Synthesis and investigation of the configurational stability of some dimethylammonium borate salts

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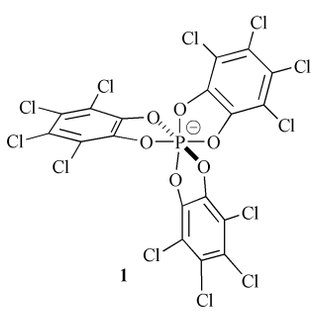
Two borate salts, dimethylammonium bis[3-isopropylbenzene-1,2-diolato(2−)-*O*,*O*′]borate and dimethylammonium 3,3″-ethylenebis(3′-methylbiphenyl-2,2′-diolato(2−)-*O*,*O*′)borate, were synthesised from the corresponding catechol and tetraphenol respectively. The configurational stability of these salts was determined by variable temperature ^{1}H NMR spectroscopy; the activation energies for the racemisation process were determined to be 85 and 79 kJ mol^{-1} respectively. Mechanisms are proposed to explain the configurational instability observed.

Introduction

Recently, Lacour and co-workers have reported the preparation and resolution of the D_3 symmetric phosphate anion TRISPHAT **1**.[1] The phosphate **1** is configurationally stable



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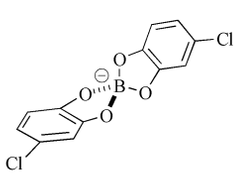


2

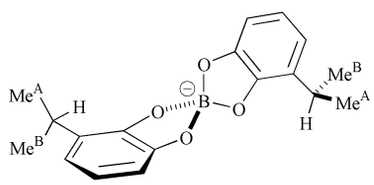
and has been used as a chiral shift reagent for determining the enantiomeric purity of chiral cationic ruthenium(II) complexes[2] and phosphonium salts.[3] TRISPHAT has also been exploited as a resolving agent for ion pair chromatography.[4]

We are interested in the preparation of configurationally stable borate salts. Previously, the brucine salt of the borate **2** has been prepared.[5] The mutarotation of a solution of the brucine salt of **2** in chloroform suggested that the **2** epimerised slowly over a number of days. In this paper, the design and synthesis of two chiral borate salts are described; their free energies of racemisation were determined using variable temperature ^{1}H NMR.

Design of the chiral borate salts

At the start of our investigation, we wanted to quantify the configurational stability of a simple borate salt such as **2** in which the boron atom was attached to two substituted catechol ligands. We chose to study the configurational stability of the borate **3**. Racemisation of **3** (Scheme 1) would result in chemical exchange of Me^A and Me^B, a process which—if it occurred—we planned to observe by dynamic NMR spectroscopy.[6] This approach would allow the configurational stability of borate **3** to be determined without the need for a resolution step.

Another class of borates in which we were interested were those based on structure **4** in which the central boron atom was coordinated by two biphenol ligands. The borate **4** has two stereogenic axes; we modelled the two conformers of **4**—*i.e.* *rac*-**4** and *meso*-**4**—in which the stereochemistry of the biaryl



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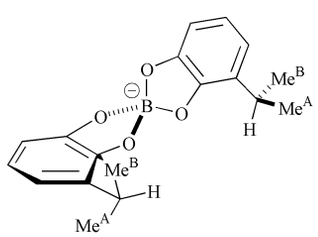

ent-**3**

Scheme 1

axes is either the same or different. Molecular modelling[7] suggested that the two diastereoisomeric conformers were very close in energy. Calculations using B3LYP/6-31G* predicted *rac*-**4** to be more stable than the *meso*-**4** by only 1.7 kJ mol^{-1} whilst calculations using HF/6-31G* suggested virtually no difference in energy between the isomers. Both methods predicted that the aryl–aryl bonds would be approximately perpendicular in the conformer *meso*-**4** (Fig. 1) and approximately parallel in the conformer *rac*-**4** (Fig. 2) and that the seven membered rings would adopt characteristic[8] twisted conformations. An X-ray crystal structure of the enantiomerically pure borate **5**, which can be considered to be a model of *rac*-**4** in which rotation about the biaryl bonds is prevented by restricted rotation, indicates that **5** also adopts a conformation in which the two aryl–aryl bonds are approximately parallel.[9] This conformational similarity reinforced our confidence in our modelling techniques.†

We wanted to synthesise configurationally stable, substituted versions of **4** in which the stereochemistry of the biaryl axes

† The B–O bond length predicted in *meso*- and *rac*-**4** using the B3LYP/631-G* method (1.45 Å) is similar to those observed (1.47–1.49 Å) in the X-ray crystal structure of the borate **23** (Fig. 3).

