Structure of bis-, tris- and tetrakispyrazolylborates in the solid state (sodium and potassium salts of tetrakispyrazolylborate by X-ray crystallography) and in solution (^{1}H, ^{11}B, ^{13}C and ^{15}N NMR)

Concepcion Lopez, Rosa Maria Claramunt*, Dionisia Sanz
Departamento de Química Orgánica, Facultad de Ciencias, UNED, Ciudad Universitaria, 28040 Madrid (Spain)

Concepcion Foces Foces, Felix H. Cano
UEI de Cristalografía, Instituto 'Rocasolano', CSIC, Serrano 117, 28006 Madrid (Spain)

Robert Faure
Laboratoire de Chimie Organique, Case 552, Université d'Aix-Marseille III, 13397 Marseille Cédex 13 (France)

Eduardo Cayon** and **Jose Elguero**
Instituto de Química Médica, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)

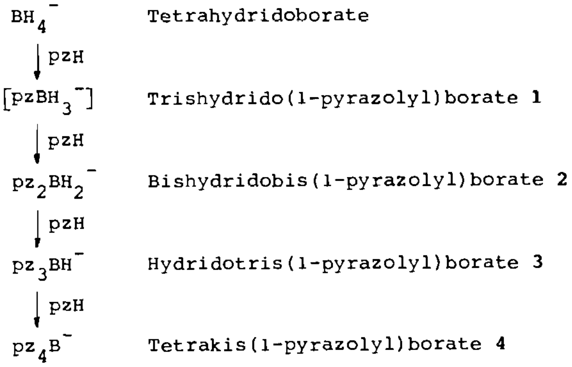
(Received March 12, 1990)

Abstract

The knowledge of the properties of pyrazolylborates has been considerably improved both in the solid state and in solution. The hydrates of the sodium and the potassium salts of tetrakis(1-pyrazolyl)borate crystallize in the space group *C2/c*, both salts being isomorphous. Regular pyrazole rings conform with a pseudosymmetry plane around a distorted tetrahedral boron atom. Chains along the *b* axis of two different octahedra of coordination, sharing water oxygens, are linked by H bonds. In solution, a careful ^{1}H, ^{13}C, ^{11}B and ^{15}N NMR study was carried out. The applicability of the rules used to assign H(3) versus H(5) and C(3) versus C(5) in the case of pyrazolylborates was reevaluated. Only for tetrakis(1-pyrazolyl)borate were couplings observed with ^{11}B in ^{1}H, ^{13}C and ^{15}N resonances. The regularity of the properties of bis-, tris- and tetrakispyrazolylborates, allows the calculation of the spectral parameters of the still unknown tris-hydrido(1-pyrazolyl)borate, $pzBH_3^-$. Finally, the electronic properties, as measured by σ_p, of the substituents BH_3^-, $pzBH_2^-$, pz_2BH^- and pz_3B^- were estimated.

Introduction

Since Trofimenko introduced the pyrazolylborate ligands in 1966 they have become one of the most popular ligands in coordination chemistry [1–4] (Scheme 1). Compound **1** has never been isolated nor characterized[†]. Amongst the three others, compound **3** is the more used ligand, being isolobal with the cyclopentadienyl anion. Surprisingly enough, very few studies deal with the free ligands, Trofimenko himself [6] describes the ^{1}H NMR of compounds **2**, **3** and **4** (potassium salts) but he does not assign H(3) and H(5) protons, and McCurdy [7] examines with more detail the case of compound **2**. The ^{11}B chemical shifts of compounds **2–4** were also reported by Trofimenko [6]. No X-ray structures of pyrazo-



Scheme 1.

---

*Author to whom correspondence should be addressed.
**Permanent address: Departamento de Química, UAB, Bellaterra, 08193 Barcelona, Spain.
[†] The corresponding structure having a 3,5-dimethylpyrazolyl residue, $dmpzBH_3^-$, has been prepared with considerable difficulty [5].

0020-1693/90/$3.50

lylborates have been reported in the literature [8] although many of their complexes have been determined [2–4]. Finally, the behaviour in mass spectrometry (FAB technique) has been the subject of a recent study [9].

TABLE 1. Final atomic coordinates and thermal parameters of **4a**

Atom	*x/a*	*y/b*	*z/c*	$U_{eq} \times 10^{3a}$
K1	0.5000	0.4806(1)	0.2500	38(1)
K2	0.5000	0.0014(2)	0.2500	58(1)
O1	0.4013(3)	0.2408(4)	0.2749(2)	59(1)
B	0.3061(3)	0.7313(5)	0.1358(2)	33(1)
N11	0.3863(2)	0.6711(4)	0.1137(1)	31(1)
N12	0.4251(2)	0.5351(4)	0.1316(1)	41(1)
C13	0.4808(3)	0.5090(5)	0.0976(2)	46(1)
C14	0.4780(3)	0.6219(6)	0.0579(2)	50(2)
C15	0.4170(3)	0.7226(5)	0.0691(2)	40(1)
N21	0.2192(2)	0.6473(4)	0.1034(1)	35(1)
N22	0.1375(2)	0.6699(5)	0.1174(2)	47(1)
C23	0.0795(3)	0.5750(6)	0.0837(2)	53(2)
C24	0.1206(3)	0.4930(6)	0.0486(2)	54(2)
C25	0.2094(3)	0.5407(5)	0.0623(2)	42(1)
N31	0.2951(2)	0.8983(4)	0.1205(1)	33(1)
N32	0.3624(2)	0.9996(4)	0.1427(2)	45(1)
C33	0.3331(4)	1.1276(5)	0.1155(2)	51(2)
C34	0.2491(4)	1.1118(5)	0.0766(2)	54(2)
C35	0.2274(3)	0.9650(5)	0.0805(2)	43(1)
N41	0.3191(2)	0.6977(4)	0.2006(1)	34(1)
N42	0.3685(3)	0.7855(4)	0.2436(1)	50(1)
C43	0.3637(4)	0.7200(6)	0.2925(2)	58(2)
C44	0.3136(3)	0.5907(6)	0.2828(2)	54(2)
C45	0.2868(3)	0.5779(5)	0.2241(2)	45(1)

[a] $U_{eq} = (1/3)\Sigma(U_{ij}a^*_i a^*_j a_i a_j \cos(a_i, a_j))$.

Experimental

Compounds **2–4** (potassium and sodium salts) were prepared according to Trofimenko [10].

Crystallography

Suitable crystals of **4a** (potassium salt) and **4b** (sodium salt) were obtained by slow evaporation at room temperature of 95% ethanolic solutions.

