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Structure of the *trans–cisoid–trans* Isomer of 2,3,11,12-Tetra-anisyl-18-crown-6: *rel*-(2*R*,3*R*,11*S*,12*S*)-2,3,11,12-Tetrakis(4-methoxyphenyl)-1,4,7,10,13,16-hexaoxacyclooctadecane

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Abstract. $C_{40}H_{48}O_{10}X$, $M_r = 701$, triclinic, $P\bar{1}$, $a = 7{\cdot}121$ (2), $b = 12{\cdot}489$ (3), $c = 13{\cdot}770$ (4) Å, $\alpha = 113{\cdot}64$ (2), $\beta = 92{\cdot}58$ (3), $\gamma = 105{\cdot}26$ (2)°, $V = 1066$ Å^3, $Z = 1$, $D_x = 1{\cdot}09$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}60$ mm^{-1}, $F(000) = 374$, room temperature, $R = 0{\cdot}073$ for 2505 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The 18-membered ring of the title compound (3) adopts a conformation with two *anti* and four *gauche* OCH_2CH_2O units which is reminiscent of the conformation of 18-crown-6: all four anisyl groups are equatorial: the vicinal groups have a *gauche* relationship to each other. [X in the formula denotes unidentified solvent fragment assigned mass of carbon atom; M_r, D_x, μ and $F(000)$ include contribution from this unidentified solvent fragment.]

Introduction. Since both the X-ray crystal structures of *trans–cisoid–trans*-2,3,11,12-tetraphenyl-18-crown-6 (8)* (Weber, Sheldrick, Burgemeister, Dietl, Mannschreck & Merz, 1984) and its 1:2 adduct with ammonia–borane (Allwood, Shahriari-Zavareh, Stoddart & Williams, 1984) have been reported, we had, with the availability (Pears, 1985) of the *trans–cisoid–trans* isomer (3) of 2,3,11,12-tetra-anisyl-18-crown-6, the ideal opportunity to establish the generality or otherwise of the structural properties of this particular configurational diastereoisomer in the 2,3,11,12-tetra-aryl-18-crown-6 series of macrocyclic polyethers. Here, we reveal that the solid-state structure of (3) is indeed similar to that of (8) in terms of the gross overall conformational features of the molecules.

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* In order to avoid repetition in the presentation of configurational formulae, the reader is referred to Fig. 1 of Pears, Shahriari-Zavareh, Stoddart, Crosby, Allwood, Slawin & Williams (1988).

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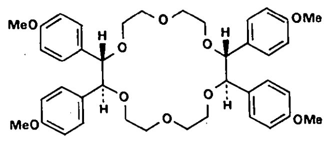

(3)

