

2,6-Dichloro-4-nitrotoluene

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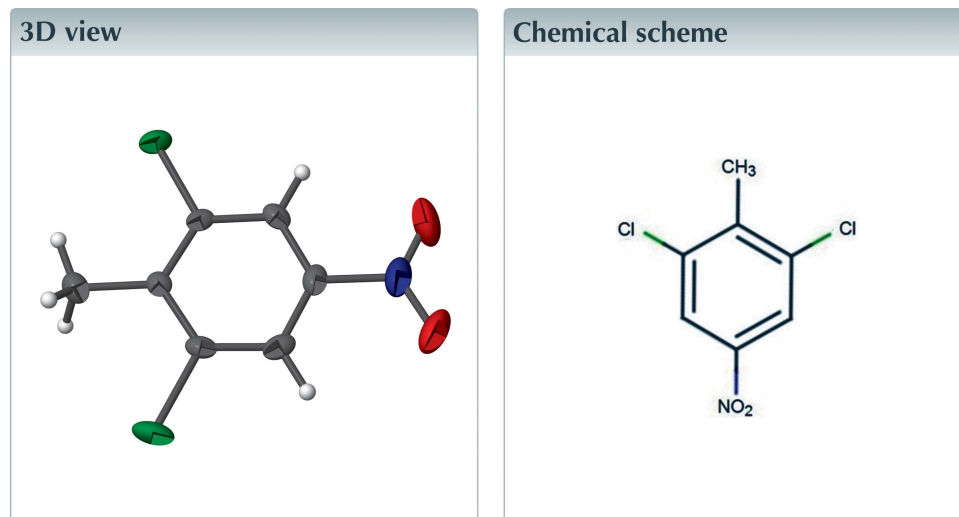
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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₇H₅Cl₂NO₂ [systematic name: 1,3-dichloro-2-methyl-5-nitrobenzene], crystallizes in the chiral space group *P*2₁2₁2₁ with a Flack parameter of −0.03 (5). The methyl C atom, the Cl atoms and the N atom of the nitro substituent all lie extremely close to the plane of the benzene ring; the deviations are 0.028 (3) Å for the methyl C atom, −0.016 (1) and 0.007 (1) Å for the two Cl atoms, and −0.017 (3) Å for the nitro N atom. Hence, no significant steric hindrance of the methyl group by the *ortho* halogen atoms is observed. The nitro group is inclined to the benzene ring by 9.8 (3)°. In the crystal, molecules are linked by weak C—H⋯O and C—H⋯Cl hydrogen bonds, forming layers parallel to the *ab* plane.



Structure description

Our group is interested in understanding the methyl radical behaviour of benzene molecules substituted by halogen and methyl substituents. Studies first focused on various mesityl halogens (Boudjada *et al.*, 2001; Tazi *et al.*, 1995; Hernandez *et al.*, 2003) to be extended thereafter to other products. In order to better identify the behaviour of the methyl group, a study of dihalogen-nitrotoluene molecules has been undertaken. The crystal structure of the dibromo analogue (DBNT) of the title compound (DCNT) was reported on recently by our group (Medjroubi *et al.*, 2016).

The molecular structure of the title compound is shown in Fig. 1. In the crystal structure of DBNT, there are two independent molecules per asymmetric unit and the methyl group H atoms are positionally disordered. For the title compound, DCNT, there is only one molecule per asymmetric unit and no disorder is observed for the methyl group H atoms. The dibromo analogue crystallizes in the centrosymmetric triclinic space