4a, $C_{12}H_{12}N_8B^- \cdot K^+ \cdot H_2O$, $M = 336.20$, transparent regular triangular plate (0.07 × 0.20 mm), monoclinic, space group *C2/c*, $a = 15.1813(5)$, $b = 8.9295(2)$, $c = 23.8818(24)$ Å, $\beta = 104.674(3)°$, $D_c = 1.426$ g cm^{-3}, $Z = 8$. Cell parameters obtained from a least-squares fit using 50 reflections up to $\theta = 45°$ and Cu Kα radiation.

4b, $C_{12}H_{12}N_8B^- \cdot Na^+ \cdot H_2O$, $M = 320.10$, transparent prism (0.23 × 0.17 × 0.10 mm), monoclinic, space group *C2/c*, $a = 14.8713(5)$, $b = 8.6823(2)$, $c = 23.8041(10)$ Å, $\beta = 106.690(3)°$, $D_c = 1.444$ g cm^{-3}, $Z = 8$. Cell parameters as for **4a** with 66 reflections.

Both compounds were analyzed in a PW1100 four-circle diffractometer with Cu Kα radiation, graphite monochromated, $\omega/2\theta$ scans, 1.5° scan width and 1 min per reflection. Good stability for both samples was checked every 90 min. With a $3\sigma(I)$ criterion 1923 and 1914 observed reflections were given, respectively, up to $\theta = 65°$. The structures were solved by Patterson and refined by full matrix least-squares procedures for 265 parameters. All hydrogen atoms were located in a difference synthesis and included isotropically. An empirical weigthing scheme was introduced to give no trends in $\langle w\Delta^2F \rangle$ versus $\langle |F_{obs}| \rangle$ or $\langle \sin \theta/\lambda \rangle$. The finals shift/error was 0.04 and 0.01 with maximum peaks in the final ΔF of 0.27 and 0.19 e Å^{-3} and the final R and R_w values were 0.055, 0.064 and 0.046, 0.048, respectively.

Most of the calculations were performed with the X-Ray76 System [11] on a Vax11/750 computer. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography [12]. Tables 1 and 2 display the final atomic coordinates for the non-hydrogen atoms with the numbering scheme appearing in Fig. 1.

NMR measurements

A Bruker AM-200 (Faculty of Sciences, University of Aix-Marseille III, France) was used to obtain ^{1}H (200.13 MHz), ^{11}B (64.21 MHz), ^{13}C (50.32 MHz) and ^{15}N (20.29 MHz) measurements.

^{1}H and ^{13}C chemical shifts (δ) are given from internal TMS with an accuracy of ±0.01 and ±0.1 ppm, respectively. Coupling constants (*J*) were measured with a digital resolution of 0.2 and 0.6 Hz, respectively. The data acquisition parameters for the heteronuclear (^{1}H–^{13}C) 2D-correlation experiments were: F_1 domain (SI1: 128 W, SW1: 500 Hz, relaxation delay D1: 3s), F_2 domain (SI2: 4 K, SW2: 2800 Hz), number of transients per FID, NS: 128, number of preparatory dummy transients per FID, DS: 0.

For ^{15}N NMR spectra, the samples were dissolved in DMSO-d_6; the concentration was 10–25% (wt./vol.) and the internal diameter of the tube was 10 mm. Nitromethane was used as external standard; chemical shifts are expressed in ppm with an accuracy of ±1 ppm and coupling constants were measured with a digital resolution of 2 Hz with the aid of the polarization transfer sequence INEPT.

^{11}B NMR chemical shifts were registered with 0.5 g of the sample in 2 ml of solvent and were measured with an accuracy of ±0.5 ppm with 10 mm tubes and referred to $BF_3 \cdot Et_2O$ as external reference. Continuous broad-band proton decoupling was used in all cases.

TABLE 2. Final atomic coordinates and thermal parameters of **4b**

Atom	*x/a*	*y/b*	*z/c*	$U_{eq} \times 10^{3\,a}$
Na1	0.5000	0.4559(2)	0.2500	41(1)
Na2	0.5000	0.0082(2)	0.2500	40(1)
O1	0.4094(2)	0.2390(3)	0.2702(1)	42(1)
B	0.3146(2)	0.7452(3)	0.1432(1)	27(1)
N11	0.3963(1)	0.6794(2)	0.1230(1)	27(1)
N12	0.4377(2)	0.5417(3)	0.1437(1)	32(1)
C13	0.4884(2)	0.5045(4)	0.1074(1)	39(1)
C14	0.4801(2)	0.6140(4)	0.0637(1)	40(1)
C15	0.4205(2)	0.7222(4)	0.0747(1)	33(1)
N21	0.2247(1)	0.6580(2)	0.1102(1)	27(1)
N22	0.1412(2)	0.6831(3)	0.1225(1)	37(1)
C23	0.0798(2)	0.5898(4)	0.0863(1)	39(1)
C24	0.1213(2)	0.5061(4)	0.0511(1)	41(1)
C25	0.2130(2)	0.5521(3)	0.0674(1)	35(1)
N31	0.3034(2)	0.9159(2)	0.1250(1)	28(1)
N32	0.3708(2)	1.0237(3)	0.1489(1)	36(1)
C33	0.3417(2)	1.1511(4)	0.1180(1)	44(1)
C34	0.2583(2)	1.1277(4)	0.0741(1)	45(1)
C35	0.2363(2)	0.9773(3)	0.0796(1)	35(1)
N41	0.3293(1)	0.7202(3)	0.2089(1)	28(1)
N42	0.3773(2)	0.8197(3)	0.2513(1)	38(1)
C43	0.3720(2)	0.7589(4)	0.3017(1)	45(1)
C44	0.3226(2)	0.6209(4)	0.2930(1)	45(1)
C45	0.2968(2)	0.5994(4)	0.2336(1)	38(1)

$^a U_{eq} = (1/3)\Sigma(U_{ij}a^*_i a^*_j a_i a_j \cos(a_i, a_j))$.

