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Transformations of thiocarbonyls into alkenes *via* Barton–Kellogg olefination

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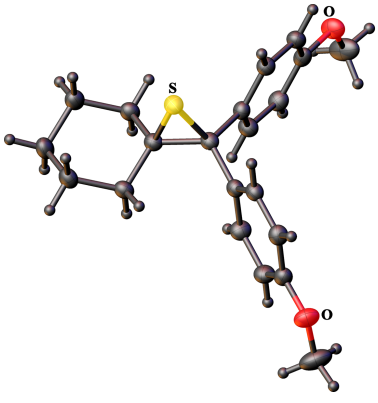
The transformation of a thiocarbonyl compound into an alkene by stepwise treatment with a diazo compound and triphenylphosphane is known as Barton–Kellogg olefination. As a model reaction, 4,4′-dimethoxythiobenzophenone and diazocyclohexane were used to prepare [bis(4-methoxyphenyl)methylidene]-cyclohexane, $C_{21}H_{24}O_2$. The crystal structure of the latter, as well as that of the intermediate thiirane, 2,2-bis(4-methoxyphenyl)-1-thiaspiro[2.5]octane, $C_{21}H_{24}O_2S$, have been determined and their molecular conformations and geometries are generally consistent with those of related structures in the literature. Variations in the influence of four substituents on crowded thiirane rings are minimal and the main differences are noted in the presence of bulky *tert*-butyl substituents. The conformation of the intermediate thiirane is influenced by weak intramolecular C—H···S interactions. A three-dimensional supramolecular structure of the methylene cyclohexane compound results from the combination of three distinct weak C—H···π interactions. Under similar reaction conditions, 5-phenyl-3*H*-1,2-dithiole-3-thione has been transformed into 3-[bis(4-methoxyphenyl)methylidene]-5-phenyl-3*H*-1,2-dithiole, $C_{24}H_{20}O_2S_2$, by treatment with bis(4-methoxyphenyl)diazomethane. The crystal structure of the 1,2-dithiole product reveals a molecule with an all-*trans* 2,4-hexadiene core, in which the Csp^2—Csp^2 bond lengths display an alternating character that suggests little delocalization of the double bonds. The 1,2-dithiole ring is nearly planar, with just a slight puckering into an envelope form. Two weak C—H···π and one C—H···O interaction link the molecules into thick two-dimensional supramolecular layers.

1. Introduction

In the synthesis of organic compounds, olefination reactions play a prominent role (see, for example, Bodwell & Nandaluru, 2012; Takeda, 2014; Hu & Wang, 2019). The most well-known ones are transformations of carbonyl compounds **1** into alkenes **2** (Scheme 1), such as, among others, the Wittig reaction (Murphy & Brennan, 1988; Maryanoff & Reitz, 1989; Byrne & Gilheany, 2013; Rocha *et al.*, 2018; Heravi *et al.*, 2020), the Peterson olefination (Ager, 1984; van Staden *et al.*, 2002; Britten & McLaughlin, 2020), the Julia–Kocienski olefination (Baudin *et al.*, 1993; Sakaine *et al.*, 2023; Chrenko & Pospíšil, 2024) and the McMurry reaction (Ephritikhine, 1998; Duan *et al.*, 2006; Bongso *et al.*, 2022).

The analogous transformation of thiocarbonyl derivatives into alkenes is known as Barton–Kellogg olefination (Barton *et al.*, 1974; Kellogg, 1976; Guziec & Sanfilippo, 1988; Schmidt & Sparr, 2021). The mechanism of this so-called 'twofold extrusion reaction' has been reported by Huisgen *et al.* (1984): the initial [3+2] cycloaddition of the thiocarbonyl compound **3** and the diazo compound **4** leads to the 1,3,4-thiadiazoline **5** (Scheme 2). Elimination of N_2 yields the thiirane **7** *via* electrocyclization of the intermediate thiocarbonyl ylide **6**, and the



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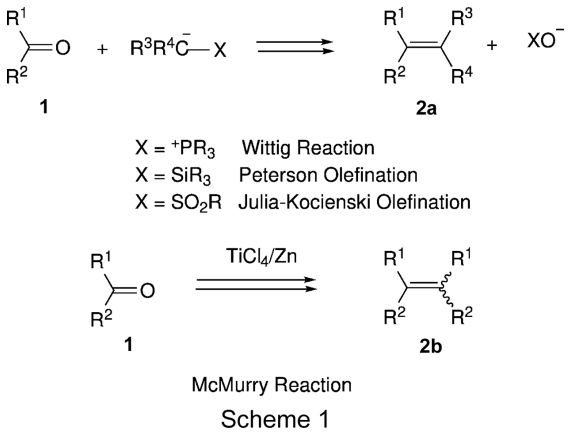
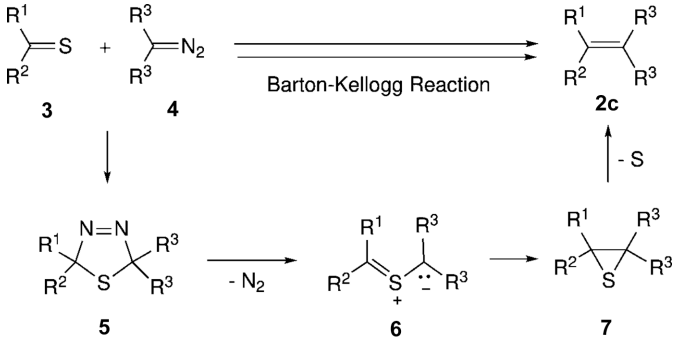
final alkene **2c** is formed by extrusion of sulfur. Recently, this reaction sequence has been supported by theoretical studies (Mlostoń *et al.*, 2020; Burns *et al.*, 2021; Seif *et al.*, 2022).



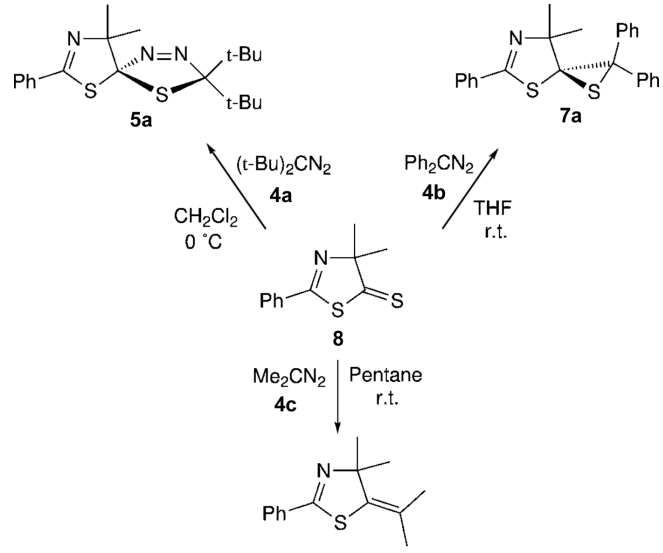
Scheme 1



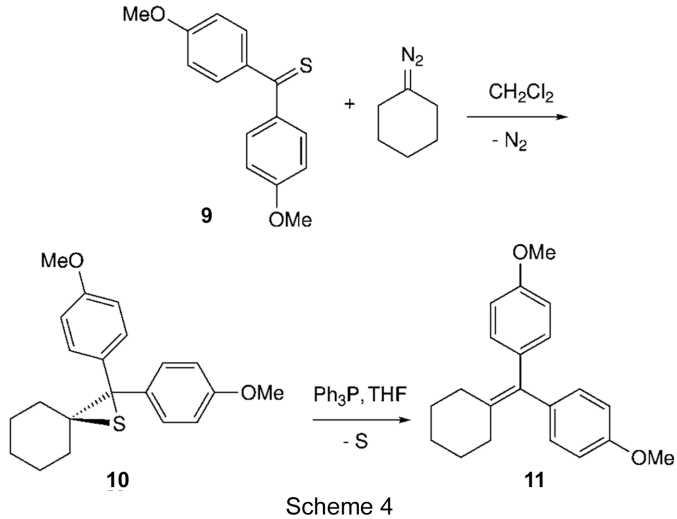
Scheme 2

It has also been communicated that the alkene **2**, as well as the intermediates **5** and **7**, can be isolated as final products depending on the kind of substituents and the reaction conditions. For example, we have shown that in the reaction of the heterocyclic thione **8**, a 1,3,4-thiadiazoline-5-thione, with bis(*tert*-butyl)diazomethane (**4a**) in dichloromethane (CH_2Cl_2) at 273 K, the primary cycloadduct **5a** can be isolated in high yield, whereas in the analogous reaction with diphenyldiazomethane (**4b**) in tetrahydrofuran (THF) at room temperature, spontaneous elimination of N_2 was observed and thiirane **7a** was obtained exclusively (Mlostoń *et al.*, 1994). Furthermore, the reaction of **8** with 2-diazopropane (**4c**) in pentane at 275–276 K and workup at room temperature yielded the alkene derivative **2d** (Mlostoń & Heimgartner, 1992) (Scheme 3). In the crude reaction mixture, the corresponding intermediates of type **5** and **7** could be detected by ^{1}H NMR spectroscopy. Finally, treatment of **8** with diazomethane in diethyl ether at 195 K led to a mixture of the corresponding thiirane and alkene derivative of type **7** and **2**, together with products of the dimerization and [3+2] cycloaddition of the intermediate thiocarbonyl ylide of type **6** (Kägi *et al.*, 1993).

Within our studies on [3+2] cycloadditions with thiocarbonyl derivatives, we used the Barton–Kellogg olefination frequently for the preparation of sterically crowded alkenes (*e.g.* Kägi, Mlostoń *et al.*, 1998; Egli *et al.*, 2007; Mlostoń *et al.*, 2002, 2016, 2018). As a model reaction, we transformed 4,4′-dimethoxythiobenzophenone (**9**) (Pedersen *et al.*, 1978) *via* the 'twofold extrusion reaction' with diazocyclohexane into [bis(4-methoxyphenyl)methylidene]cyclohexane (**11**; Scheme 4). In this case, the intermediate thiirane **10** was also isolated in a two-step reaction sequence. The crystal structures of **10** and **11** were determined by X-ray diffraction analysis.



Scheme 3



Scheme 4

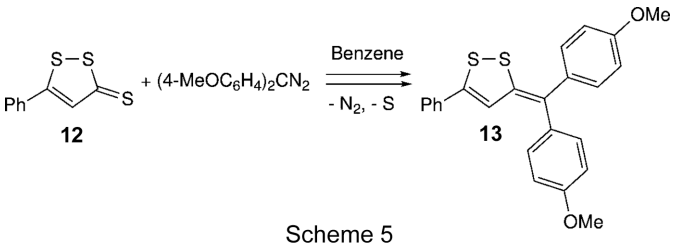
In an analogous manner, the known 5-phenyl-3*H*-1,2-dithiole-3-thione (**12**) (Wei, 1986; Mathur *et al.*, 2004; Koley *et al.*, 2016; Rakitin, 2021) was transformed into 3-[bis(4-methoxyphenyl)methylidene]-5-phenyl-3*H*-1,2-dithiole (**13**, Scheme 5) by treatment with bis(4-methoxyphenyl)diazomethane in benzene without isolation of the intermediate. The molecular structure of **13** was confirmed by a crystal structure analysis.

