Refinement

Refinement on F
$R = 0.0609$
$wR = 0.0736$
$S = 2.56$
502 reflections
117 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = -0.23$ e Å^{-3}
$\Delta\rho_{\min} = 0.36$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	1.0130 (5)	0.7134 (5)	1.3216	0.0688
O2	0.7192 (4)	0.6949 (4)	0.592 (1)	0.0551
C1	1.0889 (6)	0.8229 (6)	1.175 (2)	0.0755
C2	1.0201 (6)	0.7786 (7)	1.278 (2)	0.0552
C3	0.9643 (6)	0.7692 (6)	1.138 (2)	0.0581
C4	0.9204 (7)	0.7626 (7)	1.024 (2)	0.0615
C5	0.8677 (6)	0.7580 (6)	0.889 (2)	0.0571
C6	0.8253 (7)	0.7573 (6)	0.777 (2)	0.0534
C7	0.7753 (6)	0.7618 (6)	0.641 (2)	0.0515
C8	0.8091 (7)	0.7947 (8)	0.436 (2)	0.0891
C9	1.0154 (7)	0.8081 (7)	1.484 (3)	0.0837
C10	0.7482 (7)	0.8026 (7)	0.753 (3)	0.0899
Cl11 †	1.0	1.0	0.673 (8)	0.17 (2)
Cl12 †	0.918 (1)	0.936 (2)	1.042 (8)	0.17 (2)
C11 †	1.0	1.0	0.950 (8)	0.17 (2)

† The coordinates of these atoms were constrained in the manner described below.

Table 2. *Geometric parameters* (Å, °)

O1—C2	1.42 (2)	C4—C5	1.42 (2)
O2—C7	1.43 (1)	C5—C6	1.19 (2)
C1—C2	1.50 (2)	C6—C7	1.46 (2)
C2—C3	1.46 (2)	C7—C8	1.51 (2)
C2—C9	1.50 (2)	C7—C10	1.51 (2)
C3—C4	1.18 (2)		
O1—C2—C3	108.8 (9)	C4—C5—C6	177 (1)
C2—C3—C4	179 (1)	C5—C6—C7	176 (1)
C3—C4—C5	177 (2)	O2—C7—C6	111 (1)

2,7-Dimethyl-3,5-octadiyne-2,7-diol (1) was isolated (by flash chromatography; silica, methanol-dichloromethane as eluent) as a by-product of a palladium-catalysed coupling reaction of the parent acetylene (3) with an aryl halide. Good quality crystals were obtained by subsequent recrystallization from dichloromethane.

Disorder of the dichloromethane guest molecule was treated by constraining the C—Cl bonds to 1.77 Å and the Cl—C—Cl angles to 109°. H atoms were ignored. A C atom and one Cl atom were constrained to lie on the threefold axis parallel to c with the molecular z coordinate, rotation about z and overall vibrational parameter being allowed to refine. The group multiplicity was allowed to vary but not at the same time as the above parameters and not during the final least-squares cycle. Site occupancies for the C, Cl11 and Cl12 atoms were tied in the ratio 2:1:1, *i.e.* the dichloromethane Cl atoms were completely disordered among four tetrahedrally arranged sites. This resulted in a guest-to-host ratio of 0.060 (6):1 and site occupancy of 0.18 (2).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature search: *CSSR* (1984).

We are grateful to the SERC and GEC Marconi for a Studentship (to AEM).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71517 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1038]

References

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.
Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
Segawa, M., Mori, K. & Toda, F. (1988). *Chem. Lett.* pp. 1755-1758.
Toda, F. (1987). *Top. Curr. Chem.* **140**, 43-69.
Toda, F. & Akagi, K. (1968). *Tetrahedron Lett.* pp. 3695-3698.

