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The crystal structure of 2,3-dimethyl-1,4-dinitrobenzene – a $Z' = 4$ structure, $C_8H_8N_2O_4$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.19 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, ω
$\theta_{\max}$, completeness:	25.2°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14259, 6195, 0.056
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3792
$N(\text{param})_{\text{refined}}$:	513
Programs:	Bruker [1, 2], SHELX [3]

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Abstract

$C_8H_8N_2O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1093(5)$ Å, $b = 13.2430(8)$ Å, $c = 15.4334(10)$ Å, $\alpha = 106.544(2)^\circ$, $\beta = 98.150(2)^\circ$, $\gamma = 96.151(2)^\circ$, $V = 1745.22(18)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0508$, $wR_{\text{ref}}(F^2) = 0.1141$, $T = 173(2)$ K.

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The four crystallographically independent title molecules, forming the asymmetric unit are 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.

Source of material

The title compound was prepared by nitration of *o*-xylene. A reaction mixture was comprised of fuming nitric acid, concentrated sulfuric acid, and *o*-xylene, was stirred with 1 h over a temperature at 283 K. The reaction mixture was separated to obtain an organic phase. The organic phase was washed,

dried, distilled to give a concentrated solution. Several colorless single crystals were obtained by purifying the above solution with column chromatography on silica gel eluting with 1%, petroleum ether in ethyl acetate.

Experimental details

The coordinates of H-atoms at the benzene ring and methyl group were refined with the C–H distance fixed to 0.95 and 0.98 Å, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

Comment

Nitration of aromatic compounds is a widely used reaction to realize organic intermediates required in large tonnages for the fine chemical industry [4, 5]. The conventional nitration process, employing a nitrating mixture of nitric acid and sulfuric acid leads to overnitration or to oxidized by-products. Here we report the crystal structure of a significant by-product 2,3-dimethyl-1,4-dinitrobenzene which was prepared by nitrifying *o*-xylene [6–8].

As shown in the figure four crystallographically independent, 2,3-dimethyl-1,4-dinitrobenzene molecules are present in the asymmetric unit. The four rings are approximately planar. Owing to steric effects, the dihedral angles of the nitro groups and their parent rings are 59.3° (N1A/O1A,O2A), 45.7° (N2A/O3A,O4A), 58.1° (N1B/O1B,O2B) and 36.6° (N2B/O3B,O4B), 55.7° (N1C/O1C,O2C) and 37.1° (N2C/O3C,O4C), 48.5° (N1D/O1D,O2D), 60.15° (N2D/O3D,O4D) respectively. Bond lengths and angles are in accord with those in the isomer 1,2-dimethyl-3,5-dinitrobenzene [9] and a related trimethyl compound [10].