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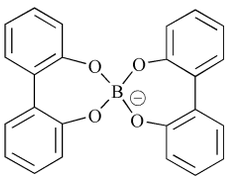

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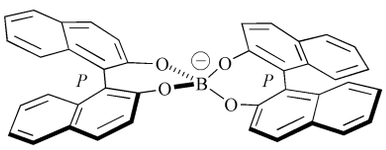

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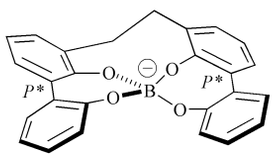
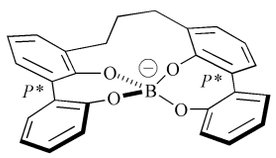
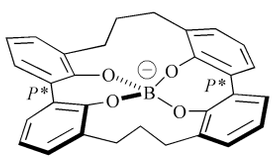


(*P**,*P**,*R**)-**6**



(*P**,*P**,*R**)-**7**



(*P**,*P**)-**8**

was the same. The borates **6**, **7** have three axes of asymmetry; these structures have three possible diastereoisomers—(*P**,*P**,*R**), (*P**,*P**,*S**) and (*P**,*M**)—all of which are chiral. The distance between the C-3 carbons was predicted to be much shorter in the conformer *rac*-**4** (C^A to C^B: 4.16 Å) than in *meso*-**4** (C^A to C^B or C^C: 5.71 Å) (Figs. 1 and 2). Therefore, we reasoned that the borates **6**–**8** would have ground states in which the stereochemistry of the biaryl axes was the same [(*P**,*P**,*R**)-**6**, (*P**,*P**,*R**)-**7** and (*P**,*P**)-**8**] because of their short chains linking the C-3 atoms. Minimisation of the geometries of the borates (*P**,*M**)-**6** and (*P**,*M**)-**8** gave only ground state conformers in which the stereochemistry of the biaryl axes was the same.

Racemisation of the borates (*P**,*P**,*R**)-**6** and (*P**,*P**,*R**)-**7** requires all three of the stereogenic axes to be epimerised. We argued that since the second most stable diastereoisomeric borates [(*P**,*M**)-**6** and **7**] were much less stable than (*P**,*P**,*R**)-**6** and **7**, epimersation of either of the biaryl axes—a process which is necessary for racemisation—was likely to be exceptionally difficult. Therefore, we reasoned that the borates (*P**,*P**,*R**)-**6**, (*P**,*P**,*R**)-**7** and (*P**,*P**)-**8** would be more configurationally stable than simple borates such as **2** and **3**.

Synthesis of chiral borate salts

ortho-Lithiation of the catechol derivative **9**, and quench with acetone gave the alcohol **10** (Scheme 2).[10] Hydrogenation of the alcohol **10**, using a 5% palladium on charcoal catalyst, gave the diether **11** in 92% yield, which was demethylated by refluxing in 45% hydrogen bromide in acetic acid to give the catechol **12** in 61% yield.

In a similar vein, the biphenol **13** was protected as the diether **14** by reaction of its sodium dianion with methyl iodide (Scheme 3). Dilithiation of **14**,[11] using *n*-butyllithium and TMEDA in refluxing ether, and reaction with methyl iodide, gave the biphenol derivative **15** in 59% yield. Radical bromination of **15**, using NBS in carbon tetrachloride with AIBN as a radical initiator, gave the bromide **16** in 96% yield.

The Würtz coupling[12] of the bromide **16** was attempted using half an equivalent of magnesium in refluxing THF (Scheme 4);

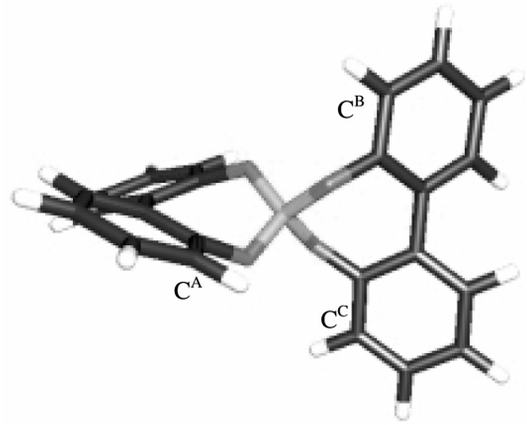


Fig. 1 Conformer *meso*-**4**.

