

*Acta Cryst.* (1999). **C55**, 1574–1575

## Cocrystallization of two conformers of (2*S*,3*S*,9*S*,10*S*)-2,3,9,10-tetraphenyl-1,4,8,11-tetraoxacyclotetradecane-6,13-dione

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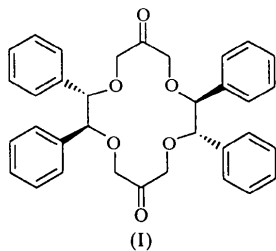
(Received 1 April 1999; accepted 19 May 1999)

### Abstract

The title compound, C<sub>34</sub>H<sub>32</sub>O<sub>6</sub>, was synthesized from the ozonolysis of (2*S*,3*S*,9*S*,10*S*)-6,13-dimethylene-2,3,9,10-tetraphenyl-1,4,8,11-tetraoxacyclotetradecane. Two different conformers of the title compound cocrystallized in a tetragonal unit cell and were structurally analyzed by X-ray crystallography.

### Comment

Chiral ketones have been shown to be remarkably promising catalysts for the oxone-mediated asymmetric epoxidation of prochiral olefins (Wang & Shi, 1998, and references therein). During our studies towards the development of new C<sub>2</sub> symmetric chiral ketones, we prepared the title compound, (I), by the ozonolysis of (2*S*,3*S*,9*S*,10*S*)-6,13-dimethylene-2,3,9,10-tetraphenyl-1,4,8,11-tetraoxacyclotetradecane, which was isolated from the reaction of the sodium salt of *trans*-(+)-stilbenediol with 3-chloro-2-chloromethyl-1-propene in *N,N*-dimethylformamide (Song *et al.*, 1997).



The X-ray crystallographic study on the title compound revealed two different conformers (Figs. 1 and 2) which are co-crystallized in a tetragonal unit cell. The two conformers are apparently distinguished by their macrocyclic ring conformations. The macrocyclic ring of the conformer *A* has a concave structure whereas that of the conformer *B* is open wide and has exact C<sub>2</sub> symmetry. The two carbonyl-O atoms in con-

former *A* are oriented in the same direction while those in the conformer *B* are oriented in the opposite direction. The asymmetric part in the tetragonal unit cell contains one full *A* and half of a *B* conformer. It seems

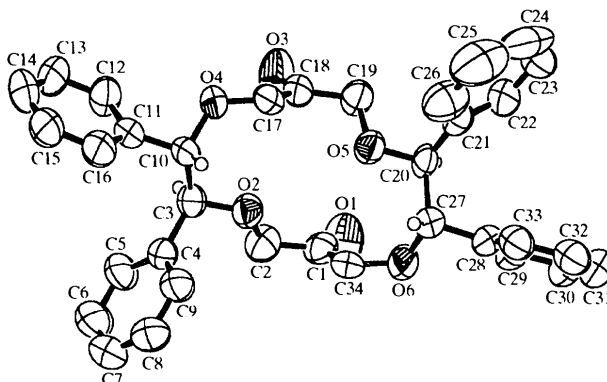


Fig. 1. The molecular structure of conformer *A* with the atom labelling scheme (top) and the ring edge-on view without the phenyl rings (bottom). Displacement ellipsoids at the 50% probability level. Non-chiral H atoms are omitted for clarity.

