



Crystal structure of (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)hydrazinecarbothioamide

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Received 22 April 2015; accepted 3 May 2015

Edited by M. Lopez-Rodriguez, Universidad de La Laguna, Tenerife

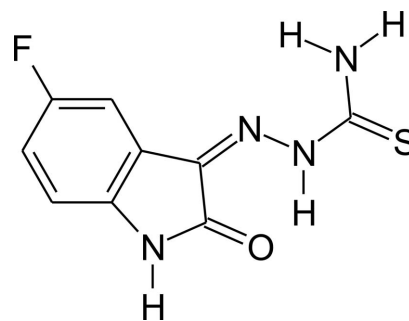
In the title compound, C₉H₇FN₄OS, the molecules are almost planar, with an r.m.s. deviation of 0.047 (3) Å from the mean plane defined by the non-H atoms and a maximum deviation of 0.123 (2) Å for the amine N atom. The torsion angle for the N—N—C—S unit is 176.57 (19)°. In the crystal, molecules are linked into inversion dimers *via* pairs of N—H...F hydrogen bonds and, additionally, through N—H...O and N—H...S hydrogen bonds, building a two-dimensional hydrogen-bond network parallel to the (103) plane. An intramolecular N—H...O interaction is also observed.

Keywords: crystal structure; thiosemicarbazone derivative; isatin; two-dimensional hydrogen-bonding network; natural product.

CCDC reference: 1062930

1. Related literature

For one of the first reports of the synthesis of thiosemicarbazone derivatives, see: Freund & Schander (1902). For the synthesis and crystal structure of a similar compound, namely (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamide, see: Ali *et al.* (2012). For a review on hydrogen bonding, see: Steiner (2002).



2. Experimental

2.1. Crystal data

C ₉ H ₇ FN ₄ OS	<i>V</i> = 1015.02 (4) Å ³
<i>M_r</i> = 238.25	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 4.7151 (1) Å	<i>μ</i> = 0.32 mm ⁻¹
<i>b</i> = 15.4517 (4) Å	<i>T</i> = 293 K
<i>c</i> = 13.9645 (4) Å	0.44 × 0.16 × 0.11 mm
<i>β</i> = 93.921 (2)°	

2.2. Data collection

Bruker X8 Kappa APEXII diffractometer	12531 measured reflections
Absorption correction: numerical (<i>SADABS</i> ; Bruker 2009)	2239 independent reflections
<i>T</i> _{min} = 0.954, <i>T</i> _{max} = 0.966	1390 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.064

2.3. Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	145 parameters
<i>wR</i> (<i>F</i> ²) = 0.140	H-atom parameters constrained
<i>S</i> = 1.01	Δ <i>ρ</i> _{max} = 0.20 e Å ⁻³
2239 reflections	Δ <i>ρ</i> _{min} = -0.29 e Å ⁻³

Table 1

Hydrogen-bond 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>
N3—H3...O1	0.86	2.12	2.781 (3)	133
N1—H1...S1 ⁱ	0.86	2.55	3.367 (2)	158
N4—H4A...F1 ⁱⁱ	0.86	2.24	2.956 (3)	140
N4—H4B...O1 ⁱⁱⁱ	0.86	2.03	2.879 (3)	171

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Acknowledgements

We gratefully thank Professor Dr Manfredo Hörner (Federal University of Santa Maria, Brazil) for his help and support with the X-ray measurements.

Supporting information for this paper is available from the IUCr electronic archives (Reference: LR2136).

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supporting information

Acta Cryst. (2015). E71, o383–o384 [doi:10.1107/S2056989015008609]

Crystal structure of (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)hydrazinecarbothioamide

