Synthesis and Chiral Recognition of Optically Active Crown Ethers incorporating a Helicene Moiety as the Chiral Centre

Koji Yamamoto,* Tetsuo Ikeda, Tomihito Kitsuki, Yoshio Okamoto, Hiroaki Chikamatsu, and Masao Nakazaki
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

The synthesis of optically active crown ethers (**8**), (**14**), and (**18**) incorporating helicene molecular frameworks is reported. Their chiral recognition properties have been examined and show that (*M*)-(−)-(**14**), although of the same helicity as (*M*)-(−)-(**8**) and (*M*)-(−)-(**18**), exhibits opposite chiral recognition for the transport of methyl phenylglycinate, 1-phenylethylamine, and 1,2-diphenylethylamine, and that the pentahelicene crown (**8**) has a higher enantiomer selectivity than the hexahelicene crown (**14**) and hexa[7]circulene crown (**18**) towards these substrates. At 6.0–6.2% transport using (**8**), the optical purity of methyl phenylglycinate and 1,2-diphenylethylamine was as high as 77–82%.

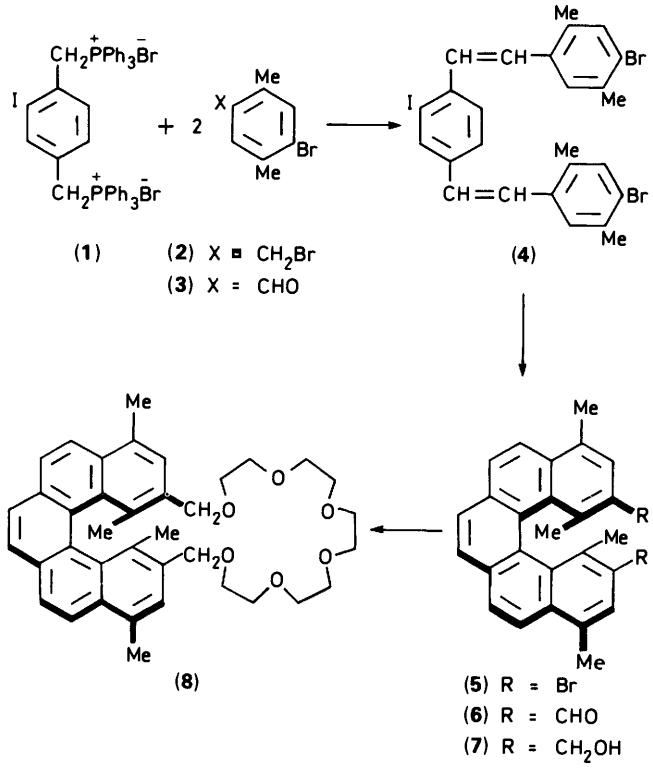
Ever since Cram's first discovery of the excellent chiral recognition properties[1] of suitably designed optically active crown ethers incorporating a 1,1′-binaphthyl chiral centre with guest organic ammonium enantiomers, an enormous amount of effort[2] has been exerted in modifying the source of chirality to study the effect of modification on the enantioselectivity of the chiral crowns. Despite this large amount of research, however, it is surprising that few studies have led to high enantiomer selectivity for organic guest ammonium ions, except for the recent publication of enantiomeric amine-selective colouration in chiral azophenolic acerands.[3]

We are interested in synthetic studies on high-symmetry chiral molecules,[4] and have described the synthesis of various chiral twisted aromatic compounds.[5] An obvious extension of our interest in these dissymmetrically twisted aromatic compounds led us to investigate the design and synthesis of optically active crown ethers incorporating chiral twisted aromatic moieties in the chiral centres.[6]

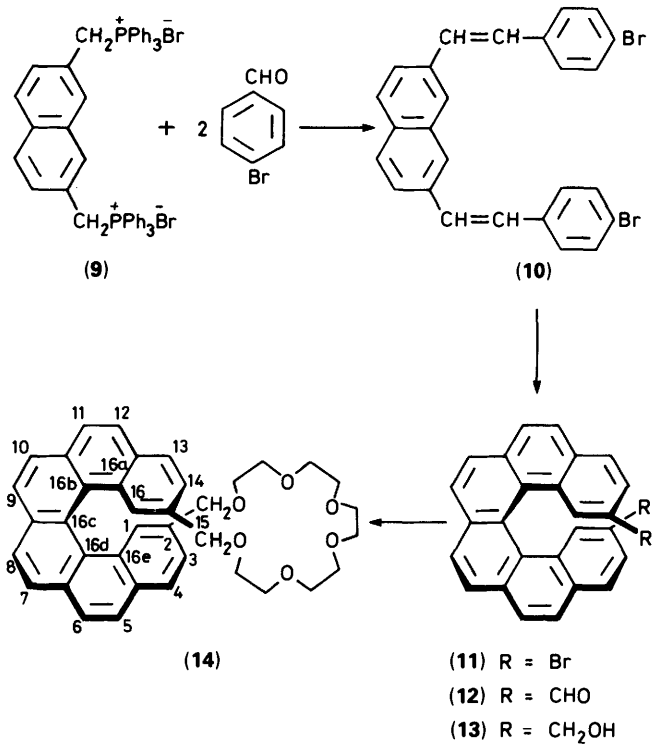
From the attractive properties of unique helicene molecules characterized by a helical structure made up of *ortho*-condensed aromatic rings and by the presence of a powerful inherently chiral chromophore, we directed our effort to the synthesis of three types of helicene crowns (**8**), (**14**), and (**18**), which should display efficient chiral recognition towards organic primary ammonium cations.

