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Synthesis of a double-stranded spiroborate helicate bearing stilbene units and its photoresponsive behaviour†

Daisuke Taura,a Heejun Min,a Claudine Katana and Eiji Yashima*a

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A novel spiroborate-based double-stranded helicate bearing photoresponsive cis-stilbene units in the middle (cis-3) was successfully synthesised from the corresponding cis-stilbene-bound tetraphenol strand in the presence of NaBH₄, whereas the tetraphenol strands with a trans-stilbene or trans-azo compound unit did not form such a double-stranded helicate. The 1H NMR and NOESY experiments revealed that cis-3 adopted contracted (cis-3•) and extended (cis-3•) forms under equilibrium in CD₃CN at 25 °C. The contracted cis-3• that accommodated a Na⁺ ion in the center showed an almost reversible extension and contraction motion by removal and addition of a Na⁺ ion. The cis-to-trans photoisomerisation of the extended cis-3• with UV light (295 nm) further induced an extension of the helicate, producing a mixture of cis-trans-3 and trans-3• at the photostationary state. However, trans-to-cis photoisomerisation of the trans-mixtures using UV light (360 nm) was irreversible in this system and produced the photooxidised aldehyde species (trans-4), resulting from the photo-cleavage of the trans-stilbene moieties of the trans-3•.

Introduction

The design and synthesis of functional molecules and polymers that exhibit a unidirectional molecular motion, such as rotary and elastic (extension and contraction) motions induced by external stimuli,1 in particular by irradiation of light have attracted a great deal of attention in the past two or three decades,2 because such photoresponsive molecular and polymeric systems can be applied for developing molecular motors,2-3 artificial muscles,4 and molecular devices and materials.2-5

We previously reported a series of ortho-linked tetraphenol strands bearing a biphenylene (1),7 bipyrpyridine,8 or bisporphyrin unit in the middle that formed unique double-stranded helicates bridged by two spiroborates in which one8,7 or two Na⁺ cations9 were accommodated in the center except for a large bisporphyrin-linked spiroborate helicate.9 Conventional optical resolution of these helicates, such as diastereomeric salt formation or chiral high-performance liquid chromatography (HPLC) separation, provided pairs of optically pure enantiomers being stable toward racemisation. Among the helicates prepared so far, the optically active biphenylene-linked spiroborate helicate (1) showed an intriguing ion-triggered reversible extension and contraction motion coupled with a unidirectional twisting motion upon release and binding of Na⁺ ions (Scheme 1A);7a the contracted helicate (1•) significantly extended through addition of [2.2.1]cryptand ([2.2.1]), resulting in the formation of extended helicate (1•) with a B–B distance of 13.0 Å that is more than two-fold when compared with that of the contracted 1• (6.0 Å). One might anticipate that if this unique spring-like motion could be controlled by irradiation of light, this would contribute to developing feasible nanoscale mechanical devices.1,b,2,5

To this end, we have designed and synthesized three novel ortho-linked tetraphenol strands linked by photoresponsive cis- and trans-stilbene bond and trans-azo compound units in the middle (Scheme 2) and investigated their double-stranded helicate formations stabilised by spiroborates with NaBH₄. We found that only the cis-stilbene-containing tetraphenol strand yielded a desired double-stranded spiroborate helicate (cis-3), whereas the tetraphenol strands with a trans-stilbene or trans-azo compound unit did not give such a helicate. We expected that the contracted helicate cis-3• would undergo an extension (cis-3•) and contraction (cis-3•) motion by the Na⁺ ion release and binding (chemical stimulus) as well as by light irradiation (physical stimulus) through cis-to-trans photoisomerisation of the stilbene units, thus producing cis-3• and more extended trans-3•, respectively (Scheme 1B). Although this cis-trans photoisomerisation was irreversible because of the photo-cleavage of the trans-stilbene moieties under irradiation of light, to the best of our knowledge, wholly-artificial double helices showing a light-triggered spring-like motion are hitherto unknown.4,b,12,13

† Electronic Supplementary Information (ESI) available: Additional spectroscopic data. See DOI: 10.1039/b000000x/
Scheme 1 Extension (E) and contraction (C) motions of spiroborate-based double-stranded helicates bearing biphenyl units (1) (A) and stilbene units (3) (B) in the middle. The contracted helicates (1C and cis-3C) including a sodium ion in their helical cavities extend upon the addition of [2.2.1] (1E and cis-3E). Further addition of NaPF₆ causes the formation of contracted forms. The cis-3E is further extended upon cis-to-trans photoisomerisation.