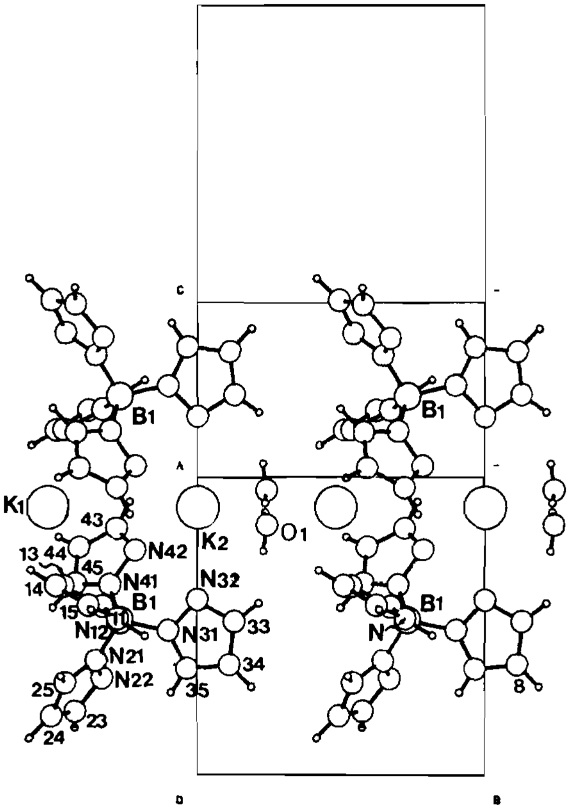


Fig. 1. A view [13] of the two crystallographically different metal coordinations along *b* axis.

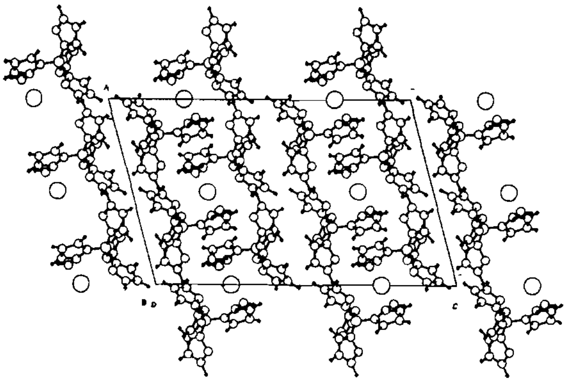


Fig. 2. A view [13] of crystal packing down *b* axis.

Results and discussion

Crystal structure

Compounds **4a** and **4b** are crystallographically isomorphous, with minor differences, thus the Figures (Figs. 1 and 2) are representative of both.

Table 3 presents the main geometrical characteristics of the structures. The geometry of the pyrazole rings compares quite well with that of the isolated pyrazole, as it appears in the Cambridge Structural Database [8], where five molecules are reported with average bonds of N–N = 1.349(8), N–C = 1.330(14), C–C = 1.373(23) Å and angles at $N_1 = C_3 = 111.7(16)$, $N_2 = C_4 = 104.6(13)$ and at $C_5 = 107.5(13)$°. The tetrahedral boron atom is distorted, the N–B–N angles ranging from 106.5(3) to 114.1(3)° (in K·[BPh$_4$] these angles range from 102.7 to 112.9° [14]). Systematically, the angles B–N–N are lower than the B–N–C ones. The pyrazole rings adopt a conformation that has a pseudosymmetry plane through N(11)–B–N(21), quite distorted, as it can be noticed from the torsion angles and from the N···N distances presented in Table 3. That conformation is far away from the tetrahedral $S_4(\bar{4})$ which, for the average Nx2–B–Nx1 angle of 27.1°, will yield an N–B–N–N torsion angle of 80.2° [15]. It is also quite distorted from the relative minimum energy form [16] which would have torsion values near the sequence −120, 120, 60, −60°.

In both structures the cations are located at two different sites, along a two-fold axis, with an octahedral coordination sharing corners occupied by N atoms and by the center of two symmetry related pyrazole rings. This coordination, responsible for the distorted conformation, leaves just N(22) out of coordination tasks but implied in a H bond, with the water molecule, which has the other hydrogen

TABLE 3. Selected geometrical parameters (Å, °)

	$x=1$		$x=2$		$x=3$		$x=4$	
	K	Na	K	Na	K	Na	K	Na
Nx1–Nx2	1.370(5)	1.370(3)	1.379(5)	1.372(4)	1.368(5)	1.369(3)	1.357(5)	1.364(3)
Nx1–Cx5	1.348(6)	1.352(4)	1.348(5)	1.347(4)	1.351(5)	1.352(3)	1.356(6)	1.358(4)
Nx2–Cx3	1.332(6)	1.338(5)	1.336(6)	1.334(4)	1.334(6)	1.329(4)	1.323(6)	1.333(4)
Cx3–Cx4	1.376(7)	1.390(5)	1.377(8)	1.383(5)	1.381(7)	1.389(4)	1.370(8)	1.390(5)
Cx4–Cx5	1.364(7)	1.368(5)	1.372(7)	1.365(4)	1.361(7)	1.362(4)	1.362(7)	1.366(4)
B–Nx1	1.541(6)	1.540(4)	1.545(5)	1.541(3)	1.534(6)	1.540(4)	1.540(5)	1.531(4)
B–Nx1–Cx5	127.8(3)	126.2(2)	129.1(4)	128.7(2)	128.0(3)	126.8(2)	127.0(3)	126.0(2)
B–Nx1–Nx2	121.2(3)	121.7(2)	120.9(3)	121.3(2)	121.6(3)	122.3(2)	123.6(3)	123.9(2)
Nx2–Nx1–Cx5	109.9(3)	110.1(2)	109.9(3)	110.0(2)	110.0(3)	110.2(2)	109.4(3)	110.1(2)
Nx1–Nx2–Cx3	104.8(3)	104.9(2)	104.9(4)	105.0(2)	104.7(4)	104.9(2)	105.6(4)	105.2(2)
Nx2–Cx3–Cx4	112.2(4)	111.9(3)	111.9(4)	111.7(3)	112.2(4)	111.9(3)	112.1(4)	111.9(3)
Cx3–Cx4–Cx5	104.7(4)	104.4(3)	105.0(4)	104.9(3)	104.5(4)	104.7(3)	104.6(5)	104.5(3)
Nx1–Cx5–Cx4	108.5(4)	108.6(3)	108.3(4)	108.4(3)	108.6(4)	108.2(3)	108.3(4)	108.3(3)
	K	Na		K	Na		K	Na
N12...N22	4.458(5)	4.465(3)	N12...N32	4.278(5)	4.312(3)	N12...N42	3.750(5)	3.811(4)
N22...N32	4.433(5)	4.424(3)	N22...N42	4.134(5)	4.118(3)	N32...N42	3.060(5)	2.994(4)
N12..B..N22	122.6(2)	122.9(1)	N12..B..N32	115.1(2)	115.7(1)	N12..B..N42	94.9(2)	96.7(1)
N22..B..N32	121.5(2)	120.7(1)	N22..B..N42	108.3(2)	107.8(1)	N32..B..N42	73.9(2)	71.8(1)
N11–B–N21	107.9(3)	107.8(2)	N11–B–N31	107.8(3)	107.5(2)	N11–B–N41	111.4(3)	111.8(2)
N21–B–N31	109.0(3)	108.8(2)	N21–B–N41	106.5(3)	107.5(2)	N31–B–N41	114.1(3)	113.3(2)
M1–O1	2.763(4)	2.443(3)	M1–N12	2.811(3)	2.544(2)	M1–Cp	3.097(6)	3.257(4)
O1–M1–N12	104.3(1)	111.0(1)	O1–M1–Cp	86.6(1)	92.5(1)	O1–M1–O1i	78.4(1)	79.1(1)
O1–M1–N12i	91.2(1)	95.4(1)	O1–M1–Cpi	157.8(1)	167.2(1)	N12–M1–Cp	76.7(1)	78.4(1)
N12–M1–N12i	160.1(1)	146.0(1)	N12–M1–Cpi	92.1(1)	79.3(1)	Cp–M1–Cpi	112.1(1)	97.3(1)
M2–O1	2.761(4)	2.536(3)	M2–N32ii	2.867(3)	2.617(2)	M2–N42ii	2.752(4)	2.458(3)
N32ii–M2–N32iii	179.4(2)	174.1(1)	O1–M2–N42ii	97.4(1)	95.0(1)	O1–M2–O1i	78.5(1)	75.6(1)
N32ii–M2–N42iii	113.5(1)	112.0(1)	O1–M2–N32iii	97.1(1)	94.3(1)	O1–M2–N32ii	83.4(1)	81.0(1)
N42ii–M2–N42iii	91.1(1)	96.5(1)	O1–M2–N42iii	163.1(1)	164.8(1)	N32ii–M2–N42ii	66.0(1)	72.2(1)
	K	Na		K	Na			
N11–B–N31–N32	−62.5(4)	−66.1(3)	N31–B–N11–N12	165.8(3)	165.1(2)			
N41–B–N21–N22	55.3(4)	54.1(3)	N21–B–N41–N42	−158.1(3)	−154.4(2)			
N11–B–N21–N22	175.1(3)	174.8(2)	N11–B–N41–N42	84.5(4)	87.5(3)			
O1–H1	0.84(9)	0.86(6)	O1...N22iv	2.852(7)	2.903(4)			
H1...N22iv	2.03(9)	2.06(6)	O1–H1...N22iv	166(7)	167(5)			