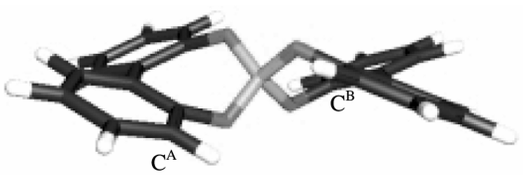
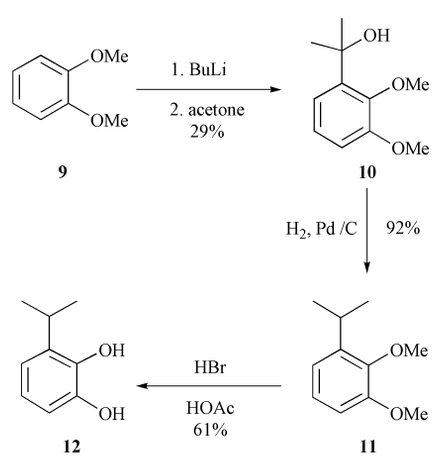
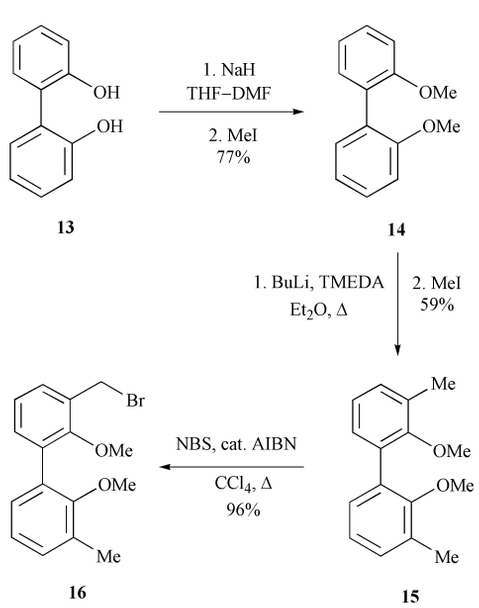


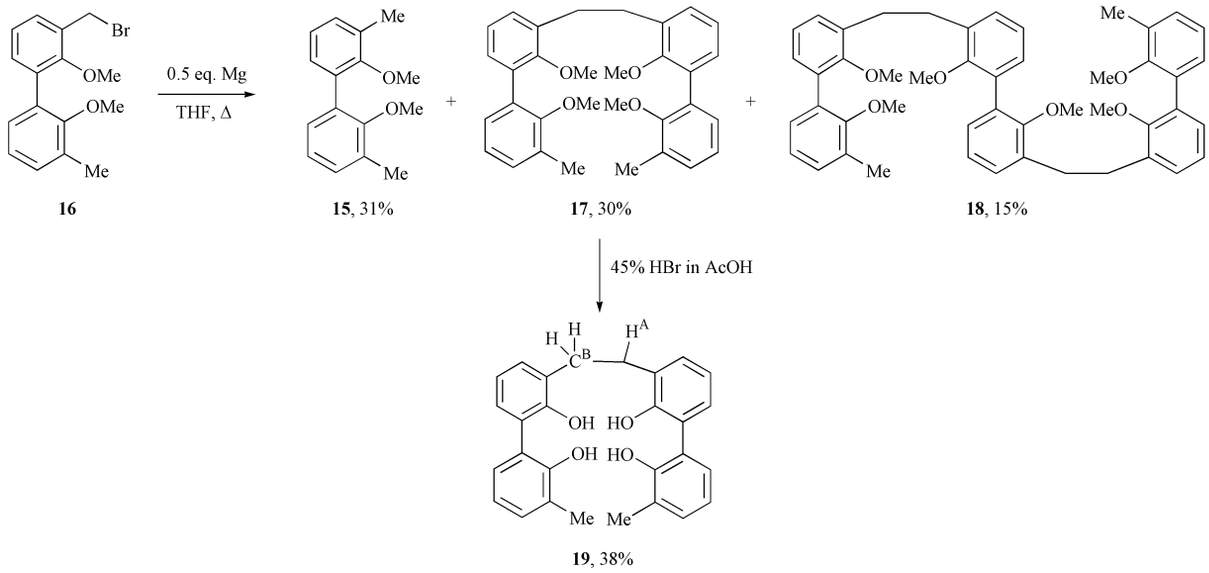
Fig. 2 Conformer *rac*-**4**.