Scheme 2 Synthesis of spiroborate-based helicates bearing trans-azobenzene (2) (a), trans-stilbene (3) (b), and cis-stilbene (cis-3) (c) units in the middle.

Results and discussion

Synthesis of tetraphenol strands linked by photoresponsive units and the corresponding spiroborate helicates

The trans-azobenzene-containing tetraphenol (8) was synthesised by Suzuki-Miyaura coupling of a boronic acid (5) with trans-4,4'-diiodoazobenzene (6), subsequently followed by deprotection of the methoxy groups using BB₃ according to a previously reported method (Scheme S1 in ESI†). The trans- and cis-stilbene-containing tetraphenols (11 and cis-11, respectively) were also synthesised in a similar way by Suzuki-Miyaura coupling of a boronic acid ester (9) with the corresponding trans- and cis-4,4'-diiodostilbenes (10 and cis-10, respectively) (Scheme S2 in ESI†).

The obtained tetraphenol strands were then allowed to react with an equimolar amount of NaBH₄ in 1,2-dichloroethane and ethanol (5/1, v/v) at 80 °C for 20 h under similar conditions used for the synthesis of the spiroborate helicates reported previously (Scheme 2). However, the products from trans-8 and trans-11 were complicated based on their 1H NMR spectra, and the electrospray ionisation (ESI) mass spectra in the negative mode indicated the formation of dimers and trimers bridged by one and two spiroborates, respectively, along with unreacted strands (Scheme 2a, b and Figs. S1 and S2 in ESI†), probably because the planar trans-azobenzene and trans-stilbene units hamper such a twisted spiroborate formation due to steric effects.

On the other hand, the cis-stilbene strand (cis-11) favourably reacted with NaBH₄, giving the corresponding helicate (cis-3) in 51.6% yield under the same condition (Scheme 2c) as supported by the ESI mass spectrum, which showed signals due to the
monovalent ($\text{cis-3}^-$) and divalent ($\text{cis-3}^{2-}$) anions at $m/z = 1581.75$ and 779.36, respectively (Fig. S3 in ESI†).

Extension and contraction motion of $\text{cis-3}$

Figs. 1B (a and b) show the $^1$H NMR spectra of $\text{cis-11}$ and $\text{cis-3}$, respectively, measured in CD$_3$CN at 25 °C. Interestingly, most of the proton resonances for $\text{cis-3}$ appeared as two sets of nonequivalent broadened signals after spiroborate helicate formation (B and B, b in Fig. 1B); such nonequivalent proton resonances have not been observed for the other spiroborate helicates prepared so far. In order to assign these signals, 2 equiv. of [2.2.1] were added to a solution of $\text{cis-3}$. As shown in c in Fig. 1B, the broad signals became sharper ones, while maintaining their chemical shifts (B) along with significant decrease in the signals marked by B in c in Fig. 1B. As reported previously, the Na$^+$ ion weakly bound in the contracted helicate ($1_C$) could be released quantitatively in the presence of [2.2.1], resulting in the formation of the extended helicate ($1_E$) (Scheme 1A). Based on these observations, the two sets of nonequivalent signals (B and B, b in Fig. 1B) could be reasonably assigned to those of the contracted ($\text{cis-3}_C$) and extended ($\text{cis-3}_E$) forms, respectively, which indicates that the Na$^+$ ion binding and release rates, in other words, the corresponding contracted and extended motions of $\text{cis-3}$ are slow in CD$_3$CN on the $^1$H NMR time scale, giving separated signals under equilibrium (b in Fig. 1B), from which the ratio of $\text{cis-3}_C$ to $\text{cis-3}_E$ and its equilibrium constant ($K$) were estimated to be 30 : 70 and $2 \times 10^3$ M$^{-1}$, respectively. In the presence of [2.2.1] (2 equiv.), the ratio of $\text{cis-3}_C$ to $\text{cis-3}_E$ changed...
to be approximately 10 : 90 (c in Fig. 1B). The further addition of [2.2.1] (3 equiv.) brought about the complete shift of the equilibrium to the extended helicate formation (cis-3).5