Symmetry code: i = 1 − x, y, ½ − z; ii = x, 1 − y, z; iii = 1 − x, −1 + y, ½ − z; iv = ½ − x, −½ + y, ½ − z. Cp is the centroid of the N41, N42, ...C45 ring.

atom free of interactions. In the above mentioned K•[BPh$_4$] salt as well as in the isomorphous Rb•[BPh$_4$] [17], the cation shows a distorted tetrahedral coordination with the centers of four phenyl rings belonging to two BPh$_4$ different anions.

NMR properties

Before discussing the NMR of pyrazolylborates, a short summary of the ^{1}H and ^{13}C NMR of N-substituted pyrazoles is imperative. We will consider only the case of pyrazole itself **5** and the case of 3(5)-substituted pyrazoles, **7**, which cover all the cases of pyrazolylborates (R = H, Me, iPr, tBu, Ph) (Scheme 2).

In the case of pyrazole **6** the problem consists in identifying the signals (^{1}H and/or ^{13}C) corresponding to positions 3 and 5. In the case of 3(5)-substituted pyrazoles the problem is to assign the structure, **8** or **9**, to the product obtained by N-substitution (in some cases, both isomers are formed and the problem is usually simpler). Both problems are related but not identical, for instance the use of $^3J(^1\mathrm{H}–^1\mathrm{H})$ coupling constants is restricted to compound **6**.

Below is a list of the criteria used to solve these problems. As we will show later on, most of them are of dubious application in the case of pyrazolylborates.

(i) ^{1}H NMR

(1) $J_{34} < J_{45}$ [18] (only for **6**)*.

(2) Relative to H(5), the proton H(3) is broadened by the quadrupolar relaxation of N(2) [18] (only for **6**).

(3) The chemical shift of proton H(5) is much more solvent dependent than that of H(3) [18].

(4) For R = methyl, the signal of this substituent in compound **9** (5-methyl) is more solvent dependent than that of compound **8** (3-methyl) [18]. In conditions of good resolution, the ^4J coupling between H(4) and CH$_3$(5) can be observed [19] [that between H(4) and CH$_3$(3) of **8** is almost nil].

(ii) ^{13}C NMR

(1) δC(3) > δC(5) [20].

(2) $^1J[\mathrm{C(3)–H(3)}] > {}^1J[\mathrm{C(5)–H(5)}]$ [20].

(3) $^2J[\mathrm{C(3)–H(4)}] < {}^2J[\mathrm{C(5)–H(4)}]$ [21].

(4) $^3J[\mathrm{C(3)–H(5)}] > {}^3J[\mathrm{C(5)–H(3)}]$ [21].

(5) $^2J[C(4)–H(5)] < {}^2J[\mathrm{C(4)–H(3)}]$ [22] (only for **6**).

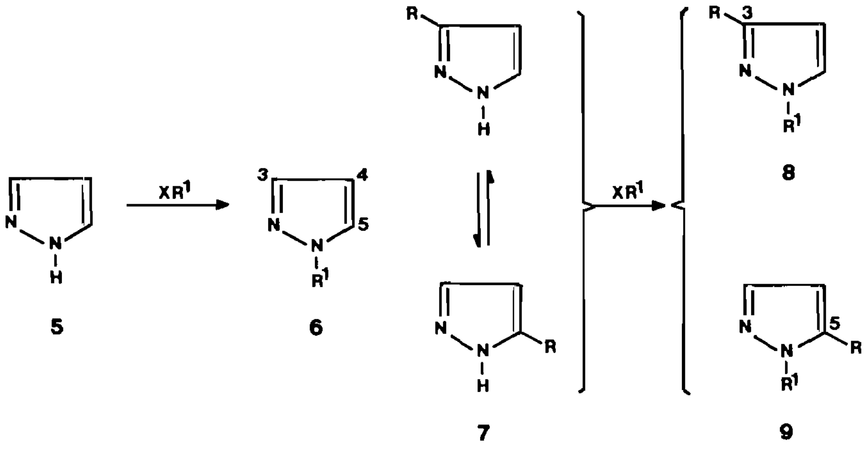
(6) When R = methyl, $\delta[\mathrm{CH_3(3)}]$ **8** > $\delta[\mathrm{CH_3(5)}]$ **9** [23].