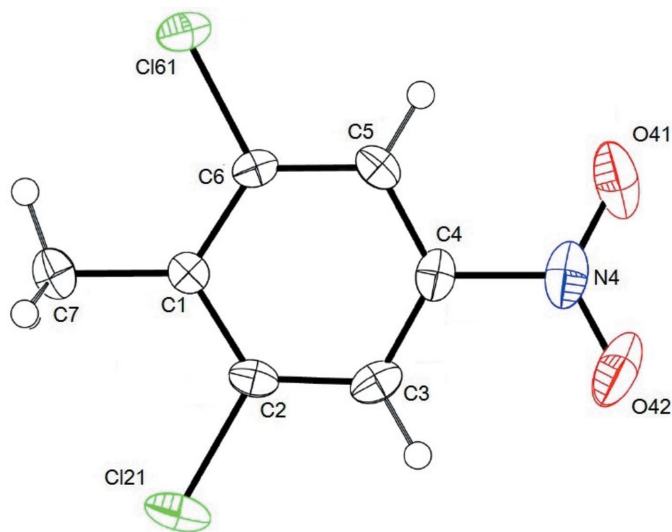


Figure 1
The molecular structure of the title compound, with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

group $P\bar{1}$, while the title dichloro analogue crystallizes in the chiral orthorhombic space group $P2_12_12_1$ [Flack parameter of -0.03 (5)].

In the DCNT molecule, the methyl C atom, the Cl atoms and the N atom of the nitro substituent all lie extremely close to the plane of the benzene ring: deviations are 0.028 (3) Å for C7, -0.016 (1) Å for Cl21, 0.007 (1) Å for Cl61 and -0.017 (3) Å for N4. Hence, no significant steric hindrance of the methyl group by the *ortho* halogen atoms is observed. The nitro group N4/O41/O42 is inclined to the benzene ring by 9.8 (3)°, compared with 2.5 (5) and 5.9 (4)° in DBNT.

In the crystal, molecules are linked by weak C—H···O and C—H···Cl hydrogen bonds forming layers parallel to the *ab* plane (Table 1 and Fig. 2).

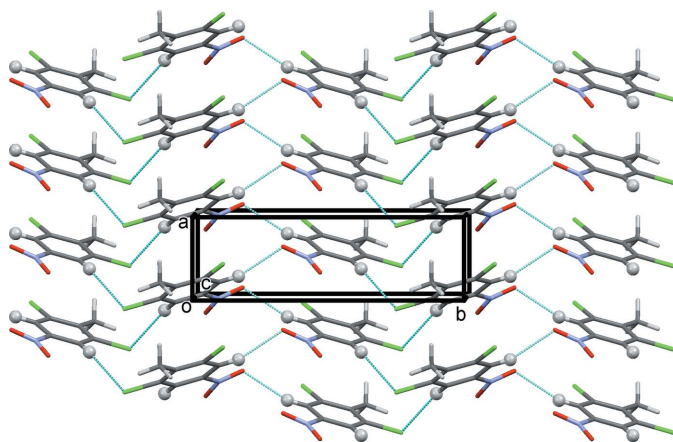


Figure 2
A view along the *c* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1) and the two H atoms involved in hydrogen bonding are shown as grey balls.

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O42 ⁱ	0.95	2.47	3.389 (3)	163
C5—H5···Cl61 ⁱⁱ	0.95	2.94	3.862 (3)	163

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₇ H ₅ Cl ₂ NO ₂
<i>M_r</i>	206.02
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.8145 (3), 12.4829 (10), 17.4438 (15)
<i>V</i> (Å ³)	830.60 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.73
Crystal size (mm)	0.26 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan
<i>T_{min}</i> , <i>T_{max}</i>	0.876, 0.964
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4472, 1879, 1756
<i>R_{int}</i>	0.028
(sin θ/λ) _{max} (Å ⁻¹)	0.651
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.066, 1.07
No. of reflections	1879
No. of parameters	110
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.23, -0.20
Absolute structure	Flack <i>x</i> determined using 640 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons et al., 2013)
Absolute structure parameter	-0.03 (5)

Computer programs: APEX2 and SAINT (Bruker, 2006), SIR2003 (Burla et al., 2005), SHELXL2013 (Sheldrick, 2015), CAMERON (Watkin et al., 1996), Mercury (Macrae et al., 2008), WinGX (Farrugia, 2012) and PLATON (Spek, 2009).

