

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.524 (3)	C5—C9	1.416 (2)
C1—C7	1.517 (3)	C6—C7'	1.414 (2)
C2—C3	1.507 (3)	C7—C8	1.375 (2)
C3—C4	1.524 (3)	C8—C9	1.435 (2)
C4—C8	1.509 (2)	C9—C9'	1.425 (3)
C5—C6	1.357 (3)		
C2—C1—C7	112.7 (2)	C6'—C7—C8	119.5 (2)
C1—C2—C3	110.0 (2)	C4—C8—C7	121.3 (2)
C2—C3—C4	110.2 (2)	C4—C8—C9	119.3 (2)
C3—C4—C8	113.8 (2)	C7—C8—C9	119.5 (2)
C6—C5—C9	121.2 (2)	C5—C9—C8	122.0 (2)
C5—C6—C7'	121.8 (2)	C5—C9—C9'	117.4 (2)
C1—C7—C6'	118.4 (2)	C8—C9—C9'	120.6 (2)
C1—C7—C8	122.1 (2)		
C1—C2—C3—C4	−63.5 (2)	C4—C8—C7—C1	−3.5 (3)
C2—C3—C4—C8	45.3 (2)	C8—C7—C1—C2	−14.6 (3)
C3—C4—C8—C7	−12.1 (3)	C7—C1—C2—C3	47.6 (3)

Symmetry code: (i)  $-x, -y, -z$ .

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

The authors acknowledge the gift of the sample of octahydrochrysene from Dr A.-U. Rahman. We thank Dr J. C. Gallucci for help of various kinds. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data and torsion angles, together with a stereoview of the unit-cell contents, have been deposited with the IUCr (Reference: FG1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A, 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 Ferrier, W. G. & Iball, J. (1958). *Acta Cryst.* **11**, 325–329.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Rahman, A.-U. & Khan, A. A. (1962). *Chem. Ber.* **95**, 1786–1791.  
 Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.  
 Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.  
 Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

*Acta Cryst.* (1996). **C52**, 1243–1248

## Structural Aspects of the Transposition Reaction of Oxatricyclo[6.5.0.0<sup>2,7</sup>]tridecane-6,7-diol Monomesylate

SANDRA IANELLI,<sup>a</sup> MARIO NARDELLI,<sup>a\*</sup> DANIELE BELLETTI,<sup>a</sup> BRIGITTE JAMART-GRÉGOIRE,<sup>b</sup> SOPHIE MERCIER-GIRARDOT<sup>b</sup> AND PAUL CAUBÈRE<sup>b</sup>

<sup>a</sup>*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy, and*  
<sup>b</sup>*Laboratoire de Chimie Organique I, UA CNRS No. 457, Université de Nancy I, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France. E-mail: nardelli@ipruniv.cce.unipr.it*

(Received 17 May 1995; accepted 18 October 1995)

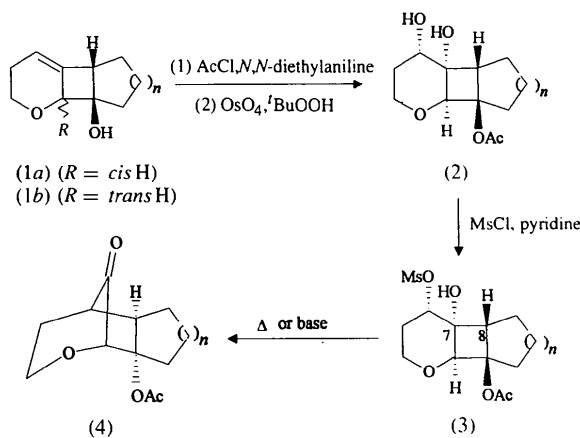
## Abstract

The structure and conformation of the molecules (1*RS*,-2*SR*,6*SR*,7*SR*,8*SR*)-6,7-dihydroxy-3-oxatricyclo[6.5.0.0<sup>2,7</sup>]tridec-1-yl acetate, (2), and (1*SR*,2*SR*,6*SR*,7*RS*)-11-oxo-10-oxatricyclo[5.3.1.0<sup>2,6</sup>]undec-2-yl acetate, (4), are illustrated and discussed. Crystals of (2) are triclinic, *P* $\bar{1}$ , with two molecules in the asymmetric unit which show small but significant differences in conformation. These molecules are joined in ribbons running along a crystallographic direction by a system of bifurcated intra- and intermolecular hydrogen bonds formed by the hydroxy groups. The tricyclic systems in the molecules of both compounds have an *anti* conformation with *cis* substitutions at the ring junctions. In (4) the keto group is transoid to the acyclic atoms at the junction of the two five-membered rings (with respect to the plane through the central ring).

