Stereospecific Syntheses of Macrobicyclic Polyethers with Carbon Bridgeheads from Chiral Glycerol Derivatives

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The [3.3.3]cryptand (**3**), prepared stereospecifically from 2,3-*O*-isopropylidene-D-glycerol D-(**1**) and 2,3-di-*O*-benzyl-L-glycerol L-(**2**), has been separated chromatographically at −5 °C into slowly interconverting *in-in ii*-(**3**) and *out-out oo*-(**3**) conformational diastereoisomers [$\Delta G^{\ddagger}_{ii\rightarrow oo}$ = *ca.* 24 kcal mol^{-1} (1 kcal = 4.184 kJ) in CD_3COCD_3 at +38 °C]; an *X*-ray structural analysis has shown (**3**) to form a crystalline 1 : 1 complex with $Ba(SCN)_2$ in which the Ba^{2+} ion is encapsulated by *oo*-(**3**) and the two SCN^- ions in an 11-co-ordinate manner.

Since the preparation of the first macrobicyclic polyethers with carbon bridgeheads was reported[1] from pentaerythritol, two reports have appeared[2,3] describing the incorporation of glycerol units at the bridgehead positions. A stereospecific synthesis starting from 2,3-*O*-isopropylidene-D-glycerol[4] D-(**1**) provides[2] a route to *in-out* isomers, whereas a non-stereospecific approach,[3] employing 1,3-dichloropropan-2-ol as the bridgehead synthon, relies upon an isomer separation† at an intermediate stage in the synthetic procedure, which affords, subsequently, only *out-out* isomers carrying fused benzo- and cyclohexano-rings.[5] In the search for a way of preparing unsubstituted *in-in* and *out-out* isomers, without having to resort to difficult isomer separations (*cf.* ref. 2), we have devised a stereospecific route where D-(**1**) constitutes one bridgehead and 2,3-di-*O*-benzyl-L-glycerol‡ L-(**2**), the other bridgehead. Here, we illustrate our approach with reference to the synthesis§ (see Scheme 1) of the [3.3.3]cryptand (**3**), which exists as chromatographically separable *in-in*, *ii*-(**3**), and *out-out*, *oo*-(**3**), isomers and then report on (*i*) the characterisation of *oo*-(**3**) by *X*-ray crystallography of its $Ba(SCN)_2$ complex and (*ii*) our preliminary investigations on the thermodynamic and kinetic stabilities of *ii*-(**3**) and *oo*-(**3**) in solution by ^{1}H and ^{13}C n.m.r. spectroscopy.

Reaction [NaH, tetrahydrofuran (THF)] of D-(**1**) with 2.3 mol. equiv. of $Ts[OCH_2CH_2]_2OTs$ (Ts = tosyl)[6] afforded (44%) the toluene-*p*-sulphonate D-(**4**), $[\alpha]_D$ + 4.6° (*c* 2.0, MeOH), after SiO_2 chromatography (CH_2Cl_2–Et_2O–light petroleum). The reaction (NaH, THF) between D-(**4**) and L-(**2**) yielded (74%) the acyclic polyether DL-(**5**), $[\alpha]_D$ + 5.2° (*c* 4.35, MeOH). Methanolysis (Zerolit 325/H$^+$) of DL-(**5**) gave the diol DL-(**6**), $[\alpha]_D$ −0.10° (*c* 4.57, MeOH), in quantitative yield after SiO_2 chromatography (Et_2O–MeOH). Hydrogenolysis (Pd/C, MeOH) of DL-(**6**) also proceeded quantitatively to give the *meso*-tetraol (**7**). Tritylation (Ph_3CCl, 4-*N*,*N*-dimethylaminopyridine, Et_3N, CH_2Cl_2)[7] of (**7**) yielded (60%) the ditrityl ether (**8**) after SiO_2 chromatography (Et_2O–light petroleum). Reaction (NaH, Me_2SO) of (**8**) with $Ts[OCH_2CH_2]_2OTs$ afforded the crude 18-crown-6 derivative (**9**), which was most easily purified by a stepwise sequence of precipitations that rely upon consecutive complexations of (**9**) with BH_3NH_3[8] and MeCN.[9] Thus, addition of pentane to a $CHCl_3$–MeOH solution of crude (**9**) and BH_3NH_3 yielded a precipitate, which was isolated and refluxed in Me_2CO–H_2O (2 M NaOH) to regenerate purified (**9**). Addition of MeCN to this sample afforded a crystalline (**9**)·2MeCN complex, m.p. 48—50 °C. Single crystals suitable for *X*-ray crystallography¶ were obtained from a MeCN solution by layering with pentane. The crystal structure (Figure 1) of (**9**)·2MeCN confirmed the *cis* stereochemistry of the 18-crown-6 derivative (**9**). Heating (*ca.* 50°C) of (**9**)·2MeCN *in vacuo* afforded pure (**9**) as an oil. This efficient isolation procedure avoids column chromatography and permits the isolation of (**9**) in 48% yield from (**8**). Deprotection (HCl, MeOH, CH_2Cl_2) of (**9**) gave (100%) the diol (**10**), which was treated (NaH, Me_2SO) with $Ts[OCH_2CH_2]_2OTs$ to afford the [3.3.3]cryptand (**3**) in 20% yield. The *out-out* isomer *oo*-(**3**) was characterised as its $Ba(SCN)_2$ complex by stirring (16 h) a solution of (**3**) in CH_2Cl_2 with excess of the salt and then layering pentane on top of the extract to afford single crystals of (**3**)·$Ba(SCN)_2$·CH_2Cl_2, m.p. 90 °C, suitable for *X*-ray crystallography.¶ The crystal structure (Figure 2)

