386 (3)		
O2—N1—O1	124.25 (16)	C3—C4—C5	121.65 (17)
O2—N1—C6	117.96 (16)	C3—C4—C11	119.64 (15)
O1—N1—C6	117.79 (16)	C5—C4—C11	118.71 (15)
C7—O4—H4A	117.5	C6—C5—C4	117.98 (18)
C6—C1—C2	116.50 (16)	C6—C5—H3	121.0
C6—C1—C7	124.11 (16)	C4—C5—H3	121.0
C2—C1—C7	119.26 (16)	C5—C6—C1	123.15 (17)
C3—C2—C1	122.11 (17)	C5—C6—N1	117.00 (16)
C3—C2—C12	118.41 (15)	C1—C6—N1	119.84 (15)
C1—C2—C12	119.48 (14)	O3—C7—O4	126.27 (17)
C4—C3—C2	118.60 (17)	O3—C7—C1	117.77 (15)
C4—C3—H5	120.7	O4—C7—C1	115.83 (15)
C2—C3—H5	120.7		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4A \cdots O3 ⁱ	0.90	1.77	2.664 (2)	173
C3—H5 \cdots O2 ⁱⁱ	0.93	2.56	3.453 (2)	160

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

Fig. 1

