# Crystal structure of (*Z*)-4,4,4-trifluoro-3-((2-hydroxyphenyl)amino)-1-(thiophen-2-yl)but-2-en-1-one, $C_{14}H_{10}F_3NO_2S$

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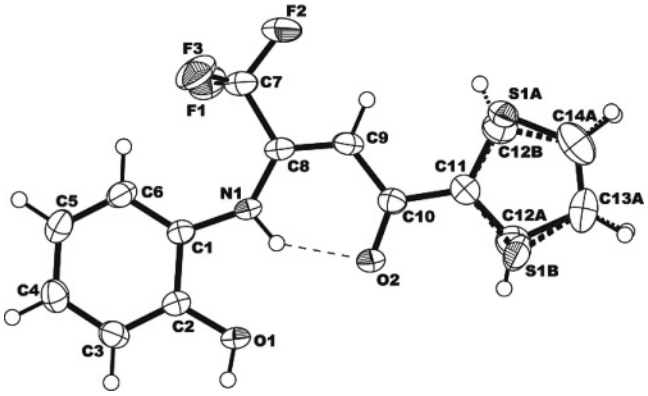


**Abstract**

$C_{14}H_{10}F_3NO_2S$, monoclinic, $P2_1/c$ (no. 14), $a$ = 13.4110(12) Å, $b$ = 6.2471(6) Å, $c$ = 16.3737(14) Å, $\beta$ = 105.423(3)°, $V$ = 1322.4 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0419, $wR_{ref}(F^2)$ = 0.1260, $T$ = 100 K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | brown blocks, size 0.263×0.283×0.701 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 2.84 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 56.71° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 26345, 3297 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2594 |
| $N(param)_{refined}$: | 203 |
| Programs: | OLEX2, SHELX [12, 13] |

## Source of material

Typical synthesis of the already known title compound TTnacPhOH [1] was carried out in a modified method. To a solution of 2-aminophenol (1.09 g, 10 mmol) in ethanol was added the equivalent amount of 2-thenoyltrifluoro acetone (2.22 g, 10 mmol), thereafter the reaction mixture was heated to reflux. After 16 hours the reaction mixture was cooled down to room temperature. The ethanol was evaporated off using a rotary evaporator to afford a reddish brown solid, Yield, 2.05g, 65.4 %. **M. p.** 132–133 ºC. Recrystallization from ethanol provided crystals suitable for X-ray diffraction. **$^1$H NMR** ($CDCl_3$, 300 MHz, ppm): 6.35 (s, 1H, –C(=O)–**CH**C=N–), 6.73–6.92 (m, 4H, –2–NH–**$C_6H_4$**–OH), 7.64–7.75 (m, 3H, 2–$C_4H_3S$), 11.30 (s, 1H, –N**H**). **$^{19}$F NMR** ($CDCl_3$, 282.4 MHz, ppm): –76.0 (s).

## Experimental details

The crystal was kept at 100 K during data collection. Using Olex2, [12] the structure was solved with the ShelXS [13] structure solution program using Direct Methods and refined with the ShelXL-2013[13] refinement package using Least-Squares minimization. The thiophene moiety of the TTnacPhOH ligand is disordered into 50:50 occupancies and was refined using PART instruction [14].

## Discussion

The phenol-imine type $\beta$-keto-imine ligands are structurally and electronically analogous to the Schiff-base type ligands derived from salicylaldehyde [2–6]. The $\beta$-ketoiminate complexes have drawn interest because of their higher thermal stability [7] than the $\beta$-diketonate analogues and their versatility, by changing the imine substituents, for tailoring their reactivity and volatility [7–11]. The condensation of equimolar amounts of the 1,3-diketone and 2-aminophenol in ethanol afforded the phenol-imino-ketone ligand. The spectroscopic data well accounted for the enol form of the ligand [15]. The proton NMR spectrum of TTnacPhOH shows a single signal at 6.35 ppm for the –C(=O)–**CH**C=N– proton and 11.3 ppm for the N**H** proton. TTnacPhOH shows a prominent –C=O stretching in the IR spectrum at 1601 cm$^{-1}$. The thiophene unit of the TTnacPhOH is disordered over two positions related by a 180° rotation (cf. Figure). The crystal structure of the molecule reveals that this compound exists in a keto-enamino phenol tautomeric form in the solid state and in the solution state (vide supra). There is an interesting hydrogen bonding pattern that leads to a spiral network along the *b* axis. This spiral network formed by the intra-molecular –N–H···O– and the inter-molecular –O–H···O– hydrogen bonding between two TTnacPhOH molecules.

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(12A) | 4*e* | 0.5 | 0.9529 | 0.0250 | 0.5914 | 0.054 |
| H(12B) | 4*e* | 0.5 | 0.6403 | 0.0010 | 0.4875 | 0.054 |
| H(1) | 4*e* | | 0.9986 | 0.7929 | 0.7955 | 0.062 |
| H(1A) | 4*e* | | 0.8110 | 0.6053 | 0.6907 | 0.035 |
| H(2) | 4*e* | | 0.9648 | 1.1064 | 0.8579 | 0.042 |
| H(9) | 4*e* | | 0.6272 | 0.2979 | 0.5651 | 0.039 |
| H(5) | 4*e* | | 0.6174 | 0.9587 | 0.7269 | 0.043 |
| H(3) | 4*e* | | 0.8355 | 1.3372 | 0.8770 | 0.045 |
| H(14) | 4*e* | 0.5 | 0.9122 | –0.3091 | 0.4880 | 0.065 |
| H(14A) | 4*e* | 0.5 | 0.9079 | –0.3172 | 0.4867 | 0.065 |
| H(13) | 4*e* | 0.5 | 0.7304 | –0.3344 | 0.4268 | 0.071 |
| H(13A) | 4*e* | 0.5 | 0.7247 | –0.3265 | 0.4253 | 0.071 |
| H(4) | 4*e* | | 0.6625 | 1.2601 | 0.8124 | 0.049 |

