International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KOBAYASHI, H., KOBAYASHI, A., SASAKI, Y., SAITO, G., ENOKI, T. & INOKUCHI, H. (1983). *J. Am. Chem. Soc.* **105**, 297–298.
MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
PAPAVASSILIOU, G. C., YIANNOPOULOS, S. Y. & ZAMBOURIS, J. S. (1985). *Mol. Cryst. Liq. Cryst.* **120**, 333–336.
PARKIN, S. S. P., ENGLER, E. M., SCHUMAKER, R. R., LAGIER, R., LEE, V. Y., SCOTT, J. C. & GREENE, R. L. (1983). *Phys. Rev. Lett.* **50**, 270–273.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHIBAEVA, R. P. (1982). *Extended Linear Chain Compounds*, pp. 435–467. New York: Plenum.
WHANGBO, M. H., WILLIAMS, J. M., BENO, M. A. & DORFMAN, J. R. (1983). *J. Am. Chem. Soc.* **105**, 645–646.

Acta Cryst. (1986). C**42**, 1587–1589

Structure of *rel*-(3*R*,3a*S*,7a*S*)-Hexahydro-4,4-dimethoxy-3-(methylthio)-3-pentyl-2(3*H*)-benzo[*b*]furanone

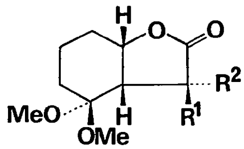
BY R. BAKER,* C. L. GIBSON, L. R. GRAY AND M. WEBSTER

Department of Chemistry, The University, Southampton SO9 5NH, England

(*Received* 18 *March* 1986; *accepted* 3 *June* 1986)

Abstract. $C_{16}H_{28}O_4S$, $M_r = 316{\cdot}5$, triclinic, $P\bar{1}$, $a = 15{\cdot}964\,(2)$, $b = 13{\cdot}261\,(2)$, $c = 9{\cdot}019\,(1)$ Å, $\alpha = 110{\cdot}82\,(1)$, $\beta = 89{\cdot}57\,(1)$, $\gamma = 103{\cdot}48\,(1)°$, $V = 1729{\cdot}5$ Å^3, $Z = 4$, $D_m = 1{\cdot}26\,(2)$ by flotation, $D_x = 1{\cdot}215$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}59$ cm^{-1}, $F(000) = 688$, room temperature, $R = 0{\cdot}066$ for 3048 reflections [$F > 2\sigma(F)$]. The structure contains two crystallographically independent molecules with similar geometry. The six-membered ring (chair conformation) is linked *cis* to the furanone. The stereochemistry of the introduced methylthio substituent is established as *endo*, bond lengths S—C(methyl) 1·797 (7) and 1·796 (5) Å, S—C(ring) 1·850 (5) and 1·842 (4) Å.

Introduction. During the course of model studies directed towards the synthesis of paniculides B and C (Baker, Gibson, Swain & Tapolczay, 1985), the title compound (2) was prepared by the treatment of bicyclic lactone (1) with lithium diisopropylamide followed by dimethyl disulfide. The stereochemistry of the introduced methylthio ether moiety could not be unequivocally elucidated from the ^{1}H NMR. As a *cis* relationship between the methylthio substituent and the adjacent methine is crucial for the generation of an endocyclic double bond (Grieco & Reap, 1974, and references therein), an X-ray structure analysis of the title compound (2) was undertaken.



(1) $R^1 = C_5H_{11}$, $R^2 = H$ (2) $R^1 = C_5H_{11}$, $R^2 = SCH_3$
(3) $R^1 = SCH_3$, $R^2 = C_5H_{11}$ (4) $R^1 = SC_6H_5$, $R^2 = C_5H_{11}$

Experimental. Enraf–Nonius CAD-4 diffractometer, ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation ($1{\cdot}5 \leq \theta \leq 22°$). Cell constants obtained by least squares from 25 accurately centred reflections; crystal dimensions 0·40 × 0·25 × 0·20 mm; 4233 unique reflections ($-16 \leq h \leq 16$, $-13 \leq k \leq 12$, $0 \leq l \leq 9$); three check reflections ($\bar{6}2\bar{1}$, $1\bar{3}\bar{3}$, $6\bar{2}1$) showed decay (18%) during the experiment and a (linear) correction was applied to the data. Lorentz–polarization correction but no absorption correction. 3048 reflections with $F > 2\sigma(F)$ were used in the refinement. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An E map based on 418 reflections with $|E| \geq 1{\cdot}66$ having the highest combined figure of merit (2·80) showed all the non-H atoms. Full-matrix least-squares refinement using *SHELX76* (Sheldrick, 1976) minimizing $\sum w(\Delta F)^2$, $w = 1/[\sigma^2(F) + 0{\cdot}0004F^2]$, anisotropic (S, O, C) atoms. A difference electron density synthesis showed many of the H atoms and these were introduced into the model in geometrically calculated positions [d(C—H) 1·08 Å] with two common refined isotropic temperature factors (one for the

---

* Author to whom correspondence should be addressed. Present address: Merck Sharp and Dohme Research Laboratories, Neuroscience Research Centre, Terlings Park, Eastwick Road, Harlow, Essex CM20 2QR, England.

