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Acta Crystallographica Section E

## Structure Reports

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ISSN 1600-5368

4-[(*E*)-(4-Fluorobenzylidene)amino]-benzoic acidBlanca M. Muñoz-Flores,<sup>a\*</sup> Víctor M. Jiménez Pérez,<sup>a</sup> Rosa L. Santillan,<sup>b</sup> Maria Eugenia Ochoa<sup>b</sup> and Noemi Waksman<sup>c</sup><sup>a</sup>Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, 66451 Nuevo León, Mexico, <sup>b</sup>Departamento de Química, Centro de Investigación y de Estudios Avanzados, del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 México, DF, Mexico, and <sup>c</sup>Departamento de Química Analítica Facultad de Medicina, Universidad Autónoma de Nuevo León, León PO Box 2316, 64841 Nuevo León, Mexico

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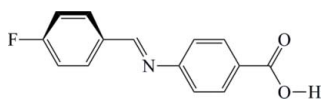
Received 16 November 2011; accepted 4 December 2011

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

In the title compound,  $\text{C}_{14}\text{H}_{10}\text{FNO}_2$ , the benzene rings make a dihedral angle of  $57.50$  ( $13$ ) $^\circ$ , and the molecule has an *E* configuration about the  $\text{C}=\text{N}$  bond. In the crystal, molecules are linked *via* pairs of  $\text{O}-\text{H}\cdots\text{O}$  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

 $\text{C}_{14}\text{H}_{10}\text{FNO}_2$  $M_r = 243.24$ Monoclinic,  $P2_1/n$  $a = 12.2787$  (5) Å $b = 5.6264$  (2) Å $c = 17.2874$  (8) Å $\beta = 105.833$  (2) $^\circ$  $V = 1148.99$  (8) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 293$  K $0.23 \times 0.2 \times 0.15$  mm

## Data collection

Nonius KappaCCD diffractometer

9975 measured reflections

2002 independent reflections

1226 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.186$ 

## 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

 $\Delta\rho_{\text{max}} = 0.18$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å,  $^\circ$ ).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}\cdots\text{O}1^i$	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*.

The authors thank the Programa de Mejoramiento del Profesorado (PROMEP; grant No. 103.5/11/4330) and the Consejo Nacional de Ciencia y Tecnología (CONACYT; grant No. 82605) for financial support.

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

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**supplementary materials**

*Acta Cryst.* (2012). E68, o175 [ doi:10.1107/S1600536811052275 ]

## 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 of a primary amine and a carbonyl compound (Schiff 1864) affords the corresponding azomethine group. This organic compound shows an important synthetic advantage 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 the nitrogen atom of the azomethine group. On the other hand, it has been reported that organic compounds containing donor and acceptor groups linked through a  $\pi$ -system delocalized exhibit promising nonlinear optical properties (Innocenzi & Lebeau 2005). We have focused our attention on the synthesis of *push-pull* organic molecules with no linear optical potential properties (Muñoz-Flores *et al.* 2008). In continuation 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-fluorobenzylideneamino)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  $15.59^\circ$  between mean planes. The carboxylic group represents a delocalized system with C(14)—O(1) and C(14)—O(2) bond lengths of 1.275 (4) and 1.293 (4) Å, respectively. The azomethine group is in the same plane as the monofluorinated ring, probably because of the short contact between the C(5)—H(5)⋯N(1) 2.633 (4) Å, [ $\angle$  C—H⋯N:  $96.8^\circ$ ]. The intermolecular O(2)—H(2)⋯O(1) [2.621 (5) Å ( $\angle$  O—H⋯O:  $156.30^\circ$ ), hydrogen bonds form a dimer with an 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):  $\delta$  = 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<sub>2</sub>O], 198 (3) [ $M^+$ —CO<sub>2</sub>], 137 (4) [ $M^+$ —FC<sub>6</sub>H<sub>8</sub>], 121 [ $M^+$ —C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>].

### 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 Å (aromatic CH). Isotropic displacement parameters for H atoms were calculated as  $U_{iso}(H) = 1.5U_{eq}(\text{carrier atom})$ .

## Figures

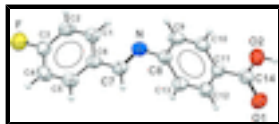


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

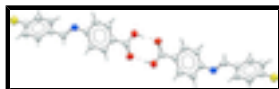


Fig. 2. Intermolecular interaction *via* hydrogen bonds.

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

### Crystal data

$C_{14}H_{10}FNO_2$

$M_r = 243.24$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 12.2787$  (5) Å

$b = 5.6264$  (2) Å

$c = 17.2874$  (8) Å

$\beta = 105.833$  (2)°

$V = 1148.99$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 504$

$D_x = 1.406$  Mg m<sup>-3</sup>

Melting point: 464 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4962 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K

Prism, yellow

$0.23 \times 0.2 \times 0.15$  mm

### Data collection

Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

CCD rotation images, thick slices scans

9975 measured reflections

2002 independent reflections

1226 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.186$

$\theta_{max} = 25.0$ °,  $\theta_{min} = 3.7$ °

$h = -14 \rightarrow 14$

$k = -6 \rightarrow 6$

$l = -17 \rightarrow 20$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.191$

$S = 1.04$

2002 reflections

166 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0979P)^2 + 0.0699P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.18$  e Å<sup>-3</sup>

1 restraint

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

## supplementary materials

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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, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2—H $\cdots$ O1 <sup>i</sup>	0.85 (1)	1.79 (2)	2.601 (3)	159 (4)

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



Fig. 1

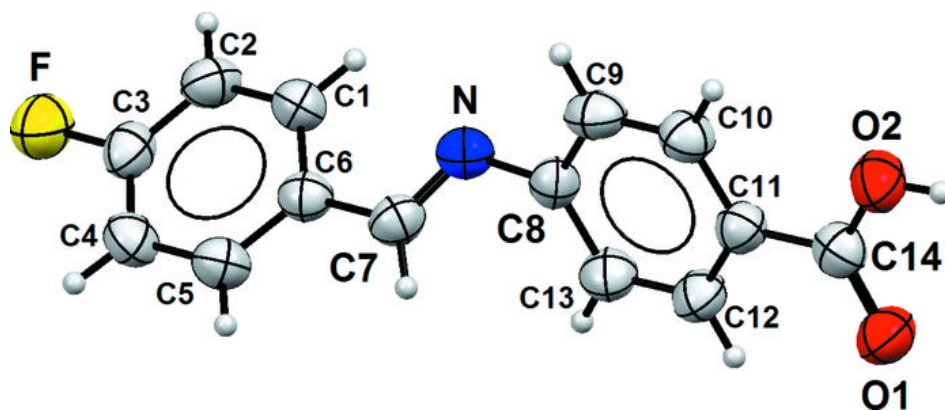


Fig. 2