Acta Cryst. (1994). C**50**, 131-133

Structure of *trans*-Methyl {2-[(Cyano)(phenylthio)methyl]-3-oxocyclopentyl}acetate, $C_{16}H_{17}NO_3S$

M. Nierlich, M. Lance and D. Vigner

CEN-Saclay, SCM, Bâtiment 125,
91191 Gif-sur-Yvette CEDEX, France

T. Strzalko and L. Wartski

ICMO, Laboratoire des carbocycles, CNRS-URA 478,
Bâtiment 420, Orsay CEDEX, France

(*Received* 3 *February* 1993; *accepted* 30 *June* 1993)

Abstract

The X-ray analysis confirms the *trans* relationship between the C(2) and C(3) substituents of the cyclopentanone ring and allows us to determine the rela-

tive configuration: 2*S*, 3*R*, 9*S* or 2*R*, 3*S*, 9*R*. Moreover, it indicates the half-chair conformation of the cyclopentanone ring and determines the methoxycarbonyl and phenylthio substituent conformations.

Comment

The present work forms part of a structural and reactivity study of 2,3-disubstituted cycloalkan-1-ones (Posner, Asirvatham, Hamill & Webb, 1990; Funk & Vollhardt, 1980; Charpin, Chevrier, Lance, Vigner, Zervos & Wartski, 1987; Zervos, Wartski, Goasdoue & Platzer, 1986; Roux, Seden-Penne, Wartski, Posner, Nierlich, Vigner & Lance, 1993). In this study, we report the synthesis and the crystal structure of the title compound.

The ^{1}H NMR data indicate a *trans* relationship between the C(2)—C(6) and C(3)—C(9) bonds and shows the C(2)—H(2) bond bisecting the H(61)—C(6)—H(62) angle. However, no information can be obtained on the relative configurations of C(9) and C(3), the conformations of the cyclopentanone ring or the carboxymethyl and thiophenyl groups. Unambiguous assignment of the structure had to be obtained from X-ray analysis. An *ORTEP*II drawing of the molecule is shown in Fig. 1, while bond distances and angles are given in Table 2.

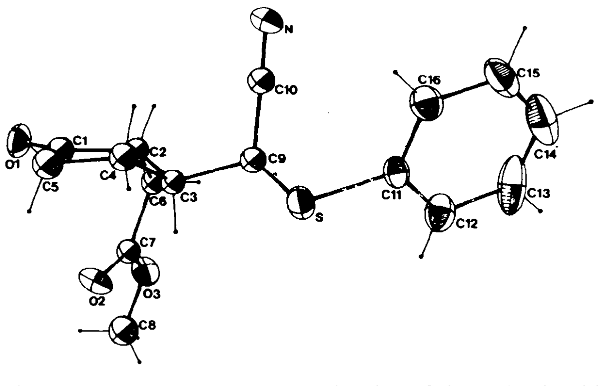

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the molecule with atom numbering.

The *trans* quasi-axial relationship between the C(2)—H(2) and C(3)—H(3) bonds is confirmed, with a value of 150.99 (7)° for the H(2)—C(2)—C(3)—H(3) torsion angle. Moreover, the H(9)—C(9)—C(3)—H(3) value of 62.69 (8)° and the H(2)—C(2)—C(6)—H(61) or H(2)—C(2)—C(6)—H(62) values of 63.48 (8) and −55.60 (8)°, respectively, are also in agreement with ^{1}H NMR data. The cyclopentanone ring adopts a half-chair conformation; the C(1), C(2), C(4), C(5), O(1) atoms lie in a plane within ±0.10 Å, C(3) and C(10) of the nitrile moiety being 0.50 and −1.40 Å, respectively, out of this least-squares plane. The C(10)—C(9)—C(3)—H(3) torsion angle of 179.77 (7)° shows that the C(9)—C(10) bond is antiparallel to C(3)—H(3). The angle between the phenyl ring and the cyclopentanone planes is 63.72 (3)°, thus revealing the particular conformation of the phenylthio group. The relative configuration of the title compound is as follows: 2*S*, 3*R*, 9*S* or 2*R*, 3*S*, 9*R*.

