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A theoretical multinuclear NMR study of pyrazolylborates*

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Abstract

The experimental chemical shifts and coupling constants of five borates of general formula BH_nPz_{4-n} [from the borohydride to tetrakis(pyrazol-1-yl)borate] anions were compared with calculations carried out at the B3LYP/6-311++G(d,p) level (GIAO for absolute shieldings), in general with satisfying results. The most stable conformations of pyrazolylborate anions are similar to those of neutral pyrazolylmethanes.

Keywords: B3LYP/6-311++G(d,p); coupling constants; GIAO; NMR; pyrazolylborates; pyrazolylmethanes.

Introduction

Pyrazolylborates are fascinating molecules that formally originate from the borohydride anion (tetrahydroborate) (**1** in Figure 1) replacing up to four H atoms for pyrazol-1-yl rings (Trofimenko, 1999). When the number of pyrazoles is 3, like in **4**, these compounds are named scorpionates (Pettinari, 2008). Tris(pyrazolyl)borates and their analogues can be considered as the tripodal equivalent of cyclopentadiene ligands and have been used in catalysis, bioinorganic models systems, metal extraction, and biomedicine.

Discovered by Swiatoslaw Trofimenko (1966) they enjoyed an enormous success as ligands in coordination chemistry. Alone or in collaboration with Trofimenko we have devoted several papers to these compounds (Aubagnac et al., 1991; López et al., 1994; Aubagnac et al., 1995; López et al., 1995; Janiak et al. 1996; Sanz et al., 1996; Claramunt et al., 2004a,b; Santa María et al., 2007; Trofimenko et al., 2007). One of the most significant of our contributions was entitled 'Structure of bis-, tris- and tetrakispyrazolylborates in the solid state (X-ray crystallography) and in solution' (López et al., 1990). On the other hand, we have been interested in the *ab initio* calculation of NMR properties, chemical shifts (Alkorta and Elguero, 1998; Alkorta et al., 2010a) and coupling constants (Alkorta and Elguero, 2003a, 2010b) for several years. A natural extension of this work was to calculate the conformations of minimum energy as well as the chemical shifts and coupling constants reported in (López et al., 1990). This paper concerns the five compounds of Figure 1.

Results and discussion

Only the X-ray structure of tetrakis(pyrazol-1-yl)borate (**5**) has been determined (sodium and potassium salts) (López et al., 1990). For all of them, we have calculated the minimum energy conformations. The calculations were carried out at the B3LYP/6-311++G(d,p) level verifying in all cases that the structures were minima (number of imaginary frequencies=0). On these geometries we calculated the absolute shieldings (σ, ppm, within the GIAO approximation) and the coupling constants (*J*, Hz) (see Computational details). B3LYP/6-311++G(d,p) calculations yield acceptable results for computed NMR properties (Alkorta and Elguero, 1998, 2003a,b; Alkorta et al., 2009, 2010a; Jacob et al., 2010).

It appears that no conformational analysis has been carried out on polypyrazolylborates (**3**, **4** and **5** and their C-substituted derivatives) while the conformation of their metal complexes have been widely examined (Trofimenko, 1971; Calderon et al., 1972; DaCruz and Zimmer, 1998; De Bari and Zimmer, 2004; Agrifoglio and Capparelli, 2005; Fraser et al., 2007; Mutseneck et al., 2010).

Conformational analysis

We carried out theoretical studies (MM2 and MNDO) of the conformational analysis of bis, tris and tetrakis(pyrazol-1-yl)methanes, related to the compounds of this work but with a central C atom instead of a B^- one (Claramunt et al., 1989). We also studied, at B3LYP/6-31G(d) computational level, the conformational space of tris(2-methylbenzimidazol-1-yl)methane, a compound related to **4** (Alkorta and Elguero, 2010c). In Table 1 are the energies associated with the different minima and in Figure 2 the corresponding geometries; to characterise the geometries we have used the same torsion angles (ϕ_A, ϕ_B,....) defined in our pyrazolylmethanes paper (Claramunt et al., 1989).

It is interesting to compare the minima found in the XH_nPz_{4-n} series (n=0–4) with X=B^- (Figure 1) and C (Figure 3) both calculated at the B3LYP/6-311++G(d,p) level.

For n=4, tetrahydroborate or borohydride (**1**) and methane (**1′**), there is a single minimum in both cases with T_d symmetry.

