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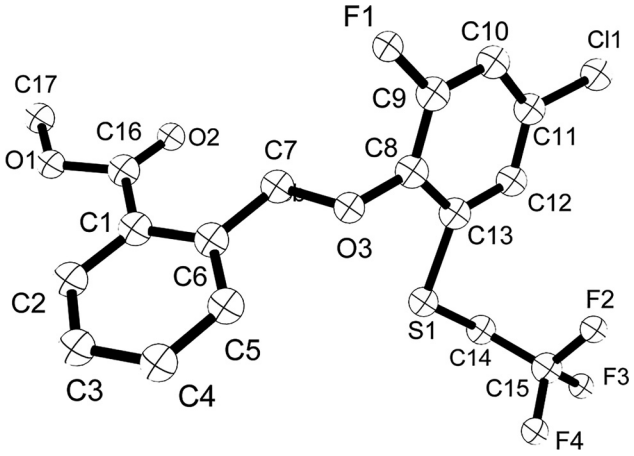
The crystal structure of methyl 2-((4-chloro-2-fluoro-6-((2,2,2-trifluoroethyl) thio)phenoxy)methyl)benzoate, $C_{17}H_{13}ClF_4O_3S$



https://doi.org/10.1515/ncrs-2022-0438
Received August 31, 2022; accepted December 5, 2022; published online December 26, 2022

Abstract

$C_{17}H_{13}ClF_4O_3S$, monoclinic, P_{21}/n (no. 14), a = 17.0097(10) Å, b = 4.4625(3) Å, c = 22.9520(19) Å, β = 102.933(7)°, V = 11698.0(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0606, $wR_{ref}(F^2)$ = 0.1605, T = 120 K.

CCDC no.: 2164983

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

Table 1: Data collection and handling.

Crystal:	Colourless needle
Size:	0.14 × 0.10 × 0.08 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	3.69 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	73.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5934, 3344, 0.060
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2294
$N(param)_{refined}$:	236
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Olex2 [4], Diamond [5]

Source of materials

To a mixture of 4-chloro-2-fluoro-6-mercaptophenol (synthesized by the procedure reported earlier [6]), K_2CO_3, sodium hydroxymethanesulphinate in DMF was added 2, 2, 2-trifluoroiodoethane dropwise at room temperature. The mixture was continuously stirred for 2 h. The mixture was added methyl 2-(chloromethyl)benzoate, stirred at 50 °C for 2 h. The reaction process was tracked by TLC. When completed, the solution was poured into water, extracted with EtOAc. The combined organic phase was washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated in vacuo to give the crude products, and then purified by column chromatography using petroleum ether: ethyl acetate (50:1, v/v) to give a white solid. M.p. 50.2–51.8 °C. Suitable crystals were obtained by slowly evaporating a mixture of methanol and chloroform at room temperature.

Experimental details

The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on the parent atoms. The U_{iso} of the H-atoms were set to 1.2 times U_{eq} of the parent atoms with C–H = 0.93 Å (aromatic) and C–H = 0.97 Å (aliphatic). The structure was solved with the Shelxt [2] structure solution program and refined with the Shelxl [3] refinement package.

Comment

Aryl trifluoroethyl sulfides(sulfoxides) are a class of compounds with acaricidal activity. In recent years, pesticide

