released from the receptor, are then extracted into the organic phase, aliquots of which were subjected to HPLC conditions developed for the analysis of carotene dioxygenase enzyme studies.[15] The reaction products were identified by retention time (co-injection with authentic samples) and by their UV spectra; external calibration curves were used for the quantification. The ratio of reaction products is given in Scheme 3.

It is evident that **1** is not only cleaved at the central double bond but also at C(12′)=C(11′) to give 12′-apocarotenal **9** and at C(10′)=C(9′) to give 10′-apocarotenal **10**. The combined yield of aldehydes **2**, **9**, and **10** was 30 %, which compares well with the efficiency of β,β-carotene 15,15′ dioxgenase which gives retinal **2** in 20 – 25 %.[4] Most interestingly, the double bond in closest proximity to the central one in **1**, C(14′)=C(13′), remains untouched. We postulated that this phenomenon is related to interactions between the end-groups of **1** and the cyclodextrin moieties, such that a lateral movement of **1** within the binding pocket exposes only three double bonds to the reactive Ru=O group (Figure 1 b). If this hypothesis is true, one would expect a carotenoid with one modified end-group to demonstrate a different selectivity in double-bond cleavage. Accordingly, we investigated the oxidation of synthetic carotenoid **8**,[16] a substrate of the native enzyme,[17] under identical conditions. The selectivity for C(15)=C(15′) cleavage is almost exclusive when one of the cyclohexene end-groups of β,β-carotene **1** is replaced by an *ortho*-dimethylphenyl group, supporting the relationship between substrate mobility and selectivity. This suggests that stronger hydrophobic interactions between the aromatic end-group of **8** and the β-cyclodextrin cavity are responsible for stabilizing the 1:1 inclusion complex with the central double bond under the reactive ruthenium center.

We have demonstrated the selective cleavage of carotenoids to provide retinal **2** with a supramoleclular enzyme mimic which shows an unusual reactivity towards olefins in the presence of TBHP. Work is currently underway to mimic the reactivity and selectivity of the enzymes responsible for excentric cleavage of β,β-carotene **1**.[18]

Experimental Section

Physical data for **4**. λ_{max} = 414 (100 %), 534 (10 %) 570 (4 %); ^{1}H NMR (600 MHz, 25 °C, [D$_6$]DMSO): δ = 8.61 (d, 4H, H-2,8,12,18, J = 4.5 Hz), 8.56 (d, 4H, H-3,7,13,17, J = 4.5 Hz), 8.06 (m, 4H, H-2″,6″), 7.94 (m, 4H, H-3″,5″), 7.58 (m, 4H, H-2′,6′), 7.33 (m, 4H, H-3′,5′), 5.9 – 5.6 (br. m, 28H, 2OH), 5.0 – 4.8 (m, 14H, anomeric H), 4.7 – 4.4 (*m*, 12H, 1OH), 3.8 – 3.25 (m, 84H, β-CD (H-2,3,4,5,6,6′)), 2.65 (*s*, 6H, ArCH$_3$); MALDI-TOF-MS: *m*/*z*: 3007 [*M*$^+$], 3024 [*M*+H$_2$O]; HPLC (LiChrospher 100 Rp-18 (5 μm), 250-4) R_t = 9.43 min (20 – 60 % acetonitrile in 20 min, flow 1.5 mL min^{-1}).

General procedure for cleavage reactions: A 25-mL round-bottomed flask which had been purged with argon and fitted with an egg-shaped magnetic stir bar was charged with a solution of dimer **4** (2.3 mg, 10 Mol-%) in H$_2$O (1 mL). TBHP (30 μL of a 70 % solution in water, 30 equiv with respect to **1**) was added. β,β-Carotene **1** (4 mg) was dissolved in hexane/chloroform (9/1; 10 mL) and added to the reaction flask to produce a biphasic system. The reaction system was closed and stirred vigorously to ensure good mixing of the two phases. At different times during the reaction, stirring was stopped to allow phase separation. Aliquots (20 μL) of the organic phase were taken and subjected to HPLC analysis (LiChrospher 100 Rp-18 5 μm, length × ID = 125 mm × 4.6 mm, 25 °C, 1 mL min^{-1}, gradient: acetonitrile:1 % NH$_4$OAc$_{(aq)}$ (1:1) (100 %) → acetonitrile:*i*PrOH (1:1) (100 %) in 10 min, then acetonitrile:*i*PrOH (1:1) (100 %) for 5 min, then acetonitrile:*i*PrOH (1:1) (100 %) → acetonitrile:1 % NH$_4$OAc$_{(aq)}$ (1:1) (100 %) in 2 min). A diode array detector was used for the detection. R_t = 10.39 (**2**), R_t = 12.05 (**9**), R_t = 12.20 min (**10**). In all reactions, carotenoids **1** (R_t = 14.0 min) and **8** (R_t = 15.3 min) were completly consumed after 24 h.