Results and Discussion

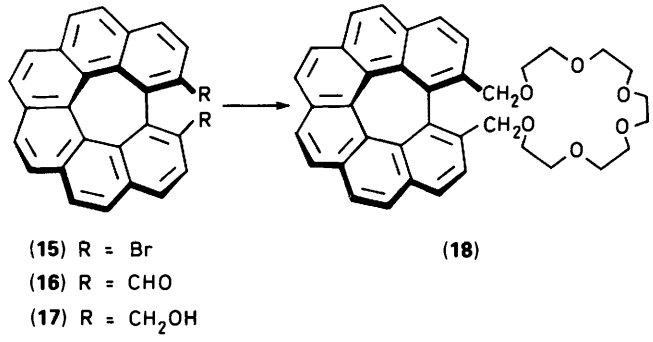
Synthesis of the Optically Active Crown Ether (**8**) *incorporating a Pentahelicene Chiral Centre* (*Scheme* 1).—Bromomethylation of 2-bromo-*p*-xylene afforded the bromomethyl derivative (**2**) which was treated with the sodium salt of 2-nitropropane[7] in ethanol to yield the aldehyde (**3**). The Wittig condensation of the aldehyde (**3**) with the bis(triphenylphosphonium) salt (**1**) (from 1,4-bisbromomethyl-2-iodobenzene)[8] using NaOMe–DMF (DMF = *N*,*N*-dimethylformamide) gave a mixture of *cis*–*cis*-, *cis*–*trans*-, and *trans*–*trans*-stereoisomeric products (**4**) (86% yield). The mixture was dissolved in benzene and irradiated with a high-pressure mercury lamp for 3 h to give 2,13-dibromo-1,4,11,14-tetramethylpentahelicene (**5**), m.p. 280–282 °C (33% yield, pale yellow prisms). Lithiation of (**5**) with Bu^{n}Li in THF (tetrahydrofuran) followed by formylation with DMF gave the dialdehyde (**6**) (69% yield), m.p. 281–282 °C, which was reduced with $LiAlH_4$ to the diol (**7**) (85% yield), m.p. 227–229 °C. Condensation of (**7**) with 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate[9] (NaH–THF) gave the pentaheliceno-crown (**8**), m.p. 116–117 °C (26% yield, pale-yellow needles) after chromatography on neutral alumina. Optical resolution of (±)-(**8**) was achieved by HPLC with a column packed with (+)-poly(triphenylmethyl methacrylate);[10] elution with methanol[11] gave optically pure (*M*)-(−)-(**8**) and (*P*)-(+)-(**8**) with $[\alpha]_D^{25}$ (MeOH) −754 and +748°, respectively. Comparison of their CD spectra with that of authentic (*M*)-(−)-pentahelicene[12] established that (−)-(**8**) and (+)-(**8**) possess the helical *M* and *P* structures, respectively. In contrast to the optical lability of (*M*)-(−)-pentahelicene, (*M*)-(−)-crown (**8**) was quite stable showing no optical rotation change after refluxing its ethanol solution for 24 h.



Scheme 1.



Scheme 2.



Scheme 3.

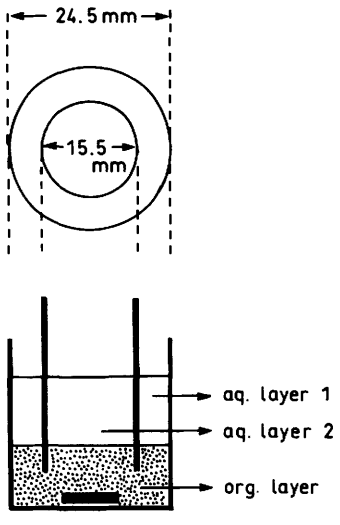


Figure 1. Transport apparatus: aqueous layer 1: 0.08M HCl; 0.4M $LiPF_6$, 0.08M guest; aqueous layer 2: 0.1M HCl; organic layer: 0.01M Host in $CHCl_3$.

