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# 4-[(*E*)-(4-Fluorobenzylidene)amino]-benzoic acid

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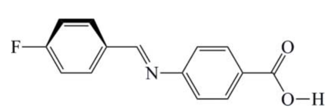
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.062; $wR$ factor = 0.191; data-to-parameter ratio = 12.1.

In the title compound, $C_{14}H_{10}FNO_2$, the benzene rings make a dihedral angle of 57.50 (13)°, and the molecule has an *E* configuration about the C═N bond. In the crystal, molecules are linked *via* pairs of O—H⋯O hydrogen bonds, forming inversion dimers.

## Related literature

For the synthesis, properties and uses of 4-(benzylidene-amino)benzoic acid, see: Borisova *et al.* (2007); Schiff (1864); Innocenzi & Lebeau (2005); Muñoz-Flores *et al.* (2008).




## Experimental

### Crystal data

$C_{14}H_{10}FNO_2$
$M_r$ = 243.24
Monoclinic, $P2_1/n$
$a$ = 12.2787 (5) Å
$b$ = 5.6264 (2) Å
$c$ = 17.2874 (8) Å
$\beta$ = 105.833 (2)°
$V$ = 1148.99 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.11 mm$^{-1}$
$T$ = 293 K
0.23 × 0.2 × 0.15 mm

### Data collection

Nonius KappaCCD diffractometer
9975 measured reflections
2002 independent reflections
1226 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.186

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.191
$S$ = 1.04
2002 reflections
166 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O2—H⋯O1$^{i}$ | 0.85 (1) | 1.79 (2) | 2.601 (3) | 159 (4) |

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *XSCANS* (Bruker, 2000); data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2486).

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## supplementary materials

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# 4-[(*E*)-(4-Fluorobenzylidene)amino]benzoic acid

B. M. Muñoz-Flores, V. M. J. Pérez, R. L. Santillan, M. E. Ochoa and N. Waksman

## Comment

Hugo Josef Schiff discovered the condensation a primary amine and a carbonyl compounds (Schiff 1864) afford the corresponding azomethine group. This organic compounds show an important synthetic advantages such as: high yields, simple synthetic route, short-time reactions, and easy isolation. Schiff base compounds have been of great importance in coordination chemistry (Borisova *et al.* 2007) due to the lone pair of electrons in an $sp^2$ hybridized orbital of nitrogen atom of the azomethine group. On the other hand, it has been reported that organic compounds containing donor and acceptor groups linked through to pi-system delocalized exhibit promising nonlinear optical properties (Innocenzi & Lebeau 2005). We have been focused our attention on synthesis of *push-pull* organic molecules with no linear optical potential properties (Muñoz-Flores *et al.* 2008). In continuous with our research, we synthesized the title compound (*E*)-4-(4-fluorobenzylideneamino)benzoic acid by condensation of 4-fluorobenzaldehyde and 4-aminobenzoic acid. In the present article, the crystal structure of (I) is being reported as shown in Fig 1. The compound, (*E*)-4-(4-fluorbenzylideneamino)benzoic acid ($C_{14}H_{10}N_2O_2F$), displays $C_1$ symmetry. The aromatic rings are not in the same plane, with a dihedral angle of 15.59° between mean planes. The carboxylic group represents a delocalized system with C(14)—O(1) and C(14)—O(2) bond lengths are 1.275 (4) and 1.293 (4) Å, respectively. The azomethine group are in the same plane as the monofluorated ring, probably because the short contact between the C(5)—H(5)···N(1) 2.633 (4) Å, [⟨ C—H···N: 96.8°]. The intermolecular O(2)—H(2)···O(1) [2.621 (5)Å (angleO-H···O: 156.30°], hydrogen bond form a dimer with a inversion center as shown in Fig 2.

