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# Pyrazabole formation by thermolysis of the free acid of the hydrotris(pyrazolyl)borate ion

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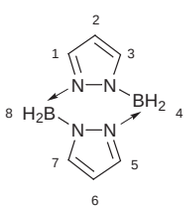
Thermolysis of the free acid of the hydrotris(pyrazolyl)borate ion resulted in one of three product pyrazaboles, depending on the reaction conditions. Melting the acid alone afforded 4,8-*trans*-(pz)HB(μ-pz)$_2$BH(pz) (pz = $C_3H_3N_2$), whilst doing so in the presence of $ZrCl_4$ resulted in the *cis* isomer. Melting the acid in a damp HCl atmosphere afforded, on alkaline work-up, the novel oxo-bridged dimeric pyrazabole [(pz)B(μ-pz)$_2$BO(pz)]$_2$. The crystal structures of all three pyrazaboles have been determined, and procedures for obtaining each compound in the pure state are described.

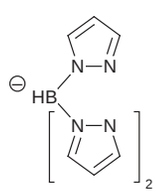
Pyrazabole **1** has been known since 1966 when it was reported contemporaneously with the poly(pyrazolyl)borate ions and their free acids.[1] Many derivatives of pyrazabole exist, of forms substituted both at the boron centres and on the pyrazolyl rings.




Of those pyrazaboles with substituents at B, the symmetrically 4,8-disubstituted derivatives are the easier to produce and syntheses often start from amine complexes of appropriately substituted boranes and pyrazoles;[1,2] another approach is to functionalise an available pyrazabole by the substitution of the B-borne hydrogens by other groups.[3,4] In the case of *gem*-B-disubstituted materials (or asymmetrically B-monosubstituted, which may also be made by the preceding method with careful regard to reaction stoichiometry[4,5]), the syntheses can be problematic, involving the sometimes unpredictable[6] reaction of the appropriate bis(pyrazolyl)borate salt with amine complexes of boranes bearing good leaving groups.[7]

Of the substitution type is the reaction of pyrazabole with 2 mol equivalents of pyrazole, with elimination of $H_2$, giving bis(pyrazolyl)pyrazabole; heteroregional disubstitution is preferable to geminal disubstitution, presumably due to steric reasons, and the formation of the known[8] 4,4-bis(pyrazolyl)-pyrazabole by this reaction is negligible.[1] However, the system does not exert a large stereochemical preference as to which of the two isomers of 4,8-bis(pyrazolyl)pyrazabole is formed, these being produced in sufficiently equal measure to mutually occlude melting points.[1] These isomers do not yet appear to have been separated or produced in isolation.

Another route to the 4,8-bis(pyrazolyl)pyrazaboles is by thermal decomposition of the free acid of the hydrotris(pyrazolyl)borate ion. The $Tp^-$ ion **2** is known to contain a hydridic B-borne hydrogen, since it readily reacts with protic materials.[3] It is curious, therefore, that the free acid HTp, which originates by protonation of the anion in aqueous solution,[1] is stable at all, ostensibly simultaneously containing hydridic and protonic hydrogens. Of further interest is the fact that, although it does decompose near its melting point, the chief products of decomposition are not $H_2$ and tetrakis(pyrazolyl)pyrazabole, as might be expected from a hydridic–protonic conproportionation, but pyrazole and a mixture of isomers of 4,8-bis-(pyrazolyl)pyrazabole.[3] Moreover, attempts to use HTp as a reagent for the synthesis of Tp complexes, by melting HTp in the presence of Zr containing materials, led to the observation that in some cases Tp will replace the cyclopentadienyl (Cp) ligand at Zr,[9] but that in others no Zr–Tp complexes are isolable, the zirconium reagent instead influencing the distribution of isomers of 4,8-bis(pyrazolyl)pyrazabole (arbitrarily denoted **A** and **B**) formed.[10]




**2**

The chemistry of HTp is virtually unreported, but initial studies[11] indicate that it is capable of replacing a wide range of easily protonated ligands with Tp at a range of metal centres. It is by these means that zirconium complexes may exert their influence over the isomer distribution of 4,8-bis(pyrazolyl)-pyrazaboles, in a proximity reaction between two Tp ligands at a Zr. Described here are stereospecific syntheses and characterisations of pure 4,8-*trans*- and 4,8-*cis*-bis(pyrazolyl)-pyrazaboles, along with those of the dimeric pyrazabole [(pz)B(μ-pz)$_2$BO(pz)]$_2$.