Experimental. The synthesis of the *trans–transoid–trans* isomer (4)* (Pears, Shahriari-Zavareh, Stoddart, Crosby, Allwood & Williams, 1988*b*) from a reaction of (±)-bis(4-methoxyphenyl)ethane-1,2-diol with diethyleneglycol bistosylate in dimethylformamide in the presence of sodium hydride as base was accompanied (Pears, 1985) by the formation of the configurational diastereoisomer (3) with the *trans–cisoid–trans* configuration. Column chromatography of the reaction product on silica gel using dichloromethane–diethyl ether as the eluant gave, first of all, fractions enriched in the *trans–transoid–trans* isomer (4) and then, later, fractions enriched in the *trans–cisoid–trans* isomer (3). On crystallization of this latter fraction from 2-methoxyethanol, single crystals of (3) with m.p. 462–464 K were obtained that were found to be suitable for X-ray structural investigation. Crystal size: 0·35 × 0·18 × 0·10 mm. Refined unit-cell parameters obtained from centring 18 refections. Nicolet $R3m$ diffractometer. 2860 independent reflections ($\theta \leq 58°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 2505 $[|F_o| > 3\sigma(|F_o|)]$ considered observed, index range h −7/7, k −13/12, l 0/14; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods. Although the intensity statistics indicated a centrosymmetric distribution, the structure did not readily solve in $P\bar{1}$. The structure was solved, however, by reverting to $P1$, an E map giving the positions of all the non-hydrogen atoms. Inspection of the coordinates revealed the presence of a centre of symmetry, so subsequent computations were carried out in $P\bar{1}$. Non-hydrogen atoms refined anisotropically. ΔF map revealed two atoms of an included solvent molecule. These were refined isotropically as 0·25 C atoms. Positions of H atoms calculated (C—H = 0·96 Å); H atoms assigned isotropic thermal parameters, $U(\mathrm{H}) = 1{\cdot}2\,U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on parent C atoms. The methoxy CH_3 groups refined as rigid bodies. 14 reflections which had $|F_o| \ll (|F_c|)$ were suspected of being affected by extinction and were removed. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0{\cdot}073$; $wR = 0{\cdot}079$ $[w^{-1} = \sigma^2(F) + 0{\cdot}00050F^2]$. $(\Delta/\sigma)_{\max}$ 0·088; residual electron density in difference map within −0·25 and 0·39 e Å^{-3}; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U/U_{eq}*
O(1)	4201 (3)	1860 (2)	−381 (2)	61 (1)
C(2)	2266 (5)	1403 (3)	−221 (3)	63 (2)
C(3)	1961 (5)	2269 (3)	846 (3)	58 (1)
O(4)	6 (3)	1763 (2)	944 (2)	62 (1)
C(5)	−576 (5)	2481 (3)	1903 (3)	63 (2)
C(6)	−2691 (5)	1851 (3)	1869 (3)	64 (2)
O(7)	−2812 (3)	719 (2)	1901 (2)	58 (1)
C(8)	−4771 (4)	−54 (3)	1760 (3)	54 (1)
C(9)	−4566 (4)	−1344 (3)	1446 (2)	54 (1)
C(10)	−5659 (4)	420 (3)	2761 (3)	52 (1)
C(11)	−4606 (5)	741 (4)	3761 (3)	72 (2)
C(12)	−5343 (6)	1166 (4)	4684 (3)	78 (2)
C(13)	−7190 (5)	1287 (4)	4658 (3)	69 (2)
C(14)	−8290 (5)	999 (3)	3688 (3)	72 (2)
C(15)	−7497 (5)	577 (3)	2739 (3)	62 (2)
C(16)	−6351 (4)	−2242 (3)	1532 (2)	53 (1)
C(17)	−8175 (5)	−2562 (3)	940 (3)	66 (2)
C(18)	−9820 (5)	−3413 (3)	995 (3)	67 (2)
C(19)	−9635 (5)	−3953 (3)	1674 (3)	63 (2)
C(20)	−7816 (6)	−3664 (3)	2270 (3)	71 (2)
C(21)	−6194 (5)	−2813 (3)	2208 (3)	61 (2)
O(22)	−7824 (4)	1701 (3)	5628 (2)	100 (2)
C(23)	−9721 (7)	1804 (5)	5669 (4)	108 (3)
O(24)	−11138 (4)	−4779 (2)	1816 (3)	90 (1)
C(25)	−13048 (6)	−5063 (4)	1267 (5)	116 (3)
X(1)	5071 (27)	4894 (18)	3964 (15)	156 (6)†
X(2)	3394 (61)	5308 (46)	5048 (38)	248 (17)†

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† U_{iso}.

Table 2. *Bond lengths* (Å), *angles* (°) *and selected torsion angles* (°)

O(1)—C(2)	1·410 (4)	O(1)—C(9′)	1·415 (4)
C(2)—C(3)	1·501 (5)	C(3)—O(4)	1·406 (4)
O(4)—C(5)	1·419 (4)	C(5)—C(6)	1·493 (5)
C(6)—O(7)	1·411 (5)	O(7)—C(8)	1·426 (4)
C(8)—C(9)	1·541 (5)	C(8)—C(10)	1·507 (5)
C(9)—C(16)	1·502 (5)	C(9)—O(1′)	1·415 (4)
C(10)—C(11)	1·387 (5)	C(10)—C(15)	1·374 (5)
C(11)—C(12)	1·356 (5)	C(12)—C(13)	1·363 (6)
C(13)—C(14)	1·378 (6)	C(13)—O(22)	1·371 (5)
C(14)—C(15)	1·405 (5)	C(16)—C(17)	1·371 (5)
C(16)—C(21)	1·397 (6)	C(17)—C(18)	1·387 (5)
C(18)—C(19)	1·375 (7)	C(19)—C(20)	1·379 (5)
C(19)—O(24)	1·359 (5)	C(20)—C(21)	1·381 (5)
O(22)—C(23)	1·392 (6)	O(24)—C(25)	1·409 (6)