## Experimental

A solution of 4-fluorobenzaldehyde (0.5 g, 4 mmol) and 4-aminobenzoic acid (0.55 g, 4 mmol) in benzene (50 ml) was heated under reflux for 6 h, with a Dean-Stark apparatus used for the azeotropic removal of water and allowed to cool to room temperature. Removal of solvent yielded a pale yellow solid, which was recrystallized from hot benzene (10 ml). Yield: 0.74 g 76%. *M*. p. 191 °C. 1H NMR (400.13 MHz, MeOD): δ = 4.9 (bs, 1H, OH), 6.62 (d, $^3J$ = 8.4 Hz, 2H, H-11/H-12), 6.80 (d, $^3J$ = 8.4 Hz, 2H, H-9/H-13), 7.10 (t, $^3J$ = 8.4 Hz, 2H, H-2/H-4), 8.05 (d, $^3J$ = 78.4 Hz, 2H, H-1/H-5), 8.53 (s, 1H, H-7). MS (DIP 20 eV) for $C_{14}H_{10}N_2O_2F$ (f. w: 243.24 g/mol) *m/z* (%): 243 (100) [$M^+$], 226 (3) [$M^+$—$H_2O$], 198 (3) [$M^+$—$CO_2$], 137 (4) [$M^+$—$FC_6H_8$], 121 [$M^+$—$C_7H_6O_2$].

## Refinement

All C-bonded H atoms were placed in calculated positions and refined as riding to their carrier atoms, with bond lengths fixed to 0.93 (aromatic CH). Isotropic displacement parameters for H atoms were calculated as $U_{iso}$(H) = 1.5$U_{eq}$(carrier atom.

**Figures**

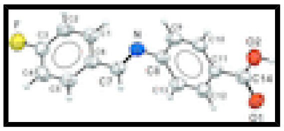

Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

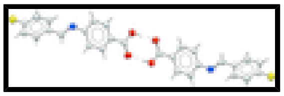

Fig. 2. Intermolecular interaction *via* hydrogen bonds.

### 4-[(*E*)-(4-Fluorobenzylidene)amino]benzoic acid

*Crystal data*

| | |
|---|---|
| $C_{14}H_{10}FNO_2$ | $F(000) = 504$ |
| $M_r = 243.24$ | $D_x = 1.406$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Melting point: 464 K |
| Hall symbol: -P 2yn | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 12.2787$ (5) Å | Cell parameters from 4962 reflections |
| $b = 5.6264$ (2) Å | $\theta = 2.9–27.5°$ |
| $c = 17.2874$ (8) Å | $\mu = 0.11$ mm$^{-1}$ |
| $\beta = 105.833$ (2)° | $T = 293$ K |
| $V = 1148.99$ (8) Å$^3$ | Prism, yellow |
| $Z = 4$ | 0.23 × 0.2 × 0.15 mm |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 1226 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.186$ |
| graphite | $\theta_{max} = 25.0°$, $\theta_{min} = 3.7°$ |
| CCD rotation images, thick slices scans | $h = -14 \rightarrow 14$ |
| 9975 measured reflections | $k = -6 \rightarrow 6$ |
| 2002 independent reflections | $l = -17 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.062$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.191$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 0.0699P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 2002 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 166 parameters | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |