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S1. Structural commentary

Concerning our interest on the study of the supramolecular chemistry of thiosemicarbazone derivatives from natural products, we report herein the crystal structure of the (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)-N-hydrazinecarbothioamide, a thiosemicarbazone derivative from 5-fluorisorisatin (Fig. 1). The molecular structure of the title compound matches the asymmetric unit and isn't planar. The maximum deviation from the mean plane of the non-H atoms amounts to 0.1229 (22) Å for N4 and the torsion angle for the N2–N3–C9–S1–entity amounts to 176.57 (19)°. All bond distances and angles are consistent with literature data of a similar compound, (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamide (Ali *et al.*, 2012). In the crystal of the title compound, the molecules are linked into dimers via pairs of N4—H4A···F1 hydrogen bonds. The dimers are linked into a two dimensional hydrogen bonded network through the N1—H1···S1, O1···H4B—N4 and S1···H1—N1 hydrogen bonds. In addition, an intramolecular N3—H3···O1 interaction is also observed and the O1 atom builds a bifurcated hydrogen bonding with the H3 and H4B atoms (Table 1, Fig. 2 and Steiner, 2002). The 2-D H-bonded polymers are stacked along the *a*-axis without any strong or relevant intermolecular interactions between themselves. The molecules of the title compound are also related by two fold screw axis parallel to the *b*-direction (Fig. 2)

S2. Synthesis and crystallization

Starting materials were commercially available and were used without further purification. The synthesis was adapted from a procedure reported previously (Freund & Schander, 1902). The hydrochloric acid catalyzed reaction of 5-fluorisorisatin (8,83 mmol) and thiosemicarbazide (8,83 mmol) in ethanol (50 ml) was refluxed for 6 h. After cooling and filtering, the title compound was obtained. Crystals suitable for X-ray diffraction of title compound were obtained in ethanol by the slow evaporation of the solvent.

S3. Refinement

All aromatic H atoms were positioned with idealized geometry and were refined isotropic with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ using a riding model with C—H = 0.93 Å. The other H atoms were located in difference map but were positioned with idealized geometry and refined isotropic with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ using a riding model with N—H = 0.86 Å.

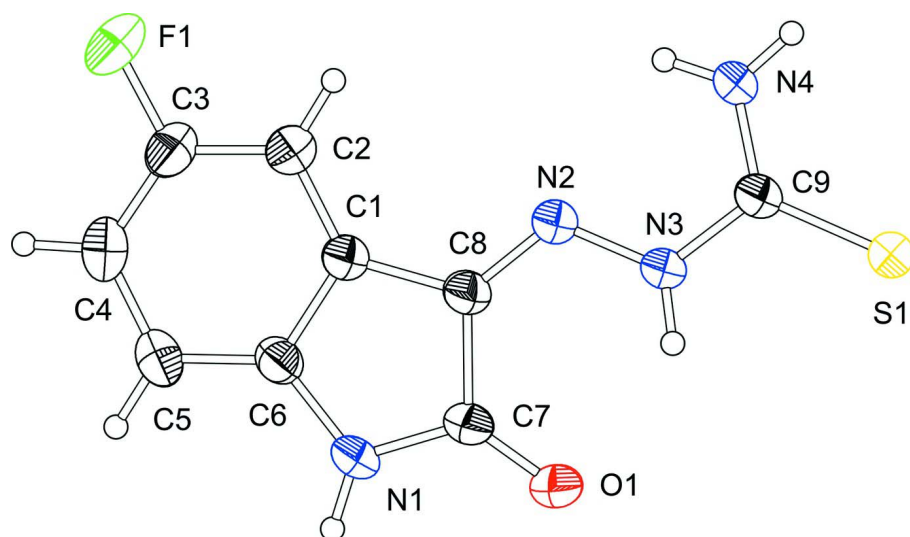


Figure 1

The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 40% probability level. H atoms are drawn isotropically.