## Comment

As part of a program dealing with new synthetic routes to heterocyclic derivatives (Caubère, 1991; Caubère, Caubère, Renard, Bizot-Espiart & Jamart-Grégoire, 1993; Caubère, Caubère, Ianelli, Nardelli & Jamart-Grégoire, 1994; Jamart-Grégoire, Léger & Caubère, 1990; Lalloz & Caubère, 1975), we previously showed that dehydropyranyl cyclobutanols (1) could be conveniently obtained by nucleophilic condensation of ketone enolates with 3,4-dihydrodihydropyran generated from 5-bromo-3,4-dihydropyran. On the other hand, we also previously showed that the carbocyclic analogues of the alcohols (1) could be easily transformed into polycyclic cyclopentane derivatives (Jamart-Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1993). Thus we thought that polycyclic tetrahydrofuran could be obtained in the same way. When the strategy previously

developed was applied to (1a), the expected tetrahydrofuran derivatives were obtained (Jamart-Grégoire, Mercier-Girardot, Ianelli, Nardelli & Caubère, 1995b). On the contrary, (1b) led to the unexpected products (4) whose structures were established with the help of the crystal structure analysis of (4) ( $n = 1$ ).



In order to understand this anomalous reaction we decided to study the structure of (3). Unfortunately we were unable to obtain suitable crystals, so we turned towards the study of the starting glycol esters and an acceptable crystal sample from them was obtained for (2) ( $n = 3$ ). Two interesting points emerged: (i) the bis-hydroxylation with OsO<sub>4</sub>-*t*BuOOH took place on the less hindered side of (1b); (ii) in contrast to what was observed with the carbocyclic series (Jamart-Grégoire *et al.*, 1993), the C7—C8 side of the four-membered ring was antiperiplanar to the C—O bond of the secondary hydroxy group. This structure explains the transposition observed and must be attributed to the presence of the O atom in the heterocyclic ring of (2).

Fig. 1 illustrates the molecular geometry for a type A molecule of (2) ( $n = 3$ ); molecules of type B are essentially identical in structure. In the following discussion, molecular geometry parameters for molecule A are given first, with those for B in square brackets. A systematic comparison of the coordinates of the two molecules has been carried out using the SYMMOL and ABRAHAMS routines of PARST (Nardelli, 1983a). This analysis showed that there are significant differences in the coordinates, particularly for the O and C atoms of the hydroxypyran ring. The half-normal probability plots (Abrahams & Keve, 1971) comparing coordinates and interatomic distances less than 4.65 Å indicate that the two molecules, although their geometry is otherwise very similar, have quite significant differences in conformation, probably because of packing effects. As indicated by the SYMMOL calculations and by the PLUTO (Motherwell & Clegg, 1976) drawing of the cell contents (Fig. 2), the two molecules are related by a pseudo twofold axis at  $y = 0.25$  (2) and  $z = 0.49$  (1) parallel to  $x$  with translation 0.30 (10).

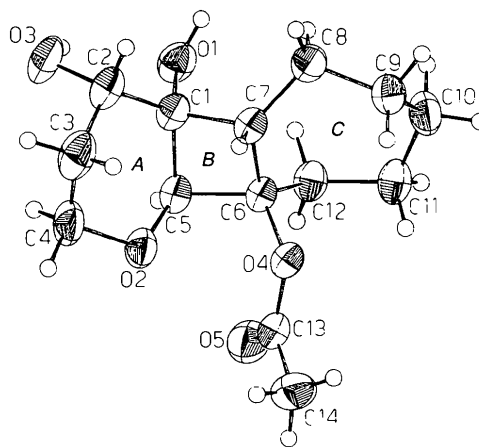


Fig. 1. ORTEP (Johnson, 1965) drawing of (2), molecule A. Ellipsoids are drawn at the 50% probability level.

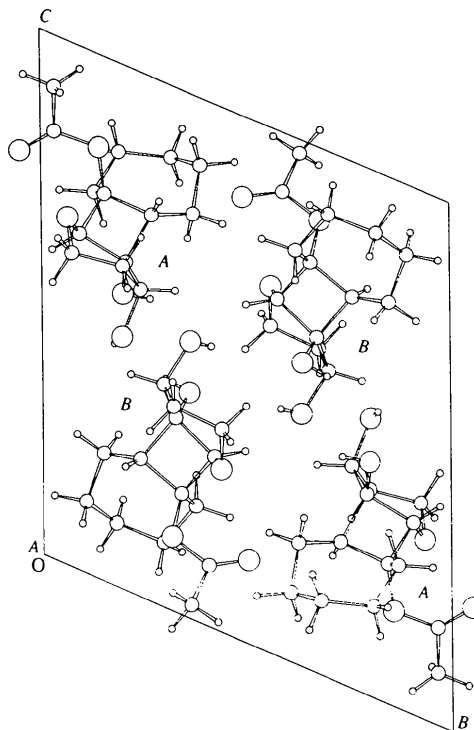


Fig. 2. Packing of the two independent molecules in the unit cell of (2).

