# 1,5-Diphenyl-4,8-bis(3-phenylpyrazol-1-yl)pyrazabole

## Fábio A. Kunrath,[a] Osvaldo L. Casagrande,[b] Loïc Toupet[c]* and Jean-François Carpentier[d]

[a]Instituto de Química de Araraquara, UNESP, CP 355, Araraquara SP, 14800-900, Brazil, [b]Laboratório de Catálise Molecular, Instituto de Química, Universidad Federal do Rio Grande do Sul, Avenida Bento Goncalves 9500, Porto Alegre RS, 90501-970, Brazil, [c]Groupe Matière Condensée et Matériaux, UMR 6626, CNRS, Université de Rennes I, Campus de Beaulieu, 35042 Rennes Cedex, France, and [d]Laboratoire Organométalliques et Catalyse, UMR 6509, CNRS, Université de Rennes 1, 35042 Rennes Cedex, France

Correspondence e-mail: loic.toupet@univ-rennes1.fr

The six-membered $B_2H_4$ ring of the title compound, $C_{36}H_{30}B_2N_8$, adopts a slightly distorted boat conformation, with the terminal B substituents in a *trans* orientation. One 3-phenylpyrazolyl group is in an equatorial position, whereas the second is in an axial position with respect to the plane defined by the B atoms.

## Comment

First introduced by Trofimenko (1967), pyrazaboles constitutes a unique class of heterocyclic compounds containing a B—N bond, mainly due to their high chemical and thermal stability (Trofimenko, 1999). In recent decades, a series of pyrazaboles have been reported in the literature (Niedenzu, 1988), and have been used as building blocks for discotic liquid crystals (Barberá *et al.*, 1994) and as bridges for ansa-ferrocenes to form active container molecules for supramolecular applications (Jäkle *et al.*, 1996; Herdtweck *et al.*, 1996). The structural characterization of these compounds has become an important tool for defining their conformational structures in the solid state. Fig. 1 shows the possible conformations of pyrazaboles.

Most of the pyrazabole derivatives which have been structurally characterized to date are related to symmetrical pyrazaboles, $R_2B(\mu\text{-pz})_2BR_2$ ($R$ = H, Et, Pz, Ph, F or Br, and pz = pyrazol-1-yl) (Barberá *et al.*, 2000; Clarke *et al.*, 1987; Hanecker *et al.*, 1985; Atwood *et al.*, 1992) or $R^1RB(\mu\text{-pz})_2$-$BRR^1$ ($R$ = Et or Ph, and $R^1$ = Pz or Br) (Niedenzu & Nöth, 1983; Bielawski *et al.*, 1986), and asymmetrical pyrazaboles, such as $R_2B(\mu\text{-pz})_2BR^1_2$ ($R$ = H or Cl, and $R^1$ = Pz or Ph) (Clarke *et al.*, 1987) or $R_2B(\mu\text{-pz})_2BR^1R^2$ ($R$ = H, $R^1$ = H, and $R^2$ = Br) (Hodgkins & Powell, 1992; Brock *et al.*, 1985). On the other hand, although several papers report the synthesis and

spectroscopic characterization of symmetrical disubstituted 4,8-bis(pyrazolyl-1-yl)pyrazaboles, $H(Pz')B(\mu\text{-pz})_2B(Pz')H$ ($Pz'$ = pyrazol-1-yl or 3,5-dimethylpyrazol-1-yl) (Trofimenko, 1967; Blosch *et al.*, 1992), only the structural characterization of $H(Pz)B(\mu\text{-pz})_2B(Pz)H$ ($Pz$ = pyrazol-1-yl), (II), has been described to date (Kresinski, 1999). Here, we describe the crystal and molecular structure of the novel $H(Pz')B(\mu\text{-pz})_2$-$zB(Pz')H$ compound ($Pz'$ = 3-phenylpyrazol-1-yl), (I). Selected bond distances and angles are listed in Table 1.
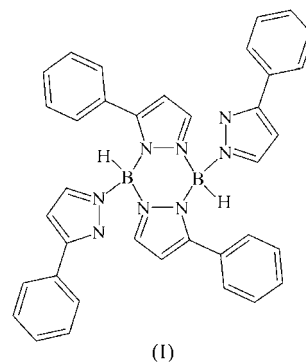


(I)