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† The recently reported (Y. Nakatsuji, T. Mori, and M. Okahara, *Tetrahedron Lett.*, 1984, **25**, 2171) separation of *cis* and *trans* isomers of several bis(bromomethyl) dimethyl crown ethers could also provide a synthetic entry into macrobicyclic polyethers with carbon bridgeheads. *Note added in proof.* Indeed, after the present communication had been accepted for publication, Nakatsuji *et al.* published a communication (*J. Chem. Soc., Chem. Commun.*, 1984, 1045) in which they reported on the syntheses of the [3.3.3]-, [3.3.2]-, and [3.2.2.]-cryptands with CMe bridgeheads and evaluated the abilities of these macrobicyclic polyethers to complex with Na$^+$ and K$^+$ ions in methanolic solution.

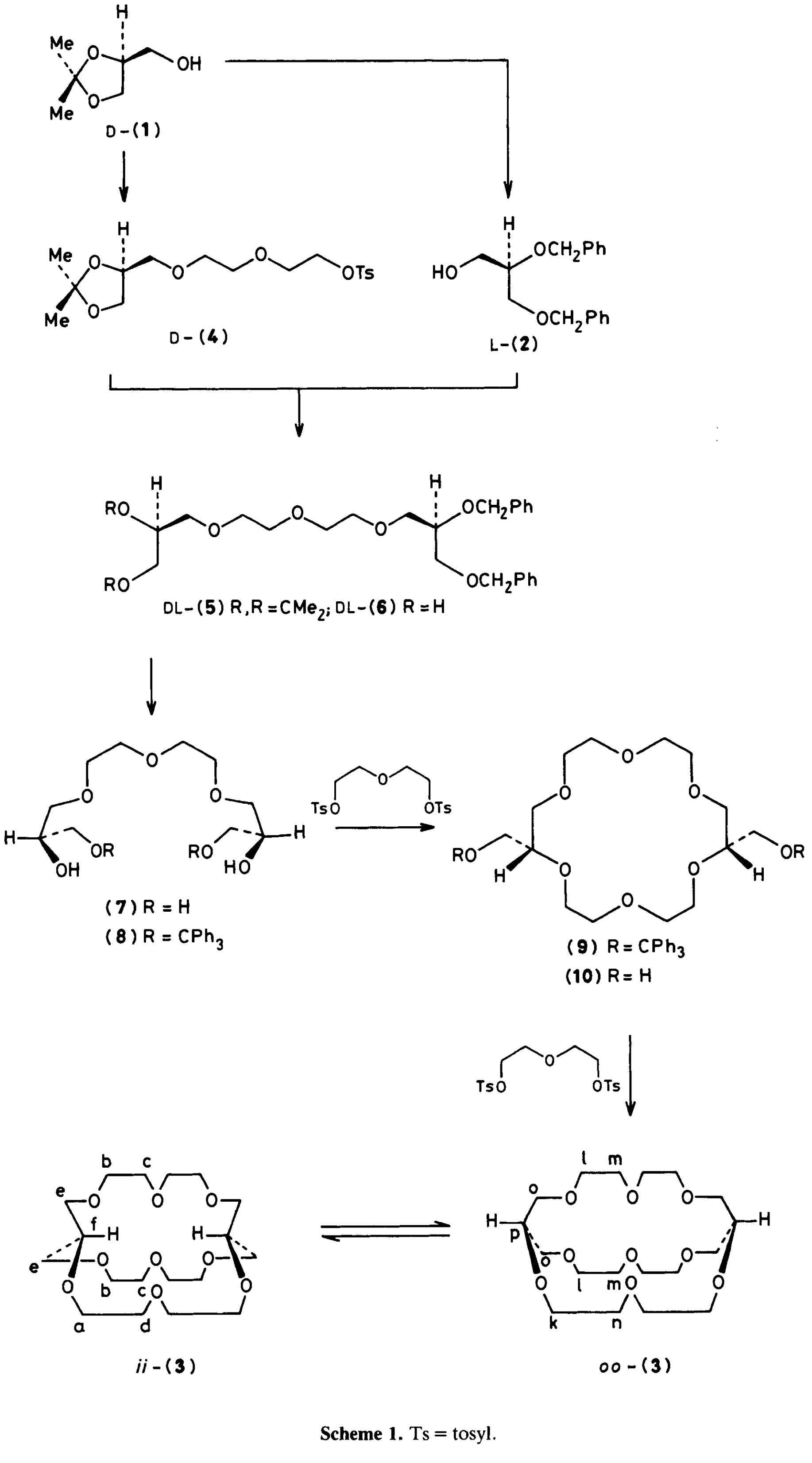
‡ The compound L-(**2**) was synthesised by a modification of a literature route (B. Wickberg, *Acta Chem. Scand.*, 1958, **12**, 1187). The optical purity of L-(**2**) was checked by conversion into its trityl derivative, $[\alpha]_D$ −8.8° (*c*, 5.0, $CHCl_3$). Recently, D-(**1**) and L-(**1**) have become commercially available from Aldrich.

