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The crystal structure of 3-methyl-2,6-dinitrophenol, $C_7H_6N_2O_5$

<https://doi.org/10.1515/ncrs-2021-0255>

Received June 22, 2021; accepted July 19, 2021;

published online August 2, 2021

Abstract

$C_7H_6N_2O_5$, monoclinic, $P2_1/n$ (no. 14), $a = 9.5931(16)$ Å, $b = 17.332(3)$ Å, $c = 9.8989(14)$ Å, $\beta = 94.902(5)^\circ$, $V = 1639.9(4)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0619$, $wR_{ref}(F^2) = 0.1784$, $T = 170$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	$0.06 \times 0.03 \times 0.02$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.14 mm^{-1}
Diffractometer, scan mode:	D8 VENTURE, φ and ω
θ_{max} , completeness:	26.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11,771, 3326, 0.063
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2064
$N(\text{param})_{\text{refined}}$:	257
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

CCDC no.: 2097360

The asymmetric unit of the title structure is shown in Figure (there are two molecules in the asymmetric unit, and hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.4598 (3)	0.42027 (19)	0.7481 (3)	0.0298 (7)
C2	0.5691 (4)	0.4594 (2)	0.8196 (3)	0.0325 (8)
H2	0.558736	0.476877	0.909190	0.039*
C3	0.6915 (3)	0.4729 (2)	0.7620 (3)	0.0319 (8)
H3A	0.764135	0.500952	0.811347	0.038*
C4	0.7117 (4)	0.44606 (19)	0.6318 (3)	0.0306 (8)
C5	0.6011 (4)	0.40670 (19)	0.5645 (3)	0.0300 (8)
C6	0.4728 (3)	0.39341 (19)	0.6167 (3)	0.0302 (8)
C7	0.8456 (4)	0.4622 (2)	0.5687 (4)	0.0400 (9)
H7A	0.907030	0.417024	0.579725	0.060*
H7B	0.892203	0.506823	0.613275	0.060*
H7C	0.824840	0.473119	0.471964	0.060*
C8	0.7221 (4)	0.7012 (2)	0.8231 (4)	0.0412 (9)
H8A	0.734605	0.649369	0.786301	0.062*
H8B	0.641970	0.701129	0.878241	0.062*
H8C	0.806690	0.716130	0.879607	0.062*
C9	0.6965 (4)	0.7571 (2)	0.7097 (3)	0.0310 (8)
C10	0.5708 (4)	0.7996 (2)	0.6924 (3)	0.0330 (8)
H10	0.502822	0.793750	0.756017	0.040*
C11	0.5451 (4)	0.8492 (2)	0.5848 (3)	0.0326 (8)
H11	0.459740	0.877214	0.574562	0.039*
C12	0.6433 (3)	0.85854 (19)	0.4914 (3)	0.0291 (7)
C13	0.7704 (3)	0.81787 (19)	0.5026 (3)	0.0279 (7)
C14	0.7902 (3)	0.76894 (19)	0.6139 (3)	0.0282 (7)
N1	0.3321 (3)	0.40750 (18)	0.8117 (3)	0.0372 (7)
N2	0.6174 (3)	0.37422 (18)	0.4297 (3)	0.0349 (7)
N3	0.9205 (3)	0.72308 (17)	0.6237 (3)	0.0338(7)
N4	0.6127 (3)	0.91292 (18)	0.3805 (3)	0.0373(7)
O1	0.3248 (3)	0.42634 (17)	0.9299 (2)	0.0481(7)
O2	0.2315 (3)	0.37747 (18)	0.7431 (3)	0.0520(8)
O3	0.3750 (3)	0.35623 (16)	0.5388 (2)	0.0404(6)
H3	0.299762	0.356210	0.576453	0.061*
O4	0.5483 (3)	0.40235 (17)	0.3324 (2)	0.0480 (7)
O5	0.6997 (3)	0.32113 (16)	0.4215 (3)	0.0485 (7)
O6	1.0106 (3)	0.73775 (16)	0.7140 (3)	0.0491 (7)
O7	0.9286 (3)	0.67116 (16)	0.5406 (3)	0.0495 (7)
O8	0.8723 (3)	0.82218 (16)	0.4190 (2)	0.0404 (6)
H8	0.843300	0.846430	0.348716	0.061*
O9	0.7043 (3)	0.92570 (16)	0.3033 (3)	0.0470 (7)
O10	0.4984 (3)	0.94305 (18)	0.3684 (3)	0.0566 (8)

atoms including atomic coordinates and displacement parameters.

Source of material

In a typical experiment 5 g of 2,4,6-trinitrotoluene (TNT) was added to 100 mL of methanol, heated to 55 °C and kept stirring to make TNT completely soluble in methanol. We used 20 mL sodium hypochlorite (NaClO) and adjusted the pH to 1 with hydrochloric acid (Tech 36%). Then the above NaClO solution

was slowly added to the reaction solution and reacted for 1 h. After the reaction, the reaction liquid was filtered. The filtrate was collected and dried to obtain solid compound **1**. Then, the solid compound **1** was washed with water, the washing liquid was collected and dried to obtain solid compound **2**. The solid compound **2** was separated by column chromatography. Finally yellow crystals were obtained. Hint: high explosives - like the title compound require considerable safety precautions during handling and experimentation.

Experimental details

Hydrogen atom was placed in their geometrically idealized positions and constrained to ride on their parent atoms. All the non-hydrogen atoms were refined anisotropically.

Comment

Hexanitrobibenzyl (HNBB) is a light yellow powder and is an important intermediate for the preparation of excellent heat-resistant explosive hexanitrostilbene (HNS) in a two-step process [5–7]. Many people have done a lot of research to improve the yield of HNBB, such as Lu Ming and others [8–10]. But for the waste liquid of synthetic HNBB, almost no information is reported. In order to study what substances are in the waste liquid, and further study the mechanism of synthesis of HNBB and provide convenience for industrial wastewater treatment we have started this study. Therefore, column chromatography is used to separate and obtain the title compound.

As shown in Figure, the crystal structure of the title compound was analyzed and refined using the SHELXL program [2–4]. In the title compound, the nitro group at position 2 of the original TNT has been removed and a hydroxyl group is added between the remaining two nitro groups. The formation of the title compound is due to the fact that in 2,4-dinitrotoluene, both nitro groups are electron-withdrawing groups, resulting in low electron density at position 3 between them, and the hydroxyl group is an electron-donating group. In the reaction, the hydroxyl group attacks the 3rd position and replaces H to form a hydroxyl group. Of course, there may be two main reasons for the formation of 2,4-dinitrotoluene. One is that TNT has removed a nitro group under alkaline conditions, the other is that this impurity still exists in the refined TNT raw materials. Bond lengths and angles are in the expected ranges [11].

Acknowledgements: We thank the Center of Testing and Analysis, Shanghai Institute, for support.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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