## Results and discussion

### Synthetic and spectroscopic studies

Initial studies of the Zr-containing systems first reported to show isomer selectivity in 4,8-bis(pyrazolyl)pyrazabole production indicated[10] that, whilst melting HTp alone appears somewhat to favour isomer **A** over **B**, the inclusion of [$ZrCp_2H(Cl)$] in the melt favours **A** still more. Conversely, the presence of $ZrCl_4$ favours **B** production.[10] Since these effects grow in magnitude with increasing proportion of the appropriate Zr-containing material in the melt, it appears that, regardless of the nature of the selective process being promoted by the zirconium material, that process must operate in competition with

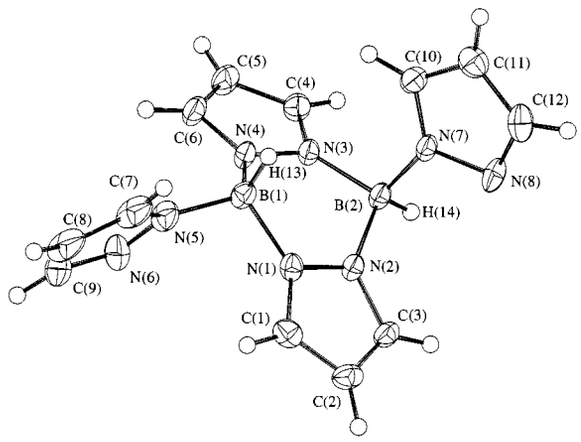



**Fig. 1** A view[12] of pyrazabole **A**, depicting atoms at the 50% probability level.

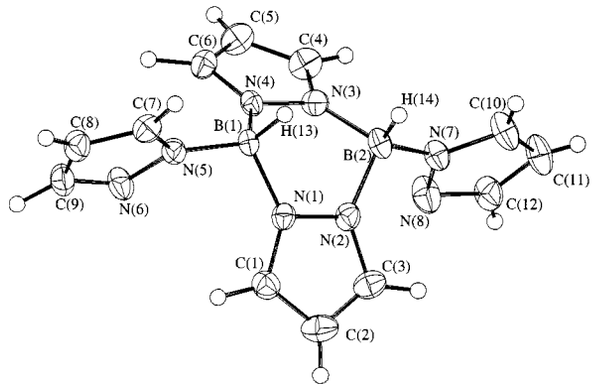



**Fig. 2** A view[12] of pyrazabole **B**, depicting atoms at the 50% probability level.

the autodecomposition of HTp. This study found that the excess of **A** formed by the melting of HTp is quite sufficient to allow for its isolation after just one recrystallisation, thereby obviating the need for zirconium mediation. Isomer **B**, however, is not isolable by this method and its production is effected by heating HTp in the presence of $ZrCl_4$ to afford very low but reproducible yields.

When the free acid was thermolysed in a HCl atmosphere, in an attempt to investigate whether the selectivity for **B** shown by the latter reaction might be caused simply by HCl arising from hydrolysis of $ZrCl_4$, the major product was **A** contaminated with a material possessing an infrared spectrum characteristic of pyrazaboles, but entirely free of B–H bands. This contaminant was found to arise from traces of moisture and with careful inclusion of water can be made to become the major product (too much water leads to complete hydrolysis to boric acid). On work-up in the same fashion as for **A** and **B**, namely the dissolution of the melt in aqueous HCl, precipitation of the crude material by basification, and crystallisation from $CH_2Cl_2$–light petroleum in ambient air, gives a material, with a different infrared spectrum, identified as $[(pz)B(\mu\text{-}pz)_2BO(pz)]_2$ **C**. The precursor of **C** is not yet characterised, but may be an oligo- or poly-meric version thereof; a B–Cl containing material also cannot be ruled out, which hydrolyses during standing in solution and crystallises as **C**. Attempts to identify this precursor are ongoing.