Table 1
Experimental details.

For all structures: $Z = 4$. Experiments were carried out at 160 K with Mo $K\alpha$ radiation using a Nonius KappaCCD area-detector diffractometer. Absorption was corrected for by the multi-scan method (Blessing, 1995). H-atom parameters were constrained.

	10	**11**	**13**
Crystal data			
Chemical formula	$C_{21}H_{24}O_2S$	$C_{21}H_{24}O_2$	$C_{24}H_{20}O_2S_2$
M_r	340.46	308.40	404.52
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, b, c (Å)	10.6815 (2), 8.3698 (1), 21.0120 (3)	12.3664 (2), 5.3819 (1), 25.5086 (5)	15.2746 (2), 6.6094 (1), 19.8754 (3)
β (°)	103.5641 (8)	93.4911 (10)	93.5489 (9)
V (Å^3)	1826.12 (5)	1694.57 (5)	2002.69 (5)
μ (mm^{-1})	0.19	0.08	0.28
Crystal size (mm)	0.28 × 0.25 × 0.15	0.25 × 0.15 × 0.08	0.30 × 0.25 × 0.15
Data collection			
T_{min}, T_{max}	0.840, 0.978	0.809, 0.999	0.863, 0.961
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36506, 4168, 3526	30267, 2994, 2356	45139, 4597, 3564
R_{int}	0.053	0.079	0.060
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.595	0.649
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.095, 1.04	0.057, 0.151, 1.06	0.042, 0.112, 1.06
No. of reflections	4165	2992	4597
No. of parameters	219	210	255
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.26	0.44, −0.21	0.29, −0.34

Computer programs: *COLLECT* (Nonius, 2000), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SIR92* (Altomare *et al.*, 1994), *SHELXL2019* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2020).



Scheme 5

2. Experimental

2.1. Synthesis and crystallization

2.1.1. 2,2-Bis(4-methoxyphenyl)-1-thiaspiro[2.5]octane (10)

To a solution of 4,4′-dimethoxythiobenzophenone (0.50 g, 2 mmol) (**9**) (Pedersen *et al.*, 1978) in CH_2Cl_2 (20 ml) at room temperature were added dropwise a solution (15 ml) of diazocyclohexane (*ca* 2–5 mmol) in CH_2Cl_2. Immediate evolution of N_2 was observed and the colour of the mixture changed from blue to yellow. After stirring for 30 min, the solvent was evaporated and the residue was purified chromatographically [MPLC, hexane/ethyl acetate (AcOEt), 8:1 *v*/*v*] and crystallized from chloroform ($CHCl_3$). Yield of **10**: 421 mg (85%). Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from $CHCl_3$.

2.1.2. [Bis(4-methoxyphenyl)methylidene]cyclohexane (11)

A solution of **10** (149 mg, 0.58 mmol) and triphenylphosphane (Ph_3P, 154 mg, 0.6 mmol) in THF (60 ml) was heated to reflux for 60 h, during which additional Ph_3P (0.6 mmol) was added after each period of 5 h. After evaporation of the solvent, the crude product was purified chromatographically (SiO_2, hexane/AcOEt, 15:1 *v*/*v*). Yield of **11**: 166 mg (92%). Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from CH_2Cl_2/hexane.

2.1.3. 3-[Bis(4-methoxyphenyl)methylidene]-5-phenyl-3*H*-1,2-dithiole (13)

To a solution of 5-phenyl-3*H*-1,2-dithiole-3-thione (*ca* 105 mg, 0.5 mmol) (**12**) in benzene (30 ml) were added bis(4-methoxyphenyl)diazomethane (*ca* 152 mg, 0.6 mmol) at room temperature. After stirring for 4 d, the mixture was heated to 323 K. Evaporation of the solvent and recrystallization of the residue from hexane/AcOEt yielded suitable crystals for X-ray crystal structure analysis.

2.2. Analytical and spectroscopic data

Compound **10**: colourless crystals, m.p. 368–369 K; IR (KBr): 2950 (*m*), 2925 (*vs*), 2851 (*s*), 2834 (*m*), 1605 (*s*), 1510 (*vs*), 1463 (*s*), 1439 (*s*), 1286 (*s*), 1246 (*vs*), 1184 (*s*), 1172 (*s*), 1114 (*m*), 1032 (*s*), 838 (*s*), 824 (*s*), 813 (*s*) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.40 (*d*, J = 8.9, 4 arom. H), 6.76 (*d*, J = 8.9, 4 arom. H), 3.73 (*s*, 2 MeO), 2.07–1.17 (*m*, 5 CH_2); ^{13}C NMR ($CDCl_3$): δ 158.3 (*s*, 2 arom. C—OMe), 134.8 (*s*, 2 arom. C), 130.3, 113.3 (2*d*, 8 arom. CH), 67.2 (*s*, C2), 62.8 (*s*, C3), 55.2 (*q*, 2 MeO), 37.1 (*t*, 2 CH_2), 26.5 (*t*, 2 CH_2), 25.8 (*t*, CH_2); CI–MS: 309 (100, $[M - S]^+$).

Compound **11**: colourless crystals, m.p. 382–383 K; IR (KBr): 2962 (*s*), 2927 (*vs*), 2913 (*m*), 2840 (*s*), 1608 (*s*), 1510 (*vs*), 1457 (*s*), 1447 (*s*), 1308 (*m*), 1301 (*s*), 1287 (*s*), 1279 (*s*), 1243 (*vs*), 1184 (*m*), 1171 (*vs*), 1107 (*m*), 1033 (*vs*), 838 (*s*), 828 (*vs*), 812 (*s*) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.02 (*d*, J = 8.9, 4 arom.

Table 2
Selected geometric parameters (Å, °) for **10** and related compounds.

The atom numbers refer to the structure model for **10**. Other atom-numbering schemes may have been used for the other structures; the entries refer to the corresponding chemical parts of the structures.

	10	MEFFAF*	DTBPTR01	NURYEE	Microwave**	22 structures without *tert*-butyl Range, mean
S1—C1	1.8381 (12)	1.8185 (15), 1.8233 (15)	1.823 (2)	1.818 (2)	1.819	1.802–1.856, 1.824 (11)
S1—C2	1.8493 (12)	1.8334 (16), 1.8245 (16)	1.847 (2)	1.841 (2)	1.819	1.785–1.854, 1.826 (17)
C1—C2	1.5041 (18)	1.516 (2), 1.508 (2)	1.549 (3)	1.539 (2)	1.492	1.508–1.556, 1.535 (13)
C1—C8	1.5152 (16)	1.512 (2), 1.507 (2)	1.516 (3)	1.505 (3)	–	1.489–1.543, 1.513 (11)
C1—C15	1.5151 (17)	1.514 (2), 1.525 (2)	1.535 (3)	1.509 (3)	–	1.489–1.543, 1.513 (11)
C2—C3	1.5160 (17)	1.530 (2), 1.528 (2)	1.588 (3)	1.567 (4)	–	1.490–1.562, 1.519 (13)
C2—C7	1.5156 (17)	1.532 (2), 1.541 (2)	1.598 (3)	1.542 (4)	–	1.490–1.562, 1.519 (13)
C1—S1—C2	48.14 (6)	49.05 (7), 48.84 (7)	49.9 (9)	49.76 (8)	65.8	48.8–50.55, 49.7 (5)
S1—C2—C1	65.54 (7)	65.99 (8), 65.62 (8)	64.2 (9)	64.35 (10)	not given	63.9–66.4, 65.3 (7)
S1—C1—C2	66.32 (7)	64.96 (8), 64.54 (8)	65.9 (9)	65.89 (11)	not given	63.9–66.2, 65.0 (7)
C8—C1—C15	113.92 (10)	112.57 (13), 112.48 (13)	104.0 (2)	108.23 (16)	–	104.0–116.7, 111 (4)
C3—C2—C7	113.01 (11)	102.50 (12), 102.54 (12)	118.3 (2)	110.94 (17)	–	102.5–118.8, 111 (5)

Notes: (*) two molecules in the asymmetric unit. (**) Structure from experimental microwave data (Cunningham *et al.*, 1951); result reproduced exactly by MO–SCF calculations (Rohmer & Roos, 1975).

H), 6.80 (*d*, *J* = 8.9, 4 arom. H), 3.78 (*s*, 2 MeO), 2.26–2.24 (*m*, 2 CH_2), 1.59–1.57 (*m*, 3 CH_2); ^{13}C NMR ($CDCl_3$): δ 157.7 (*s*, 2 arom. C—OMe), 138.3, 133. 4 (2 C), 135.9 (*s*, 2 arom. C), 130.9, 113.2 (2*d*, 8 arom. CH), 55.1 (*q*, 2 MeO), 32.5 (*t*, 2 CH_2), 28.7 (*t*, 2 CH_2), 26.9 (*t*, CH_2); CI–MS: 309 (100, $[M]^+$).

Compound **13**: red crystals.

2.3. Refinement

Crystal data, data collection and structure refinement details for **10**, **11** and **13** are summarized in Table 1. For all structures, the methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å), with U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about the parent C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (aromatic, alkene) or 0.99 Å (methylene), and U_{iso}(H) = 1.2U_{eq}(C).

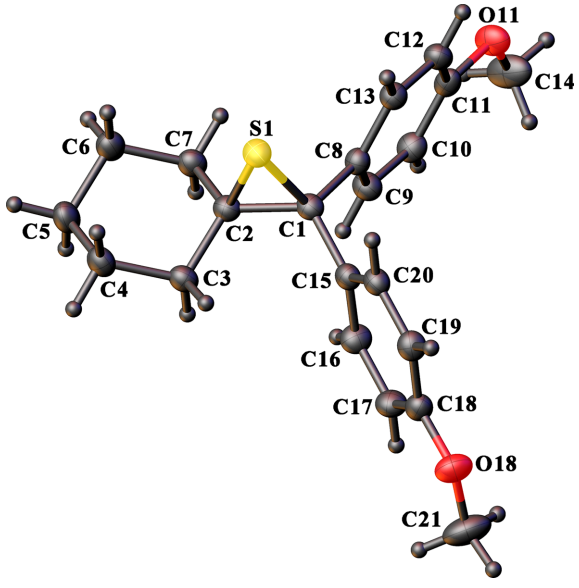


Figure 1
View of the molecule of **10**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

3. Results and discussion

The molecular structure of the intermediate **10** (Fig. 1) reveals that Barton–Kellogg olefination of the thiobenzophenone **9** (Scheme 4) initially has formed a three-membered thiirane ring, which subsequently extrudes sulfur to give the fully-substituted alkene **11**. In the crystal, the molecule of **10** has approximate noncrystallographic C_s symmetry across the plane of the thiirane ring, with a Continuous Symmetry Measure (Zabrodsky *et al.*, 1993) of 0.047 Å and a root-mean-square deviation of 0.022 Å [unit weights; calculations performed with the program *PLATON* (Spek, 2020)]. The 4-methoxy groups are nearly coplanar with their parent arene rings, with C14—O11—C11—C10 and C21—O18—C18—C17 torsion angles of −7.65 (19) and 4.9 (2)°, respectively. The mean planes of the arene rings containing atoms C8–C13 and C15–C20 make dihedral angles of 74.86 (6) and 73.65 (6)°, respectively, with the plane defined by thiirane ring atom C1 and the *ipso* and *para* C atoms of the two arene rings. Such an arrangement might be induced by one *ortho* H atom in each arene ring having a modest intramolecular interaction with atom S1 [C13—H13···S1, with H13···S1 = 2.85 Å, C13···S1 = 3.2119 (13) Å and C13—H13···S1 = 104°; C20—H20···S1 with H20···S1 = 2.83 Å, C20···S1 = 3.1963 (13) Å and C20—H20···S1 = 104°]. The consequence of this is that the distance between the other *ortho* H atoms of these two rings, H9 and H16, is 2.33 Å. There are no noteworthy intermolecular interactions of any type.