§ All new compounds gave satisfactory analytical and n.m.r. spectroscopic data. D-(**4**) δ(^{1}H, 220 MHz, $CDCl_3$) 1.35, 1.41 (2 × 3H, 2 × s, CMe_2), 2.44 (3H, s, $SO_2C_6H_4\mathit{Me}$), 3.40—3.75 (9H, m, CH_2OCH_2-CH_2OCH_2 and C*H*H in ring), 4.04 (1H, dd, *J* 6, 8 Hz, OC*H*H in ring), 4.16 (2H, t, *J* 5 Hz, $C\mathit{H}_2OSO_2C_6H_4Me$), 4.28 (1H, quintet, *J* 6 Hz, CH), 7.35, 7.81 (2 × 2H, 2 × d, *J* 8 Hz, $SO_2C_6\mathit{H}_4Me$); DL-(**5**) δ(^{1}H, 220 MHz, $CDCl_3$) 1.38, 1.45 (2 × 3H, 2 × s, CMe_2), 3.45—3.87 (16H, m, $C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}(OCH_2Ph)C\mathit{H}_2OCH_2Ph$ and OC*H*H in ring), 4.07 (1H, dd, *J* 6.0, 8.5 Hz, OCH*H* in ring), 4.30 (1H, quintet, *J* 6.0 Hz, CH in ring), 4.58, 4.73 (2 × 2H, 2 × s, $CH_2OC\mathit{H}_2Ph$ and $CHOC\mathit{H}_2Ph$ respectively), 7.20—7.42 (10H, m, 2 × Ph); DL-(**6**) δ(^{1}H, 220 MHz, $CDCl_3$) 2.75, 2.95 (2 × 1H, 2 × br. s, 2 × OH), 3.45—3.70 (16H, m, 8 × OCH_2), 3.81 (2H, quintet, 2 × OCH superimposed), 4.56, 4.72 (2 × 2H, 2 × s, $CH_2OC\mathit{H}_2Ph$ and $CHOC\mathit{H}_2Ph$, respectively), 7.25—7.40 (10H, m, 2 × Ph); (**7**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3) 64.5, 71.2, 71.3, 71.8 (CH_2), 73.8 (CH); δ(^{1}H, 220 MHz, CD_3OD) 3.40—3.72 (16H, m, 8 × OCH_2), 3.78 (2H, quintet, *J* 5.5 Hz, 2 × OCH); (**8**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3) 65.9, 71.1, 71.3, 73.8 (CH_2), 70.4 (CH), 87.0 (C), 127.7, 128.4, 129.4, 145.1 (Ph); δ(^{1}H, 400 MHz, $CDCl_3$) 3.10, 3.18 (4H, AB portion of 'ABX system', J_{AB} 9.5, J_{AX} 5.5. J_{BX} 6.0 Hz, 2 × $C\mathit{H}_2OCPh_3$), 3.50, 3.65 (4H, AB portion of 'ABX system' J_{AB} 10, J_{AX} 3.0, J_{BX} 7.0 Hz, 2 × $OC\mathit{H}_2CH$), 3.54 (2H, br. s, 2 × OH), 3.57—3.68 (8H, m, 4 × OCH_2), 3.96 (2H, br. m, 2 × OCH), 