

2-(4-Fluorophenyl)-6-phenyltetrahydro-2H-thiopyran-4-one 1-oxide

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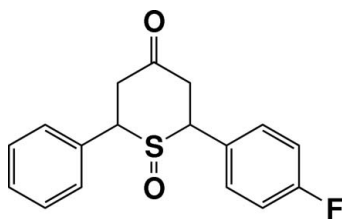
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.085; wR factor = 0.170; data-to-parameter ratio = 12.0.

In the title compound, $\text{C}_{17}\text{H}_{15}\text{FO}_2\text{S}$, a crystallographic mirror plane bisects the molecule, passing through $\text{O}=\text{S}$ and $\text{C}=\text{O}$ of the central ring, with statistical disorder of the F atom. Orientational disorder of the aromatic ring is also observed; the site occupancy factors are ca. 0.75 and 0.25. In the molecule, the thiopyran unit has a chair conformation; the geometries around the S and carbonyl C atoms are tetrahedral and planar, respectively.

Related literature

For a related crystal structure, see Thiruvalluvar *et al.* (2007). For applications of sulfoxides, see: Pandiarajan *et al.* (1993) and Yavari *et al.* (2006).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{15}\text{FO}_2\text{S}$
 $M_r = 301.35$
Orthorhombic, $Pnma$
 $a = 11.3887$ (5) Å
 $b = 24.6558$ (14) Å
 $c = 5.1828$ (2) Å
 $V = 1455.32$ (12) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.23$ mm⁻¹
 $T = 200$ K
 $0.47 \times 0.42 \times 0.22$ mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.915$, $T_{\max} = 1.000$
(expected range = 0.869–0.950)
12255 measured reflections
1297 independent reflections
1218 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.085$
 $wR(F^2) = 0.170$
 $S = 1.23$
1297 reflections
108 parameters
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.61$ e Å⁻³

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2320).

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supplementary materials

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Comment

The chemistry of organic cyclic sulfoxides continues to attract considerable attention due to their synthetic potential. The main advantage of sulfoxides over other sulfur function groups such as sulfides and sulfones is in their chirality. Sulfoxides are chiral groups which are easy to introduce and easy to remove and which give high asymmetric induction in many reactions. A large number of sulfoxides find applications in medicine and industry (Pandiarajan *et al.*, 1993; Yavari *et al.*, 2006). Thiruvalluvar *et al.* (2007) have reported a crystal structure of 2-[2,6-bis(4-methoxyphenyl)tetrahydrothiopyran-4-ylidene]malononitrile, wherein the thiopyran unit is in chair form.

The molecular structure of the title compound, (I), is shown in Fig. 1. The thiopyran unit is in the chair form. The dihedral angle between the two orientations of disordered benzene ring is $16.5(3)^\circ$. The geometry around S1 atom is tetrahedral and around C4 - planar. A crystallographic mirror plane bisects the molecule, passing through the O=S and opposite the C=O atoms of the central ring. The (*p*-fluoro)phenyl at the 2 position and the phenyl ring at the 6 position have equatorial orientations.

Experimental

A mixture of *cis*-2-(*p*-fluoro)phenyl-6-phenylthiopyran-4-one (2.82 g, 0.01 mol), diethyl ether (60 ml), bromine (3.0 g) in water (30 ml) was shaken for few minutes. The solid that separated was filtered, washed with ether and recrystallized from chloroform-carbon tetrachloride mixture (1:1 *v/v*). The yield: 2.1 g, 70%.

Refinement

The structure was solved in the space group *Pnma* with a half of molecule in the asymmetric unit. The sum of s.o.f. of F1A and F1B is 0.5. The (*p*-fluoro)phenyl group is disordered over two positions in a 0.751(2):0.249(2) ratio. All H atoms were positioned geometrically (C—H = 0.95–1.00 Å). Atom H2 was refined isotropically, while the rest H atoms were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

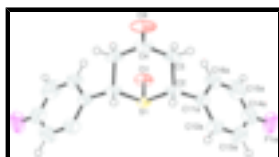


Fig. 1. The molecular structure of the title compound with the atomic numbering and 50% probability displacement ellipsoids. Only major component of the disordered (*p*-fluoro)phenyl group is shown (the occupancies of C11A—C16A and F1A atoms are 0.751(2) and 0.376(1), respectively). The unlabelled and labelled atoms are related by mirror plane [symmetry code: $x, y, 1/2 - z$].