Characterisations by mass spectrometry, elemental analysis, NMR and IR spectroscopies and single-crystal X-ray diffraction studies are reported herein for compounds **A**–**C**. However, satisfactory elemental analysis of **C** could not be obtained despite repeated recrystallisations, which may be due to the fact that **C** is observed slowly to decompose in solution to yield pyrazole as one of the products.

## Structural studies

Compounds **A**, **B** and **C** were prepared as described below, and specimens for crystallographic study were obtained by slow evaporation from near-saturated 70 : 30 $CH_2Cl_2$–light petroleum (60–80 °C) solutions. Table 4 contains important bond distances and angles for **A**–**C**.

Views of compounds **A** and **B** derived from single-crystal X-ray analyses are shown in Figs. 1 and 2. Both adopt a 'boat' conformation of the central $\{B_2N_4\}$ ring and, as may be expected, the B atoms in **A** and **B** are found at the 'bow' and 'transom' positions which offers the substituents the option of pseudo-equatorial (*pe*, or 'rudder') or pseudo-axial (*pa*, or 'bowsprit') placement. Compound **A** is clearly the 4,8-*trans* isomer, which means that one pyrazolyl substituent must be found in each of the *pe* and *pa* positions; it is the only 4,8-disubstituted pyrazabole for which this is the case. Compound **B** is the 4,8-*cis*- isomer, and the pyrazolyl substituents both adopt *pe* positions rather than *pa*. Isomers **A** and **B** are the only pyrazaboles observed preferentially to adopt a *pe* position for their pyrazolyl substituents; in 4,8-*cis*-diethylbis-(pyrazolyl)pyrazabole[13] the pyrazolyls are in *pa* positions. 4,8-*trans*-Bis(pyrazolyl)pyrazaboles have previously always been observed to adopt chair conformers with both pyrazolyls in axial positions.[4,13,14]

The $\{B_2N_4\}$ ring in compound **A** appears less puckered than in **B**; the root mean square (r.m.s.) deviation from the mean planes of these is *ca.* 0.217 Å in **A**, compared to *ca.* 0.292 Å in **B**; the B · · · B distances are consequently only 2.855(5) Å in **B** compared to 2.992(5) Å in **A**. The mean B–N (ring) distance is 1.552[2] Å in **A** and 1.561[2] Å in **B** ($[\,] = \{\sum_{i=1}^{i=n}(\sigma_i^2)\}^{\frac{1}{2}}/n$). This lengthening in **B** may be so as to minimise close across-ring N · · · N interactions, which result from the increased puckering in **B**; the closest of these in the two structures are N(2) · · · N(3) in **A** [2.475(2) Å] and N(1) · · · N(4) [2.437(3) Å] in **B**. This latter distance is longer than in only one other pyrazabole.[15]

A survey[16] of relevant precedents[4,8,13,14] reveals that the bonds from B to terminal pyrazolyls are always shorter than those to the bridging ones. The mean B–N (terminal) distances in **A** and **B** are 1.517[2] and 1.496[3] Å respectively; it appears that the longer B–N (ring) distances in **B** are offset by shorter B–N (terminal) distances, these being shorter than in any other B-pyrazolylpyrazabole. The mean value for **A** hides a remarkable difference between the distances from the B atoms to the chemically identical *pe* and *pa* pyrazolyls of 1.501(3) and 1.533(3) Å respectively (Table 1), the *pe* distance corresponding well with those in **B** and the *pa* distance being, in this sense, anomalous. This degree of difference has never before been observed, and it is difficult to rationalise its origins since there appears to be little correlation between the nature of pyrazabole B-borne substituents, the position they occupy and the length of their bonds to the B atom in preceding structures: thiolato,[4] pyrazolyl[8] or F groups[17] might be somewhat more strongly bound at *pe* than *pa* sites, Cl groups show no preference[17] and, interestingly, phenyl or large alkyls may show stronger binding at *pa* sites than *pe*.[15,18] There are no clear intermolecular interactions such as would be responsible for the difference in lengths in **A**. All 'pyridinic' N atoms in both **A** and **B** structures make intermolecular contacts with H atoms, the closest of which are 2.52(2) Å for N(8) · · · H(4) ($1 - x$, $-y$, $-z$) in **A** and 2.41(2) Å for N(8) · · · H(9) ($x - 0.5$, $y$, $0.5 - z$) in **B**; the former contact probably contributes to the difference in bond lengths in **A**, but the magnitude of the difference suggests that other factors also play a role.