Experimental

Crystal data

$C_{16}H_{17}NO_3S$
$M_r = 303.38$
Monoclinic
$P2_1/c$
$a = 10.011$ (5) Å
$b = 13.752$ (4) Å
$c = 12.182$ (3) Å
$\beta = 113.13$ (4)°
$V = 1542$ (1) Å^3
$Z = 4$

$D_x = 1.307$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$-12°
$\mu = 0.208$ mm^{-1}
$T = 295$ K
0.60 × 0.50 × 0.40 mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans [width (0.80 + 0.35tanθ)°; rate 1.2-10° min^{-1}]
Absorption correction: none
2208 measured reflections
1890 independent reflections
1196 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 22°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.056$
$wR = 0.085$
$S = 1.9$
1196 reflections
141 parameters
H atoms at calculated positions and refined as riding
$w = 1/(\sigma F)^2 = 4F^2/[\sigma I^2+(pF^2)^2]^{1/2}$ where $p = 0.4$

$(\Delta/\sigma)_{\rm max} = 0.12$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least-squares procedures based on *F*, with anisotropic thermal parameters for O, S, N and phenyl C atoms. All calculations were performed on a VAX 4200 computer with *MolEN* (Fair, 1990).

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

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.5601 (2)	0.0197 (2)	0.2767 (2)	4.69 (5)
O(1)	0.8645 (7)	0.3186 (5)	0.6945 (5)	5.9 (2)
O(2)	0.7407 (6)	0.3856 (4)	0.4186 (5)	5.2 (2)
O(3)	0.9372 (6)	0.4063 (4)	0.3798 (5)	5.6 (2)
N	0.8686 (8)	−0.0645 (5)	0.5359 (7)	5.6 (2)
C(1)	0.7915 (8)	0.2601 (6)	0.6217 (7)	4.1 (2)
C(2)	0.8430 (7)	0.2051 (6)	0.5368 (6)	3.3 (2)
C(3)	0.7001 (7)	0.1589 (6)	0.4446 (6)	3.1 (1)
C(4)	0.6090 (8)	0.1385 (6)	0.5191 (6)	3.9 (2)
C(5)	0.6404 (9)	0.2278 (7)	0.6008 (8)	4.9 (2)
C(6)	0.9321 (8)	0.2663 (6)	0.4861 (6)	3.6 (2)
C(7)	0.8525 (8)	0.3581 (6)	0.4234 (6)	3.6 (2)
C(8)	0.883 (1)	0.4976 (8)	0.3232 (8)	6.2 (2)
C(9)	0.7300 (8)	0.0690 (6)	0.3820 (6)	3.4 (2)
C(10)	0.8093 (8)	−0.0069 (6)	0.4690 (6)	3.7 (2)
C(11)	0.6263 (8)	−0.0745 (6)	0.2129 (7)	3.8 (2)
C(12)	0.664 (1)	−0.0544 (7)	0.1174 (8)	5.8 (2)
C(13)	0.719 (1)	−0.1300 (9)	0.0719 (9)	9.2 (3)
C(14)	0.738 (1)	−0.2217 (8)	0.121 (1)	8.1 (3)
C(15)	0.701 (1)	−0.2403 (7)	0.214 (1)	7.1 (3)
C(16)	0.644 (1)	−0.1670 (7)	0.2617 (8)	5.4 (3)

Table 2. *Selected bond distances* (Å) *and angles* (°)

