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Chiral Macrocycles, Part I: Synthesis and Enantioselective Transport of Carboxylic Acids as Their Li^+ Salts

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Abstract. A new series of tetrapyrazolic macrocycles with a functionalized sidearm has been prepared. Their capability to transport Li^+ salts of carboxylic acids has been examined and is shown to be strongly dependent on the functionality of the macrocycle sidearm. In the case of the Li^+ (D, L)-mandelate, chiral recognition has been observed.

Key words: Macrocycles, transport, lithium carboxylate, chiral recognition.

1. Introduction

Synthetic polydentate macrocycles containing oxygen donor atoms, such as crown ethers [1–4], cryptands [1–3, 5], and spherands [6] are well known for their ability to complex alkali and alkaline earth cations.

The transport capability of these kinds of ligands has been shown to be strongly dependent on the nature, size and geometry of the macrocyclic cavity. Furthermore, for some lariat ethers, the presence of a flexible sidearm with an electron donor site is well known to enhance the binding ability of the ligand by participation of this additional donor group in the complexation, providing a three dimensional cavity [7–16].

Recently a new class of polydentate sp^2 hybrid nitrogen donor macrocycles which includes polypyridine [17–19] and mixed pyridine–imine [20–22] ligands has been shown to form complexes with alkali ions. In our laboratory, for some years we have investigated polypyrazole macrocycles, which have the unusual property of being able to form not only stable complexes with transition metal cations [23], but also to transport alkali cations through an organic phase [24–26]; the effect of the cavity size and nature of the binding subunits on the stability of the complex and binding selectivity of different macrocycles have been studied.

Among these, we have reported the remarkable selectivity and efficiency of macrocycles containing two bipyrazolic subunits for the extraction and transport

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of alkali cations through an artificial liquid membrane [26]. Their nature is such that it allows the introduction of different kinds of sidearms without affecting the structure of the macrocycle cavity; one of them was shown to be remarkably well adapted as a Li^+ ionophore.

We have prepared a new series of macrocycles based on this same tetrapyrazolic framework, with flexible sidearms bearing donor or propyl functional groups, but with different steric hindrance to probe the effect of the sidearm on the binding ability of these ligands. We have used the potentiality of the cavity to interact with Li^+ and of the sidearm hydroxyl group to solvate the anion in order to favour the transport of the anionic species as the counterion of the cation; such a supramolecular structure has been reported in the solid state for LiNCS complexes of crown ether alcohols [27]; if such a structure occurs in solution, it may facilitate the transport of anions, the nature of which has been shown to be an important factor in cation transport [28–30]: it has been considered that organic acid anions may be good cooperative carriers depending on their lipophilicity and acidity [31, 32], so that some examples of cooperative transport of carboxylic and amino acid salts have been given [33–35]. We have taken these results into account when using macrocycles **II** and **III** as ionophores for three carboxylic acids as their Li^+ salts: phenylacetic, mandelic and methoxyphenylacetic acids, which differ only in the substituent on the carbon α to the carboxylic function: H, OH and MeO, respectively. The transport experiments have been performed under the same conditions as those described previously [25, 26].

Taking the opportunity of the chirality present in macrocycles **II** and **III**, we have tested their chiral recognition ability towards carboxylic anions in transport experiments.

2. Experimental

2.1. SYNTHESIS AND CHARACTERIZATION OF MACROCYCLES **I–III**

The synthesis of the bipyrazole **1** has already been described in a previous work [36].

2.1.1. *Synthesis of the Tetrapyrazolic Precursors* **2**

The tetrapyrazolic opened structures **2** were obtained in one step by refluxing an acetonitrile solution (200 mL) of bipyrazole **1** (8×10^{-3} mole), the appropriate amine (4×10^{-3} mole), Na_2CO_3 (4×10^{-2} mole) and an excess of KI. The corresponding heating times for the different amines are given in Table I. The inorganic matter was removed by filtration and the filtrate dried. The residue was purified by chromatography over alumina (CH_2Cl_2/EtOH 95/5) to give an oil with yields given in Table I.