Synthesis and crystallization

The commercially available title compound (DCNT; Sigma-Aldrich) was recrystallized from an ethanol solution. Colourless needle-shaped single crystals several mm in length and having a section of a few hundredths of a mm² were obtained. Examination of the crystals using polarized light and X-ray diffraction revealed that they are generally twinned and consequently it was necessary to examine a large number of crystals to find a suitable single-crystal for the present X-ray diffraction study.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170672 [<https://doi.org/10.1107/S2414314617006721>]

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1,3-Dichloro-2-methyl-5-nitrobenzene

Crystal data

$C_7H_5Cl_2NO_2$

$M_r = 206.02$

Orthorhombic, $P2_12_12_1$

$a = 3.8145$ (3) Å

$b = 12.4829$ (10) Å

$c = 17.4438$ (15) Å

$V = 830.60$ (12) Å³

$Z = 4$

$F(000) = 416$

$D_x = 1.647$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å

Cell parameters from 2377 reflections

$\theta = 2.9$ – 27.3°

$\mu = 0.73$ mm⁻¹

$T = 150$ K

Needle, colourless

$0.26 \times 0.15 \times 0.05$ mm

Data collection

Bruker APEXII

diffractometer

Graphite monochromator

CCD rotation images, thin slices scans

Absorption correction: multi-scan

$T_{\min} = 0.876$, $T_{\max} = 0.964$

4472 measured reflections

1879 independent reflections

1756 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.6^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -3 \rightarrow 4$

$k = -16 \rightarrow 15$

$l = -19 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.066$

$S = 1.07$

1879 reflections

110 parameters

0 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.1882P]$

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

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

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.20$ e Å⁻³

Absolute structure: Flack x determined using

640 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons et al., 2013)

Absolute structure parameter: -0.03 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.

_reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl21	0.9157 (2)	0.39246 (5)	0.72626 (4)	0.0367 (2)
Cl61	0.36788 (19)	0.75690 (4)	0.60731 (4)	0.03019 (17)
O41	0.3055 (7)	0.4621 (2)	0.40010 (12)	0.0573 (7)
O42	0.6101 (8)	0.32613 (16)	0.43872 (12)	0.0550 (7)
N4	0.4803 (7)	0.41449 (19)	0.44804 (14)	0.0377 (6)
C1	0.6402 (7)	0.57082 (18)	0.66257 (13)	0.0192 (5)
C2	0.7342 (7)	0.46378 (18)	0.65064 (14)	0.0225 (5)
C3	0.6879 (7)	0.41103 (18)	0.58177 (15)	0.0256 (6)
H3	0.7561	0.3384	0.5755	0.031*
C4	0.5384 (7)	0.4682 (2)	0.52239 (14)	0.0248 (6)
C5	0.4406 (7)	0.57402 (19)	0.52939 (14)	0.0226 (5)
H5	0.3402	0.6119	0.4875	0.027*
C6	0.4937 (6)	0.62324 (17)	0.59953 (14)	0.0195 (5)
C7	0.6911 (7)	0.6243 (2)	0.73951 (14)	0.0285 (6)
H7A	0.6030	0.6980	0.7371	0.043*
H7B	0.9411	0.6252	0.7524	0.043*
H7C	0.5621	0.5845	0.7789	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl21	0.0325 (4)	0.0369 (3)	0.0408 (4)	0.0052 (3)	−0.0004 (3)	0.0215 (3)
Cl61	0.0322 (4)	0.0211 (3)	0.0372 (3)	0.0057 (3)	0.0049 (3)	0.0043 (2)
O41	0.0589 (17)	0.0823 (17)	0.0307 (11)	−0.0038 (15)	−0.0097 (12)	−0.0140 (11)
O42	0.0769 (18)	0.0380 (11)	0.0502 (13)	−0.0141 (14)	0.0164 (15)	−0.0218 (10)
N4	0.0402 (16)	0.0421 (14)	0.0308 (13)	−0.0149 (12)	0.0094 (12)	−0.0116 (11)
C1	0.0140 (12)	0.0228 (10)	0.0208 (10)	−0.0033 (10)	0.0023 (11)	0.0020 (8)
C2	0.0174 (13)	0.0235 (11)	0.0264 (12)	−0.0010 (10)	0.0024 (11)	0.0093 (10)
C3	0.0220 (14)	0.0182 (11)	0.0366 (13)	−0.0021 (11)	0.0089 (12)	0.0016 (10)
C4	0.0237 (14)	0.0278 (12)	0.0229 (12)	−0.0085 (11)	0.0066 (11)	−0.0043 (10)
C5	0.0173 (13)	0.0305 (12)	0.0200 (11)	−0.0027 (11)	0.0010 (11)	0.0061 (9)
C6	0.0154 (12)	0.0170 (10)	0.0261 (12)	−0.0013 (9)	0.0065 (10)	0.0030 (9)
C7	0.0252 (14)	0.0370 (14)	0.0232 (12)	−0.0024 (12)	0.0000 (11)	0.0001 (10)