| | |
|---|---|
| 1 restraint | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.7423 (2) | 0.3339 (5) | −0.03261 (18) | 0.0515 (8) |
| H1 | 0.7623 | 0.4696 | −0.0012 | 0.062* |
| C2 | 0.7740 (2) | 0.3115 (5) | −0.10261 (19) | 0.0565 (8) |
| H2 | 0.8169 | 0.4284 | −0.1185 | 0.068* |
| C3 | 0.7407 (3) | 0.1119 (5) | −0.14822 (19) | 0.0557 (8) |
| C4 | 0.6800 (2) | −0.0683 (5) | −0.12777 (19) | 0.0567 (8) |
| H4 | 0.6588 | −0.2005 | −0.1607 | 0.068* |
| C5 | 0.6511 (2) | −0.0474 (5) | −0.05617 (18) | 0.0528 (7) |
| H5 | 0.6116 | −0.1698 | −0.0397 | 0.063* |
| C6 | 0.6803 (2) | 0.1547 (4) | −0.00823 (17) | 0.0479 (7) |
| C7 | 0.6428 (2) | 0.1789 (5) | 0.06460 (17) | 0.0506 (7) |
| H7 | 0.6186 | 0.0437 | 0.0861 | 0.061* |
| C8 | 0.6104 (2) | 0.3845 (4) | 0.17270 (17) | 0.0452 (7) |
| C9 | 0.5490 (2) | 0.5794 (4) | 0.1872 (2) | 0.0563 (8) |
| H9 | 0.5247 | 0.6939 | 0.1474 | 0.068* |
| C10 | 0.5237 (2) | 0.6054 (5) | 0.25934 (19) | 0.0534 (8) |
| H10 | 0.4824 | 0.7367 | 0.2677 | 0.064* |
| C11 | 0.5597 (2) | 0.4361 (4) | 0.32045 (17) | 0.0482 (7) |
| C12 | 0.6204 (2) | 0.2400 (5) | 0.30522 (19) | 0.0554 (8) |
| H12 | 0.6446 | 0.1251 | 0.3449 | 0.066* |
| C13 | 0.6449 (2) | 0.2136 (5) | 0.23337 (18) | 0.0546 (8) |
| H13 | 0.6849 | 0.0808 | 0.2246 | 0.065* |
| C14 | 0.5353 (2) | 0.4651 (5) | 0.39801 (18) | 0.0523 (8) |
| F1 | 0.77081 (18) | 0.0920 (3) | −0.21809 (12) | 0.0827 (7) |
| N1 | 0.64180 (18) | 0.3768 (4) | 0.10000 (15) | 0.0530 (7) |
| O1 | 0.56240 (18) | 0.3041 (4) | 0.45179 (13) | 0.0679 (7) |
| O2 | 0.48502 (19) | 0.6570 (4) | 0.41100 (13) | 0.0675 (7) |
| H | 0.487 (3) | 0.678 (7) | 0.4597 (9) | 0.101* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0568 (16) | 0.0450 (14) | 0.0523 (19) | −0.0016 (12) | 0.0142 (13) | −0.0017 (12) |
| C2 | 0.0623 (17) | 0.0512 (15) | 0.061 (2) | 0.0016 (13) | 0.0245 (15) | 0.0098 (14) |
| C3 | 0.0649 (18) | 0.0582 (17) | 0.0471 (19) | 0.0168 (14) | 0.0206 (14) | 0.0037 (14) |
| C4 | 0.0639 (17) | 0.0483 (15) | 0.058 (2) | 0.0042 (13) | 0.0177 (15) | −0.0075 (14) |
| C5 | 0.0526 (15) | 0.0457 (14) | 0.062 (2) | −0.0007 (12) | 0.0191 (13) | 0.0006 (14) |
| C6 | 0.0455 (14) | 0.0456 (14) | 0.0520 (19) | 0.0034 (11) | 0.0122 (13) | 0.0026 (12) |
| C7 | 0.0508 (15) | 0.0520 (15) | 0.0516 (18) | −0.0003 (12) | 0.0185 (13) | 0.0061 (13) |
| C8 | 0.0433 (14) | 0.0493 (15) | 0.0436 (17) | −0.0052 (11) | 0.0131 (12) | −0.0007 (12) |
| C9 | 0.0569 (16) | 0.0434 (14) | 0.066 (2) | 0.0042 (12) | 0.0116 (14) | 0.0095 (13) |
| C10 | 0.0558 (16) | 0.0470 (14) | 0.058 (2) | 0.0056 (12) | 0.0165 (14) | 0.0001 (13) |
| C11 | 0.0478 (14) | 0.0478 (14) | 0.0477 (18) | 0.0006 (11) | 0.0106 (12) | 0.0016 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C12 | 0.0628 (17) | 0.0532 (16) | 0.0474 (18) | 0.0097 (13) | 0.0106 (14) | 0.0066 (13) |
| C13 | 0.0551 (16) | 0.0503 (15) | 0.056 (2) | 0.0109 (12) | 0.0112 (14) | 0.0044 (13) |
| C14 | 0.0467 (14) | 0.0511 (15) | 0.056 (2) | 0.0011 (13) | 0.0085 (12) | −0.0023 (14) |
| F1 | 0.1162 (16) | 0.0737 (12) | 0.0682 (14) | 0.0116 (11) | 0.0420 (12) | 0.0015 (10) |
| N1 | 0.0532 (14) | 0.0494 (13) | 0.0564 (16) | 0.0016 (10) | 0.0150 (11) | 0.0027 (11) |
| O1 | 0.0832 (15) | 0.0652 (13) | 0.0558 (15) | 0.0141 (11) | 0.0198 (11) | 0.0101 (10) |
| O2 | 0.0804 (15) | 0.0660 (13) | 0.0549 (15) | 0.0158 (10) | 0.0165 (12) | −0.0040 (11) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.375 (4) | C8—C13 | 1.400 (4) |
| C1—C6 | 1.396 (4) | C8—N1 | 1.413 (4) |
| C1—H1 | 0.9300 | C9—C10 | 1.372 (4) |
| C2—C3 | 1.369 (4) | C9—H9 | 0.9300 |
| C2—H2 | 0.9300 | C10—C11 | 1.402 (4) |
| C3—C4 | 1.360 (4) | C10—H10 | 0.9300 |
| C3—F1 | 1.361 (4) | C11—C12 | 1.396 (4) |
| C4—C5 | 1.383 (4) | C11—C14 | 1.460 (4) |
| C4—H4 | 0.9300 | C12—C13 | 1.363 (4) |
| C5—C6 | 1.395 (4) | C12—H12 | 0.9300 |
| C5—H5 | 0.9300 | C13—H13 | 0.9300 |
| C6—C7 | 1.460 (4) | C14—O1 | 1.275 (4) |
| C7—N1 | 1.272 (3) | C14—O2 | 1.294 (3) |
| C7—H7 | 0.9300 | O2—H | 0.845 (10) |
| C8—C9 | 1.392 (4) | | |
| C2—C1—C6 | 120.6 (3) | C9—C8—N1 | 118.5 (2) |
| C2—C1—H1 | 119.7 | C13—C8—N1 | 123.0 (2) |
| C6—C1—H1 | 119.7 | C10—C9—C8 | 121.0 (3) |
| C3—C2—C1 | 118.0 (3) | C10—C9—H9 | 119.5 |
| C3—C2—H2 | 121.0 | C8—C9—H9 | 119.5 |
| C1—C2—H2 | 121.0 | C9—C10—C11 | 120.7 (3) |
| C4—C3—F1 | 118.0 (3) | C9—C10—H10 | 119.7 |
| C4—C3—C2 | 124.1 (3) | C11—C10—H10 | 119.7 |
| F1—C3—C2 | 117.9 (3) | C12—C11—C10 | 118.0 (3) |
| C3—C4—C5 | 117.5 (3) | C12—C11—C14 | 121.0 (2) |
| C3—C4—H4 | 121.2 | C10—C11—C14 | 121.0 (2) |
| C5—C4—H4 | 121.2 | C13—C12—C11 | 121.3 (3) |
| C4—C5—C6 | 120.9 (3) | C13—C12—H12 | 119.4 |
| C4—C5—H5 | 119.5 | C11—C12—H12 | 119.4 |
| C6—C5—H5 | 119.5 | C12—C13—C8 | 120.7 (3) |
| C5—C6—C1 | 118.8 (3) | C12—C13—H13 | 119.6 |
| C5—C6—C7 | 119.9 (2) | C8—C13—H13 | 119.6 |
| C1—C6—C7 | 121.3 (2) | O1—C14—O2 | 120.6 (3) |
| N1—C7—C6 | 122.9 (2) | O1—C14—C11 | 120.8 (2) |
| N1—C7—H7 | 118.5 | O2—C14—C11 | 118.7 (3) |
| C6—C7—H7 | 118.5 | C7—N1—C8 | 119.7 (2) |
| C9—C8—C13 | 118.3 (3) | C14—O2—H | 114 (3) |
| C6—C1—C2—C3 | 1.6 (4) | C9—C10—C11—C12 | −0.8 (4) |
| C1—C2—C3—C4 | −1.4 (4) | C9—C10—C11—C14 | 178.6 (2) |

