

Data collection

Siemens P4 diffractometer $\theta_{\max} = 27.5^\circ$
 $\theta/2\theta$ scans $h = -1 \rightarrow 34$
 Absorption correction: none $k = -1 \rightarrow 13$
 5589 measured reflections $l = -25 \rightarrow 20$
 4711 independent reflections 3 standard reflections
 1670 reflections with every 97 reflections
 $I > 2\sigma(I)$ intensity decay: <3%
 $R_{\text{int}} = 0.044$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.001$
 $R[F^2 > 2\sigma(F^2)] = 0.043$ $\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.107$ $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$
 $S = 0.740$ Extinction correction: none
 4711 reflections Scattering factors from
 262 parameters *International Tables for*
 H atoms constrained *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0318P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 2. Selected geometric parameters (\AA , $^\circ$) for (II)

N1—O3	1.218 (2)	C4—C4a	1.465 (3)
N1—O4	1.226 (2)	C4a—C9	1.505 (3)
N1—C20	1.475 (3)	C5—C5a	1.472 (3)
O1—C4	1.230 (2)	C5a—C8a	1.329 (3)
O2—C5	1.222 (2)	C5a—C9	1.514 (3)
C1a—C4a	1.337 (3)	C8a—O10	1.372 (3)
C1a—O10	1.382 (2)		
O3—N1—O4	122.5 (3)	C8a—O10—C1a	117.8 (2)
O3—N1—C20	120.3 (2)	C19—C20—N1	115.2 (2)
O4—N1—C20	117.1 (2)	C15—C20—N1	122.2 (2)
C4a—C9—C5a	109.6 (2)		

For both compounds, data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXTL (Siemens, 1996); program(s) used to refine structures: SHELXTL; molecular graphics: ORTEPIII (Johnson & Burnett, 1997); software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1174). Services for accessing these data are described at the back of the journal.

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Bis[4-(2-methoxycarbonyl-5-thienyl)]phenyl ether†

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Abstract

The title compound, $\text{C}_{24}\text{H}_{18}\text{O}_5\text{S}_2$, possesses crystallographic C_2 symmetry. The thienyl ring adopts a planar conformation. The methoxycarbonyl group is twisted $9.7(1)^\circ$ out of plane of its parent thienyl ring.

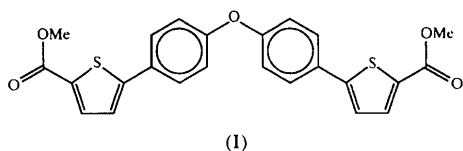
Comment

The synthesis of non-natural cavity-shaped molecules has invaded the field of molecular recognition in recent years (Haldar *et al.*, 1997). The focus on heterocyclic compounds has generated novel receptors which are capable of binding suitable guests through hydrogen bonding, π -stacking forces and van der Waals interactions. This has further enriched the field of supramolecular chemistry. In connection with our studies towards the synthesis of novel cavity-shaped receptors for the selective recognition of long-chain dicarboxylic acids, we have synthesized some bis-thiophene-5-carboxamide derivatives (Gupta *et al.*, 1999) where the diphenyl ether moiety has been used as a spacer between the two thiophene units.

The title compound, (I), is the precursor of our designed artificial receptor. In this cavity-shaped molecule,

† Alternative name: dimethyl 5,5'-(oxydi-*p*-phenylene)bis(thiophene-2-carboxylate).

two S atoms may have an 'in-in', 'in-out' or 'out-out' conformation. These conformational descriptors are normally used to define the stereochemical rotamers derivable from the positions of the S atoms of the two thiophene rings with respect to the concave curvature of the molecule at the ether-O atom. Therefore, the determination of the crystal structure is essential to confirm the actual conformation. In solution, free rotation of the C4—C7 bond enables the two S atoms to face each other, thereby allowing the receptor to bind bioactive molecules.



The structure consists of a half-molecule in the asymmetric unit and the other half is related by crystallographic C_2 symmetry. The conformation of the symmetry-related half of the molecule is defined by the torsion angle C9—C10—O3—C10ⁱ of 33.4(3)° [symmetry code (i): 2 - x, -y, z]. The bond lengths and angles are comparable with those reported for similar environments (Allen *et al.*, 1987). The slightly longer average C—S distance of 1.723(3) Å compared with 1.69(1) Å in 2-(2-aminophenylthio)-2-(2-thienyl)ethyl 2-thienyl acetone (Morgant *et al.*, 1996), 1.64(2) Å in 3-(4-methylphenyl)-1-(3-thienyl)-2-propen-1-one (Youping, Genbo & Jianqiu, 1995) and 1.694(4) Å in 3-(4-bromophenyl)-1-(3-thienyl)-2-propen-1-one (Youping, Qiangjin & Genbo, 1995) may be due to the inclusion of a methoxycarbonyl substituent on the thienyl ring. The widening of the angle at O3 [123.3(1)°] probably results from the twist between the phenyl rings. This value is comparable with 121.3(8)° for bastidin-5 tetramethyl ether (Kazlauskas *et al.*, 1981), 120.6(12)° for 3-phenyloxybenzyl *cis*-3-(2',2'-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate and 122.1(15)° for its dichloro analogue (Owen, 1976). The thienyl ring has a planar conformation and

there is no sign of the disorder that is typical of other related structures (Ray *et al.*, 1997). In the title compound, the S atoms are in the 'out-out' conformation and the planes of the two thienyl rings have an interplanar angle of 40.5(1)°. The plane of the methoxycarbonyl group is twisted by 9.7(1)° out of the plane of its parent thienyl ring. The interplanar angle between the thienyl and phenyl rings is 12.4(1)°.