The Cambridge Structural Database (CSD, Version 5.46, update of November 2024, Groom *et al.*, 2016) records 28 unique crystal structures of fully-substituted organic thiirane compounds, which have atomic coordinates in the database, no errors and R < 0.075. Of these, 24 have two aromatic substituents at one or both of the ring C atoms, albeit for 16 of

them, the aromatic rings are connected to one another as part of a spiro(dibenzo[*a*,*d*][7]annulene), spiro(xanthene), spiro(fluorene), or related, substituent, which imposes steric constraints on the $C_{ar}—C—C_{ar}$ bond angle at the spiro C atom. Concerning substituents at the other C atom of the thiirane ring, of the above 24 structures, seven have neither aromatic rings, as part of a larger spiro substituent or otherwise, nor a methylene group bonded to the thiirane ring. There is only one example (CSD refcode MEFFAF; Mlostoń *et al.*, 2006) of a spirocyclic aliphatic substituent on the thiirane ring that is not further fused with an aromatic ring, such as spiro[cyclopenta[*a*]naphthalene]. That single example contains an aliphatic spiro(norbornane) substituent on one thiirane C atom, as well as two phenyl substituents on the other thiirane ring C atom and thus may be considered as the closest relative, for which a crystal structure has been reported, to **10** with its unsubstituted spiro(cyclohexyl) group. The simplest fully-substituted thiirane structure is that of 2,2-di-*tert*-butyl-3,3-diphenylthiirane (DTBPTR01; Mugnoli & Simonetta, 1976), in which none of the substituents form a spirocyclic junction with the thiirane ring and two bulky *tert*-butyl substituents bond to one of the thiirane C atoms. One further example with a single *tert*-butyl substituent is NURYEE (Kägi, Linden *et al.*, 1998).

The geometries of the thiirane ring core of **10**, MEFFAF, DTBPTR01 and NURYEE are listed in Table 2, alongside that of unsubstituted gas-phase thiirane (ethylene sulfide) derived from its experimental microwave spectrum (Cunningham *et al.*, 1951) and matched exactly by an *ab initio* MO–SCF study (Rohmer & Roos, 1975). The geometry of the thiirane ring of **10** is consistent with that in the three other crystal structures, except that the thiirane ring C—C bond (C1—C2 in **10**) is slightly longer in the two *tert*-butyl-substituted compounds

Table 3
Selected geometric parameters (Å, °) for **11** and related compounds.

The atom numbers refer to the structure model for **11**. Other atom-numbering schemes may have been used for the other structures; the entries refer to the corresponding chemical parts of the structures.

	11	**10**	AOPCHY	DEQTOJ
C1—C2	1.340 (3)	1.5041 (18)	1.339	1.344 (3)
C1—C8	1.498 (3)	1.5152 (16)	1.495	1.511 (3)
C1—C15	1.495 (3)	1.5151 (17)	1.542	1.505 (3)
C2—C3	1.510 (3)	1.5160 (17)	1.500	1.513 (3)
C2—C7	1.514 (3)	1.5156 (17)	1.549	1.515 (3)
C8—C1–C15	113.49 (16)	113.92 (10)	115.4	117.8 (2)
C3—C2–C7	111.92 (17)	113.01 (11)	112.8	112.3 (2)

DTBPTR01 and NURYEE. Indeed, the *exo* $C_{ring}—C$ bonds are significantly longer in the two *tert*-butyl-substituted compounds than any of the other such bonds in the compounds in Table 2. These observations could be attributable to the crowding caused by the bulkiness of the *tert*-butyl substituents, whereas arene-based substituents are only bulky in one or two dimensions. None of the bond angles within the thiirane ring show any significant variation across the four crystal structures in Table 2. The *exo* $C—C_{ring}—C$ angles are less informative, as they are influenced not only by the bulkiness of the substituents, but also by potential geometrical constraints within any spirocyclic linkages.

Table 2 also lists the ranges and means of the discussed geometric parameters for the 22 structures from the above-mentioned CSD search that do not include a *tert*-butyl substituent. This shows that the molecular geometry of the core of **10** is consistent with those of a broader range of thiirane structures. On the other hand, the ring in unsubstituted thiirane obtained from microwave data and *ab initio* MO–SCF calculations shows a significantly shorter C—C bond

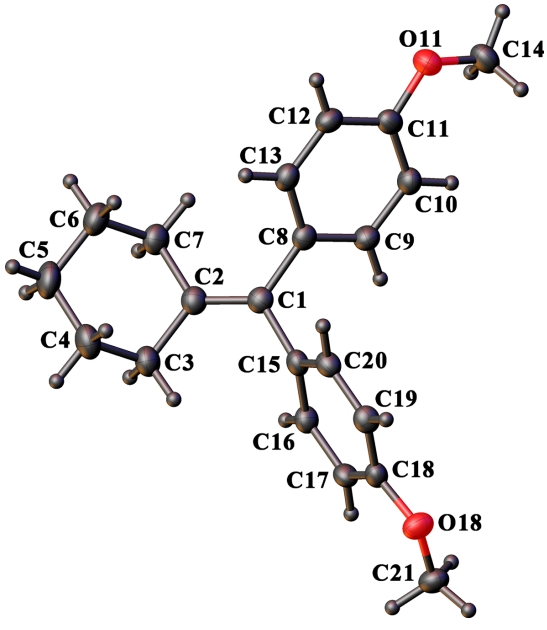


Figure 2
View of the molecule of **11**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

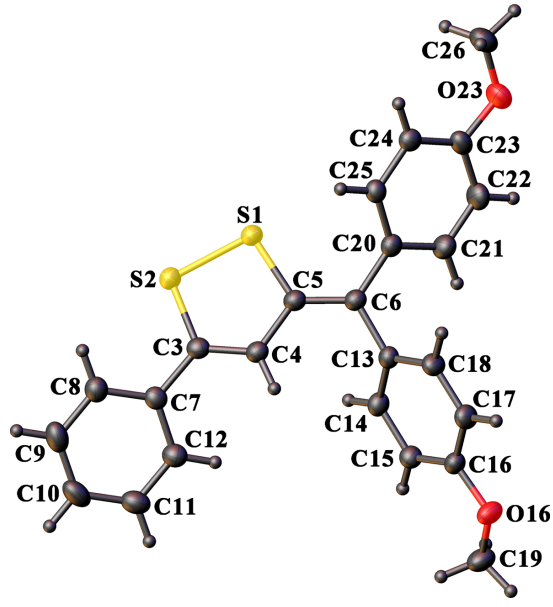


Figure 3
View of the molecule of **13**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

Table 4
Intermolecular C—H···π interactions (Å, °) for **11**.

*Cg*1 and *Cg*2 are the centroids of the C8–C13 and C15–C20 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···*Cg*2^{i}	0.99	2.96	3.888 (3)	157
C6—H6*A*···*Cg*1^{ii}	0.99	2.96	3.820 (3)	146
C14—H14*A*···*Cg*1^{iii}	0.98	2.88	3.737 (2)	147

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$.

and larger C—S—C angle than in the crystal structures listed in Table 2. The electronic influence and steric effects of the substituents are probably responsible for this observation.

The molecular structure of alkene **11** (Fig. 2), the sulfur extrusion product obtained from **10** (Scheme 4), shows *exo* C_{ring}—C_{ar} bonds slightly shorter than in **10** (Table 3). This might be attributed to some delocalization of the alkene bond with the arene rings, although the mean planes of the arene rings containing atoms C8–C13 and C15–C20 are tilted significantly out of the plane containing alkene atom C1 and both arene ring *ipso* and *para* C atoms, with dihedral angles of 52.96 (9) and 61.85 (9)°, respectively. These rings now tilt in an opposite sense to each other, unlike in **10**, thereby avoiding any short interring H···H distances. Also, the electron-withdrawing effect of the S atom in **10** could lead to the slightly longer *exo* C_{ring}—C_{ar} bonds to the arene substituents, although this does not appear to influence the length of the *exo* C_{ring}—C_{alkyl} bonds to the spiro(cyclohexyl) substituent. The substituents at each end of the central alkene bond indicate a small twist about the latter, with a dihedral angle of 7.1 (3)°. The 4-methoxy groups are nearly coplanar with their parent arene rings, with C14—O11—C11—C10 and C21—O18—C18—C17 torsion angles of 9.1 (3) and 4.1 (3)°, respectively.

The crystal structure of **11** is supported by three weak C—H···π interactions involving as donors two cyclohexyl and one methoxy C—H. Both of the 4-methoxyphenyl rings act as acceptors for these interactions (Table 4). The combination of these intermolecular interactions gives a three-dimensional supramolecular structure. There are no significant π–π interactions.

The CSD records the crystal structures of two molecules that are closely related to **11**. The relevant geometric parameters for the compounds containing bis(4-acetoxyphenyl) (AOPCHY; Precigoux *et al.*, 1972) and bis(mesityl) (DEQTOJ; Sun *et al.*, 2006) substituents, instead of the bis(4-methoxy) groups present in **11**, are included in Table 3 and are consistent with those of **11**.

An analogous Barton–Kellogg olefination starting from the dithiole-3-thione **12** led to the 3-methylene-1,2-dithiole **13** (Scheme 5). The molecular structure of **13** reveals an all-*trans* 2,4-hexadiene core from atom C7 through to C20 (Fig. 3), in which the Csp^2—Csp^2 bond lengths clearly display an alternating character that suggests little delocalization of the double bonds (Table 5). The 1,2-dithiole ring is nearly planar, with just a slight puckering into an envelope form, with atom S1 as the envelope flap being 0.1985 (5) Å out of the plane of the other four ring atoms. The mean plane of the arene substituent at atom C3 of the 1,2-dithiole ring is tilted significantly out of the plane of the 1,2-dithiole ring, calculated excluding atom S1, with a dihedral angle of 31.20 (10)°. Considering the formal alkene nature of the C5—C6 bond, there is a small twist between the planes of the substituents at each end of the alkene bond, with a dihedral angle between the planes defined by atoms S1/C4/C5 and C6/C13/C20 of 6.0 (2)°. The mean planes of the 4-methoxyphenyl rings containing atoms C13–C18 and C20–C25, calculated without considering the methoxy groups, are tilted significantly out of the plane containing alkene atom C6 and both 4-methoxyphenyl ring *ipso* and *para* C atoms, with dihedral angles of 56.58 (8) and 35.06 (8)°, respectively. These rings tilt in an opposite sense to each other, similar to the arrangement in compound **11**. The shallowness of these tilts for the arene substituent at atom C3 of the 1,2-dithiole ring and the 4-methoxyphenyl ring containing atoms C20–C25 may in part be induced by two weak intramolecular C—H···S interactions involving *ortho* C—H groups of these rings (Table 6). The 4-methoxy groups are coplanar with their parent arene rings, with C19—O16—C16—C15 and C26—O23—C23—C24 torsion angles of 2.8 (3) and −1.1 (3)°, respectively.

