Crystal structure of 2,4-dinitroanisole, $C_7H_6N_2O_5$

Gang Xue[I], Cai-Rong Gong*[,II] and Hong-Yu Chen[III]

[I] Hebei University of Technology, School of Materials Science and Engineering, Institute of Power Source and Ecomaterials Science, Tianjin 300130, P. R. China
[II] Tianjin University, School of Material Science and Engineering, Tianjin 300072, P. R. China
[III] Taishan Medical University, School of Chemistry and Chemical Engineering, Taian 271000, Shandong, P. R. China

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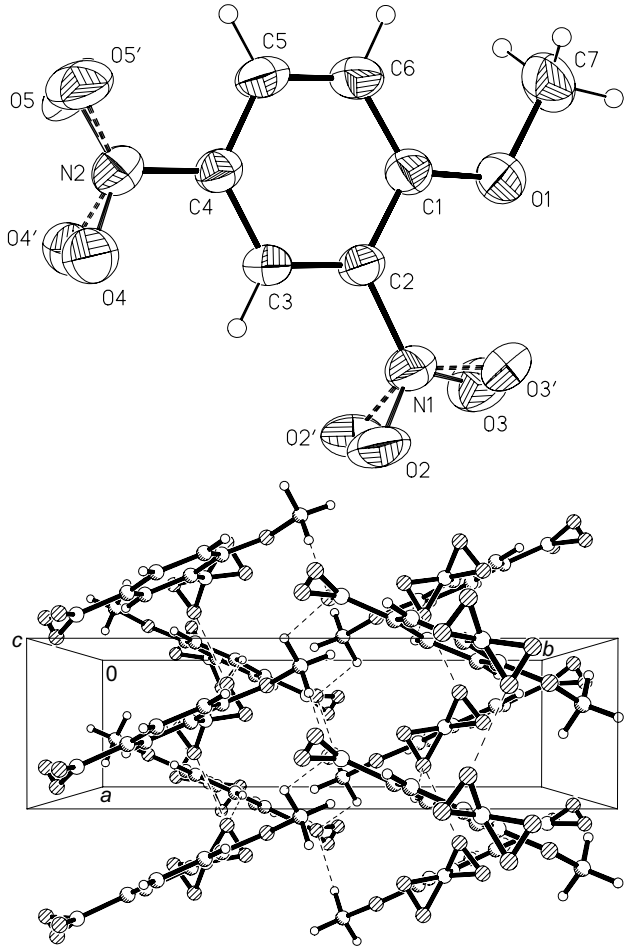

Abstract

$C_7H_6N_2O_5$, monoclinic, $P12_1/n1$ (no. 14), a = 3.9793(9) Å, b = 13.759(1) Å, c = 15.445(1) Å, β = 90.89(1)°, V = 845.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.135, T = 293 K.

Source of material

1-bromo-2,4,-dinitrobenzene, (4.92 g) and 4,5-bis-(2-cyanoethylthio)-1,3-dithiole-2-thione (6.1 g) was dissolved in 20 ml of methanol and 1.15 g of sodium was added rapidly and solution stirred for 12 h at room temperature in N_2 atmosphere. The resulting precipitate was filtered off. The title compound was recrystallized unexpectedly from the filtrate at room temperature. The synthesis of title compound belong to typical simple nucleophilic aromatic substitution of the highly labile bromide substituent with a methoxide anion.

* Correspondence author (e-mail: gcr@tju.edu.cn)

Experimental details

The two nitro groups were found to be disordered and were resolved into two sites each. The site occupancy ratios were refined using isotropic displacement parameters of the respective oxygen atoms (0.54(1)/0.46 for O2,O3/O2′,O3′ and 0.55(2)/0.45 for O4,O4/O4′,O5′). In the subsequent refinements, the occupancies were fixed at 0.50. The methyl H atoms were fitted to the electron density during the final refinement.

Discussion

DNAN (2,4-dinitroanisole) is used as an ingredient in the syntheses of dyes in industry [1]. It is also used as an insecticide by US Armed Forces [2]. Recently, some literature has shown that current interest in DNAN is predominantly as an ingredient in explosive formulations [3]. As a less sensitive melt-cast medium than TNT, DNAN is subject to less stringent transportation requirements than TNT, and it has applications in appropriate munitions requiring less sensitive melt-cast formulations [3]. One crystal structure has been already reported [4,5]. We obtained DNAN unexpectedly and found a new crystal structure. It represents a polymorphic modification.

