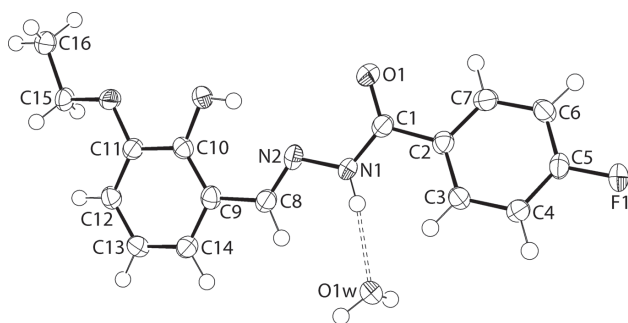




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Redetermination of the crystal structure of *N'*-(3-ethoxy-2-hydroxybenzylidene)-4-fluorobenzohydrazide monohydrate, C₁₆H₁₇FN₂O₄



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Abstract

C₁₆H₁₇FN₂O₄, monoclinic, *P*₂₁/*c* (no. 14), *a* = 9.23280(10) Å, *b* = 12.9330(2) Å, *c* = 12.3477(2) Å, β = 97.383(1)°, *V* = 1462.19(4) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0318, *wR*_{ref}(*F*²) = 0.0861, *T* = 100(2) K.

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The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents were used as purchased and used without further purification. The melting point was determined using an Electrothermal digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Perkin-Elmer RX1 spectrophotometer as a Nujol mull in a KBr cell from 4000 to 400 cm⁻¹. The ¹H NMR spectrum

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.13 × 0.07 × 0.03 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.96 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ _{max} , completeness:	67.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	17553, 2601, 0.039
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2353
<i>N</i> (<i>param</i>) _{refined} :	276
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

was recorded at room temperature in CDCl₃ solution on a Bruker AVN FT-NMR 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

3-Ethoxysalicylaldehyde (Sigma Aldrich, 0.17 g, 1 mmol) in methanol (10 mL) was added to a hot stirring methanol solution (20 mL) of 4-fluorobenzoic hydrazide (Sigma Aldrich, 0.15 g, 1 mmol). The mixture was refluxed for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. The crystal was washed with methanol and air-dried. Yield: 0.20 g (65.7%) **M.pt**: 379–381 K. **IR** (cm⁻¹): 3561 (br) ν(O–H), 1648 (s) ν(C–O), 1605 (s) ν(C–N), 1605 (s) ν(C–N), 1078 (s) ν(C–O). **¹H NMR** (CDCl₃, ppm): δ 1.39 (t, *J* = 6.9 Hz, 3H, CH₃), 3.97–4.08 (m, 2H, OCH₂), 6.60–7.11 (m, 4H, Ph-H), 8.05–8.10 (m, 3H, Ph-H), 8.66 (s, 1H, HCN), 10.90 (s, 1H, NH), 12.10 (s, 1H, OH), water-H not observed.

Experimental details

All of the H-atoms were located in a difference Fourier map and were refined without restraint.

Comment

The redetermination of the crystal structure of the title hydrazone compound (I) [5] was conducted in the context of ongoing structural studies of related Schiff base molecules [6, 7] and their organotin compounds [8–10]. With the combined advantages of Cu Kα radiation and low temperature, it was possible to refine all atoms in the molecule with the key result