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

Cl21—C2	1.735 (2)	C3—C4	1.381 (4)
Cl61—C6	1.741 (2)	C3—H3	0.9500
O41—N4	1.224 (3)	C4—C5	1.378 (3)
O42—N4	1.220 (3)	C5—C6	1.384 (3)

N4—C4	1.477 (3)	C5—H5	0.9500
C1—C6	1.396 (3)	C7—H7A	0.9800
C1—C2	1.399 (3)	C7—H7B	0.9800
C1—C7	1.512 (3)	C7—H7C	0.9800
C2—C3	1.381 (3)		
O42—N4—O41	124.7 (2)	C3—C4—N4	119.0 (2)
O42—N4—C4	117.8 (3)	C4—C5—C6	117.7 (2)
O41—N4—C4	117.5 (2)	C4—C5—H5	121.2
C6—C1—C2	115.7 (2)	C6—C5—H5	121.2
C6—C1—C7	122.9 (2)	C5—C6—C1	123.1 (2)
C2—C1—C7	121.4 (2)	C5—C6—Cl61	116.99 (18)
C3—C2—C1	123.5 (2)	C1—C6—Cl61	119.87 (18)
C3—C2—Cl21	117.87 (18)	C1—C7—H7A	109.5
C1—C2—Cl21	118.63 (19)	C1—C7—H7B	109.5
C2—C3—C4	117.3 (2)	H7A—C7—H7B	109.5
C2—C3—H3	121.4	C1—C7—H7C	109.5
C4—C3—H3	121.4	H7A—C7—H7C	109.5
C5—C4—C3	122.7 (2)	H7B—C7—H7C	109.5
C5—C4—N4	118.2 (2)		
C6—C1—C2—C3	-0.1 (4)	O42—N4—C4—C3	-9.8 (4)
C7—C1—C2—C3	179.0 (3)	O41—N4—C4—C3	170.3 (3)
C6—C1—C2—Cl21	-179.59 (19)	C3—C4—C5—C6	-0.6 (4)
C7—C1—C2—Cl21	-0.5 (3)	N4—C4—C5—C6	179.5 (2)
C1—C2—C3—C4	-0.4 (4)	C4—C5—C6—C1	0.0 (4)
Cl21—C2—C3—C4	179.05 (19)	C4—C5—C6—Cl61	-179.92 (19)
C2—C3—C4—C5	0.8 (4)	C2—C1—C6—C5	0.3 (4)
C2—C3—C4—N4	-179.3 (2)	C7—C1—C6—C5	-178.8 (2)
O42—N4—C4—C5	170.1 (3)	C2—C1—C6—Cl61	-179.73 (18)
O41—N4—C4—C5	-9.8 (4)	C7—C1—C6—Cl61	1.2 (4)

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>
C3—H3...O42 ⁱ	0.95	2.47	3.389 (3)	163
C5—H5...Cl61 ⁱⁱ	0.95	2.94	3.862 (3)	163

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