For n=3, (pyrazol-1-yl)trihydroborate (**2**) and 1-methylpyrazole (**2′**), there is a single minimum in both cases

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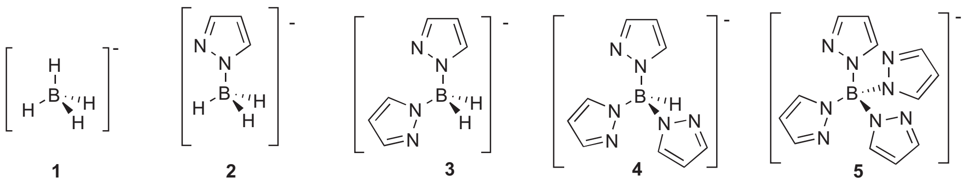
* Dedicated to Professor C. Foces-Foces on his untimely death on December 2010.



1 2 3 4 5

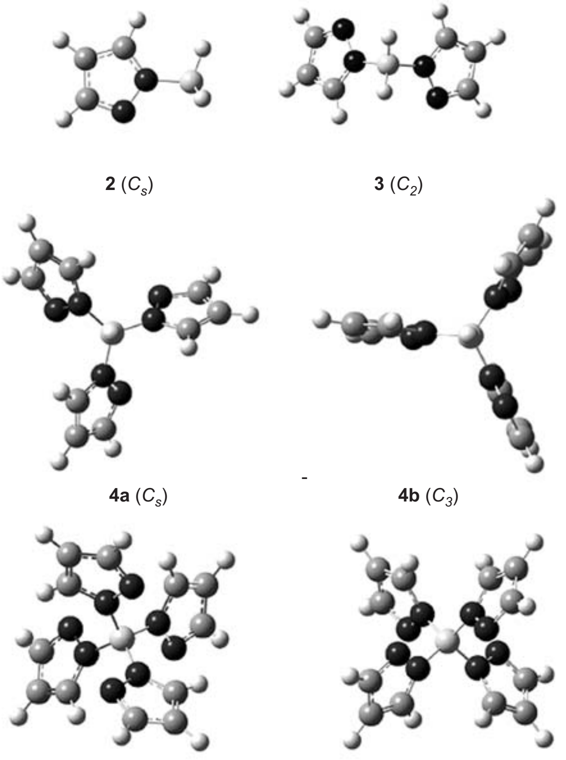
Figure 1 Borohydride and pyrazolylborate anions.

Table 1 Energies at B3LYP/6-311++G(d,p) computational level (absolute values in hartrees and relative values in kJ/mol; dipole moments in D).

Compound	SG	SCF energy	Dipole	E_{rel}	ϕ_A	ϕ_B	ϕ_C	ϕ_D
1	T_d	-27.27523	0.00	–	–	–	–	–
2	C_s	-252.39670	6.57	–	180.0	60.6	-60.6	–
3	C_2	-477.51386	2.48	–	83.6	83.6	–	–
4a	C_s	-702.61929	1.81	0.0	98.9	-143.4	-25.8	–
4b	C_3	-702.61172	2.77	19.9	117.9	-172.8	53.9	–
5a	S_4	-927.72243	0.00	0.0	-54.0	54.0	-54.0	54.0
5b	D_2	-927.70916	0.00	34.8	80.4	80.4	80.4	80.4

(**2** and **2′**) with C_s symmetry. Both minima have a similar disposition.

For n=2, X=C, **3′** has two minima, while for X=B, **3** [bishydridobis(pyrazol-1-yl)borate] has only one minimum of C_2 symmetry. The most stable minimum for X=C has C_2 symmetry, the second minimum C_1 (E_{rel} 12.7 kJ/mol) is less stable. Since the B-N bond is longer than the C-N bond in these compounds [1.54 Å vs. 1.44 Å (Claramunt et al., 1989)], the second minimum found for **3′** corresponds to a transition state, TS, in **3**.



2 (C_s) **3** (C_2)

4a (C_s) **4b** (C_3)

5a (S_4) **5b** (D_2)

Figure 2 Minimum energy conformations of pyrazolylborates.

For n=1, hydrotris(pyrazol-1-yl)borate (**4**) and the corresponding methane derivative (**4′**), two minima have been calculated in both families. The most stable one has C_s symmetry for X=B and C_1 (but actually is similar to the previous one) for X=C. The second minimum has C_3 symmetry in both families with E_{rel} 19.9 and 26.4 kJ/mol for X=B and C, respectively.

Finally, for n=0, tetrakis(pyrazol-1-yl)borate (**5**) and the corresponding methane derivative (**5′**), two minima have been located in both families having S_4 and D_2 symmetries, S_4 being always the most stable and the E_{rel} of the D_2 is 34.8 and 32.6 kJ/mol for X=B and C, respectively. Note that for **5** the X-ray structures (Na$^+$ and K$^+$ salts) (López et al., 1990) [reported in the Cambridge Structural Database with the refcode KILZEK (Allen, 2002a; Allen and Motherwell, 2002b)] are very different from the calculated ones; this is due to the pincer effect (two alkali cation linking two pyrazoles).

