Molecular Structure Corporation (1993). *TEXSAN. Crystal Structure Analysis Package*. Version 1.6. MSC, Research Forest Drive, The Woodlands, TX 77381, USA.
Reboul, J. P., Pepe, G., Siri, D., Odden, Y., Rahal, H., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 111–115.
Reboul, J. P., Rahal, H., Pepe, G., Odden, Y., Siri, D., Astier, J. P., Soyfer, J. C. & Barbe, J. (1992). *Acta Cryst.* C**48**, 2157–2160.
Sotomatsu, T., Shigemura, M., Murata, Y. & Fujita, T. (1993). *J. Pharm. Sci.* **82**, 776–781.
Suzuki, H., Ishibashi, T., Murashima, T. & Tsukamoto, K. (1991). *Tetrahedron Lett.* **32**, 6591–6594.
Wieckowski, T. & Krygowski, T. M. (1981). *Can. J. Chem.* **59**, 1622–1629.

Acta Cryst. (1997). C**53**, 746–748

4-Cyclohexanespiro{3-[2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]oxetan-2-one}†

Alan R. Kennedy, William J. Kerr and Sharon McKendry

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

(*Received 23 August 1996; accepted 27 January 1997*)

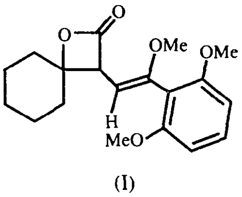
Abstract

A new and efficient route for the preparation of substituted β-lactones from chromium–carbene complexes gave the title complex, $C_{19}H_{24}O_5$, as the major stereoisomeric product.

Comment

Recently, we have discovered (Harrity, Kerr, Middlemiss & Scott, 1997) and subsequently developed (Harrity, Heron, Kerr, McKendry, Middlemiss & Scott, 1996) the reaction of α,β-unsaturated chromium–carbene complexes with propargylic alcohols to provide efficient methods for the synthesis of highly functionalized β-lactones. This entirely novel β-lactonization process further extends the use of chromium–carbene complexes in organic synthesis and, in turn, provides good to high yielding routes to this biologically important molecular sub-unit which, by our protocols, contains the synthetically attractive and highly flexible enol–ether moiety.

4-Cyclohexanespiro{3-[2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]oxetan-2-one} was prepared in 74% yield, as a 3:1 mixture of *Z* and *E* isomers, on refluxing a THF solution of pentacarbonyl[methoxy(2,6-dimethoxyphenyl)methylene]chromium(0) with an excess of 1-ethynyl-1-cyclohexanol in the presence of triethylamine and acetic anhydride. The original stereochemical assignment of the enol–ether geometry was based on ^{1}H NMR spectroscopy and NOESY studies of the mixed product and the analogous ethoxy species, 4-cyclohexanespiro{3-[2-ethoxy-2-(dimethoxyphenyl)ethenyl]oxetan-2-one}, which indicated that the major component was the *Z* isomer, (I), around the double bond. Slow recrystallization of the product from petroleum ether (303–313 K) allowed isolation of the major component (correlated by ^{1}H NMR studies) and X-ray analysis was undertaken in order to confirm that it was indeed the *Z* isomer. Subsequent ^{1}H NMR studies, supported by this structure elucidation, correlated this species with the major isomer from other lactonizations and established a more routine diagnostic process for the NMR-shift-based identification of the enol–ether isomers.



(I)

The molecular structure shown in Fig. 1 contains a near planar β-lactone four-membered ring system with a typical shortening of the O(1)—C(8) distance [O(1)—C(8) 1.351 (3) Å and O(1)—C(1) 1.504 (3) Å; see Table 1] due to the conjugation effect. The geometrical constraints of the four-membered ring leads

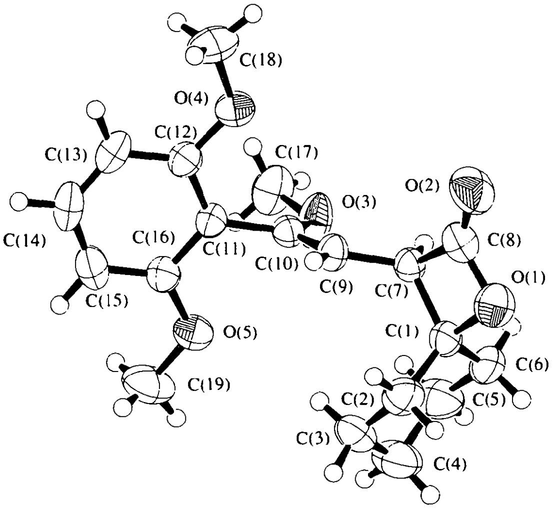


Fig. 1. *ORTEP*II (Johnson, 1976) view of compound (I). Non-H atoms are shown as 50% probability ellipsoids and H atoms are shown as small spheres of arbitrary radii.