In the title crystal structure, the bond lengths and angles are similar to those of the reported molecule structure [4,5], but the torsion angles are different. The C6–C1–O1–C7 torsion angle is 0.6(3)°, and for [4,5] the corresponding torsion angles range between 5° and 15°. Both phases crystallize in $P2_1/n$, but have different molecular packings, which result, e.g., in definitely different identity distances along the two-fold screw axis (b = 12.645(2) Å [4]). The title molecule has a planar six-membered ring (C1→C6), with the maximum deviation from its least-squares plane of 0.004(1) Å for C3 (figure, top). There are intermolecular contacts shorter than the sum of the van der Waals radii and hydrogen-bonding interactions of C–H···O type in the crystal structure (figure, bottom).

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.32 × 0.42 × 0.44 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.35 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55.00°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2976, 1942
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1109
$N(param)_{refined}$:	165
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3A)	4*e*	0.7049	0.1101	0.4958	0.072
H(5A)	4*e*	0.5295	0.1709	0.7445	0.087
H(6A)	4*e*	0.3067	0.3189	0.7056	0.088
H(7A)	4*e*	0.0336	0.5153	0.5847	0.148
H(7B)	4*e*	0.2976	0.4755	0.6522	0.148
H(7C)	4*e*	–0.0594	0.4277	0.6447	0.148

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*		0.3656(4)	0.3052(1)	0.5767(1)	0.061(1)	0.067(1)	0.060(1)	0.0002(9)	–0.0029(8)	–0.0084(8)
C(2)	4*e*		0.4875(4)	0.2400(1)	0.5149(1)	0.061(1)	0.067(1)	0.0457(8)	–0.0006(9)	0.0007(7)	0.0009(8)
C(3)	4*e*		0.6231(4)	0.1521(1)	0.5377(1)	0.066(1)	0.065(1)	0.0483(8)	–0.0007(9)	0.0068(7)	–0.0020(8)
C(4)	4*e*		0.6357(4)	0.1271(1)	0.6238(1)	0.061(1)	0.069(1)	0.0516(9)	–0.0034(9)	0.0017(8)	0.0042(8)
C(5)	4*e*		0.5184(5)	0.1889(2)	0.6865(1)	0.082(1)	0.091(2)	0.0450(9)	–0.004(1)	–0.0006(9)	–0.0023(9)
C(6)	4*e*		0.3851(5)	0.2772(2)	0.6631(1)	0.083(1)	0.084(1)	0.053(1)	0.002(1)	0.0020(9)	–0.0154(9)
C(7)	4*e*		0.1180(6)	0.4580(2)	0.6130(2)	0.104(2)	0.084(2)	0.108(2)	0.026(1)	–0.012(1)	–0.035(1)
N(1)	4*e*		0.4768(5)	0.2627(1)	0.4219(1)	0.097(1)	0.077(1)	0.0545(9)	0.012(1)	0.0035(9)	0.0070(8)
N(2)	4*e*		0.7838(5)	0.0339(1)	0.6484(1)	0.090(1)	0.081(1)	0.065(1)	0.004(1)	0.001(1)	0.0129(9)
O(1)	4*e*		0.2412(4)	0.3912(1)	0.54935(8)	0.098(1)	0.0705(9)	0.0748(8)	0.0209(8)	–0.0041(7)	–0.0117(7)
O(2)	4*e*	0.50	0.517(1)	0.1945(3)	0.3673(2)	0.156(4)	0.089(2)	0.045(2)	0.016(2)	0.003(2)	–0.007(2)
O(3)	4*e*	0.50	0.443(1)	0.3429(3)	0.3930(3)	0.158(4)	0.082(3)	0.075(2)	0.021(3)	0.011(3)	0.022(2)
O(2′)	4*e*	0.50	0.714(1)	0.2392(4)	0.3836(3)	0.130(4)	0.173(5)	0.059(2)	0.036(3)	0.041(2)	0.024(2)
O(3′)	4*e*	0.50	0.227(1)	0.3073(5)	0.3991(2)	0.124(3)	0.159(5)	0.055(2)	0.058(3)	–0.015(2)	0.003(2)
O(4)	4*e*	0.50	0.826(2)	–0.0296(7)	0.5877(7)	0.118(6)	0.074(4)	0.088(3)	0.012(3)	0.003(4)	0.001(3)
O(5)	4*e*	0.50	0.832(5)	0.021(1)	0.7234(8)	0.153(8)	0.112(7)	0.077(4)	0.006(6)	–0.033(5)	0.038(3)
O(4′)	4*e*	0.50	0.953(2)	–0.0065(7)	0.5986(7)	0.110(6)	0.074(4)	0.085(4)	0.018(3)	0.018(4)	0.010(3)
O(5′)	4*e*	0.50	0.755(5)	0.004(1)	0.7247(7)	0.17(1)	0.095(5)	0.062(3)	0.010(6)	0.017(4)	0.019(3)

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