Qualitatively, the results concerning the pyrazolylmethanes (series') are in agreement with those obtained at the MNDO level (Claramunt et al., 1989).

NMR studies

Experimental results are reported in Tables 2 and 3 and calculated ones in Tables 4 and 5.

Calculated absolute shieldings (Table 4)

Examining the data of Table 4 it appears that many σ values vary with the number of pyrazoles in a smooth manner (compounds **2–5**). When two conformations are available (**4a/4b** and **5a/5b**), **4b** and **5a** are much better than the two other ones. This has nothing to do with the energy nor with any

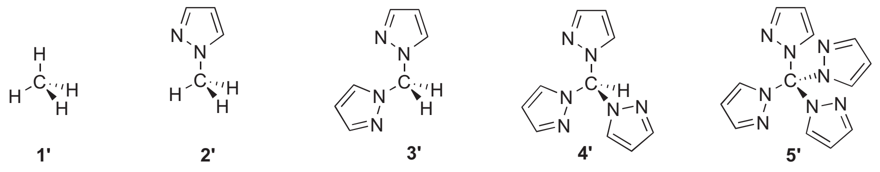
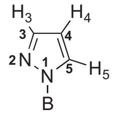


Figure 3 Methane and pyrazolylmethanes.

Table 2 Experimental chemical shifts (δ, ppm) [from reference (López et al., 1990) unless indicated otherwise].

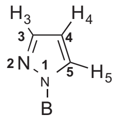


Compound	^{1}H	^{11}B	^{13}C	^{15}N
BH$_4^-$ (**1**)	-0.5[a]	-36.0[a]	–	–
PzBH$_3^-$ (**2**)	–	-9.9[b]	140.8 (C3)[b] 104.9 (C4)[b] 137.2 (C5)[b]	-132.0 (N1)[b] -71.9 (N2)[b]
Pz$_2$BH$_2^-$ (**3**)	4.0 (BH$_2$) 7.54 (H$_3$) 6.25 (H$_4$) 7.67 (H$_5$)	-6.54	141.3 (C3) 105.6 (C4) 137.1 (C5)	-137.3 (N1) -70.4 (N2)
Pz$_3$BH$^-$ (**4**)	5.5 (BH) 7.36 (H$_3$) 6.05 (H$_4$) 7.39 (H$_5$)	-0.90	141.9 (C3) 106.0 (C4) 135.7 (C5)	-141.9 (N1) -68.8 (N2)
Pz$_4$B$^-$ (**5**)	7.65 (H$_3$) 6.08 (H$_4$) 7.18 (H$_5$)	1.35	142.3 (C3) 106.9 (C4) 136.3 (C5)	-147.5 (N1) -77.3 (N2)

[a] Taken from (Fijalkowski and Grochala, 2009).

[b] Estimated values using an empirical model and the values for compounds **3**–**5** (López et al., 1990).

Table 4 Calculated absolute shielding (σ, ppm).



Compound	^{1}H	^{11}B	^{13}C	^{15}N
BH$_4^-$ (**1**)	32.12	154.17	–	–
PzBH$_3^-$ (**2**)	29.17 (BH$_3$) 24.76 (H$_3$) 26.30 (H$_4$) 24.52 (H$_5$)	124.54	44.72 (C3) 84.30 (C4) 46.22 (C5)	-32.30 (N1) -104.98 (N2)
Pz$_2$BH$_2^-$ (**3**)	27.95 (BH$_2$) 24.77 (H$_3$) 26.20 (H$_4$) 24.18 (H$_5$)	111.17	43.04 (C3) 81.53 (C4) 44.84 (C5)	-27.64 (N1) -101.45 (N2)
Pz$_3$BH$^-$ (**4a**)	26.53 (BH) 24.68 (H$_3$) 26.00 (H$_4$) 24.43 (H$_5$)	105.38	43.14 (C3) 79.54 (C4) 47.11 (C5)	-14.83 (N1) -102.12 (N2)
Pz$_3$BH$^-$ (**4b**)	26.85 (BH) 24.68 (H$_3$) 26.10 (H$_4$) 23.52 (H$_5$)	105.43	42.35 (C3) 80.74 (C4) 44.36 (C5)	-18.05 (N1) -97.73 (N2)
Pz$_4$B$^-$ (**5a**)	24.61 (H$_3$) 26.02 (H$_4$) 24.24 (H$_5$)	103.55	40.77 (C3) 80.01 (C4) 42.33 (C5)	-10.34 (N1) -94.99 (N2)
Pz$_4$B$^-$ (**5b**)	24.64 (H$_3$) 26.08 (H$_4$) 23.90 (H$_5$)	102.82	41.41 (C3) 79.54 (C4) 44.53 (C5)	-8.94 (N1) -101.81 (N2)

Table 3 Experimental coupling constants (*J*, Hz) [from reference (López et al., 1990) unless signaled].