0108-2701/86/111587-03$01.50

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (× 10³) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*(Å²)
S(1*A*)	−0·2117 (1)	0·1629 (1)	1·2154 (2)	59·3 (8)
O(1*A*)	−0·0968 (2)	−0·0301 (3)	1·0641 (3)	51·5 (20)
O(2*A*)	0·0363 (2)	0·1992 (3)	1·5275 (3)	53·3 (21)
O(3*A*)	−0·0312 (2)	0·3186 (3)	1·4639 (3)	59·9 (23)
O(4*A*)	−0·1315 (2)	0·0285 (3)	0·8772 (4)	62·5 (23)
C(1*A*)	−0·1422 (3)	−0·0271 (4)	1·3231 (6)	58·1 (33)
C(2*A*)	−0·1237 (3)	0·0397 (5)	1·5009 (6)	61·4 (37)
C(3*A*)	−0·1126 (3)	0·1640 (5)	1·5387 (5)	57·1 (34)
C(4*A*)	−0·0391 (3)	0·2070 (4)	1·4522 (5)	47·5 (31)
C(5*A*)	−0·0455 (3)	0·1413 (3)	1·2738 (5)	38·0 (26)
C(6*A*)	−0·1015 (3)	0·1591 (4)	1·1531 (5)	42·5 (28)
C(7*A*)	−0·1124 (3)	0·0494 (4)	1·0148 (6)	44·9 (31)
C(8*A*)	−0·0700 (3)	0·0153 (4)	1·2341 (5)	46·7 (30)
C(9*A*)	0·1180 (3)	0·2365 (5)	1·4756 (7)	70·0 (39)
C(10*A*)	−0·0207 (5)	0·4004 (5)	1·6229 (6)	90·5 (45)
C(11*A*)	−0·2699 (4)	0·1554 (6)	1·0405 (7)	88·6 (46)
C(12*A*)	−0·0638 (3)	0·2593 (4)	1·1044 (5)	47·4 (30)
C(13*A*)	0·0280 (3)	0·2698 (5)	1·0538 (7)	71·7 (41)
C(14*A*)	0·0630 (3)	0·3723 (4)	1·0188 (6)	59·8 (35)
C(15*A*)	0·1551 (4)	0·3907 (5)	0·9777 (7)	83·0 (46)
C(16*A*)	0·1935 (5)	0·5004 (6)	0·9659 (9)	105·9 (55)
S(1*B*)	0·3338 (1)	0·1805 (1)	1·0182 (2)	63·5 (9)
O(1*B*)	0·4081 (2)	0·4195 (3)	0·9408 (4)	59·1 (23)
O(2*B*)	0·5103 (2)	0·1062 (3)	0·8634 (3)	52·8 (21)
O(3*B*)	0·5461 (2)	0·1722 (3)	0·6574 (3)	55·4 (21)
O(4*B*)	0·3946 (2)	0·4590 (3)	1·1988 (5)	71·3 (25)
C(1*B*)	0·3517 (3)	0·2636 (4)	0·6966 (6)	61·5 (35)
C(2*B*)	0·3704 (3)	0·1591 (4)	0·5754 (6)	61·1 (34)
C(3*B*)	0·4015 (3)	0·0903 (4)	0·6583 (5)	54·3 (31)
C(4*B*)	0·4832 (3)	0·1580 (4)	0·7669 (5)	45·0 (29)
C(5*B*)	0·4768 (3)	0·2728 (4)	0·8842 (5)	42·8 (27)
C(6*B*)	0·4357 (3)	0·2869 (4)	1·0435 (5)	44·5 (28)
C(7*B*)	0·4103 (3)	0·3969 (4)	1·0732 (7)	55·2 (34)
C(8*B*)	0·4313 (3)	0·3330 (4)	0·8065 (6)	50·9 (31)
C(9*B*)	0·5167 (5)	−0·0058 (4)	0·7844 (7)	85·4 (44)
C(10*B*)	0·6330 (3)	0·2293 (5)	0·7198 (7)	80·6 (43)
C(11*B*)	0·2851 (3)	0·2305 (5)	1·2017 (6)	75·1 (39)
C(12*B*)	0·4935 (3)	0·2927 (4)	1·1831 (6)	59·2 (33)
C(13*B*)	0·5775 (3)	0·3783 (5)	1·2279 (6)	69·7 (38)
C(14*B*)	0·6267 (3)	0·3769 (5)	1·3725 (6)	68·1 (36)
C(15*B*)	0·7110 (4)	0·4616 (6)	1·4185 (7)	91·3 (47)
C(16*B*)	0·7655 (4)	0·4577 (5)	1·5495 (7)	87·6 (44)