TABLE I. Experimental and identification data for the two last steps of the synthesis of macrocycles **I–III**.

	Dimerisation			Cyclization	
R=	Reflux time	Yield(%)	m.p.	$(M+H)^+$	Yield(%)
CH_2–CH_2—CH_3	6 h	7-	151–153°C	448	65
CH_2–CHOH–CH_3	6 h	85	213–217	464	58
$CH(CH_3)$–CHOH–C_6H_5	35 h	65	viscous oil	540	26

^{1}H NMR ($CDCl_3$):

$$\begin{aligned}
\mathbf{2}R &= -C_aH_2C_bH_2C_cH_3 \\
&\quad \delta 0.86[\mathrm{t}, 3\mathrm{H}, C_c(CH_3)], 2.33[\mathrm{s}, 6\mathrm{H}, CH_3 - 3'(5')], \\
&\quad 2.43(\mathrm{d}, 6\mathrm{H}, CH_3 - 3(5)), 3.66(\mathrm{s}, 4\mathrm{H}, CH_2), \\
&\quad 6.16(\mathrm{b}, 4\mathrm{H}, \mathrm{H} - 4, 4'). \\
\mathbf{2}R &= -C_aH_2C_bH(OH)C_cH_3 \\
&\quad \delta 1.08[\mathrm{d}, 2\mathrm{H}, C_c(CH_3)], 2.30[\mathrm{s}, 6\mathrm{H}, CH_3 - 3'(5')], \\
&\quad 2.43(\mathrm{d}, 6\mathrm{H}, CH_3 - 3(5)), 3.76(\mathrm{b}, 4\mathrm{H}, CH_2), 4.0[\mathrm{m}, 1\mathrm{H}, C_bH], \\
&\quad 6.12(\mathrm{b}, 2\mathrm{H}, \mathrm{H} - 4'), 6.17(\mathrm{b}, 2\mathrm{H}, \mathrm{H} - 4). \\
\mathbf{2}R &= C_aH(CH_3)C_bH(OH)C_6H_5 \\
&\quad \delta 1.06[\mathrm{d}, 3\mathrm{H}, (CH_3)_a], 2.28[\mathrm{s}, 6\mathrm{H}, CH_3 - 3'(5')], \\
&\quad 2.46(\mathrm{d}, 6\mathrm{H}, CH_3 - 5), 3.33(\mathrm{m}, 1\mathrm{H}, C_bH), 3.76(\mathrm{s}, 4\mathrm{H}, CH_2), \\
&\quad 4.88(\mathrm{d}, 1\mathrm{H}, C_bH), 6.12(\mathrm{b}, 2\mathrm{H}, \mathrm{H} - 4'), 6.26(\mathrm{b}, 2\mathrm{H}, \mathrm{H} - 4).
\end{aligned}$$

2.1.2. *Synthesis of the Macrocycles*

Cyclization of the tetrapyrazole precursor **2** was carried out under phase transfer catalysis conditions: a toluene solution of dibromopropane (2.5×10^{-3} mole/300 mL) and precursor **2** (2.5×10^{-5} mole) in the presence of a concentrated NaOH aqueous solution (2g/2mL) and of a catalytic amount of tetrabutylammonium bromide. The mixture was refluxed for 3 h and stirred at room temperature for one night, the solution was filtered and the residue purified over alumina (95/5 CH_2Cl_2/EtOH). Yields are given in Table I.

The fast atom bombardment mass spectra were obtained with a Jeol JMX DX300 apparatus; NBA was used as a matrix.

^{1}H and ^{13}C NMR spectra were recorded on a 250 AC Bruker spectrometer; chemical shifts are given in ppm from TMS in $CDCl_3$ and are listed in Tables II and III.

TABLE II. ^1H chemical shifts of macrocycles **I–III** in $CDCl_3$ (s = singlet, d = doublet, t = triplet, b = broadened, m = multiplet).