The criteria based on the coupling constants (i1, i4, ii2–ii5) are dependent on the nature of R^1. For electron-withdrawing groups, like COCH$_3$, NO$_2$ and SO$_2$CF$_3$, the difference ΔJ is quite large and the criteria ease to apply. On the contrary, when R^1 is an electron-releasing group, the difference vanished and could even change sign. For anions, like pyrazolylborates, an inversion of these criteria is not unexpected.

Criteria based on broadening due to ^{14}N (i2) are not reliable when R^1 is a group carrying an atom with spin $I > 1/2$, like ^{10}B and ^{11}B.

Finally, criteria based on solvent effects (i3, i4) cannot be used in pyrazolylpyrazoles, where the proximity of lone pairs of another heterocycle modifies the structure of the solvation shell around the pyrazole [21].

An examination of literature results on the NMR of pyrazolylborates is quite disappointing. Three cases are found: (a) absence of NMR data of the free ligand [24–26]; (b) NMR data without assignment



Scheme 2.

---

*One of the most irritating oddities of authors describing the ^{1}H NMR of pyrazolylborates is to give for the same coupling constant, two different values, one measured on H(4) and the other on H(3) or H(5).

TABLE 4. ^1H chemical shifts (δ), ^1H–^1H and ^1H–^{11}B coupling constants (Hz) of pyrazolylborates

Compound	Solvent	H(3)	H(4)	H(5)	$^3J_{34}$	$^3J_{45}$	$^4J_{35}$	BH$^-$	$^1J(^1H–^{11}B)$
2	D_2O	7.54	6.25	7.67	1.7	2.1	0.65	3.65^a	100
	DMSO-d_6	7.21	5.90	7.31	1.65	2.05	0.6	n.o.	
3	D_2O	7.65	6.31	7.39	1.65	2.2	n.m.	5	n.m.
	DMSO-d_6	7.36	6.05	7.24	1.6	2.1	0.65	n.o.	
4	D_2O	7.65	6.30	7.34	1.7^b	2.3^b	n.m.		
	DMSO-d_6	7.44	6.08	7.18	1.6^c	2.2^c	n.m.		

n.o. = not observed; n.m. = not measurable. ^{a}Broad quartet. ^{b}Trofimenko's values [6]. ^{c}After treatment of the signal.

[6, 27]; (c) NMR data ill assigned (this is the case of McCurdy [7] which wrongly prefers the criterium based on solvent effects (i3) to that based on coupling constants (i1)). Bonati and coworkers [27] use the criteria (ii1) to assign the carbons of positions 3 and 5 of trispyrazolylborate **3**, which, as we will shown later on, is correct.

Our results concerning the ^1H NMR of pyrazolylborates are gathered in Table 4.

In bispyrazolylborate **2** the signals belonging to pyrazole protons are well resolved and even the small $^4J_{35}$ coupling constant can be measured. The signal of the hydrogens bound to the central boron atom can be observed in D_2O (contrary to protons, hydrides do not exchange with the solvent). The signal is a broad quartet (in fact, the superposition of a quartet for the ^{11}B isotopomer, 81.2%, $I=3/2$, and a septet for the ^{10}B isotopomer, 18.8%, $I=3$) [28]. The $^1J(^1H–^{11}B) \approx 100$ Hz is larger than that reported by Trofimenko for the same compound, $^1J=96$ Hz, measured in the ^{11}B NMR spectrum [6] (see later).

The trispyrazolylborate **3** presents a ^1H NMR spectrum very similar to the preceding one, the signal of the BH proton is very broad and difficult to find; the ^1J cannot be measured. Trofimenko [6] found 105 Hz, a value identical to that described by Niedenzu *et al.* [29] for the tris(3-methylpyrazolyl)borate.

The spectra, D_2O and DMSO-d_6, of tetrakispyrazolylborate are quite different. The signals seem broad, but the broadening does not disappear on heating (up to 120 °C in DMSO-d_6). In fact, after a severe treatment of the signal, it appears that they are complex multiplets due to couplings with ^{10}B and ^{11}B. The only coupling which can be measured is a $^4J(H(4)–^{11}B) = 0.9$ Hz; those of the protons H(3) and H(5) cannot be calculated due to the complexity of multiplets, which prevent also the measurement of $^4J_{35}$. It is well documented [28] that tetrahedral symmetry of tetravalent boron, through the slowing of the quadrupolar relaxation, allows the couplings with ^{11}B to be observed.

The chemical shifts of Table 4 show that when the number of pyrazole rings linked to the boron increase, H(5) is shifted to lower frequencies whereas the contrary is observed for H(3). As a consequence, $\delta H(3) > \delta H(5)$ in compounds **3** and **4** whereas in compound **2**, $\delta H(5) > \delta H(3)$.

The assignments of Table 4 for compound **2** imply that those of McCurdy [7] are wrong. With our values, the introduction of a methyl substituent at position 3 shifted the protons H(4) (−0.25 ppm) and H(5) (−0.15 ppm) upfield, similar to what was observed in *N*-methylpyrazoles [19].

Finally, amongst the different criteria of assigning ^1H NMR signals in pyrazoles, i1 is followed ($^3J_{45}/^3J_{34} \approx 1.3$); i2 cannot be used due to interactions with the boron; and i3 is not followed, at least not for D_2O and DMSO-d_6, since the solvent effects are similar for all the protons.

The results of the analysis of the ^{13}C NMR spectra of the three pyrazolylborates can be found in Table 5.

TABLE 5. ^{13}C chemical shifts (δ), ^1H–^{13}C and ^{11}B–^{13}C coupling constants (Hz) of pyrazolylborates (solvent: D_2O)

Compound	C(3)	C(4)	C(5)
2	141.3 $^1J=181.8$ $^2J=7.15$ $^3J=7.15$	105.6 $^1J=174.9$ $^2J=10.3$ $^2J=10.3$	137.1 $^1J=183.9^a$
3	141.9 $^1J=182.55$ $^2J=7.2$ $^3J=7.2$	106.0 $^1J=175.85$ $^2J=10.15$ $^2J=10.15$	135.7 $^1J=186.1^b$ $^2J=6.8$ $^3J=4.4$
4	142.3 $^1J=183.8$ $^3J(^{11}B)=2.9^c$	106.9 $^1J=176.4$ $^2J=10.1$ $^2J=9.7$ $^3J(^{11}B)=1.7^c$	136.3 $^1J=186.7$ $^2J(^{11}B)=3.5^c$

^{a}Complex signal due to additional couplings with BH_2 protons. ^{b3}J(C(5)–N–B–H) coupling of 2.4 Hz. ^{c}Measured in the ^1H-decoupled spectrum.

