Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A new polymorph of *cis–transoid–cis*-dicyclohexano-18-crown-6

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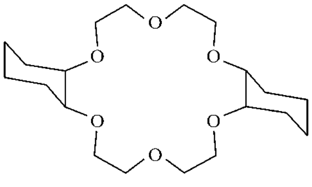
Received 5 July 2002
Accepted 3 October 2002
Online 31 October 2002

A new orthorhombic polymorphic modification of the title compound (alternative name: *cis–transoid–cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.$0^{9,14}$]hexacosane), $C_{20}H_{36}O_6$, has been found and is compared with the previously known monoclinic modification. In the structures of the two polymorphs, the crown-ether molecules are centrosymmetric and reveal essentially the same molecular shape but different packing motifs.

Comment

The title compound, (I), is well known as a versatile macrocyclic ligand suitable for the complexation of metals and neutral molecules. A search of the Cambridge Structural Database (CSD, April 2002 release; Allen & Kennard, 1993) produced a list of 90 entries covering a wide range of complexes with 20 different metal ions and 26 neutral molecules. Five stereoisomers are possible for this molecule (Mercer & Truter, 1973). However, the crystallographic information available in the CSD about the pure phases of this macrocyclic ligand is restricted to the unit-cell dimensions for the *cis–cisoid–cis* (Dalley *et al.*, 1975), *cis–transoid–cis* (monoclinic setting, $R = 0.081$; Dalley *et al.*, 1975) and *trans–cisoid–trans* (Simonov *et al.*, 1985) isomers. Only recently, the atomic coordinates for the known monoclinic polymorph of the *cis–transoid–cis* isomer became available from a private communication (Nazarenko, 2002; CCDC refcode DCHXCR04). We describe here the solid structure of a new orthorhombic polymorph of (I) and compare it with the monoclinic polymorph.

The centrosymmetric formula unit of (I) is shown in Fig. 1. The molecule is elongated in the direction of the cyclohexyl rings. The shape of the centrosymmetric molecule in the monoclinic polymorph is essentially the same. The superposition of these two polymorph molecules by fitting of all identical non-H atoms gives an r.m.s. deviation of 0.1494 Å. The separations between the *trans*-annular O atoms in (I) are O1···O1^{i} of 7.008 (3) Å, O4···O4^{i} of 4.042 (2) Å and O7···O7^{i} of 6.928 (2) Å [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$]. There is no evidence of either inter- or intramolecular hydrogen bonding; the shortest potential hydrogen-bond interaction involves atoms C6 and O4^{i} at a separation of 3.376 (2) Å, with the corresponding H···O4^{i} distance being 2.78 (2) Å.



(I)

The macrocyclic strand of the molecule in (I) displays a series of *anti* and *gauche* torsion angles for C—O and C—C bonds (Fig. 1). The individual O—C—C—O segments are $ag^{+}a$, aaa, $g^{+}g^{-}g^{-}$, $ag^{-}a$, aaa and $g^{-}g^{+}g^{+}$. Relevant torsion angles are listed in Table 1. A comparison with the data available for the pure phases of related 18-membered macrocycles shows similarities in the macrocyclic cavity shape (elliptical in all cases) and in the torsion-angle pattern along the macrocyclic strand in the molecule of 18-crown-6 (Maverick *et al.*, 1980) and those of the *cis–cisoid–cis* (Pears *et al.*, 1988*a*), *cis–transoid–cis* (Pears *et al.*, 1988*b*), *trans–cisoid–trans* (Pears *et al.*, 1988*c*) and *trans–transoid–trans* (Pears *et al.*, 1988*d*) isomers of tetraanisyl-18-crown-6.

The conformation of the dicyclohexano-18-crown-6 molecule is noticeably different in complexes with metals and cocrystals with organic molecules, where the macrocycle cavity adopts a more open shape compared with that reported above. The only exception was found in its cocrystals with 4-amino-3,5-dichlorobenzenesulfamide (Dvorkin *et al.*, 1991), where the conformation of one of the two crystallographically independent crown molecules coincides with that found in the pure phase.

The distinctive features of the crystal packing of (I) and of the monoclinic polymorph are noteworthy. In (I), the molecules are aligned along the *b* axis and form parallel piles in the perpendicular plane (Fig. 2*a*). The molecules in the piles are arranged in such a way that the polyether chains of

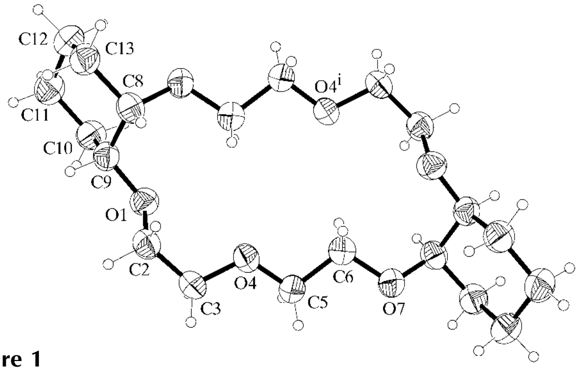


Figure 1
The structure of (I), projected on the plane of the six O atoms, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