According to this assignment, the upfield shifts of some aromatic protons for cis-3, in particular those for cis-3c (b in Fig. 1B), were explained by the shielding effect of the benzene rings of the other strand as observed in the other spirohelicates.6

The upfield shift of the stilbene protons (g′) was more significant. The calculated structures of cis-3c and cis-3e in CH3CN by using the Hartree-Fock method (HF, 6-31G*) support the upfield shifts of the stilbene protons (g′) of cis-3c, which are favourably positioned above the benzene rings of the twisted stilbene residues into one direction (Fig. 1A). The energy difference (ΔGcis) between the calculated structures in CH3CN revealed that the cis-3c is 2 kcal mol−1 more stable than the cis-3e (Fig. 1A), which is consistent with the major species (cis-3c) observed by the 1H NMR spectrum of cis-3 in CD3CN at 298 K at equilibrium (b in Fig. 1B).

The equilibrium between cis-3c and cis-3e was also unambiguously confirmed by the concentration-dependent 1H NMR and 2D NOESY (2D exchange spectroscopy (EXSY)) spectra of cis-3 in the absence and presence of [2.2.1] (2 equiv.), respectively.14 The intensities of the signals (B) derived from cis-3c gradually decreased with the decrease in the concentration of cis-3 (0.31–0.080 mM), whereas those of the signals (B) due to cis-3e rapidly increased and the signals became sharper without any changes in their chemical shifts (Fig. S4 in ESI†), from which the K value was also estimated to be 2 × 103 M−1, indicating that the equilibrium involves the sodium ion release and binding. In addition, the 2D NOESY (EXSY) spectrum of cis-3 with 2 equiv. of [2.2.1] showed clear positive exchange cross-peaks between the two species, contracted cis-3c (B) and extended cis-3e (B) forms as well as negative intrastand NOE cross-peaks for cis-3e (Figs. S6–S8 in ESI†). Although interstrand NOE cross-peaks were not observed for cis-3e, a similar tendency was reported for the other extended spirohelicates.7a

The subsequent addition of NaPF6 to the solution of cis-3e in the presence of 2 equiv. of [2.2.1] (d in Fig. 1B) regenerated the original helicates as a mixture of cis-3c and cis-3e, while new sharp signals different from those of the ligand cis-11 and the helicates (cis-3c and cis-3e) appeared in the aromatic and t-Bu proton resonance regions; the content of the new species was ca. 6% (d in Fig. 1B). We found that the identical new species also formed when a CD3CN solution of cis-3 was allowed to stand for a long time (Fig. S9A in ESI†); its ESI mass spectrum (Fig. S10 in ESI†) was identical to that measured just after dissolving cis-3 in CH3CN (Fig. S3 in ESI†). These results together with the COSY spectrum of a CD3CN solution of cis-3 after standing for ca. 36 h (Fig. S9B in ESI†) suggest that the new species is a structural isomer of the racemo-helicates (cis-3c and cis-3e) and is most likely a double-stranded meso-helicate with an extended structure (meso-cis-3e) that will be generated from the racemo-helicates in solution and reached an equilibrium within a few days. Indeed, calculations predict that meso-cis-3c is 2.7 kcal mol−1 more stable than cis-3c (Table S1 in ESI†). Although the mechanism for the present racemo-to-meso-cis isomerisation, which requires the breaking and reformulation process of the spirohelicates, remains unknown, these results reveal that the racemo-cis-3 exists as a mixture of the interconvertible contracted (cis-3c) and extended (cis-3e) forms in solution and that the ion-triggered extension and contraction motion mostly proceeds reversibly; however, the present system seems to be more complicated than before, and involves the other chemical equilibrium, i.e., racemo-to-meso-cis isomerisation.

Apparently, a further study is necessary to unambiguously elucidate the structure of the meso-cis-3 by single-crystal X-ray analysis and the mechanism of this unexpected isomerisation.