The crystal structure of **13** is supported by two weak C—H···π interactions involving as donors the *para* H atom on the phenyl ring and an *ortho* H atom on a 4-methoxyphenyl

Table 5
Selected geometric parameters (Å, °) for **13** and related compounds.

The atom numbers refer to the structure model for **13**. Other atom-numbering schemes may have been used for the other structures; the entries refer to the corresponding chemical parts of the structures.

	13	GANGUX*	CPTYBN10	XPTHYC
S1—S2	2.0826 (6)	2.041 (5), 2.051 (4)	2.072 (4)	2.053
S1—C5	1.7797 (17)	1.735 (12), 1.732 (12)	1.74 (1)	1.772
S2—C3	1.7568 (17)	1.714 (11), 1.734 (12)	1.730 (8)	1.732
C3—C4	1.342 (2)	1.36 (2), 1.36 (2)	1.35 (1)	1.379
C3—C7	1.471 (2)	1.47 (2), 1.47 (2)	1.47 (1)	1.451
C4—C5	1.446 (2)	1.40 (2), 1.41 (2)	1.42 (1)	1.404
C5—C6	1.362 (2)	1.44 (2), 1.42 (2)	1.39 (1)	1.404
C6—C13	1.492 (2)	1.41 (2), 1.39 (2)	1.40 (1)	1.451
C6—C20	1.479 (2)	1.51 (2), 1.50 (2)	–	1.394
S2—S1—C5	96.33 (6)	95.6 (9), 96.0 (4)	96.5 (9)	95.8
S1—S2—C3	94.22 (6)	96.2 (8), 95.6 (5)	95.0 (9)	96.1
S2—C3—C4	116.95 (13)	114.6 (10), 114.9 (10)	115.4 (9)	115.0
C3—C4—C5	120.21 (15)	120.6 (11), 120.1 (12)	121.2 (9)	120.4
S1—C5—C4	111.42 (12)	112.9 (11), 113.4 (9)	111.9 (9)	112.7
C13—C6—C20	116.80 (14)	126.3 (11), 124.8 (10)	–	118.2

Note: (*) two 1,2-dithiole-3*H*-3-ylidene entities in the cation.

Table 6
Intramolecular C—H···S and intermolecular C—H···O and C—H···π interactions (Å, °) for **13**.

*Cg*3 and *Cg*4 are the centroids of the C13–C18 and C20–C25 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···S2	0.95	2.77	3.1236 (19)	103
C25—H25···S1	0.95	2.59	3.0503 (19)	110
C8—H8···O16^{i}	0.95	2.59	3.413 (2)	146
C10—H10···*Cg*3^{ii}	0.99	2.96	3.888 (3)	157
C14—H14···*Cg*4^{iii}	0.99	2.96	3.820 (3)	146

Symmetry codes: (i) $x+\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+2, -y-1, -z$; (iii) $x, y-1, z$.

ring. Both of the 4-methoxyphenyl rings act as acceptors for these interactions (Table 6). Additionally, there is one intermolecular C—H···O interaction involving, as the donor, the same C8—H donor as involved in one of the intramolecular C—H···S interactions and a methoxy O atom as the acceptor. The combination of these three intermolecular interactions links the molecules into thick two-dimensional supramolecular layers which extend parallel to the $(10\bar{1})$ plane. There are no significant π–π interactions.

The CSD lists 21 unique crystal structures with an organic 1,2-dithiole-3*H*-3-ylidene core, which have atomic coordinates in the database and no errors (13 with $R < 0.075$). All of these have 5-substituted 1,2-dithiole rings. Of these structures, 18 have substituents containing S (1,2-dithiole or thione), O (carbonyl, aldehyde or nitro) or N (hydrazine, nitroso or pyridyl) atoms adjacent to the 1,2-dithiole ring, such that these heteroatoms weakly interact with a 1,2-dithiole S atom to complete an additional fused five-membered ring, thereby potentially inducing distortion of bond distances and angles and rendering comparison with those of **13** impractical. Selected geometric parameters of the remaining three structures are compared with those of **13** in Table 5. Firstly, 2-cyano-3-phenyl-4-(5-phenyl-1,2-dithiole-3-ylidene)-Δ^2-butyronitrile (CPTYBN10; Nguyen-Huy-Dong & Etienne, 1978) has just one ylidene substituent, but with potential for additional conjugation with a further alkene group, plus a phenyl substituent on the 1,2-dithiole ring. A more complex structure is that of the ionic 3-[1,3-diphenyl-3-(5-phenyl-1,2-dithiol-3-yl) propenyl-3-ylidene]-5-phenyl-1,2-dithiolium triiodide (GANGUX; Hordvik *et al.*, 1988), which is essentially a dimer of the 1,2-dithiole core, each with aryl and alkene substituents on the other end of the ylidene group, and an aryl substituent on the 1,2-dithiole ring. The authors proposed that the cationic charge is delocalized across the cation. Finally, 2,6-dimethyl-5′-*p*-methoxyphenyl-1′,2′-dithiole-3′,4-ylidene-2,5-cyclohexadienone benzene solvate (XPTHYC; Wei *et al.*, 1977), with an elevated *R* factor of 0.090, has a cyclohexadienone substituent on the other end of the ylidene group and a 4-methoxyphenyl substituent on the 1,2-dithiole ring. It can be concluded that the molecular geometry of the 1,2-dithiole-3*H*-3-ylidene core of **13** is consistent with those of these three related structures. Larger differences in the substituent C—$C_{ylidene}$ bonds are a result of variations in the electronic and chemical nature of the substituent(s) at that position.

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Transformations of thiocarbonyls into alkenes *via* Barton–Kellogg olefination

Anthony Linden, Daniel H. Egli and Heinz Heimgartner

Computing details

2,2-Bis(4-methoxyphenyl)-1-thiaspiro[2.5]octane (10)

Crystal data

$C_{21}H_{24}O_2S$
M_r = 340.46
Monoclinic, $P2_1/c$
a = 10.6815 (2) Å
b = 8.3698 (1) Å
c = 21.0120 (3) Å
β = 103.5641 (8)°
V = 1826.12 (5) Å^3
Z = 4
$F(000)$ = 728
D_x = 1.238 Mg m^{-3}
Melting point: 368 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 58148 reflections
θ = 1.0–27.5°
μ = 0.19 mm^{-1}
T = 160 K
Prism, colorless
0.28 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Nonius FR590 sealed tube generator
Horizontally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.840, T_{max} = 0.978
36506 measured reflections
4168 independent reflections
3526 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −13→13
k = −10→10
l = −26→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.095
S = 1.04
4165 reflections
219 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch
Solvent used: CHCl3 Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: on a glass fibre Mosaicity (deg.): 0.863 (1) Frames collected: 598 Seconds exposure per frame: 78 Degrees rotation per frame: 1.3 Crystal-detector distance (mm): 38.0 Client: Egli Daniel Sample code: DE281 (HG0111)

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.74158 (3)	0.71461 (4)	0.09887 (2)	0.02698 (10)
O11	0.89034 (9)	0.98043 (13)	0.40899 (4)	0.0363 (2)
O18	0.13992 (9)	0.98595 (13)	0.06303 (5)	0.0382 (2)
C1	0.64280 (12)	0.73223 (15)	0.15935 (6)	0.0238 (3)
C2	0.66885 (11)	0.56240 (15)	0.14291 (6)	0.0245 (3)
C3	0.56180 (12)	0.46440 (15)	0.10043 (6)	0.0274 (3)
H3A	0.507598	0.534466	0.067069	0.033*
H3B	0.506704	0.419516	0.127905	0.033*
C4	0.61573 (13)	0.32815 (16)	0.06628 (6)	0.0309 (3)
H4A	0.543928	0.260389	0.042478	0.037*
H4B	0.659959	0.373215	0.033868	0.037*
C5	0.71019 (14)	0.22598 (16)	0.11530 (7)	0.0338 (3)
H5A	0.747324	0.143084	0.091575	0.041*
H5B	0.663878	0.171422	0.144764	0.041*
C6	0.81856 (13)	0.32806 (17)	0.15593 (7)	0.0326 (3)
H6A	0.876451	0.259820	0.188574	0.039*
H6B	0.869730	0.374891	0.126927	0.039*
C7	0.76473 (12)	0.46177 (16)	0.19109 (6)	0.0281 (3)
H7A	0.721941	0.415001	0.223745	0.034*
H7B	0.836226	0.530316	0.214656	0.034*
C8	0.71074 (12)	0.79636 (15)	0.22593 (6)	0.0237 (2)
C9	0.67533 (13)	0.74102 (16)	0.28152 (6)	0.0291 (3)
H9	0.610411	0.661492	0.277178	0.035*
C10	0.73298 (13)	0.79965 (16)	0.34346 (6)	0.0290 (3)
H10	0.707519	0.760341	0.380925	0.035*
C11	0.82765 (12)	0.91559 (16)	0.35015 (6)	0.0271 (3)
C12	0.86493 (12)	0.97195 (16)	0.29507 (6)	0.0278 (3)
H12	0.930032	1.051250	0.299498	0.033*
C13	0.80682 (12)	0.91209 (15)	0.23369 (6)	0.0254 (3)
H13	0.833006	0.950699	0.196314	0.030*
C14	0.84186 (16)	0.9367 (3)	0.46447 (7)	0.0508 (4)
H14A	0.749170	0.958339	0.455212	0.076*
H14B	0.885966	0.999238	0.502593	0.076*
H14C	0.857201	0.822679	0.473620	0.076*