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Crystal data

$C_{17}H_{14}FO_2S$	$F_{000} = 628$
$M_r = 301.35$	$D_x = 1.375 \text{ Mg m}^{-3}$
Orthorhombic, $Pnma$	Melting point: 429 K
Hall symbol: -P 2ac 2n	Mo $K\alpha$ radiation
$a = 11.3887 (5) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 24.6558 (14) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$c = 5.1828 (2) \text{ \AA}$	$T = 200 \text{ K}$
$V = 1455.32 (12) \text{ \AA}^3$	Prism, colourless
$Z = 4$	$0.47 \times 0.42 \times 0.22 \text{ mm}$

Data collection

CrysAlis CCD diffractometer	1297 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1218 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.064$
Detector resolution: 10.5081 pixels mm^{-1}	$\theta_{\text{max}} = 25.0^\circ$
$T = 200(2) \text{ K}$	$\theta_{\text{min}} = 4.6^\circ$
φ and ω scans	$h = -13 \rightarrow 13$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)	$k = -29 \rightarrow 29$
$T_{\text{min}} = 0.915$, $T_{\text{max}} = 1.000$	$l = -6 \rightarrow 6$
12255 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.085$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.170$	$w = 1/[\sigma^2(F_o^2) + 6.1662P]$
$S = 1.23$	where $P = (F_o^2 + 2F_c^2)/3$
1297 reflections	$(\Delta/\sigma)_{\text{max}} = <0.004$
108 parameters	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$
	Extinction correction: none

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.22216 (6)	0.25000	0.26615 (12)	0.0292 (2)	
O1	0.29629 (18)	0.25000	0.0254 (3)	0.0430 (6)	
O4	0.53648 (19)	0.25000	0.7603 (5)	0.0628 (8)	
C2	0.27869 (17)	0.19474 (9)	0.4669 (4)	0.0363 (6)	
C3	0.41209 (17)	0.19809 (10)	0.4870 (4)	0.0435 (7)	
C4	0.4589 (2)	0.25000	0.6018 (5)	0.0407 (9)	
C11A	0.23702 (14)	0.14190 (6)	0.3389 (3)	0.0389 (7)	0.751 (2)
C12A	0.29790 (18)	0.11851 (8)	0.1348 (4)	0.0640 (11)	0.751 (2)
C13A	0.2563 (3)	0.07115 (9)	0.0215 (5)	0.0893 (16)	0.751 (2)
C14A	0.1539 (3)	0.04718 (8)	0.1123 (6)	0.0757 (13)	0.751 (2)
C15A	0.09301 (19)	0.07057 (9)	0.3164 (6)	0.0666 (13)	0.751 (2)
C16A	0.13457 (15)	0.11792 (8)	0.4297 (4)	0.0510 (10)	0.751 (2)
F1A	0.1134 (4)	0.00221 (17)	0.0294 (12)	0.102 (2)	0.376 (1)
F1B	0.0819 (14)	0.0004 (5)	0.184 (4)	0.102 (2)	0.124 (1)
C11B	0.2246 (4)	0.14362 (19)	0.3974 (10)	0.0389 (7)	0.249 (2)
C12B	0.2571 (6)	0.1214 (3)	0.1615 (11)	0.0640 (11)	0.249 (2)
C13B	0.2080 (8)	0.0727 (3)	0.0801 (15)	0.0893 (16)	0.249 (2)
C14B	0.1264 (8)	0.0462 (3)	0.235 (2)	0.0757 (13)	0.249 (2)
C15B	0.0938 (6)	0.0685 (3)	0.4705 (19)	0.0666 (13)	0.249 (2)
C16B	0.1430 (5)	0.1171 (3)	0.5519 (12)	0.0510 (10)	0.249 (2)
H3A	0.44573	0.19371	0.31205	0.0522*	
H3B	0.44008	0.16732	0.59314	0.0522*	
H12A	0.36791	0.13490	0.07269	0.0769*	0.751 (2)
H13A	0.29794	0.05517	-0.11800	0.1071*	0.751 (2)
H15A	0.02300	0.05418	0.37848	0.0796*	0.751 (2)
H16A	0.09297	0.13391	0.56917	0.0610*	0.751 (2)
H2	0.2454 (15)	0.2004 (7)	0.636 (3)	0.025 (5)*	
H12B	0.31295	0.13951	0.05590	0.0769*	0.249 (2)
H13B	0.23027	0.05754	-0.08116	0.1071*	0.249 (2)
H15B	0.03804	0.05035	0.57606	0.0796*	0.249 (2)
H16B	0.12072	0.13232	0.71313	0.0610*	0.249 (2)