	Macrocyclic cavity					sidearm		
	H-4, 4′	CH_3	CH_2Nsp^2	CH_2Nsp^3	$C–CH_2–C$	a	b	c
I	5.84s	2.22s	4.08t	3.68s	2.57m	2.73t	1.69m	1.0
	5.96s	2.36s						
II	5.83b	2.26s	4.10t	3.7 b d (J = 13.5 Hz)	2.62m	2.45b	3.98b	1.23
	5.90s	2.40s		3.82 b d		2.9 b		
III	5.82b	2.23s	4.15t	3.78 b d (J = 13.5 Hz)		2.61m	3.36b	5.06b
	5.91s	2.41s		3.92 b d		1.14d		7.2–7.5

TABLE III. ^{13}C chemical shifts of macrocycles **I–III** and opened structure 2 in $CDCl_3$.

	Pyrazoles				CH_2			Sidearm		
	3,3′	4,4′	5,5′	6,6′	N–	CH_2–	pz–	a	b	c
I	150.0	107.9	139.5	13.5	54.0	28.0	48.3	60.9	20.9	12.3
	148.9	97.7	137.9	11.5						
II	150.5	107.9	139.7	13.5	54.7	28.2	48.4	66.3	63.7	20.2
	149,0	97.7	138.0	11.5						
III	149.8	107.7	139.8	13.3	51.6	28.1	48.1	65.9	70.7	143.2
		97.5	138.5	11.5				10.7		128.3
										127.2
										126.7
2*	150.6	107.0	140.9	12.9	51.5			68.3	64.0	20.5
	148.7	97.7	140.9	11.2						

* R = $CH_2CHOHCH_3$.

2.2. KINETICS OF TRANSPORT

The cell used for the transport experiments is described in Figure 1. The membrane phase was continuously stirred using a magnet (230 rpm). The evolution of the concentration of the carboxylic acid salt in the receiving phase was followed by UV spectrometry with a Philips PM 8110 spectrometer. The whole spectrum of the solution (200–600 nm) was recorded every 10 min using a 1 cm quartz circulation cell. The UV data were stored on a personal computer and converted into O.D. versus time using Philips Falcon software.

1. Source phase: 25 mL of an aqueous solution of the carboxylic lithium salt 0.1 M.
2. Membrane phase: 50 mL of CH_2Cl_2 containing the macrocycle (5×10^{-4} M).
3. Receiving phase: water (10 mL).

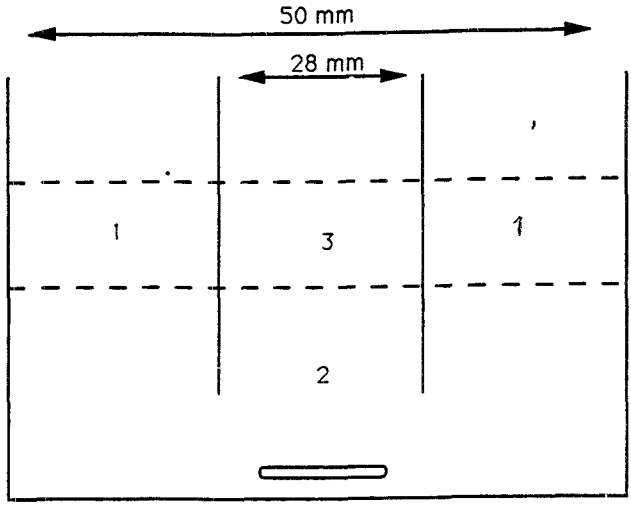

Fig. 1. Dimensions of the cell used for the transport experiments.

The spectra were compared to a reference solution of the Li^+ salt of the corresponding carboxylic acid in pure water (see Figure 2). The absorbances at different wavelengths measured from the spectra were plotted versus time. The linear part of the curve was analyzed using a least-squares adjustment program and the slope converted into transport rate (Equation 1). Correlation coefficients of the regressions are equal to or greater than 0.99.

$$v_\lambda = \mathrm{d(O.D.)}_\lambda/\mathrm{d}t \times \mathrm{Vol}/\epsilon_\lambda \tag{1}$$

where Vol = volume of the receiving phase, and ϵ_λ = molar extinction coefficient at a chosen wavelength λ.

The rates obtained at different wavelengths were compared to confirm the nature of the transported product (see Figure 3).