Synthesis of the Optically Active Hexahelicene Crown Ether (**14**) (*Scheme* 2).—The hexahelicene crown ether (**14**) was prepared in the same way as just described for the pentahelicene crown (**8**) from the phosphonium salt (**9**). The Wittig condensation of *p*-bromobenzaldehyde with the bis(triphenylphosphonium) bromide (**9**) prepared from 2,7-bis(bromomethyl)naphthalene [13] gave a mixture of stereoisomers of the stilbene derivative (**10**) (82% yield). A benzene solution of (**10**) containing iodine was irradiated with a high-pressure mercury lamp for 3 h to yield 2,15-dibromohexahelicene (**11**), m.p. 246–248 °C (30% yield, yellow prisms).

Formylation of (**11**) (Bu^nLi, DMF) gave the dialdehyde (**12**), m.p. 287–289 °C, which was reduced with $LiAlH_4$ to the diol (**13**), m.p. 233–234 °C [63% yield from (**11**)]. The alcohol (**13**) was condensed with 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate to afford the hexaheliceno-crown (**14**), m.p. 78–80 °C (54% yield, yellow needles). The racemic (**14**) could be resolved by chromatography as described for (**8**) to give optically pure (*M*)-(−)-(**14**) and (*P*)-(+)-(**14**) with $[\alpha]_D^{25}$ (MeOH) −1 269 and +1 260°, respectively, whose absolute configurations were determined by comparison of their CD spectra with that of authentic (*M*)-(−)-hexahelicene.[14]

Synthesis of the Optically Active Hexa[7]*circulene Crown Ether* (**18**) (*Scheme* 3).—1,14-Diformylhexa[7]circulene (**16**) was obtained by the lithiation of 1,14-dibromohexal[7]circulene (**15**) [15] followed by formylation with DMF. The dialdehyde (**16**) was reduced with $LiAlH_4$ to the diol (**17**), m.p. 284–286 °C (84% yield, pale yellow prisms). Condensation of the alcohol (**17**) with 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (NaH–THF) followed by chromatography gave the hexa[7]-circuleno-crown (**18**), m.p. 95–97 °C (56% yield, pale yellow needles), whose optical resolution by chromatography as described for the optically active crown (**8**) gave optically pure (*M*)-(−)-(**18**) and (*P*)-(+)-(**18**) with $[\alpha]_D^{25}$ (MeOH) −985 and +983°, respectively. Comparison of their CD spectra with that of authentic (*M*)-(−)-1,14-dimethylhexa[7]circulene [15] established their absolute configurations.

Differential Transport of Enantiomeric Molecules through Bulk Liquid Membranes containing the Optically Active Helicene Crowns (**8**), (**14**), and (**18**).—Prior to the transport experiments, the enantioselectivity of the heliceno-crown (**8**) for complexation of (±)-primary ammonium salts, especially the salt of methyl (±)-phenylglycinate, was studied by the two-phase liquid–liquid extraction method.[16]

A solution (0.5 M; 2 ml) of (*M*)-(−)-pentahelicene crown (**8**) in $CDCl_3$ was equilibrated at room temperature with an aqueous solution (2 ml) lithium hexafluorophosphate (1 M) and methyl (±)-phenylglycinate hydrochloride. Thus, the guest was extracted from water into the $CDCl_3$ by the host (**8**) to give a 1:1 complex in the organic layer. The ^1H NMR spectrum of the organic layer showed two sets of guest signals, corresponding to diastereoisomeric complexes in the ratio 8:1 [based upon guest CO_2Me signal at δ 3.58 annd 3.50 for (*S*)- and (*R*)-salts, respectively]. The organic layer was shaken with 2M-aqueous HCl and the guest concentration of the aqueous solution was determined by the UV absorbance at 262 nm; the rotation of this solution indicated that the (*S*)-guest was present in 78% optical purity. The detailed enantioselectivity of the heliceno-crowns (**8**), (**14**), and (**18**) was studied using the modified bulk liquid membrane transport method described by Cram and co-workers.[17]

The transport experiments were carried out using a conventional apparatus (Figure) [18] which consisted of an outer cylindrical glass vessel and a central glass tube maintained at 20 °C. A detailed description is given in the Experimental Section.

Table. Differential transport[a] of enantiomeric molecules through bulk liquid membranes containing (**8**), (**14**), and (**18**).

