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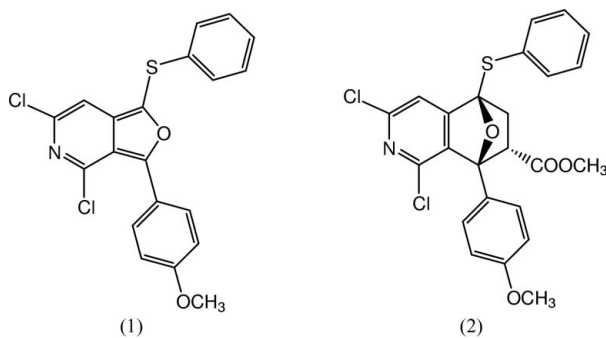
Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.030
wR factor = 0.078
Data-to-parameter ratio = 19.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Methyl (1*SR*,8*RS*,10*SR*)-3,5-dichloro-1-(4-methoxyphenyl)-8-(phenylthio)-11-oxa-4-azatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-10-carboxylate

In the title molecule, $\text{C}_{24}\text{H}_{19}\text{Cl}_2\text{NO}_4\text{S}$, the cyclohexane ring tends towards a boat conformation and the two tetrahydrofuran rings adopt envelope conformations. The crystal packing structure is built from infinite molecular chains, stabilized by an intermolecular $\text{C}-\text{H} \cdots \text{O}$ close contact, running along the *b* direction.

Comment

In contrast to the remarkable growth of the chemistry of *o*-quinoid 10- π electron isobenzofuran ring systems, isobenzofurans having a heterocyclic ring, *e.g.* furo[3,4-*c*]pyridines have not been studied so well (Padwa, 1998; Rodrigo, 1988; Bailey *et al.*, 1995; Friedrichsen, 1999). Recently, in a series of papers, Sarkar and co-workers have addressed this issue, including development of novel techniques for the generation and trapping of both stable and unstable furo[3,4-*c*]pyridines for the synthesis of polycyclic heteroaromatic ring systems (Sarkar *et al.*, 1999; Sarkar, Basak & Ghosh, 2000; Sarkar, Ghosh & Chow, 2000; Sarkar *et al.*, 2002). In this context, the title compound, (2), was synthesized by the Pummerer reaction of a pyridylmethyl substituted sulfoxide and trapping of the *in situ* generated furo[3,4-*c*]pyridine (1) in a Diels–Alder reaction with methyl acrylate. The X-ray crystal structure determination of (2) was undertaken in order to elucidate its regio- and stereochemistry, which could not be determined unambiguously by NMR spectroscopy.



The title compound, (2), has three chiral atoms; atom C6 atom is an *R*-chiral center and the atoms C8 and C9 are *S*-chiral centers (Fig. 1). The absolute configuration was determined by the Flack parameter (Flack, 1983). Since the title compound was prepared from achiral reagents, the chiral space group is the result of spontaneous resolution. All the chiral atoms belong to the oxabicycloheptane unit [O1, C3, C4, C6–C9]. The average C–O and C–C bond distances in this moiety are 1.455 Å and 1.520 Å, respectively. As a result of the

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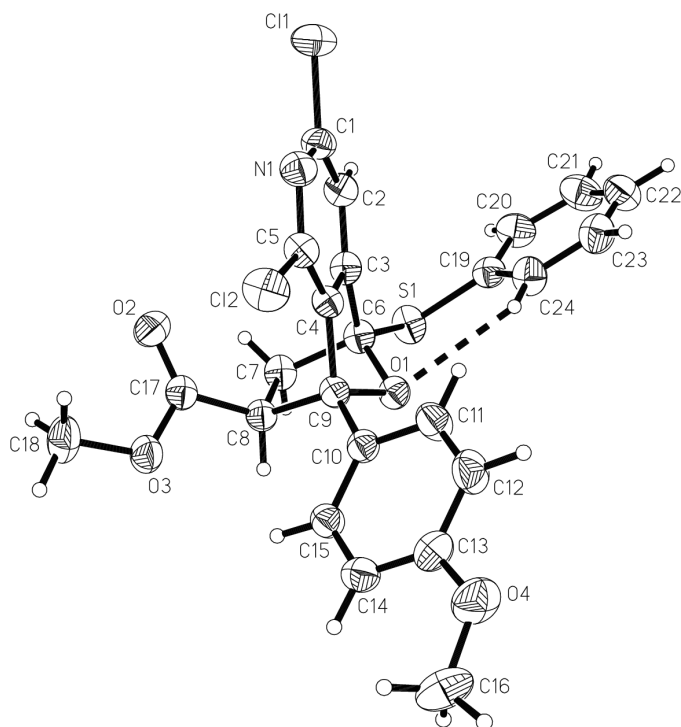


