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Crystal structural of diethyl 4-(3,5-dibromo-4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, $C_{19}H_{21}Br_2NO_5$

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Abstract

$C_{19}H_{21}Br_2NO_5$, monoclinic, $P2_1/c$ (no. 14), $a = 8.657(5)$ Å, $b = 17.150(5)$ Å, $c = 13.889(4)$ Å, $\beta = 104.807(15)^\circ$, $V = 1993.6(14)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0646$, $wR_{ref}(F^2) = 0.1732$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.26 \times 0.23 \times 0.17$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	4.1 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	25° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9761, 3493, 0.106
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1911
$N(\text{param})_{\text{refined}}$:	248
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.5943(7)	0.1264(4)	−0.0028(4)	0.0465(17)
H1	0.627845	0.147614	−0.049849	0.056*
Br1	0.90836(9)	0.31691(5)	0.33162(5)	0.0489(3)
Br2	0.66838(11)	0.10642(6)	0.57107(5)	0.0674(4)
O1	0.2408(6)	0.1233(3)	0.1981(4)	0.0492(14)
O2	0.1676(6)	0.2006(4)	0.0669(4)	0.0640(17)
O3	0.6523(7)	−0.0576(3)	0.2504(4)	0.0608(16)
O4	0.8539(8)	−0.0548(4)	0.1784(5)	0.0750(19)
O5	0.8605(7)	0.2383(4)	0.5244(3)	0.0509(15)
C1	0.3741(9)	0.2150(5)	−0.0589(5)	0.055(2)
H1A	0.430926	0.221301	−0.109435	0.082*
H1B	0.267859	0.196796	−0.088842	0.082*
H1C	0.368901	0.264237	−0.026945	0.082*
C2	0.4600(8)	0.1566(4)	0.0171(5)	0.0395(18)
C3	0.6813(8)	0.0636(5)	0.0477(5)	0.0430(19)
C4	0.8041(9)	0.0325(5)	0.0010(5)	0.055(2)
H4A	0.803914	0.062268	−0.057546	0.082*
H4B	0.907272	0.036017	0.047293	0.082*
H4C	0.780798	−0.021103	−0.017091	0.082*
C5	0.6429(8)	0.0386(4)	0.1307(4)	0.0327(16)
C6	0.5229(8)	0.0802(4)	0.1749(5)	0.0337(17)
H6	0.455516	0.040699	0.194952	0.040*
C7	0.4154(8)	0.1331(4)	0.0985(5)	0.0350(17)
C8	0.2649(8)	0.1573(5)	0.1158(5)	0.0422(19)
C9	0.0961(10)	0.1397(6)	0.2267(6)	0.064(3)
H9A	0.004214	0.124090	0.174119	0.076*
H9B	0.088070	0.195094	0.238435	0.076*
C10	0.1000(11)	0.0955(6)	0.3187(7)	0.079(3)
H10A	0.004123	0.105673	0.339242	0.118*
H10B	0.107496	0.040776	0.306331	0.118*

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H10C	0.191034	0.111511	0.370403	0.118*
C11	0.7313(10)	−0.0275(5)	0.1851(6)	0.049(2)
C12	0.7312(13)	−0.1189(6)	0.3162(7)	0.087(3)
H12A	0.799024	−0.148569	0.283817	0.104*
H12B	0.651585	−0.154122	0.329795	0.104*
C13	0.8276(14)	−0.0875(7)	0.4097(7)	0.103(4)
H13A	0.878323	−0.129507	0.451781	0.155*
H13B	0.907697	−0.053356	0.396585	0.155*
H13C	0.760408	−0.058904	0.442516	0.155*
C14	0.6093(8)	0.1249(4)	0.2676(5)	0.0322(16)
C15	0.6997(8)	0.1911(4)	0.2609(5)	0.0351(17)
H15	0.703836	0.209201	0.198509	0.042*
C16	0.7829(8)	0.2301(4)	0.3449(5)	0.0373(18)
C17	0.7811(8)	0.2041(4)	0.4390(5)	0.0372(18)
C18	0.6849(8)	0.1409(5)	0.4454(5)	0.0389(18)
C19	0.6004(8)	0.1025(4)	0.3608(5)	0.0395(18)
H19	0.535879	0.060471	0.367297	0.047*
H5	0.944(5)	0.261(4)	0.526(5)	0.04(3)*

and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of ammonium acetate (10 mmol), 3,5-bibromo-4-hydroxy-benzaldehyde (10 mmol) and ethyl acetoacetate (10 mmol) in ethanol (100 mL) was refluxed for 2–3 h and then cooled to room temperature. After filtering the precipitates, they were sequentially washed with ice-cooled water and ethanol and then dried under a vacuum.

Experimental details

H were positioned geometrically and refined using a riding model, with C–H = 0.93/0.96/0.97 Å and N–H = 0.86 Å with $U_{\text{iso}}(\text{H}) = 1.2 \text{ times } U_{\text{eq}}(\text{C})$ and 1.2 times $U_{\text{eq}}(\text{N})$.

Discussion

4-Aryl-1,4-dihydropyridines have attracted the attention of chemists because the moiety is linked to series of aromatic rings, which are biologically active and used in medicine [4, 5]. Recent research has also indicated that these heterocycles is an effective treatment to shrink liver cancer and control symptoms [6].

Geometric structure analysis of the molecule shows that the six-memberring containing nitrogen atom is folded [maximum deviation = 0.1679 Å] and the N(1)–C(1) (1.320 Å) and N(1)–C(7) (1.330 Å) bonds are significantly shorter than the typical C–N bond (1.47–1.50 Å) (*cf.* the figure).

Such cases can be rationally explained that the lone-pair electrons in N atoms participate in forming a large conjugated system between the carbonyl group and ethene bond.

In addition, the orientation of two carbonyl groups are both towards the methyl groups. These bond distances and angles are all in their normal scopes and they are similar with those previously reported compound 2,6-dimethyl-4-(3,4,5-trimethoxy-phenyl)-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester [7]. It is noting that three –OCH₃ groups presented in the compound 2,6-dimethyl-4-(3,4,5-trimethoxy-phenyl)-1,4-dihydro-pyridine-3,5-dicarboxylic acid diethyl ester was replaced by one –OCH₃ group and two Br atoms in the title compound diethyl 2,6-dimethyl-4-(3,5-bibromo-4-hydroxy-phenyl)-1,4-dihydropyridine-3,5-dicarboxylate.

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