Fig. 2 shows that the six-membered $B_2N_4$ ring adopts a slightly distorted boat conformation, with the terminal B substituents in a *trans* orientation. The B atoms are tetra-coordinated, as confirmed by the almost ideal $sp^3$-hybridization sphere around them. The two terminal pyrazolyl groups (at the 4- and 8-positions) occupy one axial position and one equatorial position. The dihedral angles between the least-squares plane through the four central atoms of the ring (N1,
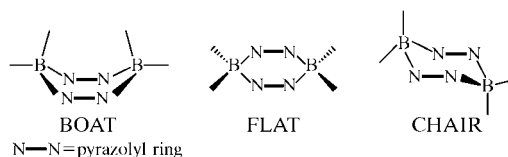
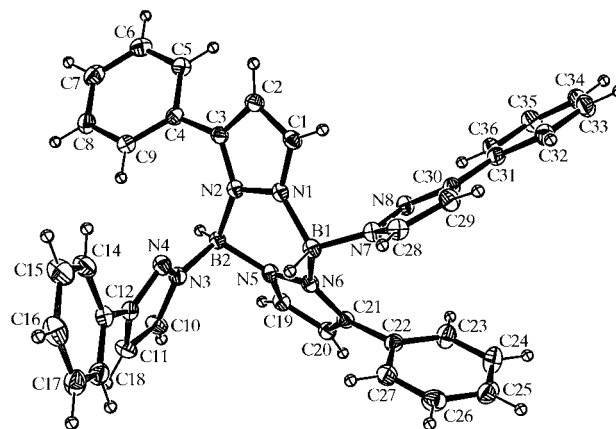

**Figure 1**
Possible conformations of pyrazaboles.



**Figure 2**
A view of the molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

# organic compounds

N2, N5 and N6) and the N2/B2/N5 and N1/B1/N6 planes are 32.42 (2) and 24.11 (2)°, respectively. The B—N [average B—N = 1.550 Å, range 1.513 (2)–1.571 (2) Å] and N—N [average N—N = 1.367 Å, range 1.3633 (17)–1.3708 (18) Å] bond distances are comparable with those found in related compound (II) (average B—N = 1.541 Å and average N—N = 1.360 Å; Kresinski, 1999). In contrast with what is observed in (II), the B—H bond distances in the pseudo-equatorial (pe) and pseudo-axial (pa) positions of (I) are very similar [B—H$_{pe}$ = 1.12 (2) Å and B—H$_{pa}$ = 1.13 (2) Å], suggesting that the negative charges on the H atoms are equally distributed. One of the four 3-phenylpyrazolyl groups features the pyrazolyl and the phenyl rings in a coplanar orientation (torsion angle N8—C30—C31—C36 = −1.98°), while the others display torsion angles ranging from 34.55 to 60.33°.

The overall structure of (I) is extended through self-complementary C—H···N hydrogen bonds that involve the bridging pyrazolyl group (C19—H19) of one molecule and an N atom (N8) of the terminal pyrazolyl unit of a second molecule. As shown in Fig. 3, this results in the formation of a dimer, with the pyrazabole rings in a mirror-like array across the centre of symmetry. The intermolecular C19—H19···N8 contacts of 2.60 Å (Table 2) are within the sum of the van der Waals radii for H and N atoms (2.75 Å; Kresinski, 1999) and are longer than the C—H···N contacts [2.41 (2) and 2.52 (2) Å for the two independent molecules] observed in related pyrazabole compound (II) which has no phenyl substituent on the pyrazolyl rings (Kresinski, 1999). Steric crowding induced by the phenyl substituents most likely accounts for the longer C—H···N contacts in (I).

Despite the presence of many aromatic rings in (I), i.e. the four phenyl substituents and the four pyrazolyl rings, only minimal π–π interactions are observed, which involve the C22–C27 phenyl ring and the N7–N8 pyrazolyl ring (Fig. 3). These observations suggest that the overall distorted-boat conformation of 4,8-disubstituted pyrazaboles, in particular the presence of pseudo-equatorial and pseudo-axial substituents, is mainly governed by the aforementioned C—H···N interactions.