Each experiment was repeated at least three times: results were reproducible to within 3–5%.

2.3. ENANTIOSELECTIVITY OF TRANSPORT

The conditions of transport are similar to those described previously. Mandelic acid Li^+ salt is used as a racemic mixture, and the macrocycles in their chiral form. The specific rotation of the macrocycles were obtained with a Perkin Elmer 241 polarimeter $[\alpha]_D^{20}$. The kinetics were followed as described earlier by UV spectroscopy; 1 mL of the receiving phase was removed every day and split into five 200 μL samples to be chromatographed on an analytical HPLC chiral

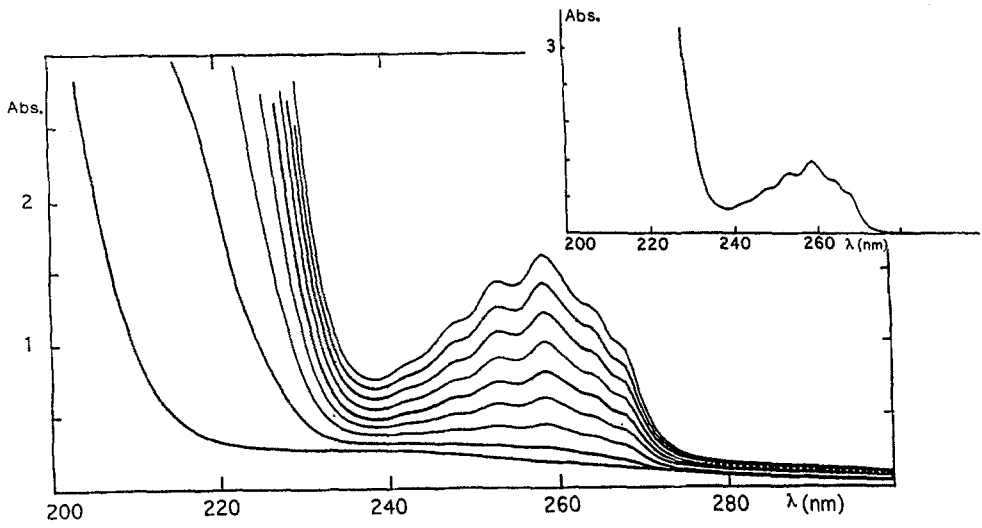

Fig. 2. Variation of the absorbance of the receiving phase versus time for the transport of Li^+ phenylacetate by macrocycle **II**. The reference solution spectrum is shown in the upper right corner.

column 250 × 4.6 mm (Chiracel OD Daicel supplied by J. T. Baker France); experimental conditions: $T = 25°C$, flow rate 0.5 mL/min, mobile phase: hexane/2-propanol/CCl_3COOH 80 : 20 : 1 [37], using a Waters instruments (510 HPLC pump, Wisp 712 automatic sample module, spectrophotometer LC455). The resulting chromatograms were analysed using a Baseline 810 chromatography workstation, including developing methods, acquiring and processing data, and manipulating chromatograms.

3. Results and Discussion

3.1. LIGAND SYNTHESES (FIG. 4)

The general method used for the synthesis of the tetrapyrazolic opened structures **2** has been described earlier [26]. The cyclization to macrocycles was carried out by condensation of **2** with dibromopropane under phase transfer catalysis conditions to favour substitution on the nitrogen atom α to the methyl group, and in high dilution conditions to favour cyclization over linear condensation. The corresponding yields

