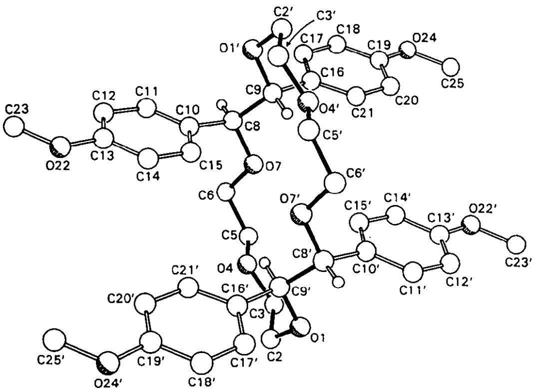

Fig. 1. Ball-and-stick representation of the structure of (2) showing the atomic numbering scheme. The 18-crown-6 ring is highlighted with solid C—C and C—O bonds.

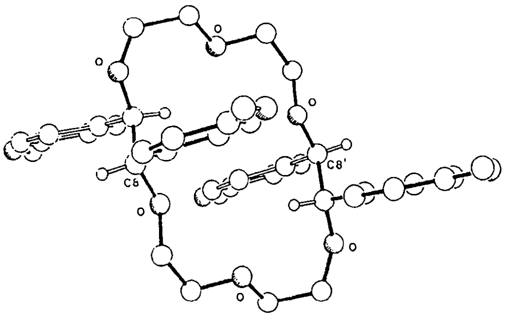

Fig. 2. A ball-and-stick representation of the structure of (2) looking down on the 18-membered ring. The macrocyclic ring, together with the two nearest anisyl groups, is highlighted with solid C—C and C—O bonds.

There are no contacts of less than normal van der Waals distances between symmetry-related molecules.

We thank the Science and Engineering Research Council and Imperial Chemical Industries PLC for financial support.

References

Blasius, E., Rausch, R. A., Andreetti, G. D. & Rebizant, J. (1984). *Chem. Ber.* **117**, 1113–1127.
Dunitz, J. D. & Seiler, P. (1974). *Acta Cryst.* B**30**, 2739–2741.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Kruse, L. I. & Cha, J. K. (1982). *J. Chem. Soc. Chem. Commun.* pp. 1329–1331.
Makriyannis, A. & Fesik, S. (1982). *J. Am. Chem. Soc.* **104**, 6462–6463.
Mersh, J. D., Saunders, J. K. M. & Matlin, S. A. (1983). *J. Chem. Soc. Chem. Commun.* pp. 306–307.
Pears, D. A. (1985). PhD Thesis. Univ. of Sheffield, England.
Pears, D. A., Shahriari-Zavareh, H., Stoddart, J. F., Crosby, J., Allwood, B. L., Slawin, A. M. Z. & Williams, D. J. (1988). *Acta Cryst.* C**44**, 1097–1100.
Pears, D. A., Shahriari-Zavareh, H., Stoddart, J. F., Crosby, J., Allwood, B. L. & Williams, D. J. (1988). *Acta Cryst.* C**44**, 1106–1109.
Sheldrick, G. M. (1983). *SHELXTL*, revision 4.0, January 1983. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.
Weber, G., Sheldrick, G. M., Burgemeister, Th., Dietl, F., Mannschreck, A. & Merz, A. (1984). *Tetrahedron*, **40**, 855–863.

Acta Cryst. (1988). C**44**, 1106–1109

A 1:2 Adduct Between the *cis–transoid–cis* Isomer of 2,3,11,12-Tetra-anisyl-18-crown-6 and Ammonia–Borane

By David A. Pears, Hooshang Shahriari-Zavareh and J. Fraser Stoddart
Department of Chemistry, The University, Sheffield S3 7HF, England

John Crosby
Organics Division, Imperial Chemical Industries PLC, Blackley, Manchester M9 3DA, England

and Billy L. Allwood and David J. Williams
Department of Chemistry, Imperial College, London SW7 2AY, England

(*Received* 7 *September* 1987; *accepted* 17 *February* 1988)

Abstract. *rel*-(2*R*,3*S*,11*S*,12*R*)-2,3,11,12-Tetrakis(4-methoxyphenyl)-1,4,7,10,13,16-hexaoxacyclooctadecane–ammonia–borane (1/2/2), $C_{40}H_{48}O_{10}.B_2H_6N_2H_6$, $M_r = 751$, monoclinic, $P2_1/c$, $a = 8{\cdot}224\,(2)$, $b = 8{\cdot}848\,(3)$, $c = 28{\cdot}47\,(1)$ Å, $\beta = 90{\cdot}56\,(3)°$, $V = 2072$ Å^3, $Z = 2$, $D_x = 1{\cdot}21$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}65$ mm^{-1}, $F(000) = 808$, room temperature, $R = 0{\cdot}051$ for 1730 unique observed

reflections with $|F_o| > 3\sigma(|F_o|)$. Two molecules of BH_3NH_3 are hydrogen bonded through their NH_3 groups, each by two-point binding, to two of the nearer O atoms on the homotopic faces of the title receptor (2) wherein the macrocycle adopts an all-*gauche* conformation: both faces carry equatorial and pseudo-axial anisyl groups.