C(2)—O(1)—C(9′)	116·2 (2)	O(1)—C(2)—C(3)	109·3 (2)
C(2)—C(3)—O(4)	106·1 (2)	C(3)—O(4)—C(5)	114·3 (2)
O(4)—C(5)—C(6)	107·8 (2)	C(5)—C(6)—O(7)	108·0 (3)
C(6)—O(7)—C(8)	114·9 (3)	O(7)—C(8)—C(9)	104·9 (3)
O(7)—C(8)—C(10)	110·7 (2)	C(9)—C(8)—C(10)	114·5 (3)
C(8)—C(9)—C(16)	113·7 (3)	C(8)—C(9)—O(1′)	111·6 (3)
C(16)—C(9)—O(1′)	107·4 (2)	C(8)—C(10)—C(11)	120·3 (3)
C(8)—C(10)—C(15)	122·7 (3)	C(11)—C(10)—C(15)	117·0 (3)
C(10)—C(11)—C(12)	122·5 (4)	C(11)—C(12)—C(13)	120·4 (4)
C(12)—C(13)—C(14)	119·5 (4)	C(12)—C(13)—O(22)	116·2 (3)
C(14)—C(13)—O(22)	124·2 (4)	C(13)—C(14)—C(15)	119·5 (4)
C(10)—C(15)—C(14)	121·0 (3)	C(9)—C(16)—C(17)	122·2 (4)
C(9)—C(16)—C(21)	120·5 (3)	C(17)—C(16)—C(21)	117·2 (3)
C(16)—C(17)—C(18)	122·5 (4)	C(17)—C(18)—C(19)	119·2 (3)
C(18)—C(19)—C(20)	119·7 (3)	C(18)—C(19)—O(24)	124·8 (3)
C(20)—C(19)—O(24)	115·5 (4)	C(19)—C(20)—C(21)	120·4 (4)
C(16)—C(21)—C(20)	120·9 (3)	C(13)—O(22)—C(23)	120·0 (4)
C(19)—O(24)—C(25)	117·9 (4)		

C(9′)—O(1)—C(2)—C(3)	−163·7 (3)	O(7)—C(8)—C(9)—O(1′)	−73·1 (3)
O(1)—C(2)—C(3)—O(4)	179·4 (3)	C(8)—C(9)—O(1′)—C(2′)	76·3 (3)
C(2)—C(3)—O(4)—C(5)	−178·4 (3)	O(7)—C(8)—C(9)—C(16)	165·3 (3)
C(3)—O(4)—C(5)—C(6)	177·9 (3)	C(10)—C(8)—C(9)—C(16)	43·7 (4)
O(4)—C(5)—C(6)—O(7)	65·2 (4)	C(10)—C(8)—C(9)—O(1′)	165·3 (2)
C(5)—C(6)—O(7)—C(8)	−173·7 (3)	C(9)—C(8)—C(10)—C(11)	69·7 (4)
C(6)—O(7)—C(8)—C(9)	161·6 (3)	C(8)—C(9)—C(16)—C(17)	60·9 (4)

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* See previous footnote.

Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. Table 1* lists the fractional atomic coordinates of the non-hydrogen atoms, Table 2 the bond lengths and angles, and selected C—C and C—O torsion angles associated with the polyether ring and substituent anisyl groups.

The structure of (3), which possesses a crystallographic centre of symmetry coincident with the centre of the macrocyclic ring, is illustrated in Fig. 1 together with the atomic numbering scheme. All four anisyl groups are equatorial and carry methoxy functions which are aligned approximately coplanar (Makriyannis & Fesik, 1982; Kruse & Cha, 1982; Mersh, Saunders & Matlin, 1983) with their associated rings. Both pairs of vicinal anisyl groups are oriented approximately *gauche* with respect to each other; however, there is a noticeable reduction in the Ar—C—C—Ar torsion angle [43·7 (4)°] from that [57·4 (3)°] reported (Weber *et al.*, 1984) for the corresponding *trans–cisoid–trans*-2,3,11,12-tetraphenyl-18-crown-6 derivative (8). By adopting a conformation with two *anti* and four *gauche* bismethylenedioxy units, the geometry of the macrocycle closely resembles that of 18-crown-6 (Dunitz & Seiler, 1974) and the *trans–cisoid–trans*-2,3,11,12-tetraphenyl-18-crown-6 derivative (8) (Weber *et al.*, 1984). In contrast with the *cis–cisoid–cis* (1) and *cis–transoid–cis* (2) isomers of 2,3,11,12-tetra-anisyl-18-crown-6 (Pears *et al.*, 1988; Pears, Shahriari-Zavareh, Stoddart, Crosby, Allwood & Williams, 1988*a*) where at least one face of the macrocycle is partially obscured by anisyl groups, here both (homotopic) faces are readily accessible.

Analysis of crystal packing reveals no contacts of less than normal van der Waals distances between symmetry-related macrocyclic receptors. The shortest contacts between receptor molecules and the disordered solvent fragments are both 4·0 Å to the methyl group, C(25), and to the methoxy oxygen atom, O(22).

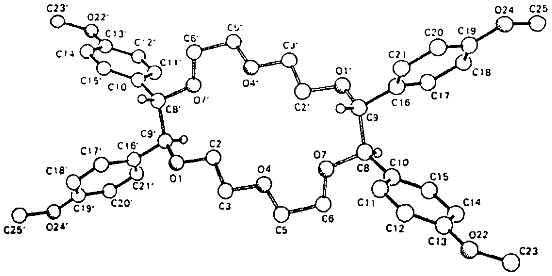

Fig. 1. Ball-and-stick representation of the structure of (3) showing the atomic numbering scheme. The anisyl substituents and the methine hydrogen atoms on the macrocycle are highlighted with solid C—C and C—H bonds.

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* Lists of structure-factor amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44787 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.