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
F1	0.17356(8)	0.75207(6)	1.22153(6)	0.0247(2)
O1	0.43989(11)	0.94056(7)	0.82362(7)	0.0251(2)
O2	0.70132(10)	0.91296(7)	0.56094(7)	0.0211(2)
H2O	0.651(2)	0.9037(16)	0.6122(16)	0.042(5)*
O3	0.86944(10)	0.91781(7)	0.40723(7)	0.0214(2)
N1	0.51705(11)	0.77511(9)	0.80658(8)	0.0182(2)
H1N	0.5191(18)	0.7126(15)	0.8264(13)	0.029(4)*
N2	0.58967(11)	0.79844(9)	0.71832(8)	0.0191(2)
C1	0.44589(13)	0.85001(10)	0.85485(9)	0.0185(3)
C2	0.37537(13)	0.81800(10)	0.95217(9)	0.0180(3)
C3	0.33094(13)	0.71721(10)	0.97067(9)	0.0186(3)
H3	0.3456(16)	0.6637(12)	0.9204(12)	0.019(3)*
C4	0.26254(13)	0.69411(10)	1.06164(10)	0.0191(3)
H4	0.2337(18)	0.6235(14)	1.0741(12)	0.027(4)*
C5	0.24076(13)	0.77353(10)	1.13235(9)	0.0191(3)
C6	0.28506(14)	0.87364(10)	1.11818(10)	0.0206(3)
H6	0.2698(17)	0.9256(13)	1.1721(12)	0.024(4)*
C7	0.35205(14)	0.89561(10)	1.02650(10)	0.0201(3)
H7	0.3833(17)	0.9652(13)	1.0161(12)	0.023(4)*
C8	0.65234(13)	0.72022(10)	0.68004(10)	0.0194(3)
H8	0.6457(17)	0.6521(13)	0.7102(12)	0.022(4)*
C9	0.73890(13)	0.72823(10)	0.58954(9)	0.0188(3)
C10	0.76169(13)	0.82141(10)	0.53635(9)	0.0180(3)
C11	0.85275(13)	0.82294(10)	0.45288(9)	0.0186(3)
C12	0.91745(14)	0.73239(10)	0.42304(10)	0.0203(3)
H12	0.9816(19)	0.7337(13)	0.3685(14)	0.030(4)*
C13	0.89223(14)	0.63949(10)	0.47478(10)	0.0221(3)
H13	0.9351(17)	0.5769(13)	0.4534(12)	0.022(4)*
C14	0.80462(14)	0.63723(10)	0.55698(10)	0.0213(3)
H14	0.7899(17)	0.5719(13)	0.5950(12)	0.025(4)*
C15	0.97702(14)	0.92450(10)	0.33209(10)	0.0201(3)
H15A	0.9538(16)	0.8763(12)	0.2733(12)	0.020(3)*
H15B	1.0717(17)	0.9103(12)	0.3719(12)	0.021(4)*
C16	0.97373(15)	1.03313(11)	0.28903(11)	0.0236(3)
H16A	0.8793(18)	1.0508(12)	0.2475(13)	0.025(4)*
H16B	1.0481(19)	1.0381(14)	0.2387(14)	0.036(4)*
H16C	0.9957(18)	1.0839(13)	0.3498(13)	0.029(4)*
O1W	0.51710(10)	0.55211(7)	0.85542(8)	0.0224(2)
H1W	0.581(2)	0.5425(14)	0.9103(16)	0.034(5)*
H2W	0.535(2)	0.5086(19)	0.8022(18)	0.059(6)*

of improved standard uncertainty values. In addition, a full description of the molecular packing of (I) is now described, an analysis which is complimented by an evaluation of the calculated Hirshfeld surfaces along with the full and delineated fingerprint plots [11, 12].

The crystallographic asymmetric unit of (I) comprises the Schiff base molecule and a water molecule, as shown in the figure (70% displacement ellipsoids). The configuration about the imine-N2—C8 [1.2852(17) Å] bond is *E*. The five non-hydrogen atoms comprising the central chromophore, i.e. C(=O)N(H)N=C, are strictly planar with the r.m.s. deviation

being 0.0033 Å. The dihedral angles formed between the central plane and the least-squares planes through the flanking hydroxy- and fluoro-phenyl rings are 4.35(9) and 23.93(6)°, respectively, indicating almost co-planar and inclined orientations. The dihedral angles formed between the outer rings is 24.26(5)°. The co-planar relationship between the central chromophore and hydroxyphenyl ring allows for the formation of an intramolecular hydroxy-O—H···N(imine) hydrogen bond [O2—H2o···N2: O2—H2o = 0.841(19) Å, H2o···N2 = 2.02(2) Å, O2···N2 = 2.7473(14) Å with angle at H2o = 144.4(19)°].