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The Spatial Demand of Dendrimers: Deslipping of Rotaxanes[**]

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Dendrimers are generally not rigid molecules because of the flexibility of their building blocks,[1] and this makes it difficult to compare their size with that of voluminous, but rather rigid "conventional" molecules. Recently we described the effect of slight changes in the size of wheels and stoppers

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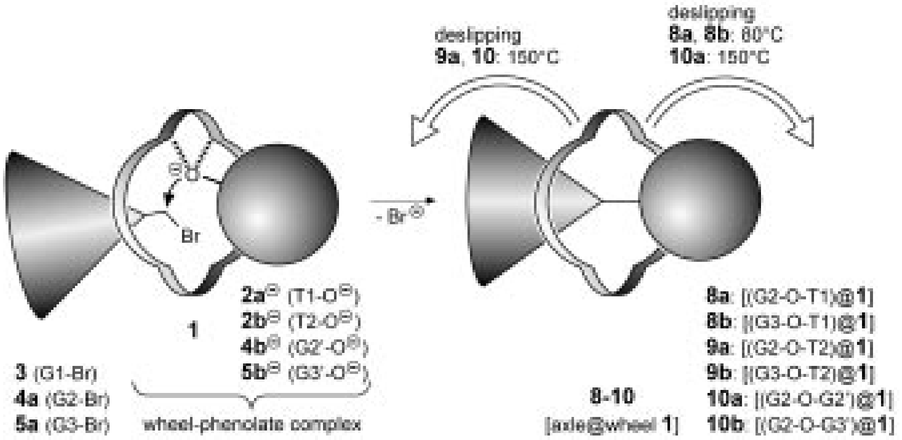
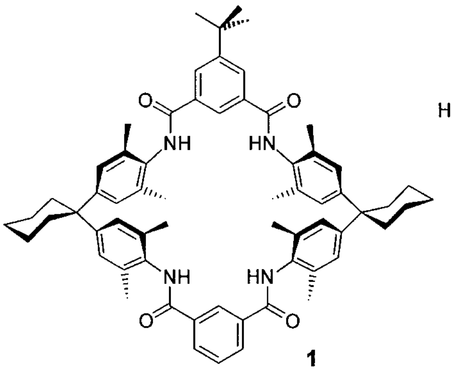
on the deslipping behavior of rotaxanes.[2–4] This investigation inspired us to compare the effective spatial demand of dendrons such as those of the Fréchet-type[5] with that of "conventional", nondendric stoppers and thus to derive a sort of size ranking by determination of the stability of the mechanical bonds in rotaxanes.[6–9]

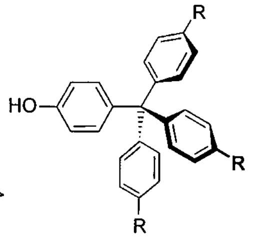


Scheme 1. Illustration of the trapping synthesis of dendritic rotaxanes by the nucleophilic attack of a wheel–phenolate complex on a stopper bromide.

