

Non-ionic [2]rotaxanes containing methylated α -cyclodextrins

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Non-ionic [2]rotaxanes have been prepared from complexes of oligoethylene derivatives with methylated α -cyclodextrins by capping them with trinitrophenyl groups as stoppers.

Recently, much attention has been focused on the construction of interlocked molecular structures, such as rotaxanes and catenanes, because of their unique structures and properties.¹ Crown ethers,² cyclodextrins (CD),³ cyclophanes⁴ and cucurbituril⁵ have been used as ring components of rotaxanes. Symmetric⁶ and asymmetric⁷ [2]rotaxanes containing α -CD and methylated β -CD have been prepared and characterized. However, all the [2]rotaxanes are ionic and in some cases their stoppers are metal complexes which are in equilibrium with dissociation states, so rings may come off. To obtain non-ionic [2]rotaxanes, it is necessary to design a dumbbell part which consists of neutral stoppers and a neutral axle. We chose a 2,4,6-trinitrobenzenesulfonic acid sodium salt (TNBS) as a stopping agent and diaminohexaethylene dihydrochloride (DAHE-2HCl) as an axle because TNBS is large enough to prevent dethreading and DAHE-2HCl is long enough to penetrate a methylated α -CD cavity. Moreover, TNBS and the amino groups of DAHE react easily with each other to give a covalent C–N bond in aqueous solution under mild conditions. 2,6-Di-*O*-methyl- α -CD (DM- α -CD) and 2,3,6-tri-*O*-methyl- α -CD (TM- α -CD) were chosen as ring molecules, because they are highly soluble in water and are able to form complexes with oligoethylene derivatives in aqueous solutions. Here we report the first preparation of non-ionic [2]rotaxanes based on the formation of the inclusion complexes.

α -CD forms complexes with ω , ω' -diaminoalkanes to give crystalline complexes. However, DM- α -CD and TM- α -CD did not form crystalline complexes, forming instead soluble complexes with ω , ω' -diaminoalkanes in an aqueous solution, although DAHE is insoluble in water. DAHE could be dissolved in aqueous solutions of DM- α -CD or TM- α -CD. The molar ratio of DAHE dissolved to the methylated α -CD is 1:1, indicating formation of 1:1 complexes. The complexes were allowed to react with TNBS to prevent dethreading of the cyclodextrins (Scheme 1). The products precipitated from water and were collected and purified by preparative thin layer chromatography (TLC) on SiO₂. This gave two kinds of [2]rotaxanes containing DM- α -CD and TM- α -CD, respectively. The [2]rotaxanes were obtained in high yields; 42% for DM- α -CD-[2]rotaxane and 48% for TM- α -CD-[2]rotaxane.

The products were characterized by elemental analysis, UV–VIS, ¹H NMR, ¹³C NMR and FAB mass spectra.† TLC of the products on SiO₂ plates (90:10, CHCl₃–MeOH) revealed single spots in each case. The products showed absorptions at 417 and 347 nm, indicating that the 2,4,6-trinitrophenyl groups were substituted on the axles. The UV–VIS spectra as well as the ¹H NMR spectra and elemental analyses revealed that the ratio between the methylated α -CD and DAHE-TNP₂ was 1:1.

The ¹H NMR spectrum of TM- α -CD-[2]rotaxane shows that it is composed of TM- α -CD, an HE chain and trinitrophenyl end groups in the proper ratios, that is, a single TM- α -CD unit, one HE chain and two TNP end groups. The peaks of TM- α -CD and DAHE-TNP₂ in the spectrum of [2]rotaxane show some shifts compared with those of its components, indicating that TM- α -CD and a HE chain are imprisoned in a single molecule. The

