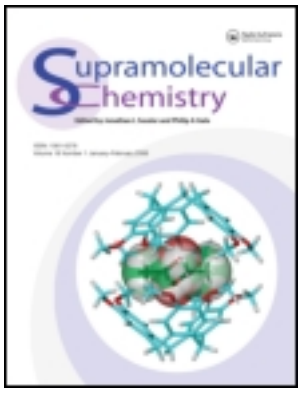

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# Synthesis, physico-chemical, structure and supramolecular properties of pinacolophanes: versatile synthetic precursors to stilbenophanes

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Novel pinacolophanes tethered by methyl and ethyl chains were synthesised and characterised. The stereochemistry of these small-sized cyclophanes was determined by NMR spectral data as well as by single-crystal X-ray analysis. Intramolecular hydrogen bondings in the crystal structure of the molecules play an important role in holding their configuration, while the intermolecular hydrogen bondings lead to a designed arrangement of the molecules. The stereoselective transformation of pinacolophanes to stilbenophanes in improved yield is also reported.

**Keywords:** pinacolophanes; pinacol coupling; X-ray structure; molecular tectonics; stilbenophanes



## 1. Introduction

The design and synthesis of cyclophanes possessing rigidly defined cavities and shape-persistent structures attract current interest in view of supramolecular chemistry (*1*). Stilbenophanes, cyclophanes containing stilbene moieties, with well-defined cavities are intriguing molecules from both physico-chemical and supramolecular points of view (*2–11*).

In this context, we have synthesised a series of ortho-stilbenophanes **3**, possessing stilbene unit and alkyl chains, to study their structure, conformation and supramolecular properties (*12–16*). Their conformation is depended on the alkyl chain length and Z/E stereochemistry of the olefins.

We have also studied the supramolecular properties of **3** and their related compounds (*12, 14, 16*). As the best example, a saddle-shaped stilbenophane forms inclusion complex with $Ag^+$ ion, which can be confirmed by both NMR and theoretical analyses (*12*).

On the other hand, stilbenophanes **3** could serve as key precursors in synthetic approaches to the corresponding tolanophanes by bromination/dehydrobromination method (*13, 18*).

To understand the novel supramolecular properties of **3** more deeply, development of its practical synthesis has become an important problem of the study.

Stilbenophanes **3** have been prepared from the McMurry coupling of the corresponding dialdehydes **1**, which are usually the mixtures of geometric isomers (*12–17*). However, the availability of **3** has been unsatisfactory, because the synthesis of them using the McMurry reaction suffered from the difficulty in purification. Therefore, improvement of the synthesis of **3** was desired.

Pinacolophanes **2**, cyclophanes containing pinacol moieties, are possible intermediates in the alkene-forming process for the synthesis of the corresponding stilbenophanes **3** (Scheme 1). Exploration of the new strategy for stilbenophanes **3** synthesis, therefore, begins with investigations on the synthesis of **2** as key precursors. On the other hand, the physico-chemical, supramolecular properties of **2** together with their potentially application in asymmetric syntheses (*11, 19*) attracted our interest.

Here, we report on the synthesis of *cis*- and *trans*-pinacolophanes **2**. To the best of our knowledge, only the *trans*-isomers **2** have been synthesised and characterised (*20*). In order to establish with great certainty the stereochemistry of each isomer, the X-ray crystal structure of the cyclic diols **2** was determined. The generation of H-bonded molecular networks in their solid state introduces **2** as new molecular tectons. Finally, we report an effective synthesis of **3** from **2** in improved yields.

## 2. Results and discussion

### 2.1 Synthesis and characterisation of pinacolophanes 2

The starting material for the pinacol coupling, the bis(carbaldehydes) **1a–b**, was obtained from the reaction of 2-hydroxybenzaldehyde with the diiodomethane and 1,2-dibromoethane, respectively, under reflux conditions (*21*).