7.17—7.43 (30H, m, 2 × CPh_3); (**9**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3) 64.7, 70.7, 71.3, 71.6, 71.8, 72.4 (CH_2), 79.5 (CH), 87.2 (C), 127.7, 128.5, 129.4, 145.1 (Ph); δ(^{1}H, 400 MHz, $CDCl_3$) 3.11, 3.17 (4H, AB portion of 'ABX system' J_{AB} 9.5, J_{AX}, J_{BX} 5.5 Hz, 2 × $C\mathit{H}_2OCPh_3$), 3.55—3.80 (22H, m, 10 × OCH_2, 2 × OCH), 7.19—7.45 (30H, m, 2 × CPh_3); (**10**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3) 62.6, 70.2, 71.4, 71.5, 71.5, 72.3 (CH_2), 80.9 (CH); δ(^{1}H, 400 MHz, $CDCl_3$) 3.30 (2H, br. s, 2 × OH), 3.60—3.85 (26H, m 12 × OCH_2, 2 × OCH); *ii*-(**3**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3, −40 °C) 69.7 (CH_2-a), 71.2 (2 × CH_2-b, 2 × CH_2-c), 71.9 (CH_2-d), 72.9 (2 × CH_2-e), 77.2 (CH-f); δ(^{1}H, 400 MHz, $CDCl_3$, −5 °C) 3.53—3.62 (8H, AB portion of 'ABX system', J_{AB} 10, J_{AX}, J_{BX} 6.0 Hz, 4 × CH_2-e), 3.62—3.72 (16H, m, 4 × CH_2-b, 4 × CH_2-c), 3.74, 3.91 (8H, AA′BB′ system, 2 × CH_2-a, 2 × CH_2-d), 4.35 (2H, quintet, *J* 6.0 Hz, 2 × CH-f); *oo*-(**3**) δ(^{13}C{^{1}H}, 25.15 MHz, CD_3COCD_3, −40 °C) 70.0 (CH_2-k), 71.2, 71.5, 71.5, 71.7 (2 × CH_2-l, 2 × CH_2-m, CH_2-n, 2 × CH_2-o), 79.9 (CH-p); δ(^{1}H, 400 MHz, $CDCl_3$, −5 °C) 3.50—3.92 (all protons); *oo*-(**3**)·$Ba(SCN)_2$ δ(^{13}C{^{1}H}, 62.90 MHz, CD_3COCD_3) 68.6 (CH_2-k), 70.7, 71.9, 72.9 (2 × CH_2-l, 2 × CH_2-m, 2 × CH_2-o), 71.5 (CH_2-n), 77.0 (CH-p); δ(^{1}H, 400 MHz, $CDCl_3$) 3.52, 3.69—3.76, 3.84, 4.31 (16H, ABCD system, J_{AB} J_{AC} J_{BD} 10, J_{AD} J_{BC} J_{CD} 2.5 Hz, 4 × CH_2-l, 4 × CH_2-m), 3.59 (2H, br.t, *J* 4, 1 Hz, 2 × CH-p), 3.69—3.76, 3.90 (12H, AA′BB′ system and B portion of 'ABX system', 2 × CH_2-k, 2 × CH_2-n, 4 × C*H*H-o), 3.99 (4H, A portion of 'ABX system', J_{AB} 10, J_{AX} 4 Hz, 4 × CH*H*-o).