### Photosomerisation of cis-11

Cis/trans photosomerisation of the single strand cis-11 was first investigated by 1H NMR and absorption spectroscopies in CD3CN (Figs. S11-S12 and S13-S14, respectively in ESI†). Upon irradiation of UV light at 295 nm, the intensities of the cis-11 protons decreased with time, while the new peaks due to trans-11 appeared with a gradual increase in their intensities and the cis/trans ratio reached a constant value (8 : 92) after irradiation for 120 min as estimated from the integral ratio of the cis- and trans-stilbene protons (t1 and g2) (Table 1 and Fig. S11a in ESI†). Subsequent irradiation with UV light at 360 nm, which induces the trans-to-cis isomerisation, produced a mixture of cis- and trans-11 (Fig. S11b in ESI†); its ratio changed with time and reached an almost constant value (42 : 56) at the photostationary state after 120 min irradiation (Table 1 and Fig. S12 in ESI†), indicating that the trans-to-cis photosomerisation did not take place efficiently as reported for typical stilbene derivatives.15

The changes in the absorption spectra of cis-11 in a dilute CD3CN solution during the course of the cis-to-trans followed by the trans-to-cis photosomerisations were also measured (Fig. S13 in ESI†). An absorption peak at 335 nm due to the formation of trans-11 gradually increased with time accompanied with a

### Table 1 Results of the photoisomerisation of cis-11 and cis-3 in CD3CN upon irradiation of UV light at 295 and subsequently at 360 nm

<table>
<thead>
<tr>
<th></th>
<th>cis-11 /</th>
<th>cis-3 /</th>
<th>cis-trans-3e /</th>
<th>trans-3e /</th>
<th>trans-4 /</th>
<th>cis-trans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Before irradiation</td>
<td>99 : 1</td>
<td>97</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>98.5 : 1.5</td>
</tr>
<tr>
<td>After irradiation with 295 nm light (cis-to-trans)</td>
<td>8 : 92</td>
<td>21</td>
<td>39</td>
<td>38</td>
<td>2</td>
<td>40.5 : 58.5</td>
</tr>
<tr>
<td>After irradiation with 360 nm light (trans-to-cis)</td>
<td>42 : 56e</td>
<td>24</td>
<td>43</td>
<td>20</td>
<td>13</td>
<td>45.5 : 48.0</td>
</tr>
</tbody>
</table>

* Product ratios were estimated by 1H NMR analyses. † 0.65 mM at 25 °C under air (see Figs. S11 and S12 in ESI†). ‡ 0.25 mM cis-3 in the presence of 2 equiv. [2.2.1] at 25 °C under argon (see Fig. 3 and Fig. S15 in ESI†). § Overall cis and trans ratio of the stilbene units of 3 and 4. ¶ A trace amount of oxidised aldehydes (ca. 2%) was produced during the photosomerisation (see Fig. S11b in ESI†).

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(a) cis-3

(b) 295 nm light for 60 min

(c) 360 nm light for 60 min

Fig. 2 1H NMR spectral changes of cis-3 (500 MHz, CD3CN, 25 °C, 0.25 mM) in the presence of 2 equiv. [2.2.1] before (a) and after irradiation of UV light at 295 nm for 60 min (b), followed by irradiation of UV light at 360 nm for 60 min under argon (c) (see Fig. S15 in ESI†). B, H, J, and F denote the signals for cis-3E, cis,trans-3E, trans-3E, and trans-4, respectively. The peak assignments were done on the basis of the ESI-MS spectrum of the mixture (Fig. S16 in ESI†) and gCOSY and NOESY spectra (Figs. S17–S19 in ESI†).

Scheme 3 Photoisomerisation of cis- and trans-stilbene helicates.

Clear isosbestic point at 298 nm upon irradiation of UV light at 295 nm, affording the trans-11 in 94% yield. Further irradiation with UV light at 360 nm gave a mixture of cis- and trans-11 (43 : 57) at the photostationary state (Fig. S13b and c in ESI†); the cis/trans ratio was estimated by using a calibration curve obtained from the plots for the absorption intensity ratio at 335 and 298 nm as a function of the trans-11 content estimated from the 1H NMR analyses. The results were fully consistent with those obtained from the 1H NMR analyses, although a trace amount of a photooxidised product (aldehydes) (ca. 2%) was produced upon irradiation of UV light at 360 nm under air as shown in Fig. S11 (ESI†). As anticipated, the fluorescence intensity of 11 significantly increased during the cis-to-trans photoisomerisation (Fig. S14b in ESI†).

