# Synthesis of bis(*p*-phenylene)-32-crown-4 and bis(*m*-phenylene)-30-crown-4 macrocycles for the preparation of polyrotaxanes

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The predominantly hydrocarbon macrocycles bis(*p*-phenylene)-32-crown-4 and bis(*m*-phenylene)-30-crown-4 have been synthesized in one step from hydroquinone and resorcinol, respectively, and 1,10-dibromodecane in the presence of sodium hydroxide in dioxane/1-butanol.

**(Keywords: macrocycles; synthesis; polyrotaxanes)**

## *Introduction*

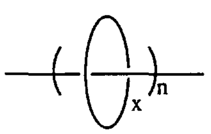
Our objective is to prepare polymeric rotaxanes. Polyrotaxanes are molecular composites comprised of rings threaded by linear polymer backbones with no covalent bonds between the two components as shown in *Scheme 1*[1–4]. By independent variation of the linear and cyclic components of polyrotaxanes an intriguing new family of polymer architectures with 'tunable' properties is at hand. The ability of the cyclic species to move laterally and circumferentially with respect to the backbone offers opportunities for design not currently available in traditional copolymers.

To be threaded by a polymethylene chain a ring size of at least 22 or 23 atoms (C, O, N) is required[5]. We are particularly interested in the synthesis of macrocycles in the range of 30–40 ring atoms with different polarities, rigidities and hydrophilicities[6–9]. Incorporation of *m*- or *p*-phenylene units into crown ethers with a predominantly hydrocarbon structure will produce stiffer macrocycles in comparison with flexible ethyleneoxy analogues. Syntheses of two such large predominantly hydrocarbon macrocycles are described in this paper for ultimate threading by hydrophilic linear macromolecules.

## *Experimental*

*Materials.* Reagent grade reactants and solvents were used as received from chemical suppliers.

*General comments.* The melting points were taken in capillary tubes with a Haake-Buchler melting point apparatus and have been corrected. The $^1$H nuclear magnetic resonance (n.m.r.) spectra were obtained at ambient temperature in deuteriochloroform solution with $Me_4Si$ as internal standard ($\delta = 0$ ppm) and recorded on a Bruker WP high resolution spectrometer operating at 270 mHz. The infra-red (i.r.) spectra were recorded (KBr pellets) on a Nicolet MX-1 FTIR spectrometer. The mass spectra were measured with a VGA 7070E analytical mass spectrometer.



**Scheme 1**

*Bis*(p-*phenylene*)-*32-crown-4* (**4**). Following a literature procedure used for other crown ethers[10], in a 2 litre three-necked flask equipped with a mechanical stirrer and reflux condenser under nitrogen was placed hydroquinone (**1**) (12.6 g, 110 mmol) dissolved in 1-butanol (450 ml) and sodium hydroxide (9.1 g, 230 mmol) in water (20 ml) was added. To this solution 1,10-dibromodecane (**3**) (30 g, 100 mmol) in dioxane/1-butanol (500 ml, 3:2 v/v) was added and the mixture was refluxed for 24 h, cooled, filtered and evaporated to give 30 g of brown viscous oil, which was chromatographed on 700 g of acidic alumina with diethyl ether as eluting agent. The residue from the column eluate crystallized from ethyl acetate to give 1.9 g (8%) of **4**, white crystalline solid, m.p. 97–98°C. I.r. (KBr): 1586 (C=C), 1231 (C–O–C) cm$^{-1}$. $^1$H n.m.r.: 1.27 (s, 16 H, $\delta$-$CH_2$), 1.42 (m, 8 H, $\gamma$-$CH_2$), 1.72 (p, 8 H, $\beta$-$CH_2$), 3.93 (t, 8 H, $\alpha$-$CH_2$), 6.81 (s, 8 H, $H_{arom.}$); $m/z$ (%): 496 ($M^+$, 100%); anal. calc. for $C_{32}H_{48}O_4$ ($M_W$ 496.72): C, 77.38; H, 9.74. Found: C, 77.12; H, 9.64.