C15	0.50846 (12)	0.79871 (15)	0.13383 (6)	0.0240 (2)
C16	0.40710 (13)	0.74695 (17)	0.16004 (6)	0.0299 (3)
H16	0.423268	0.668698	0.193729	0.036*
C17	0.28309 (13)	0.80669 (17)	0.13825 (7)	0.0304 (3)
H17	0.215689	0.769833	0.157030	0.036*
C18	0.25829 (12)	0.92048 (16)	0.08888 (6)	0.0280 (3)
C19	0.35817 (13)	0.97422 (16)	0.06218 (6)	0.0282 (3)
H19	0.341838	1.052592	0.028545	0.034*
C20	0.48113 (12)	0.91381 (15)	0.08450 (6)	0.0252 (3)
H20	0.548440	0.951492	0.065830	0.030*
C21	0.03735 (15)	0.9424 (3)	0.09253 (9)	0.0544 (5)
H21A	0.022375	0.827032	0.087960	0.082*
H21B	−0.041139	0.999579	0.070816	0.082*
H21C	0.060354	0.970774	0.139073	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02968 (17)	0.02958 (18)	0.02390 (16)	−0.00255 (12)	0.01074 (12)	−0.00057 (12)
O11	0.0338 (5)	0.0515 (6)	0.0216 (5)	−0.0032 (4)	0.0026 (4)	−0.0073 (4)
O18	0.0261 (5)	0.0487 (6)	0.0380 (5)	0.0047 (4)	0.0040 (4)	0.0065 (5)
C1	0.0263 (6)	0.0266 (6)	0.0198 (6)	−0.0030 (5)	0.0079 (5)	0.0005 (5)
C2	0.0254 (6)	0.0268 (6)	0.0217 (6)	−0.0016 (5)	0.0062 (5)	0.0008 (5)
C3	0.0268 (6)	0.0283 (6)	0.0253 (6)	−0.0036 (5)	0.0025 (5)	−0.0001 (5)
C4	0.0341 (7)	0.0284 (7)	0.0279 (6)	−0.0030 (5)	0.0026 (5)	−0.0034 (5)
C5	0.0364 (7)	0.0245 (6)	0.0377 (7)	−0.0001 (5)	0.0029 (6)	−0.0026 (6)
C6	0.0310 (7)	0.0290 (7)	0.0347 (7)	0.0023 (5)	0.0016 (5)	−0.0006 (6)
C7	0.0276 (6)	0.0293 (7)	0.0252 (6)	−0.0009 (5)	0.0014 (5)	0.0005 (5)
C8	0.0260 (6)	0.0244 (6)	0.0209 (6)	0.0011 (5)	0.0058 (5)	−0.0010 (5)
C9	0.0313 (7)	0.0310 (7)	0.0258 (6)	−0.0037 (5)	0.0084 (5)	−0.0007 (5)
C10	0.0321 (7)	0.0347 (7)	0.0212 (6)	0.0015 (5)	0.0085 (5)	0.0014 (5)
C11	0.0262 (6)	0.0325 (7)	0.0206 (6)	0.0058 (5)	0.0018 (5)	−0.0030 (5)
C12	0.0250 (6)	0.0294 (7)	0.0277 (6)	−0.0015 (5)	0.0034 (5)	−0.0017 (5)
C13	0.0271 (6)	0.0266 (6)	0.0226 (6)	0.0003 (5)	0.0063 (5)	0.0018 (5)
C14	0.0411 (8)	0.0889 (14)	0.0228 (7)	−0.0074 (9)	0.0079 (6)	−0.0129 (8)
C15	0.0262 (6)	0.0247 (6)	0.0211 (6)	−0.0021 (5)	0.0058 (5)	−0.0024 (5)
C16	0.0317 (7)	0.0315 (7)	0.0277 (6)	−0.0005 (5)	0.0096 (5)	0.0059 (5)
C17	0.0276 (6)	0.0344 (7)	0.0308 (7)	−0.0034 (5)	0.0101 (5)	0.0014 (5)
C18	0.0258 (6)	0.0299 (7)	0.0267 (6)	0.0008 (5)	0.0029 (5)	−0.0033 (5)
C19	0.0327 (7)	0.0286 (7)	0.0228 (6)	0.0008 (5)	0.0055 (5)	0.0021 (5)
C20	0.0288 (6)	0.0252 (6)	0.0227 (6)	−0.0033 (5)	0.0080 (5)	−0.0017 (5)
C21	0.0283 (7)	0.0824 (13)	0.0529 (10)	0.0085 (8)	0.0107 (7)	0.0151 (9)

Geometric parameters (Å, º)

S1—C1	1.8381 (12)	C8—C13	1.3927 (17)
S1—C2	1.8493 (12)	C9—C10	1.3921 (18)
O11—C11	1.3723 (15)	C9—H9	0.9500

O11—C14	1.4296 (18)	C10—C11	1.3846 (19)
O18—C18	1.3681 (16)	C10—H10	0.9500
O18—C21	1.4269 (18)	C11—C12	1.3916 (18)
C1—C2	1.5041 (18)	C12—C13	1.3871 (17)
C1—C15	1.5151 (17)	C12—H12	0.9500
C1—C8	1.5152 (16)	C13—H13	0.9500
C2—C7	1.5156 (17)	C14—H14A	0.9800
C2—C3	1.5160 (17)	C14—H14B	0.9800
C3—C4	1.5300 (19)	C14—H14C	0.9800
C3—H3A	0.9900	C15—C16	1.3939 (18)
C3—H3B	0.9900	C15—C20	1.3949 (17)
C4—C5	1.5241 (19)	C16—C17	1.3892 (19)
C4—H4A	0.9900	C16—H16	0.9500
C4—H4B	0.9900	C17—C18	1.3872 (19)
C5—C6	1.5280 (19)	C17—H17	0.9500
C5—H5A	0.9900	C18—C19	1.3914 (18)
C5—H5B	0.9900	C19—C20	1.3826 (18)
C6—C7	1.5258 (19)	C19—H19	0.9500
C6—H6A	0.9900	C20—H20	0.9500
C6—H6B	0.9900	C21—H21A	0.9800
C7—H7A	0.9900	C21—H21B	0.9800
C7—H7B	0.9900	C21—H21C	0.9800
C8—C9	1.3889 (17)		

C1—S1—C2	48.14 (6)	C13—C8—C1	122.32 (11)
C11—O11—C14	116.09 (11)	C8—C9—C10	121.37 (12)
C18—O18—C21	117.23 (12)	C8—C9—H9	119.3
C2—C1—C15	118.47 (10)	C10—C9—H9	119.3
C2—C1—C8	118.20 (10)	C11—C10—C9	119.63 (12)
C15—C1—C8	113.92 (10)	C11—C10—H10	120.2
C2—C1—S1	66.32 (7)	C9—C10—H10	120.2
C15—C1—S1	115.75 (8)	O11—C11—C10	123.99 (12)
C8—C1—S1	116.01 (8)	O11—C11—C12	116.16 (12)
C1—C2—C7	120.28 (10)	C10—C11—C12	119.85 (11)
C1—C2—C3	119.47 (10)	C13—C12—C11	119.86 (12)
C7—C2—C3	113.01 (11)	C13—C12—H12	120.1
C1—C2—S1	65.54 (7)	C11—C12—H12	120.1
C7—C2—S1	114.82 (9)	C12—C13—C8	121.12 (11)
C3—C2—S1	115.18 (8)	C12—C13—H13	119.4
C2—C3—C4	111.37 (10)	C8—C13—H13	119.4
C2—C3—H3A	109.4	O11—C14—H14A	109.5
C4—C3—H3A	109.4	O11—C14—H14B	109.5
C2—C3—H3B	109.4	H14A—C14—H14B	109.5
C4—C3—H3B	109.4	O11—C14—H14C	109.5
H3A—C3—H3B	108.0	H14A—C14—H14C	109.5
C5—C4—C3	111.32 (11)	H14B—C14—H14C	109.5
C5—C4—H4A	109.4	C16—C15—C20	117.50 (12)
C3—C4—H4A	109.4	C16—C15—C1	120.33 (11)

C5—C4—H4B	109.4	C20—C15—C1	122.17 (11)
C3—C4—H4B	109.4	C17—C16—C15	121.79 (12)
H4A—C4—H4B	108.0	C17—C16—H16	119.1
C4—C5—C6	111.01 (11)	C15—C16—H16	119.1
C4—C5—H5A	109.4	C18—C17—C16	119.59 (12)
C6—C5—H5A	109.4	C18—C17—H17	120.2
C4—C5—H5B	109.4	C16—C17—H17	120.2
C6—C5—H5B	109.4	O18—C18—C17	124.65 (12)
H5A—C5—H5B	108.0	O18—C18—C19	115.79 (12)
C7—C6—C5	111.01 (11)	C17—C18—C19	119.56 (12)
C7—C6—H6A	109.4	C20—C19—C18	120.15 (12)
C5—C6—H6A	109.4	C20—C19—H19	119.9
C7—C6—H6B	109.4	C18—C19—H19	119.9
C5—C6—H6B	109.4	C19—C20—C15	121.41 (12)
H6A—C6—H6B	108.0	C19—C20—H20	119.3
C2—C7—C6	110.89 (10)	C15—C20—H20	119.3
C2—C7—H7A	109.5	O18—C21—H21A	109.5
C6—C7—H7A	109.5	O18—C21—H21B	109.5
C2—C7—H7B	109.5	H21A—C21—H21B	109.5
C6—C7—H7B	109.5	O18—C21—H21C	109.5
H7A—C7—H7B	108.1	H21A—C21—H21C	109.5
C9—C8—C13	118.17 (11)	H21B—C21—H21C	109.5
C9—C8—C1	119.50 (11)		

C2—S1—C1—C15	−111.49 (11)	C1—C8—C9—C10	−178.37 (12)
C2—S1—C1—C8	111.11 (12)	C8—C9—C10—C11	0.0 (2)
C15—C1—C2—C7	−146.87 (11)	C14—O11—C11—C10	−7.65 (19)
C8—C1—C2—C7	−2.38 (16)	C14—O11—C11—C12	172.89 (13)
S1—C1—C2—C7	105.57 (11)	C9—C10—C11—O11	−179.80 (12)
C15—C1—C2—C3	1.31 (16)	C9—C10—C11—C12	−0.3 (2)
C8—C1—C2—C3	145.80 (11)	O11—C11—C12—C13	179.68 (11)
S1—C1—C2—C3	−106.25 (11)	C10—C11—C12—C13	0.19 (19)
C15—C1—C2—S1	107.56 (10)	C11—C12—C13—C8	0.31 (19)
C8—C1—C2—S1	−107.95 (10)	C9—C8—C13—C12	−0.63 (19)
C1—S1—C2—C7	−113.57 (11)	C1—C8—C13—C12	178.18 (12)
C1—S1—C2—C3	112.54 (12)	C2—C1—C15—C16	71.48 (15)
C1—C2—C3—C4	156.42 (11)	C8—C1—C15—C16	−74.46 (15)
C7—C2—C3—C4	−53.23 (14)	S1—C1—C15—C16	147.25 (10)
S1—C2—C3—C4	81.48 (12)	C2—C1—C15—C20	−109.30 (13)
C2—C3—C4—C5	53.57 (15)	C8—C1—C15—C20	104.76 (13)
C3—C4—C5—C6	−55.72 (16)	S1—C1—C15—C20	−33.53 (15)
C4—C5—C6—C7	56.76 (16)	C20—C15—C16—C17	0.06 (19)
C1—C2—C7—C6	−155.75 (11)	C1—C15—C16—C17	179.31 (12)
C3—C2—C7—C6	54.17 (14)	C15—C16—C17—C18	0.3 (2)
S1—C2—C7—C6	−80.72 (12)	C21—O18—C18—C17	4.9 (2)
C5—C6—C7—C2	−55.42 (15)	C21—O18—C18—C19	−175.48 (14)
C2—C1—C8—C9	−70.72 (15)	C16—C17—C18—O18	179.08 (12)
C15—C1—C8—C9	75.32 (15)	C16—C17—C18—C19	−0.5 (2)

