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Z. Kristallogr. NCS 2020; 235(5): 1257–1258

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Crystal structure of hexanedihydrazide, $C_6H_{14}N_4O_2$
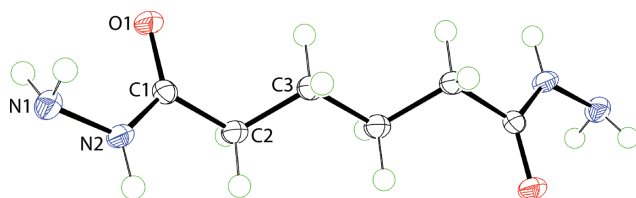
Abstract

$C_6H_{14}N_4O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 12.2878(3)$ Å, $b = 4.8442(1)$ Å, $c = 7.0931(1)$ Å, $\beta = 97.546(2)°$, $V = 418.557(15)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0290$, $wR_{ref}(F^2) = 0.0829$, $T = 100(2)$ K.

CCDC no.: 2014865

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 crystals of the title compound were the unreacted adipic acid dihydrazide obtained from the reaction of adipic acid dihydrazide (Sigma-Aldrich, 0.17 g, 1 mmol) with 4-hydroxysalicylaldehyde (Merck, 0.27 g, 2.0 mmol) in ethanol (30 mL).

Yield: 0.03 g (17%). **M.pt** (Mel-temp II digital melting point apparatus): 452–454 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 3376 (br) ν(OH) & ν(NH), 1728(s) ν(C=O), 1653(m) ν(C=N), 1465(m) ν(C−O), 1089 (m) ν(N−N). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me$_4$Si, DMSO-d$_6$ solution at 40 °C; ppm): 1.56–1.57 (m, 4H, CH$_2$), 2.05–2.06 (m, 4H, CH$_2$), 4.05 (s, 4H, NH$_2$), 8.97 (s, 2H, NH). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 24.4 (CH$_2$), 34.1 (CH$_2$CO), 172.6 (CN).

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.12 \times 0.09 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	0.88 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9520, 747, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 692
$N(param)_{refined}$:	65
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.22676(7)	0.82232(18)	0.39671(13)	0.0171(3)
N1	0.07234(9)	0.4738(2)	0.20003(16)	0.0162(3)
H1N	0.0913(13)	0.543(3)	0.0930(16)	0.019*
H2N	0.0446(12)	0.614(3)	0.258(2)	0.019*
N2	0.17031(9)	0.3906(2)	0.31416(15)	0.0147(3)
H3N	0.1830(13)	0.213(2)	0.326(2)	0.018*
C1	0.24186(10)	0.5696(3)	0.40318(17)	0.0128(3)
C2	0.34380(10)	0.4456(3)	0.51277(18)	0.0139(3)
H2A	0.341970	0.242617	0.496574	0.017*
H2B	0.344997	0.486234	0.649818	0.017*
C3	0.44803(10)	0.5601(3)	0.44510(17)	0.0143(3)
H3A	0.446770	0.518220	0.308222	0.017*
H3B	0.449129	0.763354	0.459953	0.017*

Experimental details

The C-bound H atoms were geometrically placed (C−H = 0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H atoms were refined with N−H = 0.88 ± 0.01 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. A correction for secondary extinction was made [coefficient = 0.0089(16)].

Comment

The title compound, H$_2$NN(H)C(=O)(CH$_2$)$_4$C(=O)N(H)NH$_2$, commonly known as adipic acid dihydrazide (ADH; alternative name: adipohydrazide), is a widely used, water-soluble chemical for cross-linking of species such as chitosan oligomers [5] and lipid-polymer hybrid nanoparticles for drug delivery [6]. Despite the wide use of ADH, no crystal structure determination has yet been reported for this molecule. Indeed, the only crystal structure containing ADH

is that of a one-dimensional coordination polymer with a ladder topology, i.e. $[Zn_2(ADH)_3]_n \cdot 4n(NO_3)_2 \cdot 2nDMF$, where the octahedrally coordinated Zn atoms are chelated by the carbonyl-O and hydrazide-N atoms of each end of a bridging ADH molecule to form a five-membered ring [7]. In the present study, crystals of ADH, (I), became available during the reaction of adipic acid dihydrazide with 4-hydroxysalicylaldehyde.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) $1 - x$, $1 - y$, $1 - z$). The molecule is disposed around a centre of inversion with the C-backbone having an all-trans ($+$ anti-periplanar) conformation as seen in the values of the $C1-C2-C3-C3^i = 179.48(12)°$ and $C2-C3-C3^i-C2^i = 180°$, from symmetry, torsion angles. A kink in the molecule is noted about the $C1-C2$ bond, i.e. the $N2-C1-C2-C3$ torsion angle $= 122.88(12)°$, indicating an $+$ anti-clinal conformation. The key geometric parameters are $N1-N2 = 1.4181(15)$ Å, $C1-O1 = 1.2380(16)$ Å and $C1-N2 = 1.3334(17)$ Å.

The molecular packing of (I) is dominated by conventional hydrogen bonding which leads to a three-dimensional architecture. A supramolecular tape is formed through the agency of amide-$N-H\cdots O$(carbonyl) hydrogen bonds [$N2-H3n\cdots O1^{ii}$: $H3n\cdots O1^{ii} = 2.013(10)$ Å, $N2\cdots O1^{ii} = 2.8802(13)$ Å, angle at $H3n = 170.1(13)°$ for (ii) x, $-1 + y$, z]. These are connected into a supramolecular layer parallel to $(-1\ 0\ 2)$ by hydrazide-$N-H\cdots N$(hydrazide) hydrogen bonds [$N1-H2n\cdots N1^{iii}$: $H2n\cdots N1^{iii} = 2.303(15)$ Å, $N1\cdots N1^{iii} = 3.1402(15)$ Å with angle at $H2n = 157.8(13)°$ for (iii) $-x$, $1/2 + y$, $1/2 - z$]. The layers thus formed are connected along the c-axis by hydrazide-$N-H\cdots O$(carbonyl) interactions [$N1-H1n\cdots O1^{iv}$: $H1n\cdots O1^{iv} = 2.397(15)$ Å, $N1\cdots O1^{iv} = 3.2058(14)$ Å with angle at $H1n = 151.5(13)°$ for (iv) x, $3/2 - y$, $-1/2 + z$], indicating the carbonyl-O1 atom accepts two hydrogen bonds.

A further analysis of the Hirshfeld surfaces and two-dimensional fingerprint plots (overall and decomposed) was conducted in order to ascertain the influence of non-hydrogen bonding contacts upon the molecular packing.

Calculations were performed using Crystal Explorer 17 [8] and standard procedures [9]. While $O\cdots H/H\cdots O$ [25.0%] and $N\cdots H/H\cdots N$ [13.0%] make significant percentage contributions to the calculated Hirshfeld surface, $H\cdots H$ contacts dominate, contributing 58.6% of all contacts. The only other contribution to the surface contacts $>1\%$ is from $C\cdots H/H\cdots C$ contacts [2.2%].

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