The three-ring system is *cis,anti,cis* with the C1—C2 bond (–)antiperiplanar to C7—C8 and O2—C5 (+)antiperiplanar to C6—C12. The configurations at the chiral centres as shown in Fig. 1 are *S*(C1), *S*(C2), *S*(C5), *R*(C6), *S*(C7); the enantiomer is also present in the crystal, the space group being centrosymmetric. The relevant parameters describing the conformation of the three-ring system forming the core of the molecule are: for ring A,  $Q_T = 0.522$  (2) [0.520 (2) Å], DAP,  $\Delta_S$ (C1) = 0.008 (1) [0.034 (1)], sofa; for ring B,  $Q_T = 0.0645$  (5) [0.0567 (6) Å]; for ring C,  $Q_T = 0.811$  (2) [0.792 (2) Å],

DAP,  $\Delta_2(\text{C7}) = 0.0312(7)$  [0.0381(7)], twisted chair [where  $Q_T$  = total puckering amplitude (Cremer & Pople, 1975) and DAP = minimum displacement asymmetry parameter (Nardelli, 1983b)]. The dihedral angles formed by the least-squares planes through the rings are:  $A/B = 63.3(1)$  [62.2(1)],  $B/C = 36.6(1)$  [35.8(1)],  $A/C = 44.0(1)$  [39.2(1)°]. The cycloheptane ring approximates the TC conformation for which Hendrickson (1967) calculates a total strain energy of 27.9 kJ mol<sup>-1</sup>.

Fig. 3 shows the cisoid configuration at the junction of the two five-membered rings in (4) ( $n = 1$ ), with the keto group transoid to the acyclic atoms at that junction with respect to the plane through the central ring. The configurations at the chiral centres are  $S(\text{C1})$ ,  $R(\text{C5})$ ,  $R(\text{C6})$ ,  $S(\text{C7})$ ; the enantiomer is also present in the crystal, the space group being centrosymmetric.

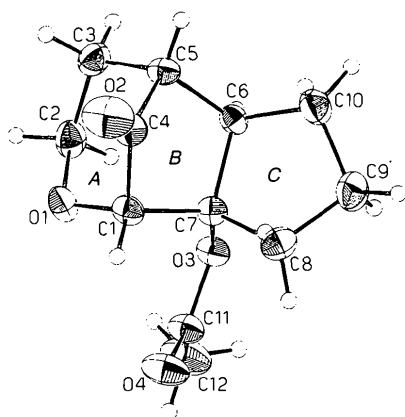


Fig. 3. ORTEP (Johnson, 1965) drawing of (4). Ellipsoids are drawn at the 50% probability level.

The values of the total puckering amplitudes of the three rings are 0.646(2) Å for the sofa conformation of the tetrahydropyran ring A, 0.455(2) Å for the cyclopentanone ring B, and 0.418(2) Å for the cyclopentane ring C, the latter two having envelope conformations. From the conformation point of view and not considering the acetoxy substituent, there is a local pseudo mirror along C2, C4, C9 and the midpoint of the C6—C7 bond. The least-squares planes through the three rings form the dihedral angles  $A/B = 84.1(1)$ ,  $B/C = 61.1(1)$  and  $A/C = 34.9(1)^\circ$ , with the C3—C5 bond (+)antiperiplanar to C6—C10 [C3—C5—C6—C10 = 157.6(2)°] and C1—O1 (–)antiperiplanar to C7—C8 [O1—C1—C7—C8 = –162.0(1)°].

The plane through the acetoxy group is approximately perpendicular to the mean plane through the B,C rings in both compounds, the O—C(acetoxy) bond being antiperiplanar to the C6—C7 junction: C13—O4—C6—C7 = 156.1(2) [159.6(2)°] in (2), C11—O3—C7—C6 = –171.6(1)° in (4).

To see to what extent packing forces in the crystal influence the molecular conformation, molecular-

mechanics calculations were carried out using both *MMX* and *MM+* force-fields of the *PCMODEL* (Serena Software, 1989) and *HYPERCHEM* (Autodesk Inc., 1992) systems of programs, respectively, considering isolated molecules with default parameters and starting the energy minimization process from the molecular structure experimentally found by the X-ray diffraction analysis. Comparison in terms of bond distances, bond angles and torsion angles with the averaged values from the experimental analysis (deposited) allows the following general comments. Firstly, a rough general evaluation of the disagreement between the experimental and calculated models is given by the following averages of the absolute values of the differences  $|\Delta|$ : compound (2)  $|\Delta|(\text{MMX})$  distances 0.013(2) Å, angles 1.2(2), torsions 2.7(2)°;  $|\Delta|(\text{MM+})$  0.023(5) Å, 1.6(3), 6.0(5)°; compound (4)  $|\Delta|(\text{MMX})$  distances 0.012(2) Å, angles 1.0(2), torsions 1.6(2)°;  $|\Delta|(\text{MM+})$  0.014(2) Å, 0.8(1), 1.4(2)°. Secondly, negative differences for bond distances can possibly be justified by the fact that the experimental values are not corrected for thermal motion. Third, for (2), the most relevant differences in bond angles are observed for angles (C6—O4—C13, C5—C6—C12, C1—C7—C8) involving the acetoxy substituent attachment; for (4), the largest difference in bond angles is observed for the value of C7—O3—C11 calculated by *MMX*. Fourth, as commonly observed, the torsion angles are the parameters showing the largest discrepancies, probably produced by packing interactions not considered in the calculated models.