Photoisomerisation of cis-3

With all the above photoisomerisation results of cis-11 in mind, we then investigated the photoisomerisation behaviour of the double-stranded helicate cis-3 composed of two cis-11 strands with 1H NMR and absorption spectroscopies in a manner similar to that for cis-11. Fig. 2 shows the 1H NMR spectral changes of cis-3 in CD3CN in the presence of 2 equiv. of [2.2.1] before and

Fig. 3 Time-dependent changes in the product ratio during the photoisomerisation of cis-3 (0.25 mM) in the presence of 2 equiv. [2.2.1] upon irradiation of UV light at 295 nm, followed by irradiation of UV light at 360 nm under argon (see Fig. S15 in ESI†).
after irradiation of UV light at 295 nm for 90 min under air (c) (see Fig. S21b in ESI†). Magnified chromatograms corresponding to the areas indicated by the squares in (a) and (c) are shown in (b) and (d), respectively. HPLC conditions: column, Chiralpak IB (Daicel, 0.46 (i.d.)×25 cm); eluent: hexane/CHCl₃ (6:4, v/v) containing 0.5 mg/mL tetrabutylammonium bromide (TBAB); flow rate, 1.0 mL min⁻¹; column temperature, 25 °C. The peak assignments were performed by fractionation of each peak, followed by measurements of the ¹H NMR spectra. We note that photoirradiation of cis-3E in air produced a larger amount of the photooxidised trans-4E.

Fig. 4 HPLC chromatograms for the resolution of cis-3 in CH₃CN (a) and cis-3E in the presence of 7 equiv. [2.2.1] in CD₃CN after irradiation of UV light at 295 nm for 90 min under air (c) (see Fig. S21b in ESI†). Magnified chromatograms corresponding to the areas indicated by the squares in (a) and (c) are shown in (b) and (d), respectively. HPLC conditions: column, Chiralpak IB (Daicel, 0.46 (i.d.)×25 cm); eluent: hexane/CHCl₃ (6:4, v/v) containing 0.5 mg/mL tetrabutylammonium bromide (TBAB); flow rate, 1.0 mL min⁻¹; column temperature, 25 °C. The peak assignments were performed by fractionation of each peak, followed by measurements of the ¹H NMR spectra. We note that photoirradiation of cis-3E in air produced a larger amount of the photooxidised trans-4E.

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Optical resolution of helicates

As mentioned above, the cis-3 just after preparation undergoes the ion-triggered extension and contraction motion in acetonitrile, which further changes its structure to a new species in acetonitrile under equilibrium. We tentatively assigned the cis-3 and the new species as racemo- and meso-cis-3 helicates, respectively, on the basis of their NMR spectra. Obviously, the racemo-cis-3 helicate is chiral, whereas the meso-cis-3 helicate is achiral, and in order to confirm these structural assignments, we investigated if the chiral cis-3 could be resolved into enantiomers by HPLC using a chiral column (Chiralpak IB, Daicel).

Fig. 4a shows the chromatogram of the resolution of cis-3, showing a single peak detected by UV, although the circular dichroism (CD)-detected chromatogram indicated a partial separation with negative and positive CDs; their CD intensities were too weak to evidence the enantioseparation (Fig. 4b). Next, a CH₃CN solution of a mixture of cis,trans-3ₓ, trans-3ₓ, and trans-4 prepared from cis-3ₓ through the photoisomerisation under air was injected into the chiral HPLC system (Fig. S21 in ESIF). As shown in Fig. 4d, the trans-3ₓ and trans-4 were not completely but rather were partially separated into a pair of enantiomers with the first positive and second negative CD signs. Importantly, the trans-3ₓ and trans-4 were converted from cis-3ₓ via photoisomerisation without any breaking and reformation process of the spiroborate groups, leading to the conclusion that the cis-3 is a racemo-helicate with a double-stranded spiroborate structure and the new species formed from the cis-3 in CDCl₃ may possess a meso structure.

Conclusions

In summary, we have successfully synthesised the photoresponsive spiroborate-based double-stranded helicate (cis-3) bearing cis-stilbene units in the middle, which underwent an extension (cis-3ₓ) and contraction (cis-3ₓ) motion by the Na⁺ ion release and binding. Although photo-induced cis/trans isomerisation of cis-3 did not efficiently nor reversibly take place because of its highly strained spiroborated duplex structure in addition to the oxidative photo-cleavage of the trans-stilbene moieties under irradiation of UV light, the present results provide further design strategy for developing novel photoresponsive spiroborate-based helicates that exhibit light-triggered spring-like motions by introducing an overcrowded double bond into the helicates as a photo- and thermo-responsive linker.²⁵,²⁶,²⁷,³³

Experimental section

1. Materials and instruments

Materials. All starting materials and dehydrated solvents were purchased from commercial suppliers and were used without further purification unless otherwise noted. Silica gel (SiO₂) for the flash chromatography was purchased from Merck. The boronic acid (5),¹⁸ (E)-4,4’-diodoazobenzene (6),¹⁸ the boronic acid pinacol ester (9),⁹ and (Z)-4,4’-diodostilbene (10)²⁹ were prepared according to the literature.