* $U_{eq} = \frac{1}{3}$trace **U**.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A* ($X = A$)	Molecule *B* ($X = B$)
S(1*X*)—C(11*X*)	1·797 (7)	1·796 (5)
S(1*X*)—C(6*X*)	1·850 (5)	1·842 (4)
O(1*X*)—C(7*X*)	1·352 (7)	1·333 (8)
O(1*X*)—C(8*X*)	1·460 (5)	1·457 (6)
O(2*X*)—C(4*X*)	1·429 (6)	1·409 (7)
O(2*X*)—C(9*X*)	1·421 (6)	1·429 (7)
O(3*X*)—C(4*X*)	1·421 (7)	1·431 (6)
O(3*X*)—C(10*X*)	1·440 (5)	1·426 (6)
O(4*X*)—C(7*X*)	1·197 (6)	1·205 (6)
$C—C_{min}$	1·483 (10)	1·489 (7)
$C—C_{max}$	1·537 (7)	1·544 (6)
$C—C_{average}$	1·52 (2)	1·52 (2)
C(6*X*)—S(1*X*)—C(11*X*)	103·6 (2)	104·2 (2)
C(8*X*)—O(1*X*)—C(7*X*)	111·0 (3)	110·9 (4)
O(1*X*)—C(7*X*)—C(6*X*)	111·0 (4)	112·0 (4)
C(7*X*)—C(6*X*)—C(5*X*)	100·7 (4)	99·7 (4)
C(6*X*)—C(5*X*)—C(8*X*)	104·7 (3)	104·5 (4)
C(5*X*)—C(8*X*)—O(1*X*)	103·4 (4)	104·0 (4)
S(1*X*)—C(6*X*)—C(5*X*)	112·1 (3)	111·7 (2)
S(1*X*)—C(6*X*)—C(7*X*)	105·2 (3)	106·3 (3)
S(1*X*)—C(6*X*)—C(12*X*)	109·5 (4)	109·5 (4)
C(4*X*)—O(2*X*)—C(9*X*)	118·2 (4)	116·4 (4)
C(4*X*)—O(3*X*)—C(10*X*)	115·9 (4)	118·2 (4)
O(2*X*)—C(4*X*)—O(3*X*)	110·0 (3)	110·5 (4)
Internal C—C—C angles of cyclohexane residue		
min.	109·8 (4)	110·3 (4)
max.	115·8 (4)	116·5 (4)

methyl H atoms and one for the CH and CH_2 groups). Final $R = 0·066$, $wR = 0·066$; 405 parameters (2 blocks); max. shift/e.s.d. 0·48; max. and min. residual electron density 0·45 and −0·51 e Å^{-3}; scattering factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); diagrams produced with *ORTEP* (Johnson, 1965). Calculations were performed on ICL 2970 and CDC 7600 computers.

Discussion. Final atomic coordinates are given in Table 1* and selected bond lengths and angles are in Table 2. The structure contains two crystallographically independent molecules (labelled *A* and *B*), both with essentially the same geometry. Fig. 1 shows molecule *A* and the atom-numbering scheme. The methylthio substituent has been introduced unexpectedly from the concave α face to yield the *endo* sulfide (2) rather than the required *exo* sulfide (3). The *endo* stereochemistry generated in lactone (2) establishes a *trans* relationship between the methylthio moiety and the adjacent bridgehead methine. Consequently oxidative elimination of the methylthio substituent would be expected to afford an exocyclic olefin rather than the required endocyclic isomer. In direct contrast to the formation of *endo* methyl sulfide (2) the *exo* phenyl sulfide (4) is formed exclusively when the enolate derived from lactone (1) is treated with diphenyl disulfide (Gibson, 1983). Thus, phenylsulfenylation of the enolate of (1) occurs from the convex β face while methylsulfenylation proceeds from the sterically congested α face

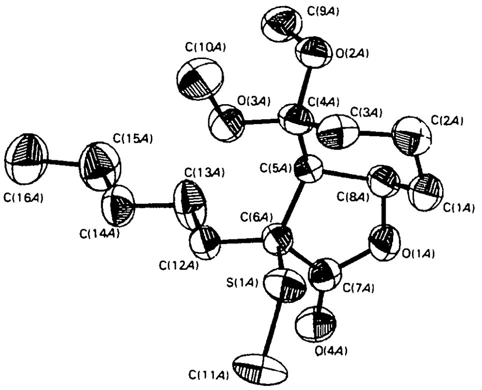


Fig. 1. View of molecule *A* with the atom-numbering scheme. The atoms are drawn with 50% probability thermal ellipsoids and H atoms excluded for clarity. Molecule *B* has the same numbering scheme and is very similar in conformation.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43136 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

yielding the *exo* (4) and *endo* (2) sulfides respectively. The cyclohexane residue is in the chair conformation with a *cis* junction to the furanone ring. The furan ring has an envelope conformation with four of the atoms being coplanar [max. deviation 0·015 (5) Å] and the fifth atom [C(5*A*), C(5*B*)] 0·47 (1) Å out of the plane.