Figure 1
The structure of (2), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed line denotes the intramolecular C—H···O close contact.

bulky substituents attached to the oxabicycloheptane in (2), the average C—O bond distance is slightly longer, whereas that of C—C is shorter, compared with the corresponding values in the related structure of methyl 7-oxabicyclo[2.2.1]-heptane-2,3,5,6-tetracarboxylate [C—O 1.433 Å and C—C 1.555 Å; Kohnke *et al.*, 1988]. The cyclohexane ring (C3, C4, C6–C9) tends towards a boat conformation and the two tetrahydrofuran rings [O1, C3, C4, C6, C9 and O1, C6–C9] adopt envelope conformations, which are similar to those in the related structure. Also comparable are the dihedral angles between the O1/C6/C9 and C3/C4/C6/C9 planes [127.6 (1)°], the O1/C6/C9 and C6/C7/C8/C9 planes [121.5 (1)°], and the C3/C4/C6/C9 and C6/C7/C8/C9 planes [110.9 (1)°]; the corresponding values in the related structure are 124°, 124° and 112° (Kohnke *et al.*, 1988).

Atoms C11 and C12 are displaced on opposite sides of the pyridine ring by 0.046 (1) Å and 0.142 (1) Å. The relative configuration of the other three substituents, methyl carboxylate (O2, O3, C17, C18), thiophenyl (S1, C19–C24) and methoxyphenyl (O4, C10–C16), with respect to the oxabicycloheptane are influenced by the sp^3 hybridization of atoms C6, C8 and C9. The carbomethoxy group is twisted about the C8—C17 bond by an angle of 28.7 (1)° out of the C6/C7/C8/C9 mean plane.

Within these substituents, atom S1 exhibits sp^3 hybridization; the angle subtended at this atom is 104.4 (1)°, while the methoxy substituent (atoms O4 and C16), is approximately coplanar with the attached phenyl [being twisted by 5.3 (1)°], as is usually observed in anisoles (Domiano *et al.*, 1979).