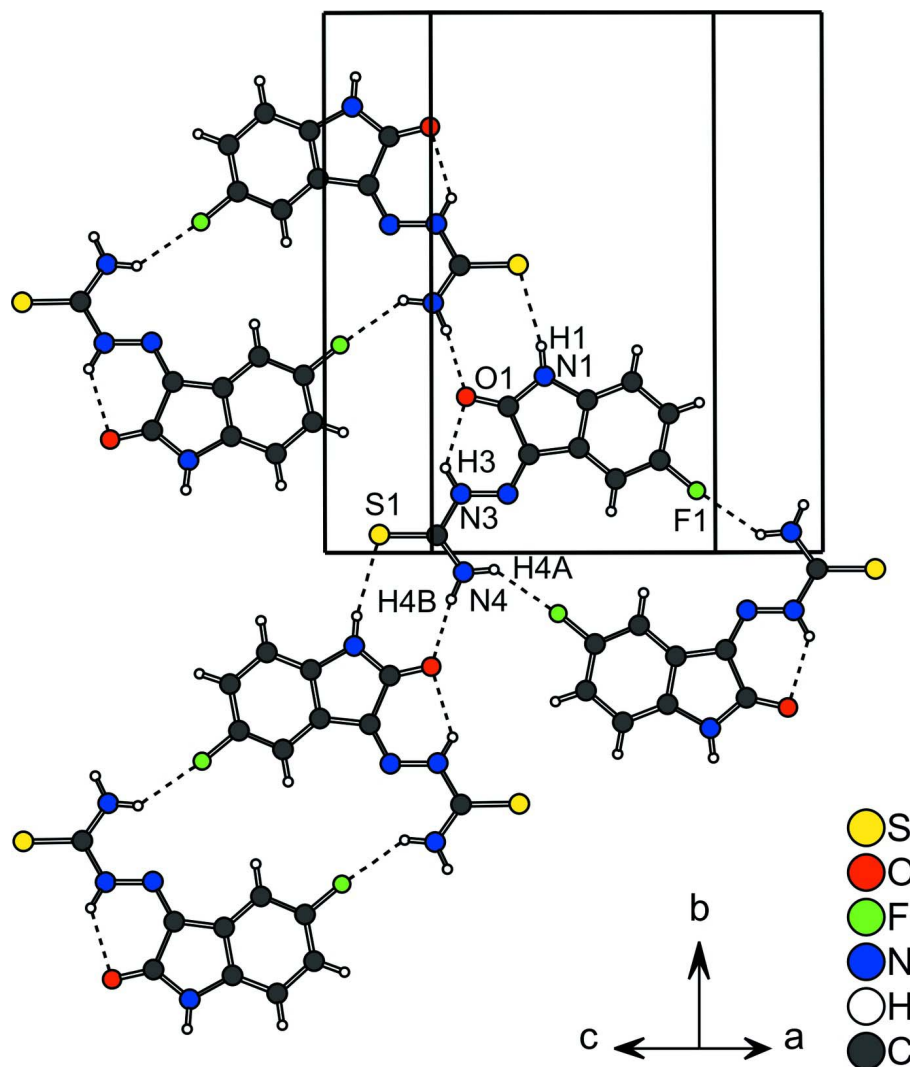


Figure 2

A view, down the *c* axis, of the packing of the title compound showing the two dimensional hydrogen-bond network. Hydrogen bonds are shown as dashed lines.

(*Z*)-2-(5-Fluoro-2-oxoindolin-3-ylidene)hydrazinecarbothioamide

Crystal data

$C_9H_7FN_4OS$

$M_r = 238.25$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 4.7151(1)\ \text{\AA}$

$b = 15.4517(4)\ \text{\AA}$

$c = 13.9645(4)\ \text{\AA}$

$\beta = 93.921(2)^\circ$

$V = 1015.02(4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 488$

$D_x = 1.559\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1744 reflections

$\theta = 2.6\text{--}22.4^\circ$

$\mu = 0.32\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, orange

$0.44 \times 0.16 \times 0.11\ \text{mm}$

Data collection

Bruker X8 Kappa APEXII
diffractometer

Radiation source: fine-focus sealed tube, Bruker
X8 Kappa APEX II

Graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

0.5 ° ω & φ scans

Absorption correction: numerical

(SADABS; Bruker 2009)

$T_{\min} = 0.954$, $T_{\max} = 0.966$

12531 measured reflections

2239 independent reflections

1390 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.064$

$\theta_{\max} = 27.2^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -3 \rightarrow 6$

$k = -19 \rightarrow 19$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.140$

