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

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Two chiral crown ethers (−)-(*S*)-(**5**) and (−)-(*R,R*)-(**6**) with a biphenanthryl moiety as the chiral centre have been prepared; examination of their chiral recognition behaviour showed that (−)-(*S*)-(**5**) has a very high enantiomer selectivity for 1,2-diphenylethylamine.

As an extension of our recent synthetic studies on optically active crown ethers incorporating helicene frameworks,[1] we report here the preparation and chiral recognition properties of two novel chiral crown ethers (**5**) and (**6**) having a biphenanthryl chiral centre.

9-Phenanthrol (**3**)[2] was prepared *via* a sequence of conversions involving oxidation of 9-phenanthrylmagnesium bromide (**1**)[3] with t-butyl perbenzoate and hydrolysis of the resulting t-butyl ether (**2**)[4] (65% overall yield). Oxidative coupling[5] of (**3**) was carried out with manganese tris(acetylacetonate) to give 10,10′-dihydroxy-9,9′-biphenanthryl (**4**),† m.p. 240—242 °C (84% yield); ^{1}H n.m.r. ($CDCl_3$) δ 5.55 (s, ArOH, 2H), 7.18—7.82 (m, ArH, 10H), and 8.38—8.80 (m, Ar, 6H). Optical resolution of (±)-(**4**) was achieved by h.p.l.c. with a column packed with (+)-poly(triphenylmethyl methacrylate);[6] elution‡ with methanol gave optically pure (−)-(*S*)-(**4**)§ and (+)-(*R*)-(**4**)¶ with $[\alpha]_D^{23}$ ($CHCl_3$) −71.5 and +71.8°, respectively. Condensation of (−)-(**4**) with 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (Bu^{t}OK–tetrahydrofuran) afforded the (−)-(*S*)-biphenanthryl crown ether (**5**), m.p. 178—180 °C (40% yield), $[\alpha]_D^{24}$ −5.4° ($CHCl_3$); ^{1}H n.m.r. ($CDCl_3$) δ 3.10—4.10 (m, CH_2, 20H), 7.20—7.85 (m, ArH, 10H), and 8.45—8.95 (m, ArH, 6H). The crown ether (−)-(*R,R*)-(**6**) with two biphenanthryl

† Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

‡ Compound (−)-(*S*)-(**4**) was eluted first.

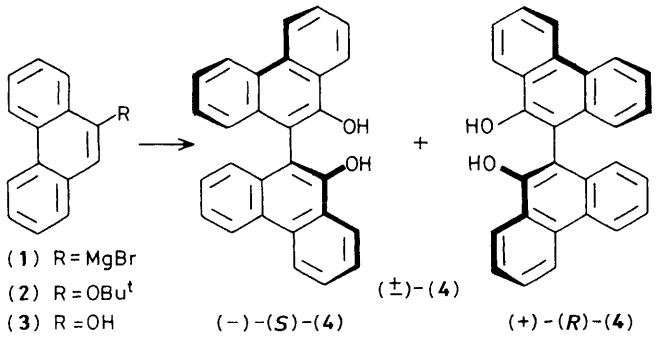
§ The (*S*)-configuration of (−)-(**4**) was determined by chemical correlation with (−)-(*S*)-2,2′-dihydroxy-3,3′-dimethyl-1,1′-binaphthyl (ref. 8; presented in part at the 49th Annual Meeting of the Chemical Society of Japan, April 1984, Tokyo).

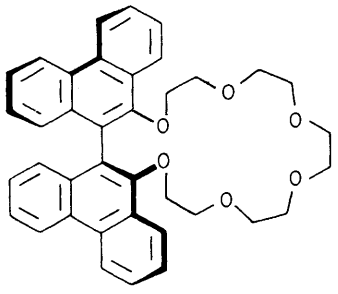
¶ Optically active (**4**) was found to be quite stable and showed no change in optical rotation after refluxing in methanol for 24 h.

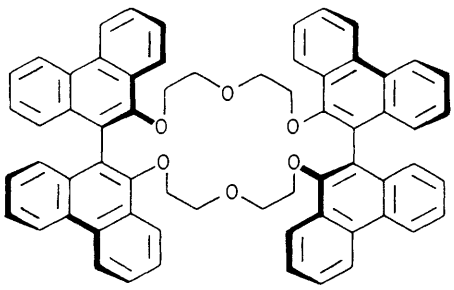
Table 1. Differential transport (ref. 9) of enantiomeric molecules through bulk liquid membranes containing (−)-(*S*)-(**5**) and (−)-(*R,R*)-(**6**).[a]

Host[b]	Guest	Temp./°C	Time/h	Transport (%)	Configuration of dominant enantiomer	Optical purity (%)
(−)-(*S*)-(**5**)	[c]	19	1	2.8	*R*	24
	[d]	19	0.5	3.7	*S*	31
	[d]	−5	0.5	2.5	*S*	45
	[e]	19	0.5	2.5	*S*	32
	[e]	−5	0.5	3.8	*S*	78
(−)-(*R,R*)-(**6**)	[c]	19	24	2.6	*S*	19
	[d]	19	12	3.2	*R*	21
	[e]	19	12	3.0	*R*	20
	[e]	−5	12	3.2	*R*	23

[a] Differential transport of the hexafluorophosphate salt of racemic guests with optically active crown ethers was carried out in conventional apparatus (ref. 10) which consisted of an outer cylindrical glass vessel (24.5 mm inner diameter) and a central glass tube (15.5 mm inner diameter). The 0.01 M $CHCl_3$ solution of the host separated the inner aqueous phase (0.1 M HCl) and the outer aqueous phase (0.08 M HCl) which contained $LiPF_6$ (0.4 M) and the racemic guest (0.08 M). The organic layer was stirred at a constant speed (60 r.p.m.), and transport was followed by monitoring the absorbance at 262 nm and $[\theta]_{262}$ of the inner aqueous phase. [b] In the absence of crown ethers, there was no detectable transfer of the substrates. [c] Methyl (±)-phenylglycinate hydrochloride. [d] (±)-1-Phenylethylamine hydrochloride. [e] (±)-1,2-Diphenylethylamine hydrochloride.







units was prepared by condensation of (+)-(*R*)-(**4**) with 3-oxapentane-1,5-diyl bistoluene-*p*-sulphonate {(−)-(*R,R*)-(**6**): m.p. 131—132 °C (23% yield), $[\alpha]_D^{23}$ −64° ($CHCl_3$); ^1H n.m.r. ($CDCl_3$) δ 2.60—3.85 (m, CH_2, 16H), 7.00—7.70 (m, ArH, 20H), and 8.15—8.90 (m, ArH, 12H)}.

Table 1 gives the chiral recognition behaviour of (−)-(*S*)-(**5**) and (−)-(*R,R*)-(**6**) with methyl (±)-phenylglycinate hydrochloride, (±)-1-phenylethylamine hydrochloride, and (±)-1,2-diphenylethylamine hydrochloride. These results indicate that (i) (−)-(*S*)-(**5**) and (−)-(*R,R*)-(**6**) exhibit opposite enantiomer selectivities, (ii) (−)-(*S*)-(**5**) shows higher enantiomer selectivity than (−)-(*R,R*)-(**6**), and (iii) (−)-(*S*)-(**5**) has a very high selectivity for 1,2-diphenylethylamine.[7]

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