DOI: 10.1107/S0108270102018206

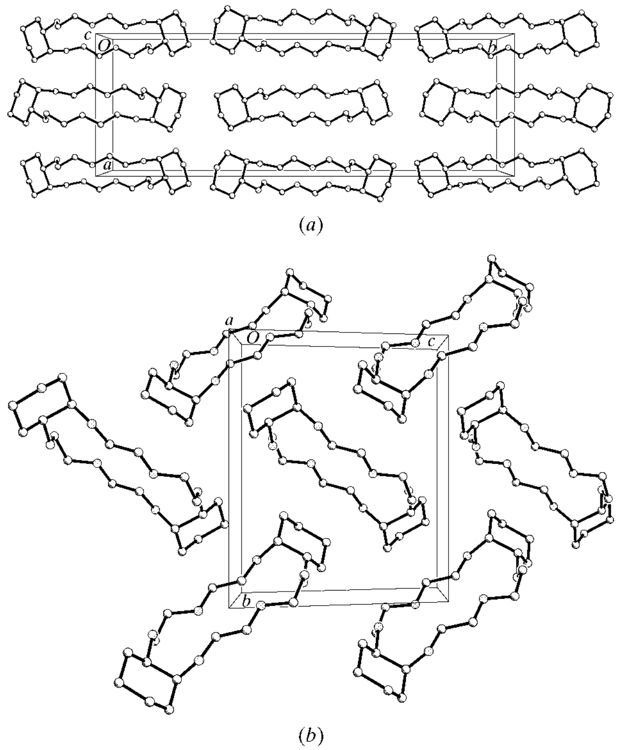


Figure 2
Packing diagrams for (*a*) (I) and (*b*) the monoclinic polymorph.

neighbouring macrocycles approach the same cavity from both sides. The dihedral angle between the planes of their six O atoms is 62.3°.

In the monoclinic polymorph, the cyclohexane moieties of adjacent molecules approach the same polyether cavity from both sides and the herring-bone packing motif is clearly observed (Fig. 2*b*). The dihedral angle between the planes of the six O atoms of two neighbouring molecules mutually arranged in the T-shape mode is 61.0°.

Experimental

Crystals of (I) were obtained serendipitously as by-products during cocrystallization of the macrocycle with tin tetrafluoride in methanol.

Crystal data

$C_{20}H_{36}O_6$
M_r = 372.49
Orthorhombic, *Pccn*
a = 9.7563 (3) Å
b = 28.5733 (10) Å
c = 7.2263 (2) Å
V = 2014.47 (11) Å^3
Z = 4
D_x = 1.228 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2312 reflections
θ = 1.0–27.9°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.4 × 0.4 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and *ω* scans
4105 measured reflections
2320 independent reflections
1092 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.054
$\theta_{\max}$ = 27.9°
h = 0 → 12
k = −37 → 37
l = 0 → 9

Table 1
Selected torsion angles (°).

C8—C9—O1—C2	81.62 (17)	O4—C5—C6—O7	163.91 (14)
C9—O1—C2—C3	−174.24 (13)	C5—C6—O7—C8$^{\rm i}$	149.65 (14)
O1—C2—C3—O4	72.42 (18)	C6—O7—C8$^{\rm i}$—C9$^{\rm i}$	72.90 (18)
C2—C3—O4—C5	−175.48 (14)	O7—C8$^{\rm i}$—C9$^{\rm i}$—O1$^{\rm i}$	−61.32 (17)
C3—O4—C5—C6	173.39 (14)		

Symmetry code: (i) 1 − *x*, 1 − *y*, 1 − *z*.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.102
S = 0.90
2320 reflections
190 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.12 e Å^{-3}
$\Delta\rho_{\min}$ = −0.14 e Å^{-3}

H atoms were found in a difference Fourier synthesis and were refined freely; C—H distances were in the range 0.967 (16)–1.022 (17).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *maXus* (Mackay *et al.*, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

The authors thank the MRDA–CRDF for financial support (research grant No. MP2-3021).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1116). Services for accessing these data are described at the back of the journal.

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A new polymorph of *cis–transoid–cis*-dicyclohexano-18-crown-6. Erratum

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In the *Comment* of the paper by Kravtsov *et al.* [*Acta Cryst.* (2002), C**58**, o683–o684], there in an error in a cited Cambridge Structural Database (Allen, 2002) refcode. The correct text is ‘Only recently, the atomic coordinates for the known monoclinic polymorph of the *cis–transoid–cis* isomer became available from a private communication (Nazarenko, 2002; CCDC refcode DCHXCS01).’ The updated reference is given below.

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