## Experimental

The title compound was obtained as a co-product from the reaction of anhydrous YCl$_3$ (0.25 g, 1.28 mmol) and potassium hydrotris(3-phenylpyrazolyl)borate (KTp$^{ph}$) (0.61 g, 1.28 mmol) in tetrahydrofuran. The mixture was stirred at 293 K for 7 d, over which time the amount of insoluble material decreased. Volatiles were removed under vacuum and the residue was extracted with toluene (2 × 20 ml). The resulting colourless filtrate was evaporated under vacuum and the residue washed with pentane. Crystals of (I) suitable for X-ray diffraction were grown from a 1:2 toluene–pentane solution at 239 K.

### Crystal data

| | |
|---|---|
| C$_{36}$H$_{30}$B$_2$N$_8$ | $D_x$ = 1.294 Mg m$^{-3}$ |
| $M_r$ = 596.30 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 7153 |
| $a$ = 11.3980 (2) Å | reflections |
| $b$ = 22.6068 (4) Å | $\theta$ = 1.0–27.5° |
| $c$ = 13.1547 (2) Å | $\mu$ = 0.08 mm$^{-1}$ |
| $\beta$ = 115.4290 (10)° | $T$ = 120 (1) K |
| $V$ = 3061.21 (9) Å$^3$ | Prism, colourless |
| $Z$ = 4 | 0.20 × 0.18 × 0.10 mm |

### Data collection

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | $\theta_{max}$ = 27.5° |
| | $h$ = 0 → 14 |
| $\omega$ scans (1.4°) | $k$ = 0 → 29 |
| 6995 measured reflections | $l$ = −17 → 15 |
| 6995 independent reflections | |
| 5037 reflections with $I > 2\sigma(I)$ | |



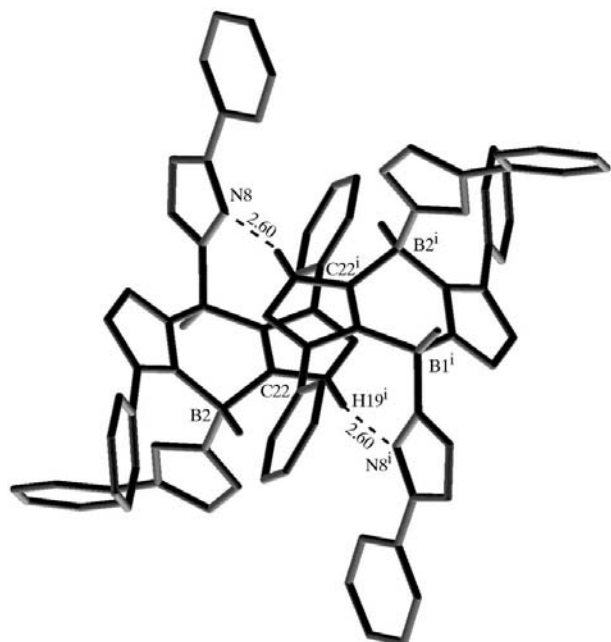**Figure 3**
A view of (I), showing the dimeric aspect of the structure [symmetry code: (i) 1 − x, −y, 1 − z]. Distances are given in Å.