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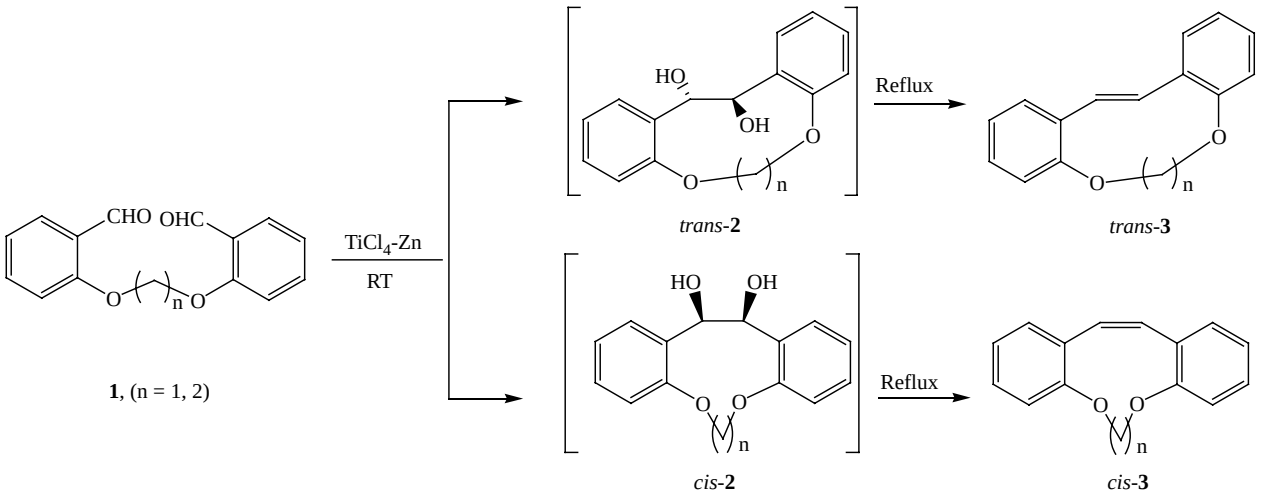



Scheme 1. The chemoselectivity of the titanium-induced macrocyclisation of the bis-carbaldehyde **1** at different reaction temperatures.

As shown in Scheme 2, the intramolecular pinacol coupling of **1** with low-valent titanium (LVT), prepared from $TiCl_4$ and Zn in tetrahydrofuran (THF) (*14, 22*), at room temperature gave a mixture of *trans*- and *cis*-isomers of **2**.

The *cis*- and *trans*-isomers of **2** could be rapidly isolated in useful yields by column chromatography. The *trans*-**2a** and *cis*-**2a** can be separated from the product mixtures by column chromatography in 25 and 40% yields, respectively, as fine colourless needles. In a similar manner, *trans*-**2b** and *cis*-**2b** were also prepared from the corresponding dicarbaldehyde **1b** in 25 and 50% yields, respectively (Scheme 2).

The $^1H$ and $^{13}C$ NMR spectra of the *cis*- and *trans*-isomers of **2** are in accord with the symmetry of these molecules. The aromatic protons appear as two doublets and two triplets, while non-aromatic protons of *trans*-**2** and *cis*-**2** appear in different patterns. In **2a**, the benzylic protons of *trans*-isomer (unlike in *cis*-isomer) appear as two doublets, because of their different positions relative to the etheric oxygen (5.7 and 5.4 ppm), but the methylene protons of both isomers are observed as a singlet around 5.5 ppm.

In contrast to **2a**, the benzylic protons of both isomers **2b** appeared as one sharp singlet, while the methylene protons are not equivalent. The stereochemical assignment deduced from NMR is in agreement with the X-ray structure analysis of molecules **2** (*22, 23*).

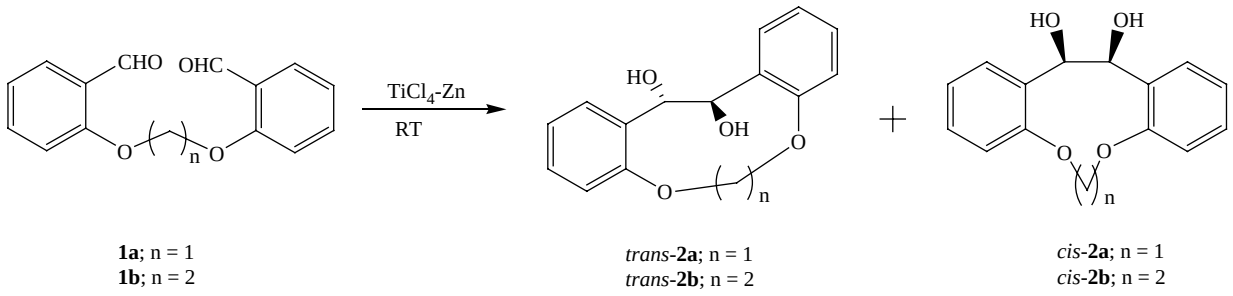
### *2.2 The molecular structure of pinacolophanes 2*

The structures of compounds *trans*-**2a**, *cis*-**2a** and *cis*-**2b** were confirmed by X-ray diffraction studies. The ORTEP drawing and crystal data are shown in Figure 1 and Table 1, respectively.[1] According to the Mo-Kα radiation, the Flack parameter for *trans*-**2a** and *cis*-**2b** could not be calculated accurately, in case of *cis*-**2b** with a large standard deviation, −0.2(6). The *cis* configuration of the molecules can be described as 'open scallop'.