Instruments. The melting points were measured on an MPA100 OptiMelt automated melting point apparatus or a Yanaco MP-500D melting point apparatus (Kyoto, Japan), and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500 AS spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C or a Varian INOVA 700 spectrometer operating at 700 MHz for ¹H and 175 MHz for ¹³C using tetramethylsilane (TMS) or a solvent residual peak as the internal standard. The electron spray ionization (ESI) mass spectra were recorded using a JEOL JMS-T100CS spectrometer (Akishima, Japan). The absorption spectra were measured in a 1- or 10-mm quartz cell on a JASCO V-570 spectrophotometer. The photoradiation for cis/trans isomerisation was performed on a JASCO FP-6500 spectrofluorometer with a 150 W xenon lamp under argon unless otherwise noted. The slit width used in the experiments was 20 nm. The chiral HPLC analyses were performed on a JASCO PU-2080 liquid chromatograph equipped with UV-visible (JASCO MD-2010) and CD detectors (JASCO CD-2095) using a Chiralpak IB column (0.46 (i.d.) x 25 cm, Daicel, Osaka, Japan).

2. Synthetic procedures

trans-7. To a mixture of 5 (427 mg, 1.15 mmol), trans-6 (200 mg, 0.461 mmol), and Pd(PPh₃)₄ (133 mg, 0.115 mmol) in toluene (7.2 mL) was added 2 M aqueous K₂CO₃ (7.2 mL). The reaction mixture was stirred at 110 °C for 36 h under nitrogen. After being cooled to room temperature, the mixture was extracted with EtOAc. The organic layer was washed with H₂O and dried over anhydrous MgSO₄. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO₂, 12 g) with n-hexane/EtOAc (10/0 to 10/1 (v/v)) to afford trans-7 (289 mg, 75.5% yield) as an orange solid. Mp: 275.1–276.0 °C. ¹H NMR (500 MHz, CDCl₃, r.t.): δ 8.00 (d, J = 8.5 Hz, 4H, ArH), 7.80 (d,
trans-8. To a solution of trans-7 (200 mg, 0.241 mmol) in CH$_2$Cl$_2$ (5.0 mL) was added a CH$_2$Cl$_2$ solution of BBr$_3$ (1.0 M, 2.41 mL, 2.41 mmol) at -78 °C under nitrogen. After being warmed to room temperature, the reaction mixture was stirred for 19 h. The mixture was then quenched with H$_2$O (10 mL) at 0 °C and stirred at room temperature for 1 h. After the solvent was evaporated, the residue was extracted with EtOAc. The organic layer was washed with H$_2$O and dried over anhydrous MgSO$_4$.

After filtration, the solvent was evaporated under reduced chromatography with $n$-hexane/EtOAc (10/0 to 20/1 (v/v)) to afford trans-8 (170 mg, 90.9% yield) as a dark orange solid. Mp: 156.5–158.1 °C (dec). $^1$H NMR (500 MHz, CDCl$_3$, r.t.): δ 8.06 (d, $J$ = 8.5 Hz, 4H, ArH), 7.77 (d, $J$ = 8.5 Hz, 4H, ArH), 7.44 (d, $J$ = 2.5 Hz, 2H, ArH), 7.32 (dd, $J$ = 2.5, 8.5 Hz, 2H, ArH), 7.13 (m, 4H, ArH), 7.01 (d, $J$ = 8.5 Hz, 2H, ArH), 5.55 (s, 2H, ArOH), 5.47 (s, 2H, ArOH), 4.39 (s, 18H, C(CH$_3$)$_3$), 1.35 (s, 18H, C(CH$_3$)$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$, r.t.): δ 152.03, 151.13, 147.67, 146.58, 144.49, 141.02, 130.35, 128.38, 128.15, 128.08, 128.00, 127.23, 124.26, 123.42, 121.41, 116.56, 34.55, 34.43, 31.71 (19 signals out of 20 expected ones). HRMS (negative mode ESI): m/z calcd for [M(C$_5$H$_9$N$_3$O$_2$)$^-$]$,^+$, 773.4318; found 773.4311.

