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MULTINUCLEAR MAGNETIC RESONANCE STUDY (^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{31}P, ^{119}Sn, ^{207}Pb NMR) OF SOME *N*-PYRROLYL DERIVATIVES

BERND WRACKMEYER

Institut für Anorganische Chemie der Universität München, Meiserstr. 1, D-8000 München 2 (F.R.G.)

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Summary

A multinuclear magnetic resonance study (^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{31}P, ^{119}Sn, ^{207}Pb NMR) of *N*-pyrrolyl derivatives, $E(NC_4H_4)_n$ ($E = (CH_3)_2B$, $(C_2H_5)_2B$, C_2H_5B, $(CH_2S)_2B$, $C_2H_5B(NC_5H_5)$, $n = 1, 2, 3$; $E = (CH_3)_3Si$; $(CH_3)_3Sn$, $(CH_3)_2Sn$, $n = 1, 2$; $E = (CH_3)_3Pb$) has been carried out. Changes in the chemical shifts and coupling constants are discussed in terms of the influence of the various substituents on the electronic structure of the pyrrole system. It is shown that $\delta(^{13}C)$ and $\delta(^{15}N)$ data, in particular, act as indicators of mesomeric and/or inductive substituent effects. This is supported by comparison with $\delta(^{13}C)$ data for analogous benzene derivatives.

Introduction

The importance of pyrroles as a structural unit in many natural products is reflected to some extent in the numerous studies of the chemistry and spectroscopy of simple pyrrole derivatives. We have previously studied the synthesis and some NMR parameters of pyrrole derivatives of Group III, IV, V elements [1–5]. Thus, we reported ^{13}C (2-pyrrolylboranes [3]), ^{11}B and ^{14}N NMR data (1-pyrrolyl-, 2-pyrrolylboranes [1,2,4]), and recently we carried out an extensive study of *N*-pyrrolylphosphorus compounds [5] (^{13}C, ^{14}N, ^{15}N and ^{31}P NMR). In the present work we present ^{13}C NMR data for various 1-pyrrolyl derivatives together with ^{15}N NMR data and the NMR parameters of nuclei (^{11}B, ^{29}Si, ^{31}P, ^{119}Sn, ^{207}Pb) linked to the pyrrole nitrogen atom. The various *N*-substituents can be regarded as π-acceptors and/or as inductive donors. The objective was to use the information from the NMR parameters to throw light on the changes in the electronic structure of the pyrrole system. The widely differing nature of the *N*-substituents studied should help to reveal which NMR parameters are most sensitive and useful in this respect.

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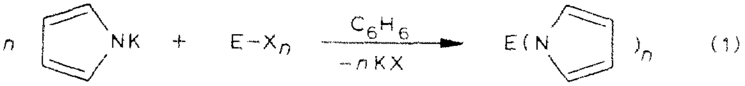
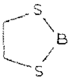
Results and Discussion

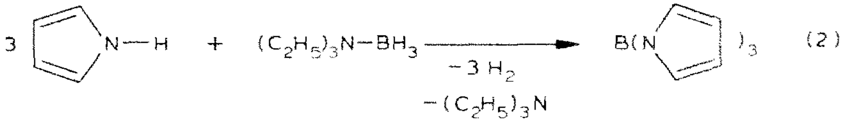
Synthesis

The *N*-pyrrolyl derivatives **1a–e** [1], **2a–d** [6] and **3a**, **b** [5] were prepared by the reaction of potassium pyrrole with the corresponding element halides (eq. 1):



E	n	Nr.	E	n	Nr.
$(CH_3)_2B$	1	**1a**	$(CH_3)_3Si$	1	**2a**
$(C_2H_5)_2B$	1	**1b**	$(CH_3)_3Sn$	1	**2b**
C_2H_5B	2	**1c**	$(CH_3)_2Sn$	2	**2c**
	1	**1d**	$(CH_3)_3Pb$	1	**2d**
			$(CH_3)_2P$	1	**3a**
B	3	**1e**	$(CH_3)_2P(S)$	1	**3b**

The yield was in general between 60–80%, except for **1c**, **1d** and **2c** (ca. 25%, < 5%, and < 5%, respectively). Low yields from this route appear to be general if there is more than one halogen atom to be substituted [5], and so tris(*N*-pyrrolyl)borane (**1e**), was prepared by the reaction of pyrrole with triethylamine-borane [7] (eq. 2).



(**1e**)

Addition of pyridine to **1c** (1/1 ratio) gave the borane adduct **1f** [7].