BH$_4^-$ (**1**)	^1J(BH)=83 (Fijalkowski and Grochala, 2009), ^1J(BH)=81.0 (Ruman et al., 2007)
PzBH$_3^-$ (**2**)	$^1J(C_3H_3)$=180.7*, $^1J(C_4H_4)$=174.2*, $^1J(C_5H_5)$=182.8*, $^3J(H_3H_4)/^3J(H_4H_5)$=0.83*
Pz$_2$BH$_2^-$ (**3**)	^1J(BH)=100, ^1J(BH)=96 (Trofimenko, 1967), $^3J(H_3H_4)$=1.7, $^3J(H_4H_5)$=2.1, $^4J(H_3H_5)$=0.65, $^1J(C_3H_3)$=181.8, $^2J(C_3H_4)$=7.15, $^3J(C_3H_5)$=7.15, $^1J(C_4H_4)$=174.9, $^2J(C_4H_3)$=10.3, $^2J(C_4H_5)$=10.3, $^1J(C_5H_5)$=183.9, $^3J(N_1H_3)$=6.7, $^3J(N_1H_4)$=6.7, $^2J(N_2H_3)$=12.8
Pz$_3$BH$^-$ (**4**)	^1J(BH)=105 (Trofimenko, 1967), $^3J(H_3H_4)$=1.65, $^3J(H_4H_5)$=2.2, $^1J(C_3H_3)$=182.55, $^2J(C_3H_4)$=7.2, $^3J(C_3H_5)$=7.2, $^1J(C_4H_4)$=175.85, $^2J(C_4H_3)$=10.15, $^2J(C_4H_5)$=10.15, $^1J(C_5H_5)$=186.1, $^2J(C_5H_4)$=6.8, $^3J(C_5H_3)$=4.4, $^3J(C^5\text{-N-B-H})$=2.4, $^3J(N_1H_3)$=7.7, $^3J(N_1H_4)$=7.7, $^2J(N_2H_3)$=13.0
Pz$_4$B$^-$ (**5**)	$^4J(BH_4)$=0.9, $^3J(H_3H_4)$=1.7, $^3J(H_4H_5)$=2.3, $^1J(C_3H_3)$=183.8, $^3J(C_3B)$=2.9, $^1J(C_4H_4)$=176.4, $^2J(C_4H_3)$=10.1**, $^2J(C_4H_5)$=9.7**, $^3J(C_4B)$=1.7, $^1J(C_5H_5)$=186.7, $^2J(C_5B)$=3.5, $^1J(N_1B)$=30.0, $^3J(N_1H_3)$=6.0, $^3J(N_1H_4)$=5.5, $^2J(N_1H_5)$=5.5, $^2J(N_2H_3)$=13.4

All couplings involving boron refer to ^{11}B.

*Estimated values using an empirical model and the values for compounds **3**–**5** (López et al., 1990); **unassigned.

Table 5 Calculated coupling constants (J, Hz) corresponding to those of Table 3.

