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The crystal structure of 1,5-dinitro-2,3,4-trichlorobenzene, $C_6H_1Cl_3N_2O_4$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.12 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.00 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II
$\theta_{\max}$, completeness:	26.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9849, 1781, 0.037
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1660
$N(\text{param})_{\text{refined}}$:	136
Programs:	Bruker [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6007(3)	0.84918(14)	0.34092(10)	0.0176(4)
C2	0.7613(3)	0.75122(12)	0.33642(11)	0.0164(4)
C3	0.7579(3)	0.66768(15)	0.40326(11)	0.0157(4)
C4	0.6125(3)	0.67841(14)	0.47497(10)	0.0152(3)
H4	0.619929	0.621216	0.521013	0.018*
C5	0.4540(3)	0.77585(14)	0.47798(11)	0.0145(4)
C6	0.4420(3)	0.86066(13)	0.41110(11)	0.0162(4)
Cl1	0.24736(8)	0.98063(4)	0.41471(3)	0.02057(19)
Cl2	0.60413(10)	0.95600(4)	0.26157(3)	0.0276(2)
Cl3	0.95002(9)	0.73801(4)	0.24913(3)	0.02327(19)
N1	0.3036(3)	0.78546(11)	0.55618(9)	0.0169(3)
N2	0.9210(3)	0.56219(12)	0.40275(9)	0.0170(3)
O1	0.8240(2)	0.46825(10)	0.42099(8)	0.0239(3)
O2	1.1420(2)	0.57620(11)	0.38715(8)	0.0237(3)
O3	0.4106(2)	0.76399(11)	0.62787(8)	0.0234(3)
O4	0.0816(2)	0.81191(11)	0.54383(8)	0.0243(3)

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Abstract

$C_6H_1Cl_3N_2O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 5.3193(2)$ Å, $b = 11.3307(4)$ Å, $c = 15.1131(5)$ Å, $\beta = 93.329(1)^\circ$, $V = 909.35(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0264$, $wR_{\text{ref}}(F^2) = 0.1098$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

An amount of 5.7 g of nitric acid (Tech 97%) was added to 39.9 g of sulfuric acid (AR 98%) below 40°. Then 1.84 g of

m-dichlorobenzene at 110° was added and the mixture was stirred for 10 min. The reaction was completed at 140° for 4 h. After the reaction, the reaction solution (90°) was poured into ice water. A pale yellow solid was collected, washed and dried.

1,5-dinitro-2,3,4-trichlorobenzene is a by-product of the preparation of 1,3,5-trinitro-2,4-dichlorobenzene. The pure 1,5-dinitro-2,3,4-trichlorobenzene obtained by column chromatography. At room temperature in ethanol solvent crystallization was performed to obtain crystals suitable for single crystal X-ray diffraction.

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Experimental details

All H atoms were identified in difference Fourier syntheses. With C—H bond lengths constrained to 0.95° and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

The chlorine atoms on the benzene ring of nitrochlorobenzene compound are susceptible to ortho-pair nitro groups [4, 5]. It can produce high-energy compounds with excellent properties through Ullmann condensation and coupling reaction, so it is an important organic intermediate [6]. The title compound 1,5-dinitro-2,3,4-trichlorobenzene, as a by-product of the *m*-dichlorobenzene nitration to 2,4-dichloro-1,3,5-trinitrobenzene, is a colorless solid with a melting point of 92–93°, soluble in ethanol or acetone but insoluble in water.

As shown in the figure, the crystal structure of the title compound was determined. The two nitro groups are attached to C1 and C5, respectively. And the dihedral angles with the benzene ring are 44.9° and 46.0°, respectively. Three chlorines are coplanar with the benzene ring. The bond length of C2—Cl1 and C4—Cl3 is increased compared to 1,3-dichloro-2,4,6-trinitrobenzene because the halogen atom has a smaller steric hindrance than the nitro group [7]. Compared with 1,5-dichloro-2,4-dinitrobenzene, the dihedral angle increases by 10° between the benzene ring and the nitro group on C3.

Compared with 1,3-DNTCB [8], the dihedral angle of the two nitro groups and the benzene ring is reduced due to the small steric hindrance of H.

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