¶ *Crystal data:* for (**9**)·2MeCN, $C_{56}H_{62}O_8N_2$, $M = 891.1$, monoclinic, space group *Cc*, $a = 7.593(2)$, $b = 16.819(7)$, $c = 38.89(1)$ Å, $\beta = 93.77(2)°$, $U = 4955$ Å^3, $Z = 4$, $D_c = 1.20$ g cm^{-3}. The structure was solved by direct methods and the positions of the MeCN hydrogen atoms were clearly located in a ΔF map. The non-hydrogen atoms were refined anisotropically and the MeCN methyl groups were refined as rigid bodies. Refinement converged to $R = 0.049$, $R_w = 0.053$ for 3186 independent observed reflections [$\theta \leqslant 58°$, $|F_O| > 3\sigma(|F_O|)$].

For *oo*-(**3**)·$Ba(SCN)_2$·CH_2Cl_2, $C_{21}H_{36}O_9N_2Cl_2S_2Ba$, $M = 732.9$, orthorhombic, space group $P2_12_12_1$, $a = 10.846(2)$, $b = 13.980(5)$, $c = 20.132(6)$ Å, $U = 3053$ Å^3, $Z = 4$, μ(Cu-K_α) = 136 cm^{-1}, $D_c = 1.60$ g cm^{-3}. The structure was solved by the heavy atom method and the non-hydrogen atoms were refined anisotropically using absorption corrected data to $R = 0.056$, $R_w = 0.060$ for 2272 independent reflections [$\theta \leqslant 58°$, $|F_O| > 3\sigma(|F_O|)$]. There is disorder both in the dichloromethane and in the region around C(13) in the host.

In both cases, data were measured on a Nicolet R3m diffractometer using the ω-scan routine with graphite-monochromated Cu-K_α radiation. The atomic co-ordinates are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1. Ts = tosyl.

demonstrates the *out-out* stereochemistry of the hydrogen atoms at the bridgehead positions of this [3.3.3]cryptate.

T.l.c. (Al_2O_3–EtOAc) of (**3**) indicated the presence of a major fast-moving (fraction 1) and a minor slow-moving (fraction 2) component: n.m.r. spectroscopic data revealed that these components are slowly interconverting ($t_{\frac{1}{2}}$ = *ca.* 2 h at 20 °C) conformational diastereoisomers, *i.e.* atropisomers. Fractions 1 and 2 were separated in the form of oils by Al_2O_3