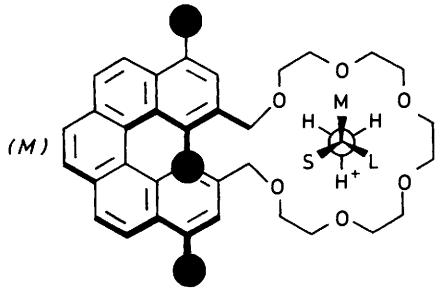
Host[a]	Guest[b]	Time/h	% Transport	Configuration	% Optical purity
(*M*)-(−)-(**8**)	A	6.0	6.0	*S*	75
	B	2.5	5.8	*R*	26
	C	5.0	6.2	*R*	80
(*P*)-(+)-(**8**)	A	6.0	6.0	*R*	77
	B	2.5	5.8	*S*	29
	C	5.0	6.2	*S*	82
(*M*)-(−)-(**14**)	A	10.0	5.8	*R*	27
	B	4.5	6.1	*S*	20
	C	8.0	5.8	*S*	45
(*P*)-(+)-(**14**)	A	10.0	5.8	*S*	28
	B	4.5	6.1	*R*	18
	C	8.0	5.9	*R*	46
(*M*)-(−)-(**18**)	A	10.0	5.8	*S*	28
	B	4.5	6.0	*R*	23
	C	8.0	5.9	*R*	41
(*P*)-(+)-(**18**)	A	10.0	5.9	*R*	30
	B	4.5	6.1	*S*	22
	C	8.0	6.0	*S*	42

[a] In the absence of crown ethers, there was no detectable transfer of the substrates. [b] A = Methyl (±)-phenylglycinate hydrochloride; B = (±)-1-phenylethylamine hydrochloride; C = (±)-1,2-diphenylethylamine hydrochloride.

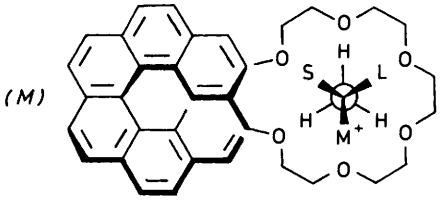
The table lists the chiral recognition behaviour of the three types of helicene crown (**8**), (**14**), and (**18**) with methyl (±)-phenylglycinate hydrochloride, (±)-1-phenylethylamine hydrochloride, and (±)-1,2-diphenylethylamine hydrochloride. The degree of chiral recognition in transport varied widely with variation in the structures of the three hosts and guests. More interesting is the ability of the hosts to discriminate between enantiomers, especially when they contain a pentahelicene chiral centre. The table shows that the pentaheliceno-crown (**8**) has a higher enantiomer selectivity than the hexaheliceno-crown (**14**) and the hexa[7]circuleno-crown (**18**) towards the three substrates, and for methyl phenylglycinate and 1,2-diphenylethylamine at 6.0–6.2% transport, the optical purity of the transported amines was as high as 77–82%. The higher enantiomer selectivity of (**8**) is comparable to that of the previously reported binaphthyl crown ether[19] which is known to have excellent chiral recognition properties. Inspection of Corey–Pauling–Koltun (CPK) space-filling molecular models suggests that the inner methyl groups in the pentahelicene framework play an important role in enantiomeric differentiation owing to the chiral recognition barrier between them and the guest salt.

The configuration of the more rapidly transported enantiomer was predicted *a priori* by examination of CPK molecular models of the diastereoisomeric complexes which were assumed to have the general structure (**19**) and (**20**) for the pentaheliceno-crown (*M*)-(−)-(**8**) and hexaheliceno-crown (*M*)-(−)-(**19**) in which L, M, and S stand for large, medium, and small groups attached to the chiral centre of the guest salt. These hosts all have C_2 symmetry, so that the same complexes are formed by attachment of the guest to either face of the macrocycle. Diastereoisomers (**19**) and (**20**) (or their enantiomers) on steric grounds would appear to be more stable. In (**19**) and (**20**), the S group extends alongside a helicene wall, and the L group occupies a large cavity by itself. Structures diastereoisomeric to (**19**) and (**20**) appear in models to be more crowded and to be more unstable.

From these considerations of the diastereoisomeric complexes



(**19**)



(**20**)

of assumed structure (**19**) and (**20**), although the pentaheliceno-crown (**8**) and hexaheliceno-crown (**14**) are of the same helicity, they should exhibit opposite chiral recognition properties, as shown in the Table for the three substrates. These results are also compatible with examination of CPK models for (**8**), (**14**), and (**18**) which reveal that the ether parts of (*M*)-(−)-pentahelicene crown (**8**) and (*M*)-(−)-hexa[7]circulene crown (**18**) have *P*-helicity while that of (*M*)-(−)-hexahelicene crown (**14**) has *M*-helicity.

We are currently checking the use of these chiral crown ethers to separate enantiomers when covalently fixed on silica gel and a suitable polymer support.[20]

Experimental

General.—All m.p.s are uncorrected. IR data were obtained with a Hitachi 260-10 spectrophotometer. ^{1}H NMR spectra were recorded for $CDCl_3$ solutions with a JNM-MH-100 spectrometer, with tetramethylsilane as internal standard. UV spectra were determined on a Hitachi EPS-3T spectrometer. Mass spectral data were measured on a RMS-4 spectrometer. CD spectra were obtained from a JASCO J-40 spectropolarimeter. Elemental analyses were performed on a Yanagimoto CHN-Corder, Type II. Merck alumina or Merck silica gel was used for column chromatography. Progress of most reactions was followed by TLC using Merck precoated silica gel. A Halos ET-300 high-pressure mercury lamp (Eikosha Co., Osaka, Japan) was used for irradiations.

