Synthesis and Chiral Recognition of Optically Active Crown Ethers incorporating a 4,4′-Biphenanthryl Moiety as the Chiral Centre

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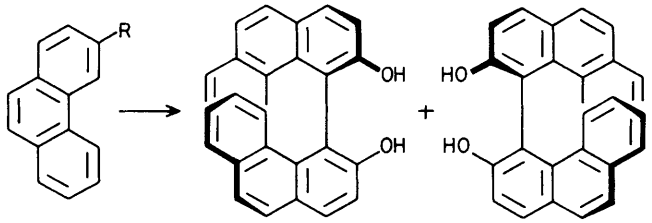
Two chiral crown ethers (+)-(*S*)-(**4**) and (−)-(*R,R*)-(**5**) with a 4,4′-biphenanthryl moiety as the chiral centre have been prepared, and their chiral recognition properties were examined to show that (+)-(*S*)-(**4**) has a high enantiomer selectivity for 2-aminotetralin and 1,2-diphenylethylamine.

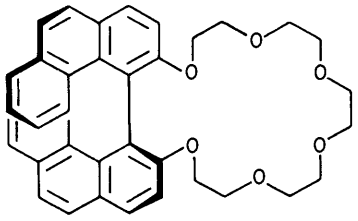
As an extension of our recent synthetic studies on optically active crown ethers incorporating 9,9′-biphenanthryl molecular frameworks,[1] we report here the preparation and chiral recognition properties of two novel chiral ethers (**4**) and (**5**) having a 4,4′-biphenanthryl chiral centre.

3-Phenanthrol (**2**) was prepared *via* a sequence of conversions involving sulphonation[2] of phenanthrene with sulphuric acid and alkali fusion of the resulting phenanthrene-3-sulphonic acid (**1**) (24% overall yield). Oxidative coupling of (**2**) was carried out with 1,2-diphenylethylamine–copper(II) complex[3] to give 3,3′-dihydroxy-4,4′-biphenanthryl (**3**),† m.p. 246—247 °C (65% yield); ^{1}H n.m.r. ($CDCl_3$) δ 5.10 (s, ArOH, 2H) and 6.80—8.13 (m, ArH, 16H). Optical resolution of (±)-(**3**) was achieved by h.p.l.c. with a column packed with (+)-poly(triphenylmethyl methacrylate);[4] elution‡ with methanol gave optically pure (+)-(*R*)-(**3**)§ and (−)-(*S*)-(**3**)¶ with $[\alpha]_D^{25}$ ($CHCl_3$) +70.8 and −70.2°, respectively. Condensation of (−)-(*S*)-(**3**) with 3,6,9,12-tetraoxatetradecane-1,14-diyl bistoluene-*p*-sulphonate (Bu^{t}OK–tetrahydrofuran) afforded the (+)-(*S*)-4,4′-biphenanthryl crown ether (**4**), m.p.

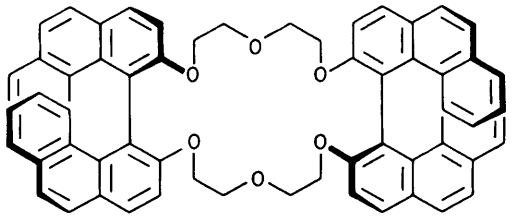


(**1**) R = SO_3H
(**2**) R = OH

(+)-(*R*)-(3) (−)-(*S*)-(3)



(+)-(*S*)-(4)



(−)-(*R,R*)-(5)

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

‡ (+)-(*R*)-(**3**) was the first moving fraction.

§ The absolute configuration of (−)-(**3**) was determined by the chiral recognition method developed by Miyano and co-workers.[5] Intramolecular Ullmann reaction of (+)-3,3′-bis(1-bromo-2-naphthylcarbonyloxy)-4,4′-biphenanthryl followed by hydrolysis gave recovered (−)-(**3**) and (−)-(*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid {$[\alpha]_D^{22}$ −89° (0.1 M NaOH), 81% optical yield}. This result unequivocally indicates that (−)-(**3**) has the same *S*-configuration; presented in part at the 50th Annual Meeting of the Chemical Society of Japan, April 1985, Tokyo.

¶ Optically active (**3**) was found to be quite stable and showed no change in optical rotation after refluxing in ethanol for 24 h.

Table1. Differential transport[8] of enantiomeric molecules through bulk liquid membrances containing (+)-(*S*)-(**4**) and (−)-(*R,R*)-(**5**).[a]

Host[b]	Guest[c]	Time/h	% Transport	Configuration of dominant enantiomer	% Optical purity
(−)-(*S*)-(**4**)	A	0.5	1.4	*S*	21
	B	0.5	1.6	*S*	66
	C	0.5	2.5	*R*	74
(−)-(*R,R*)-(**5**)	A	24.0	2.7	*R*	25
	B	0.5	1.4	*R*	35
	C	0.5	2.1	*S*	42

[a] Carried out in conventional apparatus[9] 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.) at 20 °C, 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] A, Methyl (±)-phenylglycinate hydrochloride; B, (±)-1,2-diphenylethylamine hydrochloride; C, (±)-2-aminotetralin hydrochloride.

88—89 °C (49% yield), $[\alpha]_D^{22}$ +185° ($CHCl_3$); ^{1}H n.m.r. ($CDCl_3$) 2.75—3.96 (m, CH_2, 20H) and 6.70—8.14 (m, ArH, 16H). The crown ether (−)-(*R,R*)-(**5**) with two biphenanthryl units was prepared by condensation of (+)-(*R*)-(**3**) with 3-oxapentane-1,5-diyl bistoluene-*p*-sulphonate {(−)-(*R,R*)-(**5**): m.p. 111—112 °C (43% yield), $[\alpha]_D^{25}$ −253° ($CHCl_3$); ^{1}H n.m.r. ($CDCl_3$) δ 2.47—2.73 (m, CH_2, 8H), 3.15—3.59 (m, CH_2, 8H), 6.60—6.90 (m, ArH, 4H), 7.05—7.33 (m, ArH, 8H), and 7.45—8.06 (m, ArH, 20H)}.

Table 1 lists the chiral recognition behaviour of (**4**) and (**5**) with methyl (±)-phenylglycinate hydrochloride, (±)-1,2-diphenylethylamine hydrochloride, and (±)-2-aminotetralin hydrochloride: (+)-(*S*)-(**4**) and (−)-(*R,R*)-(**5**) exhibit opposite enantiomer selectivities; (+)-(*S*)-(**4**) shows higher enantiomer selectivity than (−)-(*R,R*)-(**5**); (+)-(*S*)-(**4**) has a high selectivity for 1,2-diphenylethylamine[6] and 2-aminotetralin.[7]

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