Compound **2** shows a ^{1}H-decoupled spectrum with very narrow signals. A first-order analysis of the proton-coupled spectrum yields the coupling constants of Table 5. The signal corresponding to C(5) is complex due to long-range couplings with the BH_2 protons and cannot be analyzed.

The trispyrazolylborate study is of crucial importance since its ^{1}H-coupled spectrum shows a ^3J(C(5)–N–B–H) = 2.4 Hz very similar to that observed in 1-methylpyrazole (^3J(C(5)–N–C–H) = 2.7 Hz) [21]. This allows C(5) to be assigned with certainty and, by self-consistency, all other signals of Table 5. Since heteronuclear (^{1}H–^{13}C) COSY experiments relate the carbons of Table 5 to the protons of Table 4, these last values are also assigned without ambiguity.

In contrast to compounds **2** and **3**, which show very narrow signals in the ^{1}H-decoupled spectra, the tetrakispyrazolylborate **4** presents beautiful quartets corresponding to couplings with ^{11}B*. As in ^{1}H NMR, the tetrahedral symmetry of **4** explains why these couplings appear only in it. In Scheme 3 we report these couplings together with some related values.

In phenyl derivatives, like tetraphenylborate, $^3J > {}^2J$, whereas the reverse is observed for **4**. A similar situation is found for ^{1}H–^{13}C coupling constants: in phenyl derivatives $^3J \gg {}^2J$ and in pyrazoles (see Table 5), $^2J \simeq {}^3J$.

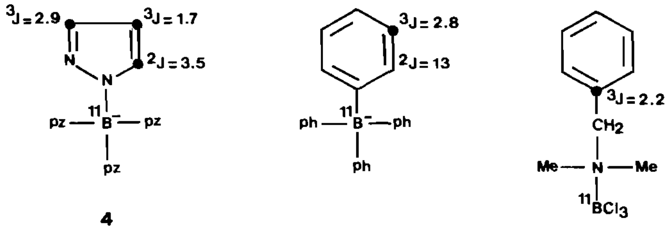
We have recorded the ^{13}C NMR spectrum of tetrakispyrazolylborate **4** in the solid state at 100 MHz (CP/MAS technique): four narrow signals are observed of intensities near 1:1:0.5:0.5 at $\delta = 107.5$ (C(4)), 137.8 (C(5)), 141.3 and 143.3 (C(3)). These are close to those of Table 5. The splitting of C(3) into two signals of the same intensity could correspond to a residual dipolar coupling with N(2), similar to that observed in other ^{14}N derivatives [31], or to a conformational origin (two classes of pyrazoles in the crystal).

Concerning the assignment criteria, the results of Table 5 show that criterium i1 is followed (δC(3) > δC(5)); criterium ii2 (^1J) is also followed but the difference in coupling constants ($\Delta J = 2.8$ Hz) is smaller than the difference in chemical shifts ($\Delta\delta = 5.5$ ppm). Both δ and J are quite sensible to solvent effects, but the sign of $\Delta\delta$ and ΔJ remains unchanged. Criteria using long-range coupling constants (ii2–ii5) are either false or useless.

The ^{11}B NMR spectra of compounds **2**, **3** and **4** in D_2O were reported by Trofimenko [6]. Correcting the chemical shifts from the older reference, $B(OMe)_3$, used by Trofimenko, to the new one, $BF_3 \cdot Et_2O$ [32] ($\Delta\delta = 18.3$ ppm), the Trofimenko values are **2**, $\delta^{11}B = -7.4$ ($^1J = 96$ Hz); **3**, $\delta^{11}B = -1.3$ ($^1J = 105$ Hz), **4**, $\delta^{11}B = 1.0$. Our results in DMSO-d_6 of the ^{1}H-decoupled spectra are (between parentheses the linewidth at half-height, $\Delta\nu 1/2$, in Hz): **2**, $\delta^{11}B = -6.54$ ($\Delta\nu 1/2 = 248$ Hz); **3**, $\delta^{11}B = -0.90$ ($\Delta\nu 1/2 = 175$ Hz); **4**, $\delta^{11}B = 1.35$ ($\Delta\nu 1/2 = 4.4$ Hz), values very similar to those of Trofimenko showing a very small solvent effect (-0.5 ppm) and a great sensibility of the linewidth to the symmetry.

Finally, the ^{15}N NMR spectroscopy of pyrazolylborates was studied (no previous reports) using DMSO-d_6 as solvent. The assignment of N(1) (pyrrol-like) and N(2) (pyridine-like) is straightforward [33, 34]. The results on compounds **2**–**4** together with those of an *N*-R^1 pyrazole doubly labelled with ^{15}N (**6**, $R^1 = C(CH_3)_2OH$) [33] are reported in Table 6.

The evolution of NMR parameters with the increasing number of pyrazoles (**2**→**3**→**4**) is very regular, to the point that it is possible to predict the values for $pzBH_3^-$ (**1**): δ[N(1)] = -132.2 to -133.7, δ[N(2)] = -72.0, ^2J[N(2)–H(3)] = 12.6 Hz. The ^1J(^{11}B–^{15}N) coupling found in compound **4** and not in compounds **2** and **3** is still an example of the extraordinary importance of tetrahedral symmetry to observe couplings with nuclei of $I > 1/2$. The value we obtained, 30 Hz, is similar to those described in



4

From ref. [30]

From ref. [28]

Scheme 3.

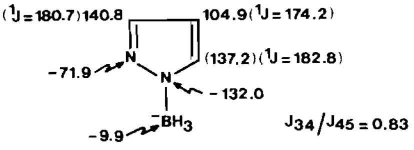
---

*The septet due to ^{10}B is not observed. Its minor intensity (18.8%) and the smaller value of the coupling constant (0.335 times that with ^{11}B) made its direct observation very difficult [28].

TABLE 6. ^{15}N chemical shifts (δ)[a], ^{1}H–^{15}N and ^{11}B–^{15}N coupling constants (Hz) of pyrazolylborates and related compounds (solvent: DMSO-d_6)

Compound	N(1)	N(2)
2	−137.3 $^{3}J[H(3)]=6.7$ $^{3}J[H(4)]=6.7$	−70.4 $^{2}J[H(3)]=12.8$
3	−141.9 $^{3}J[H(3)]=7.7$ $^{3}J[H(4)]=7.7$	−68.8 $^{2}J[H(3)]=13.0$
4	−147.5[b] $^{3}J[H(3)]=6.0$ $^{3}J[H(4)]=5.5$ $^{2}J[H(5)]=5.5$	−67.3 $^{2}J[H(3)]=13.4$
6	−140.3 $^{3}J[H(3)]=7.5$[c] $^{3}J[H(4)]=5.2$[c] $^{2}J[H(5)]=4.0$[c]	−80.6 $^{2}J[H(3)]=12.9$[c] $^{3}J[H(4)]=1.1$[c] $^{3}J[H(5)]=0$[c]

[a] From nitromethane external reference, 200 mg of CH_3NO_2 in 1 ml of DMSO-d_6. [b] A $^{1}J(^{11}B–^{15}N)$ coupling of 30.0 Hz is observed. [c] Calculated from the ^{1}H sub-spectra using a double labelled pyrazole [33].