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1A	0.2726(3)	0.38606(18)	0.40512(17)	0.0227(6)
C2A	0.3792(3)	0.33848(18)	0.44621(17)	0.0238(6)
C3A	0.4213(3)	0.37687(19)	0.54265(17)	0.0243(6)
C4A	0.3519(3)	0.45921(19)	0.58844(18)	0.0264(6)
C5A	0.2470(3)	0.5067(2)	0.54595(18)	0.0289(6)
H5A	0.2041	0.5636	0.5809	0.035*
C6A	0.2068(3)	0.46924(19)	0.45206(18)	0.0275(6)
H6A	0.1357	0.4996	0.4202	0.033*
C7A	0.4512(3)	0.2501(2)	0.39086(19)	0.0343(7)
H7A1	0.4182	0.2392	0.3252	0.051*
H7A2	0.4215	0.1840	0.4050	0.051*
H7A3	0.5607	0.2696	0.4065	0.051*
C8A	0.5412(3)	0.3312(2)	0.5908(2)	0.0347(7)
H8A1	0.5797	0.3800	0.6528	0.052*
H8A2	0.6233	0.3219	0.5560	0.052*
H8A3	0.4982	0.2619	0.5949	0.052*
C1B	0.0856(3)	0.58481(19)	−0.09746(17)	0.0241(6)
C2B	0.1807(3)	0.54845(19)	−0.03846(17)	0.0236(6)
C3B	0.2066(3)	0.60570(19)	0.05642(17)	0.0237(6)
C4B	0.1324(3)	0.69329(19)	0.08205(17)	0.0248(6)
C5B	0.0374(3)	0.72635(19)	0.02172(18)	0.0293(6)
H5B	−0.0118	0.7858	0.0436	0.035*
C6B	0.0145(3)	0.67240(19)	−0.07052(18)	0.0302(6)
H6B	−0.0480	0.6946	−0.1141	0.036*
C7B	0.2591(3)	0.4542(2)	−0.0726(2)	0.0362(7)
H7B1	0.2113	0.3928	−0.0579	0.054*
H7B2	0.3649	0.4716	−0.0429	0.054*
H7B3	0.2519	0.4368	−0.1394	0.054*
C8B	0.3062(3)	0.5684(2)	0.12355(19)	0.0376(7)
H8B1	0.2968	0.4905	0.1017	0.056*
H8B2	0.2759	0.5904	0.1838	0.056*
H8B3	0.4107	0.5999	0.1290	0.056*
C1C	0.7727(3)	0.95188(18)	0.49828(17)	0.0230(6)
C2C	0.8336(3)	0.86820(18)	0.44575(17)	0.0229(6)
C3C	0.9421(3)	0.82443(18)	0.49233(17)	0.0225(6)
C4C	0.9785(3)	0.86907(18)	0.58772(18)	0.0231(6)
C5C	0.9177(3)	0.95348(19)	0.63803(18)	0.0255(6)
H5C	0.9479	0.9812	0.7029	0.031*
C6C	0.8130(3)	0.99616(19)	0.59243(18)	0.0263(6)
H6C	0.7695	1.0544	0.6246	0.032*
C7C	0.7904(3)	0.8283(2)	0.34223(18)	0.0373(7)
H7C1	0.7205	0.7611	0.3238	0.056*
H7C2	0.8806	0.8165	0.3152	0.056*
H7C3	0.7420	0.8814	0.3205	0.056*
C8C	1.0153(3)	0.7368(2)	0.4373(2)	0.0383(7)
H8C1	0.9462	0.6692	0.4181	0.057*
H8C2	1.1075	0.7302	0.4752	0.057*
H8C3	1.0398	0.7541	0.3828	0.057*
C1D	0.2709(3)	0.95801(18)	0.03558(18)	0.0234(6)
C2D	0.3906(3)	0.94318(18)	0.09544(17)	0.0242(6)
C3D	0.4831(3)	0.87017(19)	0.05626(17)	0.0244(6)
C4D	0.4481(3)	0.82063(19)	−0.03786(18)	0.0252(6)
C5D	0.3307(3)	0.83882(19)	−0.09655(18)	0.0265(6)
H5D	0.3137	0.8037	−0.1608	0.032*
C6D	0.2404(3)	0.90915(19)	−0.05859(18)	0.0258(6)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H6D	0.1586	0.9241	−0.0960	0.031*
C7D	0.4273(3)	1.0031(2)	0.19690(18)	0.0344(7)
H7D1	0.3616	1.0573	0.2112	0.052*
H7D2	0.5323	1.0378	0.2132	0.052*
H7D3	0.4117	0.9532	0.2322	0.052*
C8D	0.6155(3)	0.8499(2)	0.1162(2)	0.0402(7)
H8D1	0.5796	0.8081	0.1543	0.060*
H8D2	0.6734	0.9181	0.1558	0.060*
H8D3	0.6796	0.8103	0.0773	0.060*
N1A	0.2235(2)	0.34924(17)	0.30451(15)	0.0289(5)
N2A	0.3846(3)	0.5015(2)	0.68959(16)	0.0364(6)
N1B	0.0567(3)	0.52774(19)	−0.19735(15)	0.0334(6)
N2B	0.1550(3)	0.75968(17)	0.17929(16)	0.0368(6)
N1C	0.6579(2)	0.99891(19)	0.45219(16)	0.0324(6)
N2C	1.0908(3)	0.82835(19)	0.64295(17)	0.0343(6)
N1D	0.1638(2)	1.02742(17)	0.07249(16)	0.0316(6)
N2D	0.5414(3)	0.74398(19)	−0.08129(17)	0.0381(6)
O1A	0.1643(2)	0.25661(14)	0.26728(13)	0.0406(5)
O2A	0.2420(2)	0.41563(15)	0.26431(13)	0.0384(5)
O3A	0.4046(2)	0.59850(16)	0.72426(14)	0.0514(6)
O4A	0.3860(3)	0.43800(18)	0.73352(14)	0.0566(6)
O1B	0.0858(2)	0.57918(16)	−0.24863(13)	0.0447(5)
O2B	0.0028(3)	0.43345(16)	−0.22335(14)	0.0507(6)
O3B	0.2804(3)	0.77616(16)	0.22711(14)	0.0532(6)
O4B	0.0470(3)	0.79794(15)	0.20603(14)	0.0496(6)
O1C	0.6817(2)	1.09516(16)	0.46559(16)	0.0501(6)
O2C	0.5439(2)	0.94060(16)	0.40555(15)	0.0484(6)
O3C	1.0935(2)	0.73256(16)	0.62167(16)	0.0514(6)
O4C	1.1739(2)	0.89391(17)	0.70888(15)	0.0529(6)
O1D	0.1284(2)	1.09149(14)	0.03276(14)	0.0405(5)
O2D	0.1111(2)	1.01379(16)	0.13786(14)	0.0446(5)
O3D	0.6042(2)	0.76432(16)	−0.14018(16)	0.0528(6)
O4D	0.5479(3)	0.66504(18)	−0.05650(16)	0.0697(8)

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References

1. Bruker. SMART Ver. 5.05 data collection and SAINT-Plus Ver. 6.45 a data processing software for the SMART system. Bruker Analytical X-ray Instruments, Madison, WI, USA (2003).
2. Bruker. S.: SAINT. Area Detector Control and Integration Software. Bruker Analytical X-ray Instruments, Madison, WI, USA, (1997).
3. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **64A** (2008) 112–122.
4. Choudary, B. M.; Sateesh, M.; Kantam, M. L.; Rao, K. K.; Prasad, K. V. R.; Raghavan, K. V.; Sarma, J. A. R. P.: Selective nitration of aromatic compounds by solid acid catalysts. *Chem. Commun.* **1** (2000) 25–26.
5. Pokhodenko, V. D.; Pavlishchuk, V. V.: Green chemistry and modern technology. *Theor. Exp. Chem.* **38** (2002) 69–87.
6. 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.
7. 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.
 8. Kantam, M. L.; Choudary, B. M.; Kumar, N. S., Ramprasad, K. V.: Beta zeolite: an efficient and eco-friendly catalyst for the nitration of *o*-xylene with high regio-selectivity in liquid phase. *J. Mol. Catal. A: Chem.* **229** (2005) 67–70.
 9. Wang, J.; Xue, S.; Shen, F.; Xu, Z.: Crystal structure of 1,2-dimethyl-3,5-dinitrobenzene, $C_8H_8N_2O$. *Z. Kristallogr. NCS* **233** (2018) 909–910.
 10. Brihi, O.; Hamdouni, N.; Boudjada, A.; Meinel, J.: Crystal structure of 1,3,5-trimethyl-2,4-dinitrobenzene. *Acta Crystallogr. E* **71** (2015) o670–o671.