**Table 1**
Selected geometric parameters (Å, °).

| N1—C1 | 1.3403 (19) | N6—B1 | 1.571 (2) |
|---|---|---|---|
| N1—N2 | 1.3677 (17) | N7—C28 | 1.356 (2) |
| N1—B1 | 1.567 (2) | N7—N8 | 1.3708 (18) |
| N2—C3 | 1.360 (2) | N7—B1 | 1.513 (2) |
| N2—B2 | 1.539 (2) | N8—C30 | 1.3420 (19) |
| N3—C10 | 1.351 (2) | C1—C2 | 1.378 (2) |
| N3—N4 | 1.3657 (17) | C2—C3 | 1.389 (2) |
| N3—B2 | 1.542 (2) | C10—C11 | 1.362 (2) |
| N4—C12 | 1.342 (2) | C11—C12 | 1.404 (2) |
| N5—C19 | 1.3441 (19) | C19—C20 | 1.381 (2) |
| N5—N6 | 1.3633 (17) | C20—C21 | 1.390 (2) |
| N5—B2 | 1.571 (2) | C28—C29 | 1.362 (2) |
| N6—C21 | 1.3550 (19) | C29—C30 | 1.411 (2) |
| | | | |
| C1—N1—N2 | 108.33 (12) | C21—N6—N5 | 108.44 (12) |
| C1—N1—B1 | 126.86 (13) | C21—N6—B1 | 131.37 (13) |
| N2—N1—B1 | 124.80 (12) | N5—N6—B1 | 119.88 (12) |
| C3—N2—N1 | 108.14 (12) | C28—N7—N8 | 110.41 (12) |
| C3—N2—B2 | 132.66 (13) | C28—N7—B1 | 126.45 (13) |
| N1—N2—B2 | 118.83 (12) | N8—N7—B1 | 121.68 (12) |
| C10—N3—N4 | 110.24 (12) | C30—N8—N7 | 105.42 (12) |
| C10—N3—B2 | 125.39 (13) | N1—C1—C2 | 109.27 (14) |
| N4—N3—B2 | 124.08 (12) | C1—C2—C3 | 106.17 (14) |
| C12—N4—N3 | 105.34 (12) | C10—C11—C12 | 104.60 (14) |
| C19—N5—N6 | 108.47 (12) | C19—C20—C21 | 106.28 (13) |
| C19—N5—B2 | 128.48 (13) | C28—C29—C30 | 104.99 (14) |
| N6—N5—B2 | 122.34 (12) | | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0684P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | $+ 0.647P]$ |
| $wR(F^2) = 0.131$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.05$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 6995 reflections | $\Delta\rho_{max} = 0.22$ e Å$^{-3}$ |
| 422 parameters | $\Delta\rho_{min} = -0.27$ e Å$^{-3}$ |
| H atoms treated by a mixture of | Extinction correction: *SHELXL97* |
| independent and constrained | (Sheldrick, 1997) |
| refinement | Extinction coefficient: 0.0085 (9) |

## Table 2
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| C19—H19⋯N8$^i$ | 0.93 | 2.60 | 3.489 (2) | 160 |

Symmetry code: (i) $1 - x, -y, 1 - z$.

All H atoms were located in a difference Fourier synthesis, but those attached to C atoms were treated as riding on their parent C atoms, with C—H = 0.93 Å and $U_{iso}$(H) = $1.2U_{eq}$(C). H atoms attached to B atoms were freely refined with a fixed $U_{iso}$ value.

Data collection: *KappaCCD Server Software* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

## References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1998). *J. Appl. Cryst.* **31**, 74–77.

Atwood, V. O., Atwood, D. A., Cowley, A. H. & Trofimenko, S. (1992). *Polyhedron*, **11**, 711–714.

Barberá, J., Giménez, R. & Serrano, J. L. (1994). *Adv. Mater.* **6**, 470–476.

Barberá, J., Giménez, R. & Serrano, J. L. (2000). *Chem. Mater.* **12**, 481–489.

Bielawski, J., Hanecker, M. K., Das, E., Niedenzu, K. & Nöth, H. (1986). *Inorg. Chem.* **25**, 4623–4628.

Blosch, L. L., Gamble, A. S., Abboud, K. & Boncella, J. M. (1992). *Organometallics*, **11**, 2342–2344.

Brock, C. P., Niedenzu, K., Hanecker, E. & Nöth, H. (1985). *Acta Cryst.* C**41**, 1458–1463.

Clarke, C. A., Mariategui, J. F., Bielawski, J., Hanecker, M. K., Das, E., Niedenzu, K., Niedenzu, P. M., Nöth, H. & Warnert, K. R. (1987). *Inorg. Chem.* **26**, 2310–2317.

Hanecker, E., Hodgkins, T. G., Niedenzu, K. & Nöth, H. (1985). *Inorg. Chem.* **24**, 459–462.

Herdtweck, E., Jäkle, F., Opromolla, G., Spiegler, M., Wagner, M. & Zanello, P. (1996). *Organometallics*, **15**, 5524–5535.

Hodgkins, G. T. & Powell, D. R. (1992). *Acta Cryst.* C**48**, 1260–1262.

Jäkle, F., Priermeier, T. & Wagner, M. (1996). *Organometallics*, **15**, 2033–2040.

Kresinski, R. A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 401–405.

Niedenzu, K. (1988). *Adv. Boron Boranes*, **5**, 357–372.

Niedenzu, K. & Nöth, H. (1983). *Chem. Ber.* **116**, 1132–1135.

Nonius (1999). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 3165–3170.

Trofimenko, S. (1999). *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*. London: Imperial College Press.