In the past, reactivity[6] and structural studies[8,19] have given rise to speculation that, where the pyrazabole contains *pa* and *pe* hydrogens, the B–H (*pa*) bond is weaker than the B–H(*pe*); however the structural evidence is weak and not without contradictory examples.[5] This study allows another opportunity to

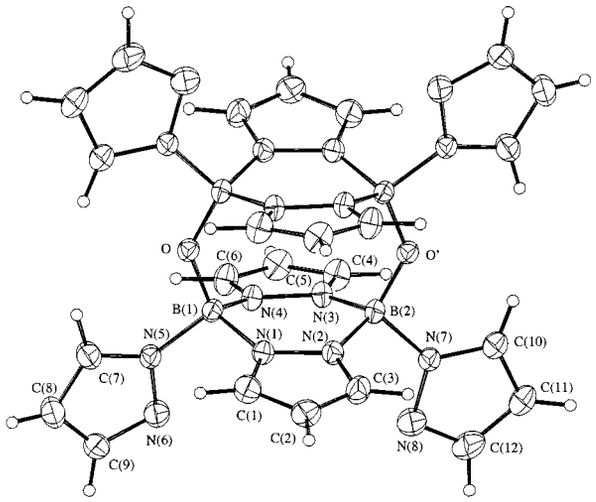



**Fig. 3** A view[12] of pyrazabole **C**, depicting atoms at the 30% probability level. Hydrogens are unlabelled, but carry the same numerical suffix as do their parent carbons. The symmetry-related half of the dimer ($' = -x, 1 - y, 1 - z$) is also mostly unlabelled.

test this hypothesis, in that **A** contains both *pe* and *pa* B–H bonds. These distances are 1.06(2) and 1.14(2) Å respectively, which would appear to offer the hypothesis some support were it not that the two B–H distances in **B**, which are both *pa*, also appear to be different, at 1.05(2) and 1.15(2) Å! It has been noted that the conformation of the central $\{B_2N_4\}$ ring is sensitive to general packing effects,[8] but elsewhere one also sees that the near-planar 2,6-dibromo-4,4,8,8-tetraethylpyrazabole exhibits a very large range of 1.47(8) to 1.76(9) Å in the lengths of its B–C bonds;[20] the cause of such a difference, if significant, must also lie in packing forces, and its magnitude would suggest that packing forces likely outweigh other bonding considerations in determining not only the conformation of the central ring, but also the bonding to its substituents.

Despite this, some structural aspects of pyrazaboles seem to be fairly universal. In both **A** and **B** (and indeed **C**, below) the *pe* pyrazolyl substituents adopt an orthogonal orientation with respect to the central ring. The angles between the planes of the $\{B_2N_4\}$ ring and the *pe* rings are in every case close to 90°; the largest deviation is that in **A**, of less than 9°. It is absolutely commonplace for planar substituents in equatorial or *pe* positions to adopt this orthogonal orientation,[4,8,17,18] but what is notable about *pe* pyrazolyls is that the torsional angle between the pyridinic N and the B *pa* substituent is close to 180° in all cases; in terms of the nautical analogy, the pyridinic N is always lowest down on the 'rudder'.[8] There is also a preferred alignment of *pa* pyrazolyls, but there are several exceptions. In **A** the *pa* pyrazolyl is approximately orthogonal to that of the central ring but is rotated approximately 54° relative to the B1 · · · B2 vector so as to be aligned approximately with the B(2)–N(3) bond. This arrangement is similar to that in many other pyrazaboles bearing pyrazolyls[4,13] or other planar *pa* substituents[8,17] but several structures, among them 4,4-bis(pyrazolyl)-pyrazabole,[4] show no such alignment.

