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Crystal structure of 2,4-pentanedione bis(2,4-dinitrophenylhydrazone), $C_{17}H_{16}N_8O_8$

Table 1: Data collection and handling.

Crystal:	Needles, orange
Size:	0.56 × 0.29 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, 0.5° φ and ω -scans
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	47896, 4645, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4474
$N(\text{param})_{\text{refined}}$:	302
Programs:	Bruker programs [1], SHELX [2], WinGX and ORTEP [3]

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Abstract

$C_{17}H_{16}N_8O_8$, orthorhombic, $Pna2_1$ (no. 33), $a = 13.2406(3)$ Å, $b = 21.0883(5)$ Å, $c = 7.1364(2)$ Å, $V = 1992.64(9)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0285$, $wR_{\text{ref}}(F^2) = 0.0802$, $T = 173(2)$ K.

CCDC no.: 1897170

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared adding of 2,4-pentadione (4.875 g, 0.04875 mol) into a 100 mL round-bottom flask containing 2,4-dinitrophenylhydrazine (9.659 g, 0.04875 mol). A brick red colour was observed and the contents of the flask were refluxed with continuous stirring overnight. Two layers were observed in the flask; an upper colourless layer and a lower red coloured layer. After the reflux, the flask was left to stand for two hours in an ice-water bath. A brown-orange

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.12874(11)	0.96896(6)	0.1818(2)	0.0338(3)
O2	0.27712(11)	0.94063(7)	0.0837(2)	0.0356(3)
O3	−0.10620(10)	0.81460(6)	0.3784(2)	0.0292(3)
O4	−0.08118(9)	0.71373(6)	0.34241(19)	0.0243(3)
O5	0.53844(10)	0.40681(6)	0.3334(2)	0.0324(3)
O6	0.61629(11)	0.31851(8)	0.3831(3)	0.0403(4)
O7	0.48678(15)	0.12102(7)	0.2014(3)	0.0532(5)
O8	0.33548(16)	0.11237(7)	0.0870(2)	0.0488(5)
N1	0.19170(12)	0.92861(7)	0.1406(2)	0.0255(3)
N2	−0.05413(10)	0.76982(6)	0.3247(2)	0.0197(3)
N3	0.08197(10)	0.67142(6)	0.1768(2)	0.0193(3)
H3	0.027855	0.658065	0.236496	0.023*
N4	0.14432(11)	0.62943(6)	0.0822(2)	0.0208(3)
N5	0.27611(11)	0.43459(6)	0.0947(2)	0.0201(3)
N6	0.35752(10)	0.40773(6)	0.1875(2)	0.0184(3)
H6A	0.400833	0.431756	0.248438	0.022*
N7	0.54301(11)	0.34860(8)	0.3252(2)	0.0246(3)
N8	0.40548(16)	0.14355(8)	0.1523(3)	0.0376(4)
C1	0.16322(12)	0.86172(7)	0.1568(2)	0.0202(3)
C2	0.07121(13)	0.84650(7)	0.2311(2)	0.0190(3)
H2	0.027103	0.878780	0.274979	0.023*
C3	0.04309(11)	0.78289(7)	0.2414(2)	0.0168(3)
C4	0.10707(12)	0.73369(7)	0.1743(2)	0.0168(3)
C5	0.20221(11)	0.75260(8)	0.1012(2)	0.0189(3)
H5	0.247811	0.721124	0.057483	0.023*
C6	0.22971(12)	0.81499(8)	0.0924(3)	0.0203(3)
H6	0.293690	0.826581	0.042831	0.024*
C7	0.12319(12)	0.57035(8)	0.0988(3)	0.0217(3)
C8	0.03931(14)	0.54271(8)	0.2137(3)	0.0307(4)
H8A	−0.025750	0.553498	0.156511	0.046*
H8B	0.042182	0.560048	0.340977	0.046*
H8C	0.046654	0.496496	0.218707	0.046*