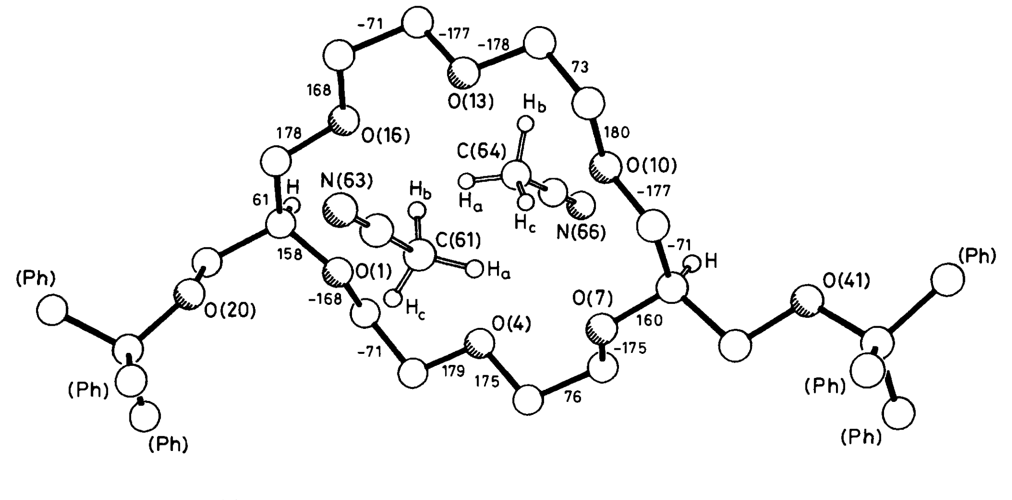


Figure 1. The solid state structure of (**9**)·2MeCN, omitting the phenyl rings associated with the trityl groups for the sake of clarity. The torsional angles (°) around the macrocyclic ring are shown beside the relevant bonds. The shortest distances *R*[C(61) . . . . O] are 3.24 and 3.20 Å to O(1) and O(13), respectively, and *R*[C(64) . . . . O] are 3.17 and 3.31 Å to O(4) and O(10), respectively. All other [C(Me) . . . . O] distances are greater than 3.42 Å. Although the angle (174°) between the two axes of the MeCN guest molecules reflects a near parallel alignment, the individual MeCN axes deviate by 39° [C(61)N] and 35° [C(64)N] from the normal to the mean plane of the six ring oxygen atoms. The [C(61) . . . . C(64)] distance between the two MeCN guest molecules of 3.952 Å may be compared with that of 3.93 Å for the [C(Me) · · · · C(Me)] distance in {[*trans*-Ir(CO)(MeCN)(PPh$_3$)$_2$]$_2$$^+$·18-crown-6}[PF$_6$]$^-_2$ (H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 1426).

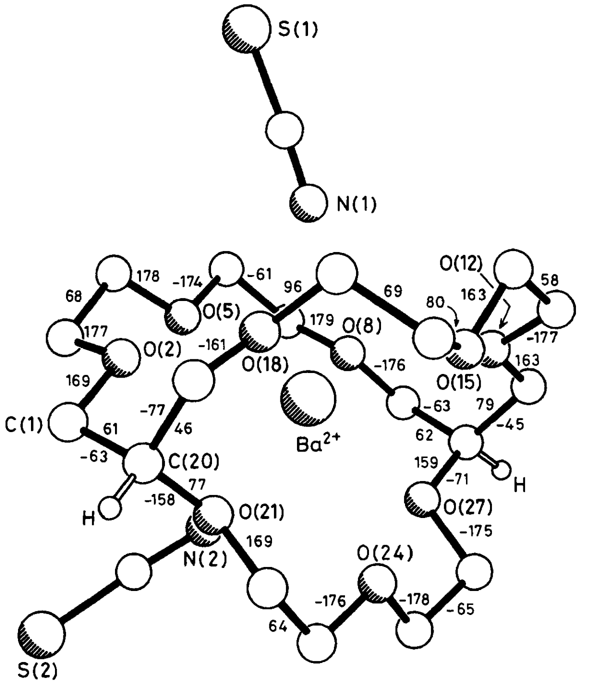


Figure 2. The solid state structure of *oo*-(**3**)·Ba(SCN)$_2$. The torsional angles (°) are shown beside the relevant bonds. The barium co-ordination distances are as follows: O(2), 2.866; O(5), 2.932; O(8), 2.862; O(12), 2.917; O(15), 3.067; O(18), 2.921; O(21), 2.814; O(24), 2.929; O(27), 2.862; N(1), 2.848; N(2), 2.813 Å. Note the rare 11-fold co-ordination of the Ba^{2+} ion: for another example involving a barium [3.2.2]cryptate thiocyanate dihydrate, see B, Metz, D. Moras, and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1388.

chromatography (EtOAc) at −5 °C and were characterised as the *in-in*, *ii*-(**3**), and *out-out*, *oo*-(**3**), isomers, respectively, on the basis of the following evidence.

(i) Chromatographic mobility: whereas the *X*-ray structure (Figure 2) of *oo*-(**3**)·Ba(SCN)$_2$ reveals that the 18-membered ring in the host incorporating O(2), O(5), O(8), O(27), O(24), and O(21) adopts an all-*gauche* conformation with local pseudo D_{3d} symmetry, molecular model inspection shows that this complex-forming conformation is denied to both 18-membered rings in *ii*-(**3**); thus, *oo*-(**3**) should form complexes with guest species readily and, as a consequence, exhibit low chromatographic mobility characteristic[10] of 18-crown-6 derivatives which can assume this conformation.

(ii) ^{1}H N.m.r. spectroscopic data in CDCl$_3$: whereas *ii*-(**3**) gives rise to a low field quintet at δ 4.35 for the bridgehead protons (H-f), the signal for H-p in *oo*-(**3**), and for the methine protons in the precursors (**9**) and (**10**), resonate at much higher field, *i.e.* below δ 3.92; at equilibrium at ambient temperature, *ii*-(**3**) : *oo*-(**3**) is 58 : 42.