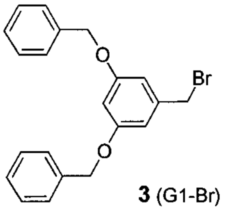
We used our newly developed trapping procedure for the template synthesis of the new rotaxanes **8**–**10** (see Scheme 1). This method is based on the complexation of intermediate anionic stopper building blocks by neutral macrocyclic isophthalamides such as **1** and their subsequent reaction with electrophilic stoppers to give rotaxanes with phenyl ether axles.[10] First, *p*-tritylphenol (**2a**, T1-OH) was treated with the first, second, and third generation dendritic bromides **3**, **4a**, and **5a** (G1-Br, G2-Br, and G3-Br) in the presence of the tetralactam **1**[11] and K_2CO_3. The rotaxanes **8a** and **8b** with the G2 and G3 stoppers, respectively, were formed (Scheme 1) in yields of 14 and 7%, respectively, while no rotaxane could be isolated with the G1 stopper; only the free axle was obtained. Clearly the first generation (G1) is too small to prevent the (pseudo-) rotaxane that is probably formed as an intermediate from deslipping. The yields of the analogous rotaxanes **9a** and **9b** with the bulkier *tert*-butyl-substituted tritylstopper **2b** (T2-OH)[12] were 15 and 17%, respectively. In order that the medium-sized G2 and T2 building blocks could be ranked the "doubly dendritic" rotaxane **10b** with G2-O-G3′ as the axle had to be prepared so that its deslipping could be compared with that of the G2-O-T2 rotaxane **9a**. Therefore, the previously unknown phenolic dendron **5b** (G3′-OH) was synthesized from 5-acetoxyresorcinol[13] and G2-Br **4a**.[14] The reaction of the new nucleophilic dendron **5b** with **4a** in the presence of the macrocycle **1** yielded 1.5% of the rotaxane **10b**. Analogously, 1% of the rotaxane **10a** with the G2-O-G2′ axle was obtained from the reaction of **1**, **4a**, and the likewise new G2′-phenol **4b**. The yields of the rotaxanes were considerably lower here than in previously reported trapping syntheses, which were nearly quantitative in some cases,[10] probably as a result of the steric shielding of the bromomethyl group by the voluminous, flexible dendritic groups and the shielding of the phenolate oxygen atom in the complex with the wheel. Complexation of the dendritic phenolates **4b** and **5b** is possibly also sterically hindered and the effectivity of the template assistance reduced consequently.[15]



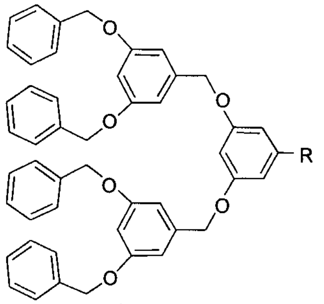
1



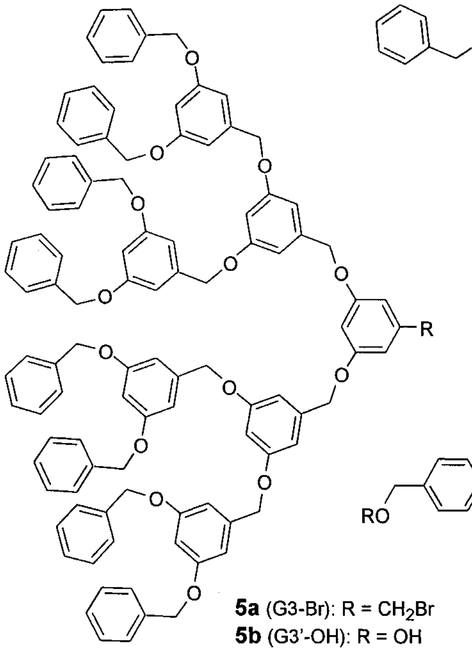
2a (T1-OH): R = H
2b (T2-OH): R = *t*Bu



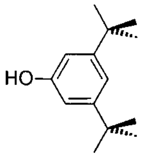
3 (G1-Br)



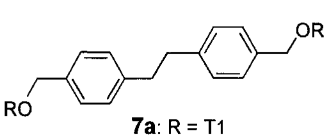
4a (G2-Br): R = CH_2Br
4b (G2′-OH): R = OH



5a (G3-Br): R = CH_2Br
5b (G3′-OH): R = OH



6 (D*t*BP-OH)



7a: R = T1
7b: R = D*t*BP

All of the rotaxanes were stable indefinitely at room temperature. However, the spectra of the rotaxanes **8a** and **8b**, the axles of which (G2-O-T1 and G3-O-T1, repectively) each carry one trityl stopper, clearly showed signals of the free components after a few hours at 80°C. Quantification of the data gave a half-life of eleven hours for **8a** and twelve hours for **8b**, which is not a significant difference considering the accuracy of the method. The rotaxane [**7a**@**1**],[10a] which has a comparitively long bibenzyl central part in the axle, was mechanically more stable with a half-life of 34 h at 80°C, even though its wheel has the possibility of slipping over both T1 stoppers. The slower deslipping kinetics is clearly caused by the longer and more flexible axle. The analogous rotaxane [**7b**@**1**] with the smaller 3,5-di-*tert*-butylphenyl (D*t*BP) stoppers, however, slowly deslipped even at room temperature (ca. 10% in 48 h).[10a]

