organic compounds

2,4-Dichloro-6-nitrobenzoic acid

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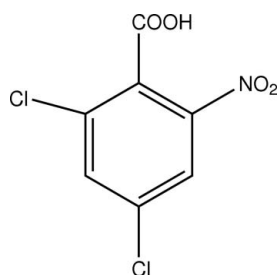
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The title compound, $C_7H_3Cl_2NO_4$, was prepared by the reaction of 2,4-dichloro-6-nitrotoluene with 20% HNO_3 solution at 430 K. The carboxyl and nitro groups are twisted by 82.82 (12) and 11.9 (2)°, respectively, with respect to the benzene ring. The crystal structure is stabilized by O—H···O hydrogen bonding between carboxyl groups and weak C—H···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

$C_7H_3Cl_2NO_4$	Triclinic, $P\bar{1}$
$M_r = 236.00$	$a = 4.6930$ (7) Å
$b = 7.5590$ (11) Å	$Z = 2$
$c = 13.0721$ (19) Å	Mo $K\alpha$ radiation
$\alpha = 97.120$ (2)°	$\mu = 0.71$ mm^{-1}
$\beta = 95.267$ (2)°	$T = 295$ (2) K
$\gamma = 100.631$ (2)°	$0.40 \times 0.30 \times 0.20$ mm
$V = 449.11$ (11) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2415 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	1641 independent reflections
$T_{min} = 0.765$, $T_{max} = 0.872$	1457 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	127 parameters
$wR(F^2) = 0.086$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
1641 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3^i	0.90	1.77	2.664 (2)	173
C3—H5···O2^{ii}	0.93	2.56	3.453 (2)	160

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

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).

References

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Langer, R., Rodefeld, L. & Neumann, K. H. (2006). US Patent No. 7 094 923.

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supporting information

2,4-Dichloro-6-nitrobenzoic acid

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S1. 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.
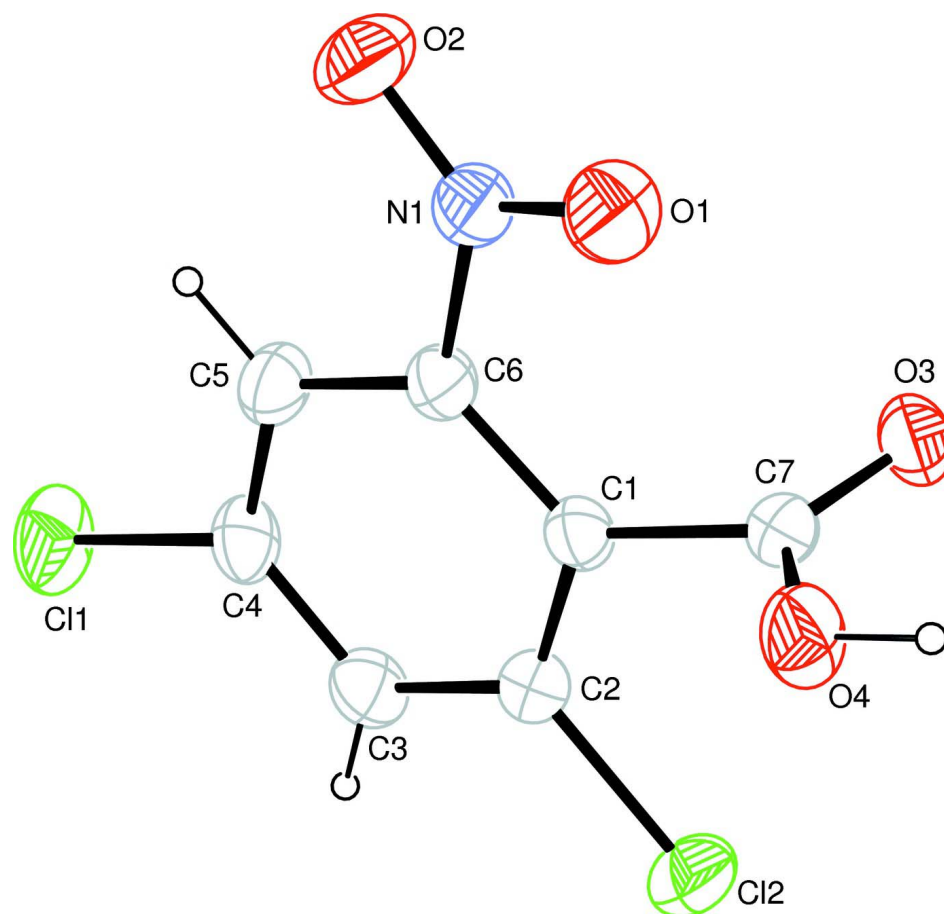
The molecular structure of the title compound is shown in Fig. 1. The molecule displays a non-planar structure. The carboxyl and nitro groups are twisted with respect to the benzene ring by 82.82 (12) and 11.9 (2)°, respectively. Within the carboxyl group, the O3—C7 bond distance is appreciably shorter 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).

S2. Experimental

The title compound was prepared by a reaction of 2-nitro-4,6-dichlorotoluene (1 mmol) with 20% HNO_3 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.

S3. Refinement

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

Figure 1

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

2,4-Dichloro-6-nitrobenzoic acid

Crystal data

$C_7H_3Cl_2NO_4$	$Z = 2$
$M_r = 236.00$	$F(000) = 236$
Triclinic, $P\overline{1}$	$D_x = 1.745$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.6930\ (7)$ Å	Cell parameters from 2069 reflections
$b = 7.5590\ (11)$ Å	$\theta = 2.8–27.5°$
$c = 13.0721\ (19)$ Å	$\mu = 0.71$ mm^{-1}
$\alpha = 97.120\ (2)°$	$T = 295$ K
$\beta = 95.267\ (2)°$	Prism, colorless
$\gamma = 100.631\ (2)°$	$0.40 \times 0.30 \times 0.20$ mm
$V = 449.11\ (11)$ Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
Radiation source: fine-focus sealed tube	$T_{min} = 0.765$, $T_{max} = 0.872$
Graphite monochromator	2415 measured reflections
φ and ω scans	1641 independent reflections
	1457 reflections with $I > 2\sigma(I)$

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

$\theta_{\text{max}} = 25.5°$, $\theta_{\text{min}} = 2.8°$

$h = -5 \rightarrow 5$

$k = -9 \rightarrow 9$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.087$	
$S = 1.06$	H-atom parameters constrained
1641 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.1228P]$ where $P = (F_o^2 + 2F_c^2)/3$
127 parameters	
0 restraints	$(\Delta/\sigma)_{\text{max}} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{max}} = 0.22$ e Å^{-3}
	$\Delta\rho_{\text{min}} = -0.34$ e Å^{-3}

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}
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 (Å^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)
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, º)

Cl1—C4	1.7309 (18)	C1—C2	1.390 (3)
Cl2—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—Cl1	119.64 (15)
O1—N1—C6	117.79 (16)	C5—C4—Cl1	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—Cl2	118.41 (15)	C1—C6—N1	119.84 (15)
C1—C2—Cl2	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, º)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3[i]	0.90	1.77	2.664 (2)	173
C3—H5···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.