(iii) ^{13}C{^{1}H} N.m.r. spectroscopic data in CD$_3$COCD$_3$: whereas the bridgehead carbon atoms (CH-f) in *ii*-(**3**) resonate at δ 77.2, the signal for these carbon atoms (CH-p) in *oo*-(**3**), and for the methine carbon atoms in the precursors (**9**) and (**10**) appear at δ 79.9, 79.5, and 80.9, respectively, *i.e.* at lower field; at equilibrium at +38 °C, *ii*-(**3**) : *oo*-(**3**) is 68 : 32. Employing the signals for CH-f in *ii*-(**3**) and CH-p in *oo*-(**3**) as quantitative ^{13}C probes, direct equilibration experiments[11] afforded a $\Delta G^{\ddagger}_{ii \rightarrow oo}$ value of *ca.* 24 kcal mol^{-1} (1 kcal = 4.184 kJ) at + 38 °C. We propose that conformational interconversion between *ii*-(**3**) and *oo*-(**3**) involves passage of the 7-atom chain containing O(21), O(24), and O(27) through the 20-membered ring [C(1)—C(20)].

(iv) ^{13}C Chemical shift changes on complexation: the upfield shifts exhibited by most of the resonances in *oo*-(**3**), when it forms a 1 : 1 complex with Ba(SCN)$_2$, are in accordance with the previously observed[2] effect on ^{13}C{^{1}H} spectra of macrobicyclic polyethers when 1 mol. equiv. of KSCN is present.

(v) ^{1}H Chemical shift changes on complexation: in particular, the appearance of a high field quintet at δ 3.59 for the bridgehead protons (H-p) in *oo*-(**3**)·Ba(SCN)$_2$ is in accord with expectation.

The control of stereochemistry illustrated here in the preparation of *ii/oo*-(**3**) is capable of further development, *e.g.* in the stereospecific synthesis of *macropolycyclic* polyethers from carbohydrate precursors.

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References

1 A. C. Coxon and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1974, 537; *Carbohydr. Res.*, 1975, **44**, C1; *J. Chem. Soc., Perkin Trans. 1*, 1977, 767.

2 B. T. Gregory, A. H. Haines, and P. Karntiang, *J. Chem. Soc., Chem Commun.*, 1977, 918; A. H. Haines and P. Karntiang, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2577.

3 D. G. Parsons, *J. Chem. Soc., Perkin Trans. 1*, 1978, 451; 1984, 1193.

4 See, for example, J. J. Baldwin, A. W. Raab, K. Mensler, B. A. Arison, and D. E. McClure, *J. Org. Chem.*, 1978, **43**, 4876; H. Eibl, *Chem. Phys. Lipids*, 1981, **28**, 1; T. Mukaiyama, Y. Tanabe, and M. Shimizu, *Chem. Lett.*, 1984, 401.

5 For *X*-ray crystal structures of these cryptands and derived cryptates, see: I. R. Hanson, D. G. Parsons, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1979, 486; J. A. Herbert and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1253; I. R. Hanson and M. R. Truter, *ibid.*, 1981, 1; J. D. Owen, *ibid.*, 1981, 12; I. R. Hanson, J. D. Owen, and M. R. Truter, *ibid.*, 1981, 1606; J. A. Bandy, D. G. Parsons, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1981, 729; J. A. Bandy and M. R. Truter, *Acta Crystallogr., Sect. B*, 1982, **38**, 2639; J. A. Bandy, D. L. Hughes, and M. R, Truter, *ibid.*, 1982, **38**, 2648; J. D. Owen, *ibid.*, *Sect. C*, 1983, **39**, 579; J. A. Bandy, C. H. L. Kennard, D. G. Parsons, and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1984, 309; F. Benetollo, G. Bombieri, G. de Paoli, D. L. Hughes, D. G. Parsons, and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1984, 425.

6 J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, 1972, **26**, 1471.

7 *Cf.* S. K. Chaudhary and O. Hernandez, *Tetrahedron Lett.*, 1979, 95; O. Hernandez, S. K. Chaudhary, R. H. Cox, and J. Porter, *ibid.*, 1981, **22**, 1491.

8 *Cf.* H. M. Colquhoun, G. Jones, J. M. Maud, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1984, 63.

9 *Cf.* G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, 1974, **39**, 2445.

10 J. F. Stoddart, *Progress in Macrocyclic Chemistry*, 1981, **2**, 173.

11 A. Hoorfar, W. D. Ollis, J. A. Price, J. S. Stephanatou, and J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1649.