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Molecular Modelling and Chemical Synthesis of Molecular 'Mappemondes' Designed from a Calix[4]-*bis*-crown

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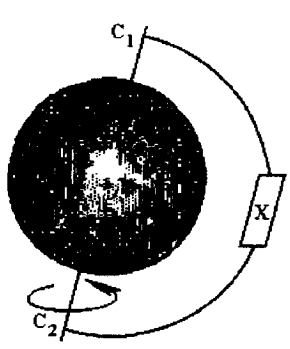
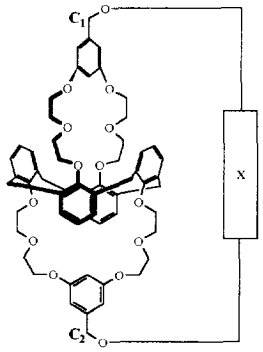
Abstract: The syntheses of molecular 'mappemondes' **10-12** have been designed from a calix[4]-*bis*-crown. The assembling of molecular segments toward **10-12** has been assisted by molecular modelling. Copyright © 1996 Elsevier Science Ltd

One branch of supramolecular chemistry deals with the development of synthetic strategies for constructing artificial systems with a desire behaviour. The term of 'molecular machines' has been given to desired chemical systems presenting mechanical properties with reference to classical mechanics as for example motions of part of molecules in self-assembled molecular architectures. [1] Obtention of catenanes, rotaxanes, and molecular shuttles relies upon the formation of mechanically interlocked molecular components[2,3]. Molecular clips derived from glycoluril have a binding conformation induced by addition of a metal salt[4]. A molecular brake constructed from a 2,2'-bipyridine attached to a triptycene acts as a wheel prevented from spining around the triptycene-pyridine bond by metal-complexation of the 2,2'-bipyridine[5]. A molecular pendulum deriving from a calixarene-analogous presents a type motion steered by intramolecular hydrogen bonding.[6]

In the present Note we describe the construction of molecular systems **10-12** looking like a 'mappemonde'. The general concept and the molecular objects are presented below :

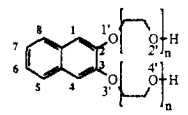




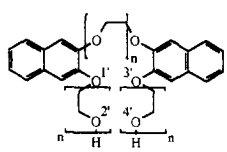
10 - 12

A calix[4]-*bis*-crown-6[7] moiety represents the earth ball which poles (C1 and C2) are linked by a polyether loop X serving as an arm.

Mechano Construction. In a preliminary step we have optimized[8] the geometrical calix[4]-*bis*-crown-6 or model I. The distance between the two terminal carbons C1-C2 was founded 19.82 Å (see Fig. 1a). In a second step, we performed a systematic conformational study of different 2,3-naphthyl-di-polyethylene glycol **1-5** with n varying from 3 to 7, in order to determine the low-energy conformers with intermolecular O2'-O4' distances matching the C1-C2 distance of model I. As shown in the Table, we noticed that the distance O2'-O4' increased regularly with n whereas the angle O2'-center of Ar1-O4' decreased from 137° to 64°. From a topological point of view all the diols seemed suitable for 1+1 bridging C1 to C2, except the stuctures **1** (n=3) and **2** (n=4) because of steric hindrance with the aromatic rings of the calix unit. And in fact, C1-C2 bridging occured in very low yields with these diols (cf *vide infra* 2% and 8% respectively). Untill now we have been unable to prepare **3-5** in acceptable yields to perform the bridging. We therefore prepared di-naphthyl-di-polyethylene glycol **6** very similar to **5** in its conformational behaviour with O2'-O4' distance equal to ~19-20 Å giving the best fit (Fig. 1b). In this case the C1-C2 bridging occured in 33% yield. Optimized structure of **12** is presented in Fig 1c.

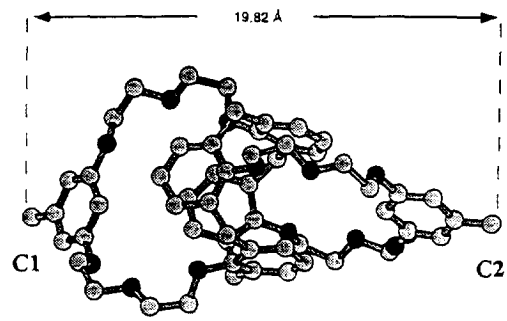


1-5 (n = 3-7)