As shown in Table 1, *trans*-**2a** crystallises in the orthorhombic space group $P2_12_12_1$, *cis*-**2a** in the monoclinic space group $P2_1/c$ and *cis*-**2b** in the orthorhombic space group $Pna2_1$.

#### *2.2.1 The molecular structure of* trans-*2a*

Although the Mo-Kα radiation of the absolute structure could not be refined, the planar *trans*-**2a** possesses a *meso*-configuration.




Scheme 2. Synthesis of pinacolophanes **2**.

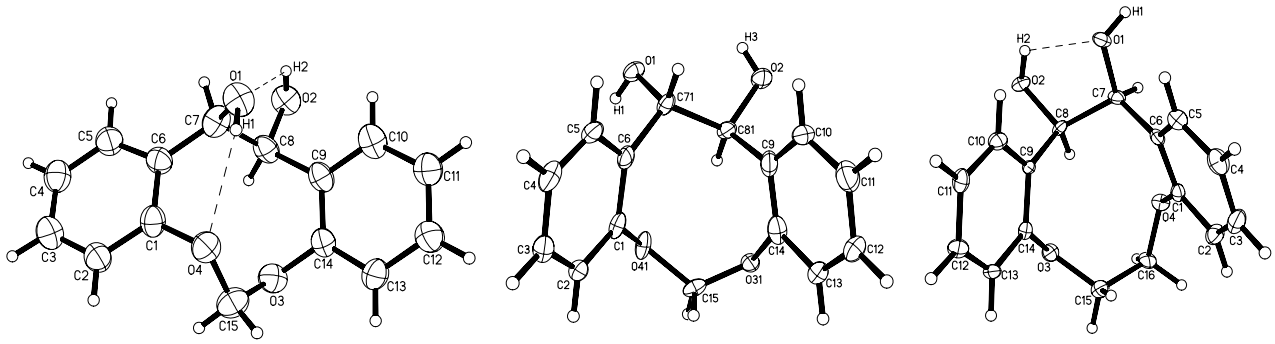



Figure 1. ORTEP drawing of *trans*-**2a** (left), *cis*-**2a** (middle, major specimen) and one of the crystallographic molecules in *cis*-**2b** (right).



As shown in Figure 1, two intramolecular H bridges fix an *exo*-conformation (O1···O4: 3.03(8), O2···O1: 3.22(8) Å) and lead to an angle of 15° between the two phenylene rings. While one benzylic proton is towards the centre of a molecule with a short intramolecular C—H···O bond facing oxygen atom (2.43 Å), the other one is directed out having a short hydrogen bond with the neighbouring hydroxyl group (2.28 Å).

The crystal packing of *trans*-**2a** includes four molecules in which pinacol units overlap each other not only in a face-to-face interaction, but also in an edge-to-face interaction. The intermolecular H bonding forms columns along [100] (O1···O2a: 2.95(7) Å (Figure 2).

### 2.2.2 *The molecular structure of* cis-***2a***

The molecule of *cis*-**2a** possesses approximate $C_s$-symmetry (Figure 1). The phenyl rings are in a face-to-face configuration with a dihedral angle of about 93°. There is a disorder in the molecule. The sequences C71/O31/H1/O41/H3/C81 and O31/C15/C41 as shown in Figure 1 belong to the major specimen (occupation parameter 0.65). The bridge C6-C71-C81-C9 as well as the bridge of the minor specimen C6-C72-C82-C9 exhibits a *twist*-conformation concerning the corresponding OH-groups. A short intramolecular O—H···O bond (O2···O1 = 2.81(2) Å) and two short intermolecular hydrogen bonds O1—H1···O2a (O1···O2a = 2.78(2) Å) and O2—H3···O41a (O2···O41a = 2.84(9) Å) were found. The first one stabilises the *twist*-configuration and the latter ones are responsible for the connection of the molecules in the unit cell.

In the crystal structure of *cis*-**2a**, the molecules are stacked in columns along [010] connected by various C—H···O and O—H···O hydrogen bonds (Figure 2).

