

4-(Diethylamino)salicylaldehyde

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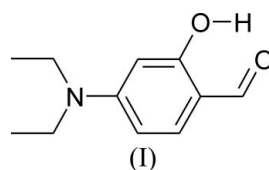
Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.036
wR factor = 0.103
Data-to-parameter ratio = 13.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{11}\text{H}_{15}\text{NO}_2$, contains a planar diethylamine group with an sp^2 -hybridized N atom bonded to a nearly planar salicylaldehyde fragment. Electron density from the diethylamine group is transferred to a pseudo-ring formed by an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond involving the aldehyde and hydroxy groups. In the crystal structure, the molecules form $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonded centrosymmetric dimers.

Comment

Structure–activity and structure–property relationships are two of the basic principles of current medicinal chemistry and chemical technology. These principles are the basis for the research and development of new, more active, drugs or more efficient high-throughput multifunctional materials. One way to modify the structure of a drug is by the insertion of a diethylaminochromogen, or a combination of pull–push chromophores, into the molecule (Reyes *et al.*, 2004). Such modifications lead to changes in the lipo–hydrophilic properties, as well as other interesting physicochemical properties. For example, new types of intermolecular interactions in the formation of structures of higher order (Cariati *et al.*, 2002), or changes in the UV–VIS spectra (Averseng *et al.*, 2001), contribute to unique optical properties with possible applications in non-linear optics (Borbone *et al.*, 2004; Lenoble *et al.*, 1998; Averseng *et al.*, 1999).



The title compound, (I), has been used several times as a reactant for the preparation of organic or metal–organic compounds. Such Schiff bases and their metal complexes (Moloney *et al.*, 1990; Averseng *et al.*, 2001) have interesting properties, *e.g.* catalase-like activity of an Fe^{II} complex (Chen *et al.*, 2001). Inspired by these findings, and in order to prepare new bioactive compounds in a similar manner to that described previously (Marek *et al.*, 2003; Švajlenová *et al.*, 2004; Krätzmár-Šmogrovič *et al.*, 1990; Vančo *et al.*, 2004), the reactant 4-diethylaminosalicylaldehyde, (I), was prepared and its structure is described here.

The molecular structure of compound (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The molecule consists of a diethylamine group bonded to atom C5 of salicylaldehyde. The salicylaldehyde

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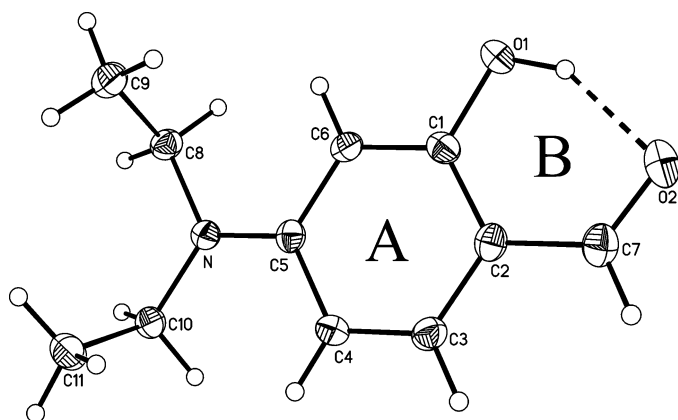


Figure 1
A plot of compound (I), showing the labelling scheme and with displacement ellipsoids at the 50% probability level.

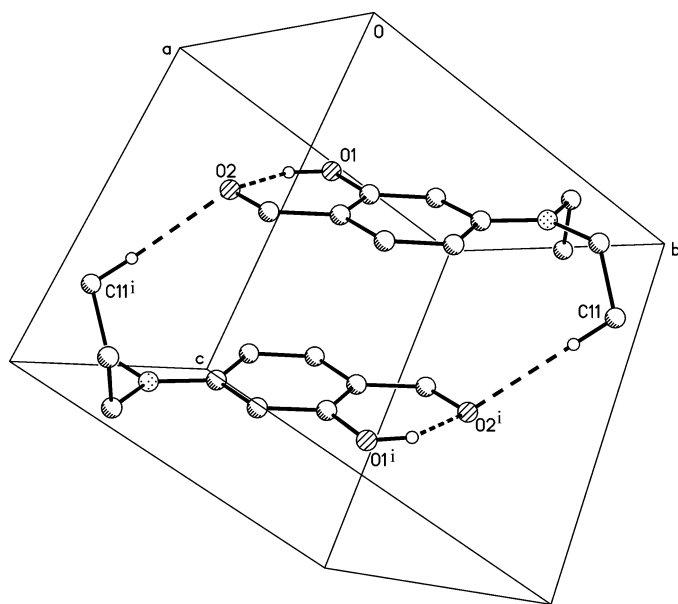


Figure 2
Part of the crystal structure of (I), showing the intermolecular C—H...O hydrogen bonds between molecules related by a centre of symmetry [symmetry code: (i) $1 - x, 1 - y, 1 - z$]. C-bound H atoms have been omitted for clarity.