In contrast to this, no changes were observed in the spectra of the rotaxanes with the larger *tert*-butyl-substituted trityl stopper (T2) or two dendritic stoppers (G2 or G3) even after many hours at 80 °C. Deslipping experiments were, therefore, carried out at even higher temperatures (150 °C) so that the spatial demands of these three stoppers could be compared.[16] After a short time signals corresponding to the free components appeared in the NMR spectra of the rotaxanes **9a**, **10a**, and **10b**, which all carry at least one dendron of the second generation on their axles (G2-O-T2, G2-O-G2′, and G2-O-G3′, respectively). Only the spectra of the G3-O-T2 rotaxane **9b** with a third generation dendron and a substituted trityl stopper showed hardly any changes. Pronounced line broadening and signal overlapping in the spectra of the "doubly dendritic" rotaxanes **10a** and **10b** prevented an exact quantification of the rate of deslipping, but half-lifes of about 15–20 h could be estimated. These results lead to the conclusion that the wheel slips over the second generation dendrons in rotaxanes **9a**, **10a**, and **10b** and that this consequently has a lower spatial demand than the substituted trityl group (T2).

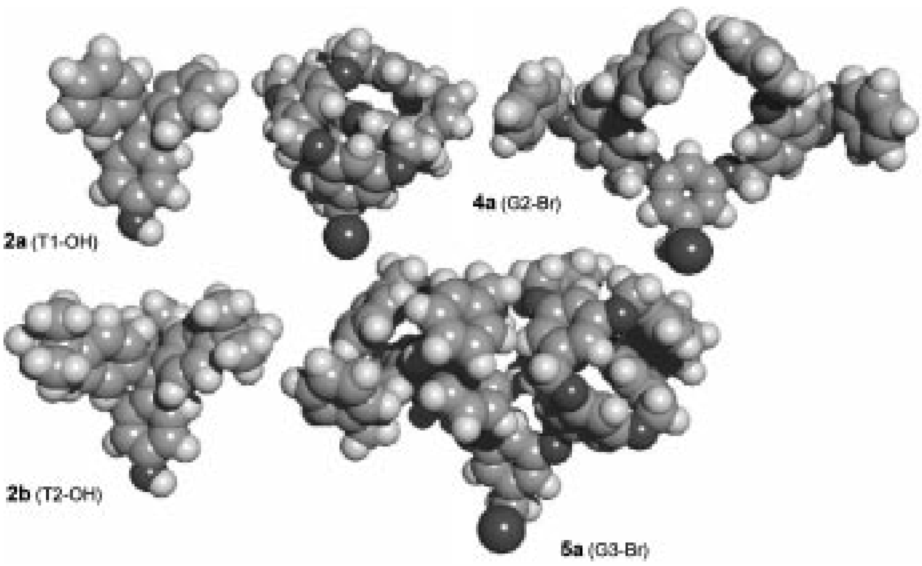


Figure 1. MM2 energy-minimized space-filling models of the stopper units; heteroatoms are shaded dark. The G2 bromide **4a** is shown in a "collapsed" and an (energetically unfavorable) "extended" conformation to illustrate the problem of the size estimation. The models of the dendrons were obtained from arbitrarily chosen starting conformations.

Figure 1 shows the space-filling models of the stopper groups used here. They illustrate in particular that the "size" of G2 cannot be estimated intuitively like the two trityl stoppers whereas the deslipping behavior allows a ranking. On the basis of the models it can be said that the third Fréchet generation has the largest spatial demand of all the stoppers used here. Thus the following empirical ranking list of voluminous substituents can be derived from the results: G1 < D*t*BP < T1 < G2 < T2 < G3.

This comparison of the size of molecules shows that the "rotaxanation" of dendrons and the subsequent deslipping is a suitable method for obtaining a clearer conception of the "dynamic spatial demand" of other types of dendrimers, and to come to an extensive ranking list of different types of wheels and stoppers in the future. This knowledge would be important, for example, for membrane reactors with dendritic catalysts that have to be larger than the pores to prevent them from being washed out with the products.[17] The surprisingly pronounced dependency of the deslipping kinetics on the length and, probably, the flexibility of the central part of the axle as observed by comparison of rotaxanes **8a** and **8b** with [**7a**@**1**] is currently under investigation and likewise the stability of rotaxanes with dendritic stoppers built from aliphatic units of different length. A comparison of the molecular dynamics simulations of the deslipping of dendritic stoppers with those of conventional building blocks would be a useful supplement to the experimental results.