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**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S(1A) | 4*e* | 0.5 | 0.6929(2) | –0.0416(4) | 0.4880(2) | 0.0305(7) | 0.0387(7) | 0.0341(6) | –0.0048(5) | 0.0039(5) | –0.0063(4) |
| C(12A) | 4*e* | 0.5 | 0.8865(9) | –0.017(2) | 0.5578(9) | 0.042(4) | 0.050(3) | 0.043(3) | –0.004(2) | 0.012(2) | 0.000(2) |
| S(1B) | 4*e* | 0.5 | 0.9044(2) | –0.0186(5) | 0.5591(2) | 0.046(1) | 0.0471(8) | 0.0433(8) | 0.0190(8) | 0.0087(7) | –0.0061(6) |
| C(12B) | 4*e* | 0.5 | 0.7120(7) | –0.031(2) | 0.4997(7) | 0.042(4) | 0.050(3) | 0.043(3) | –0.004(2) | 0.012(2) | 0.000(2) |
| O(2) | 4*e* | | 0.86771(8) | 0.3724(2) | 0.64303(7) | 0.0218(5) | 0.0344(6) | 0.0429(6) | 0.0014(4) | 0.0005(4) | –0.0046(5) |
| O(1) | 4*e* | | 0.93900(8) | 0.7529(2) | 0.76878(8) | 0.0183(5) | 0.0458(7) | 0.0555(7) | 0.0001(5) | 0.0015(5) | –0.0162(6) |
| N(1) | 4*e* | | 0.75098(9) | 0.6607(2) | 0.69153(8) | 0.0171(5) | 0.0320(7) | 0.0355(6) | 0.0017(5) | 0.0029(4) | –0.0021(5) |
| C(2) | 4*e* | | 0.8942(1) | 1.0756(3) | 0.8316(1) | 0.0316(8) | 0.0386(9) | 0.0340(7) | –0.0061(7) | 0.0086(6) | –0.0041(6) |
| C(6) | 4*e* | | 0.7637(1) | 0.8474(2) | 0.74173(8) | 0.0236(6) | 0.0296(7) | 0.0273(6) | –0.0002(6) | 0.0071(5) | 0.0028(5) |
| F(3) | 4*e* | | 0.53135(9) | 0.7874(2) | 0.60470(8) | 0.0398(6) | 0.0834(9) | 0.0627(7) | 0.0287(6) | –0.0005(5) | 0.0000(6) |
| F(1) | 4*e* | | 0.54854(9) | 0.6131(2) | 0.72071(8) | 0.0442(6) | 0.0638(8) | 0.0790(8) | –0.0039(5) | 0.0365(6) | –0.0053(6) |
| C(8) | 4*e* | | 0.6719(1) | 0.5445(3) | 0.6447(1) | 0.0197(6) | 0.0370(8) | 0.0347(7) | –0.0010(6) | 0.0040(5) | 0.0006(6) |
| C(1) | 4*e* | | 0.8680(1) | 0.8942(3) | 0.78208(9) | 0.0239(7) | 0.0332(8) | 0.0299(6) | 0.0007(6) | 0.0074(5) | 0.0011(6) |
| C(9) | 4*e* | | 0.6864(1) | 0.3682(3) | 0.5994(1) | 0.0224(7) | 0.0378(9) | 0.0353(7) | –0.0057(6) | 0.0021(5) | –0.0028(6) |
| C(10) | 4*e* | | 0.7862(1) | 0.2847(2) | 0.60121(9) | 0.0270(7) | 0.0292(7) | 0.0277(6) | –0.0018(6) | 0.0042(5) | 0.0039(5) |
| C(5) | 4*e* | | 0.6882(1) | 0.9869(3) | 0.7536(1) | 0.0254(7) | 0.0394(9) | 0.0425(8) | 0.0045(6) | 0.0088(6) | 0.0010(7) |
| C(3) | 4*e* | | 0.8176(1) | 1.2127(3) | 0.8429(1) | 0.0459(9) | 0.0347(9) | 0.0361(8) | –0.0024(7) | 0.0162(7) | –0.0050(6) |
| C(11) | 4*e* | | 0.7930(1) | 0.0887(3) | 0.55356(9) | 0.0375(8) | 0.0319(8) | 0.0270(6) | –0.0021(7) | 0.0074(6) | 0.0033(6) |
| C(14) | 4*e* | | 0.8625(2) | –0.2118(3) | 0.4985(1) | 0.074(1) | 0.042(1) | 0.0493(9) | 0.016(1) | 0.0233(9) | –0.0015(8) |
| C(13) | 4*e* | | 0.7606(2) | –0.2218(4) | 0.4642(1) | 0.084(2) | 0.051(1) | 0.0380(9) | –0.019(1) | 0.0103(9) | –0.0060(8) |
| C(4) | 4*e* | | 0.7151(1) | 1.1671(3) | 0.8042(1) | 0.0398(9) | 0.0386(9) | 0.0470(9) | 0.0087(8) | 0.0184(7) | –0.0014(7) |
| C(7) | 4*e* | | 0.5616(1) | 0.6008(4) | 0.6427(1) | 0.0232(8) | 0.059(1) | 0.064(1) | –0.0047(8) | 0.0085(7) | –0.018(1) |
| F(2) | 4*e* | | 0.49495(9) | 0.4548(3) | 0.6016(1) | 0.0265(6) | 0.104(1) | 0.138(1) | –0.0170(6) | 0.0159(7) | –0.0631(9) |

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