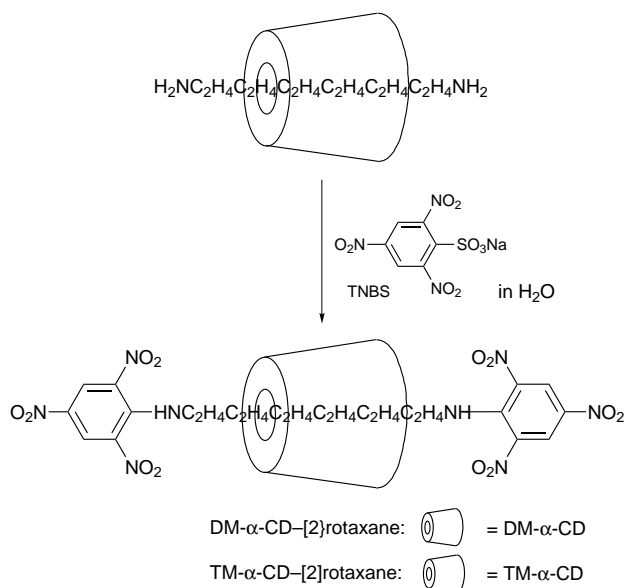
¹H NMR spectrum of DM- α -CD-[2]rotaxane showed similar results.

Fig. 1 shows the ¹³C NMR spectrum of DM- α -CD-[2]rotaxane together with those of DM- α -CD and DAHE-TNP₂. The spectrum shows that the compound is composed of a single DM- α -CD and a single DAHE-TNP₂ unit. The C(c) and C(d) resonances of the TNP group split into two peaks, respectively. One is due to the TNP group at the small side of DM- α -CD and another is due to the TNP group at the larger cavity side. The C(e) resonance of the HE chain also separates into two peaks for the same reason. The resonances of the HE backbone split into a more complex pattern indicating that the HE chain is included in the cavity of DM- α -CD.

The FAB MS spectra of the two [2]rotaxanes are characteristic of DM- α -CD-[2]rotaxane and TM- α -CD-[2]rotaxane, respectively. In addition to peaks for the molecular ions and those with sodium, fragmentation peaks for the components are also observed.

The solubilities of the two [2]rotaxanes are quite different from those of their components. The [2]rotaxanes are insoluble in water, although DM- α -CD, TM- α -CD, TNBS and even complexes of DAHE with methylated α -CDs are soluble in water. The rotaxanes are soluble in most organic solvents such as chloroform, benzene, DMSO and DMF. The solubilities of the rotaxanes in organic solvents are higher than the thread and stopper molecule DAHE-TNP₂. The rotaxanes do not dethread into their components in any solvents, because the stopper group is covalently bound to the thread.

In conclusion, new neutral non-ionic [2]rotaxanes containing methylated CDs were prepared by utilizing the complex formation of derivatives of ω , ω' -diaminoalkane and methylated α -CDs in high yields. The rotaxanes obtained here have the simplest structures of such supramolecular compounds containing CDs reported, which enables us to study the basis of



Scheme 1

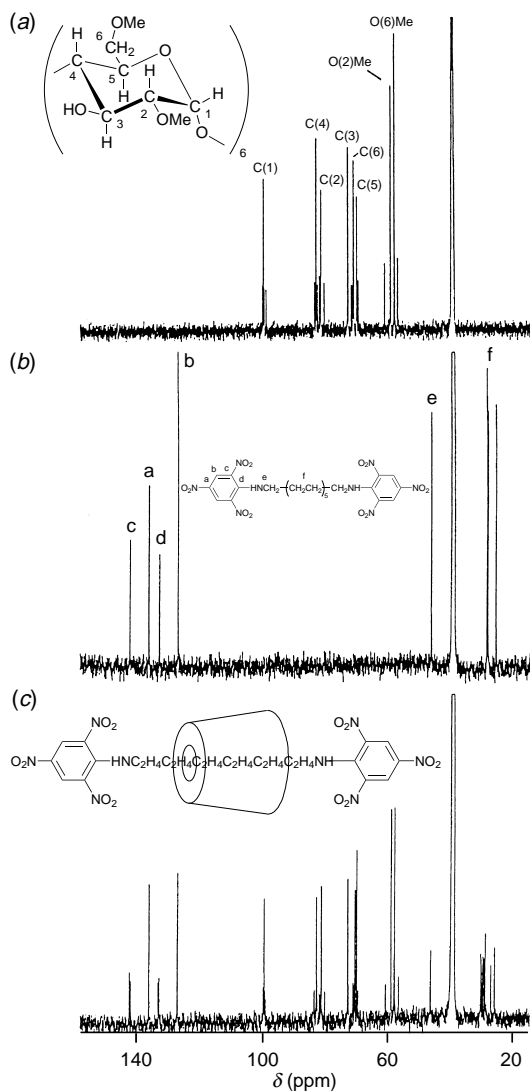


Fig. 1 125.65 MHz ^{13}C CP MAS NMR spectra of (a) DM- α -CD, (b) DAHE-TNP₂ and (c) DM- α -CD-[2]rotaxane in $[\text{D}_6]\text{DMSO}$ at 30 °C

rotaxane chemistry. This work also provides new methods for the synthesis of more complexed rotaxanes and catenanes using such non-covalent self-assembly processes.