Non-bonded energy calculations show that the orientation of the acetoxy group in both compounds is mainly determined by intramolecular steric hindrance, as the minima of the energy profiles calculated by rotating the group about the C(junction)—O(acetoxy) bond for the isolated molecules are displaced by not more than ca 5° with respect to the orientations found in the crystals.

In both molecules of (2) the O3 hydroxy group acts as a donor in an intramolecular hydrogen bond and an acceptor in an intermolecular hydrogen bond (see Table 2); the latter joins the molecules about the pseudo twofold axis relating the two independent molecules to form ribbons running in the  $x$  direction. Packing of these ribbons is due to van der Waals contacts (Fig. 2).

The analysis of 'thermal' motion of the molecules in the crystals, carried out in terms of the Schomaker & Trueblood (1968) TLS rigid-body approximation using the *THMV* program (Trueblood, 1984), gives the following values for the residual disagreement index  $R_{wU} \{= [\sum(w\Delta U)^2/\sum(wU_o)^2]^{1/2}$ , where  $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})\}$ : 0.090 [0.104] for (2) and 0.107 for (4). These values improve to 0.065 [0.085] and 0.092, respectively, if internal motions are taken into account according to Dunitz & White (1973). No particular indication is found for static disorder, as evidenced by the values of  $U_{eq}$  and anisotropy ratios.

## Experimental

Compound (2) ( $n = 3$ ) was obtained by esterification (Hogle, Treglich & Vorbroggen, 1972) followed by bishydroxylation (Minato, Yamamoto & Tsuji, 1990) of (1*RS*,2*SR*,8*SR*)-3-oxatricyclo[6.5.0.0<sup>2,7</sup>]tridec-6-en-1-ol, synthesized as described by Jamart-Grégoire, Mercier-Girardot, Ianelli, Nardelli & Caubère (1995a). Full details of this preparation will be published elsewhere. Compound (4) ( $n = 1$ ) was prepared by monomesylation of (1*RS*,2*SR*,6*SR*,7*SR*,8*SR*)-3-oxatricyclo[6.3.0.0<sup>2,7</sup>]undec-6,7-diol (1.2 equiv. MsCl, 16 equiv. pyridine in CH<sub>2</sub>Cl<sub>2</sub>, 24 h at room temperature) followed by action of 3 equiv. of NaH in tetrahydrofuran for 48 h at room temperature (Jamart-Grégoire, Mercier-Girardot, Ianelli, Nardelli & Caubère, 1995a).

## Compound (2)

### Crystal data

C<sub>14</sub>H<sub>22</sub>O<sub>5</sub> $M_r = 270.33$ 

Triclinic

 $P\bar{1}$  $a = 7.909 (3) \text{ \AA}$  $b = 12.608 (9) \text{ \AA}$  $c = 15.303 (11) \text{ \AA}$  $\alpha = 112.13 (4)^\circ$  $\beta = 104.58 (5)^\circ$  $\gamma = 91.52 (4)^\circ$  $V = 1355 (2) \text{ \AA}^3$  $Z = 4$  $D_x = 1.325 \text{ Mg m}^{-3}$ 

### Data collection

Siemens AED diffractometer

 $\theta$ - $2\theta$  scans

Absorption correction:

none

5167 measured reflections

5167 independent reflections

3235 observed reflections

 $[I > 2\sigma(I)]$ Cu  $K\alpha$  radiation $\lambda = 1.54178 \text{ \AA}$ 

Cell parameters from 29

reflections

 $\theta = 18.92\text{--}37.24^\circ$  $\mu = 0.825 \text{ mm}^{-1}$  $T = 293 (2) \text{ K}$ 

