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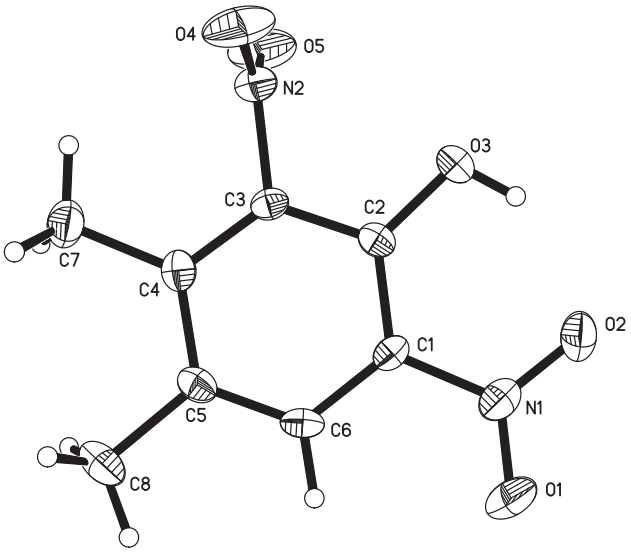
Crystal structure of 3,4-dimethyl-2,6-dinitrophenol, $C_8H_8N_2O_5$



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Abstract

$C_8H_8N_2O_5$, monoclinic, $P2_1/n$ (no. 14), $a = 10.7951(12)$ Å, $b = 8.1053(9)$ Å, $c = 10.8626(9)$ Å, $\beta = 100.371(4)°$, $V = 934.92(17)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0686$, $wR_{ref}(F^2) = 0.1382$, $T = 293(2)$ K.

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The asymmetric unit of the crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.24 × 0.18 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.13 mm^{-1}
Diffractometer, scan mode:	Photon 100 Detector, ω
θ_{max}, completeness:	25.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5351, 1700, 0.081
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 954
$N(param)_{refined}$:	141
Programs:	Bruker [5], SHELX [6], Olex2 [7]

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.4868(3)	0.2230(4)	0.0374(3)	0.0316(8)
C2	0.3664(3)	0.1977(4)	−0.0321(3)	0.0320(8)
C3	0.2882(3)	0.0970(4)	0.0229(3)	0.0300(8)
C4	0.3211(3)	0.0204(4)	0.1378(3)	0.0331(9)
C5	0.4445(3)	0.0492(4)	0.2046(3)	0.0369(9)
C6	0.5241(3)	0.1492(4)	0.1532(3)	0.0365(9)
H6	0.6050	0.1680	0.1972	0.044*
C7	0.2296(4)	−0.0883(5)	0.1891(3)	0.0528(11)
H7A	0.1492	−0.0845	0.1344	0.079*
H7B	0.2209	−0.0501	0.2707	0.079*
H7C	0.2603	−0.1997	0.1948	0.079*
C8	0.4881(4)	−0.0297(5)	0.3314(3)	0.0625(13)
H8A	0.5727	0.0050	0.3642	0.094*
H8B	0.4859	−0.1476	0.3228	0.094*
H8C	0.4335	0.0036	0.3875	0.094*
N1	0.5765(3)	0.3260(4)	−0.0116(3)	0.0464(8)
N2	0.1604(3)	0.0730(4)	−0.0512(3)	0.0434(8)
O1	0.6798(3)	0.3491(4)	0.0508(3)	0.0745(10)
O2	0.5439(3)	0.3881(4)	−0.1168(3)	0.0617(9)
O3	0.3198(2)	0.2611(3)	−0.1449(2)	0.0492(8)
H3A	0.376(3)	0.318(4)	−0.168(3)	0.059*
O4	0.0773(3)	0.1602(4)	−0.0281(3)	0.0799(11)
O5	0.1469(3)	−0.0321(4)	−0.1309(3)	0.0845(12)

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Source of material

The title compound was prepared by the nitration of *o*-xylene with fuming nitric acid and concentrated sulfuric acid [1], and treatmented with ice water and dilute sodium hydroxide solution. The water phase was collected and acidifide with hydrochloric acid. The dark precipitate was obtained, which

was recrystallized from methylene chloride solution at room temperature to give yellow crystals suitable for single-crystal X-ray diffraction.

Experimental details

All H atoms were placed in geometrically position and were refined using the riding model, with $C\text{-}H_{\text{aromatic}} = 0.93$ Å; $C\text{-}H_{\text{methyl}} = 0.96$ Å; $O\text{-}H_{\text{hydroxyl}} = 0.8369$ Å. The $U_{\text{iso}}(\text{H}) = 1.2\ U_{\text{eq}}(\text{C})$ for aromatic and hydroxyl group, $U_{\text{iso}}(\text{H}) = 1.5\ U_{\text{eq}}(\text{O})$ for methyl group.

Comment

4-Nitro *o*-xylene is an important intermediate for preparing dyes, perfume and agrochemical [2–4], which was prepared by the nitration of *o*-xylene. The title compound is a significant dinitro by-product of the synthesis of 4-nitro *o*-xylene.

As shown in the figure, the asymmetric unit of the title compound consists of one molecule. The arene ring is planar, the two nitro groups are twisted with respect to the plane of the central ring, making dihedral angles of 1.8 (N1/O1,O2) and 84.2 (N2/O4,O5)°, respectively. All bond lengths and angles are in the expected ranges.

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References

1. Sengupta, S. K.; Schultz, J. A.; Walck, K. R.; Corbin, D. R.; Ritter, J. C.: Synthesis of 4-nitro-*o*-xylene by selective nitration of *o*-xylene. Top. Catal. **55** (2012) 601–605.
2. Liu, H.; Ji, C.; Dong, X.; Peng, X.; Shi, C.: Regioselective preparation of 4-nitro-*o*-xylene using nitrogen dioxide/molecular oxygen over zeolite catalysts. Remarkable enhancement of para-selectivity. Chem. Lett. **43** (2014) 817–819.
3. Liu, Y. H.; Zhang, T. L.; Zhang, J. G.; Guo, J. Y.; Yu, K. B.: Preparation, structural characterization and the molecular structure of 2,3,5-trinitro-*p*-xylene. Struct. Chem. **16** (2005) 475–483.
4. Patil, P. T.; Malshe, K. M.; Dagade, S. P.; Dongare, M. K.: Regioselective nitration of *o*-xylene to 4-nitro-*o*-xylene using nitric acid over solid acid catalysts. Catal. Commun. **4** (2003) 429–434.
5. Bruker. APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2016).
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
7. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. **42** (2009) 339–341.