Footnotes

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† Selected data for DM- α -CD-[2]rotaxane: ^1H NMR (CDCl_3 , 270 MHz): δ 9.02 (d, 4 H, Ph), 8.94 (d, 2 H, PhNH), 4.95 [m, 12 H, C(2)OH and C(1)H

of CD], 3.69–3.98 [m, 18 H, C(3)H and C(6)H of CD], 3.61 [s, 18 H, C(2)OCH₃ of CD], 3.40–3.57 [m, 6 H, C(5)H of CD], 3.36 [s, 18 H, C(6)OCH₃ of CD], 3.11–3.27 [m, 12 H, C(2)H and C(4)H of CD], 3.03 [d, 4 H, H(α) of hexaethylene chain], 1.24–1.77 (m, 20 H, hexaethylene backbone); ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 125.65 MHz): δ 141.87 [C(2) of Ph], 136.00 [C(4) of Ph], 132.94 [C(1) of Ph], 127.07 [C(3) of Ph], 99.61 [C(1) of CD], 82.91 [C(4) of CD], 81.36 [C(2) of CD], 72.99 [C(3) of CD], 70.75 [C(6) of CD], 70.17 [C(5) of CD], 59.39 [MeO of C(2) of CD], 58.28 [MeO of C(6) of CD], 46.62 [C(α) of HE chain], 26.12–30.50 (HE backbone); Positive ion FAB MS: m/z 1799.7 ($M + \text{CH}_2 + \text{Na}^+$), 1777.7 ($M^+ + \text{CH}_2$), 1763.7 ($M^+ + 1$), 1759.7, 1745.7, 1729.7, 1714.7. Calc. for $\text{C}_{72}\text{H}_{115}\text{N}_8\text{O}_{42}$: C, 49.00; H, 6.57; N, 6.35. Found: C, 49.01; H, 6.53; N, 6.36%.

For TM- α -CD-[2]rotaxane: ^1H NMR (CDCl_3 , 270 MHz): δ 9.01 (d, 4 H, Ph), 8.91 (d, 2 H, PhNH), 5.02 [d, 6 H, C(1)OH of CD], 3.40–3.85 [m, 24 H, C(3)H, C(5)H and C(6)H of CD], 3.48 [s, 18 H, C(3)OCH₃ of CD], 3.37 [C(6)OCH₃ of CD], 3.11–3.18 [m, 12 H, C(2)H and C(4)H of CD], 3.03 [m, 4 H, H(α) of hexaethylene chain], 1.25–1.70 (m, 20 H, hexaethylene backbone); ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 125.65 MHz): δ 141.67 [C(2) of Ph], 136.07 [C(4) of Ph], 133.02 [C(1) of Phenyl], 126.99 [C(3) of Ph], 99.18 [C(1) of CD], 82.09 [C(4) of CD], 81.82 [C(2) of CD], 80.75 [C(3) of CD], 70.91 [C(6) of CD], 70.86 [C(5) of CD], 60.94 [MeO of C(3) of CD], 58.26 [MeO of C(2) of CD], 56.93 [MeO of C(6) of CD], 46.31 [C(α) of HE chain], 26.40–30.85 (HE backbone); Positive ion FAB MS: m/z 1869.8 ($M + \text{Na}^+$), 1848.8 ($M^+ + 1$), 1847.8 (M^+), 1831.8 ($M - \text{CH}_2$), 1830.8, 1829.9, 1814.8. Calc. for $\text{C}_{78}\text{H}_{126}\text{N}_8\text{O}_{42}$: C, 50.70; H, 6.87; N, 6.06. Found: C, 50.47; H, 6.84; N, 6.09%.

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