

N-[3,5-Bis(trifluoromethyl)phenyl]-3-methoxysalicylaldimine

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Key indicators

Single-crystal X-ray study

$T = 180\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.069

wR factor = 0.195

Data-to-parameter ratio = 10.2

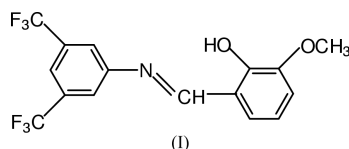
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{16}\text{H}_{11}\text{NO}_2\text{F}_6$, the two aromatic rings are somewhat twisted with respect to each other, forming a dihedral angle of $35.12(4)^\circ$. The $\text{N}=\text{C}$ bond distance of $1.287(5)\text{ \AA}$ is typical for a double bond. In the crystal structure, the molecules are linked by intramolecular $\text{O}-\text{H}\cdots\text{N}$ and intermolecular $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds.

Comment

Solvent extraction is now widely accepted as a process for the recovery of metal ions from aqueous solution in hydrometallurgical and environmental applications (El Aamrani *et al.*, 1999), with new interest in the processing of heavy metals by chelation in combination with supercritical fluid (SCF) extraction processing. Carbon dioxide is commonly employed in SCF processing because it is readily available, inexpensive, non-toxic and non-flammable (Yazdı *et al.*, 1996; Cross *et al.*, 1996). Solubilities of known ligands in supercritical CO_2 are generally low compared to solubilities in organic solvents. Data indicate that fluorination of chelating agents results in dramatic enhancement of solubility. In this work, we have designed a novel Schiff base type chelating agent, by attaching a CO_2 -philic fluoroalkyl group; this has been synthesized, and characterized for supercritical CO_2 extraction of heavy metals.

Most aromatic compounds which contain a trifluoromethyl group are known to have higher melting points, in some cases significantly higher, than the corresponding methyl-substituted compounds. The latter, however, despite their lower molecular weight, generally have higher boiling points. Apparently, forces exist in the crystalline state between molecules containing a CF_3 group which are stronger than in the corresponding methyl-substituted compounds, but which are absent in the liquid state (Boitsov *et al.*, 2002).



The molecular structure of (I) is shown in Fig. 1. The $\text{C9}-\text{N1}$ and $\text{C7}-\text{C6}$ bond lengths are $1.412(4)$ and $1.442(4)\text{ \AA}$; these are in agreement with the corresponding distances in *trans*-4-[(4-dimethylaminophenyl)iminomethyl]-*N*-methylpyridinium *p*-toluenesulfonate [$1.413(3)$ and $1.461(3)\text{ \AA}$; Coe *et al.*, 2001] and *N*-[3,5-bis(trifluoromethyl)phenyl]salicylaldimine [$1.417(4)$ and $1.439(4)\text{ \AA}$; Karadayı *et al.*, 2003]. The $\text{O1}-\text{C5}$, $\text{O2}-\text{C4}$ and $\text{O2}-\text{C8}$ bond lengths are $1.352(3)$, $1.361(4)$ and $1.430(4)\text{ \AA}$, respectively, and agree with the

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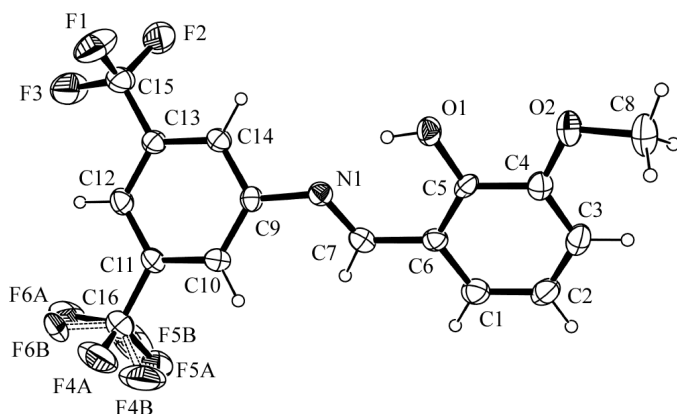


Figure 1

An ORTEP (Burnett & Johnson, 1996) drawing of the title compound, (I), showing the atomic numbering scheme. Displacement ellipsoids of non-H atoms are drawn at the 30% probability level.