Experimental Section

Synthesis of the phenolic dendrimers G2′-OH (**4b**) and G3′-OH (**5b**): A mixture of 5-acetoxyresorcinol (0.5 mmol), the respective bromides (**3** or **4a**; 1 mmol), dibenzo[18]crown-6 (0.1 mmol), and K_2CO_3 (1 mmol) in acetone (15 mL) was stirred at room temperature for 7 d. The inorganic salts were filtered off and the filtrate evaporated. The residue was then refluxed with NaOMe (1 mmol) in MeOH (15 mL) for 1 d. After removal of the solvent the residue was dissolved in CH_2Cl_2 and extracted with water and the organic phase dried with $MgSO_4$. Column chromatography with CH_2Cl_2 on silica gel gave about 60% of a colorless solid in both cases. Analytical data of **5b** is given as an example: $R_f = 0.15$ (CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 4.89$, 4.94, and 5.01 (3s, 4H, 8H, and 16H, respectively, OCH_2), 6.05 (s, 2H, phloroglucinol-H-2/6), 6.21 (s, 1H, phloroglucinol-H-4), 6.53 and 6.63 (2s, 2H and 4H, resorcinol-H2), 6.57 and 6.67 (2s, 4H and 8H, resorcinol-H4/6), 7.3–7.4 (m, 40H, phenyl); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 69.84$ and 69.98 (OCH_2), 94.74 and 95.40 (phloroglucinol-CH), 101.52 and 106.31 (resorcinol-CH), 127.12, 127.89, and 128.47 (phenyl-CH), 136.69, 139.17, 157.48, 160.03, 160.54 (all C_q); FAB-MS: m/z: 1579.5 [MH^+].

The rotaxanes **8**–**10** were synthesized in an analogous manner to other rotaxanes with phenylether axles.[10a] FAB-MS: **4b**: $m/z = 731.2$ [$M+H^+$]; **5b**: $m/z = 1579.5$ [$M+H^+$]. MALDI-TOF-MS: **8a**: m/z: 2045.2 [$M+Na^+$]; **8b**: m/z: 2895.5 [$M+Na^+$]; **9a**: m/z: 2213.9 [$M+Na^+$], 2230.2 [$M+K^+$]; **9b**: m/z: 3063.1 [$M+Na^+$]; **10b**: m/z: 3285.1 [$M+Na^+$].

The deslipping experiments were carried out in [D_6]DMSO and followed by NMR spectroscopy by integration of suitable signals of the rotaxanes and the resulting free components.

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[16] To make sure that under these severe conditions the spectral changes were caused by mechanical deslipping and not by chemical decomposition, we exposed the free components of the rotaxanes, that is the tetralactam **1** and the axles, to the same conditions. Indeed, there was a slow color change of the solutions and slight changes in the spectra were observed, however, these processes were significantly slower than the changes observed in the spectra of the rotaxanes.

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Bishomoaromatic 1,2,4-Triboracyclopentane Dianions: Strong Three-Center, Two-Electron Bonds between Three Boron Atoms[**]

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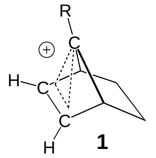
The three-center, two-electron (3c,2e) bonding of bishomoaromatic cations of type **1**[1–4] are known to be weakened by R = C_6H_5[2b, 3a] and displaced by R = p-$MeOC_6H_4$ and R = OH.[4] Evidently, cations **1** are stabilized by the 3c,2e bonds, whereas cations **2** are stabilized by donor substituents R. According to computational estimates, **1u** (R = H) is more stable than **2u** (R = H) by 15 kcal mol^{-1}.[2a] The energy difference between the prototypes **3u** and **4u**, neither of which is known experimentally, is only 10.1 kcal mol^{-1}.[5]



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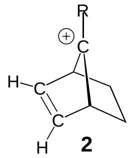

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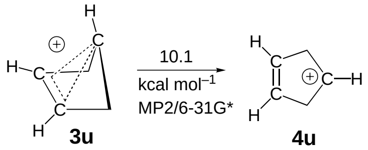
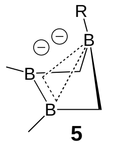


3u **4u**



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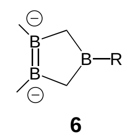

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We now report on bishomoaromatic dianions **5** of 1,2,4-triboracyclopentanes that have skeletons isoelectronic to that of **3u**.[6, 7] The 3c,2e bonds of dianions of type **5** remain intact even in the presence of strong donor substituents like R = NR_2. Hence, the energy difference between **5** and **6** must be larger than the 26 kcal mol^{-1} stabilization afforded to a tricoordinate boron atom by a dialkylamino substituent.[8] Calculations at the MP2/6-31+G* level[9] confirm this conclusion.

The dianions **5a–c** (Dur = 2,3,5,6-tetramethylphenyl) are obtained by reduction of **7a–c** with lithium in diethyl ether.

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