Scheme 2



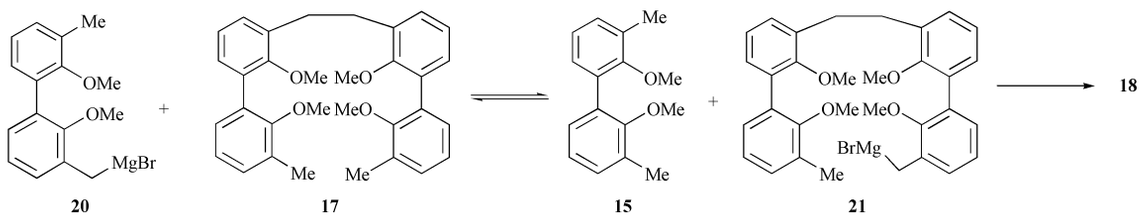
Scheme 3



16 **15**, 31% **17**, 30% **18**, 15%

19, 38%

Scheme 4

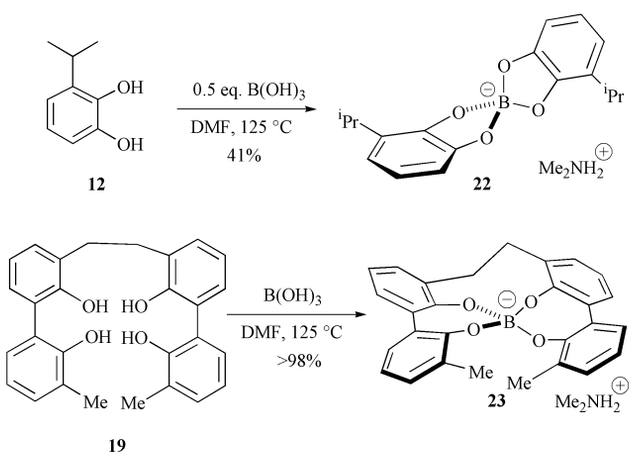


20 **17** **15** **21**

Scheme 5

to our surprise, the required tetraphenol derivative **17** was obtained in a rather low 30% yield along with the biphenol derivative **15** (31% yield) and the hexaphenol derivative **18** (15% yield). We have interpreted this result in terms of the mechanism outlined in Scheme 5. Equilibration of the Grignard reagent **20** and the initial product **17**, by deprotonation of a benzylic position of **17**, would give the diether **15** and the Grignard reagent **21**; coupling of **21** with the bromide **16** would give the observed hexaphenol derivative **18**. The tetraether **17** was demethylated with 45% hydrogen bromide in acetic acid to give the tetraphenol **19**. The structure of the tetraphenol **19** was confirmed by the observation of an HMBC crosspeak between H^A and C^B (see Scheme 4).

The dimethylammonium borate salts **22** and **23** were prepared from the catechol **12** and the tetraphenol **19** respectively by treatment with boric acid in DMF at 125 °C for 16 h (Scheme 6). The borate **22** was obtained in 41% yield after two recrystallisations from ether and the borate **23** was obtained in >98% yield after removal of the DMF by distillation and recrystallisation from chloroform. An X-ray crystal structure of the borate **22** was obtained (Fig. 3).



12 **22**

19 **23**

Scheme 6

Determination of the free energy of activation for the racemisation of the dimethylammonium borates 22 and 23

Racemisation of **3** and **24**, the anions of the salts **22** and **23**, would result in chemical exchange of diastereotopic groups (Schemes 1 and 7), a property which should allow configurational stability to be probed by dynamic NMR spectroscopy. The anions **3** and **24** are both C_2-symmetric; racemisation of **3** would result in chemical exchange of Me^A and Me^B (Scheme 1) and racemisation of **24** would result in exchange of H^A and H^B (Scheme 7).‡

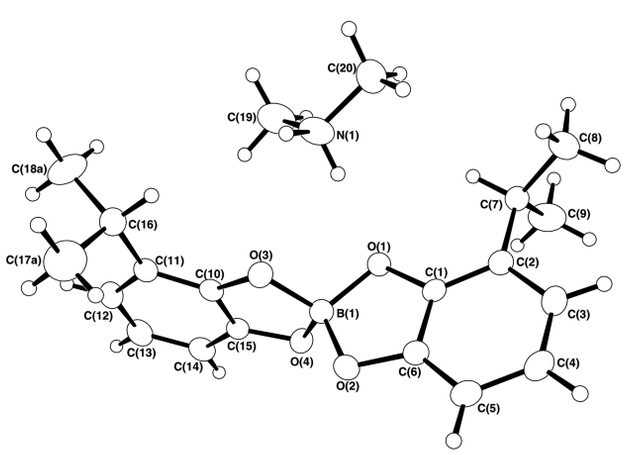
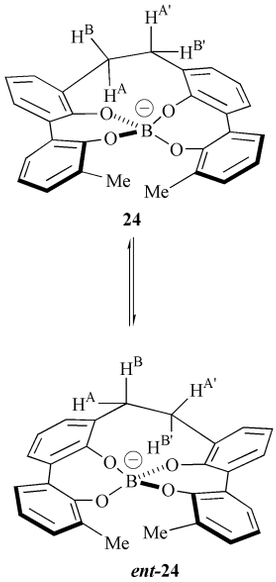


Fig. 3 X-Ray crystal structure of the borate **22**.

‡ For a borate similar to **3** with diastereotopic protons on the side chains of the two catechol units, see ref. 13.



Scheme 7

The borate **22** was dissolved in DMSO-d_6, and the coalescence of its methyl doublets was observed by variable temperature 400 MHz ^{1}H NMR spectroscopy. The coalescence of the doublets corresponding to Me^A and Me^B occurred at 366 K, indicating that the activation energy for racemisation, $\Delta G^‡$, was 85 kJ mol^{-1}.§ Assuming that $\Delta G^‡$ is approximately independent of temperature, this barrier translates into a half-life of approximately two minutes at room temperature (293 K). This process was acid-catalysed: the free energy of racemisation, $\Delta G^‡$, was 81 kJ mol^{-1} with 16 mM benzoic acid in DMSO-d_6.