### 2.2.3 *The molecular structure of* cis-***2b***

The molecules of **2b** have an approximate $C_s$-symmetry (Figure 1). The phenyl rings have a face-to-face arrangement with dihedral angles in the range of 104°–122°. There are four crystallographic independent asymmetric molecules (shown in blue, green, red and violet) in tetrameric unit and all of them are meso, which are connected *via* hydrogen bonds to each other (Figure 3). This tetramer forms further hydrogen bonds to neighbours. A very short intramolecular O2—H2···O1 interaction between hydrogen of a hydroxyl group with the oxygen atom of the neighbouring hydroxyl group (O2···O1 2.62(3) Å) is observed.

The crystal packing of *cis*-**2b** includes 16 molecules per unit cell, in which four asymmetric molecules are connected via strong hydrogen bonding. As shown in Figure 3(A) and (B), two molecules (shown in blue and violet) are in a back-to-back arrangement having one highly short intermolecular H-bond interaction (O1—H1···O2 = 2.00 Å).

In contrast, two other asymmetric molecules (shown in red and green) are in a nearly face-to-face interaction without any intermolecular H-bond interaction. However, both red and green molecules have a short H-bond interaction with the violet (H···O = 2.21 and 2.03 Å, respectively) and also with the blue (H···O = 1.92 and 2.36 Å, respectively). Therefore, the molecules in crystal are arranged in a designed shape, which is resulted from the various intra- and intermolecular hydrogen bondings of the molecules (Figure 3(C) and (D)).

## 2.3 *The stereoselective transformation of 2–3*

Pinacolophanes **2** may serve as key intermediates in synthetic approaches to the corresponding stilbenophanes **3**. Although a variety of **3** have been prepared using the McMurry coupling reactions as a key step (*12–18*), the route was flawed by the difficulty in purification and the need for sophisticated procedures.

Exploration of the new strategy for stilbenophanes synthesis begins with investigations using pinacolophanes **2** as starting materials. Treatment of *cis*- and *trans*-isomer **2** with LVT, generated by the reaction of

Table 1. Crystal data for colourless *trans*-**2a**, *cis*-**2a** and *cis*-**2b**.

| File | ga207 (*trans*-**2a**) | ga209 (*cis*-**2a**) | ga210 (*cis*-**2b**) |
|---|---|---|---|
| Instrument | IPDS II (Stoe) | IPDS II (Stoe) | IPDS II (Stoe) |
| Radiation | Mo-Kα | Mo-Kα | Mo-Kα |
| Formula | $C_{15}H_{14}O_4$ | $C_{15}H_{14}O_4$ | $C_{16}H_{16}O_4$ |
| Formular weight ($g\,mol^{-1}$) | 258.26 | 258.26 | 272.29 |
| Crystal size (mm) | $0.34 \times 0.1 \times 0.05$ | $0.48 \times 0.08 \times 0.07$ | $0.48 \times 0.11 \times 0.10$ |
| $a$ (pm) | 526.4(1) | 827.6(1) | 1729.0(1) |
| $b$ (pm) | 991.9(2) | 832.7(1) | 1735.6 |
| $c$ (pm) | 2340.9(5) | 1821.4(2) | 1774.7(1) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 99.69(1) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 |
| Unit cell volume ($pm^3$) | $1222.3(4) \times 10^6$ | $1237.3(3) \times 10^6$ | $5325.6(5) \times 10^6$ |
| $Z$ | 4 | 4 | 16 |
| dcalc ($g\,cm^{-3}$) | 1.403 | 1.386 | 1.358 |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic |
| Space group (No.) | $P2_12_12_1$ (19 [ ]) | $P2_1/c$ (14 [ ]) | $Pna2_1$ (33 [ ]) |
| Absorption correction | Numerical | Numerical | Numerical |
| $\mu$ ($cm^{-1}$) | 1.02 | 1.01 | 0.97 |
| Temperature (K) | 193 | 100 | 100 |
| $2\theta_{max}$ (°) | 52.3 | 52.02 | 51.98 |
| hkl values | $-6 \le h \le 6$, $-9 \le k \le 12$, $-28 \le l \le 28$ | $-10 \le h \le 10$, $-10 \le k \le 10$, $-22 \le l \le 22$ | $-21 \le h \le 21$, $-21 \le k \le 21$, $-21 \le l \le 21$ |
| Measured reflection | 6245 | 16,913 | 73,157 |
| Unique reflections | 2390 | 2418 | 10,388 |
| $R_{int}$ | 0.2065 | 0.1028 | 0.1534 |
| Reflections with $F_o > 4\sigma(F_o)$ | 820 | 1179 | 4811 |
| Parameter | 173 | 209 | 746 |
| Structure solution | Direct methods (SIR-92) | Direct methods (SIR-92) | Direct methods (SIR-92) |
| Refinement against $F_2$ | SHELXL-97 | SHELXL-97 | SHELXL-97 |
| H atoms | Calculated positions with common displacement parameter | Calculated positions with common displacement parameter | Calculated positions with common displacement parameter. Coordinates of $H_1$–$H_8$ were refined |
| Flack parameter | Could not be refined because of Mo-Kα radiation | – | −0.2(6) |
| $R_1$ | 0.0759 | 0.0403 | 0.0296 |
| $wR_2$ (all data) | 0.2142 | 0.0610 | 0.0416 |
| Max. residual electron density ($10^{-6}$ e $pm^{-3}$) | 0.303 | 0.149 | 0.157 |