BH_4^- (**1**)	$^{1}J(BH)=78.8$
$PzBH_3^-$ (**2**)	$^{1}J(C_3H_3)=165.1$, $^{1}J(C_4H_4)=156.8$, $^{1}J(C_5H_5)=170.3$, $^{3}J(H_3H_4)/^{3}J(H_4H_5)= 0.79$
$Pz_2BH_2^-$ (**3**)	$^{1}J(BH)=97.4$, $^{3}J(H_3H_4)=1.05$, $^{3}J(H_4H_5)=1.54$, $^{4}J(H_3H_5)=0.13$, $^{1}J(C_3H_3)=166.5$, $^{2}J(C_3H_4)=6.5$, $^{3}J(C_3H_5)=7.0$, $^{3}J(C_3B)=3.1$, $^{1}J(C_4H_4)=158.3$, $^{2}J(C_4H_3)=11.8$, $^{2}J(C_4H_5)=9.6$, $^{1}J(C_5H_5)=178.6$, $^{3}J(N_1H_3)=4.5$, $^{3}J(N_1H_4)=2.8$, $^{2}J(N_2H_3)=9.0$
Pz_3BH^- (**4a**)	$^{1}J(BH)=98.0$, $^{3}J(H_3H_4)=1.03$, $^{3}J(H_4H_5)=1.68$, $^{1}J(C_3H_3)=169.2$, $^{2}J(C_3H_4)=6.4$, $^{3}J(C_3H_5)=7.0$, $^{3}J(C_3B)=3.2$, $^{1}J(C_4H_4)=159.1$, $^{2}J(C_4H_3)= 11.8$, $^{2}J(C_4H_5)=9.6$, $^{1}J(C_5H_5)=170.7$, $^{2}J(C_5H_4)=8.7$, $^{3}J(C_5H_3)=4.0$, $^{3}J(C^5\text{-N-B-H})=2.6$, $^{3}J(N_1H_3)=4.5$, $^{3}J(N_1H_4)=2.6$, $^{2}J(N_2H_3)=9.0$
Pz_3BH^- (**4b**)	$^{1}J(BH)=102.5$, $^{3}J(H_3H_4)=1.06$, $^{3}J(H_4H_5)=1.69$, $^{1}J(C_3H_3)=170.3$, $^{2}J(C_3H_4)=6.6$, $^{3}J(C_3H_5)=7.1$, $^{3}J(C_3B)=2.3$, $^{1}J(C_4H_4)=159.4$, $^{2}J(C_4H_3)=11.6$, $^{2}J(C_4H_5)=10.2$, $^{1}J(C_5H_5)=174.8$, $^{2}J(C_5H_4)=8.8$, $^{3}J(C_5H_3)$ $=3.8$, $^{3}J(C^5\text{-N-B-H})=5.4$, $^{3}J(N_1H_3)=4.4$, $^{3}J(N_1H_4)=2.6$, $^{2}J(N_2H_3)=8.9$
Pz_4B^- (**5a**)	$^{4}J(BH_4)=0.5$, $^{3}J(H_3H_4)=1.04$, $^{3}J(H_4H_5)=1.94$, $^{1}J(C_3H_3)=168.8$, $^{3}J(C_3B)=3.8$, $^{1}J(C_4H_4)=160.6$, $^{2}J(C_4H_3)=11.4$, $^{2}J(C_4H_5)=9.8$, $^{3}J(C_4B)=1.9$, $^{1}J(C_5H_5)=178.6$, $^{2}J(C_5B)=3.8$, $^{1}J(N_1B)=20.2$, $^{3}J(N_1H_3)=4.5$, $^{3}J(N_1H_4)=2.8$, $^{2}J(N_1H_5)=3.6$, $^{2}J(N_2H_3)=9.0$
Pz_4B^- (**5b**)	$^{4}J(BH_4)=0.4$, $^{3}J(H_3H_4)=1.02$, $^{3}J(H_4H_5)=1.90$, $^{1}J(C_3H_3)=169.4$, $^{3}J(C_3B)=2.7$, $^{1}J(C_4H_4)=160.4$, $^{2}J(C_4H_3)=11.7$, $^{2}J(C_4H_5)=9.5$, $^{3}J(C_4B)=1.8$, $^{1}J(C_5H_5)=175.6$, $^{2}J(C_5B)=3.8$, $^{1}J(N_1B)=20.2$, $^{3}J(N_1H_3)=4.6$, $^{3}J(N_1H_4)=2.7$, $^{2}J(N_1H_5)=3.8$, $^{2}J(N_2H_3)=9.2$

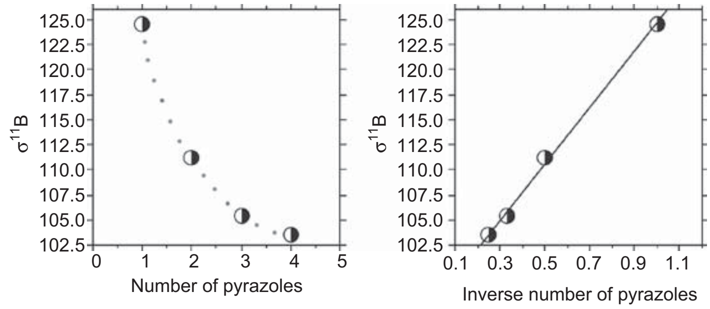


Figure 4 The trendline of the figure on the right corresponds to: $\sigma^{11}B=(96.5\pm0.5)+(28.2\pm0.9)$ 1/no. of pyrazoles, n=4, $R^2=0.998$ [eq. 3].

experimental data but with a consistent way to introduce successively pyrazole rings on the boron atom.

For instance, the central boron atom shows a curvilinear variation (Figure 4, left) that can be transformed into a linear one by using 1/number of pyrazoles. A similar variation was observed with the absolute shielding of the ^{1}H of BH: $\sigma^{1}H=(24.8\pm0.9)+(1.7\pm0.3)$ no. of H atoms, n=4, $R^2=0.936$ [eq. 1]. The correlation coefficient is not very good because the relation was curvilinear; a better agreement is obtained using the square of the number of H atoms: $\sigma^{1}H=(26.4\pm0.3)+(0.34\pm0.03)$ no. of H atoms^2, n=4, $R^2=0.988$ [eq. 2].