In a similar vein, the configurational stability of the borate **23** was determined by variable temperature 500 MHz ^{1}H NMR spectroscopy. In this case coalescence temperature was 383 K, which indicated that the activation energy for racemisation, $\Delta G^‡$, was 79 kJ mol^{-1}. The borate **23**, with its two-carbon chain linking the biphenol ligands, was, in fact, *less* configurationally stable than the borate **22**.

Proposed mechanisms of racemisation of the borates 22 and 23

We propose that **22** racemises *via* the following acid-catalysed process. Protonation of **3**, the anion of **22**, and ring-opening would give the achiral trigonal borate **26** (Scheme 8). The phenol of **26** can re-attack either face of the boron atom, leading to either enantiomer of **3**.

In the design phase of the borate **23**, we argued that racemisation would be difficult because epimerisation of either biaryl axis would give a highly strained diastereoisomer. However, the free energy of racemisation of **23** was found to be less than that of the borate **22**. The mechanism which we propose to account for this configurational instability is shown in Scheme 9. Protonation of **24**, the anion of **23**, and ring-opening, would give the borate **28** in which two of **24**'s chiral axes have been destroyed: the boron atom of **28** is trigonal and the transition state for rotation about the exocyclic biaryl bond only requires the two *ortho* substituents to slip past a hydrogen atom.[15] Epimerisation of the remaining chiral axis of **28** (→*ent*-**28**) simply requires its seven-membered ring to flip. The rather low barrier to racemisation of **23**, therefore, stems from the strained ring system which destabilises its ground state.

§ The relationship $\Delta G^‡ = RT_c\{23 + \ln[T_c\sqrt{(\Delta\nu^2 + 6J^2)}]\}$ was used to determine the activation energy, $\Delta G^‡$, for a symmetrical coupled system, from the coalescence temperature, T_c (K), the gas constant, R, the frequency separation of the peaks, $\Delta\nu$ (Hz) and the coupling constant between the nuclei, J (Hz).[14]

Summary

The configurational stability of the dimethylammonium borate salts **22** and **23** were investigated in DMSO-d_6 by variable temperature ^{1}H NMR spectroscopy; the free energies of racemisation were found to be 85 and 79 kJ mol^{-1} respectively. Mechanisms for the racemisation processes were proposed which involved protonation of one of the ligands attached to boron, followed by ring-opening to give a trigonal borate. The configurational instability of **23** was attributed to ring strain in its ground state.

Experimental

All solvents were distilled before use. THF and Et_2O were freshly distilled from lithium aluminium hydride whilst CH_2Cl_2 and toluene were freshly distilled from calcium hydride. Ether refers to diethyl ether and petrol refers to petroleum spirit (bp 40–60 °C) unless otherwise stated. Diisopropylamine was purified prior to use by distillation from calcium hydride. Solvents were removed under reduced pressure using a Büchi rotary evaporator at water aspirator pressure. Triphenylmethane was used as indicator for THF. *n*-Butyllithium was titrated against diphenylacetic acid before use. All non-aqueous reactions were carried out under argon using oven-dried glassware.

Flash column chromatography was carried out using silica (35–70 μm particles) according to the method of Still, Kahn and Mitra.[16] Thin layer chromatography was carried out on commercially available pre-coated plates (Merck silica Kieselgel $60F_{254}$). Unless otherwise stated, R_f values were measured with ethyl acetate as eluant. Proton and carbon NMR spectra were recorded on a Bruker WM 250, DPX 300, WM 400 or DRX 500 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million downfield of tetramethylsilane and values of coupling constants (J) are given in Hz. Carbon NMR spectra were recorded with broad band proton decoupling.

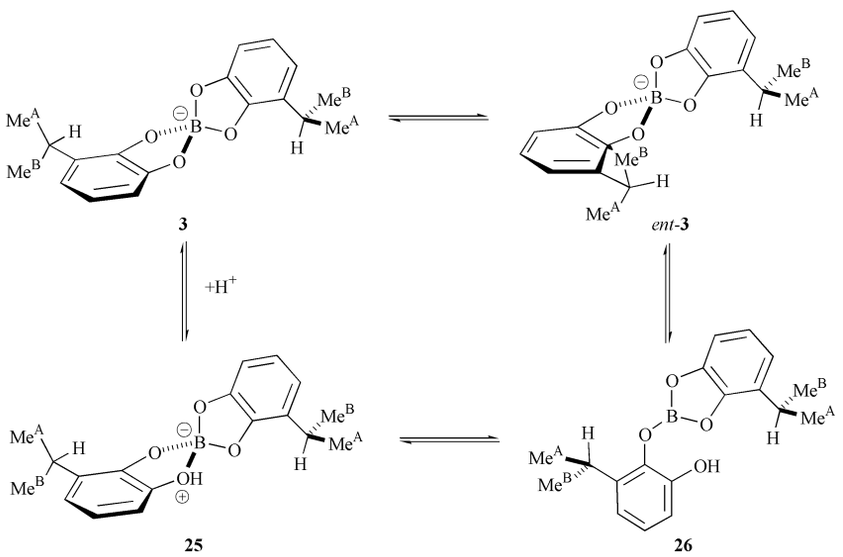
Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR ESP infrared spectrophotometer and signals were referenced to the polystyrene 1601 cm^{-1} absorption. Mass spectra were recorded on a VG autospec mass spectrometer, operating at 70 eV, using both the electron impact and fast atom bombardment methods of ionisation. Accurate molecular weights were obtained by peak matching using perfluorokerosene as a standard. Electron Impact was used unless Fast Atom Bombardment (+FAB) is indicated. Microanalyses were carried out by the staff of the School of Chemistry using a Carlo Erba 1106 automatic analysers.