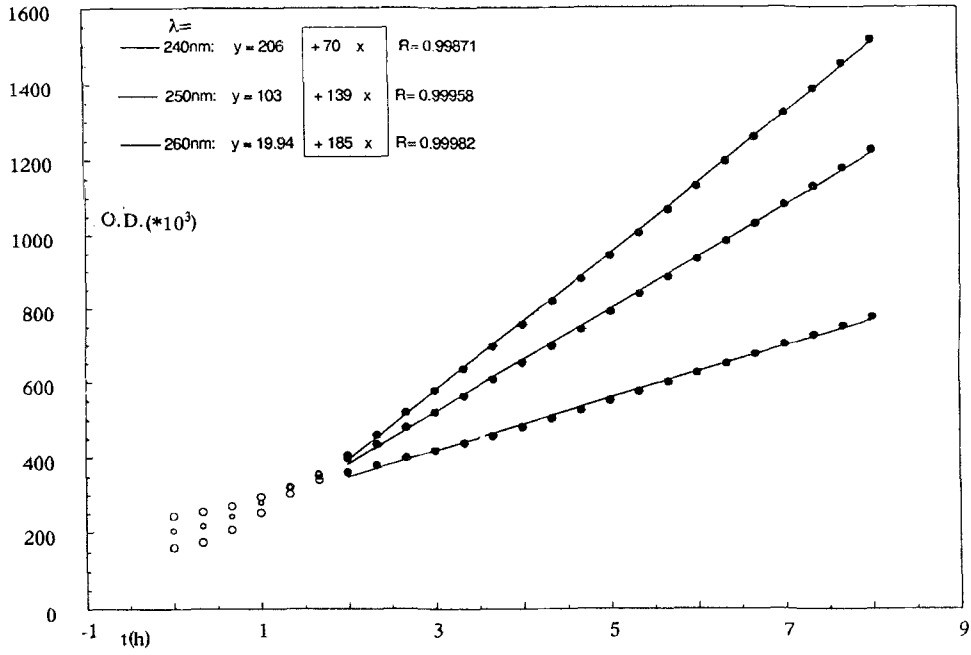

Fig. 3. Absorbance vs time plot at three different wavelengths extracted from Figure 2.

obtained in these two steps depending on the sidearm nature are summarized in Table I, the lower yield and longer heating time for compound **III** is probably due to the steric hindrance present in the primary amine which defavours its dialkylation.

The structure of macrocycles **I–III** has been determined by mass spectrometry (Table I) and by ^{1}H and ^{13}C NMR spectroscopy (Tables II and III). In the case of macrocycles **II** and **III** two points should be stressed: the dissymmetry present on the sidearm is reflected not only in its signals but also by the macrocycle CH_2–Nsp^3 protons, which are nonequivalent. The second point concerns the broadening observed for some protons of the sidearms and of the macrocycle (Table II) in $CDCl_3$ which disappears in protic solvents; the appearance of two new signals at low field which move downfield as the temperature decreases may be attributed to the OH group and to one molecule of water; at low temperatures, the exchange phenomenon between the sidearm OH function and two pyrazolic nitrogen atoms involving one molecule of water, becomes slow; such a conformation having the sidearm lying over the cavity and hydrogen bonded to macrocyclic donor sites has been suggested to explain the unexpected reactivity of some *N*-pivot lariat ethers [38, 39].

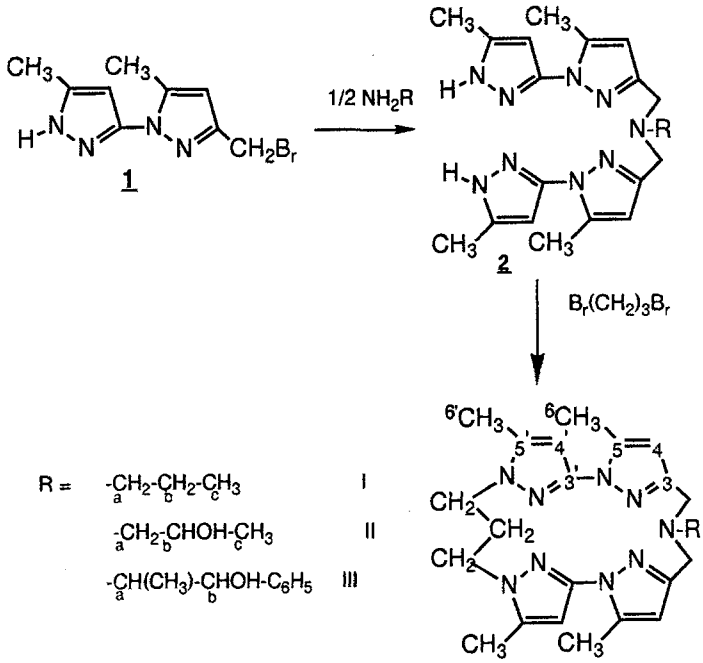

Fig. 4. General scheme for the synthesis of macrocycles **I–III**.

