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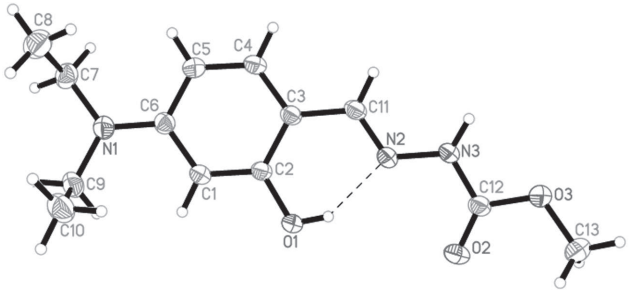
Crystal structure of methyl (*E*)-2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazine-1-carboxylate, $C_{13}H_{19}N_3O_3$



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Abstract

$C_{13}H_{19}N_3O_3$, monoclinic, $P2_1/c$ (no. 14), $a = 11.594(5)$ Å, $b = 11.311(5)$ Å, $c = 11.688(5)$ Å, $\beta = 117.347(19)°$, $V = 1361.4(10)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0479$, $wR_{ref}(F^2) = 0.1630$, $T = 296$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Methyl hydrazinecarboxylate (0.9 g, 10 mmol) and 4-diethylamino-2-hydroxybenzaldehyde (1.93 g, 10 mmol) were dissolved in stirred methanol (25 mL). The reaction mixture was refluxed for 7–8 h with TLC monitoring (ethyl acetate:hexane = 1:1). The resulting solid was filtered off and recrystallized from ethanol to give the title compound.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.24 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.9 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	60.2°, 98.9%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17068, 3958, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2992
$N(param)_{refined}$:	180
Programs:	Bruker programs [1], SHELX [2], ORTEP [3], DIAMOND [4]

Experimental details

The nitrogen bound hydrogen atoms were located from the difference Fourier map, and refined freely. All other H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 or 0.96 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ and $1.5U_{eq}(C_{methyl})$.

Comment

Benzaldehydehydrazone derivatives and their complexes have become a hot topic of coordination chemistry due to their unique structure and catalytic activity [5]. Meanwhile, it is an important intermediate in the synthethic protocol of 1,3,4-oxadiazoles, which have interesting properties [6]. In our recent report, a benzaldehydehydrazone is involved in a key step of the synthesis of dimethyl-3,6-di(aryl)-1,4-dihydro-1,2,4,5-tetrazine-1,4-dicarboxylates which was proved to have antitumour activity [7]. We have been interested in this type of derivatives and reported several crystallographic studies of the products [8–11]. As a continuation of our work, an unsymmetrical benzaldehydehydrazone derivative, (*E*)-2-(4-(diethylamino)-2-hydroxybenzylidene)hydrazine-1-carboxylate was synthesized from methyl hydrazinecarboxylate and the corresponding aromatic aldehyde.

The compound crystallizes with one independent molecule in the asymmetric unit. In the crystal structure, the aryl ring C(1)/C(2)/C(3)/C(4)/C(5)/C(6) is almost coplanar

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N2	0.48723(10)	0.36020(8)	0.24475(10)	0.0442(2)
O1	0.57485(9)	0.17518(7)	0.39031(8)	0.0501(2)
H1	0.5384	0.2116	0.3222	0.075*
C1	0.70334(11)	0.20682(9)	0.61165(11)	0.0410(2)
H1A	0.7099	0.1252	0.6220	0.049*
C3	0.61876(10)	0.37703(9)	0.46903(11)	0.0382(2)
C11	0.54562(10)	0.42820(9)	0.34214(12)	0.0414(3)
H11	0.5411	0.5098	0.3315	0.050*
C4	0.68182(11)	0.44845(9)	0.57802(12)	0.0449(3)
H4	0.6748	0.5301	0.5677	0.054*
C6	0.76706(10)	0.27989(10)	0.72080(11)	0.0404(3)
N3	0.41933(11)	0.40789(9)	0.12330(10)	0.0490(3)
C2	0.63149(10)	0.25331(9)	0.48985(11)	0.0379(2)
O3	0.30823(10)	0.38593(8)	−0.08885(9)	0.0557(3)
N1	0.83844(10)	0.23193(9)	0.84182(10)	0.0489(3)
C12	0.36091(11)	0.32926(10)	0.02564(12)	0.0446(3)
C5	0.75395(12)	0.40329(10)	0.69998(12)	0.0469(3)
H5	0.7945	0.4546	0.7694	0.056*
O2	0.35480(10)	0.22431(8)	0.03875(10)	0.0600(3)
C7	0.90316(13)	0.30488(13)	0.95615(12)	0.0526(3)
H7A	0.9085	0.2607	1.0296	0.063*
H7B	0.8501	0.3742	0.9462	0.063*
C9	0.86748(14)	0.10614(12)	0.85665(13)	0.0539(3)
H9A	0.7881	0.0626	0.8056	0.065*
H9B	0.8971	0.0847	0.9462	0.065*
C13	0.24988(16)	0.30997(14)	−0.19979(14)	0.0643(4)
H13A	0.3026	0.2407	−0.1856	0.096*
H13B	0.2434	0.3514	−0.2742	0.096*
H13C	0.1647	0.2871	−0.2135	0.096*
C10	0.96982(16)	0.06824(15)	0.81657(17)	0.0677(4)
H10A	0.9420	0.0899	0.7284	0.102*
H10B	0.9814	−0.0159	0.8257	0.102*
H10C	1.0506	0.1068	0.8704	0.102*
C8	1.03847(15)	0.34520(16)	0.98522(17)	0.0705(4)
H8A	1.0927	0.2774	0.9975	0.106*
H8B	1.0741	0.3924	1.0621	0.106*
H8C	1.0343	0.3914	0.9145	0.106*
H20	0.4233(16)	0.4836(17)	0.1058(17)	0.065(5)*

with the O atoms of the hydroxy group within 0.013 Å. The dihedral angle between the aryl ring and the plane C(11)/C(12)/C(13)/O(2)/O(3)/N(2)/N(3) is 8.6°. The angles of C(7)—C(8)—N(1) and C(10)—C(9)—N(1) are almost similar with 114.94(12)° and 114.15(12)°, respectively. The intramolecular N—H···O hydrogen bonding is most predominant and observed mostly in molecules having a CH = N—NH chain in which the hydrogen atom of the secondary amine acts as a proton donor. In the crystal, weak intermolecular hydrogen bonds further stabilize the structure.

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