Introduction. In view of the fact that the *cis–transoid–cis* isomer (2) of 2,3,11,12-tetra-anisyl-18-crown-6 has a much stronger complexing ability [Pears, Shahriari-Zavareh, Stoddart, Crosby, Allwood, Slawin & Williams, 1988 (paper I); Pears, Shahriari-Zavareh, Stoddart, Crosby, Allwood & Williams, 1988*a*,*b* (papers II, III)] than the diastereoisomeric *cis–cisoid–cis* isomer (1),* it was of considerable interest to us to compare the solid-state structures of their ammonia–borane (BH_3-NH_3) adducts. The first point of interest surrounds the stoichiometries of the crystalline adduct: while (1) forms a 1:1 adduct, (2) is isolated (Pears, 1985) as the 1:2 adduct, $[(2).(BH_3NH_3)_2]$. Here, we report on the crystal structure of this adduct and comment on its structural relationship (*a*) to the free macrocycle (2) (Pears *et al.*, 1988*b*), (*b*) to the adduct $[(1).BH_3NH_3]$ (Pears *et al.*, 1988*a*), and (*c*) to the 1:1 complex formed between *cis–transoid–cis*-2,3,11,12-tetraphenyl-18-crown-6 (7)† and sodium iodide (Weber, Sheldrick, Burgemeister, Dietl, Mannschreck & Merz, 1984).

Experimental. A solution of ammonia–borane (1 mg) in methanol (0·5 ml) was added to a solution of (2) (10 mg) in dichloromethane (1 ml). The solvents were removed under vacuum to afford a white solid, which was redissolved in dichloromethane (0·5 ml) and layered with *n*-pentane. After 2 days, single crystals of $[(2).(BH_3NH_3)_2]$ had formed with m.p. 428–430 K and were found to be suitable for X-ray structural investigation (Pears, 1985). Crystal size: 0·63 × 0·27 × 0·03 mm. Refined unit-cell parameters obtained from centring 16 reflections. Nicolet *R*3*m* diffractometer, 2124 independent reflections ($\theta \leq 50°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 1730 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range h −8/8, k 0/8, l 0/28; two check reflections every 50 reflections, net count constant; Lorentz and polarization correction, no absorption correction. Structure solved by direct methods; non-hydrogen atoms refined anisotropically. Positions of NH_3 and BH_3 hydrogen atoms clearly resolved in ΔF map; CH_3, BH_3 and NH_3 groups refined as rigid bodies (B—H = 1·08, N—H = 0·96 Å); positions of other H atoms calculated (C—H = 0·96 Å); H atoms assigned isotropic thermal parameters, $U(H) = 1{\cdot}2\ U_{eq}(X)$ (X = C, N, B) and allowed to ride on parent X atoms. An empirical extinction correction was applied (g = 0·00284). Refinement using F magnitudes by block-cascade full-matrix least squares; R = 0·051; wR = 0·053 [$w^{-1} = \sigma^2(F) + 0{\cdot}0008F^2$]. $(\Delta/\sigma)_{max}$ = 0·084; residual electron density in difference map within −0·18 and 0·19 e Å^{-3}; atomic scattering factors and dispersion correction from *International Tables for X-ray Crystallography* (1974). 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 torsion angles.

The structure of $[(2).(BH_3NH_3)_2]$ is illustrated in Fig. 1 which includes the atomic numbering scheme. Fig. 2 shows a space-filling representation of the 1:2 adduct viewed normal to the plane of the macrocyclic ring.