Compound **C**, shown in Fig. 3, is the sole dimeric pyrazabole structure known to date. It is an example of the class of pyrazaboles which are bridged between *pa* 4,8-*cis* positions, most of which have bridges not more than three atoms long. The bridge in **C** imparts little strain such as would pucker the boat conformer and bring the B atoms closer together. The B(1) · · · B(2) separation is 3.171(4) Å, which is longer than in any of [(R)B(μ-Z)(μ-pz)$_2$B(R)] where R = Et, Z = $O_2$BEt,[21] ($pz^+$),[22] Se[23] or $Se_2$;[23] R = Me, Z = $S_2$[24] or ferrocenyl.[25] Indeed, the r.m.s. deviation of the atoms in the $\{B_2N_4\}$ ring from its mean plane is *ca.* 0.138 Å, which makes it rather less puckered than either **A** or **B**. The B–N (ring) distances are slightly longer than those in **A** or **B**, averaging 1.569[2] Å; the B–N (terminal) distances are more so, at a mean of 1.529[2] Å. This overall lengthening of B–N bonds in **C** relative to **A** or **B** indicates that the B in **C** is less acidic to the nitrogen lone pairs, which is presumably an effect of increased electron donation from the O atom. The B–O distances in **C** are indeed short compared to, for example,[21] those in [($C_2H_5$)B(μ-$O_2$B$CH_2CH_3$)(μ-pz)$_2$B($C_2H_5$)] but the geometry around B is almost tetrahedral and it is thus difficult to envisage π-basic behaviour of O in this situation.

As in compounds **A** and **B**, the *pe* pyrazolyls are 'rudder-like', their maximum inclination to the best plane through the $\{B_2N_4\}$ ring being less than 7° in both cases.

**Table 1** Selected bond lengths (Å) and angles (°) for compounds **A**–**C**

| | **A** | **B** | **C** |
|---|---|---|---|
| **A**, **B**: X = H(13), Y = H(14). **C**: X = O, Y = O′ ($' = -x,1 - y,1 - z$) | | | |
| B(1)–X | 1.14(2) | 1.15(2) | 1.405(3) |
| B(1)–N(5) | 1.501(3) | 1.491(4) | 1.533(3) |
| B(1)–N(4) | 1.556(3) | 1.560(4) | 1.564(3) |
| B(1)–N(1) | 1.560(3) | 1.559(4) | 1.566(3) |
| B(2)–Y | 1.06(2) | 1.05(2) | 1.411(3) |
| B(2)–N(7) | 1.533(3) | 1.500(4) | 1.524(3) |
| B(2)–N(2) | 1.546(3) | 1.570(4) | 1.566(3) |
| B(2)–N(3) | 1.548(3) | 1.556(4) | 1.580(3) |
| N(1)–N(2) | 1.359(2) | 1.362(3) | 1.358(2) |
| N(3)–N(4) | 1.360(2) | 1.367(3) | 1.362(2) |
| X–B(1)–N(5) | 109.7(9) | 115.1(10) | 108.4(2) |
| X–B(1)–N(4) | 109.3(9) | 108.8(11) | 114.0(2) |
| N(5)–B(1)–N(4) | 111.1(2) | 111.3(3) | 107.9(2) |
| X–B(1)–N(1) | 111.6(8) | 106.6(11) | 113.0(2) |
| N(5)–B(1)–N(1) | 109.9(2) | 111.5(3) | 108.1(2) |
| N(4)–B(1)–N(1) | 105.2(2) | 102.7(2) | 105.3(2) |
| Y–B(2)–N(7) | 112.0(10) | 112.6(11) | 108.8(2) |
| Y–B(2)–N(2) | 109.3(10) | 108.2(12) | 113.7(2) |
| N(7)–B(2)–N(2) | 109.5(2) | 110.7(3) | 108.6(2) |
| Y–B(2)–N(3) | 111.0(10) | 109.8(2) | 113.1(2) |
| N(7)–B(2)–N(3) | 108.6(2) | 111.3(3) | 107.1(2) |
| N(2)–B(2)–N(3) | 106.2(2) | 103.8(2) | 105.3(2) |
| C(1)–N(1)–N(2) | 108.6(2) | 107.9(3) | 107.5(2) |
| C(1)–N(1)–B(1) | 129.8(2) | 133.7(3) | 126.9(2) |
| N(2)–N(1)–B(1) | 121.3(2) | 118.3(2) | 125.4(2) |
| C(3)–N(2)–N(1) | 107.8(2) | 108.3(3) | 107.5(2) |
| C(3)–N(2)–B(2) | 129.5(2) | 133.0(3) | 127.0(2) |
| N(1)–N(2)–B(2) | 122.2(1) | 118.6(3) | 125.4(2) |
| C(4)–N(3)–N(4) | 108.5(2) | 107.0(3) | 107.4(2) |
| C(4)–N(3)–B(2) | 129.3(2) | 133.8(3) | 126.9(2) |
| N(4)–N(3)–B(2) | 122.3(2) | 119.2(3) | 125.7(2) |
| C(6)–N(4)–N(3) | 107.7(2) | 108.8(3) | 107.5(2) |
| C(6)–N(4)–B(1) | 130.8(2) | 133.3(3) | 127.7(2) |
| N(3)–N(4)–B(1) | 121.0(2) | 117.8(3) | 124.3(2) |
| B–O–B′ | | | 133.6(2) |