Computational details

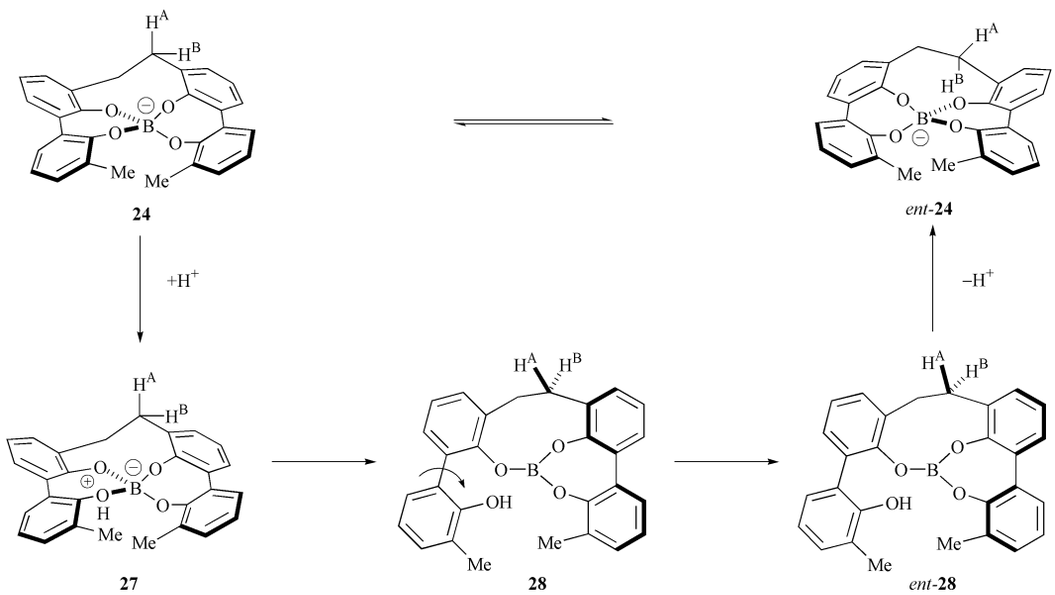
Starting structures for the two isomers were first minimised at the AM1 level. These structures were then optimised at the HF/6-31G* and B3LYP/6-31G* level. All calculations used the Gaussian software[7] running on a dual processor Pentium III-500 machine running redhat 6.0 linux. Default convergence criteria were used in all minimisations.

Dimethylammonium bis[3-isopropylbenzene-1,2-diolato(2−)-*O*,*O′*]borate 22

Boric acid (66 mg, 1.07 mmol) was added to a stirred solution of 3-isopropylbenzene-1,2-diol[10] **12** (320 mg, 2.13 mmol) in dry DMF (5 ml). The reaction was heated at 125 °C for 48 h. The DMF was removed by evaporation under reduced pressure, ether (5 ml) was added, the solution was placed in the freezer for 12 h, filtered and recrystallised from ether to give the *borate* **22** (154 mg, 43%) as colourless cubes, mp >250 °C (Found: C, 67.2; H, 8.00; N, 3.9; $C_{20}H_{28}BNO_4$ requires C, 67.2; H, 7.90; N, 3.9%); ν_{max}/cm^{-1} (Nujol) 2925, 1648, 1557 and 1460; δ_H (300



Scheme 8



Scheme 9

MHz, DMSO-d_6) 6.55 (4 H, m), 6.47 (2 H, dd, *J* 8.5 and 2.0 Hz), 3.55 (2 H, $Me_2N\mathit{H}_2$), 3.12 (2 H, sept, *J* 7.1 Hz, C*H*Me_2), 2.40 (6H, s, Me_2NH_2), 1.28 (6 H, d, *J* 7.1, CH$\mathit{Me}_A\mathrm{Me_B}$) and 1.27 (6 H, d, *J* 7.1, $\mathrm{CHMe_A}\mathit{Me}_B$).

Single crystals of **22** were obtained by slow evaporation from ether–dichloromethane.