| | | | |
|---|---|---|---|
| C1—C2—C3—F1 | 179.0 (2) | C10—C11—C12—C13 | 0.4 (4) |
| F1—C3—C4—C5 | 179.2 (2) | C14—C11—C12—C13 | −179.0 (3) |
| C2—C3—C4—C5 | −0.3 (4) | C11—C12—C13—C8 | 0.5 (4) |
| C3—C4—C5—C6 | 1.9 (4) | C9—C8—C13—C12 | −1.0 (4) |
| C4—C5—C6—C1 | −1.8 (4) | N1—C8—C13—C12 | 174.3 (2) |
| C4—C5—C6—C7 | 176.2 (2) | C12—C11—C14—O1 | −4.7 (4) |
| C2—C1—C6—C5 | 0.0 (4) | C10—C11—C14—O1 | 175.9 (2) |
| C2—C1—C6—C7 | −178.0 (2) | C12—C11—C14—O2 | 175.7 (2) |
| C5—C6—C7—N1 | −162.4 (3) | C10—C11—C14—O2 | −3.7 (4) |
| C1—C6—C7—N1 | 15.6 (4) | C6—C7—N1—C8 | −176.5 (2) |
| C13—C8—C9—C10 | 0.6 (4) | C9—C8—N1—C7 | −143.9 (3) |
| N1—C8—C9—C10 | −174.9 (2) | C13—C8—N1—C7 | 40.8 (4) |
| C8—C9—C10—C11 | 0.3 (4) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H···O1$^{i}$ | 0.85 (1) | 1.79 (2) | 2.601 (3) | 159 (4) |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