## Conclusion

The presence of zirconium materials is known to affect the isomer distribution of 4,8-bis(pyrazolyl)pyrazaboles formed during the thermolysis of the free acid of the hydrotris(pyrazolyl)borate ion. Since the enhancement in yield of one isomer over another has at times been shown to exceed the quantity of zirconium complex present,[10] the process appears to be to some extent catalytic. If it is indeed a proximity reaction at the Zr, this would mean that the formation of a pyrazabole from two Tp ligands followed by its elimination from the co-ordination sphere of Zr is likely to be an exoergonic process with a low activation barrier, and militates against the possibility of forming stable $\{Tp_2Zr\}$-containing species.

There is only one report of complexes of Zr containing two poly(pyrazolyl)borate ligands, namely that of [$ZrX_2${B(pz)$_4$}$_2$] (X = halide).[26] However, the irreproducibility of the syntheses of these materials,[27] and the poor agreement between their spectral assignments and those made since for other poly(pyrazolyl)-

**Table 2** Crystal data and structure refinement for compounds **A**–**C**

| | **A** | **B** | **C** |
|---|---|---|---|
| Empirical formula | $C_{12}H_{14}B_2N_8$ | $C_{12}H_{14}B_2N_8$ | $C_{24}H_{24}B_4N_{16}O_2$ |
| *M* | 291.93 | 291.93 | 611.83 |
| *T*/K | 150 | 150 | 295 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_1/c$ | *Pbca* | *Pbca* |
| *a*/Å | 8.7432(11) | 12.0191(9) | 9.4165(13) |
| *b*/Å | 8.5509(9) | 10.8998(6) | 16.383(2) |
| *c*/Å | 19.423(2) | 22.799(3) | 18.6033(9) |
| *β*/° | 96.942(9) | | |
| *V*/Å$^3$ | 1441.5(3) | 2986.8(4) | 2870.0(5) |
| *Z* | 4 | 8 | 4 |
| $D_c$/Mg m$^{-3}$ | 1.345 | 1.298 | 1.416 |
| $\mu$/mm$^{-1}$ | 0.088 | 0.085 | 0.097 |
| *F*(000) | 608 | 1216 | 1264 |
| Data collected | 4162 | 10454 | 10031 |
| Independent data | 2167 | 2368 | 2264 |
| Data with $I > 2\sigma(I)$ | 1309 | 878 | 1042 |
| *R*(int), $R_\sigma$ | 0.0424, 0.2186 | 0.1104, 0.4196 | 0.1330, 0.2735 |
| Restraints/parameters | 0/255 | 0/255 | 0/257 |
| Goodness of fit on $F^2$ | 0.398 | 0.602 | 0.557 |
| *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.0312, 0.0759 | 0.0354, 0.0585 | 0.0351, 0.0559 |
| (all data) | 0.0528, 0.1040 | 0.1573, 0.0701 | 0.1165, 0.0656 |
| Peak, hole/e Å$^{-3}$ | 0.141, −0.139 | 0.181, −0.206 | 0.145, −0.166 |

borate complexes of Zr,[9,28,29] must leave the nature of "[$ZrX_2$-{$B(pz)_4$}$_2$]" open to question. If it is assumed that the existence of complexes of Zr containing two poly(pyrazolyl)borate ligands is not proven, the production of 4,8-bis(pyrazolyl)-pyrazaboles by zirconium complexes may go some way to show why this is so.