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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0222 (3)	0.0475 (4)	0.0180 (3)	0.0000	-0.0027 (3)	0.0000
O1	0.0384 (10)	0.0743 (14)	0.0162 (9)	0.0000	0.0048 (9)	0.0000
O4	0.0290 (10)	0.124 (2)	0.0355 (11)	0.0000	-0.0096 (10)	0.0000
C2	0.0271 (9)	0.0576 (12)	0.0242 (9)	0.0057 (9)	-0.0001 (9)	0.0059 (9)
C3	0.0257 (9)	0.0688 (14)	0.0360 (11)	0.0067 (10)	-0.0032 (10)	0.0015 (11)
C4	0.0204 (12)	0.077 (2)	0.0247 (14)	0.0000	0.0015 (12)	0.0000
C11A	0.0380 (11)	0.0472 (12)	0.0316 (12)	0.0079 (10)	-0.0068 (11)	0.0057 (10)
C12A	0.051 (2)	0.0641 (16)	0.0770 (19)	-0.0027 (16)	0.0194 (19)	-0.0227 (16)
C13A	0.080 (3)	0.079 (2)	0.109 (3)	0.013 (2)	-0.007 (3)	-0.042 (2)
C14A	0.0651 (19)	0.0520 (16)	0.110 (3)	0.0069 (16)	-0.024 (2)	-0.005 (2)
C15A	0.0582 (16)	0.0645 (17)	0.077 (3)	-0.0136 (15)	-0.015 (2)	0.018 (2)
C16A	0.0455 (13)	0.0615 (16)	0.046 (2)	-0.0030 (13)	-0.0031 (16)	-0.0034 (18)
F1A	0.099 (3)	0.0493 (17)	0.159 (5)	-0.007 (2)	-0.035 (3)	-0.039 (3)
F1B	0.099 (3)	0.0493 (17)	0.159 (5)	-0.007 (2)	-0.035 (3)	-0.039 (3)
C11B	0.0380 (11)	0.0472 (12)	0.0316 (12)	0.0079 (10)	-0.0068 (11)	0.0057 (10)
C12B	0.051 (2)	0.0641 (16)	0.0770 (19)	-0.0027 (16)	0.0194 (19)	-0.0227 (16)
C13B	0.080 (3)	0.079 (2)	0.109 (3)	0.013 (2)	-0.007 (3)	-0.042 (2)
C14B	0.0651 (19)	0.0520 (16)	0.110 (3)	0.0069 (16)	-0.024 (2)	-0.005 (2)
C15B	0.0582 (16)	0.0645 (17)	0.077 (3)	-0.0136 (15)	-0.015 (2)	0.018 (2)
C16B	0.0455 (13)	0.0615 (16)	0.046 (2)	-0.0030 (13)	-0.0031 (16)	-0.0034 (18)

Geometric parameters (\AA , $^\circ$)