trans-11. To a solution of 9 (93 mg, 0.22 mmol), trans-10 (43 mg, 0.10 mmol), and Pd(PPh$_3$)$_2$ (23 mg, 0.020 mmol) in toluene (5.0 mL) was added 2 M aqueous K$_2$CO$_3$ (5.0 mL). The reaction mixture was stirred at 110 °C for 22 h under nitrogen. After being cooled to room temperature, the mixture was extracted with EtOAc. The organic layer was washed with H$_2$O and aqueous HCl, and dried over anhydrous MgSO$_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO$_2$, 12 g) with $n$-hexane/EtOAc (10/0 to 6/4 (v/v)) to afford trans-11 (27 mg, 35% yield) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, r.t.) δ 7.67 (d, $J$ = 8.5 Hz, 4H, ArH), 7.59 (d, $J$ = 8.5 Hz, 4H, ArH), 7.39 (d, $J$ = 2.5 Hz, 2H, ArH), 7.37 (dd, $J$ = 2.5, 8.5 Hz, 2H, ArH), 7.33 (d, $J$ = 2.5 Hz, 2H, ArH), 7.31 (d, $J$ = 2.5 Hz, 2H, ArH), 7.23 (s, 2H, HC=CH), 7.01 (d, $J$ = 8.5 Hz, 4H, ArH), 5.56 (s, 2H, OH), 5.52 (s, 2H, OH), 1.37 (s, 18H, C(CH$_3$)$_3$), 1.34 (s, 18H, C(CH$_3$)$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$, r.t.): δ 151.22, 147.28, 144.49, 144.26, 136.74, 136.73, 130.35, 128.38, 128.15, 128.08, 128.00, 127.23, 124.26, 123.42, 121.41, 116.56, 34.55, 34.43, 31.71 (20 signals out of 21 expected ones). HRMS(ESI): m/z calcd for [M(C$_5$H$_9$N$_3$O$_2$)$^-$]$,^+$, 771.4413; found 771.4379.

cis-11. To a solution of 9 (216 mg, 0.509 mmol), cis-10 (100 mg, 0.231 mmol), and Pd(PPh$_3$)$_2$ (58.8 mg, 0.0509 mmol) in toluene (5.0 mL) was added 2 M aqueous K$_2$CO$_3$ (5.0 mL). The reaction mixture was stirred at 105 °C for 29 h under nitrogen. After being cooled to room temperature, the solvent was extracted with EtOAc. The organic layer was washed with H$_2$O and dried over anhydride MgSO$_4$. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (SiO$_2$, 12 g) with $n$-hexane/EtOAc (10/0 to 8/2 (v/v)) to afford cis-11 (80.0 mg, 44.7% yield) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, r.t.): δ 7.30–7.45 (m, 8H, ArH), 7.36 (d, $J$ = 2.5 Hz, 2H, ArH), 7.35 (dd, $J$ = 2.5, 8.5 Hz, 2H, ArH), 7.31 (d, $J$ = 2.4 Hz, 2H, ArH), 7.29 (d, $J$ = 2.5 Hz, 2H, ArH), 6.99 (d, $J$ = 8.5 Hz, 2H, ArH), 6.68 (s, 2H, HC=CH), 5.57 (s, 2H, OH), 5.54 (s, 2H, OH), 1.35 (s, 18H, C(CH$_3$)$_3$), 1.33 (s, 18H, C(CH$_3$)$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$, r.t.): δ 151.22, 147.28, 144.49, 144.26, 136.74, 136.73, 130.27, 129.59, 129.38, 128.30, 128.13, 128.11, 127.80, 127.00, 124.14, 123.93, 116.62, 34.51, 34.39, 31.71, 31.70. HRMS(ESI): m/z calcd for [M(C$_5$H$_9$N$_3$O$_2$)$^-$]$,^+$, 771.4413; found 771.4380.

