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The crystal structure of 1,4-dinitroso-2,3,5,6-tetraacetoxy-piperazine, $C_{12}H_{16}N_4O_{10}$

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Abstract

$C_{12}H_{16}N_4O_{10}$, monoclinic, $C2/c$ (no. 15), $a = 21.953(3)$ Å, $b = 7.0292(9)$ Å, $c = 13.5984(19)$ Å, $\beta = 127.569(4)^\circ$, $V = 1663.23(40)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0555$, $wR_{ref}(F^2) = 0.1224$, $T = 122(2)$ K.

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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:	Colourless plate
Size:	$0.21 \times 0.17 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.13 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, ω
$\theta_{\max}$, completeness:	25.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4558, 1522, 0.069
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1025
$N(\text{param})_{\text{refined}}$:	139
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N2 ^a	1.0579(11)	0.242(2)	0.9259(15)	0.018(3)
O1 ^a	1.0962(2)	0.1669(6)	0.8967(4)	0.0302(13)
N2 ^b	1.0655(16)	0.206(3)	0.924(2)	0.025(5)
O1 ^b	1.0400(3)	0.3713(9)	0.8940(5)	0.0293(19)
C1	0.99682(16)	0.2028(4)	1.0206(3)	0.0177(6)
H1	0.9777	0.3311	0.9815	0.021*
C2	0.92969(15)	0.0723(4)	0.9768(3)	0.0183(7)
H2	0.9044	0.1114	1.0149	0.022*
C4	1.09630(15)	0.3466(4)	1.2136(3)	0.0196(7)
C5	1.13626(18)	0.3368(5)	1.3493(3)	0.0305(8)
H5A	1.1839	0.4109	1.3930	0.046*
H5B	1.1484	0.2039	1.3766	0.046*
H5C	1.1029	0.3891	1.3677	0.046*
C6	0.80813(15)	0.1786(4)	0.7964(3)	0.0202(7)
C7	0.76145(16)	0.1946(4)	0.6597(3)	0.0266(7)
H7A	0.7253	0.0880	0.6206	0.040*
H7B	0.7954	0.1917	0.6355	0.040*
H7C	0.7329	0.3147	0.6324	0.040*
N1	1.04447(12)	0.1225(3)	0.9910(2)	0.0165(5)
O2	1.03780(11)	0.2162(2)	1.15220(17)	0.0190(5)
O3	1.11001(11)	0.4519(3)	1.15972(19)	0.0252(5)
O4	0.87641(10)	0.0875(3)	0.84454(18)	0.0205(5)
O5	0.79117(11)	0.2320(3)	0.8609(2)	0.0303(6)

^aOccupancy: 0.581(7), ^bOccupancy: 0.419(7).

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Source of material

40% Glyoxal solution (6.00 mL) was added to an aqueous solution (30.00 mL) of potassium sulfamate (14.85 g), the mixture was stirred at a low temperature for about 3 days. After filtering and drying, a white solid (HKIW, 4.38 g) was obtained.

98% nitric acid (4.63 g) was added to a certain amount of acetic anhydride at low temperatures. HKIW (3.50 g) was added to the mixed acid and reaction for 4 h at 328 K. The mixture was poured into deionized water, filtered at room temperature and dried under vacuum in a drying oven. Then a white solid (1,4-dinitroso-2,3,5,6-tetraacetoxy-piperazine, 0.74 g) was obtained. Colorless transparent crystals were obtained by slow evaporation from a dichloromethane solution at room temperature.

Experimental details

Hydrogen atoms were placed in calculated positions using the riding model. $U_{\text{iso}}(\text{H})$ were constrained to $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2 U_{\text{eq}}(\text{C})$ for other H atoms. The asymmetric unit contains a half molecule and the whole molecule is sited on a crystallographic inversion centre. The nitroso group is disordered over two positions, with refined occupancies of 0.581(7) and 0.419(7).

Comment

Piperazine derivatives have important applications in the fields of medicinal chemistry and materials [4–10]. The molecular structure of the title compound (*cf.* the figure) has two nitroso groups and four acetoxy groups, which are bonded to two nitrogen atoms and four carbon atoms on the piperazine ring, respectively. All bond lengths and angles are within normal ranges and in good agreement with those found for the structure of 1,4-diformyl-2,3,5,6-tetraacetoxy-piperazine, which crystallises in space group $P2_1/n$ and has been previously reported in the literature [11]. The planes defined by the nitroso group (N1, N2, O1) and by C1, N1, C2 are almost coplanar for the angle between the two planes is 3.52° . The dihedral angle between the two acetoxy groups (C1, O2, C4, O3, C5 and C2, O4, C6, O5, C7) and the plane (C1, C2, C1', C2') is 87.41° and 78.73° respectively. The dihedral angle between the plane defined by the nitroso group (N1, N2, O1) and the plane (C1, C2, C1', C2') is 49.00° .

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