The crystal of (I) features significant hydrogen bonding involving the water molecule of crystallisation that leads to the formation of a supramolecular double-layer in the *bc*-plane. As shown in the figure, the water molecule accepts a hydrogen bond from the amide-N—H atom [N1—H1n···O1w: N1—Hn = 0.844(19) Å, H1n···O1w = 2.107(19) Å, N1···O1w = 2.9464(15) Å with angle at H1n = 173.0(16)°]. This arrangement is supported by a significant fluorophenyl-C—H···O(water) interaction [C3—H3···O1w: C3—H3 = 0.951(15) Å, H3···O1w = 2.358(15) Å, C3···O1w = 3.1886(15) Å with angle at H3 = 145.7(12)°]. The water molecule also donates hydrogen bonds to the hydroxy-oxygen [O1w—H1w···O2ⁱ: O1w—H1w = 0.849(19) Å, H1w···O2ⁱ = 2.120(19) Å, O1w···O2ⁱ = 2.9030(13) Å with angle at H1w = 153.3(17)° for symmetry operation (i) *x*, 3/2 − *y*, 1/2 + *z*] and the carbonyl-oxygen atom [O1w—H2w···O1ⁱⁱ: O1w—H2w = 0.90(2) Å, H2w···O1ⁱⁱ = 1.83(2) Å, O1w···O1ⁱⁱ = 2.7115(13) Å with angle at H2w = 169(2)° for (ii) 1 − *x*, −1/2 + *y*, 3/2 − *z*]. The most prominent interactions between the layers along the *a*-axis are of the type parallel fluoride···π(hydroxyphenyl) [C5—F1···Cg(C9—C14)ⁱⁱⁱ: F1···Cg(C9—C14)ⁱⁱⁱ = 3.8932(9) Å with angle at F1 = 81.52(6)° for (iii) −1 + *x*, 3/2 − *y*, 1/2 + *z*].

With the aid of Crystal Explorer 17 [11] and literature precedents [12], an analysis of the calculated Hirshfeld surfaces was also conducted as well as the calculation of the full and decomposed two-dimensional fingerprint plots. For the entire asymmetric unit of (I), H···H contacts predominate, accounting for 40.4% of all contacts. Prominent contributions to the surface are also made by O···H/H···O [21.7%] and C···H/H···C [16.2%] contacts. Notable contacts of the type F···H/H···F [8.9%], C···C [5.2%] and N···C/C···N [4.7%] are also apparent but, at separations greater than the sum of the respective van der Waals radii. An analysis was also conducted on the individual components of the asymmetric unit. When the surface contacts for the Schiff base molecule alone were calculated, only very minor changes in percentage contributions were apparent. The major change were noted in a decrease in O···H/H···O [20.3%] contacts. To compensate this, the C···H/H···C [16.7%] and F···H/H···F

[9.4%] surface contacts rose by 0.5%. For the water molecule, only two contacts are noted, namely O...H/H...O and H...H with percentage contributions of 56.8 and 42.8%, respectively.

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References

1. Agilent Technologies. CrysAlis^{PRO}. Agilent Technologies, Santa Clara, CA, USA (2010).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
5. Li, L.; Lv, K.-W.; Li, Y.-T.; Jiang, G.-F.; Xin, Y.; Ye, L.; Zhang, Y.; Liu, H.; Shang, C.-N.; You, Z.-L.: Syntheses, crystal structures and insulin-like activity of maltolato- and ethylmaltolato-coordinated oxovanadium(V) complexes derived from 4-fluoro-*N'*-(3-ethoxy-2-hydroxybenzylidene)benzohydrazide. *Chin. J. Inorg. Chem.* **33** (2017) 905–912.
6. Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: *N'*-[1-(5-Bromo-2-hydroxyphenyl)ethylidene]isonicotinohydrazide monohydrate: crystal structure and Hirshfeld surface analysis. *Acta Crystallogr. E* **73** (2017) 630–636.
7. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of 4-Chloro-*N'*-[(1*E*)-(3-ethoxy-2-hydroxyphenyl)methylidene]benzohydrazide – a *Z'* = 3 structure, C₁₆H₁₅ClN₂O₃. *Z. Kristallogr. NCS* **234** (2019) 1341–1344.
8. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of bis(2-fluorobenzyl) (4-chloro-*N'*-[(2-oxido-5-chlorophenyl)methylidene]benzene-carbohydrazonato)tin(IV), C₂₈H₂₀Cl₂F₂N₂O₂Sn. *Z. Kristallogr. NCS* **235** (2020) 151–153.
9. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of benzyl-chlorido-(4-chloro-*N'*-[(2-oxidophenyl)methylidene]benzenecarbohydrazonato)-methanol-tin(IV), C₂₂H₁₉Cl₂N₂O₃Sn. *Z. Kristallogr. NCS* **234** (2019) ncrs-2019-0530.
10. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of aqua-chlorido-(4-fluorobenzyl)-(*N'*-(4-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato-*N,O,O'*)-tin(IV), C₂₆H₂₂ClFN₂O₅Sn. *Z. Kristallogr. NCS* **235** (2020) 155–157.
11. Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: *Crystal Explorer v17*. The University of Western Australia, Australia (2017).
12. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr. E* **75** (2019) 308–318.