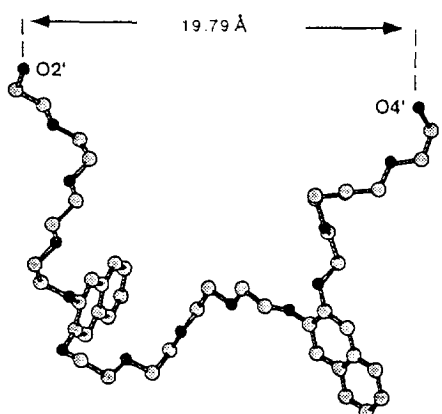


6 (n = 4)

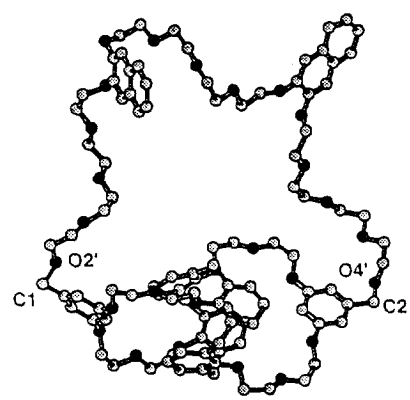
Link	n	d(O1'-O2')	d(O2'-O4')	Angle(O2'-Ar1-O4')
1	3	8.19 Å	18.83 Å	137°
2	4	10.93 Å	20.24 Å	124°
3	5	13.73 Å	20.12 Å	80°
4	6	16.43 Å	20.79 Å	70°
5	7	19.12 Å	21.96 Å	64°



(a) model I



(b) link **6**

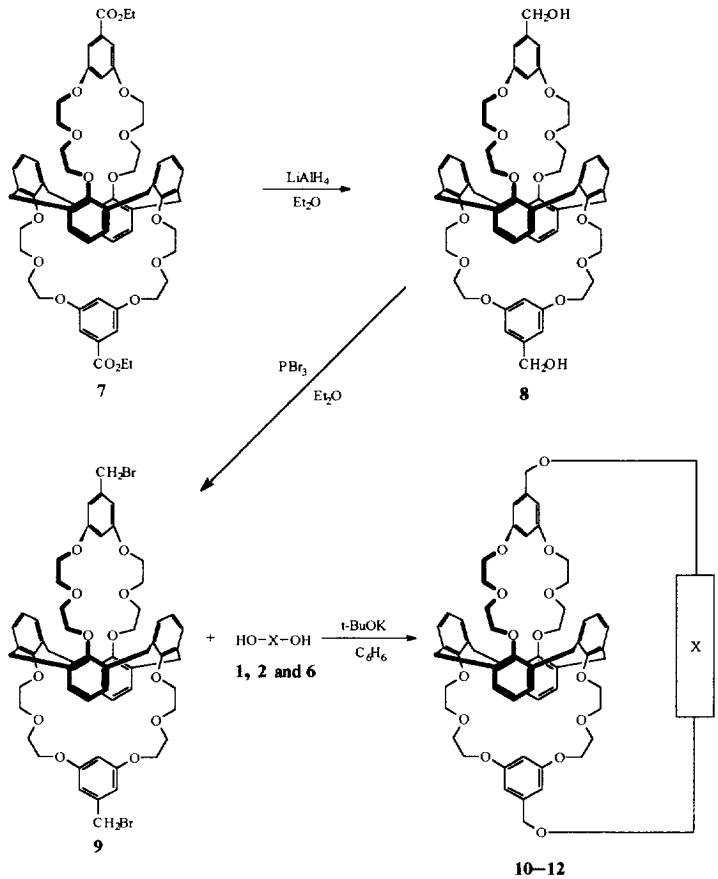


d(O2'-O4') = 19.27Å d(C1-C2) = 19.80Å

(c) optimized structure of **12**

Figure 1. Optimized structures of : (a) model I, (b) link **6**, (c) molecule **12**

Chemical Synthesis. The synthesis of **10-12** was conducted as outlined below. Diethyl ester calix[4]-*bis*-crown-6[9] **7** was reduced with ~ 40 equivs of $LiAlH_4$ in Et_2O (6 h-reflux) into the diol **8** (66% yield recrystallized from CH_2Cl_2) which was converted into the dibromo **9** with a large excess of PBr_3 in Et_2O (17 h-stirring at rt) in a quantitative yield. Reaction of **9** with diols **1**, **2** and **6** in the presence of t-BuOK in benzene (5 days-reflux in high dilution conditions) provided bridged-adducts **10-12** in 2%, 8% and 33% yields respectively.[10] This order of 1+1 bridging is in agreement with the mechano estimation.