Crystal structure determination of 22

Molecular formula $C_{20}H_{28}BNO_4$ (M_r = 357.24), orthorhombic, *a* = 12.9858(4), *b* = 11.7576(3), *c* = 25.6292(8) Å, *V* = 3913.1(2) Å^3, *T* = 180 K, space group *Pbca*, *Z* = 8, μ(Cu-Kα) = 0.664 mm^{-1}, 5132 reflections collected, 3170 unique (merging with *R* = 0.099) and all were retained in calculations. Refinement, based on F^2 (SHELXL93) converged at $rR_2 = 0.1098$ for all data, $R_1 = 0.0415$ for relections with $F^2 > 2.0\sigma(F^2)$. CCDC reference number 207/489. See http://www.rsc.org/suppdata/p1/b0/b005954o/ for crystallographic files in .cif format.

2,2′-Dimethoxy-3,3′-dimethylbiphenyl 15

Butyllithium (1.6 M solution in hexanes, 12.5 ml, 20.0 mmol) was added dropwise to a stirred solution of the diether[11] **14** (1.0 g, 4.6 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (3.4 ml, 23.0 mmol) in dry ether (60 ml) at 0 °C. The reaction was stirred at 0 °C for 1 h, warmed to 40 °C and refluxed for 16 h. The reaction mixture was cooled to 0 °C, methyl iodide (1.55 ml, 25 mmol) added dropwise, stirred for 1.5 h, dilute aqueous hydrochloric acid (4 M, 20 ml) added and stirred for 30 min. The layers were separated and the organic layer was washed with dilute aqueous hydrochloric acid (0.5 M, 100 ml), saturated sodium bicarbonate solution (100 ml) and brine (80 ml), dried (Na_2SO_4), filtered and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 1:7 ethyl acetate–petrol to give the diether **15** (800 mg, 77%) as a yellow oil, R_f 0.30 (12% EtOAc in petrol) (Found: C, 79.2; H, 7.60; $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.50%); ν_{max}/cm^{-1} (Nujol) 2927, 2855, 1460, 1413, 1255, 1223 and 1170; δ_H (300 MHz, $CDCl_3$) 7.19 (4 H, m), 7.04 (2 H, t, *J* 7.4 Hz, 5-H and 5′-H), 3.40 (6 H, s, Me) and 2.34 (6 H, s, Me); δ_C (75 MHz, $CDCl_3$) 156.6, 132.6, 131.6, 130.8, 129.5, 123.8, 60.4 and 16.8; *m*/*z* (EI) 242 (100%, M^+) and 212 (30).

3-Bromomethyl-2,2′-dimethoxy-3′-methylbiphenyl 16

A solution of the diether **15** (1.35 g, 5.6 mmol), *N*-bromosuccinimide (1.98 g, 11 mmol) and AIBN (15 mg) in carbon tetrachloride (80 ml) was refluxed for 2 days. The reaction was filtered and evaporated under reduced pressure to give a crude product which was redissolved in dichloromethane (100 ml),

washed with saturated aqueous sodium bicarbonate solution (20 ml) and water (20 ml), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 1:7→1:4 ethyl acetate–petrol to give the *bromide* **16** (2.12 g, 96%) as a yellow oil, R_f 0.30 (12% EtOAc in petrol) (Found: $M^+ - H$, 319.0340; $C_{16}H_{17}BrO_2$ requires $M - H$, 319.0342); ν_{max}/cm^{-1} (Nujol) 2927, 2855, 1460, 1233 and 1008; δ_H (300 MHz, $CDCl_3$) 7.43–7.04 (6H, m), 4.65 (2 H, d, *J* 0.4 Hz, CH_2Br), 3.49 (3H, s, OMe), 3.40 (3H, s, OMe) and 2.35 (3 H, d, *J* 0.7 Hz, Me); *m*/*z* (EI) 319 (100%, $M^+ - H$), 239 (35), 225 (50) and 209 (45).

1,2-Bis(2,2′-dimethoxy-3′-methylbiphenyl-3-yl)ethane 17

The bromide **16** was dried by azeotropic removal from dry toluene (3 × 50 ml) and dissolved in dry THF (50 ml). Magnesium turnings (65 mg, 2.7 mmol) were added and the reaction was stirred for 30 min and then refluxed for 16 h. The solvent was removed by evacuation under reduced pressure and the residue was dissolved in dichloromethane (100 ml), washed with water (50 ml), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 1:9 ethyl acetate–petrol to give 1,2-bis(2,2′-dimethoxy-3′-methylbiphenyl-3-ylethane **17** (390 mg, 30%) as a yellow oil, R_f 0.25 (10% EtOAc in petrol) (Found: M^+, 482.2456; $C_{32}H_{34}BrO_4$ requires *M*, 482.2456); ν_{max}/cm^{-1} (Nujol) 2926, 2855, 1460, 1255, 1223, 1011 and 906; δ_H (500 MHz, $CDCl_3$) 7.22–7.06 (12 H, m), 3.41 (6 H, s, OMe), 3.40 (6 H, OMe), 3.05 (4 H, CH_2CH_2) and 2.36 (6 H, Me); δ_C (125 MHz, $CDCl_3$) 156.1, 135.1, 132.3, 132.1, 131.3, 129.7, 129.6, 129.5, 129.1, 123.5, 123.4, 60.7, 60.0, 31.5 and 16.4 (one peak missing); *m*/*z* (EI) 482 (55%, M^+) and 241 (100). The HMBC spectrum showed a crosspeak between CH_2CH_2 and CH_2CH_2.