Scheme 4.

the literature (12–70 Hz) [32]. For the complex 1-methylimidazole-BMe_3, it was concluded from the appearance of the ^{15}N NMR spectrum [32] that $^{1}J(N(3)–^{11}B)$ is very small (< 5 Hz), but the possibility that the lack of symmetry prevents its observation must not be ruled out.

The fact that N(2) is coupled with H(3) but not with H(5) can be used to determine if a substituent is at position 3 or 5, i.e. to differentiate **8** and **9**.

Assuming that the NMR properties of pyrazolylborates **2**–**4** are linearly related to the number of pyrazoles, $P=a+bn$ (n = 1–3), it is possible to calculate those a of $pzBH_3^-$ ($n=0$). The results of these calculations are shown in Scheme 4.

The electronic structure of pyrazolylborates with regard to other substituents on the nitrogen and the σ_p value of BH_3^-, $pzBH_2^-$, pz_2BH^- and pz_3B^- substituents

In a preceding paper dealing with ^{13}C NMR of azoles carrying different substituents on the nitrogen [20], we have shown that the three $^{1}J(^{1}H–^{13}C)$ coupling constants of pyrazoles **6** are related. For a set of 17 different R^1 substituents we found that $^{1}J(C(3)–H(3)) = -27.7+1.2\ ^{1}J(C(4)–H(4))$ and $^{1}J(C(5)–H(5)) = -216.3+2.28\ ^{1}J(C(4)–H(4))$. The values of Table 5 obey these equations; taking $^{1}J(C(4)–H(4))$ as the 'true' value, the calculated values for $^{1}J(C(3)–H(3))$ and $^{1}J(C(5)–H(5))$ differ from the experimental ones by 0.4 and −1.2 Hz, respectively. For compound **1**, the value of $^{1}J=174.2$ for C(4) (Scheme 4) and the above mentioned equations led to the values of 181.3 and 180.9 for the ^{1}J coupling constants of C(3) and C(5), a little different from those calculated linearly (Scheme 4).

We have gathered in Table 7 two NMR properties of pyrazoles that we empirically found to be related with Hammett σ_p: the ratio of the ^{3}J coupling constants in ^{1}H NMR and the chemical shift of C(4) in ^{13}C NMR.

For the eleven substituents of Table 7, the following equation was found by linear regression

$$J_{34}/J_{45}=0.76-0.30\ \sigma_p,\ r^2=0.94$$

With this equation and the J_{34}/J_{45} ratios of compounds **2**–**4** determined in DMSO-d_6 (Table 4) and that of **1** linearly calculated (Scheme 4), the σ_p values of Table 7 (first column) were determined. The $^{1}J(C(4)–H(4))$ of the four pyrazolylborates, including **1** ($^{1}J=174.2$ Hz, Scheme 4), are linearly related to the σ_p values thus determined

$$^{1}J(C(4)–H(4))=175.8+6.58\ \sigma_p,\ r^2=0.997$$

The chemical shift of C(4) of the eleven modeling compounds and σ_p were related by the equation

$$\delta C(4)=106.7+5.1\ \sigma_p,\ r^2=0.92$$

TABLE 7. Hammett relationships in pyrazoles **6**

R^1	σ_p [35]		J_{34}/J_{45}	δC(4)
$-N{=}PPh_3$	−0.75		1 [36]	102.2 [36]
–NHMe	−0.70		0.92 [37]	103.7 [37]
$-NH_2$	−0.66		1 [38]	104.2 [20]
–Me	−0.17		0.86 [38]	105.1 [20]
–Adamantyl	−0.13		0.76 [39]	104.3 [41]
–Ph	−0.01		0.76 [38]	107.3 [20]
–2.4,6-Trinitrophenyl	0.30		0.73 [38]	109.4 [20]
$-CONH_2$	0.36		0.59 [38]	108.6 [20]
–COMe	0.50		0.55 [38]	109.3 [20]
$-NO_2$	0.78		0.55 [38]	109.8 [20]
$-SO_2CF_3$	0.93		0.50 [40]	111.9 [20]
1	−0.24	−0.36	(0.83)	(104.9)
2	−0.13	−0.21	0.80	105.6
3	0.00	−0.13	0.76	106.0
4	0.10	0.04	0.73	106.9

which, in turn, leads to another estimation of the σ_p of the substituents BH_3^- (−0.36), $pzBH_2^-$ (−0.21), pz_2BH^- (−0.13) and pz_3B^- (0.04). Both sets of σ_p values do not perfectly agree although they are related (σ_p (2nd column) = −0.09 + 1.1 σ_p (1st column of Table 7), $r^2 = 0.97$).

In conclusion the $[pz_nBH_{3-n}]^-$ substituents are moderate electron-releasing substituents, comparable to alkyl groups, the electron-releasing ability diminishing with the increase of pyrazole residues on the boron.

Acknowledgments

This work was supported by the CICYT of Spain (Project No PB87-0094-CO2). One of us (C.L.) is indebted to the 'Secretaría General Técnica de la Consejería de Educación y Juventud de la Comunidad de Madrid' for a grant. Another of the authors (D.S.) thanks the Ministeries of Education of Spain (MEC) and France (MRES) for a fellowship during her stage at the University of Marseille.