S1—C1—C8—C9	−146.51 (10)	O18—C18—C19—C20	−179.23 (11)
C2—C1—C8—C13	110.48 (13)	C17—C18—C19—C20	0.37 (19)
C15—C1—C8—C13	−103.48 (13)	C18—C19—C20—C15	−0.03 (19)
S1—C1—C8—C13	34.69 (16)	C16—C15—C20—C19	−0.18 (18)
C13—C8—C9—C10	0.47 (19)	C1—C15—C20—C19	−179.42 (11)

1-[Cyclohexylidene(4-methoxyphenyl)methyl]-4-methoxybenzene (11)

Crystal data

$C_{21}H_{24}O_2$
M_r = 308.40
Monoclinic, $P2_1/c$
a = 12.3664 (2) Å
b = 5.3819 (1) Å
c = 25.5086 (5) Å
β = 93.4911 (10)°
V = 1694.57 (5) Å^3
Z = 4
$F(000)$ = 664
D_x = 1.209 Mg m^{-3}
Melting point: 382 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4255 reflections
θ = 2.0–27.5°
μ = 0.08 mm^{-1}
T = 160 K
Prism, colorless
0.25 × 0.15 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Nonius FR590 sealed tube generator
Horizontally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
φ and ω scans with κ offsets
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.809, T_{max} = 0.999
30267 measured reflections
2994 independent reflections
2356 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 25.0°, θ_{min} = 3.2°
h = −14→14
k = −6→6
l = −30→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.151
S = 1.06
2992 reflections
210 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 1.1639P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch
Solvent used: CH2Cl2 / n-hexane Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: on a glass fibre Mosaicity (deg.): 0.716 (1) Frames collected: 798 Seconds exposure per frame: 50 Degrees rotation per frame: 1.0 Crystal-detector distance (mm): 35.0 Client: Daniel Egli Sample code: 29 (HG0117)

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O11	0.90829 (12)	0.2799 (3)	0.31845 (5)	0.0376 (4)
O18	0.92248 (12)	0.3067 (3)	−0.04335 (5)	0.0364 (4)
C1	0.64944 (16)	0.2691 (4)	0.12690 (8)	0.0278 (5)
C2	0.54097 (16)	0.2577 (4)	0.12404 (8)	0.0309 (5)
C3	0.47346 (17)	0.2191 (5)	0.07335 (8)	0.0368 (5)
H3A	0.521496	0.205427	0.043817	0.044*
H3B	0.425127	0.363738	0.066663	0.044*
C4	0.40570 (19)	−0.0168 (5)	0.07653 (10)	0.0431 (6)
H4A	0.454433	−0.162793	0.079172	0.052*
H4B	0.358589	−0.033957	0.043936	0.052*
C5	0.33549 (19)	−0.0130 (5)	0.12374 (10)	0.0482 (7)
H5A	0.296986	−0.173613	0.125959	0.058*
H5B	0.280496	0.120017	0.118972	0.058*
C6	0.40395 (19)	0.0315 (5)	0.17474 (9)	0.0418 (6)
H6A	0.355901	0.047537	0.204216	0.050*
H6B	0.452314	−0.112584	0.181998	0.050*
C7	0.47193 (17)	0.2670 (4)	0.17102 (9)	0.0358 (5)
H7A	0.423453	0.413335	0.167978	0.043*
H7B	0.519283	0.285675	0.203492	0.043*
C8	0.71732 (15)	0.2738 (4)	0.17757 (7)	0.0262 (5)
C9	0.79499 (17)	0.4594 (4)	0.18697 (8)	0.0307 (5)
H9	0.803376	0.582818	0.160904	0.037*
C10	0.86048 (17)	0.4697 (4)	0.23322 (8)	0.0303 (5)
H10	0.912170	0.599029	0.238816	0.036*
C11	0.84906 (16)	0.2876 (4)	0.27108 (7)	0.0283 (5)
C12	0.77454 (16)	0.0977 (4)	0.26199 (8)	0.0308 (5)
H12	0.768087	−0.028892	0.287563	0.037*
C13	0.70958 (16)	0.0915 (4)	0.21598 (8)	0.0302 (5)
H13	0.658690	−0.039548	0.210418	0.036*
C14	0.97417 (19)	0.4906 (4)	0.33229 (9)	0.0394 (6)
H14A	1.035188	0.497781	0.309560	0.059*
H14B	1.001698	0.476234	0.369009	0.059*
H14C	0.930815	0.642385	0.327793	0.059*
C15	0.71438 (15)	0.2783 (4)	0.07937 (7)	0.0268 (5)
C16	0.70617 (16)	0.4752 (4)	0.04383 (8)	0.0282 (5)
H16	0.654014	0.601918	0.048273	0.034*
C17	0.77306 (16)	0.4895 (4)	0.00194 (7)	0.0272 (5)
H17	0.766256	0.624770	−0.021964	0.033*
C18	0.84965 (15)	0.3058 (4)	−0.00477 (7)	0.0280 (5)
C19	0.85706 (16)	0.1052 (4)	0.02960 (8)	0.0292 (5)
H19	0.907458	−0.024442	0.024417	0.035*
C20	0.79125 (16)	0.0947 (4)	0.07113 (8)	0.0286 (5)
H20	0.798320	−0.041196	0.094858	0.034*
C21	0.92289 (19)	0.5200 (4)	−0.07642 (8)	0.0359 (5)
H21A	0.855084	0.526514	−0.098361	0.054*

H21B	0.984219	0.510006	−0.098917	0.054*
H21C	0.929641	0.670099	−0.054729	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0360 (8)	0.0474 (10)	0.0286 (8)	−0.0034 (7)	−0.0033 (6)	0.0028 (7)
O18	0.0365 (8)	0.0419 (9)	0.0316 (8)	0.0035 (7)	0.0097 (6)	0.0034 (7)
C1	0.0286 (11)	0.0254 (11)	0.0295 (10)	−0.0004 (9)	0.0029 (8)	−0.0001 (8)
C2	0.0276 (11)	0.0302 (12)	0.0349 (11)	0.0004 (9)	0.0015 (9)	0.0013 (9)
C3	0.0269 (11)	0.0446 (14)	0.0386 (12)	−0.0028 (10)	−0.0013 (9)	0.0006 (10)
C4	0.0311 (12)	0.0480 (15)	0.0492 (14)	−0.0067 (11)	−0.0052 (10)	−0.0044 (11)
C5	0.0296 (12)	0.0532 (16)	0.0617 (16)	−0.0122 (11)	0.0023 (11)	0.0034 (13)
C6	0.0301 (12)	0.0476 (15)	0.0483 (14)	−0.0059 (11)	0.0080 (10)	0.0050 (11)
C7	0.0267 (11)	0.0410 (13)	0.0399 (12)	0.0024 (10)	0.0043 (9)	−0.0001 (10)
C8	0.0238 (10)	0.0275 (11)	0.0277 (10)	0.0017 (9)	0.0047 (8)	−0.0016 (8)
C9	0.0305 (11)	0.0337 (12)	0.0278 (10)	−0.0027 (9)	0.0023 (8)	0.0038 (9)
C10	0.0270 (11)	0.0337 (12)	0.0303 (11)	−0.0050 (9)	0.0018 (8)	−0.0020 (9)
C11	0.0243 (10)	0.0365 (12)	0.0243 (10)	0.0044 (9)	0.0023 (8)	−0.0025 (9)
C12	0.0304 (11)	0.0347 (12)	0.0279 (10)	0.0004 (10)	0.0059 (8)	0.0053 (9)
C13	0.0266 (10)	0.0320 (12)	0.0325 (11)	−0.0031 (9)	0.0054 (8)	−0.0016 (9)
C14	0.0372 (13)	0.0482 (15)	0.0318 (11)	−0.0032 (11)	−0.0059 (10)	−0.0058 (10)
C15	0.0223 (10)	0.0300 (11)	0.0278 (10)	−0.0030 (9)	−0.0019 (8)	−0.0020 (9)
C16	0.0225 (10)	0.0300 (12)	0.0318 (11)	0.0012 (9)	0.0004 (8)	0.0000 (9)
C17	0.0266 (10)	0.0291 (11)	0.0254 (10)	−0.0010 (9)	−0.0031 (8)	0.0052 (8)
C18	0.0228 (10)	0.0361 (12)	0.0249 (10)	−0.0032 (9)	0.0002 (8)	−0.0033 (9)
C19	0.0276 (11)	0.0287 (11)	0.0312 (11)	0.0031 (9)	0.0012 (8)	−0.0023 (9)
C20	0.0279 (11)	0.0284 (11)	0.0289 (10)	−0.0013 (9)	−0.0035 (8)	0.0023 (9)
C21	0.0401 (13)	0.0419 (14)	0.0263 (11)	−0.0034 (10)	0.0062 (9)	0.0023 (10)

Geometric parameters (Å, º)

O11—C11	1.375 (2)	C9—C10	1.391 (3)
O11—C14	1.428 (3)	C9—H9	0.9500
O18—C18	1.374 (2)	C10—C11	1.389 (3)
O18—C21	1.425 (3)	C10—H10	0.9500
C1—C2	1.340 (3)	C11—C12	1.386 (3)
C1—C15	1.495 (3)	C12—C13	1.382 (3)
C1—C8	1.498 (3)	C12—H12	0.9500
C2—C3	1.510 (3)	C13—H13	0.9500
C2—C7	1.514 (3)	C14—H14A	0.9800
C3—C4	1.526 (3)	C14—H14B	0.9800
C3—H3A	0.9900	C14—H14C	0.9800
C3—H3B	0.9900	C15—C16	1.395 (3)
C4—C5	1.527 (3)	C15—C20	1.396 (3)
C4—H4A	0.9900	C16—C17	1.393 (3)
C4—H4B	0.9900	C16—H16	0.9500
C5—C6	1.527 (3)	C17—C18	1.387 (3)

C5—H5A	0.9900	C17—H17	0.9500
C5—H5B	0.9900	C18—C19	1.390 (3)
C6—C7	1.527 (3)	C19—C20	1.376 (3)
C6—H6A	0.9900	C19—H19	0.9500
C6—H6B	0.9900	C20—H20	0.9500
C7—H7A	0.9900	C21—H21A	0.9800
C7—H7B	0.9900	C21—H21B	0.9800
C8—C13	1.394 (3)	C21—H21C	0.9800
C8—C9	1.396 (3)		