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.91695 (6)	−0.0121 (3)	0.43916 (5)	0.0341 (3)
S1	0.59003 (6)	0.0971 (3)	0.42309 (5)	0.0300 (3)
F1	0.73286 (15)	0.6325 (6)	0.28602 (11)	0.0372 (6)
F2	0.70681 (14)	0.1829 (6)	0.54888 (11)	0.0372 (6)
F3	0.66108 (17)	−0.1928 (7)	0.58997 (12)	0.0483 (8)
F4	0.58288 (15)	0.1786 (6)	0.55610 (11)	0.0408 (7)
O1	0.39193 (17)	0.1786 (7)	0.10544 (12)	0.0303 (7)
O2	0.50701 (16)	0.0350 (7)	0.16813 (13)	0.0296 (7)
O3	0.59929 (16)	0.4843 (6)	0.32799 (12)	0.0296 (7)
C1	0.4217 (2)	0.3971 (9)	0.20039 (17)	0.0226 (9)
C2	0.3452 (2)	0.5258 (9)	0.18629 (19)	0.0273 (9)
H2	0.3108 (2)	0.4808 (9)	0.14982 (19)	0.0328 (11)*
C3	0.3194 (2)	0.7184 (10)	0.22512 (19)	0.0301 (10)
H3	0.2684 (2)	0.8050 (10)	0.21482 (19)	0.0361 (12)*
C4	0.3706 (2)	0.7805 (10)	0.27968 (19)	0.0314 (10)
H4	0.3534 (2)	0.9069 (10)	0.30656 (19)	0.0377 (12)*
C5	0.4470 (2)	0.6570 (9)	0.29467 (18)	0.0268 (9)
H5	0.4806 (2)	0.7011 (9)	0.33155 (18)	0.0321 (11)*
C6	0.4741 (2)	0.4682 (9)	0.25539 (18)	0.0238 (9)
C7	0.5595 (2)	0.3441 (10)	0.27191 (17)	0.0267 (9)
H7a	0.5881 (2)	0.3903 (10)	0.24090 (17)	0.0320 (11)*
H7b	0.5583 (2)	0.1282 (10)	0.27655 (17)	0.0320 (11)*
C8	0.6739 (2)	0.3610 (9)	0.35242 (18)	0.0260 (9)
C9	0.7422 (2)	0.4405 (9)	0.33201 (18)	0.0272 (9)
C10	0.8170 (2)	0.3264 (10)	0.35724 (19)	0.0288 (9)
H10	0.8619 (2)	0.3766 (10)	0.34241 (19)	0.0345 (11)*
C11	0.8236 (2)	0.1347 (10)	0.40533 (19)	0.0269 (9)
C12	0.7576 (2)	0.0567 (10)	0.42828 (18)	0.0271 (9)
H12	0.7639 (2)	−0.0713 (10)	0.46096 (18)	0.0326 (11)*
C13	0.6819 (2)	0.1717 (9)	0.40202 (18)	0.0251 (9)
C14	0.6182 (3)	−0.1521 (10)	0.48547 (19)	0.0324 (10)
H14a	0.5731 (3)	−0.2838 (10)	0.48636 (19)	0.0389 (12)*
H14b	0.6627 (3)	−0.2758 (10)	0.47972 (19)	0.0389 (12)*
C15	0.6425 (3)	0.0040 (11)	0.5446 (2)	0.0324 (10)
C16	0.4463 (2)	0.1851 (10)	0.15794 (18)	0.0261 (9)
C17	0.4078 (3)	−0.0342 (10)	0.06198 (19)	0.0327 (10)
H17a	0.3668 (10)	−0.017 (5)	0.0258 (5)	0.0491 (15)*
H17b	0.4596 (8)	0.007 (4)	0.0536 (10)	0.0491 (15)*
H17c	0.4075 (18)	−0.2336 (11)	0.0776 (6)	0.0491 (15)*

producing companies such as BASF, Bayer, Sumitomo Chemical and Combinatorial Chemical have successively published dozens of related patents on a series of these acaricidal compounds [6–9]. Flupentiofenox is an aryl trifluoroethyl sulfoxide acaricide developed by the Japanese Combination Chemical Company, and its mechanism of action has not been elucidated yet. This compound has an excellent biological activity against adults of the two-spotted spider mite and brown planthopper [10, 11]. Therefore, a trifluoroethyl sulfide analogue, i.e., methyl 2-((4-chloro-2-fluoro-6-((2,2,2-trifluoroethyl)thio)phenoxy)-methyl)benzoate, was synthesized.

The crystal structure of the title crystal structure of methyl 2-((4-chloro-2-fluoro-6-((2,2,2-trifluoroethyl)thio)-phe-noxy)methyl)benzoate is shown in figure. The dihedral angles of the two benzene rings were 68.5°. The C–C bond lengths of the aromatic rings and bond angles of the phenyl rings were within normal ranges. The C–F bond lengths of the benzene ring and CF_3 were between 1.340(5) and 1.352(5) Å. The bond distances of O(1)–C(17) and O(3)–C(7) exhibited typical single bonds, 1.446(5) and 1.455(4) Å, respectively. The O(1)–C(16) [1.345(4) Å] and O(3)–C(8) [1.382(4) Å] were slightly shorter compared with the standard single C–O bond. The bond lengths of S1–C13 and S1–C14 are 1.767(4) and 1.791(4) Å, respectively.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was financially supported by Nanning Scientific Research and Technology Development Program Project Funding, Major Science and Technology Project (20201043); Nanning Innovation and Entrepreneurship Leading Talent "Yongjiang Plan" Entrepreneurship Project (2020002-1).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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