The presence of only one well-resolved singlet at 4.54, 4.52 and 4.54 ppm for the methylene protons of the Ar-C*H*$_2$-O- in **10-12** respectively let us assume that the globular calixcrown spins around these bonds.

Preliminary complexation studies showed that ligand **12** extracted more rapidly (one week) $NH_4^+Pic^-$ from the solid into chloroform than calix[4]-*bis*-crown **7** (one month) probably due to the presence of the additional polyether loop. The both receptors formed 1:1 complexes as determined from the singlet of the aromatic picrate anion and the triplet of the *para*-proton on the aromatic unit of calix unit by a procedure already described by us.[11] The metal was located in the calix unit on the view of upfield shifts of ~ 0.14 ppm of the singlets at 6.97 ppm and 6.63 ppm corresponding to the Ar*H*-benzo protons in **7** and **12** respectively.

Work is in progress to show evidence of a spining slow-down by multi-complexation of small cations and by complexation of R-NH_3^+ with *n*-alkyl chains with various lengths.

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8. All molecular modelling calculations were carried out with the SYBYL 6.1 program from Tripos Inc. The geometrical parameters of the different models were calculated on a Silicon Graphics Indigo/2 worstation, with help of the Tripos force field and the MAXIMIN2 energy minimizer.
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10. **Data of 10-12** : Compound **10** : White solid. Mp 89-91 °C. *200 MHz* ^{1}H-NMR ($CDCl_3$) δ in ppm 7.63 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.32 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.13 (s, 2H, Ar*H*-naphtho); 6.94 (d, 8H, J = 7.5 Hz, *meta*-Ar*H*-calix); 6.67 (s, 6H, Ar*H*-benzo); 6.05 (t, 4H, J = 7.5 Hz, *para*-Ar*H*-calix); 4.54 (s, 4H, ArCH_2O); 4.31 (m, 8H, ArOCH_2CH_2); 4.18 (t, 4H, J = 5.9 Hz, ArOCH_2CH_2); 3.97 (m, 8H, $ArCH_2OCH_2CH_2O$); 3.81-3.75 (m, 20H, CH_2CH_2O); 3.57 (s, 8H, ArCH_2Ar); 3.44-3.37 (m, 16H, CH_2CH_2O). Mass spectrum (FAB$^+$, NAB): *m/z* 1373.6 (M^+ *calc.* 1372.6). **Yield 2%**.
Compound **11** : White solid. Mp 72-75 °C. *200 MHz* ^{1}H-NMR ($CDCl_3$) δ in ppm 7.65 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.31 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.15 (s, 2H, Ar*H*-naphtho); 7.08 (d, 8H, J = 7.5 Hz, *meta*-Ar*H*-calix); 6.67 (s, 2H, Ar*H*-benzo); 6.61 (s, 4H, Ar*H*-benzo); 6.44 (t, 4H, J = 7.5 Hz, *para*-Ar*H*-calix); 4.52 (s, 4H, ArCH_2O); 4.29 (m, 12H, ArOCH_2CH_2); 4.01-3.64 (m, 52H, CH_2CH_2O); 3.64 (s, 8H, ArCH_2Ar). Mass spectrum (FAB$^+$, NAB): *m/z* 1461.4 (M^+ *calc.* 1460.7). **Yield 8%**.
Compound **12** White solid. Mp 121-123 °C. *200 MHz* ^{1}H-NMR ($CDCl_3$) δ in ppm 7.62 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.29 (dd, 2H, J = 3.3 Hz, Ar*H*-naphtho); 7.12 (s, 4H, Ar*H*-naphtho); 7.02 (d, 8H, J = 7.5 Hz, *meta*-Ar*H*-calix); 6.63 (s, 6H, Ar*H*-benzo); 6.29 (t, 4H, J = 7.5 Hz, *para*-Ar*H*-calix); 4.54 (s, 4H, ArCH_2O); 4.25 (m, 16H, ArOCH_2CH_2); 4.00 (s, 8H, ArOCH_2CH_2); 3.91 (m, 16H, $ArCH_2OCH_2CH_2O$); 3.79-3.62 (m, 40H, CH_2CH_2O); 3.42 (s, 8H, ArCH_2Ar). Mass spectrum (FAB$^+$, NAB): *m/z* 1779.8 (M^+ *calc.* 1780.1). *Anal. Found* C, 68.58; H, 7.17. *Calc.* for $C_{102}H_{122}O_{27}$: C, 68.82; H, 6.91. **Yield 33%**.
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