*Bis*(m-*phenylene*)-*30-crown-4* (**5**). The same procedure as above was followed and 1,10-dibromodecane (**3**) (30 g, 100 mmol) was treated with resorcinol (**2**) (12.6 g, 110 mmol) and sodium hydroxide (9.1 g, 230 mmol). After the solution was refluxed for 24 h, filtered and evaporated *in vacuo*, 30 g of residue was chromatographed on acidic alumina with ether as eluting agent. The residue from the column eluate crystallized from ethyl acetate to give 1.9 g (8%) of **5**, white crystalline solid, m.p. 102–105°C (lit.[11], 105–106°C). I.r. (KBr): 1600 (C=C), 1279 (C–O–C) cm$^{-1}$. $^1$H n.m.r.: 1.27 (s, 16 H, $\delta$-$CH_2$), 1.42 (m, 8 H, $\gamma$-$CH_2$), 1.72 (p, 8 H, $\beta$-$CH_2$), 3.95 (t, 8 H, $\alpha$-$CH_2$), 6.47 (d, 4 H, $H_{arom.4,6}$), 6.50 (s, 2 H, $H_{arom.2}$), 7.15 (t, 2 H, $H_{arom.5}$); $m/z$ (%); 496 ($M^+$, 100%).

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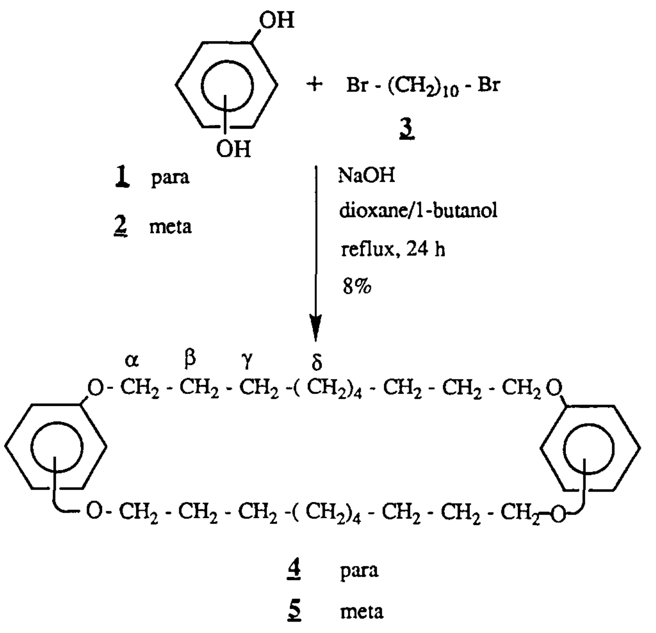


**Scheme 2**

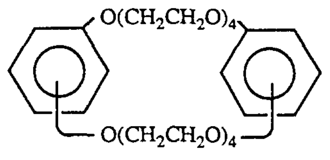
### *Results and discussion*

Here we report the synthesis of bis(*p*-phenylene)-32-crown-4 (**4**) from hydroquinone (**1**) and 1,10-dibromodecane (**3**) and NaOH in dioxane/1-butanol (*Scheme 2*). The yield of pure isolated macrocycle in this one step procedure is 8%. Despite the fact that there is not any significant chance of a template effect in the formation of this hydrophobic type macrocycle, the yield is comparable with the yields of bis(1,4-phenylene)-34-crown-10 (**6**) made in similar fashion (8%[10], 10.5%[12]).

The bis(*m*-phenylene)-30-crown-4 (**5**) was synthesized in 1937 by Luttringhaus and Ziegler[11] as a by-product from the reaction of resorcinol (**2**), 1,10-dibromodecane (**3**) and KOH in $C_2H_5OH$ (no yield reported). We have synthesized this macrocycle in one step via the reaction of resorcinol (**2**) with 1,10-dibromodecane (**3**) and NaOH in dioxane/1-butanol in 8% yield (*Scheme 2*). Again, even though the template effect cannot be operative, this yield is comparable to those obtained in the similar syntheses of bis(1,3-phenylene)-32-crown-10 (**7**) (9%)[8] and its 5,5′-dimethyl derivative (9%)[9].

Both macrocycles have been characterized by spectroscopic methods. Comparison of the asymmetric stretching frequencies of C=C and C–O–C bands of the *para*- and *meta*-substituted macrocycles show big differences. In other words, because of conjugation and lengthening of these bonds in the *para* isomer **4** relative to the *meta* isomer **5** they shift 14 and 48 $cm^{-1}$ to lower wave numbers, respectively. There are differences in the frequencies of the other bands as well.

The melting points of the above hydrocarbon macrocycles are also different from the corresponding ethyleneoxy crowns having similar ring size; for example, compare 32-membered **4**, m.p. 97–98°C, and 30-membered **5**, m.p. 102–105°C, to bis(*m*-phenylene)-32-crown-10 (**7**), m.p. 72–74°C[8,13]. These differences show that the hydrocarbon macrocycles have a more rigid structure, as anticipated on the basis of the restricted conformational properties bestowed by $-CH_2-$ relative to $-O-$.



**6** para
**7** meta

### *Acknowledgement*

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