Prism

 $0.40 \times 0.32 \times 0.23 \text{ mm}$ 

Colourless

O4A	0.2781 (2)	-0.1427 (1)	-0.82117 (8)	0.0443 (5)
O5A	0.3530 (2)	0.0510 (1)	-0.7507 (1)	0.0655 (7)
C1A	0.3559 (2)	-0.2071 (2)	-0.6233 (1)	0.0429 (7)
C2A	0.2156 (3)	-0.2436 (2)	-0.5829 (1)	0.0534 (8)
C3A	0.0445 (3)	-0.1992 (2)	-0.6126 (2)	0.0638 (11)
C4A	0.0790 (3)	-0.0745 (2)	-0.5964 (2)	0.0603 (11)
C5A	0.3466 (2)	-0.0935 (2)	-0.6395 (1)	0.0414 (8)
C6A	0.3948 (2)	-0.1555 (1)	-0.7368 (1)	0.0379 (7)
C7A	0.3392 (2)	-0.2724 (2)	-0.7347 (1)	0.0407 (7)
C8A	0.4365 (3)	-0.3747 (2)	-0.7706 (1)	0.0503 (9)
C9A	0.4691 (3)	-0.3935 (2)	-0.8699 (1)	0.0529 (9)
C10A	0.6355 (3)	-0.3213 (2)	-0.8610 (2)	0.0589 (10)
C11A	0.6320 (3)	-0.1921 (2)	-0.8288 (2)	0.0565 (10)
C12A	0.5875 (2)	-0.1302 (2)	-0.7317 (1)	0.0463 (8)
C13A	0.2634 (3)	-0.0341 (2)	-0.8160 (1)	0.0511 (9)
C14A	0.1210 (4)	-0.0350 (3)	-0.9011 (2)	0.0743 (13)
O1B	0.0992 (2)	-0.3624 (2)	-0.4255 (1)	0.0654 (7)
O2B	-0.1951 (2)	-0.4387 (1)	-0.30496 (9)	0.0502 (5)
O3B	-0.2328 (3)	-0.3657 (2)	-0.5246 (1)	0.0758 (9)
O4B	0.0516 (2)	-0.3181 (1)	-0.13891 (8)	0.0466 (5)
O5B	0.0375 (2)	-0.5047 (1)	-0.1569 (1)	0.0683 (8)
C1B	-0.0182 (2)	-0.3283 (2)	-0.3659 (1)	0.0458 (7)
C2B	-0.1883 (3)	-0.2994 (2)	-0.4205 (1)	0.0562 (9)
C3B	-0.3424 (3)	-0.3235 (2)	-0.3857 (2)	0.0555 (9)
C4B	-0.3442 (3)	-0.4402 (2)	-0.3812 (2)	0.0533 (9)
C5B	-0.0325 (2)	-0.4223 (2)	-0.3237 (1)	0.0435 (7)
C6B	0.1064 (2)	-0.3420 (2)	-0.2274 (1)	0.0418 (7)
C7B	0.0737 (3)	-0.2403 (2)	-0.2592 (1)	0.0429 (7)
C8B	0.2253 (3)	-0.1502 (2)	-0.2397 (1)	0.0557 (9)
C9B	0.3481 (3)	-0.1059 (2)	-0.1347 (2)	0.0600 (10)
C10B	0.4886 (3)	-0.1805 (2)	-0.1185 (2)	0.0641 (10)
C11B	0.4274 (3)	-0.2975 (2)	-0.1214 (2)	0.0630 (10)
C12B	0.2892 (3)	-0.3773 (2)	-0.2160 (2)	0.0539 (10)
C13B	0.0157 (2)	-0.4072 (2)	-0.1145 (1)	0.0519 (9)
C14B	-0.0552 (4)	-0.3643 (3)	-0.0268 (2)	0.0704 (13)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (2)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O3A—H30A $\cdots$ O1A	0.81 (2)	2.13 (3)	2.647 (3)	122 (2)
O3B—H30B $\cdots$ O1B	0.86 (3)	2.18 (3)	2.672 (3)	116 (3)
O1B—H10B $\cdots$ O3A	0.84 (3)	2.11 (3)	2.913 (3)	160 (3)
O1A—H10A $\cdots$ O3B	0.89 (3)	2.18 (3)	2.973 (3)	148 (3)

Symmetry code: (i)  $1 + x, y, z$ .

### Refinement

Refinement on  $F^2$  $R(F) = 0.0343$  $R(F^2) = 0.0980$  $S = 1.050$ 

5167 reflections

520 parameters

All H-atom parameters

refined

 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} = -0.004$  $\theta_{\text{max}} = 70.25^\circ$  $h = -9 \rightarrow 9$  $k = -15 \rightarrow 0$  $l = -17 \rightarrow 18$ 

1 standard reflection

monitored every 50

reflections

intensity decay: none

 $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$ 

Extinction correction:

*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:

0.0034 (3)

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
O1A	0.5279 (2)	-0.1992 (1)	-0.56044 (9)	0.0534 (6)
O2A	0.1742 (2)	-0.0649 (1)	-0.66177 (9)	0.0527 (6)
O3A	0.2715 (2)	-0.1968 (2)	-0.4773 (1)	0.0670 (8)

Table 3. Comparison of selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for the two independent molecules of (2)

	A	B	Average
O1—C1	1.431 (2)	1.425 (3)	1.429 (3)
O2—C4	1.431 (3)	1.428 (3)	1.429 (2)
O2—C5	1.411 (2)	1.412 (3)	1.411 (2)
O3—C2	1.437 (3)	1.435 (3)	1.436 (2)
O4—C6	1.452 (2)	1.452 (3)	1.452 (2)
O4—C13	1.351 (3)	1.355 (3)	1.353 (2)
O5—C13	1.203 (2)	1.195 (3)	1.201 (4)
C1—C2	1.535 (3)	1.527 (3)	1.531 (4)
C1—C5	1.544 (3)	1.561 (3)	1.553 (8)
C1—C7	1.557 (3)	1.555 (2)	1.556 (2)
C2—C3	1.508 (3)	1.513 (4)	1.510 (2)
C3—C4	1.503 (4)	1.499 (4)	1.501 (3)
C5—C6	1.550 (3)	1.551 (2)	1.551 (2)
C6—C7	1.542 (3)	1.540 (3)	1.541 (2)
C6—C12	1.525 (3)	1.512 (3)	1.518 (7)
C7—C8	1.514 (3)	1.520 (3)	1.517 (3)
C8—C9	1.536 (4)	1.532 (3)	1.533 (2)
C9—C10	1.527 (4)	1.508 (4)	1.518 (9)
C10—C11	1.518 (4)	1.521 (4)	1.520 (3)
C11—C12	1.531 (3)	1.533 (3)	1.532 (2)
C13—C14	1.488 (4)	1.501 (4)	1.495 (7)
C4—O2—C5	112.5 (2)	113.3 (2)	112.9 (4)
C6—O4—C13	117.4 (2)	118.9 (2)	118.2 (8)
O1—C1—C7	113.7 (2)	113.4 (2)	113.5 (1)
O1—C1—C5	107.2 (2)	106.6 (2)	106.9 (3)
O1—C1—C2	109.7 (2)	111.3 (2)	110.5 (8)