Also obtained was the diether **15** (0.41 g, 31%), spectroscopically identical to that obtained previously.

Also obtained was 2,2′-dimethoxy-3,3′-bis[2-(2,2′-dimethoxy-3′-methylbiphenyl-3-yl)ethyl]biphenyl **18** (200 mg, 15%) as a yellow oil, R_f 0.20 (10% EtOAc in petrol) (Found: MH^+, 723.3705; $C_{48}H_{51}O_6$ requires *MH,* 723.3686); ν_{max}/cm^{-1} (Nujol) 2935, 1461, 1255, 1223, 1011 and 906; δ_H (300 MHz, $CDCl_3$) 7.22–6.98 (18 H, m), 3.42 (12 H, s, OMe), 3.41 (6 H, OMe), 3.05 (8 H, CH_2CH_2) and 2.35 (6 H, Me); *m*/*z* (EI) 722 (90%, M^+), 481 (50) and 241 (100); (ES+) 740 (100%, MNH_4^+) and 723 (15, MH^+).

1,2-Bis(2,2′-dihydroxy-3′-methylbiphenyl-3-yl)ethane 19

The tetraether **17** (147 mg, 0.3 mmol) was dissolved in 48% aqueous hydrogen bromide (4 ml) and acetic acid (4 ml) and refluxed for 48 h. The reaction was cautiously quenched with saturated sodium carbonate solution (20 ml), extracted with ether (2 × 20 ml), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 1:3 ethyl acetate–petrol to give the *tetraphenol* **19** (55 mg, 38%) as a yellow oil, R_f 0.25 (25% EtOAc in petrol) (Found: MH^+, 427.1916; $C_{28}H_{27}O_4$ requires *MH,* 427.1909); ν_{max}/cm^{-1} (Nujol) 3600, 3465, 2984, 2909, 1446, 1373, 1238 and 1045; δ_H (300 MHz, $CDCl_3$) 7.2–7.1 (6H, m), 7.10 (2 H, d, *J* 7.5 Hz), 6.97 (2 H, t, *J* 7.5 Hz), 6.93 (2 H, t, *J* 7.5 Hz), 6.23 (2 H, br s, OH), 5.60 (2 H, br s, OH), 3.00 (4 H, s, CH_2) and 2.31 (6 H, s, Me); δ_C (75 MHz, $CDCl_3$) 151.7, 151.5, 131.6, 130.8, 130.0, 129.0, 128.8, 126.1, 124.1, 123.5, 121.6, 121.3, 31.9 and 16.7; *m*/*z* (ES+) 444 (45%, MNH_4^+), 427 (100, MH^+). The HMBC spectrum showed a crosspeak between CH_2CH_2 and CH_2CH_2.

Dimethylammonium 3,3″-ethylenebis(3′-methylbiphenyl-2,2′-diolato(2−)-*O*,*O*′)borate 23

The tetraphenol **19** (55 mg, 0.12 mmol) was heated in DMF (1 ml) at 125 °C for 48 h. The DMF was removed by evaporation under reduced pressure; recrystallisation from chloroform gave the *borate* **23** (62 mg, >98%) as brown plates, mp >250 °C, (Found: C, 74.9; H, 6.00; N, 2.8. $C_{30}H_{30}BNO_4$ requires C, 75.2; H, 6.30; N, 2.9%); ν_{max}/cm^{-1} (Nujol) 2925, 1645, 1557, 1461, 1377 and 1149; δ_H (300 MHz, DMSO-d_6) 8.23 (2 H, br s, Me_2NH_2), 7.28 (2 H, dd, *J* 7.6 and 1.6), 7.14 (4 H, m), 7.12 (2 H, dd, *J* 7.6 and 1.7), 6.94 (2 H, t, *J* 7.4), 6.90 (2 H, t, *J* 7.4), 3.41 (6 H, Me_2NH_2), 2.94 (2 H, d, *J* 10 Hz, $CH_AH_BCH_{A'}H_{B'}$), 2.84 (2 H, d, *J* 10 Hz, $CH_AH_BCH_{A'}H_{B'}$) and 2.63 (6 H, s, Me); δ_B (80 MHz, DMSO-d_6) 9.1; *m*/*z* (EI) 434 (MH^+, 30%), 322 (35) and 149 (100).

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