There is a crystallographic centre of symmetry at the centre of the macrocyclic ring. On adduct formation with two molar equivalents of BH_3NH_3 the macrocycle changes from a geometry closely similar to that of 18-crown-6 in the crystalline state (Dunitz & Seiler, 1974) to a distorted all-*gauche* conformation with local pseudo-D_{3d} symmetry. The reduced magnitudes [161·6 (3) and 151·2 (3)°] of the '*anti*' C—O—C—C [O(1)—C(2) and O(7)—C(6) respectively] torsion angles produce a slight splaying of the axial anisyl substituents at C(8) and C(8′), thus preventing their obscuring both faces of the macrocycle. This distortion is probably a result of steric repulsion (Fig. 2) between the BH_3 groups on the substrates and one of the *ortho* H atoms on each of the pseudo-axial anisyl substituents. The C(9) and C(9′) anisyl substituents are both equatorial and *gauche* to their vicinal partners. Both BH_3NH_3 molecules are bound (Figs. 1 and 2) in perching modes (Trueblood, Knobler, Lawrence & Stevens, 1982) to opposite faces of the macrocycle.

The NH_3 group in the BH_3NH_3 substrate is hydrogen bonded to O(1), O(7) and O(4′) with N···O distances of 3·34 (1), 3·04 (1) and 3·13 (1) Å respectively. The corresponding N—H···O angles at H(*c*), H(*a*) and H(*b*) are 168, 172 and 161°. The angles between the COC planes and the HO vectors are 19, 23 and 9° for H(*c*), H(*a*) and H(*b*) respectively. The NH_3 and BH_3 groups in the substrate are in almost staggered relationship with respect to each other, the smallest H—N—B—H torsion angle being 51°. The N atom is displaced 1·61 Å from the best mean plane of the six O atoms in

---

* In order to avoid repetition in the presentation of configurational formulae, the reader is referred to paper III and to Fig. 1 in paper I.

† See previous footnote.

* 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 44786 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²×10³)

	x	y	z	U_{eq}*
O(1)	7256 (3)	−774 (3)	5821 (1)	52 (1)
C(2)	8795 (4)	−128 (4)	5700 (1)	64 (2)
C(3)	8562 (4)	1471 (4)	5560 (1)	60 (1)
O(4)	7856 (3)	1535 (2)	5102 (1)	49 (1)
C(5)	7704 (4)	3047 (4)	4937 (1)	53 (1)
C(6)	7058 (4)	3042 (4)	4450 (1)	54 (1)
O(7)	5452 (3)	2397 (3)	4453 (1)	49 (1)
C(8)	4433 (4)	2964 (4)	4086 (1)	45 (1)
C(9)	2723 (4)	2391 (4)	4183 (1)	47 (1)
C(10)	5089 (4)	2601 (4)	3600 (1)	43 (1)
C(11)	4932 (4)	3644 (4)	3246 (1)	48 (1)
C(12)	5545 (4)	3387 (4)	2800 (1)	50 (1)
C(13)	6337 (4)	2065 (4)	2710 (1)	52 (1)
C(14)	6504 (4)	993 (4)	3061 (1)	58 (1)
C(15)	5871 (4)	1264 (4)	3498 (1)	51 (1)
C(16)	1525 (4)	3091 (4)	3843 (1)	44 (1)
C(17)	762 (4)	4414 (4)	3959 (1)	46 (1)
C(18)	−212 (4)	5204 (4)	3647 (1)	50 (1)
C(19)	−424 (4)	4629 (4)	3199 (1)	48 (1)
C(20)	262 (4)	3264 (4)	3080 (1)	53 (1)
C(21)	1229 (4)	2494 (4)	3396 (1)	51 (1)
O(22)	7039 (3)	1706 (3)	2289 (1)	74 (1)
C(23)	6999 (6)	2811 (5)	1932 (1)	84 (2)
O(24)	−1299 (3)	5337 (3)	2850 (1)	62 (1)
C(25)	−2138 (5)	6672 (4)	2972 (2)	75 (2)
N	4105 (3)	1116 (3)	5360 (1)	52 (1)
B	3296 (6)	2400 (5)	5672 (2)	68 (2)