trans-2. To a solution of trans-8 (3.0 g, 3.9 µmol) in 1,2-dichloroethane (625 µL) was added a solution of NaBH$_4$ in ethanol (31.2 mM, 125 µL, 3.90 µmol). The reaction mixture was stirred at 80 °C for 20 h under argon. After being cooled to room temperature, the solvents were evaporated under reduced pressure and the residue was dried in vacuo. The negative ESI mass spectrum of the residue dissolved in CD$_3$CN was then measured using CH$_3$CN as the eluent (Fig. S1 in ESI†).

trans-3. To a solution of trans-11 (3.3 mg, 4.3 µmol) in 1,2-dichloroethane (486 µL) was added a solution of NaBH$_4$ in ethanol (44.0 mM, 98 µL, 4.3 µmol). The reaction mixture was
stirred at 80 °C for 20 h under argon, resulting in a precipitate. After being cooled to room temperature, the solvents were evaporated under reduced pressure and the residue was dried in vacuo. The negative ESI mass spectrum was measured after the residue was dissolved in DMSO-d6 and then diluted with CH3CN (Fig. S2 in ES1).

cis-3. To a solution of cis-11 (20.5 mg, 26.5 µmol) in 1,2-dichloroethane (3.0 mL) was added a solution of NaNH4 in ethanol (44.5 mM, 0.60 mL, 27 µmol). The reaction mixture was stirred at 80 °C for 20 h under argon. The precipitate obtained from the mixture during the reaction was collected by filtration, washed with 1,2-dichloroethane, and dried in vacuo to afford cis-3 as a white solid in 51.6% yield (11.0 mg). Mp: > 300 °C. 1H NMR (500 MHz, DMSO-d6, 25 °C) δ 7.33 (d, J = 8.5 Hz, 8H, ArH), 7.19 (d, J = 2.5 Hz, 4H, ArH), 7.09 (dd, J = 2.5, 8.5 Hz, 4H, ArH), 7.06 (d, J = 2.5 Hz, 4H, ArH), 6.79 (d, J = 8.5 Hz, 8H, ArH), 6.56 (d, J = 8.5 Hz, 4H, ArH), 6.27 (s, 4H, CH=CH), 1.30 (s, 36H, C(CH3)3), 1.25 (s, 36H, C(CH3)2). 13C NMR (175 MHz, DMSO-d6, 40 °C): δ 154.90, 152.16, 140.82, 140.38, 139.23, 133.79, 131.23, 130.86, 130.78, 129.00, 126.92, 125.54, 124.93, 124.34, 124.80, 120.67, 33.57, 33.52, 31.47, 31.34 (20 signals out of 21 expected ones). HRMS(ESI): m/z calcd for [M(C10H11B2Na2O4)−Na]+, 1581.8470; found 1581.8462.

3. Computational calculations

We used quantum chemical approaches, as implemented in the Gaussian 09 package,21 to construct model double-stranded spiroboborolate helicates. Geometry optimisations were performed at different levels of theory, namely Hartree-Fock (HF) and density functional theory (DFT) using the hybrid oB97X-D functional,22 for dianions, monoanions and neutral helicates. For all optimised geometries, a subsequent frequency calculation was performed to verify that geometries correspond to energy minimums. The effect of basis set on geometries and properties was checked by increasing the basis set from the standard 3-21G basis up to the 6-31G*. Calculations were conducted both in vacuum and in the presence of solvent (CH3CN) using the Polarizable Continuum Model (PCM) as implemented in Gaussian 09.

For several helicates, we have first verified at the HF/3-21G level of theory in vacuum that substitution of the Bu groups with hydrogen atoms does not significantly change the optimised geometries and respective stability of the structures. For these simplified structures, we were able to increase the basis set up to 6-31G* and at the same time afford frequency calculations for solvated structures. In fact, relying solely on differences of electronic energies or on geometries optimized in vacuum appears to be insufficient to properly describe the relative stability of such double-stranded spiroboborolate helicates. In addition, geometry optimization was found to be more involved with the oB97X-D functional than at the HF level but leads to consistent results whenever available. We thus retained the HF/6-31G* level of theory in CH3CN and summarize the main results in Table S1. Comparison of the monoanion cis-3c with the dianion cis-3c and a free sodium cation needs to be corrected for basis set superposition errors (BSSE). This could be qualitatively estimated from electronic energies in vacuum where BSSE amounts to ca. 3 kcal mol−1.

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Notes and references