Experimental

The title compound (Gupta *et al.*, 1998) was obtained by condensation of methyl thioglycolate (Kar *et al.*, 1991) with the bis-chloroaldehyde bis[4-(1-chloro-2-formylethenyl)-phenyl] ether, which in turn was prepared by treatment of bis(4-acetylphenyl) ether with POCl₃/*N,N*-dimethylformamide at 273–323 K for 4 d. X-ray quality crystals were obtained by slow evaporation from benzene (m.p. 476–478 K).

Crystal data

C₂₄H₁₈O₅S₂

$M_r = 450.50$

Orthorhombic

*Aba*2

$a = 7.3785(2) \text{ \AA}$

$b = 47.9241(10) \text{ \AA}$

$c = 5.9069(2) \text{ \AA}$

$V = 2088.7(1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.433 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5357 reflections

$\theta = 0.85\text{--}28.34^\circ$

$\mu = 0.290 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Slab

$0.44 \times 0.34 \times 0.06 \text{ mm}$

Colourless

Data collection

Siemens SMART CCD area detector diffractometer

ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

$T_{\min} = 0.883$, $T_{\max} = 0.983$

6884 measured reflections

1414 independent reflections

(plus 1003 Friedel-related reflections)

2164 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 28.23^\circ$

$h = -8 \rightarrow 9$

$k = -63 \rightarrow 61$

$l = -7 \rightarrow 7$

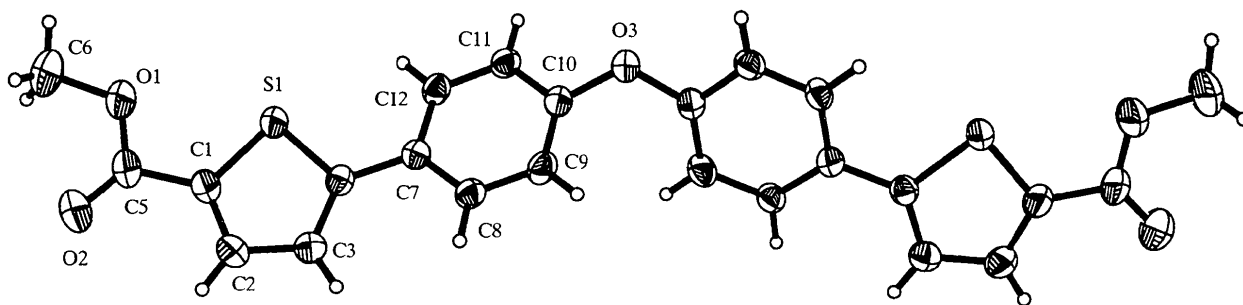


Fig. 1. A 50% probability displacement ellipsoid plot of (1) (the molecule possesses crystallographic C_2 symmetry).

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.095$
 $S = 1.083$
 2417 reflections
 166 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.251 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.242 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 0.04 (8)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$$

	x	y	z	U_{eq}
S1	0.94722 (7)	0.136182 (8)	0.05891 (11)	0.03939 (14)
O1	0.9504 (3)	0.19534 (3)	-0.0037 (4)	0.0662 (6)
O2	1.0364 (3)	0.20886 (4)	0.3435 (4)	0.0798 (7)
O3	1	0	-0.1333 (4)	0.0404 (4)
C1	1.0021 (3)	0.16063 (4)	0.2608 (4)	0.0397 (4)
C2	1.0612 (3)	0.14842 (4)	0.4572 (4)	0.0426 (5)
C3	1.0646 (3)	0.11879 (4)	0.4423 (4)	0.0389 (4)
C4	1.0074 (2)	0.10899 (4)	0.2350 (4)	0.0302 (4)
C5	0.9978 (4)	0.19091 (4)	0.2105 (4)	0.0501 (6)
C6	0.9571 (5)	0.22377 (5)	-0.0819 (7)	0.0847 (11)
C7	0.9994 (2)	0.08004 (3)	0.1510 (4)	0.0286 (3)
C8	1.0826 (2)	0.05803 (4)	0.2674 (3)	0.0328 (4)
C9	1.0803 (2)	0.03076 (4)	0.1847 (4)	0.0343 (4)
C10	0.9953 (2)	0.02546 (3)	-0.0218 (4)	0.0303 (4)
C11	0.9110 (2)	0.04687 (4)	-0.1404 (4)	0.0326 (4)
C12	0.9138 (2)	0.07378 (4)	-0.0547 (3)	0.0322 (4)

Table 2. Selected geometric parameters (Å , $^\circ$)

S1—C1	1.720 (2)	O1—C6	1.439 (3)
S1—C4	1.7255 (19)	O2—C5	1.199 (3)
O1—C5	1.330 (4)	O3—C10	1.387 (2)
C1—S1—C4	92.05 (11)	O2—C5—C1	124.5 (2)
C5—O1—C6	116.6 (2)	O1—C5—C1	110.7 (2)
O2—C5—O1	124.9 (2)		

The H atoms of the methyl groups were placed in geometrically optimized positions and constrained to ride on their parent C atom, while all other H atoms were refined freely (x , y , z and U_{iso}); C—H distances are in the range 0.89 (2)–0.94 (2) Å .

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1085). Services for accessing these data are described at the back of the journal.

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Methyl 1-(4-chlorobenzyl)-2-oxocyclohexane-1-carboxylate and methyl (2*RS*,4*aRS*,8*aRS*)-2-(4-chlorobenzyl)-3-oxoperhydropthalene-2-carboxylate

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Abstract

In the title compounds, methyl 1-(4-chlorobenzyl)-2-oxocyclohexane-1-carboxylate, $C_{15}H_{17}ClO_3$, (I), and methyl (2*RS*,4*aRS*,8*aRS*)-2-(4-chlorobenzyl)-3-oxoper-

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