## Experimental

### Materials

The salt NaTp was prepared according to a previously described method;[30] $ZrCl_4$ was used as supplied by Aldrich Chemicals Ltd.

### Physical measurements

The FT-IR spectra were recorded as KBr dispersions using an ATI Mattson Genesis spectrometer, $^1$H NMR spectra using a JEOL JNM FX270 spectrometer and mass spectra using a Kratos MS80RF instrument. Melting points were measured in open glass capillaries and are uncorrected.

### Preparations

**HTp.** The salt NaTp (10 g, 42 mmol), was dissolved in water (100 ml). A calibrated pH electrode was inserted into the solution and aqueous 4 M HCl added dropwise until the pH had fallen to 8.0 from the initial 9.5. The precipitated HTp (2.2 g, 24%) was collected by filtration, washed well with distilled water and dried overnight in a vacuum desiccator over $H_2SO_4$ and NaOH [a further batch of HTp (*ca.* 1.5 g) can be collected down to pH 6.5, but appears prone to decomposition over several days].

**4,8-*trans*-Bis(pyrazolyl)pyrazabole (isomer A).** The compound HTp (1.02 g, 4.77 mmol) was placed in a Schlenk tube maintained with a nitrogen atmosphere. The tube was then placed into an oil-bath maintained at 110–120 °C. A mobile melt was obtained after a few minutes, and after 1 h the tube was removed and allowed to cool. The contents were dissolved in 4 M HCl (*ca.* 10 ml) and this solution was filtered and promptly made basic with concentrated $NH_3$. The initial fine precipitate coagulated after about 20 s and was collected by suction–filtration. The material **A** was recrystallised from 70 : 30 $CH_2Cl_2$–light petroleum (bp 60–80 °C) by slow evaporation (0.06 g, 9%), mp 174–176 °C (Found: C, 49.2; H, 4.8; N, 38.6. $C_6H_7BN_4$ requires C, 49.3; H, 4.8; N, 38.4%); $\tilde{\nu}_{max}$/cm$^{-1}$ 3144, 3117, 3102, 2473, 1517, 1424, 1413, 1386, 1331, 1304, 1241, 1224, 1205, 1149, 1101, 1089, 1037, 956, 786, 762, 745 and 727; $\delta_H(CDCl_3)$ 7.71, 7.56, 6.30 [2 H, d, *J*(HH) = 1.5; 2 H, d, *J*(HH) = 2.2; 2 H, t, *J*(HH) = 2.2, 1.7] (terminal pyrazolyl, assigned by decoupling), 7.58 and 6.47 [4 H, d, *J*(HH) = 2.5; 2 H, t, *J*(HH) = 2.2 Hz] (bridging pyrazolyl); *m*/*z* 291, $[M - H]^+$; 225, $[M - pz - 2H]^+$; 157, $[\{(pz)B\}_2H]^+$; and 68 $[pzH]^+$ (electron impact).