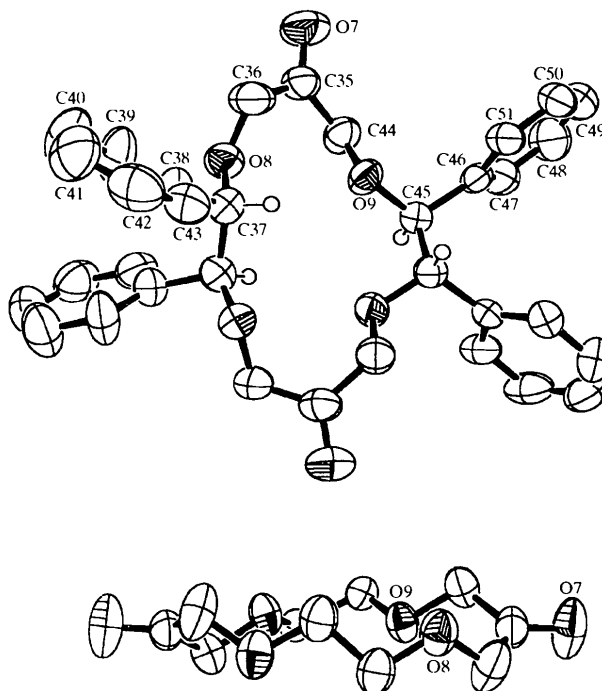


Fig. 2. The molecular structure of conformer *B* with the atom labelling scheme (top) and the ring edge-on view without the phenyl rings (bottom). Displacement ellipsoids at the 50% probability level. Non-chiral H atoms are omitted for clarity.

to be a rare case that two macrocyclic conformations can be structurally analysed in one crystal. The contact distances between the carbonyl-O atom and *ortho* protons of phenyl rings, which may be the important chiral sensors in the asymmetric epoxidation of olefins catalyzed by chiral ketones, vary from 4.08 (O1...H29) to 6.37 (O1...H33) for the conformer *A*, and from 4.75 (O7...H51) to 6.46 Å (O7...H43) for the conformer *B*.

## Experimental

(2*S*,3*S*,9*S*,10*S*)-6,13-Dimethylene-2,3,9,10-tetraphenyl-1,4,8,11-tetraoxacyclotetradecane (1.51 g, 1.89 mmol) was ozonized at 195 K by passing an O<sub>3</sub>/O<sub>2</sub> stream through until the solution was saturated with O<sub>3</sub>. Excess O<sub>3</sub> was removed by the O<sub>2</sub> stream, and the triphenylphosphine (0.50 g, 1.89 mmol) was added portionwise to the reaction mixture. After stirring for 30–40 min at 195 K, the mixture was allowed to warm to room temperature, and the solvent was evaporated *in vacuo*. The product was purified chromatographically on silica gel (eluant ethyl acetate:hexane 2:1) and recrystallized from diethyl ether solution (yield 68%, m.p. 451–456 K).

### Crystal data

C<sub>34</sub>H<sub>32</sub>O<sub>6</sub>  
*M<sub>r</sub>* = 536.60  
 Tetragonal  
*P*4<sub>3</sub>2<sub>1</sub>2  
*a* = 14.945 (2) Å  
*c* = 39.572 (2) Å  
*V* = 8838.5 (17) Å<sup>3</sup>  
*Z* = 12  
*D<sub>x</sub>* = 1.210 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 7–14°  
 $\mu$  = 0.082 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Octahedron  
 0.65 × 0.50 × 0.40 mm  
 Colourless

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: none  
 4476 measured reflections  
 4476 independent reflections  
 2158 reflections with  $I > 2\sigma(I)$

$\theta_{\max}$  = 24.97°  
 $h$  = 0 → 12  
 $k$  = 0 → 17  
 $l$  = 0 → 47  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.150$   
*S* = 0.999  
 4476 reflections  
 541 parameters  
 H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.153 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.166 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

O1—C1	1.195 (6)	O6—C34	1.414 (6)
O2—C2	1.408 (6)	O6—C27	1.428 (6)
O2—C3	1.434 (6)	C1—C2	1.494 (7)

O3—C18	1.206 (6)	C1—C34	1.502 (7)
O4—C17	1.394 (5)	C3—C10	1.519 (7)
O4—C10	1.436 (5)	C17—C18	1.490 (7)
O5—C19	1.417 (5)	C18—C19	1.492 (7)
O5—C20	1.430 (5)	C20—C27	1.544 (6)

The absolute configuration of the structure was determined by the chemical used.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.2* (Hall *et al.*, 1994). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *ORTEPIII* (Johnson, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1289). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 1575–1577

## Methyl 1-(*tert*-butoxycarbonyl-L-alanyl-L-leucylamino)cyclooctane-1-carboxylate

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(Received 2 February 1999; accepted 13 April 1999)

## Abstract

In the title compound, C<sub>24</sub>H<sub>33</sub>N<sub>3</sub>O<sub>6</sub>, an end-protected tripeptide, the peptide backbone adopts an incipient 3<sub>10</sub> helical conformation. The peptide units are *trans*