1-*Bromo*-4-*bromomethyl*-2,5-*dimethylbenzene* (**2**).—A stirred mixture of 2-bromo-*p*-xylene (50 g, 0.254 mol), paraformaldehyde (11 g, 0.282 mol of formaldehyde), acetic acid (65 ml), 85% phosphoric acid (20 ml), and 47% hydrobromic acid (65 ml) was heated under reflux for 1 h. The cooled mixture was poured into cold water and extracted with ether. The ether solution was washed with water, 3% aqueous sodium hydrogen carbonate, and water again, and dried ($MgSO_4$). After removal of the solvent, the product was distilled to give the *bromomethyl compound* (**2**) (32 g, 42%), b.p. 139–140 °C (3 mmHg), n_D^{21} 1.5796; δ 2.35 (s, 6 H, CH_3), 4.44 (s, 2 H, CH_2), 7.20 (s, 1 H, ArH), and 7.40 (s, 1 H, ArH) (Found: C, 38.9; H, 3.5; Br, 57.5. $C_9H_{10}Br_2$ requires C, 38.9; H, 3.6; Br, 57.5%).

4-*Bromo*-2,5-*dimethylbenzaldehyde* (**3**).—2-Nitropropane (12.6 g, 0.143 ml) was added to a solution of sodium ethoxide, prepared from sodium (4.6 g atom) and absolute ethanol (135 ml). The nitronate salt was brought into solution by the addition of absolute ethanol (250 ml). To this ethanol solution, the bromide (**2**) (34.2 g, 0.123 mol) was added and the mixture was stirred for 30 h. The mixture was poured into cold water and then extracted with ether. The ether extract was washed with 10% sodium hydroxide solution and water, and then dried. Removal of the solvent yielded a solid which on crystallization from hexane gave the *bromoaldehyde* (**3**) (20 g, 51%), m.p. 59–60 °C; *m/z* 213 (M^+); ν_{max}(KBr) 1 686 cm^{-1} (C=O); δ 2.43 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 7.49 (s, 1 H, ArH), 7.65 (s, 1 H, ArH), and 10.24 (s, 1 H, CHO) (Found: C, 50.7; H, 4.3; Br, 37.6. C_9H_9OBr requires C, 50.7; H, 4.3; Br, 37.5%).

2-*Iodo*-1,4-*bis*(4-*bromo*-2,5-*dimethylstyryl*)*benzene* (**4**).—To a stirred solution of the phosphonium salt (**1**)[13] (22.7 g, 0.025 mol) and the aldehyde (**3**) (10.8 g, 0.05 mol) in dry dimethylformamide (DMF) (140 ml) was added dropwise a solution of NaOMe (8.7 g, 0.16 mol) in dry DMF (60 ml). After being stirred for 13 h at room temperature, the mixture was poured into water and extracted with chloroform. The organic layer was washed with water and then dried. After evaporation of the solvent, the residual solid was chromatographed on neutral alumina. Elution with hexane–benzene (1:1) produced a mixture of the *cis–cis*-, *cis–trans*-, and *trans–trans*-isomers of (**4**), m.p. 164–169 °C (13.4 g, 86%); *m/z* 622 (M^+); δ 2.18 (6 H, s, CH_3), 2.40 (6 H, s, CH_3), and 6.47—8.06 (11 H, m, ArH).

2,13-*Dibromo*-1,4,11,14-*tetramethylpentahelicene* (9,12-*Dibromo*-7,10,11,14-*tetramethyldibenzo*[c,d]*phenanthrene*) (**5**).—The diene mixture (**4**) (0.3 g) was dissolved in benzene (350 ml), and the solution was irradiated with a high-pressure mercury lamp under nitrogen for 3 h. The solvent was removed, and the residue was chromatographed over alumina. Benzene eluates were collected, and removal of the solvent left a yellow solid which was recrystallized from benzene–hexane to give the *helicene* (**5**) (0.1 g, 33%), m.p. 280–282 °C; *m/z* 492 (M^+); ν_{max}(KBr) 3 050, 2 960, 2 935, 1 570, 1 450, 970, 870, 845, 795, 729, and 720 cm^{-1}; δ 0.86 (6 H, s, CH_3), 2.76 (6 H, s, CH_3), 7.63 (2 H, s, ArH), and 7.78–8.13 (6 H, m, ArH) (Found: C, 63.5; H, 4.1; Br, 32.4. $C_{26}H_{20}Br_2$ requires C, 63.4; H, 4.1; Br, 32.5%).