**4,8-*cis*-Bis(pyrazolyl)pyrazabole (isomer B).** The compound HTp (1.75 g, 8.18 mmol) and $ZrCl_4$ (0.78 g, 3.35 mmol) were ground thoroughly under $N_2$, mixed thoroughly and placed in a Schlenk tube maintained with a nitrogen atmosphere. The whole was heated in an oil-bath at 110–120 °C whereupon the mixture partially melted and frothed to 300% of its original volume. After 2 h it was left to cool, and the resulting hard mass ground and dissolved in 4 M HCl (*ca.* 10 ml). This was filtered to clarity and made basic with concentrated $NH_3$. The resulting precipitate was collected by suction–filtration, dried *in vacuo* and ground under $CH_2Cl_2$. The liquid was removed, filtered, and evaporated. The resulting material was recrystallised from 70 : 30 $CH_2Cl_2$–light petroleum (bp 60–80 °C) by slow evaporation (0.06 g, 5%), mp 154–155 °C (Found: C, 49.6; H, 4.7; N, 38.1. $C_6H_7BN_4$ requires C, 49.3; H, 4.8; N, 38.4%); $\tilde{\nu}_{max}$/cm$^{-1}$ 3153, 3139, 3128, 3113, 3091, 2456, 2434, 1513, 1422, 1397, 1387, 1327, 1305, 1238, 1219, 1152, 1100, 1069, 1038, 954, 778 and 745; $\delta_H(CDCl_3)$ 7.81, 6.40 [4 H, dd, *J*(HH) = 2.2, 1.4; 2 H, t, *J*(HH) = 2.2, 1.4] (terminal pyrazolyl), 7.22, 6.34 [4 H, d, *J*(HH) = 2.5; 2 H, t, *J*(HH) = 2.4 Hz] (bridging pyrazolyl); *m*/*z* 293 $[M + H]^+$; 225, $[M - pz]^+$; 79, $[(pz)BH]^+$ (FAB, 3-nitrobenzyl alcohol matrix).

**Bis(pyrazolyl)boron oxide dimer C.** Distilled water (30 μl) was placed into the bottom of a small Schlenk tube, followed by HTp (0.82 g, 3.8 mmol). Hydrogen chloride ($H_2SO_4$/NaCl generator) was passed into the tube slowly, resulting in a collapse in volume, and apparent partial liquefaction, of the contents. The flow of HCl was continued until the material had assumed a stable glossy appearance (60 min), whereafter the whole was placed in an oil-bath at 150 °C for 2 h. After this time the temperature was raised to 180 °C over 35–40 min, and then the tube allowed to cool. The contents were dissolved in water and the resulting solution was filtered and made basic with dilute $NH_3$

until the solution smelt thereof. The resulting precipitate was collected by suction–filtration, dried *in vacuo* and crystallised from 60 : 10 $CH_2Cl_2$–toluene by slow evaporation (0.14g, 20%); mp 258–261 °C. IR ($cm^{-1}$): 3149, 3126, 1506, 1411, 1386, 1210, 1149, 1101, 1027, 935, 871, 781, 757 and 642. $^1H$ NMR: $\delta(CDCl_3)$ 8.46, 7.63, 6.41 [4 H, d, $J$(HH) = 2.3; 4 H, d, $J$(HH) = 1.3; 4 H, t, $J$(HH) = 2.3, 1.3] (terminal pyrazolyl), 7.08, 6.11 [8 H, d, $J$(HH) = 2.7; 4 H, t, $J$(HH) = 2.6 Hz] (bridging pyrazolyl). Mass spectrum, *m/z* 634, $[M + Na - 1]^+$; 612, $[M + H]^+$; 545, $[M - pz]^+$; 333, $[(pz)_4B_3O_2]^+$; 239, $[(pz)_3B_2O]^+$ (or dimer) (FAB, 3-nitrobenzyl alcohol matrix) (Found: C, 44.6; H, 3.6; N, 34.7. $C_{12}H_{12}B_2N_8O$ requires C, 47.1; H, 4.0; N, 36.6%).

### Crystallography

Data were collected on a FAST TV Area detector diffractometer ($\lambda = 0.71069$Å), following previously described procedures.[31] Systematic absences indicated the appropriate space groups, given a 'data rotation' for compound **B** (transformation matrix [0 1 0 1 0 0 0 0 1]). The positions of most non-H atoms were estimated by direct methods,[32] and all other atoms were found from subsequent Fourier difference syntheses interspersed with full-matrix least-squares refinement[33] cycles based on merged data. Non-H atoms were refined anisotropically, and H atoms isotropically with no restraints on positional or displacement parameters. The data were corrected[34] for absorption effects based on these converged models and refinement resumed to convergence giving satisfactory structures in all cases.

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See http://www.rsc.org/suppdata/dt/1999/401/ for crystallographic files in .cif format.

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