---

† Alternative name: 3-[(*Z*)-2-methoxy-2-(2,6-dimethoxyphenyl)ethenyl]-1-oxaspiro[3.5]nonan-2-one.

to the closure of the internal bond angles, however, all geometric parameters of the cyclic lactone are in good agreement with those found in similar systems (Adam *et al.*, 1991; Dou, Basaran, Paulus & Weiss, 1993; Hegmann, Christl, Peters, Peters & von Schnering, 1987). The inclination of the lactone group to the plane of the vinylic group is described by the torsion angles C(1)—C(7)—C(9)—C(10) and C(8)—C(7)—C(9)—C(10), which have values of −117.3 (3) and 141.0 (3)°, respectively. The plane of the aryl ring approaches the normal to the plane of the vinylic group [C(9)—C(10)—C(11)—C(12) 81.0 (3) and C(9)—C(10)—C(11)—C(16) −97.8 (3)°]. All other geometric parameters are unexceptional, with the bond distances comparing well with the average values given in the compilation by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987).

Experimental

The crude product was purified by flash column chromatography (eluant petrol/ether, 4:1). FTIR (CH_2Cl_2): 1829 (C═O) and 1600 (C═C) cm^{-1}.

Crystal data

$C_{19}H_{24}O_5$
$M_r = 332.40$
Monoclinic
$P2_1/n$
$a = 7.390\,(1)$ Å
$b = 12.490\,(2)$ Å
$c = 19.223\,(3)$ Å
$\beta = 91.75\,(1)°$
$V = 1773.4\,(4)$ Å^3
$Z = 4$
$D_x = 1.245$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 10.3$–$13.4°$
$\mu = 0.089$ mm^{-1}
$T = 295$ K
Block
0.70 × 0.45 × 0.20 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3938 measured reflections
3650 independent reflections
2112 reflections with $I > \sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 26°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = -23 \rightarrow 23$
3 standard reflections every 150 reflections intensity decay: <0.5%

Refinement

Refinement on *F*
$R = 0.0605$
$wR = 0.0539$
$S = 1.517$
2112 reflections
218 parameters
H atoms not refined

$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: Zachariasen (1968) type 2, Gaussian isotropic
Extinction coefficient: $9\,(2) \times 10^{-7}$
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.001$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O(1)—C(1)	1.504 (3)	C(7)—C(8)	1.512 (4)
O(1)—C(8)	1.351 (3)	C(7)—C(9)	1.489 (3)
O(2)—C(8)	1.196 (3)	C(9)—C(10)	1.321 (3)
O(3)—C(10)	1.363 (3)	C(10)—C(11)	1.484 (3)
C(1)—C(7)	1.549 (3)		
C(1)—O(1)—C(8)	91.7 (2)	C(8)—C(7)—C(9)	117.8 (2)
O(1)—C(1)—C(2)	109.9 (2)	O(1)—C(8)—O(2)	126.4 (3)
O(1)—C(1)—C(6)	110.1 (2)	O(1)—C(8)—C(7)	95.7 (2)
O(1)—C(1)—C(7)	88.3 (2)	O(2)—C(8)—C(7)	137.9 (3)
C(2)—C(1)—C(6)	112.1 (2)	C(7)—C(9)—C(10)	124.0 (2)
C(2)—C(1)—C(7)	117.7 (2)	O(3)—C(10)—C(9)	117.6 (2)
C(6)—C(1)—C(7)	116.0 (2)	O(3)—C(10)—C(11)	119.3 (2)
C(1)—C(7)—C(8)	84.1 (2)	C(9)—C(10)—C(11)	123.0 (2)
C(1)—C(7)—C(9)	122.9 (2)		

Data were averaged after correction for Lorentz–polarization only. Subsequently, reflections with $I<\sigma(I)$ were disregarded. The structure was solved by direct methods and Fourier techniques, with all atoms observed after a series of difference syntheses. All H atoms were placed in calculated positions, with C—H = 0.96 Å and $B_{\rm iso} = 1.2B_{\rm eq}$ of the ridden atom. Methyl-group orientations were derived from the difference synthesis. Final refinement to convergence was by full-matrix least squares. All calculations were performed on a Silicon Graphics Indy R4600.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The authors are grateful for the financial support of the EPSRC for a studentship (SMcK).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Adam, W., Albert, R., Grau, N. D., Hasemann, L., Nestler, B., Peters, E.-M., Peters, K., Prechtl, F. & von Schnering, H. G. (1991). *J. Org. Chem.* **56**, 5778–5781.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Dou, S., Basaran, R., Paulus, H. & Weiss, A. (1993). *Z. Naturforsch. Teil A*, **48**, 491–496.

Harrity, J. P. A., Heron, N. M., Kerr, W. J., McKendry, S., Middlemiss, D. & Scott, J. S. (1996). *Synlett*, pp. 1184–1186.