The same happens with the ^{13}C absolute shieldings (Figure 5). The absolute shieldings of C4 show a curvature that fit better with $\sigma^{13}C=(78.7\pm0.1)+(5.6\pm0.2)$ 1/no. of pyrazoles, n=4, $R^2=0.997$ [eq. 4]. Since the slopes of Figure 3 are very similar it is possible to adjust all the data to $\sigma^{13}C=-(1.3\pm0.1)$ no. of pyrazoles$+(45.9\pm0.4)$C3$+(84.8\pm0.4)$C4$+(47.6\pm0.4)$C5, n=12, $R^2=1.00$ [eq. 5].

When ^{15}N absolute shieldings were considered it appears that **4b** and **5a** fit much better than **4a** and **5b** the correlation with the number of pyrazoles (Figure 6).

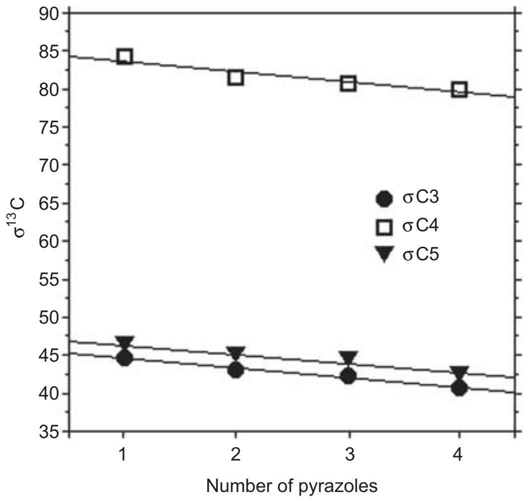


Figure 5 Plot of $\sigma^{13}C$ vs. the number of pyrazoles.
The trendlines of the figure are: C3, $\sigma^{13}C=(45.9\pm0.4)-(1.3\pm0.1)$ no. of pyrazoles, n=4, $R^2=0.978$ [eq. 6]; C4, $\sigma^{13}C=(85.0\pm1.0)-(1.4\pm0.4)$ no. of pyrazoles, n=4, $R^2=0.884$ [eq. 7]; C5, $\sigma^{13}C=(47.5\pm0.6)-(1.2\pm0.2)$ no. of pyrazoles, n=4, $R^2=0.948$ [eq. 8].

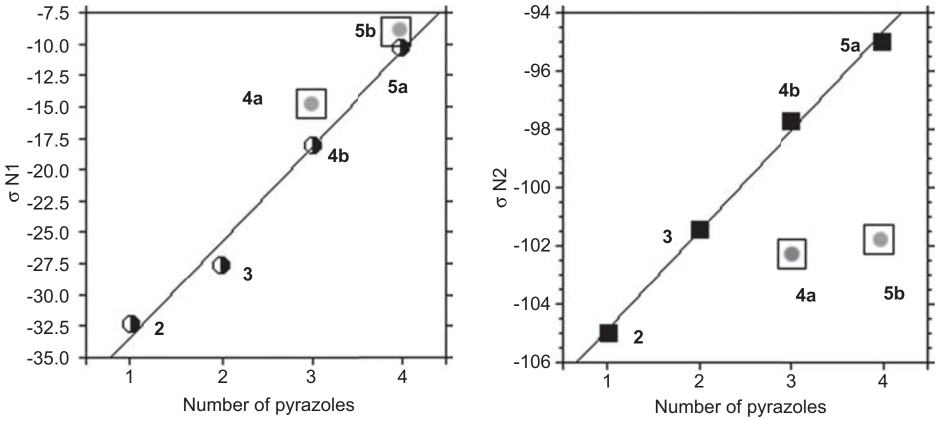


Figure 6 Plot of $\sigma^{15}N$ vs. the number of pyrazoles.
The trendlines of the figure are: N1, $\sigma^{15}N=-(40.9\pm1.9)+(7.5\pm0.7)$ no. of pyrazoles, n=4, $R^2=0.984$ [eq. 9]; N2, $\sigma^{15}N=-(108.2\pm0.4)+(3.4\pm0.2)$ no. of pyrazoles, n=4, $R^2=0.996$ [eq. 10].

Experimental chemical shifts vs. calculated absolute shieldings (Tables 2 and 4)

We have tried different proportions of **4a**/**4b** and **5a**/**5b** for different nuclei and the best results (in a statistical sense) were obtained with 80% **4a** –20% **4b** and 100% **5a**. According to Table 1 calculations, **4b** is less stable than **4a** (19.9 kJ/mol) but has a larger dipole moment (2.77 vs. 1.81 D). In the case of **5a** vs. **5b** the energy difference is more important (34.8 kJ/mol) and both have 0 D dipole moments. In all comparisons between experimental and calculated properties (δ and J) we will use **1**, **2**, **3**, **4a,b** (80% **4a** –20% **4b**) and **5a**.