A number of hexahydrobenzofuranone derivatives have been studied by X-ray diffraction. $C_{10}H_{16}O_3$* (Burnett & Rossmann, 1971) shows a chair cyclohexane with *trans* ring junction and also shows the disparate C—O distances in the furanone rings observed in the present case. The C—O bond adjacent to the carbonyl group is very much shorter than the other C—O bond. A chair conformation with a *cis* junction is found in $C_{19}H_{26}O_3$† (Andriamialisoa, Fetizon, Hanna, Pascard & Prange, 1984).

We acknowledge a CASE award from May and Baker (CLG) and financial support from the University of Southampton (LRG). We thank Dr M. B. Hursthouse for the X-ray data collection on the QMC/SERC diffractometer.

References

Andriamialisoa, R. Z., Fetizon, M., Hanna, I., Pascard, C. & Prange, T. (1984). *Tetrahedron*, **40**, 4285–4295.
Baker, R., Gibson, C. L., Swain, C. J. & Tapolczay, D. J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1509–1516.
Burnett, R. M. & Rossmann, M. G. (1971). *Acta Cryst.* B**27**, 1378–1387.
Gibson, C. L. (1983). PhD Thesis. Univ. of Southampton.
Grieco, P. A. & Reap, J. J. (1974). *Tetrahedron Lett.* pp. 1097–1100.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
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.* Univs. of York, England, and Louvain, Belgium.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

---

* Hexahydro-6-hydroxy-6,7a-dimethyl-2(3*H*)-benzo[*b*]furanone.

† Hexahydro-3-(6,6-dimethyl-3-oxocyclohex-1-en-5-yl)-4-methyl-4-vinyl-2(3*H*)-benzo[*b*]furanone.

Acta Cryst. (1986). C**42**, 1589–1591

2-Chlorobiphenyl-4-carbonitrile

By H. H. Sutherland, Z. Ali-Adib and S. Basu

Physics Department, The University of Hull, Hull HU6 7RX, England

(*Received* 3 *April* 1986; *accepted* 29 *May* 1986)

Abstract. $C_{13}H_8ClN$, $M_r = 213·7$, monoclinic, $P2_1/c$, $a = 14·31$ (2), $b = 6·96$ (3), $c = 11·67$ (2) Å, $\beta = 110·1$ (2)°, $V = 1091·5$ Å^3, $Z = 4$, $D_m = 1·33$, $D_x = 1·30$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2·7$ mm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0·066$ for 1012 observed densitometer-measured equi-inclination Weissenberg data. The average C—C bond in the phenyl rings is 1·396 Å. The molecule is non-planar; the angle between the phenyl rings is 51·9 (1)°; the C—Cl bond is 1·743 (7) Å; the C—C≡N bonds are 1·439 (13) and 1·149 (15) Å, the C—C bond making an angle of 3·4 (1)° with the phenyl plane.

Introduction. The structure determination of the title compound forms part of an investigation into liquid-crystal compounds and their chemical precursors.

Experimental. D_m measured by flotation in aqueous cadmium *n*-dodecatungstoborate. Pale-yellow opaque crystals used in data collection, dimensions 0·09 × 0·08 × 0·28 and 0·17 × 0·07 × 0·15 mm, respectively, for *c*- and *b*-axis Weissenberg data. 1070 reflections measured by the SERC Microdensitometer Service, Daresbury Laboratory, from multiple-film photographs using Cu $K\alpha$ radiation. $-15 \le h \le 15$; $0 \le k \le 8$; $0 \le l \le 9$; 1012 unique observed reflections, $R_{\text{int}} = 0·05$. Structure solved by Patterson synthesis and refined (on *F*) by blocked-matrix least squares with anisotropic thermal parameters for the non-H atoms; H-atom positions, initially obtained from a difference synthesis and placed at geometrically reasonable positions, refined with constrained C—H bond distances and isotropic thermal parameters; final $R = 0·066$, unit weights, $wR = 0·066$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·004 for positional and 0·013 for thermal parameters. Max. and min. heights in final $\Delta\rho$ map +0·6 and −0·3 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs used: *SHELX76* (Sheldrick, 1976) and local programs supplied by HHS and Drs C. Morgan and M. J. Mottram.

0108-2701/86/111589-03$01.50