NMR data

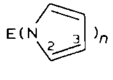
The NMR data of the pyrroles **1–3** are given in Table 1. Selected $\Delta(^{15}N)$, $\Delta(^{13}C(2, 3))$ data of pyrroles and $\Delta(^{13}C$ $(i, o, m, p))$ data of corresponding phenyl compounds are given in Table 2.

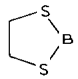
For the *N*-pyrrolylboranes (**1**) the ^{14}N NMR spectra were satisfactory, as reported previously [1,4]. In the case of **1a** we recorded the ^{15}N NMR spectrum using the refocused INEPT [8] and the basic INEPT [9] pulse sequence. The latter was more efficient inspite of the unresolved multiplet structure of the broad ^{15}N resonance. This is a consequence of the partially relaxed scalar coupling $J(^{15}N^{11}B)$ [10], which leads to efficient scalar relaxation of the second kind [11]. The ^{15}N NMR spectra (refocused INEPT) for compounds **2a, b, d** gave accurate $\delta(^{15}N)$ data and the coupling constants $^1J(^{119}Sn^{15}N)$, $^1J(^{207}Pb^{15}N)$. The signal to noise ratio in the case of **2a** was insufficient for observing $^1J(^{29}Si^{15}N)$.

The assignment of the ^{13}C resonances is straightforward [5]. All other NMR spectra were recorded using standard conditions: ^{29}Si (^1H decoupled refocused INEPT, $^2J(^{29}Si^1H)$ 7.3 Hz), ^{119}Sn (^1H inverse gated decoupling for NOE suppression) and ^{11}B, ^{207}Pb NMR (^1H decoupled).

TABLE 1

^{13}C, ^{15}N, ^{11}B, ^{29}Si, ^{31}P, ^{119}Sn, ^{207}Pb-NMR PARAMETERS [a] OF *N*-PYRROLYL DERIVATIVES



Nr.	E	$\delta(^{13}C)$(pyrrole)			$\delta(^{15}N)$ ($^1J(^{15}NX)$) (Hz)	X (in E)	other $\delta(^{13}C)$ in E ($^1J(^{13}CX)$ (Hz))	Solvent
		C(2)	C(3))	$^1J(^{13}C(2)^{13}C(3))$ [b] (Hz)				
1a	$(CH_3)_2B$	124.6	114.2	68.0	−187 (< 10)	54.2	6.5 (> 58 ± 3) $^1J(^{13}C^{11}B)$	$CDCl_3$
1b	$(C_2H_5)_2B$	124.1	113.6	67.5	−185 [c]	57.6	11.9, 8.6 (br)	$CDCl_3$
1c	C_2H_5B	125.2	113.4	67.5	−195 [c]	39.3	9.5, 9.5 (br)	$CDCl_3$
1e	B	126.6	113.6	n.o.	−207 [c]	27.8	–	$CDCl_3$
1d		125.6	113.7	68.0	−201 [c]	53.3	36.7	$CDCl_3$
1f	$C_2H_5B(NC_5H_5)$	123.0	108.5	n.o.	n.o.	5.0	14.7, 9.5 (br)	$CDCl_3$
2a	$(CH_3)_3Si$	127.7	114.4	67.5	−216.0	11.0	−0.5 (58.1) $^1J(^{29}Si^{13}C)$	C_6D_6
2b	$(CH_3)_3Sn$	124.4	109.8	65.0	−216.2 (6.4)	+72.9	−5.8 (397.7) $^1J(^{119}Sn^{13}C)$	C_6D_6
2c	$(CH_3)_2Sn$	124.1	110.1	n.o.	n.o.	+15.2	−4.6 (511.0) $^1J(^{119}Sn^{13}C)$	$CDCl_3$
2d	$(CH_3)_3Pb$	125.4	108.8	63.5	−206.7 (290.0)	+204.0	9.0 (312.1) $^1J(^{207}Pb^{13}C)$	C_6D_6
3a	$(CH_3)_3P$ [d]	123.1	111.3	n.o.	−219.3 (+55.6)	+34.4	17.9 (15.5) $^1J(^{31}P^{13}C)$	C_6D_6
3b	$(CH_3)_2P(S)$ [d]	122.0	113.0	n.o.	−212.6 (+13.2)	+63.0	24.2 (66.0) $^1J(^{31}P^{13}C)$	C_6D_6

[a] Solutions of 10–30% (w/v), 27–28°C; values $\delta(^{13}C)$, $\delta(^{15}N)$, $\delta(^{31}P)$, $\delta(^{29}Si)$ and $\delta(^{119}Sn) \pm 0.1$ ppm; $\delta(^{11}B)$ ±0.3 ppm; $\delta(^{14}N)$ ±1 to ±5 depending on the ^{14}N-linewidth; $\delta(^{119}Sn)$, $\delta(^{207}Pb)$ ±0.3 ppm; n.o. = not observed. [b] From the ^{13}C-satellites ±0.5 Hz. [c] ^{14}N NMR. [d] Ref. 5.