C5—C1—C7	88.6 (2)	88.4 (2)	88.5 (1)
C2—C1—C7	117.7 (2)	116.9 (2)	117.3 (4)
C2—C1—C5	118.3 (2)	118.2 (2)	118.2 (1)
O3—C2—C1	110.8 (2)	111.9 (2)	111.3 (5)
C1—C2—C3	111.2 (2)	111.3 (2)	111.2 (1)
O3—C2—C3	106.8 (2)	107.5 (2)	107.2 (3)
C2—C3—C4	110.2 (2)	110.1 (2)	110.1 (1)
O2—C4—C3	109.5 (2)	109.4 (2)	109.4 (1)
O2—C5—C1	113.8 (2)	115.0 (2)	114.4 (6)
C1—C5—C6	88.4 (2)	88.6 (2)	88.5 (1)
O2—C5—C6	108.8 (2)	110.2 (2)	109.5 (7)
O4—C6—C5	113.9 (1)	114.4 (2)	114.0 (2)
C5—C6—C12	115.3 (2)	114.3 (2)	114.8 (5)
C5—C6—C7	88.9 (2)	89.3 (2)	89.1 (2)
O4—C6—C12	110.9 (2)	111.6 (2)	111.2 (3)
O4—C6—C7	109.9 (2)	108.5 (2)	109.2 (7)
C7—C6—C12	116.2 (2)	117.1 (2)	116.6 (5)
C1—C7—C6	88.2 (2)	89.2 (2)	88.7 (5)
C6—C7—C8	121.1 (2)	120.8 (2)	120.9 (1)
C1—C7—C8	121.2 (2)	120.3 (2)	120.7 (4)
C7—C8—C9	112.6 (2)	113.4 (2)	113.0 (4)
C8—C9—C10	113.8 (2)	114.7 (2)	114.2 (4)
C9—C10—C11	116.7 (2)	116.9 (2)	116.8 (1)
C10—C11—C12	116.2 (2)	115.7 (2)	115.9 (3)
C6—C12—C11	114.4 (2)	114.5 (2)	114.4 (1)
O4—C13—O5	124.0 (2)	124.6 (3)	124.2 (3)
O5—C13—C14	125.3 (2)	125.9 (2)	125.6 (3)
O4—C13—C14	110.7 (2)	109.5 (2)	110.1 (6)

C4—O2—C5—C6	144.4 (2)	141.0 (2)	142.7 (17)
C4—O2—C5—C1	47.6 (2)	42.8 (2)	45 (2)
C6—O4—C13—C14	-171.9 (2)	-174.4 (2)	-173.1 (13)
C13—O4—C6—C7	156.1 (2)	159.6 (2)	157.9 (18)
O1—C1—C2—O3	33.7 (3)	30.3 (3)	32.0 (17)
O1—C1—C5—O2	-154.1 (2)	-150.4 (2)	-152.2 (19)
C2—C1—C5—O2	-29.4 (3)	-24.2 (3)	-27 (3)
O1—C1—C7—C8	35.9 (3)	34.5 (3)	35.2 (7)
C2—C1—C7—C8	-94.4 (2)	-97.1 (2)	-95.7 (13)
O2—C5—C6—O4	15.1 (2)	10.0 (2)	13 (3)
O2—C5—C6—C12	145.0 (2)	140.4 (2)	143 (2)
C7—C6—C12—C11	78.1 (2)	77.0 (3)	77.8 (5)
C12—C6—C7—C8	-26.3 (3)	-24.4 (3)	-25.3 (9)
C6—C7—C8—C9	-46.5 (3)	-46.7 (3)	-46.6 (2)
C7—C8—C9—C10	85.3 (3)	83.8 (3)	84.6 (8)
C8—C9—C10—C11	-70.3 (3)	-69.8 (3)	-70.1 (3)
C9—C10—C11—C12	55.4 (3)	56.6 (3)	56.0 (6)
C10—C11—C12—C6	-72.3 (3)	-73.3 (3)	-72.8 (5)

**Compound (4)***Crystal data*C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>M<sub>r</sub> = 224.26

Orthorhombic

*Pbca*

a = 14.815 (2) Å

b = 14.264 (2) Å

c = 10.550 (2) Å

V = 2229.4 (6) Å<sup>3</sup>

Z = 8

D<sub>x</sub> = 1.336 Mg m<sup>-3</sup>*Data collection*

Siemens AED diffractometer

θ-2θ scans

Absorption correction:

none

4122 measured reflections

2114 independent reflections

1961 observed reflections

[I &gt; 2σ(I)]