S—C(9)	1.812 (7)	C(3)—C(4)	1.54 (1)
S—C(11)	1.769 (9)	C(3)—C(9)	1.54 (1)
O(1)—C(1)	1.208 (9)	C(4)—C(5)	1.53 (1)
O(2)—C(7)	1.16 (1)	C(6)—C(7)	1.53 (1)
O(3)—C(7)	1.34 (1)	C(11)—C(12)	1.38 (1)
O(3)—C(8)	1.43 (1)	C(11)—C(16)	1.39 (1)
N—C(10)	1.13 (1)	C(12)—C(13)	1.39 (2)
C(1)—C(2)	1.53 (1)	C(13)—C(14)	1.38 (2)
C(1)—C(5)	1.50 (1)	C(14)—C(15)	1.36 (2)
C(2)—C(3)	1.566 (9)	C(15)—C(16)	1.39 (2)
C(2)—C(6)	1.52 (1)	C(9)—C(10)	1.48 (1)
C(9)—S—C(11)	100.1 (4)	O(2)—C(7)—C(6)	126.7 (8)
C(7)—O(3)—C(8)	116.3 (7)	O(3)—C(7)—C(6)	108.6 (7)
O(1)—C(1)—C(2)	124.0 (8)	S—C(9)—C(3)	109.8 (5)
O(1)—C(1)—C(5)	127.0 (9)	S—C(9)—C(10)	109.5 (5)
C(2)—C(1)—C(5)	109.0 (6)	C(3)—C(9)—C(10)	111.5 (6)
C(1)—C(2)—C(3)	103.3 (6)	N—C(10)—C(9)	179 (1)
C(1)—C(2)—C(6)	114.2 (6)	S—C(11)—C(12)	119.7 (7)
C(3)—C(2)—C(6)	116.7 (6)	S—C(11)—C(16)	119.3 (8)
C(2)—C(3)—C(4)	103.7 (5)	C(12)—C(11)—C(16)	121.0 (9)
C(2)—C(3)—C(9)	112.3 (5)	C(11)—C(12)—C(13)	117.9 (9)
C(4)—C(3)—C(9)	114.8 (6)	C(12)—C(13)—C(14)	121 (1)
C(3)—C(4)—C(5)	102.6 (7)	C(13)—C(14)—C(15)	120 (1)
C(1)—C(5)—C(4)	106.5 (8)	C(14)—C(15)—C(16)	120 (1)
C(2)—C(6)—C(7)	112.7 (6)	C(11)—C(16)—C(15)	119 (1)
O(2)—C(7)—O(3)	124.5 (7)		

The title compound was prepared by Michael addition of lithiated phenylthioacetonitrile to 2-cyclopentenone followed by methyl bromoacetate alkylation. After the usual treatment of the reaction medium, the residue was dissolved in the minimum amount of ether. After 48 h at room temperature, a solid had precipitated; crystals were grown by slow evaporation of an etheral solution at room temperature; m.p. 382 K.

References

Charpin, P., Chevrier, G., Lance, M., Vigner, D., Zervos, M. & Wartski, L. (1987). *Acta Cryst.* C**43**, 1647–1648.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.

Funk, R. L. & Vollhardt, K. P. C. (1980). *J. Am. Chem. Soc.* **102**, 5253–5261.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Posner, G. H., Asirvatham, E., Hamill, T. G. & Webb, K. S. (1990). *J. Org. Chem.* **55**, 2132–2137.

Roux, M. C., Seden-Penne, J., Wartski, L., Posner, G. H., Nierlich, M., Vigner, D. & Lance, M. (1993). *J. Org. Chem.* **58**, 3969–3973.

Zervos, M., Wartski, L., Goasdoue, N. & Platzer, N. (1986). *J. Org. Chem.* **51**, 1293–1298.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71450 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1045]

Acta Cryst. (1994). C**50**, 133–136

A Chiral Tetrahydro-γ-pyranonecarboxylate Ester for Asymmetric Nazarov Cyclization

CHARLES S. BOND, GORDON A. LEONARD,
ANDREW C. REGAN AND WILLIAM N. HUNTER

Department of Chemistry, University of Manchester, Manchester M13 9PL, England

JOHN F. P. ANDREWS†

The Chemical Laboratory, University of Kent, Canterbury CT2 7NH, England

(*Received* 12 *March* 1993; *accepted* 23 *June* 1993)

Abstract

(1*S*,2-*exo*)-1-[(*N*,*N*-Dicyclohexylamino)sulfonylmethyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-yl [2*R*(2α,3β,5β,6α)]-tetrahydro-2,5,6-trimethyl-4-oxo-2*H*-pyran-3-carboxylate, $C_{31}H_{51}NO_6S$, has an asymmetric unit containing two unique but similarly conformed molecules (*A* and *B*). In molecule *A* the cyclohexyl rings are free to crystallize in either of the approximately coplanar conformations, whereas in molecule *B* only one conformation is allowed. The N atoms in

---

† Present address: Department of Chemistry, University of Loughborough, Loughborough, Leicester LE11 3TU, England.