In general, ^1H chemical shifts are too sensitive to solvent effects to afford good correlations with calculated absolute shieldings, however, the data of Tables 2 and 4 are fairly well correlated: $\delta^1H=(30.8\pm1.1)-(0.96\pm0.04)\ \sigma^1H$, n=12, $R^2=0.980$ [eq. 11].

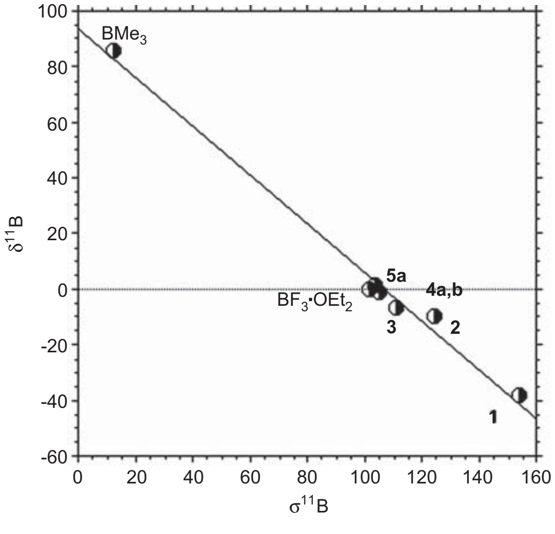


Figure 7 Plot of $\delta^{11}B$ vs. $\sigma^{11}B$.
Trendline $\delta^{11}B=(94.1\pm4.3)-(0.88\pm0.04)\ \sigma^{11}B$, n=7, $R^2=0.990$ [eq. 12] [includes BMe_3 and $BF_3{\cdot}OEt_2$, the reference, $\delta^{11}B=0.0$ (Alkorta and Elguero, 1998)].

To discuss ^{11}B chemical shifts, we have included two other boron derivatives to increase the range. The results are reported in Figure 7.

Figure 8 represents the ^{13}C NMR results. The worst points are C5 of **5a** and C3 of **2** (but its 140.8 ppm value was an estimated value not a measured one). Similarly, we found for ^{15}N data: $\delta^{15}N=-(157.6\pm1.7)-(0.85\pm0.02)\ \sigma^{15}N$, n=8, $R^2=0.995$ [eq. 14].

Experimental vs. calculated coupling constants (Tables 3 and 5)

At difference from chemical shifts, all coupling constants can be compared irrespective of the nuclei involved (Figure 9). One problem is that small values for the cluster near 0 are not a good

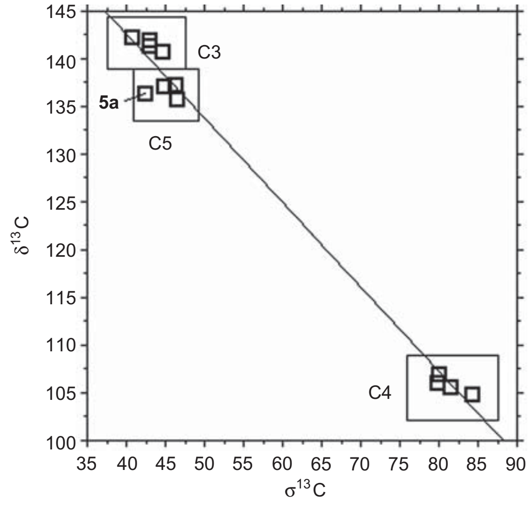


Figure 8 Plot of $\delta^{13}C$ vs. $\sigma^{13}C$.
Trendline $\delta^{13}C=(177.9\pm1.8)-(0.88\pm0.03)\ \sigma^{13}C$, n=12, $R^2=0.988$ [eq. 13].

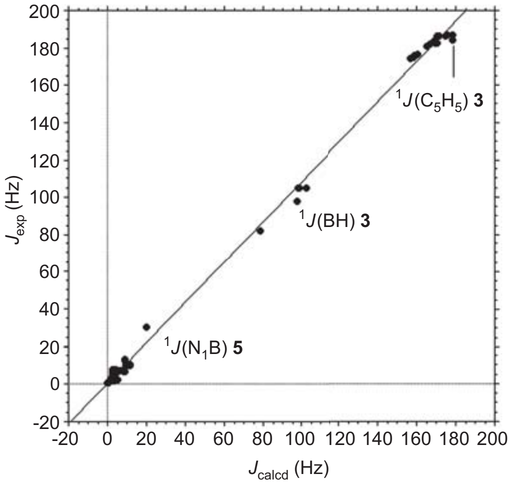


Figure 9 Equation of the trendline: J_{exp} (Hz)=(1.079±0.005) J_{calcd} (Hz), n=53, R^2=0.999 [eq. 17]. calcd., calculated.

criteria of quality. The main problem is that the sign of experimental SSCC (spin-spin coupling constants) has not been determined, thus we have two possibilities; (1) to assume that all of them are positive, i.e. to discuss the absolute values, or (2) to assume that the calculated sign is correct. In the present case it happens, by coincidence, that all the coupling constants that have been measured have positive calculated values.