C11—O11—C14	117.29 (16)	C8—C9—H9	118.9
C18—O18—C21	116.93 (16)	C11—C10—C9	118.89 (19)
C2—C1—C15	122.85 (18)	C11—C10—H10	120.6
C2—C1—C8	123.65 (18)	C9—C10—H10	120.6
C15—C1—C8	113.49 (16)	O11—C11—C12	115.97 (18)
C1—C2—C3	123.51 (19)	O11—C11—C10	124.13 (19)
C1—C2—C7	124.49 (19)	C12—C11—C10	119.90 (18)
C3—C2—C7	111.92 (17)	C13—C12—C11	120.42 (19)
C2—C3—C4	110.22 (19)	C13—C12—H12	119.8
C2—C3—H3A	109.6	C11—C12—H12	119.8
C4—C3—H3A	109.6	C12—C13—C8	121.2 (2)
C2—C3—H3B	109.6	C12—C13—H13	119.4
C4—C3—H3B	109.6	C8—C13—H13	119.4
H3A—C3—H3B	108.1	O11—C14—H14A	109.5
C3—C4—C5	111.8 (2)	O11—C14—H14B	109.5
C3—C4—H4A	109.3	H14A—C14—H14B	109.5
C5—C4—H4A	109.3	O11—C14—H14C	109.5
C3—C4—H4B	109.3	H14A—C14—H14C	109.5
C5—C4—H4B	109.3	H14B—C14—H14C	109.5
H4A—C4—H4B	107.9	C16—C15—C20	117.61 (18)
C4—C5—C6	111.20 (18)	C16—C15—C1	122.07 (18)
C4—C5—H5A	109.4	C20—C15—C1	120.20 (18)
C6—C5—H5A	109.4	C17—C16—C15	121.17 (19)
C4—C5—H5B	109.4	C17—C16—H16	119.4
C6—C5—H5B	109.4	C15—C16—H16	119.4
H5A—C5—H5B	108.0	C18—C17—C16	119.82 (18)
C7—C6—C5	110.86 (19)	C18—C17—H17	120.1
C7—C6—H6A	109.5	C16—C17—H17	120.1
C5—C6—H6A	109.5	O18—C18—C17	124.63 (19)
C7—C6—H6B	109.5	O18—C18—C19	115.69 (18)
C5—C6—H6B	109.5	C17—C18—C19	119.67 (18)
H6A—C6—H6B	108.1	C20—C19—C18	119.87 (19)
C2—C7—C6	111.16 (19)	C20—C19—H19	120.1
C2—C7—H7A	109.4	C18—C19—H19	120.1
C6—C7—H7A	109.4	C19—C20—C15	121.82 (19)
C2—C7—H7B	109.4	C19—C20—H20	119.1
C6—C7—H7B	109.4	C15—C20—H20	119.1
H7A—C7—H7B	108.0	O18—C21—H21A	109.5

C13—C8—C9	117.31 (18)	O18—C21—H21B	109.5
C13—C8—C1	122.39 (18)	H21A—C21—H21B	109.5
C9—C8—C1	120.25 (18)	O18—C21—H21C	109.5
C10—C9—C8	122.21 (19)	H21A—C21—H21C	109.5
C10—C9—H9	118.9	H21B—C21—H21C	109.5
C15—C1—C2—C3	8.3 (3)	C9—C10—C11—C12	1.1 (3)
C8—C1—C2—C3	−171.7 (2)	O11—C11—C12—C13	178.76 (18)
C15—C1—C2—C7	−175.3 (2)	C10—C11—C12—C13	−1.5 (3)
C8—C1—C2—C7	4.7 (3)	C11—C12—C13—C8	0.3 (3)
C1—C2—C3—C4	120.3 (2)	C9—C8—C13—C12	1.4 (3)
C7—C2—C3—C4	−56.4 (2)	C1—C8—C13—C12	178.82 (18)
C2—C3—C4—C5	55.4 (2)	C2—C1—C15—C16	63.1 (3)
C3—C4—C5—C6	−54.9 (3)	C8—C1—C15—C16	−116.9 (2)
C4—C5—C6—C7	54.3 (3)	C2—C1—C15—C20	−121.1 (2)
C1—C2—C7—C6	−119.9 (2)	C8—C1—C15—C20	58.9 (2)
C3—C2—C7—C6	56.8 (2)	C20—C15—C16—C17	−0.7 (3)
C5—C6—C7—C2	−55.2 (2)	C1—C15—C16—C17	175.20 (18)
C2—C1—C8—C13	55.1 (3)	C15—C16—C17—C18	−0.2 (3)
C15—C1—C8—C13	−124.9 (2)	C21—O18—C18—C17	4.1 (3)
C2—C1—C8—C9	−127.6 (2)	C21—O18—C18—C19	−174.90 (17)
C15—C1—C8—C9	52.4 (3)	C16—C17—C18—O18	−177.26 (18)
C13—C8—C9—C10	−1.9 (3)	C16—C17—C18—C19	1.7 (3)
C1—C8—C9—C10	−179.38 (18)	O18—C18—C19—C20	176.66 (17)
C8—C9—C10—C11	0.7 (3)	C17—C18—C19—C20	−2.4 (3)
C14—O11—C11—C12	−171.17 (18)	C18—C19—C20—C15	1.6 (3)
C14—O11—C11—C10	9.1 (3)	C16—C15—C20—C19	0.0 (3)
C9—C10—C11—O11	−179.28 (18)	C1—C15—C20—C19	−175.98 (18)

3-[Bis(4-methoxyphenyl)methylidene]-5-phenyl-3H-1,2-dithiole (13)

Crystal data

$C_{24}H_{20}O_2S_2$	$F(000) = 848$
$M_r = 404.52$	$D_x = 1.342$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.2746$ (2) Å	Cell parameters from 89387 reflections
$b = 6.6094$ (1) Å	$\theta = 2.0$–$27.5°$
$c = 19.8754$ (3) Å	$\mu = 0.28$ mm^{-1}
$\beta = 93.5489$ (9)°	$T = 160$ K
$V = 2002.69$ (5) Å^3	Prism, red
$Z = 4$	0.30 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer	Absorption correction: multi-scan (Blessing, 1995)
Radiation source: Nonius FR590 sealed tube generator	$T_{min} = 0.863$, $T_{max} = 0.961$
Horizontally mounted graphite crystal monochromator	45139 measured reflections
Detector resolution: 9 pixels mm^{-1}	4597 independent reflections
φ and ω scans with κ offsets	3564 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.060$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$

$h = -19 \rightarrow 19$
$k = -8 \rightarrow 8$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 1.06$
4597 reflections
255 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch
Solvent used: n-hexane / EtOAc Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: on a glass fibre Mosaicity (deg.): 0.736 (1) Frames collected: 792 Seconds exposure per frame: 14 Degrees rotation per frame: 0.8 Crystal-detector distance (mm): 30.0 Client: Daniel Egli Sample code: 546-2 (HG0565)

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.81169 (3)	0.02969 (7)	0.18723 (2)	0.03566 (14)
S2	0.89382 (3)	−0.21239 (7)	0.21415 (2)	0.03574 (14)
O16	0.67096 (9)	−0.1967 (2)	−0.21293 (6)	0.0389 (3)
O23	0.51306 (9)	0.6949 (2)	0.13085 (7)	0.0441 (3)
C3	0.90450 (11)	−0.2908 (3)	0.13060 (8)	0.0279 (4)
C4	0.85607 (11)	−0.1924 (3)	0.08229 (8)	0.0279 (4)
H4	0.860230	−0.228548	0.036344	0.033*
C5	0.79763 (11)	−0.0314 (3)	0.10002 (8)	0.0279 (4)
C6	0.73775 (11)	0.0630 (3)	0.05719 (8)	0.0277 (4)
C7	0.96095 (11)	−0.4669 (3)	0.11990 (8)	0.0283 (4)
C8	1.03456 (12)	−0.5078 (3)	0.16258 (9)	0.0359 (4)
H8	1.049269	−0.420049	0.199431	0.043*
C9	1.08669 (14)	−0.6753 (3)	0.15186 (10)	0.0441 (5)
H9	1.137079	−0.700957	0.181060	0.053*
C10	1.06553 (14)	−0.8044 (3)	0.09904 (11)	0.0449 (5)
H10	1.100868	−0.919655	0.091785	0.054*
C11	0.99230 (14)	−0.7647 (3)	0.05653 (10)	0.0407 (5)
H11	0.977848	−0.852939	0.019764	0.049*
C12	0.94032 (12)	−0.5997 (3)	0.06684 (9)	0.0339 (4)
H12	0.889852	−0.575731	0.037556	0.041*
C13	0.72244 (11)	−0.0118 (3)	−0.01340 (8)	0.0281 (4)
C14	0.70204 (11)	−0.2129 (3)	−0.02748 (8)	0.0297 (4)

H14	0.699560	−0.306181	0.008715	0.036*
C15	0.68516 (11)	−0.2810 (3)	−0.09324 (8)	0.0297 (4)
H15	0.671967	−0.419523	−0.101704	0.036*
C16	0.68770 (12)	−0.1455 (3)	−0.14638 (8)	0.0304 (4)
C17	0.70759 (13)	0.0561 (3)	−0.13345 (9)	0.0354 (4)
H17	0.709595	0.149219	−0.169745	0.042*
C18	0.72452 (12)	0.1222 (3)	−0.06784 (9)	0.0336 (4)
H18	0.737784	0.260725	−0.059609	0.040*
C19	0.64583 (15)	−0.4012 (3)	−0.22711 (10)	0.0436 (5)
H19A	0.694770	−0.491668	−0.213957	0.065*
H19B	0.630435	−0.416033	−0.275459	0.065*
H19C	0.595035	−0.436246	−0.201640	0.065*
C20	0.68241 (11)	0.2331 (3)	0.07760 (8)	0.0283 (4)
C21	0.59439 (12)	0.2448 (3)	0.05283 (9)	0.0360 (4)
H21	0.571730	0.145202	0.022003	0.043*
C22	0.54040 (12)	0.3977 (3)	0.07233 (10)	0.0386 (4)
H22	0.480747	0.400656	0.055705	0.046*
C23	0.57236 (12)	0.5480 (3)	0.11616 (9)	0.0326 (4)
C24	0.65936 (12)	0.5441 (3)	0.14044 (8)	0.0294 (4)
H24	0.682115	0.647347	0.169811	0.035*
C25	0.71305 (11)	0.3863 (3)	0.12117 (8)	0.0274 (4)
H25	0.772490	0.383138	0.138299	0.033*
C26	0.54322 (15)	0.8527 (3)	0.17532 (11)	0.0490 (5)
H26A	0.561511	0.795153	0.219408	0.074*
H26B	0.495745	0.950193	0.180498	0.074*
H26C	0.593130	0.921443	0.156637	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0446 (3)	0.0360 (3)	0.0255 (2)	0.0130 (2)	−0.00476 (18)	−0.00565 (18)
S2	0.0447 (3)	0.0368 (3)	0.0250 (2)	0.0121 (2)	−0.00345 (18)	−0.00208 (18)
O16	0.0573 (9)	0.0346 (7)	0.0240 (6)	0.0020 (6)	−0.0041 (6)	−0.0017 (5)
O23	0.0405 (8)	0.0475 (8)	0.0444 (8)	0.0173 (6)	0.0041 (6)	−0.0042 (6)
C3	0.0298 (9)	0.0265 (9)	0.0275 (8)	−0.0008 (7)	0.0016 (7)	−0.0023 (7)
C4	0.0298 (9)	0.0287 (9)	0.0250 (8)	0.0004 (7)	0.0006 (6)	−0.0022 (7)
C5	0.0307 (9)	0.0277 (9)	0.0250 (8)	0.0008 (7)	0.0010 (7)	−0.0023 (7)
C6	0.0296 (9)	0.0287 (9)	0.0245 (8)	0.0013 (7)	0.0002 (6)	−0.0019 (7)
C7	0.0305 (9)	0.0264 (8)	0.0283 (8)	0.0012 (7)	0.0043 (7)	0.0028 (7)
C8	0.0366 (10)	0.0384 (10)	0.0326 (9)	0.0062 (8)	0.0002 (7)	0.0017 (8)
C9	0.0391 (11)	0.0498 (12)	0.0435 (11)	0.0153 (9)	0.0039 (9)	0.0108 (9)
C10	0.0504 (12)	0.0377 (11)	0.0478 (12)	0.0175 (9)	0.0141 (9)	0.0042 (9)
C11	0.0475 (12)	0.0343 (10)	0.0411 (11)	0.0045 (9)	0.0090 (9)	−0.0053 (8)
C12	0.0355 (10)	0.0317 (10)	0.0346 (9)	0.0014 (8)	0.0022 (7)	−0.0025 (7)
C13	0.0288 (9)	0.0303 (9)	0.0249 (8)	0.0045 (7)	−0.0011 (6)	0.0005 (7)
C14	0.0322 (9)	0.0308 (9)	0.0258 (8)	0.0007 (7)	−0.0007 (7)	0.0034 (7)
C15	0.0328 (9)	0.0266 (9)	0.0294 (8)	0.0001 (7)	−0.0003 (7)	0.0000 (7)
C16	0.0336 (9)	0.0336 (9)	0.0236 (8)	0.0062 (8)	−0.0015 (7)	−0.0011 (7)

