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The crystal structure of 1,2-dimethyl-3,4-dinitrobenzene, $C_8H_8N_2O_4$

Table 1: Data collection and handling.

Crystal:	Colorless column
Size:	0.30 × 0.15 × 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.12 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, ω [4]
$\theta_{\max}$, completeness:	25.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13096, 3282, 0.102
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1811
$N(\text{param})_{\text{refined}}$:	285
Programs:	Bruker [1, 2], SHELX [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1A	1.1441(3)	0.3081(2)	0.23964(19)	0.0308(7)
C2A	1.1138(3)	0.34172(19)	0.15757(19)	0.0279(7)
C3A	1.0610(4)	0.2851(2)	0.08892(19)	0.0345(8)
C4A	1.0335(4)	0.1907(2)	0.1050(2)	0.0384(8)
C5A	1.0639(4)	0.1583(2)	0.1869(2)	0.0394(8)
H5A	1.0462	0.0944	0.1971	0.047*
C6A	1.1191(4)	0.2154(2)	0.2543(2)	0.0369(8)
H6A	1.1397	0.1913	0.3102	0.044*
C7A	1.0347(5)	0.3228(2)	0.0003(2)	0.0528(10)
H7A1	0.9127	0.3197	−0.0236	0.079*
H7A2	1.1010	0.2858	−0.0344	0.079*
H7A3	1.0734	0.3874	0.0013	0.079*
C8A	0.9743(5)	0.1239(3)	0.0340(2)	0.0621(11)
H8A1	0.9560	0.0626	0.0575	0.093*
H8A2	1.0619	0.1194	−0.0029	0.093*
H8A3	0.8666	0.1462	0.0012	0.093*
C1B	0.6326(4)	0.3808(2)	0.1312(2)	0.0371(8)
C2B	0.6367(3)	0.3193(2)	0.1971(2)	0.0337(8)
C3B	0.5990(4)	0.2261(2)	0.1842(2)	0.0411(8)
C4B	0.5524(4)	0.1962(2)	0.1005(2)	0.0480(10)
C5B	0.5519(4)	0.2595(3)	0.0352(2)	0.0546(10)
H5B	0.5239	0.2385	−0.0216	0.066*
C6B	0.5906(4)	0.3512(3)	0.0499(2)	0.0499(9)
H6B	0.5882	0.3934	0.0041	0.060*
C7B	0.6082(5)	0.1599(3)	0.2572(3)	0.0715(13)
H7B1	0.6787	0.1869	0.3071	0.107*
H7B2	0.6595	0.1014	0.2426	0.107*
H7B3	0.4923	0.1482	0.2694	0.107*
C8B	0.5037(5)	0.0964(2)	0.0805(3)	0.0870(16)
H8B1	0.4676	0.0894	0.0194	0.131*
H8B2	0.4091	0.0787	0.1102	0.131*
H8B3	0.6028	0.0564	0.0991	0.131*
N1A	1.1908(3)	0.3688(2)	0.31266(18)	0.0406(7)

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Abstract

$C_8H_8N_2O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 7.8936(7)$ Å, $b = 14.4210(13)$ Å, $c = 16.0109(15)$ Å, $V = 1799.5(3)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0590$, $wR_{\text{ref}}(F^2) = 0.1293$, $T = 173(2)$ K.

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One of two crystallographic independent molecules of the title 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.

Source of material

The title compound was prepared by nitration reaction of *o*-xylene. It is recrystallized from the ethyl acetate solution at

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
N2A	1.1402(3)	0.44083(17)	0.13973(17)	0.0379(7)
N2B	0.6776(4)	0.3490(2)	0.28623(19)	0.0546(8)
O1A	1.2353(3)	0.33283(18)	0.38171(15)	0.0578(7)
O2A	1.1809(3)	0.45230(17)	0.30191(16)	0.0609(7)
O3A	1.2848(3)	0.46599(15)	0.13367(16)	0.0557(7)
O4A	1.0147(3)	0.49054(15)	0.12921(18)	0.0610(8)
O3B	0.5581(3)	0.3687(2)	0.32266(17)	0.0725(9)
O4B	0.8267(3)	0.3480(3)	0.31930(18)	0.1039(13)
N1B ^a	0.6641(8)	0.4803(3)	0.1517(5)	0.0497(14)
O1B ^a	0.6499(7)	0.5347(3)	0.0921(6)	0.0639(19)
O2B ^a	0.7031(10)	0.5029(5)	0.2252(5)	0.078(2)
N1Y ^b	0.662(3)	0.4820(11)	0.1213(19)	0.056(6)
O1Y ^b	0.680(4)	0.511(2)	0.052(2)	0.066(7)
O2Y ^b	0.668(4)	0.5262(15)	0.187(3)	0.064(6)

^aOccupancy: 0.83(2), ^bOccupancy: 0.17(2).

room temperature to give colourless crystal for single-crystal X-ray diffraction.

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 $U_{\text{eq}}(\text{C})$. There is a disorder at the nitro group N1B (Table 2).

Comment

A nitrating mixture comprising sulfuric acid and fuming nitric acid produce approximately equal amount of isomer mixtures involving 3-nitro-*o*-xylene and 4-nitro-*o*-xylene [4–6]. Mixed-acid nitration systems are corrosive and used in excess often lead to overnitration or to oxidized by-products. Here we report the crystal structure of a significant by-product, 1,2-dimethyl-3,4-dinitrobenzene. The title compound was separated from the reaction mixture and the structure was characterized. (*cf.* the figure).

Two crystallographically independent, 1,2-dimethyl-3,4-dinitrobenzene molecules are present in the asymmetric unit. The two rings are approximately planar as expected. Owing to space steric effect, the dihedral angle of the nitro groups and their parent rings are 12.4° (N1A/O1A,O2A), 83.1° (N2A/O3A,O4A), 3.9° (N1B/O1B,O2B), 14.3° (N1Y/O1Y,O2Y) 88.2° (N2B/O3B,O4B), respectively. The geometric parameter are in accord with those in the isomer 1,2-dimethyl-3,5-dinitrobenzene [7] and a structurally related trimethyl compound [8].

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