$S = 1.01$

2239 reflections

145 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 0.1779P]$

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

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

$\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.29 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.02917 (16)	0.03364 (5)	0.86791 (6)	0.0558 (3)
O1	0.3669 (4)	0.28879 (12)	0.73620 (14)	0.0506 (5)
F1	1.2874 (4)	0.11434 (14)	0.40106 (15)	0.0840 (7)
N3	0.3467 (4)	0.10914 (14)	0.74614 (16)	0.0452 (6)
H3	0.2958	0.1572	0.7708	0.054*
N1	0.6921 (4)	0.32661 (14)	0.62633 (16)	0.0472 (6)
H1	0.6864	0.3820	0.6319	0.057*
N2	0.5310 (4)	0.10861 (14)	0.67623 (16)	0.0433 (5)
N4	0.3217 (5)	-0.03703 (14)	0.73181 (19)	0.0587 (7)
H4A	0.4327	-0.0322	0.6857	0.070*
H4B	0.2628	-0.0872	0.7481	0.070*
C1	0.8212 (5)	0.19327 (16)	0.57361 (19)	0.0411 (6)
C8	0.6233 (5)	0.18194 (16)	0.64722 (19)	0.0402 (6)
C7	0.5406 (5)	0.27122 (16)	0.67762 (19)	0.0413 (6)
C6	0.8603 (5)	0.28250 (17)	0.56272 (19)	0.0412 (6)
C5	1.0436 (6)	0.31552 (19)	0.4996 (2)	0.0502 (7)

H5	1.0706	0.3748	0.4936	0.060*
C3	1.1423 (6)	0.1702 (2)	0.4555 (2)	0.0549 (8)
C2	0.9634 (5)	0.13570 (19)	0.5189 (2)	0.0507 (7)
H2	0.9393	0.0762	0.5246	0.061*
C9	0.2420 (5)	0.03249 (16)	0.7774 (2)	0.0431 (6)
C4	1.1869 (6)	0.2569 (2)	0.4450 (2)	0.0553 (8)
H4	1.3129	0.2766	0.4015	0.066*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0683 (5)	0.0365 (4)	0.0666 (5)	−0.0055 (3)	0.0331 (4)	−0.0047 (3)
O1	0.0629 (11)	0.0349 (10)	0.0560 (12)	0.0082 (9)	0.0181 (10)	−0.0011 (9)
F1	0.0816 (12)	0.0853 (15)	0.0906 (15)	0.0084 (11)	0.0470 (11)	−0.0180 (12)
N3	0.0534 (12)	0.0273 (11)	0.0571 (15)	0.0001 (9)	0.0209 (11)	−0.0011 (10)
N1	0.0558 (13)	0.0259 (11)	0.0614 (15)	−0.0024 (9)	0.0153 (12)	0.0024 (10)
N2	0.0457 (11)	0.0331 (12)	0.0526 (14)	0.0004 (9)	0.0150 (10)	−0.0001 (10)
N4	0.0721 (15)	0.0292 (12)	0.0798 (18)	−0.0060 (11)	0.0412 (14)	−0.0022 (12)
C1	0.0408 (13)	0.0347 (14)	0.0484 (16)	0.0003 (11)	0.0082 (12)	−0.0001 (11)
C8	0.0407 (13)	0.0317 (14)	0.0486 (16)	0.0020 (11)	0.0064 (12)	0.0014 (11)
C7	0.0489 (14)	0.0289 (13)	0.0466 (15)	0.0025 (11)	0.0062 (12)	0.0000 (11)
C6	0.0422 (13)	0.0339 (14)	0.0478 (16)	−0.0016 (11)	0.0037 (12)	0.0036 (11)
C5	0.0495 (15)	0.0470 (17)	0.0544 (18)	−0.0081 (13)	0.0065 (13)	0.0096 (14)
C3	0.0513 (16)	0.060 (2)	0.0551 (19)	0.0032 (14)	0.0170 (14)	−0.0062 (15)
C2	0.0497 (14)	0.0437 (16)	0.0604 (19)	0.0022 (13)	0.0157 (13)	−0.0020 (14)
C9	0.0452 (14)	0.0314 (13)	0.0537 (17)	−0.0003 (11)	0.0106 (12)	0.0004 (12)
C4	0.0484 (15)	0.068 (2)	0.0514 (18)	−0.0079 (14)	0.0127 (14)	0.0075 (15)