1,4,11,14-*Tetramethylpentahelicene*-2,3-*dicarbaldehyde* (7,10,11,14-*Tetramethyldibenzo*[c,d]*phenanthrene*-9,12-*dicarbaldehyde*) (**6**).—n-Butyl-lithium (1.6M solution in hexane) (6.8 ml, 10.9 mmol) was added dropwise under nitrogen by syringe to a stirred solution of (**5**) (2 g, 4.06 mmol) in dry tetrahydrofuran (THF) (9 ml) at −78 °C. The mixture was stirred at this temperature for 30 min, dry DMF (4.1 ml, 52.7 mmol) was added dropwise, and the mixture stirred for 1 h. Saturated aqueous ammonium chloride (200 ml) was added to quench the reaction. The mixture was extracted with chloroform and the extracts were washed with brine and then dried. Removal of the solvent afforded a solid which was chromatographed on a silica gel column. Elution with benzene afforded the *dialdehyde* (**6**) (1.1 g, 69%) which was recrystallized from benzene–hexane, m.p. 281–282 °C; *m/z* 390 (M^+); ν_{max}(KBr) 1 673 cm^{-1} (C=O); δ 1.12 (6 H, s, CH_3), 2.87 (6 H, s, CH_3), 7.92–8.25 (8 H, m, ArH), and 10.08 (2 H, s, CHO) (Found: C, 86.1; H, 5.7. $C_{28}H_{22}O_2$ requires C, 86.1; H, 5.7%).

2,13-*Bis*(*hydroxymethyl*)-1,4,11,14-*tetramethylpentahelicene* {9,12-*Bis*(*hydroxymethyl*)-7,10,11,14-*tetramethyldibenzo*[c,d]-*phenanthrene*} (**7**).—A solution of the dialdehyde (**6**) (1.47 g, 3.73 mmol) in dry THF (150 ml) was added to a suspension of $LiAlH_4$ in dry THF (150 ml). The stirred mixture was heated under reflux for 5 h, and the excess of reducing agent was decomposed with water (4 ml). Aluminium hydroxide was filtered off. Recrystallization of the solid product from benzene gave the *diol* (**7**) (1.2 g, 85%), m.p. 227–229 °C; *m/z* 394 (M^+); ν_{max}(KBr) 3 250 cm^{-1} (OH); δ 0.78 (6 H, s, CH_3), 2.88 (6 H, s, CH_3), 4.57 (4 H, ABq, *J* 11.4 Hz, CH_2), and 7.38—8.11 (8 H, m, ArH) (Found: C, 85.3; H, 6.6. $C_{28}H_{26}O_2$ requires C, 85.2; H, 6.6%).

Pentahelicene Crown Ether (6,8,9,11,12,14,15,17,18,20,21,23-*Dodecahydro*-4,25,31,34-*tetramethyl*-3,5:24,26-*diethenophenanthro*[4,5-tuv][1,4,7,10,13,16]*hexaoxacyclohexacosin*) (**8**).—To 40 ml of dry THF under nitrogen was added NaH (0.17 g, 4.2 mmol) as a 60% mineral oil dispersion. To this boiling suspension was added a solution of (**7**) (0.5 g, 1.3 mmol) and 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (0.65 g, 13 mmol) in dry THF (45 ml) dropwise during 8 h under nitrogen. The mixture was heated under reflux for a further 12 h, cooled in an ice bath, and quenched with water. The product was extracted with chloroform, and the chloroform extract was washed with dilute aqueous sodium hydrogen carbonate and with water and then dried. After removal of the solvent, the residue was chromatographed on neutral alumina (activity III). Elution with benzene–ether (3:2) gave the *helicene crown ether* (**8**) (0.2 g, 26%, pale yellow needles), m.p. 116–117 °C; *m/z* 596 (M^+); ν_{max}(KBr) 3 040, 2 950, 1 604, 1 460, 1 130, and 855 cm^{-1}; λ_{max}(hexane) 246 (log ε 4.80), 250.2sh (4.35), 273sh (4.35), 283 (4.43), 292 (4.50), 316 (4.46), 333sh (4.13), 352 (4.62), and 368 nm (4.02); δ 0.72 (6 H, s, CH_3), 2.83 (6 H, s, CH_3), 3.48–3.85 (20 H, m, OCH_2CH_2O), 4.37 (4 H, ABq, *J* 11.4 Hz, $ArCH_2$), 7.50 (2 H, s, ArH), and 7.78–8.70 (6 H, m, ArH) (Found: C, 76.5; H, 7.4. $C_{38}H_{44}O_6$ requires C, 76.5; H, 7.4%).

Optically Active Pentahelicene Crown Ether (**8**).—Optical resolution of (±)-(**8**) was achieved by HPLC with a column packed with (+)-poly(triphenylmethyl methacrylate)[10] on silica gel as described.[11] A solution of (±)-(**8**) (20 mg) in methanol (15 ml) was injected on the column (30 × 2.2 i.d. mm); elution with methanol gave first the (−)-isomer and then the (+)-isomer. The procedure was repeated to process a total

of 200 mg of (**8**), and recrystallization of the resolved enantiomeric compounds from benzene–hexane afforded optically pure (*M*)-(−)-(**8**) and (*P*)-(+)-(**8**): (*M*)-(−)-(**8**) (80 mg): m.p. 106–108 °C, $[\alpha]_D^{25}$ −754° (MeOH), CD (MeOH) $[\theta] \times 10^{-5}$ (λ/nm) −23.0 (250), +9.44 (283), +10.24 (292), −9.8sh (313), −15.5 (324), −8.07 (352), and −6.13 (369); (*P*)-(+)-(**8**) (80 mg): m.p. 107–109 °C, $[\alpha]_D^{25}$ +748° (MeOH).