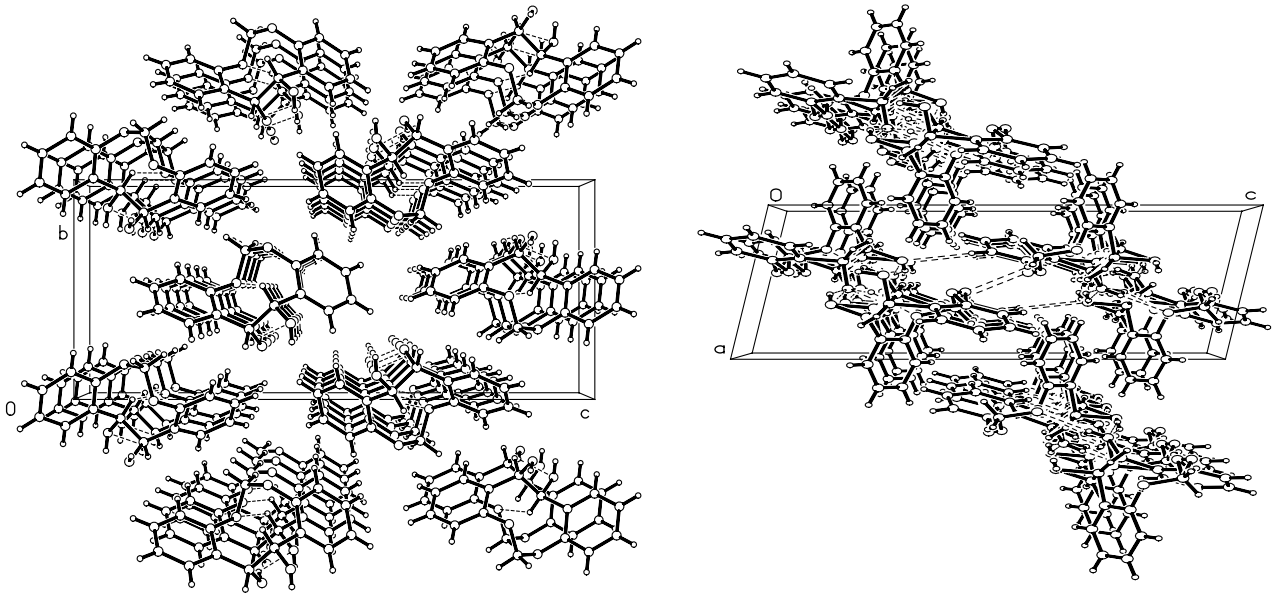



Figure 2. View of the packing of *trans*-**2a** (left) and *cis*-**2a** (right) along *a*- and *b*-axes, respectively, *via* hydrogen-bonded network.

titanium(IV) chloride with zinc in THF, led to the high yield formation of pure *cis*- and *trans*-isomer **3**, respectively (Scheme 3).

As shown in Table 2, the overall yield of each isomer in this two-step sequence is higher than those previously reported for the direct McMurry coupling of **1** in the same solvent (THF) (*12, 15*). Notably, the yields of *cis*- and *trans*-isomer **3a** were significantly improved as compared with those in the previous procedures (*12–16*). The products **3** were readily obtained in almost pure forms simply by a flash chromatographic filtration through silica gel.