**Fig. 1**

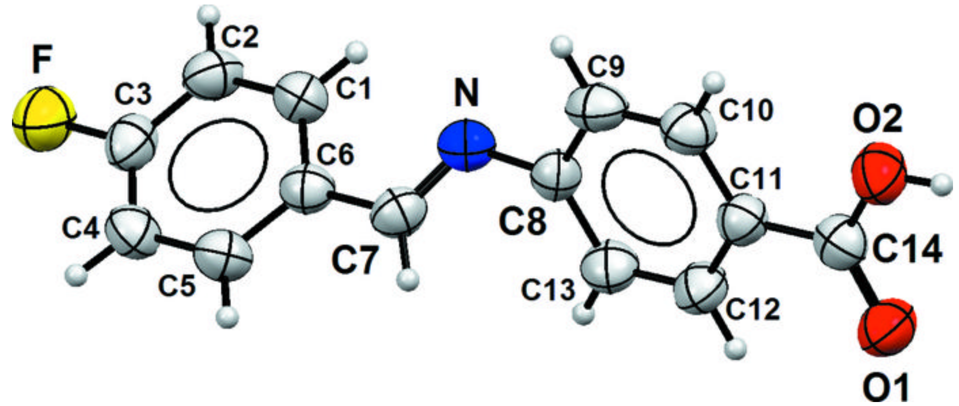

**Fig. 2**