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

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

O(1)—C(2)	1·433 (4)	O(1)—C(9′)	1·431 (4)
C(2)—C(3)	1·483 (5)	C(3)—O(4)	1·423 (4)
O(4)—C(5)	1·422 (4)	C(5)—C(6)	1·480 (5)
C(6)—O(7)	1·439 (4)	O(7)—C(8)	1·424 (4)
C(8)—C(9)	1·523 (4)	C(8)—C(10)	1·524 (5)
C(9)—C(16)	1·506 (5)	C(9)—O(1′)	1·431 (4)
C(10)—C(11)	1·371 (5)	C(10)—C(15)	1·379 (5)
C(11)—C(12)	1·391 (5)	C(12)—C(13)	1·365 (5)
C(13)—C(14)	1·384 (5)	C(13)—O(22)	1·373 (4)
C(14)—C(15)	1·373 (5)	C(16)—C(17)	1·370 (5)
C(16)—C(21)	1·398 (5)	C(17)—C(18)	1·380 (5)
C(18)—C(19)	1·383 (5)	C(19)—C(20)	1·377 (5)
C(19)—O(24)	1·373 (4)	C(20)—C(21)	1·376 (5)
O(22)—C(23)	1·411 (5)	O(24)—C(25)	1·413 (5)
N—B	1·593 (6)		
C(2)—O(1)—C(9′)	112·7 (2)	O(1)—C(2)—C(3)	109·5 (3)
C(2)—C(3)—O(4)	109·6 (3)	C(3)—O(4)—C(5)	111·9 (2)
O(4)—C(5)—C(6)	109·6 (3)	C(5)—C(6)—O(7)	108·5 (3)
C(6)—O(7)—C(8)	113·0 (2)	O(7)—C(8)—C(9)	106·8 (3)
O(7)—C(8)—C(10)	112·3 (3)	C(9)—C(8)—C(10)	115·5 (3)
C(8)—C(9)—C(16)	110·3 (3)	C(8)—C(9)—O(1′)	108·7 (3)
C(16)—C(9)—O(1′)	114·5 (3)	C(8)—C(10)—C(11)	119·5 (3)
C(8)—C(10)—C(15)	122·9 (3)	C(11)—C(10)—C(15)	117·6 (3)
C(10)—C(11)—C(12)	121·9 (3)	C(11)—C(12)—C(13)	119·3 (3)
C(12)—C(13)—C(14)	119·7 (3)	C(12)—C(13)—O(22)	124·6 (3)
C(14)—C(13)—O(22)	115·7 (3)	C(13)—C(14)—C(15)	119·9 (3)
C(10)—C(15)—C(14)	121·5 (3)	C(9)—C(16)—C(17)	119·7 (3)
C(9)—C(16)—C(21)	122·4 (3)	C(17)—C(16)—C(21)	117·8 (3)
C(16)—C(17)—C(18)	122·9 (3)	C(17)—C(18)—C(19)	118·3 (3)
C(18)—C(19)—C(20)	120·1 (3)	C(18)—C(19)—O(24)	124·1 (3)
C(20)—C(19)—O(24)	115·8 (3)	C(19)—C(20)—C(21)	120·6 (3)
C(16)—C(21)—C(20)	120·2 (3)	C(13)—O(22)—C(23)	117·5 (3)
C(19)—O(24)—C(25)	117·3 (3)		
C(9′)—O(1)—C(2)—C(3)	161·6 (3)	O(7)—C(8)—C(9)—O(1′)	−60·5 (3)
O(1)—C(2)—C(3)—O(4)	−74·9 (4)	C(8)—C(9)—O(1′)—C(2′)	176·0 (3)
C(2)—C(3)—O(4)—C(5)	−176·2 (3)	O(7)—C(8)—C(9)—C(16)	173·3 (3)
C(3)—O(4)—C(5)—C(6)	176·6 (3)	C(10)—C(8)—C(9)—C(16)	−61·1 (4)
O(4)—C(5)—C(6)—O(7)	63·2 (3)	C(10)—C(8)—C(9)—O(1′)	65·2 (4)
C(5)—C(6)—O(7)—C(8)	151·2 (3)	C(9)—C(8)—C(10)—C(15)	−86·4 (4)
C(6)—O(7)—C(8)—C(9)	−170·7 (3)	C(8)—C(9)—C(16)—C(21)	84·8 (4)

the macrocycle and the B—N bond is inclined 7·7° to the normal to this plane. The through-the-ring N···N′ distance is 3·21 (1) Å. All the N—H···O hydrogen bonds are noticeably longer than those in the 1:1 adduct (Pears *et al.*, 1988*a*) of BH_3NH_3 with the *cis–cisoid–cis* isomer (1) of 2,3,11,12-tetra-anisyl-18-crown-6. Also, there is a marked asymmetry in the N···O distances indicating a tendency towards two-point rather than three-point binding geometry. This feature is also present (Allwood, Shahriari-Zavareh, Stoddart & Williams, 1984; Shahriari-Zavareh, Stoddart, Williams, Allwood & Williams, 1985) in other 1:2 adducts between 18-crown-6 derivatives and BH_3NH_3. In [(2).$(BH_3NH_3)_2$], the weakest – and longest – hydrogen bonds [to O(1) and O(1′)] are directed towards those portions of the macrocycle that carry the pseudo-axial anisyl groups [at C(8′) and C(8) respectively]: this results in the tilting of the BH_3NH_3 substrates away from these substituents, presumably in order to reduce steric interactions with them. Thus, it would appear that (2) carries two equally poor binding sites for BH_3NH_3 substrates in contrast with (1) which carries (Pears *et al.*, 1988*a*) one highly efficient binding site. The solid-state structure of [(2).$(BH_3NH_3)_2$] is not comparable with that (Weber *et al.*, 1984) of [(7).NaI], which is clearly quite a different situation altogether.