C17	0.0476 (11)	0.0299 (9)	0.0283 (9)	0.0060 (8)	0.0000 (8)	0.0050 (7)
C18	0.0453 (11)	0.0250 (9)	0.0300 (9)	0.0048 (8)	−0.0017 (7)	0.0006 (7)
C19	0.0607 (13)	0.0381 (11)	0.0311 (9)	−0.0001 (10)	−0.0041 (9)	−0.0069 (8)
C20	0.0314 (9)	0.0297 (9)	0.0237 (8)	0.0019 (7)	0.0004 (6)	0.0025 (7)
C21	0.0326 (10)	0.0407 (11)	0.0339 (9)	0.0027 (8)	−0.0036 (7)	−0.0048 (8)
C22	0.0271 (9)	0.0469 (12)	0.0412 (10)	0.0073 (8)	−0.0020 (8)	−0.0016 (9)
C23	0.0340 (9)	0.0353 (10)	0.0290 (9)	0.0113 (8)	0.0069 (7)	0.0039 (7)
C24	0.0350 (9)	0.0291 (9)	0.0241 (8)	0.0018 (7)	0.0028 (7)	0.0026 (7)
C25	0.0276 (8)	0.0285 (9)	0.0262 (8)	0.0023 (7)	0.0018 (6)	0.0038 (7)
C26	0.0588 (14)	0.0428 (12)	0.0458 (12)	0.0206 (10)	0.0057 (10)	−0.0052 (9)

Geometric parameters (Å, º)

S1—C5	1.7797 (17)	C13—C18	1.400 (2)
S1—S2	2.0826 (6)	C14—C15	1.392 (2)
S2—C3	1.7568 (17)	C14—H14	0.9500
O16—C16	1.374 (2)	C15—C16	1.387 (2)
O16—C19	1.428 (2)	C15—H15	0.9500
O23—C23	1.371 (2)	C16—C17	1.387 (3)
O23—C26	1.425 (3)	C17—C18	1.384 (2)
C3—C4	1.343 (2)	C17—H17	0.9500
C3—C7	1.471 (2)	C18—H18	0.9500
C4—C5	1.446 (2)	C19—H19A	0.9800
C4—H4	0.9500	C19—H19B	0.9800
C5—C6	1.362 (2)	C19—H19C	0.9800
C6—C20	1.479 (2)	C20—C25	1.394 (2)
C6—C13	1.492 (2)	C20—C21	1.405 (2)
C7—C8	1.392 (2)	C21—C22	1.375 (3)
C7—C12	1.393 (2)	C21—H21	0.9500
C8—C9	1.388 (3)	C22—C23	1.390 (3)
C8—H8	0.9500	C22—H22	0.9500
C9—C10	1.375 (3)	C23—C24	1.386 (3)
C9—H9	0.9500	C24—C25	1.395 (2)
C10—C11	1.384 (3)	C24—H24	0.9500
C10—H10	0.9500	C25—H25	0.9500
C11—C12	1.372 (3)	C26—H26A	0.9800
C11—H11	0.9500	C26—H26B	0.9800
C12—H12	0.9500	C26—H26C	0.9800
C13—C14	1.389 (2)		

C5—S1—S2	96.33 (6)	C16—C15—H15	120.2
C3—S2—S1	94.22 (6)	C14—C15—H15	120.2
C16—O16—C19	117.06 (14)	O16—C16—C15	124.15 (16)
C23—O23—C26	117.24 (15)	O16—C16—C17	116.15 (15)
C4—C3—C7	125.56 (15)	C15—C16—C17	119.70 (16)
C4—C3—S2	116.95 (13)	C18—C17—C16	120.22 (16)
C7—C3—S2	117.35 (12)	C18—C17—H17	119.9
C3—C4—C5	120.21 (15)	C16—C17—H17	119.9

C3—C4—H4	119.9	C17—C18—C13	121.12 (17)
C5—C4—H4	119.9	C17—C18—H18	119.4
C6—C5—C4	125.84 (15)	C13—C18—H18	119.4
C6—C5—S1	122.73 (13)	O16—C19—H19A	109.5
C4—C5—S1	111.42 (12)	O16—C19—H19B	109.5
C5—C6—C20	123.39 (15)	H19A—C19—H19B	109.5
C5—C6—C13	119.74 (15)	O16—C19—H19C	109.5
C20—C6—C13	116.80 (14)	H19A—C19—H19C	109.5
C8—C7—C12	118.38 (16)	H19B—C19—H19C	109.5
C8—C7—C3	121.58 (16)	C25—C20—C21	117.06 (16)
C12—C7—C3	120.03 (16)	C25—C20—C6	123.17 (15)
C9—C8—C7	120.70 (18)	C21—C20—C6	119.78 (16)
C9—C8—H8	119.7	C22—C21—C20	121.28 (17)
C7—C8—H8	119.7	C22—C21—H21	119.4
C10—C9—C8	120.12 (19)	C20—C21—H21	119.4
C10—C9—H9	119.9	C21—C22—C23	120.56 (17)
C8—C9—H9	119.9	C21—C22—H22	119.7
C9—C10—C11	119.43 (18)	C23—C22—H22	119.7
C9—C10—H10	120.3	O23—C23—C24	124.82 (17)
C11—C10—H10	120.3	O23—C23—C22	115.35 (16)
C12—C11—C10	120.82 (19)	C24—C23—C22	119.80 (16)
C12—C11—H11	119.6	C23—C24—C25	119.07 (16)
C10—C11—H11	119.6	C23—C24—H24	120.5
C11—C12—C7	120.54 (18)	C25—C24—H24	120.5
C11—C12—H12	119.7	C20—C25—C24	122.21 (16)
C7—C12—H12	119.7	C20—C25—H25	118.9
C14—C13—C18	117.70 (16)	C24—C25—H25	118.9
C14—C13—C6	121.75 (15)	O23—C26—H26A	109.5
C18—C13—C6	120.49 (16)	O23—C26—H26B	109.5
C13—C14—C15	121.67 (16)	H26A—C26—H26B	109.5
C13—C14—H14	119.2	O23—C26—H26C	109.5
C15—C14—H14	119.2	H26A—C26—H26C	109.5
C16—C15—C14	119.59 (17)	H26B—C26—H26C	109.5

S1—S2—C3—C4	−5.04 (14)	C18—C13—C14—C15	0.7 (3)
S1—S2—C3—C7	178.96 (12)	C6—C13—C14—C15	178.01 (16)
C7—C3—C4—C5	174.91 (16)	C13—C14—C15—C16	−0.7 (3)
S2—C3—C4—C5	−0.7 (2)	C19—O16—C16—C15	2.8 (3)
C3—C4—C5—C6	−171.60 (18)	C19—O16—C16—C17	−176.79 (17)
C3—C4—C5—S1	7.5 (2)	C14—C15—C16—O16	−179.13 (16)
S2—S1—C5—C6	170.12 (15)	C14—C15—C16—C17	0.4 (3)
S2—S1—C5—C4	−9.01 (13)	O16—C16—C17—C18	179.34 (16)
C4—C5—C6—C20	−177.17 (16)	C15—C16—C17—C18	−0.2 (3)
S1—C5—C6—C20	3.8 (3)	C16—C17—C18—C13	0.3 (3)
C4—C5—C6—C13	5.9 (3)	C14—C13—C18—C17	−0.5 (3)
S1—C5—C6—C13	−173.05 (13)	C6—C13—C18—C17	−177.85 (17)
C4—C3—C7—C8	152.20 (18)	C5—C6—C20—C25	39.0 (3)
S2—C3—C7—C8	−32.2 (2)	C13—C6—C20—C25	−144.05 (17)

C4—C3—C7—C12	−29.1 (3)	C5—C6—C20—C21	−140.87 (18)
S2—C3—C7—C12	146.55 (14)	C13—C6—C20—C21	36.1 (2)
C12—C7—C8—C9	0.9 (3)	C25—C20—C21—C22	−1.8 (3)
C3—C7—C8—C9	179.62 (17)	C6—C20—C21—C22	178.06 (17)
C7—C8—C9—C10	−0.6 (3)	C20—C21—C22—C23	1.5 (3)
C8—C9—C10—C11	0.4 (3)	C26—O23—C23—C24	−1.1 (3)
C9—C10—C11—C12	−0.6 (3)	C26—O23—C23—C22	−179.63 (18)
C10—C11—C12—C7	0.9 (3)	C21—C22—C23—O23	178.62 (17)
C8—C7—C12—C11	−1.0 (3)	C21—C22—C23—C24	0.0 (3)
C3—C7—C12—C11	−179.76 (17)	O23—C23—C24—C25	−179.54 (16)
C5—C6—C13—C14	53.4 (2)	C22—C23—C24—C25	−1.1 (3)
C20—C6—C13—C14	−123.65 (18)	C21—C20—C25—C24	0.7 (2)
C5—C6—C13—C18	−129.38 (19)	C6—C20—C25—C24	−179.14 (15)
C20—C6—C13—C18	53.5 (2)	C23—C24—C25—C20	0.7 (3)