3.2. KINETICS OF CARBOXYLIC ACID SALT TRANSPORT

We have chosen to use an artificial liquid membrane for the transport experiments to allow comparison with our previous results [25, 26, 36, 40] and literature data. The transport was carried out through a CH_2Cl_2 membrane separating two aqueous solutions as described previously [36].

The three macrocycles reported here are all based on the same tetrapyrazolic skeleton, and as long as the nature of the flexible sidearm does not interfere with the cavity size, geometry and binding ability of the four pyrazolic subunits, they are equivalent; the difference in their binding ability, reflected in the transport rate, is only due to the nature of the sidearm. Different factors may be taken into account to rationalize the influence of the sidearm on the transport rate, such as:

- the OH polar group on the sidearm may stabilize the complex in the membrane phase in two ways: direct interaction with the ring bound cation and, because of the intimate ion pair structure of the macrocycle-acid salt couple, hydrogen bond formation with the hydroxy group of the acid salt.
- the hydrophilic character of the OH group-bearing sidearm and its flexibility may favour the approach of the macrocycle at the interfaces.

Transport rate values are reported in Table IV.

TABLE IV. Transport rate values of the carboxylic acids in 10^{-6} mol/h.

Macrocycle:	Phenylacetic salt	Mandelic salt
I	2	0
II	10	(see text)
III	5	12

Transport experiments for the phenylacetic acid salt show an enhancement of the transport rate for macrocycle **II** compared to **I**. The presence of a hydroxyl group on the sidearm can affect the transport in two ways: it may favour a better approach of the macrocycle at the source phase interface and/or a better stabilization of the Li^+ salt, compared to the propyl group of **I**, which is inert from that point of view.

Macrocycle **III** also possesses a hydroxyl group, which is sterically hindered by a phenyl substituent, so that its transport efficiency decreases.

The absence of measurable transport in the case of methoxyphenylacetic acid salt may be explained by the enhancement of its hydrophilic character and of the steric hindrance due to the methoxy group, which is moreover totally unable to create stabilizing interactions with the macrocycle.

The hydroxyl group present in the mandelate is expected to enhance its hydrophilic character, and then, in the absence of any kind of stabilizing interaction with the macrocycle, to reduce the transport rate. This is in accord with the absence of transport observed for macrocycle **I**, its propyl group being unable to interact with the hydroxyl group of the acid salt. For macrocycle **III** we have observed an increase of the transport rate compared to phenylacetic acid, which suggests that the hydrophilic character of mandelic acid is counterbalanced by the stabilizing effect of a hydrogen bond between the hydroxyl group of the macrocycle and the acid salt.

The transport of mandelic acid by macrocycle **II** has shown unusual behavior (Figure 5): the UV spectra obtained from the receiving phase were not comparable with the spectrum of the mandelic acid reference solution, while the variation of absorbance versus time was at least ten times faster than for the other systems. Nevertheless, the chromatogram of the receiving phase on a chiral column (see next paragraph) shows only the presence of the two acid enantiomers; and a comparison of the transport rate approximation obtained from these measurements gives a value superior to the one obtained with the other macrocycles. The NMR and mass spectra of the receiving solution show only the presence of the expected acid and of the macrocycle which makes us reject the hypothesis of a supramolecular catalytic reaction leading to an unknown product. Furthermore the comparison of the NMR data (listed in Table V), for the free macrocycle alone in water and for the receiving phase mixture of the macrocycle and acid salt (ratio $\sim$ 1/10) shows some significant shifts of the pyrazolic and CH_2–Nsp^3 proton signals suggesting that the macrocycle is still complexed to the Li^+ mandelate.