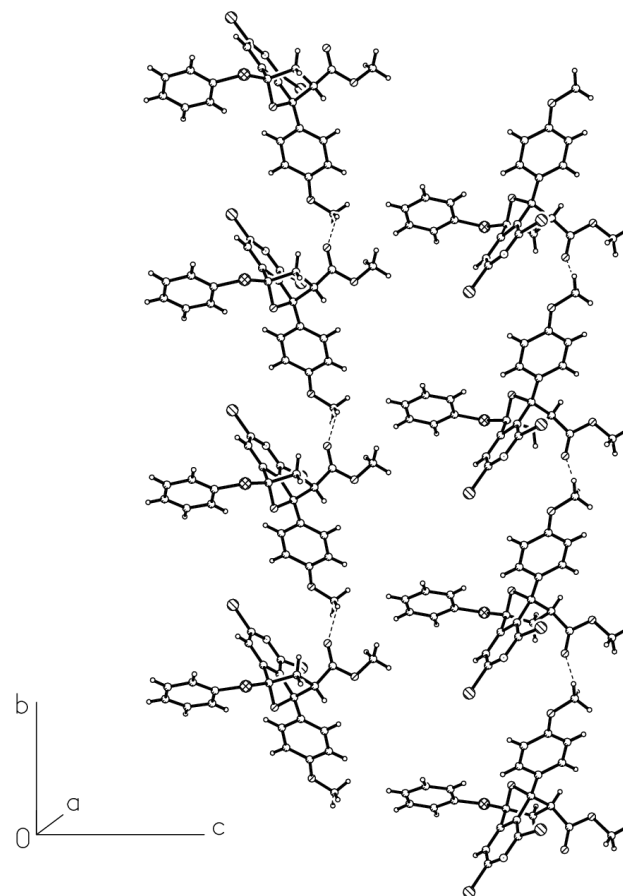


Figure 2
The packing of (2), viewed down the *a* axis, showing the molecular chains running along the *b* direction. Dashed lines denote the intermolecular C—H···O close contacts.

An intramolecular C—H···O close contact is observed in (2), linking atom H24 of the thiophenyl to O1 of the oxabicycloheptane (Fig. 1). In the crystal packing, the molecules are linked by intermolecular C16—H16B···O2ⁱ (*i*: $x, y - 1, z$) close contacts (Table 2) into one-dimensional molecular chains: in this manner a *C*(11) chain (Bernstein *et al.*, 1995) is generated running along the *b* direction (Fig. 2). Short contacts C12···O3ⁱⁱ [3.20 Å; *ii*: $-\frac{1}{2} + x, \frac{3}{2} - y, -z$] are observed in the crystal, connecting the molecular chains into a three-dimensional network.

Experimental

A mixture of 5 ml of dry toluene and 0.13 ml acetic anhydride containing a catalytic amount of *p*-toluenesulfonic acid and 0.1 ml methyl acrylate was refluxed under argon. To this mixture, 60 mg of *o*-benzoyl-substituted pyridylmethyl sulfoxide in 5 ml toluene was added dropwise over a period of 10 min. The yellow solution was refluxed for an additional 1 h. The bright yellow solution was cooled and washed with saturated aqueous NaHCO₃ and dried (Na₂SO₄). After removal of solvent, the residue was purified by preparative thin-layer chromatography, and finally crystallized from ethyl acetate–petroleum ether (1:20) to give colorless crystals of (2) (m.p. 390–392 K).

Crystal data

C₂₄H₁₉Cl₂NO₄S
M_r = 488.36
 Orthorhombic, *P*2₁2₁2₁
a = 9.0330 (4) Å
b = 10.2107 (5) Å
c = 24.5414 (12) Å
V = 2263.53 (19) Å³
Z = 4
D_x = 1.433 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 8828 reflections
 $\theta = 2.6\text{--}28.3^\circ$
 $\mu = 0.41 \text{ mm}^{-1}$
T = 293 (2) K
 Block, colorless
 0.42 × 0.40 × 0.40 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.846, *T_{max}* = 0.853
 14401 measured reflections

5601 independent reflections
 5068 reflections with *I* > 2σ(*I*)
R_{int} = 0.016
 $\theta_{\text{max}} = 28.3^\circ$
h = −12 → 10
k = −13 → 13
l = −32 → 26

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.030
wR(*F*²) = 0.078
S = 1.07
 5601 reflections
 291 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.2526P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$
 Absolute structure: (Flack, 1983),
 2408 Friedel pairs
 Flack parameter = 0.02 (4)

Table 1
 Selected geometric parameters (Å).

O1—C6	1.450 (2)	C7—C8	1.548 (2)
O1—C9	1.4600 (18)	C8—C9	1.579 (2)
C6—C7	1.556 (2)		

Table 2
 Short contact 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>
C16—H16 <i>B</i> ...O2 ⁱ	0.96	2.56	3.377 (3)	142
C24—H24...O1	0.93	2.51	3.205 (2)	132

Symmetry code: (i) *x*, *y* − 1, *z*.

All the H-atoms were fixed geometrically and were treated as riding atoms, with C—H distances 0.93–0.98 Å and *U_{iso}*(H) = 1.2–1.5*U_{eq}*(C). The methyl H atoms were constrained, but allowed to rotate about the C—C bonds.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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