Harrity, J. P. A., Kerr, W. J., Middlemiss, D. & Scott, J. S. (1997). *J. Organomet. Chem.* **503**. In the press.

Hegmann, J., Christl, M., Peters, K., Peters, E.-M. & von Schnering, H. G. (1987). *Tetrahedron Lett.* **28**, 6429–6432.

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

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1997). **C53**, 748–749

meso-3,3′-Bi(1,2,4-trithiacyclohex-5-enyl)†

Toshio Shimizu, Kazuko Iwata, Mitsuru Kondo, Susumu Kitagawa and Nobumasa Kamigata

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan. E-mail: kamigata-nobumasa@c.metro-u.ac.jp

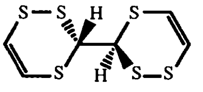
(*Received 11 October 1996; accepted 4 February 1997*)

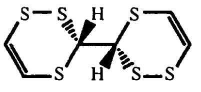
Abstract

The stereochemistry of the title compound, $C_6H_6S_6$, was determined to have *meso* geometry. The molecule has C_i symmetry with a dihedral angle around the disulfide moiety of −64.25 (10)°, a reduction from the normal strain-free geometry (*ca* 90°) of the disulfide.

Comment

Cyclic polysulfides have been the subject of considerable interest (Sato, 1990). In the course of our work on sulfur-containing unsaturated cyclic compounds, 3,3′-bi(1,2,4-trithiacyclohex-5-enyl) was obtained as a diastereomeric mixture (Shimizu, Iwata & Kamigata, 1996). One isomer, the title compound, could be isolated by recrystallization of the diastereomeric mixture. However, if the compound had *meso* or *dl* geometry [(I) and (II), respectively], it could not be determined from spectral data such as ^{1}H and ^{13}C NMR, IR and MS. The geometry of the title compound, isolated as yellow prisms, was therefore determined by X-ray crystallographic analysis to be *meso* form.


(I)


(II)

The atoms of the six-membered ring, except for an S atom at the 2 position, are nearly planar. The dihedral angle around the disulfide moiety is −64.25 (10)°, a reduction from the normal strain-free geometry of the disulfide (*ca* 90°; Dixon, Zeroka, Wendoloski & Wasserman, 1985; Block & Jansen, 1985; Rauk, 1984; Shimizu, Iwata, Kamigata & Ikuta, 1997), whereas the S—C═C—S torsion angle is 2.0 (3)°, indicating an almost strain-free geometry of this part of the molecule.

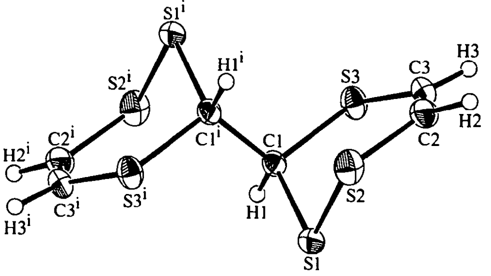


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. [Symmetry code: (i) $-x$, $-y$, $1-z$].

Experimental

3,3′-Bi(1,2,4-trithiacyclohex-5-enyl) was obtained as a diastereomeric mixture by oxidation of *cis*-disodium ethene-1,2-dithiolate and photochemical reaction of 1,2,5,6-tetrathiacycloocta-3,7-diene. The title compound was isolated as yellow prisms by recrystallization from chloroform (m.p. 400.5–401.5 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (*d*, 2H, J = 9.5 Hz), 6.62 (*d*, 2H, J = 9.5 Hz), 4.94 (*s*, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.5, 115.4, 56.1; IR (KBr): 3030, 3020, 2905, 1540, 1125, 810 cm^{-1}; UV (cyclohexane): 325 (*sh*, ε 1.4 × 10^3), 247 (ε 6.1 × 10^3) nm; EI MS: *m/z* 271 (M^+ + 1), 207, 180, 147, 135, 116, 90, 58; calculated for $C_6H_6S_6$: C 26.64, H 2.24%; found: C 27.14, H 2.36%.

Crystal data

$C_6H_6S_6$
M_r = 270.47
Monoclinic
$P2_1/c$
a = 8.111 (2) Å
b = 6.146 (1) Å
c = 10.242 (1) Å
β = 103.19 (1)°
V = 497.1 (1) Å^3
Z = 2
D_x = 1.807 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 19.7–19.9°
μ = 1.313 mm^{-1}
T = 293 K
Prism
0.40 × 0.30 × 0.30 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.572, $T_{\max}$ = 0.674
1340 measured reflections
1257 independent reflections

1073 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.0123
$\theta_{\max}$ = 27.55°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -13 \rightarrow 12$
3 standard reflections
every 150 reflections
intensity decay: 0.29%

---

† Alternative name: 3,3′-bi(3*H*-1,2,4-trithiinyl).