Geometric parameters (Å, °)

S1—C9	1.667 (3)	C1—C2	1.377 (4)
O1—C7	1.227 (3)	C1—C6	1.401 (4)
F1—C3	1.365 (3)	C1—C8	1.446 (3)
N3—N2	1.351 (3)	C8—C7	1.503 (3)
N3—C9	1.366 (3)	C7—O1	1.227 (3)
N3—H3	0.8600	C6—C5	1.374 (3)
N1—C7	1.351 (3)	C5—C4	1.388 (4)
N1—C6	1.407 (3)	C5—H5	0.9300
N1—H1	0.8600	C3—C4	1.365 (4)
N2—C8	1.289 (3)	C3—C2	1.371 (4)
N4—C9	1.316 (3)	C2—H2	0.9300
N4—H4A	0.8600	C4—H4	0.9300
N4—H4B	0.8600		
N2—N3—C9	119.3 (2)	C5—C6—C1	121.9 (2)
N2—N3—H3	120.3	C5—C6—N1	129.2 (3)
C9—N3—H3	120.3	C1—C6—N1	108.9 (2)
C7—N1—C6	111.7 (2)	C6—C5—C4	117.4 (3)

C7—N1—H1	124.2	C6—C5—H5	121.3
C6—N1—H1	124.2	C4—C5—H5	121.3
C8—N2—N3	118.0 (2)	F1—C3—C4	118.3 (3)
C9—N4—H4A	120.0	F1—C3—C2	117.9 (3)
C9—N4—H4B	120.0	C4—C3—C2	123.8 (3)
H4A—N4—H4B	120.0	C3—C2—C1	116.8 (3)
C2—C1—C6	120.2 (2)	C3—C2—H2	121.6
C2—C1—C8	132.8 (2)	C1—C2—H2	121.6
C6—C1—C8	107.0 (2)	N4—C9—N3	115.6 (2)
N2—C8—C1	125.3 (2)	N4—C9—S1	125.6 (2)
N2—C8—C7	128.2 (2)	N3—C9—S1	118.83 (19)
C1—C8—C7	106.4 (2)	C3—C4—C5	119.8 (3)
O1—C7—N1	127.9 (2)	C3—C4—H4	120.1
O1—C7—C8	126.1 (2)	C5—C4—H4	120.1
N1—C7—C8	106.0 (2)		
C9—N3—N2—C8	179.0 (2)	C2—C1—C6—N1	179.9 (2)
N3—N2—C8—C1	179.8 (2)	C8—C1—C6—N1	-0.5 (3)
N3—N2—C8—C7	-3.6 (4)	C7—N1—C6—C5	-179.5 (3)
C2—C1—C8—N2	-1.7 (5)	C7—N1—C6—C1	-1.0 (3)
C6—C1—C8—N2	178.8 (3)	C1—C6—C5—C4	1.1 (4)
C2—C1—C8—C7	-178.9 (3)	N1—C6—C5—C4	179.5 (3)
C6—C1—C8—C7	1.5 (3)	F1—C3—C2—C1	179.4 (3)
C6—N1—C7—O1	-177.1 (3)	C4—C3—C2—C1	0.6 (5)
C6—N1—C7—C8	1.9 (3)	C6—C1—C2—C3	0.5 (4)
N2—C8—C7—O1	-0.2 (5)	C8—C1—C2—C3	-178.9 (3)
C1—C8—C7—O1	176.9 (3)	N2—N3—C9—N4	-3.3 (4)
N2—C8—C7—N1	-179.2 (3)	N2—N3—C9—S1	176.57 (19)
C1—C8—C7—N1	-2.1 (3)	F1—C3—C4—C5	-179.8 (3)
C2—C1—C6—C5	-1.4 (4)	C2—C3—C4—C5	-0.9 (5)
C8—C1—C6—C5	178.2 (2)	C6—C5—C4—C3	0.0 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 \cdots O1	0.86	2.12	2.781 (3)	133
N1—H1 \cdots S1 ⁱ	0.86	2.55	3.367 (2)	158
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