R<sub>int</sub> = 0.0410

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 30

reflections

θ = 18.32–39.89°

μ = 0.827 mm<sup>-1</sup>

T = 293 (2) K

Thick tablet

0.31 × 0.26 × 0.23 mm

Colourless

θ<sub>max</sub> = 70.09°

h = -18 → 17

k = -9 → 17

l = -1 → 12

1 standard reflection

monitored every 50

reflections

intensity decay: none

*Refinement*Refinement on F<sup>2</sup>

R(F) = 0.0493

R(F<sup>2</sup>) = 0.1309

S = 1.119

2111 reflections

210 parameters

All H-atom parameters

refined

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.04P)<sup>2</sup>

+ 0.89P]

where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3(Δ/σ)<sub>max</sub> < 0.001Δρ<sub>max</sub> = 0.29 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.23 e Å<sup>-3</sup>

Extinction correction:

SHELXL93 (Sheldrick,  
1993)

Extinction coefficient:

0.0049 (4)

Atomic scattering factors

from *International Tables*  
for *Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (4)
$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U <sub>eq</sub>
O1	0.94758 (8)	0.13859 (9)	0.5081 (1)	0.0438 (4)
O2	0.7813 (1)	0.0229 (1)	0.6316 (1)	0.0694 (6)
O3	0.86143 (8)	0.28458 (8)	0.3799 (1)	0.0346 (3)
O4	0.9092 (1)	0.3566 (1)	0.5581 (1)	0.0575 (5)
C1	0.8573 (1)	0.1611 (1)	0.5462 (2)	0.0339 (5)
C2	0.9554 (1)	0.0988 (1)	0.3827 (2)	0.0453 (6)
C3	0.8885 (1)	0.0212 (1)	0.3580 (2)	0.0452 (6)
C4	0.8050 (1)	0.0692 (1)	0.5428 (2)	0.0390 (5)
C5	0.7936 (1)	0.0497 (1)	0.4038 (2)	0.0357 (5)
C6	0.7664 (1)	0.1465 (1)	0.3516 (2)	0.0309 (5)
C7	0.8048 (1)	0.2192 (1)	0.4492 (1)	0.0299 (4)
C8	0.7216 (1)	0.2689 (1)	0.5029 (2)	0.0433 (6)
C9	0.6528 (1)	0.2639 (2)	0.3954 (2)	0.0552 (8)
C10	0.6642 (1)	0.1642 (2)	0.3478 (2)	0.0464 (6)
C11	0.9116 (1)	0.3469 (1)	0.4453 (2)	0.0409 (5)
C12	0.9704 (2)	0.4018 (2)	0.3578 (3)	0.0645 (9)

Table 5. Selected geometric parameters (Å, °) for (4)

O1—C1	1.432 (2)	C3—C5	1.540 (3)
O1—C2	1.444 (2)	C4—C5	1.502 (2)
O2—C4	1.200 (2)	C5—C6	1.541 (2)
O3—C7	1.452 (2)	C6—C7	1.568 (2)
O3—C11	1.349 (2)	C6—C10	1.536 (2)
O4—C11	1.199 (2)	C7—C8	1.530 (2)
C1—C4	1.523 (2)	C8—C9	1.527 (3)
C1—C7	1.530 (2)	C9—C10	1.518 (3)
C2—C3	1.509 (3)	C11—C12	1.491 (3)
C1—O1—C2	114.83 (13)	C10—C6—C5	114.46 (15)
C11—O3—C7	118.94 (13)	C10—C6—C7	105.46 (13)
O1—C1—C4	106.01 (13)	O3—C7—C1	113.03 (12)
O1—C1—C7	114.11 (13)	O3—C7—C6	107.65 (12)
C4—C1—C7	101.03 (13)	O3—C7—C8	110.77 (13)
O1—C2—C3	113.2 (2)	C1—C7—C6	105.37 (12)
C2—C3—C5	110.60 (15)	C1—C7—C8	114.40 (14)
O2—C4—C1	127.2 (2)	C8—C7—C6	104.91 (13)
O2—C4—C5	128.9 (2)	C9—C8—C7	103.94 (15)
C5—C4—C1	103.89 (13)	C8—C9—C10	102.5 (2)
C4—C5—C3	104.65 (15)	C6—C10—C9	104.72 (15)
C3—C5—C6	111.26 (14)	O3—C11—C12	110.6 (2)
C4—C5—C6	102.23 (13)	O4—C11—O3	124.6 (2)
C5—C6—C7	105.27 (12)	O4—C11—C12	124.9 (2)
C2—O1—C1—C7	-50.2 (2)	C2—C3—C5—C6	50.8 (2)
C11—O3—C7—C1	-55.7 (2)	C3—C5—C6—C10	157.6 (2)
C11—O3—C7—C6	-171.6 (1)	C5—C6—C10—C9	137.2 (2)
C11—O3—C7—C8	74.2 (2)	C1—C7—C8—C9	-143.6 (2)
O1—C1—C7—C8	-162.0 (1)		

For both compounds the integrated intensities were obtained by a modified version (Belletti, Uguzzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure, and corrected for Lorentz and

polarization effects, but not for absorption. The scan speed was 3–12° min<sup>-1</sup> with width (1.2 + 0.14tanθ)°. The structures were solved by direct methods and refined by anisotropic full-matrix least squares. All the H atoms were found from Δρ maps and refined isotropically.