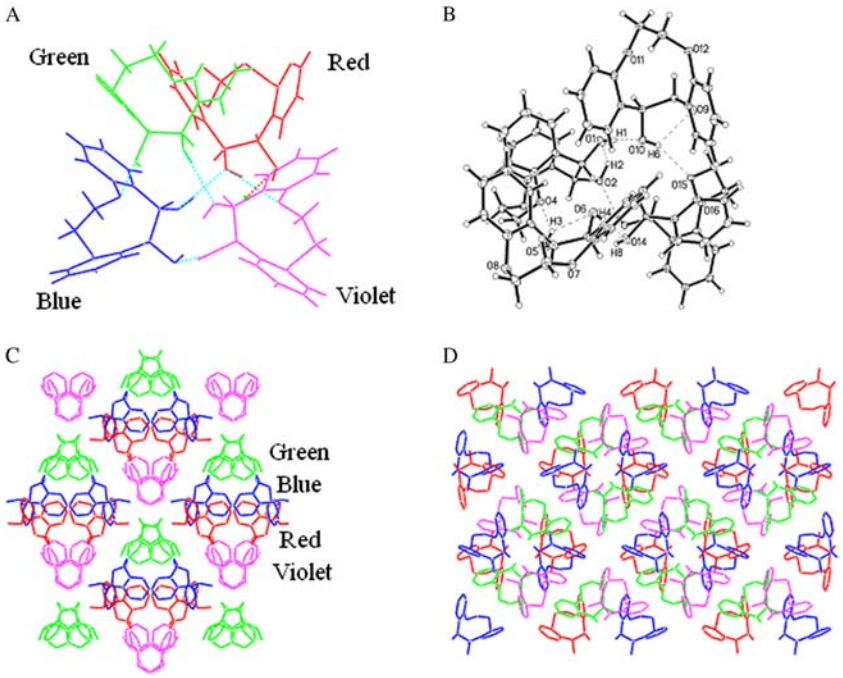



Figure 3. Crystal structure of **2b**: hydrogen-bonded network in tetrameric unit with four asymmetric molecules (A and B); Arrangement of molecules in the crystallographic direction along *a*-axis (C) and *c*-axis (D). Hydrogen atoms have been omitted for clarity.

Table 2. A comparison between the present work and the previous procedure for the preparation of **3**.

| | Product (%) | | | |
|---|---|---|---|---|
| Synthetic method | *trans*-**3a** | *cis*-**3a** | *trans*-**3b** | *cis*-**3b** |
| McMurry of **1** | 1 (*15*) | 2 (*15*) | 25 (*12*) | 20 (*12*) |
| Present work | 20 | 30 | 23 | 48 |

The success of this new procedure will expand the range and availability of **3** that can be prepared for the studies aimed at elucidating their properties.

## 3. Conclusion

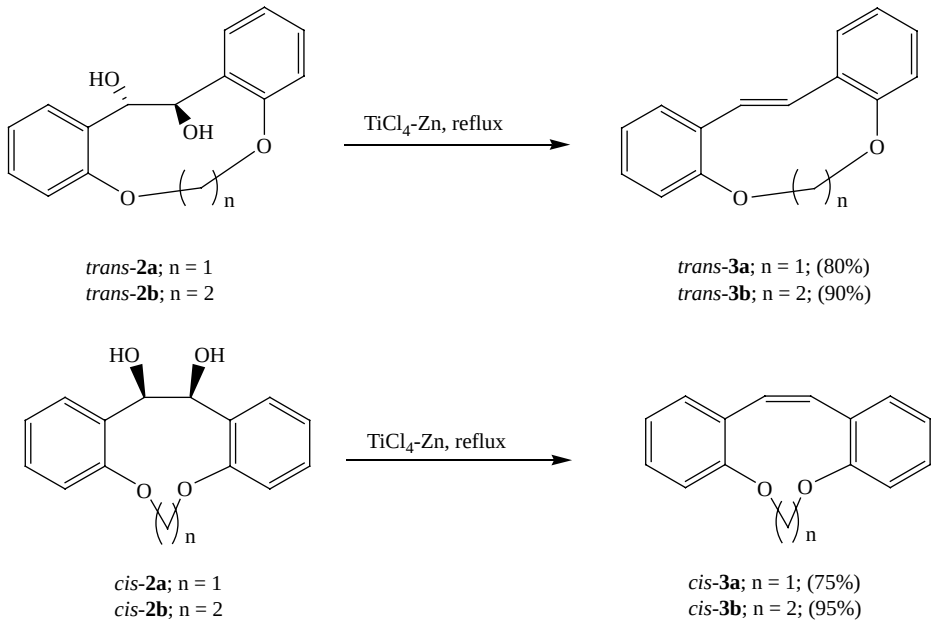
The smallest members of pinacolophanes **2a–b** were synthesised by intramolecular reductive coupling in the presence of LVT at room temperature. The *cis*- and *trans*-configuration of products was confirmed by both $^1$H NMR and X-ray structure analyses. The self-assembly between hydroxyl groups via hydrogen bonding generates H-bonded networks that were structurally characterised by X-ray diffraction studies on single crystals. The different interactions between the 1,2-dihydroxy type in pinacols **2** as tectons with different locations of H-bond sites in *cis*- and *trans*-configuration lead to different arrangements, in the crystal, which is due to the tetragonal angles of 1,2-dihydroxy groups in the molecules. Furthermore, the pinacolophanes **2** are easily converted into the stilbenophanes **3** with high stereoselectivity and improved yield with an easier work-up.

