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## **(E)-N-Benzylidene-3-chloro-4-fluoroaniline**

**K. V. Arjuna Gowda *et al.***

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**(E)-N-Benzylidene-3-chloro-4-fluoro-aniline**K. V. Arjuna Gowda,<sup>a</sup> M. K. Kokila,<sup>a</sup> Puttaraja,<sup>a</sup> M. V. Kulkarni<sup>b</sup> and N. C. Shivaprakash<sup>c\*</sup><sup>a</sup>Department of Physics, Bangalore University, Jnanabharathi Campus, Bangalore 560 056, India, <sup>b</sup>Department of Organic Chemistry, Karnataka University, Dharwad 580 003, India, and <sup>c</sup>Department of Instrumentation, Indian Institute of Science, Bangalore 560 012, India

Correspondence e-mail: shiv@isu.iisc.ernet.in

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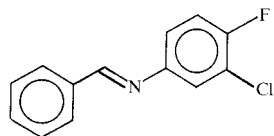
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The title molecule, C<sub>13</sub>H<sub>9</sub>ClFN, is substantially planar. The phenyl and 3-chloro-4-fluorophenyl rings are on opposite sides of the C=N bond. There is an intermolecular C—H...F short contact with a C...F distance of 3.348 (2) Å and a C—H...F angle of 137.4 (1)°. The molecules are held in layers parallel to the *bc* plane.

**Comment**

The title compound, (I), belongs to the family of fluorine-substituted benzylidene anilines. It displays anti-inflammatory activity in mice (Nargund & Srinivasmurthy, 1994) and has been found to orient butadienes, styryl coumarins for photo-dimerization, and also not to accept hydrogen bonds. Interest in these compounds has stemmed from the fact that they are useful models in the development of the principles of crystal engineering (Guru Row, 1999). It has been pointed out that organofluorine has low proton affinity (Dunitz & Taylor, 1997; Shimoni & Glusker, 1994) and hardly accepts hydrogen bonds. The introduction of fluorine into organic molecules has been found to enhance crystal densities and solid-state photochemical reactivity (Vishnumurthy *et al.*, 1996). In light of the



(I)

above observations, we are currently involved in analysing structures which contain fluorine as a substituent to explore the types of weak interactions fluorine can form in drugs and drug intermediates. The crystal structure of the title compound, (I), has been determined in this regard.

The C atoms in (I) are in a state of *sp*<sup>2</sup> hybridization and there are no significant deviations except the angles at C1;

C2—C1—N 124.8 (1)° and C6—C1—N 116.2 (1)°. This variation is reflected in the distances of nitrogen from corresponding H atoms; the interatomic N...H2 bond distance of 2.695 (2) Å is greater than N...H6 of 2.512 (2) Å.

The C1—N single-bond distance of 1.416 (2) Å is, as expected, longer than the C7=N double-bond distance of 1.249 (2) Å. The C7—C1' bond distance of 1.466 (2) Å is also longer than the expected value and these variations keep interelectronic repulsions to a minimum.

The larger C3—Cl bond distance of 1.731 (2) Å also minimizes the repulsion between the *ortho*-substituted fluorine and also reduces the dipole–dipole repulsive forces.

The bond lengths associated with the bridging atoms C1—N—C7—C1' are of significance in reflecting the effects of substituents present in the aniline–benzylidene system. The torsion angle C1—N—C7—C1' of −177.4 (2)° indicates the antiperiplanar disposition of the two phenyl rings. Atoms H7 and C1 are *cis* with respect to each other about C7—N, and H7 and C2' are *anti* with respect to each other [C1—N—C7—H7 2.6 (3)° and C2'—C1'—C7—H7 178.5 (2)°]

The F and Cl atoms attached to the aniline ring have deviations of 0.022 (1) and 0.044 (1) Å, respectively. An important factor in the solid-state molecular configuration and the twisting of the aniline and benzylidene rings from the C1—N—C7—C1' plane which has been observed in benzylidene anilines (Burgi & Dunitz, 1969) but it is interesting that in case of the title compound, the entire molecule is planar. The geometry and planarity of the molecule indicates a close spatial proximity between H2' and N, and the observed distance is 2.593 (2) Å. It is also interesting to note that the two *ortho*-H atoms, H2 and H2', are almost equidistant [2.651 (2) and 2.657 (2) Å, respectively] from the azomethine C7 atom. The hydrogen bond C4'—H4'...F [3.348 (2) Å, angle 137.4 (1)°] is weak with a marginal H4'...F bond distance of 2.603 (1) Å. The molecules are held together in parallel layers in the *bc* plane.

**Experimental**

The title compound was synthesized by the reaction of 3-chloro-4-fluoroaniline dissolved in absolute ethanol (30 ml). Benzaldehyde (0.01 M) was added and this mixture was refluxed gently for 3 h in the presence of 2–3 drops of glacial acetic acid. Afterwards, the reaction mixture was cooled to room temperature and poured onto crushed ice. The precipitate obtained was filtered, washed with ice-cooled water, dried in air and finally recrystallized from dimethylformamide.

**Crystal data**

C <sub>13</sub> H <sub>9</sub> ClFN	$D_m = 1.408 \text{ Mg m}^{-3}$
$M_r = 233.66$	$D_m$ measured by flotation
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 5.7874 (7) \text{ \AA}$	Cell parameters from 25 reflections
$b = 7.5327 (7) \text{ \AA}$	$\theta = 30\text{--}40^\circ$
$c = 25.3418 (19) \text{ \AA}$	$\mu = 2.936 \text{ mm}^{-1}$
$\beta = 94.227 (8)^\circ$	$T = 293 (2) \text{ K}$
$V = 1101.76 (19) \text{ \AA}^3$	Needle, pale yellow
$Z = 4$	$0.2 \times 0.1 \times 0.1 \text{ mm}$
$D_x = 1.409 \text{ Mg m}^{-3}$	

## Data collection

Nonius CAD-4 diffractometer  
 $\omega$ -2 $\theta$  scans  
 2285 measured reflections  
 2082 independent reflections  
 1798 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 69.86^\circ$

$h = 0 \rightarrow 7$   
 $k = 0 \rightarrow 9$   
 $l = -30 \rightarrow 30$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 1%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.123$   
 $S = 0.976$   
 2082 reflections  
 146 parameters  
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.2845P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.016$   
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0098 (10)

The H-atom positional parameters were calculated geometrically and fixed with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ .

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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