The shortest non-hydrogen contact between symmetry-related adducts is 3·21 (1) Å between the methoxy oxygen atom O(24) and the anisyl-group carbon atom at C(12). There are no other intermolecular contacts of less than normal van der Waals distances.

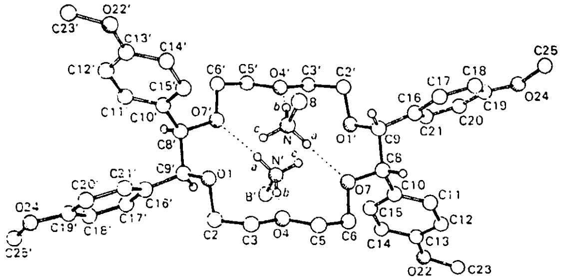

Fig. 1. Ball-and-stick representation of the structure of [(2).(BH_3-$NH_3)_2$] showing the atomic numbering scheme. The 18-crown-6 ring is highlighted with solid C—C and C—O bonds.

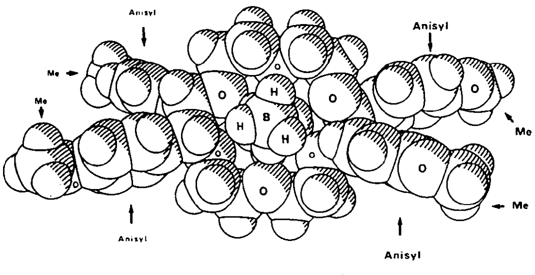

Fig. 2. Space-filling representation of [(2).$(BH_3NH_3)_2$] viewed normal to the plane of the macrocyclic ring.

We thank the Science and Engineering Research Council and Imperial Chemical Industries PLC for financial support.

References

ALLWOOD, B. L., SHAHRIARI-ZAVAREH, H., STODDART, J. F. & WILLIAMS, D. J. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1461–1464.

DUNITZ, J. D. & SEILER, P. (1974). *Acta Cryst.* **B30**, 2739–2741.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

PEARS, D. A. (1985). PhD Thesis. Univ. of Sheffield, England.

PEARS, D. A., SHAHRIARI-ZAVAREH, H., STODDART, J. F., CROSBY, J., ALLWOOD, B. L., SLAWIN, A. M. Z. & WILLIAMS, D. J. (1988). *Acta Cryst.* **C44**, 1097–1100.

PEARS, D. A., SHAHRIARI-ZAVAREH, H., STODDART, J. F., CROSBY, J., ALLWOOD, B. L. & WILLIAMS, D. J. (1988*a*). *Acta Cryst.* **C44**, 1101–1104.

PEARS, D. A., SHAHRIARI-ZAVAREH, H., STODDART, J. F., CROSBY, J., ALLWOOD, B. L. & WILLIAMS, D. J. (1988*b*). *Acta Cryst.* **C44**, 1104–1106.

SHAHRIARI-ZAVAREH, H., STODDART, J. F., WILLIAMS, M. K., ALLWOOD, B. L. & WILLIAMS, D. J. (1985). *J. Inclusion Phenom.* **3**, 355–377.

SHELDRICK, G. M. (1983). *SHELXTL*, revision 4.0, January 1983. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

TRUEBLOOD, K. N., KNOBLER, C. B., LAWRENCE, D. S. & STEVENS, R. V. (1982). *J. Am. Chem. Soc.* **104**, 1355–1362.

WEBER, G., SHELDRICK, G. M., BURGEMEISTER, TH., DIETL, F., MANNSCHRECK, A. & MERZ, A. (1984). *Tetrahedron*, **40**, 855–863.

Acta Cryst. (1988). C**44**, 1109–1111

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

BY DAVID A. PEARS, HOOSHANG SHAHRIARI-ZAVAREH AND J. FRASER STODDART

Department of Chemistry, The University, Sheffield S3 7HF, England

JOHN CROSBY

Organics Division, Imperial Chemical Industries PLC, Blackley, Manchester M9 3DA, England

AND BILLY L. ALLWOOD AND DAVID J. WILLIAMS

Department of Chemistry, Imperial College, London SW7 2AY, England

(*Received 7 September* 1987; *accepted* 17 *February* 1988)

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.

---

[*] 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).

0108-2701/88/061109-03$03.00