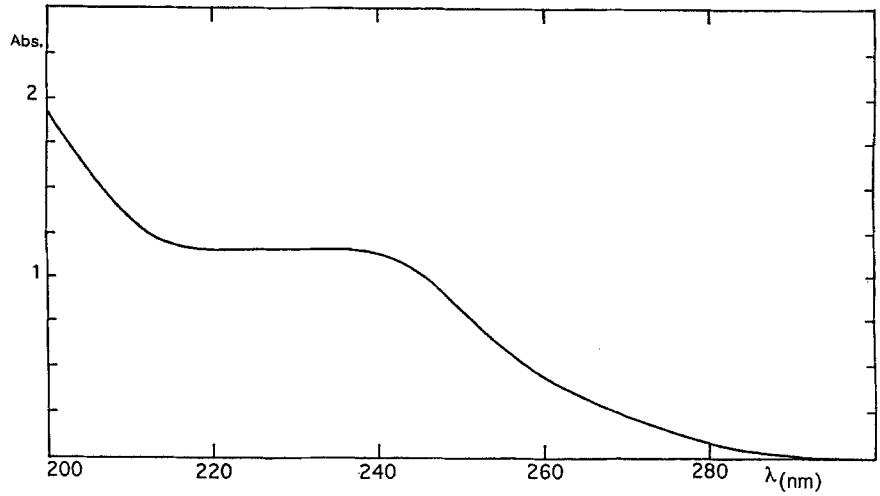

Fig. 5. UV spectra of a 10^{-3} M solution of mandelic acid salt and macrocycle **II**.

TABLE V. Chemical shifts of macrocycle **II** in water, (1) alone, (2) concentrated from the receiving phase.

	H 4′	CH_3	CH_2Nsp^2	CH_2Nsp^3	CH_2–CH_2	a	b	c
(1)	6.12	2.29	4.16	3.73	2.80	2.55	2.9	1.15
	5.69	2.23						
(2)	6.24	2.26	4.15	3.52		2.52	2.9	1.32
	5.97	2.23						

This implies that the stability of the complex between the macrocycle and the acid salt is high enough for this complex to be present in a significant amount in the receiving phase. This complex has its own absorption band around 300 nm (Figure 5) which is intense enough to mask the low intensity band of mandelic acid at those wavelengths; this new absorbance probably results from an interaction between the π systems of the macrocycle and the acid, the molar extinction coefficient of this band has been estimated to be greater than or equal to 10^3 M^{-1} L^{-1}; the upfield shift (-0.2 ppm) observed in this complex for the CH_2–Nsp^3 protons corroborates the occurence of a stacking interaction.

The spectra of the receiving phase of the other macrocycles were only slightly distorted, and the absorbance vs time plot has been successfully analyzed.

3.3. ENANTIOSELECTIVITY OF TRANSPORT

The transport rate of the acid salts is shown to be strongly dependent on the nature of the sidearm, so we could expect that, for the Li^+ mandelate, it would be also

TABLE VI. Percentage of mandelate *D* enantiomer transported by the chiral macrocycles **II** and **III**.

Macrocycle	*%D*
II	46.6 ± 0.1
III	47.7 ± 0.1

sensitive to the chirality of the macrocycle: both hydroxyl groups of the macrocycle and of the acid are borne by asymmetric carbons.

In order to show the influence of the chirality of the macrocyclic sidearm on the transport rate, we have carried out transport experiments under the same conditions as those described previously, but using the chiral form *R* of the macrocycle and a racemic source phase. The receiving phase was then chromatographed on a chiral column to allow determination of the enantiomeric percentages of mandelate *D* enantiomer in the receiving phase for the two chiral macrocycles (Table VI).

A significant enhancement of the transport of the L form from the racemic source phase is observed, especially if we consider that this selectivity appears in a one step process.

4. Conclusion

We have shown that the binding ability of our macrocycles is strongly dependent on the nature of their flexible sidearms, which can stabilize the Li^+ ion in the cavity or establish hydrogen bonds with the hydroxyl group of the acid if present. To our knowledge, it is the first time that an enhancement of transport due to a hydrogen bond between the counter anion and the macrocycle, is reported. Furthermore, we have shown that the introduction of an asymmetric center on this sidearm can induce a chiral recognition of the counteranion enantiomers: this result suggests an application for our compounds when linked to a chromatographic support.

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