S1—O1	1.5065 (18)	C13B—C14B	1.391 (12)
S1—C2	1.831 (2)	C14A—C15A	1.390 (4)
S1—C2 ⁱ	1.831 (2)	C14B—C15B	1.389 (14)
F1A—C14A	1.275 (5)	C15A—C16A	1.390 (3)
F1B—C14B	1.266 (15)	C15B—C16B	1.389 (10)
O4—C4	1.206 (3)	C2—H2	0.965 (16)
C2—C11B	1.448 (5)	C3—H3A	0.9900
C2—C3	1.525 (3)	C3—H3B	0.9900
C2—C11A	1.537 (3)	C12A—H12A	0.9500
C3—C4	1.509 (3)	C12B—H12B	0.9500
C11A—C16A	1.390 (2)	C13A—H13A	0.9500
C11A—C12A	1.390 (3)	C13B—H13B	0.9500
C11B—C16B	1.390 (8)	C15A—H15A	0.9500
C11B—C12B	1.390 (8)	C15B—H15B	0.9500
C12A—C13A	1.390 (3)	C16A—H16A	0.9500
C12B—C13B	1.390 (11)	C16B—H16B	0.9500
C13A—C14A	1.390 (4)		
O1—S1—C2	105.88 (8)	C11B—C16B—C15B	120.1 (6)
O1—S1—C2 ⁱ	105.88 (8)	S1—C2—H2	105.7 (10)
C2—S1—C2 ⁱ	96.15 (10)	C3—C2—H2	108.8 (10)
S1—C2—C3	110.41 (15)	C11A—C2—H2	113.2 (10)

S1—C2—C11A	106.07 (13)	C11B—C2—H2	100.6 (11)
S1—C2—C11B	110.9 (2)	C2—C3—H3A	108.00
C3—C2—C11A	112.52 (17)	C2—C3—H3B	108.00
C3—C2—C11B	119.2 (2)	C4—C3—H3A	108.00
C2—C3—C4	115.14 (18)	C4—C3—H3B	108.00
O4—C4—C3	121.82 (11)	H3A—C3—H3B	107.00
O4—C4—C3 ⁱ	121.82 (11)	C11A—C12A—H12A	120.00
C3—C4—C3 ⁱ	116.1 (2)	C13A—C12A—H12A	120.00
C2—C11A—C12A	121.74 (15)	C13B—C12B—H12B	120.00
C2—C11A—C16A	118.26 (15)	C11B—C12B—H12B	120.00
C12A—C11A—C16A	119.99 (16)	C14A—C13A—H13A	120.00
C12B—C11B—C16B	120.0 (5)	C12A—C13A—H13A	120.00
C2—C11B—C12B	116.7 (5)	C14B—C13B—H13B	120.00
C2—C11B—C16B	123.4 (5)	C12B—C13B—H13B	120.00
C11A—C12A—C13A	120.0 (2)	C16A—C15A—H15A	120.00
C11B—C12B—C13B	120.0 (6)	C14A—C15A—H15A	120.00
C12A—C13A—C14A	120.0 (2)	C16B—C15B—H15B	120.00
C12B—C13B—C14B	120.0 (7)	C14B—C15B—H15B	120.00
C13A—C14A—C15A	120.0 (2)	C15A—C16A—H16A	120.00
C13B—C14B—C15B	120.0 (7)	C11A—C16A—H16A	120.00
C14A—C15A—C16A	120.0 (2)	C11B—C16B—H16B	120.00
C14B—C15B—C16B	120.1 (7)	C15B—C16B—H16B	120.00
C11A—C16A—C15A	120.00 (19)		
O1—S1—C2—C3	48.52 (17)	C2—C3—C4—O4	135.9 (2)
O1—S1—C2—C11A	-73.65 (13)	C2—C3—C4—C3 ⁱ	-50.3 (3)
C2 ⁱ —S1—C2—C3	-59.94 (16)	C2—C11A—C12A—C13A	-179.0 (2)
C2 ⁱ —S1—C2—C11A	177.89 (13)	C16A—C11A—C12A—C13A	0.0 (3)
S1—C2—C3—C4	59.5 (2)	C2—C11A—C16A—C15A	179.01 (19)
C11A—C2—C3—C4	177.76 (17)	C12A—C11A—C16A—C15A	0.0 (3)
S1—C2—C11A—C12A	83.40 (18)	C11A—C12A—C13A—C14A	0.0 (4)
S1—C2—C11A—C16A	-95.60 (17)	C12A—C13A—C14A—C15A	0.0 (4)
C3—C2—C11A—C12A	-37.4 (2)	C13A—C14A—C15A—C16A	0.0 (4)
C3—C2—C11A—C16A	143.58 (18)	C14A—C15A—C16A—C11A	0.0 (4)

Symmetry codes: (i) $x, -y+1/2, z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O1 ⁱⁱ	0.965 (16)	2.430 (16)	3.206 (3)	137.2 (13)

Symmetry codes: (ii) $x, y, z+1$.

Fig. 1