References

1 S. Trofimenko, *J. Am. Chem. Soc., 92* (1970) 5118.
2 S. Trofimenko, *Prog. Inorg. Chem., 34* (1986) 115.
3 K. Niedenzu and S. Trofimenko, *Top. Curr. Chem., 131* (1986) 1.
4 R. Han, A. Looney and G. Parkin, *J. Am. Chem. Soc., 111* (1989) 7276; M. K. Chan and W. H. Armstrong, *Inorg. Chem., 28* (1989) 3777; C. K. Gosh and W. A. G. Graham, *J. Am. Chem. Soc., 111* (1989) 375; A. H. Cowley, R. L. Geerts, C. M. Nunn and S. Trofimenko, *J. Organomet. Chem., 365* (1989) 19; R. E. Marsch, *Acta Crystallogr., Sect. C, 45* (1989) 1269; N. A. Obaidi, A. J. Edwards, C. J. Jones, J. A. McCleverty, B. N. Neaves, F. E. Mabbs and D. Collison, *J. Chem. Soc., Dalton Trans.,* (1986) 127; M. A. J. Moss, C. J. Jones and A. J. Edwards, *J. Chem. Soc., Dalton Trans.,* (1989) 1413; M. J. Fernández, M. J. Rodríguez, L. A. Oro and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.,* (1989) 2073; C. A. Kipke, W. E. Cleland, S. A. Roberts and J. H. Enemark, *Acta Crystallogr., Sect. C, 45* (1989) 870; R. A. Kresinski, T. A. Hamor, L. Isam, C. J. Jones and J. A. McCleverty, *Polyhedron, 8* (1989) 845; S. J. Davies, A. F. Hill, M. U. Pilotti and F. G. A. Stone, *Polyhedron, 8* (1989) 2265; M. A. J. Moss and C. J. Jones, *Polyhedron, 8* (1989) 2367; R. A. Doyle and R. J. Angelici, *J. Am. Chem. Soc., 112* (1990) 194; I. B. Gorrell, A. Looney and G. Parkin, *Chem. Commun.,* (1990) 220.
5 E. Frauendorfer and G. Agrifolio, *Inorg. Chem., 21* (1982) 4122.
6 S. Trofimenko, *J. Am. Chem. Soc., 89* (1967) 3170.
7 W. H. McCurdy, *Inorg. Chem., 14* (1975) 2292.
8 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res., 16* (1983) 146; Cambridge Structural Database, Version Jan. 1990.
9 J. L. Aubagnac, R. M. Claramunt, C. López and J. Elguero, *Rapid Commun. Mass Spectrom.,* submitted for publication.
10 S. Trofimenko, *Inorg. Synth., 12* (1970) 99.
11 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, *The X-Ray System, Tech. Rep. TR-446,* Computer Science Center, University of Maryland, MD, U.S.A., 1976.
12 *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
13 W. D. S. Motherwell and W. Clegg, *PLUTO,* a program for plotting crystal and molecular structures, Cambridge University, U.K., 1978.
14 K. Hoffmann and E. Weiss, *J. Organomet. Chem., 67* (1974) 221.
15 F. H. Cano, J. Fayos and C. Foces-Foces, *J. Mol. Struct., 204* (1990) 111.
16 R. M. Claramunt, J. Elguero, M. J. Fabre, C. Foces-Foces, F. H. Cano, I. H. Fuentes, C. Jaime and C. López, *Tetrahedron, 45* (1989) 7805.
17 Y. A. Ozols, I. Tetere, S. G. Vimba and A. Ievins, *Latv. PSR Zinat. Akad.,* (1975) 517; *Chem. Abstr., 84* (1976) 52461.
18 J. Elguero and R. Jacquier, *J. Chim. Phys., 63* (1966) 1242.
19 J. Elguero, R. Jacquier and H. C. N. Tien Duc, *Bull. Soc. Chim. Fr.,* 3727 (1966).
20 M. Begtrup, J. Elguero, R. Faure, P. Camps, C. Estopá, D. Ilavský, A. Fruchier, C. Marzin and J. de Mendoza, *Magn. Reson. Chem., 26* (1988) 134.
21 M. Bruix, J. de Mendoza and J. Elguero, *Tetrahedron, 43* (1987) 4663.
22 M. Bruix, R. M. Claramunt, J. Elguero, J. de Mendoza and C. Pascual, *Spectrosc. Lett., 17* (1984) 757.
23 P. Cabildo, R. M. Claramunt and J. Elguero, *Org. Magn. Reson., 22* (1984) 603.
24 J. C. Calabrese, S. Trofimenko and J. S. Thompson, *J. Chem. Soc., Chem. Commun.,* (1986) 1123.
25 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem., 26* (1987) 1507.
26 S. Trofimenko, J. C. Calabrese, P. J. Domaille and J. S. Thompson, *Inorg. Chem., 28* (1989) 1091.
27 G. G. Lobbia, F. Bonati, P. Cecchi, A. Cingolani and A. Lorenzotti, *J. Organomet. Chem., 378* (1989) 139.
28 J. Atchekzaï, B. Bonnetot, J. C. Duplan, B. Fenet, B. Frange and H. Mongeot, *Magn. Reson. Chem., 27* (1989) 699.
29 K. Niedenzu, P. M. Niedenzu and K. R. Warner, *Inorg. Chem., 24* (1985) 1604.
30 J. L. Aubagnac, F. H. Cano, R. Claramunt, J. Elguero, R. Faure, C. Foces-Foces and P. Raj, *Bull. Soc. Chim. Fr.,* (1988) 905.
31 R. K. Harris, P. Jonsen, K. J. Packer and C. D. Campbell, *Magn. Reson. Chem., 24* (1986) 977; A. C. Olivieri, L. Frydman and L. E. Díaz, *J. Magn. Reson., 75* (1987) 50.
32 B. Wrackmeyer, *Annual Reports on NMR Spectroscopy,* Vol. 20, Academic Press, New York, 1986, p. 61.
33 I. I. Schuster, C. Dyllick-Brenzinger and J. D. Roberts, *J. Org. Chem., 44* (1978) 1765; D. S. Wofford, D. M. Forkey and J. D. Russell, *J. Org. Chem., 47* (1982)

5132; B. C. Chen, W. von Philipsborn and K. Nagarajan, *Helv. Chim. Acta, 66* (1983) 1537; L. Stefaniak, J. D. Roberts, M. Witanowski and G. A. Webb, *Org. Magn. Reson., 22* (1984) 215; W. von Philipsborn and R. Müller, *Angew. Chem., Int. Ed. Engl., 25* (1986) 383.

34 A. Fruchier, V. Pellegrin, R. M. Claramunt and J. Elguero, *Org. Magn. Reson., 22* (1984) 473.

35 C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology,* Wiley, New York, 1979.

36 C. López, R. M. Claramunt and P. Molina, unpublished results.

37 D. Sanz, R. M. Claramunt, J. Elguero, L. Salazar and M. Espada, *J. Chem. Soc., Perkin Trans., 1* (1990) 809.

38 J. Elguero, in A. R. Katritzky and C. W. Rees (eds.), *Pyrazoles and their Benzo Derivatives,* Vol. V, *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, 1984.

39 P. Cabildo, R. M. Claramunt and J. Elguero, *J. Heterocycl. Chem., 21* (1984) 249.

40 P. Camps and J. Elguero, unpublished results.

41 R. M. Claramunt, P. Cabildo, D. Sanz and J. Elguero, *Spectrosc. Int. J., 4* (1985) 109.