2,7-*Bis*(p-*bromostyryl*)*naphthalene* (**10**).—The Wittig reaction of the bistriphenylphosphonium salt (**9**) (27.3 g, 32.5 mmol) [from 2,7-bis(bromomethyl)naphthalene][13] and *p*-bromobenzaldehyde (13 g, 70 mmol) followed by the usual isolation and separation yield a mixture of the *cis–cis*-, *cis–trans*-, and *trans–trans*-isomers of (**10**) (13 g, 82%), m.p. 145–152 °C; *m/z* 490 (M^+); ν_{max}(KBr) 2 940, 1 580, 1 480, 965, 750, and 710 cm^{-1}.

2,15-*Dibromohexahelicene* (11,14-*Dibromophenanthro*[3,4-c]*phenanthrene*) (**11**).—A solution of the mixture (**10**) (0.2 g, 0.4 mmol) in benzene (300 ml) containing a small amount of iodine was irradiated with a 300 W high-pressure mercury lamp under nitrogen for 2 h. Removal of the solvent followed by column chromatography on alumina (benzene as eluant) afforded the *helicene* (**11**) (60 mg, 30%) which was recrystallized from benzene–hexane to give pale yellow prisms, m.p. 246–248 °C; *m/z* 486 (M^+); ν_{max}(KBr) 3 040, 1 595, 1 468, 1 435, 1 246, 1 210, 1 140, 1 110, 1 040, 960, 908, 860, 820, 812, and 745 cm^{-1}; δ 7.33–7.97 (m, ArH) (Found: C, 64.2; H, 2.9; Br, 32.9. $C_{26}H_{14}Br_2$: requires C, 64.2; H, 2.9; Br, 32.9%).

Hexahelicene-2,15-*dicarbaldehyde* (*Phenanthro*[3,4-c]*phenanthrene*-11,14-*dicarbaldehyde*) (**12**).—Compound (**12**) was prepared by the method described for (**6**), using the dibromide (**11**) (1.5 g, 3.1 mmol), n-butyl-lithium (1.6M solution in hexane; 5 ml, 8 mmol), and DMF (2.8 g, 36 mmol). The product was recrystallized from benzene to give the *dialdehyde* (**12**) (0.884 g, 74%), m.p. 287–289 °C; *m/z* 384 (M^+); ν_{max}(KBr) 1 690 cm^{-1} (C=O); δ 7.38–7.96 (14 H, m, ArH) and 10.01 (2 H, s, CHO) (Found: C, 87.4; H, 4.2. $C_{28}H_{16}O_2$ requires C, 87.5; H, 4.2%).

2,15-*Bis*(*hydroxymethyl*)*hexahelicene*{11,14-*Bis*(*hydroxymethyl*)*phenanthro*[3,4-c]*phenanthrene*} (**13**)—The reduction of the dialdehyde (**12**) (464 mg, 1.2 mmol) was carried out as described for (**7**), providing an 85% yield of the *diol* (**13**) (400 mg), m.p. 232–235 °C; *m/z* 388 (M^+); ν_{max}(KBr) 3 300 cm^{-1} (OH); δ 4.01 (4 H, ABq, *J* 7.2 Hz, $ArCH_2$) and 7.12–8.20 (14 H, m, ArH) (Found: C, 84.5; H, 5.2. $C_{28}H_{20}O_2$ requires C, 86.6; H, 5.2%).

Hexahelicene Crown Ether (*Hexaheliceno*[2,1,15-rstuvwxy][1,4,7,10,13,16]*hexaoxacycloheptacosin*) (**14**).—Compound (**14**) was prepared by the method described for (**8**), using the diol (**13**) (0.38 g 1 mmol), tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (0.5 g, 1 mmol), NaH (0.13 g, 3.2 mmol) as a 60% mineral oil dispersion, and dry THF (50 ml). The resulting product was chromatographed on neutral alumina (activity III). Elution with benzene–ether (3:2) gave the *helicene crown ether* (**14**) (0.32 g, 54%) which was recrystallized from benzene–hexane to give pale yellow needles, m.p. 78—80 °C; *m/z* 590 (M^+); ν_{max} (KBr) 3 050, 2 880, 1 620, 1 590, 1 460, 1 258, 1 160, 1 105, and 840 cm^{-1}; δ 3.67 (20 H, br s, OCH_2CH_2O), 3.92 (4 H, ABq, *J* 14 Hz, $ArCH_2$), and 7.32–8.04 (14 H, m, ArH); λ_{max}(hexane) 232sh (log ε 4.74), 258 (4.79), 265 (4.78), 303 (4.38), 316 (4.42), 3.27 (4.32), and 349 nm (4.03) (Found: C, 77.2; H, 6.5. $C_{38}H_{38}O_6$ requires C, 77.3; H, 6.5%).