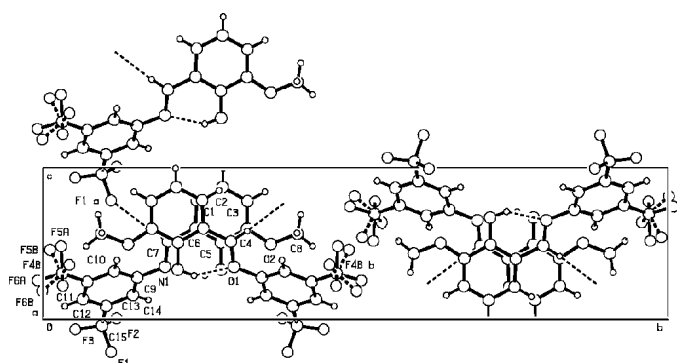


Figure 2

PLATON plot (Spek, 1997), viewed down the *c* axis, showing part of the hydrogen-bond network and the stacking of molecules.

corresponding distances in (*E*)-2-hydroxy-3,3',4'-trimethoxystilbene [1.369 (2), 1.371 (2) and 1.427 (3) Å; Stomberg *et al.*, 1998]. The N1=C7 bond length is 1.287 (5) Å, approximately equal to previously reported C=N double-bond lengths (Elerman & Elmali, 1998; Karadayı *et al.*, 2003; Kazak *et al.*, 2000).

One intramolecular O—H···N hydrogen bond and one intermolecular C—H···F hydrogen bond are present in the crystal structure (Table 2).

Experimental

An ethanol solution of 3,5-bis(trifluoromethyl)aminobenzene (2.29 g, 20 ml ethanol) was added dropwise, at room temperature, to a solution of 3-methoxysalicylaldehyde (*o*-vanillin) (1.52 g, 0.01 mol) in ethanol (20 ml), yielding large amounts of a pale yellow precipitate. The mixture was stirred for 30 min at this temperature and filtered under vacuum. Crystallization from toluene gave a spectroscopically pure product as a pale yellow, plate-like, crystalline compound (yield: 91%, m.p.: 394–396 K); elemental analysis calculated for C₁₆H₁₁F₆N: C 52.89, H 3.03, N 3.85%; found: C 52.82, H 2.89, N 3.83%; ¹H NMR (CDCl₃, 400 MHz): δ = 3.8 (*s*, 3H, O—CH₃), 6.6–7.4 (*m*, 6H, Ar—H), 8.4 (*s*, 1H, H—C=N), 12.4 (*s*, 1H, OH). IR (KBr): 3600–3300 (*br*, Ph—OH), 2950 (H—CN), 1650 (C=N), 1600 (Ar—CH). UV–vis (CHCl₃): λ = 245 (ε: 2125), 305 (max., ε: 3163), 368 nm (ε: 1088).

Crystal data

C₁₆H₁₁F₆NO₂
M_r = 363.26
 Monoclinic, *P*2₁/*a*
a = 7.2130 (14) Å
b = 29.196 (4) Å
c = 7.8870 (16) Å
 β = 116.140 (5)°
V = 1491.0 (5) Å³
Z = 4

D_x = 1.618 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 35 reflections
 θ = 5–25°
 μ = 0.16 mm⁻¹
T = 180 (2) K
 Plate, yellow
 0.20 × 0.20 × 0.01 mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 17689 measured reflections
 2591 independent reflections
 1891 reflections with *I* > 2σ(*I*)
R_{int} = 0.044

θ_{max} = 25.0°
h = −8 → 8
k = −34 → 34
l = −9 → 9
 1 standard reflection
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.070
wR (*F*²) = 0.195
S = 1.13
 2591 reflections
 255 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0926*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.060
 Δρ_{max} = 0.40 e Å⁻³
 Δρ_{min} = −0.30 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0051 (3)

Table 1

Selected geometric parameters (Å, °).

O1—C5	1.352 (3)	N1—C7	1.280 (4)
O2—C4	1.361 (4)	N1—C9	1.412 (4)
O2—C8	1.430 (4)	C6—C7	1.442 (4)
C12—C11—C16	119.3 (3)	C5—C6—C7	121.6 (3)
C10—C11—C16	119.5 (3)	C1—C6—C7	119.1 (3)
C4—O2—C8	116.6 (3)	N1—C7—C6	123.2 (3)
C7—N1—C9	118.9 (3)	C14—C9—N1	117.3 (3)
O2—C4—C5	115.5 (3)	C10—C9—N1	123.3 (3)
O1—C5—C6	122.4 (3)	C12—C13—C15	119.7 (3)
O1—C5—C4	118.1 (3)	C14—C13—C15	119.6 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···N1	0.82	1.91	2.635 (3)	146
C7—H7···F1 ⁱ	0.93	2.46	3.387 (4)	175

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

The H atoms were refined with riding-model constraints. One of the CF₃ groups showed rotational disorder. The disordered F atoms were refined anisotropically, using distance and angle restraints. For atoms F4A, F5A and F6A the site-occupancy factor is 0.62 (1) and for atoms F4B, F5B and F6B the site-occupancy factor is 0.38 (1).

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1997).

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