## 4. Experimental section

### *4.1 General*

All reactions were carried out under nitrogen (Schlenk conditions). Unless otherwise noted, all chemicals were obtained from commercial sources and used as received without further purification. Solvents were purified and dried by using common methods. Column chromatography was carried out using Merck silica gel 60, 70-230 mesh ASTM. NMR spectra were recorded on a Bruker DRX-500 spectrometer in $CDCl_3$ using TMS as an internal standard.

*4.1.1 General procedure for the preparation of pinacolophanes **2**.* Anhydrous THF (100 ml) was added to Zn dust (2.2 g, 34 mmol) under an argon atmosphere. $TiCl_4$ (3 ml, 27 mmol) was added to the mixture at 0°C, and the black suspension thus obtained was warmed to room temperature and then refluxed for 2 h. A solution of dialdehyde **1** (10 mmol) in THF (50 ml) was added dropwise to the above black reaction mixture at room temperature, and the resulting mixture was stirred for an additional 12 h. The reaction mixture was quenched with 10% aqueous $K_2CO_3$ (30 ml). The organic layer was separated, and the aqueous suspension was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated to afford a




*trans*-**2a**; n = 1
*trans*-**2b**; n = 2

*trans*-**3a**; n = 1; (80%)
*trans*-**3b**; n = 2; (90%)

*cis*-**2a**; n = 1
*cis*-**2b**; n = 2

*cis*-**3a**; n = 1; (75%)
*cis*-**3b**; n = 2; (95%)

Scheme 3. The synthesis of pure isomers **3** from the corresponding isomers **2**.

syrupy liquid, which was purified by chromatography on silica gel using a 1:1 mixture of ethyl acetate and hexane to afford pure *cis*- and *trans*-isomers **2**.

*4.1.1.1 Pinacolophane trans-**2a***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 2.99 (br s, 2H), 5.36 (d, 1H, $J = 12$ Hz), 5.55 (br s, 2H), 5.74 (d, 1H, $J = 12$ Hz), 6.91 (d, 2H), 7.09 (t, 2H), 7.19 (t, 2H), 7.48 (d, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ 73.2, 122.6, 124.5, 127.6, 128.4, 132.2, 133.5, 158.1; MS(EI), *m/z* (rel. intensity, %) 258 ($M^+$, 5), 136 (100); $\nu$ (KBr, $cm^{-1}$): 3535 (OH, sh), 3477 (OH, br), 3055, 2956, 1600, 1580; anal. calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.97; H, 5.22.

*4.1.1.2 Pinacolophane cis-**2a***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 3.26 (s, 2H), 5.45 (s, 2H), 5.54 (s, 2H), 6.83 (d, 2H), 6.98 (t, 2H), 7.16 (t, 2H), 7.28 (d, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ 70.1, 101.4, 121.6, 125.6, 129.5, 130.1, 134.9, 156.0; MS(EI), *m/z* (rel. intensity, %) 258 ($M^+$, 5), 136 (100); $\nu$ (KBr, $cm^{-1}$): 3473 (OH, sh), 3354, 3300 (OH, br), 3018, 2935, 2885, 1604, 1584; anal. calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.89; H, 5.62.

*4.1.1.3 Pinacolophane cis-**2b***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 3.15 (s, 2H), 4.18 (ddd, 2H, $J = 12$ Hz), 4.42 (ddd, 2H, $J = 12$ Hz), 5.81 (s, 2H), 6.76 (d, 2H), 6.89 (t, 2H), 7.05 (t, 2H), 7.42 (d, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ 70.2, 70.7, 118.0, 123.4, 128.3, 128.6, 133.0, 155.5; MS(EI), *m/z* (rel. intensity, %) 272 ($M^+$, 20), 254 (15), 149 (50), 120 (100), 76 (95); $\nu$ (KBr, $cm^{-1}$): 3421 (OH, sh), 3320 (OH, br), 3068, 3034, 2982, 2875, 1581; anal. calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.25; H, 6.11.