First, we have used all the calculated values, **4a**, **4b**, **4a,b** (80% **4a**/20% **4b**), **5a** and **5b** obtaining the following equation: J_{exp}=(0.56±0.32)+(1.076±0.004) J_{calcd}, n=103, R^2=0.999 [eq. 15]. Since, the largest residues belong to **5b**, the corresponding calculations were removed: J_{exp}=(0.46±0.35)+(1.076±0.004) J_{calcd}, n=87, R^2=0.999 [eq. 16]. In a second step, we analysed the residuals of equation 16 for compounds **4a**, **4b** and **4a,b**. The small residual corresponds to **4a,b**, therefore we removed the points corresponding to **4a** and **4b** obtaining equation 17 reported in Figure 9.

The experimental value of $^1J(C_5H_5)$ of **3** (183.9 Hz, Table 2) is dubious because it has been measured in a complex signal. There are two couplings not well reproduced ^1J(BH) of **3** (100 Hz) and $^1J(N_1B)$ of **5** (30.0 Hz). In general, $^1J_{CH}$ SSCC are underestimated by the calculations by 10 Hz on average; therefore we decided to examine these couplings separately. We report in Figure 10 a plot of $^1J_{CH}$ experimental vs. $^1J_{CH}$ calculated for $^1J_{C3H3}$ (half-filled circles), $^1J_{C4H4}$ (black squares) and $^1J_{C5H5}$ (empty squares).

Although experimental values could contain some uncertainties, the large deviations observed for $^1JC_5H_5$ (white squares) are due to the inability of the method to calculate this coupling which involved H atoms closest to other pyrazole rings.

Predicted values

There are several chemical shifts and many coupling constants that have no experimental counterpart: they can be used as such or using the empirical equations we have described along this paper, to predict with acceptable accuracy their values, including the outsiders.

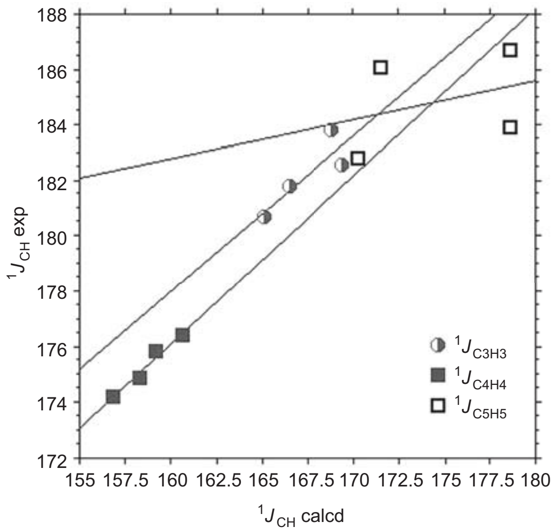


Figure 10 Equation of the trendlines: $^1JC_3H_3$ exp.=(88±39)+(0.56±0.23) $^1JC_3H_3$ calcd., n=4, R^2=0.74 [eq. 18]; $^1JC_4H_4$ exp.=(79±12)+(0.60±0.08) $^1JC_4H_4$ calcd., n=4, R^2=0.97 [eq. 19]. The $^1JC_5H_5$ values are not correlated. exp., exponential.

Conclusions

The large collection of NMR properties previously determined for pyrazolylborates (López et al., 1990) is well reproduced by DFT calculations. Some irregularities were detected that are not due to solvent effects and not to diferent counterions, since the experimental values were determined in high dissociating solvents (DMSO-d_6 and D_2O). Many other calculated values are available that can be used for predictive purposes.

Computational details

All calculations were carried out using the facilities of the Gaussian 03 package (Frisch et al., 2003). The geometry of the molecules has been fully optimised at the B3LYP computational method (Becke, 1988; Lee et al., 1988; Becke, 1993) with the 6-311++G(d,p) basis set (Ditchfield et al., 1971; Frisch et al., 1984). Harmonic frequency calculations were carried out to verify that all the structures were minima or transition states (TS) (McIver and Komornicki, 1972). Absolute shieldings were calculated within the GIAO approximation (London, 1937; Ditchfield, 1974). Absolute shieldings (σ, ppm) and coupling constants (Hz) of compounds **1–5** can be obtained on request to one of the authors.

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