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980) for (2) and *SIR92* (Altomare *et al.*, 1994) for (4). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1976). Programs for checking the space group of (2): *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988), *MISSYM* (Le Page, 1987) and the *SYMMOL* option of *PARST* (Nardelli, 1983a). Software used for geometrical calculations and to prepare material for publication: *PARST*, *PARSTCIF* (Nardelli, 1991). The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma) and on a COMPAQ-486c portable computer.

Financial support from the European Commission under contract N. SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.  
 Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.  
 Autodesk Inc. (1992). *HYPERCHEM*. Version 2.0. Autodesk Inc., 2320 Marinship Way, Sansalito, CA 94965, USA.  
 Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffratometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo 220*. Internal Report 1–3/79. Centro di Studio per la Strutturistica Diffattometrica del CNR, Parma, Italy.  
 Caubère, P. (1991). *Rev. Heteroatom. Chem.* **4**, 78–139.  
 Caubère, C., Caubère, P., Ianelli, S., Nardelli, M. & Jamart-Grégoire, B. (1994). *Tetrahedron*, **54**, 11903–11920.  
 Caubère, C., Caubère, P., Renard, P., Bizot-Espiart, J. G. & Jamart-Grégoire, B. (1993). *Tetrahedron Lett.* **34**, 6889–6892.  
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.  
 Dunitz, J. D. & Withe, D. N. J. (1973). *Acta Cryst.* **A29**, 148–150.  
 Hendrickson, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7043.  
 Hogle, G., Treglich, W. & Vorbroggen, H. (1972). *Synthesis*, pp. 619–621.  
 Jamart-Grégoire, B., Brosse, N., Ianelli, S., Nardelli, M. & Caubère, P. (1993). *J. Org. Chem.* **58**, 4572–4578.  
 Jamart-Grégoire, B., Léger, C. & Caubère, P. (1990). *Tetrahedron Lett.* **31**, 7599–7602.  
 Jamart-Grégoire, B., Mercier-Girardot, S., Ianelli, S., Nardelli, M. & Caubère, P. (1995a). *Synlett*, **7**, 742–744.  
 Jamart-Grégoire, B., Mercier-Girardot, S., Ianelli, S., Nardelli, M. & Caubère, P. (1995b). *Tetrahedron*, **51**, 1973–1984.  
 Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 Lalloz, L. & Caubère, P. (1975). *J. Chem. Soc. Chem. Commun.* p. 745.

- Lawton, S. L. & Jacobson, R. A. (1965). *The Reduced Cell and its Crystallographic Applications*. Ames Laboratory. Available from the Clearinghouse for Federal Scientific and Technical Information, National Institute of Standards and Technology, US Department of Commerce, Springfield, Virginia, USA.  
 Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–589.  
 Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.  
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.  
 Minato, M., Yamamoto, K. & Tsuji, J. (1990). *J. Org. Chem.* **55**, 766–768.  
 Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.  
 Mugnoli, A. (1985). *J. Appl. Cryst.* **18**, 183–184.  
 Nardelli, M. (1983a). *Comput. Chem.* **7**, 95–98.  
 Nardelli, M. (1983b). *Acta Cryst.* **C39**, 1141–1142.  
 Nardelli, M. (1991). *PARSTCIF. Program for Creating a CIF from the Output of PARST*. University of Parma, Italy.  
 Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.  
 Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.  
 Serena Software (1989). *PCMODEL*. Version 4.0. Serena Software, Bloomington, IN 47402–3076, USA.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Spek, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.  
 Trueblood, K. N. (1984). *THMV. Program for Thermal Motion Analysis*. University of California, Los Angeles, USA.

*Acta Cryst.* (1996). **C52**, 1248–1250

## 2,3,6,7-Tetrakis(methylthio)benzo[b]thiophene

M. PARVEZ,\* S. T. E. MESHER AND P. D. CLARK

Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4.  
 E-mail: parvez@acs.ucalgary.ca

(Received 21 July 1995; accepted 17 November 1995)

## Abstract

Crystals of the title compound, C<sub>12</sub>H<sub>14</sub>S<sub>5</sub>, are composed of independent molecules separated by normal van der Waals distances. The benzothiophene moiety is essentially planar and substituted by four methylthio groups, two of which, those at positions 2 and 6, lie almost in the plane, with the remaining two, those at positions 3 and 7, lying almost perpendicular to the plane. The mean values of the important bond distances are S—C<sub>sp<sup>3</sup></sub>, 1.805 (17) and S—C<sub>sp<sup>2</sup></sub>, 1.767 (19) Å.

## Comment

The one-step thioalkylation of heteroaromatic compounds is a desirable process as it can lead to the for-