fragment is nearly planar, with a maximum out-of-plane deviation of 0.0314 (9) Å for atom O2. The Cremer & Pople puckering parameters (Cremer & Pople, 1975) for the benzene ring are $Q = 0.026$ (1) Å, $\theta = 111$ (3)° and $\varphi_2 = 68$ (3)°, and these indicate a slight boat deformation of the ring. A trigonal-planar arrangement about the N atom of the diethylamine group and the sp^2 hybridization of this atom should favour electron donation from the N atom to ring B (Fig. 1) formed by atoms H—O1, C1, C2 and C7=O2. This is consistent with the observed shortening of the C2—C7 bond: 1.4280 (17) Å in (I), compared with the average bond length of 1.482 (1) Å in 220 salicylaldehyde derivatives reported in the Cambridge Structural Database (Version 5.26.2; Allen, 2002). The dihedral angle between the mean plane through the benzene ring and the plane defined by atoms N, C8 and C10 is 2.44 (6)°.

In the crystal structure of compound (I), the molecular packing (Fig. 2) is stabilized by intermolecular C—H...O hydrogen bonds between molecules related by a centre of symmetry, and stacking interactions between the A and B rings (see Fig. 1 for definitions). The distance between the planes of rings A and Aⁱ [symmetry code: (i) $1 - x, 1 - y, 1 - z$] is 3.429 Å.

Experimental

The crystals of compound (I) were prepared by recrystallization in conjunction with the slow hydrolysis of the Schiff base of (I). A solution of 4-diethylaminosalicylaldehyde, (I) (Sigma–Aldrich; 10 mmol, 1.93 g) in ethanol (40 ml, 96% *v/v*) was mixed vigorously with a solution of β -alanine (10 mmol, 0.89 g) in water (10 ml) and heated to 333 K for 60 min. During the reaction, the colour of the solution turned to dark red. After the reaction, the system was left to cool to room temperature and water (30 ml) was added. After 3 d of hydrolysis, light-brown well developed crystals of compound (I) were isolated. Analysis (Carlo–Erba 1180 instrument), calculated for $C_{11}H_{15}NO_2$: C 68.37, H 7.82, N 7.25%; found: C 68.82, H 7.59, N 7.55%.

Crystal data

$C_{11}H_{15}NO_2$
 $M_r = 193.24$
Triclinic, $P\bar{1}$
 $a = 7.0605$ (11) Å
 $b = 8.1633$ (11) Å
 $c = 9.2352$ (13) Å
 $\alpha = 94.103$ (11)°
 $\beta = 107.421$ (13)°
 $\gamma = 97.215$ (12)°
 $V = 500.49$ (12) Å³

$Z = 2$
 $D_x = 1.282$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2035 reflections
 $\theta = 2.3$ – 28.3 °
 $\mu = 0.09$ mm⁻¹
 $T = 120$ (2) K
Prism, light brown
0.40 × 0.40 × 0.15 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
 ω scans
Absorption correction: none
3791 measured reflections
1755 independent reflections

1454 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.039$
 $\theta_{max} = 25.0$ °
 $h = -8 \rightarrow 7$
 $k = -9 \rightarrow 9$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.103$
 $S = 1.08$
1755 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.03P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.017$
 $\Delta\rho_{max} = 0.18$ e Å⁻³
 $\Delta\rho_{min} = -0.25$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3617 (14)	N—C8	1.4680 (14)
O2—C7	1.2433 (15)	N—C10	1.4694 (14)
N—C5	1.3635 (15)	C2—C7	1.4280 (17)
C5—N—C8	120.60 (9)	N—C8—C9	113.96 (10)
C5—N—C10	122.54 (9)	N—C10—C11	113.93 (10)
C8—N—C10	116.78 (9)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O2	0.93 (1)	1.77 (1)	2.6107 (12)	149 (2)
C11—H11A \cdots O2 ⁱ	0.98	2.56	3.5090 (17)	162

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

The H atom attached to O1 was refined isotropically, with the O \cdots H distance restrained to 0.95 (1) Å. H atoms attached to C atoms were positioned geometrically, with C—H distances in the range 0.95–0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH and CH₂, and $1.5U_{\text{eq}}(\text{C})$ for CH₃.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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