*4.1.1.4 Pinacolophane trans-**2b***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 2.96 (s, 4H), 4.22 (dd, 4H, $J = 18$ Hz), 4.42 (dd, 4H, $J = 18$ Hz), 5.39 (s, 4H), 6.82 (d, 4H), 6.91 (t, 4H), 7.10 (t, 4H), 7.23 (d, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ 71.0, 76.1, 118.8, 123.7, 129.2, 129.3, 133.5, 156.5; MS(EI), *m/z* (rel. intensity, %) 272 ($M^+$, 45), 254 (15), 149 (55), 121 (100), 105 (15); $\nu$ (KBr, $cm^{-1}$): 3530 (OH, sh), 3400 (OH, br), 3062, 2940, 2881, 1600, 1583; anal. calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.85; H, 6.22.

*4.1.2 General procedure for the stereoselective transformation of the pinacolophanes **2** to stilbenophanes **3***. Anhydrous THF (30 ml) was added to Zn dust (0.4 g, 6 mmol) under an argon atmosphere. $TiCl_4$ (0.35 ml, 3 mmol) was added to the mixture at 0°C, and the black suspension thus obtained was warmed to room temperature and then refluxed for 2 h. A solution of *cis*- or *trans*-isomers **2** (0.36 mmol) in THF (10 ml) was added dropwise to the above black reaction mixture at room temperature. The reaction mixture was stirred at reflux temperature. After disappearance of the substrate (TLC), the reaction mixture was treated with aqeous. $K_2CO_3$ (10%) and stirred open to the atmosphere, until oxidation of the titanium was completed (off-white suspension). The organic layer was separated, and the aqueous suspension was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated. A flash column chromatography on silica gel (ethyl acetate:hexane; 1:8) afforded pure *cis*- or *trans*-isomers **3**.

We have already reported the spectral data of stilbenophanes **3** (*12, 15*).

*4.1.2.1 Stilbenophane trans-**3a***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 5.12 (d, 1H), 5.43 (d, 1H), 5.49 (s, 2H), 6.88 (d, 2H), 6.95 (t, 2H), 7.19 (t, 2H), 7.25 (d, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 153.96, 128.40, 125.14, 121.56, 121.27, 117.09, 90.30, 76.23; MS(EI), *m/z* (rel. intensity, %) 224 (20), 223 (90), 210 (80), 181 (60), 152 (50).

*4.1.2.2 Stilbenophane cis-**3a***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 5.02 (s, 1H), 5.05 (s, 1H) 6.90 (d, 2H), 6.93 (t, 2H), 7.14 (t, 2H), 7.37 (d, 2H), $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 145.91, 130.30, 127.17, 126.02, 124.48, 123.49, 123.46, 121.02, 120.79, 117.50, 117.44, 115.14, 111.03, 103.30, 73.98; MS(EI) *m/z* (rel. intensity, %) 224 (10), 210 (90), 152 (5), 135 (15).

*4.1.2.3 Stilbenophane trans-**3b***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 4.22 (s, 4H), 6.81 (s, 2H), 6.95 (m, 4H), 7.02 (dd, 2H), 7.13 (td, 2H). $^{13}$C NMR (500 MHz, $CDCl_3$) $\delta$ 71.6, 120.2, 123.1, 128.2, 129.9, 130.0, 131.4, 156.1; MS(EI), *m/z* (rel. intensity, %) 266 ($M^+$, 45).

*4.1.2.4 Stilbenophane cis-**3b***. Colourless solid, $^1$H NMR (300 MHz, $CDCl_3$, 25°C): $\delta$ 4.16 (s, 4H), 7.05 (s, 2H), 7.13 (m, 4H), 7.20 (td, 2H), 7.33 (dd, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 73.2, 122.6, 124.5, 127.6, 128.4, 132.2, 133.5, 158.1; MS(EI), *m/z* (rel. intensity, %) 266 ($M^+$, 45), 181 (34), 165 (56), 55 (100).

## Supporting Information

X-ray structure analyses *trans*-**2a**, *cis*-**2a** and *cis*-**2b** and NMR, mass and IR spectra of all of pinacolophanes **2** and stilbenophanes **3** are available online.

## Note

1. Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (0)1223 336033; Email: deposit@ccdc.cam.ac.uk) quoting the depository nos. CCDC 776726 (*trans*-**2a**), 776727 (*cis*-**2a**) and 776728 (*cis*-**2b**).

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(22) The stereochemistry of each product was determined by NMR spectral data as well as by X-ray structural analyses. Therefore, we found that the reported *trans* configurations for small-ring pinacolophanes **2a–b** by Tashiro *et al.* (*20*) have *cis* configurations. This is in agreement with the McMurry explanation for intramolecular pinacolisation that small rings prefer a *cis* configuration, while larger cyclic compounds adopt a *trans* configuration; McMurry, J.E. *Chem. Rev.* **1989**, *89*, 1513–1524.

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