Optically Active Hexahelicene Crown Ether (**14**).—Optical resolution of (±)-(**14**) (200 mg) was carried out as described for the preparation of optically active (**8**). (*M*)-(−)-(**14**) (80 mg): m.p. 72–74 °C, $[\alpha]_D^{25}$ −1 269° (MeOH), CD (MeOH) $[\theta] \times 10^{-5}$ (λ/nm) −0.54 (231), +6.51 (248), −0.14 (293), −1.56 (310sh), and −6.24 (327); (*P*)-(+)-(**14**) (80 mg): m.p. 73–75 °C, $[\alpha]_D^{25}$ +1 260° (MeOH).

1,14-*Bis*(*hydroxymethyl*)*hexa*[7]*circulene*{7,8-*Bis*(*hydroxymethyl*)*benzo*[no]*naphtho*[2,1,8,9-ghij]*pleiadene*} (**17**).—The dialdehyde (**16**) [from the dibromide (**15**)[15]] (0.4 g, 1 mmol) was reduced as described for (**7**), providing a 84% yield of the *diol* (**17**) (0.33 g), m.p. 264–266 °C; *m/z* 386 (M^+); ν_{max}(KBr) 3 400 cm^{-1} (OH); δ 4.10 (4 H, ABq, *J* 7.8 Hz, $ArCH_2$), 7.84–8.34 (12 H, m, ArH), and 8.60 (2 H, s, ArH) (Found: C, 86.9; H, 4.7. $C_{38}H_{18}O_2$ requires C, 87.0; H, 4.7%).

Hexa[7]*circulene Crown Ether*{11,13,14,16,17,19,20,22,23,25,26,28-*Dodecahydro*-1,29-*etheno*-8,9,10-(*penta*[1,3]*diene*[1,3]-*diyl* [5]*ylidene*)*phenanthro*[4′,5′:21,22,23,24]*cyclohepta*[5] [1,4,7,10,13,16]*cyclodocosin* (**18**).—The crown (**18**) was prepared as described for (**8**), using the diol (**17**) (0.3 g, 0.77 mmol), NaH (0.1 g, 2.5 mmol) as a 60% mineral oil, tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (0.38 g, 0.77 mmol), and dry THF (40 ml). The product was chromatographed on neutral alumina followed by recrystallization (benzene–hexane) to give the *crown* (**18**) as pale yellow needles (0.25 g, 56%), m.p. 95–96 °C; *m/z* 588 (M^+); ν_{max}(KBr) 3 030, 2 940, 1 605, 1 594, 1 450, 1 100, 845, and 750 cm^{-1}; δ 3.68br (20 H, s, OCH_2CH_2O), 4.03 (4 H, ABq, *J* 7.6 Hz, $ArCH_2$), and 7.78–8.55 (12 H, m, ArH); λ_{max}(hexane) 343 (log ε 4.70), 268sh (4.62), 273 (4.63), 282 (4.60), 307 (4.40), and 325 nm (4.34) (Found: C, 77.4; H, 6.2. $C_{38}H_{36}H_6$ requires C, 77.5; H, 6.2%).

Optically Active Hexa[7]*circulene Crown Ether* (**18**).—Optical resolution of (±)-(**18**) was carried out as described for the preparation of optically active (**8**): (*M*)-(−)-(**18**) (84 mg), m.p. 86–88 °C, $[\alpha]_D^{25}$ −985° (MeOH), CD (MeOH) $[\theta] \times 10^{-5}$ (λ/nm) +1.79 (248), −0.66 (265), +1.72 (280), and −2.14 (326); (*P*)-(+)-(**18**) (85 mg): m.p. 87–89 °C, $[\alpha]_D^{25}$ +983° (MeOH).

Enantiomer Differential Transport.—The transport experiments were carried out in a conventional apparatus (Figure 1)[18] which consisted of an outer cyclindrical glass vessel (24.5 mm i.d.) and a central glass tube (15.5 mm i.d.). A $CHCl_3$ solution (0.01M) of the host separated the inner aqueous phase (0.1M HCl) and the outer aqueous phase (0.08M HCl) which contained $LiPF_6$ (0.4M) and the racemic guest (0.08M). The organic layer was stirred at a constant speed (60 rpm) at 20.0 ± 0.5 °C, and transport was monitored by UV and CD spectroscopy ($[\theta]_{262}$) at 262 nm of the inner aqueous phase for the determination of concentrations and optical purities.

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