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C9	0.19058(15)	0.52658(8)	−0.0126(3)	0.0257(4)
H9A	0.223207	0.551078	−0.114245	0.031*
H9B	0.148521	0.493262	−0.071385	0.031*
C10	0.27151(12)	0.49534(8)	0.1050(3)	0.0200(3)
C11	0.34250(14)	0.53693(8)	0.2130(3)	0.0258(4)
H11A	0.412005	0.528672	0.172635	0.039*
H11B	0.336122	0.527790	0.347159	0.039*
H11C	0.325780	0.581526	0.189981	0.039*
C12	0.36940(11)	0.34394(7)	0.1832(2)	0.0156(3)
C13	0.29113(12)	0.30435(8)	0.1137(2)	0.0191(3)
H13	0.229938	0.322934	0.071106	0.023*
C14	0.30241(14)	0.23966(8)	0.1071(3)	0.0236(3)
H14	0.249234	0.213740	0.061029	0.028*
C15	0.39219(15)	0.21232(7)	0.1681(3)	0.0261(4)
C16	0.46970(14)	0.24787(8)	0.2391(2)	0.0243(3)
H16	0.530028	0.228129	0.281407	0.029*
C17	0.45868(12)	0.31356(7)	0.2483(2)	0.0191(3)

solid was obtained by vacuum filtration and washed with two portions of 2 mL of methanol. The crude product of 9.5450 g was then obtained. The crude (1.0 g) was transferred into two separate 100 mL narrow necked round-bottom flasks. In one flask, the crude was recrystallized from 40 mL of acetone and in the other flask the crude was recrystallized from a mixture of dichloromethane (30 mL) and methanol (10 mL). The orange needles of the title compound {systematic name: 2,2'-(pentane-2,4-diylidene)bis(1-(2,4-dinitrophenyl)hydrazine)} had formed and were isolated by vacuum filtration.

M.p. 193 – 197 °C; IR: $\nu(\text{cm}^{-1})$ 3329 (s), 3108 (m), 1615 (vs), 1587 (vs), 1499 (vs), 1415 (s), 1360 (s), 1331 (vs), 1303 (vs), 1269 (vs), 1222 (m), 1133 (s), 1088 (s), 1061 (s), 916 (s), 831 (s), 763 (m), 726 (m), 671 (w). ¹H NMR: (400 MHz, d₆-DMSO): δ = 11.13 p.p.m. (s, 2H, NH), 9.14 – 9.13 p.p.m. (d, 2H, J = 2.00 Hz, aromatic H's), 8.34 – 8.31 p.p.m. (dd, 2H, J = 9.5 Hz, 2.0 Hz, aromatic H's), 7.94 – 7.91 p.p.m. (d, 2H, J = 9.5 Hz, aromatic H's), 3.56 p.p.m. (s, 2H, CH₂). 2.15 p.p.m. (s, 6H, CH₃) ¹³C NMR: δ = 16.01 p.p.m., 48.27 p.p.m., 116.30 p.p.m., 123.30 p.p.m., 130.20 p.p.m., 138.31 p.p.m., 144.93 p.p.m., 152.72 p.p.m.

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer [1]. The structure was solved by the direct method using the SHELXS [2] program and refined. The visual crystal structure information was performed using ORTEP-3 [3] system software. All hydrogen atoms were placed in idealized positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C–H were constrained to 0.95 Å for all the aromatic H atoms, 0.98 Å for methyl hydrogens, 0.99 Å for methylene hydrogens and 0.88 Å for imine hydrogens.

Discussion

The title compound is a polymorph of a previously reported $P\bar{1}$ structure [4] and a polymorph of a Pn structure [5]. The crystals are yellow in colour compared to the red blocks of the $P\bar{1}$ and Pn structures. The molecular overlay of the title compounds and the previously reported $P\bar{1}$ structure show an r.m.s. deviation of 1.5826 Å while that of the title compound and the Pn structure is 0.5105 Å. In the former, the conformations of the two molecules are completely different while in the latter, the molecular conformations are similar. All three polymorphs enjoy intra molecular N–H...O hydrogen bonds.

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