^{13}C NMR

Recent solid state NMR measurements [11] support the relationship between π-electron charge densities and isotropic ^{13}C chemical shifts in 6π-electron ring systems originally proposed by Spiesecke and Schneider [12]. It is assumed that this relationship is valid also for $\delta(^{13}C)$ values of the pyrroles, at least for $\delta(^{13}C(3, 4))$ values which are least prone to neighbouring effects exerted by the *N*-substituents. The resonance structures **A** to **C** are common to all pyrrole derivatives studied, whereas structure **D** is restricted to *N*-substituents capable of π-interaction with the nitrogen atom. Any significant contribution of **D** will reduce the probability of **B** or

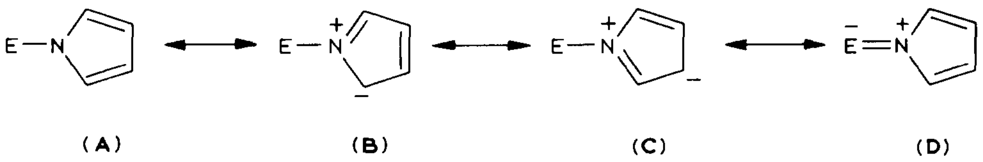
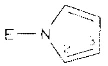
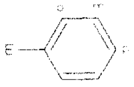


TABLE 2

SHIFT DIFFERENCES $\Delta(^{15}N)$, $\Delta(^{13}C)$ FOR CORRESPONDING *N*-PYRROLYL AND PHENYL COMPOUNDS RELATIVE TO THOSE FOR H-NC$_4$H$_4$ [a] and C$_6$H$_6$ [b,c]

E							
	$\Delta(^{15}N)$	$\Delta(^{13}C(2))$	$\Delta(^{13}C(3))$	$\Delta(^{13}C(i))$	$\Delta(^{13}C(o))$	$\Delta(^{13}C(m))$	$\Delta(^{13}C(p))$
CH$_3$	4.1 [d]	3.2	−0.1	9.2	0.7	−0.1	−3.0
C$_6$H$_5$	16.0	1.2	2.6	13.1	−1.1	0.4	−1.1
(CH$_3$)$_2$B	52.2	6.8	6.4	12.2	5.1	−0.9	3.4
	33.2	7.8	6.1	4.1	5.9	−1.1	2.9
(CH$_3$)$_3$Si	18.2	4.9	3.6	11.6	4.9	−0.7	0.4
(CH$_3$)$_3$Sn	18.0	6.6	2.0	13.4	7.4	−0.2	−0.3
(CH$_3$)$_3$Pb	27.5	7.6	1.0	20.1	8.0	−0.1	−1.0
(CH$_3$)$_2$P	14.9	5.3	3.5	13.6	1.6	−0.6	−1.0
(CH$_3$)$_2$P(S)	21.6	4.2	5.2	6.7	2.0	0.2	2.9

[a] $\Xi(^{15}N)$ (pyrrole) = 10 134 384 in acetone-d_6 (M.M. King, H.J.C. Yeh and G.O. Dudek, Org. Magn. Reson., 8 (1976) 208; conversion to the external CH$_3$NO$_2$-^{15}N chemical shift scale gives $\delta(^{15}N)$ −234.2; $\delta(^{13}C(2))$ 117.8, $\delta(^{13}C(3))$ 107.8 in C$_6$D$_6$. [b] $\delta(^{13}C)$ (C$_6$H$_6$) 128.5 [13]. [c] Except for the phenyl boranes [3] the $\Delta(^{13}C)$ data are taken from ref. 14. [d] 0.5 *M* in (CH$_3$)$_2$SO with 0.01 *M* Cr(acac)$_3$, L. Stefaniak, J.D. Roberts, M. Witanowski and G.A. Webb, Org. Magn. Reson., 22 (1984) 214.

C, and therefore reduce the π-electron charge density at C(2, 3). The $\delta(^{13}C)$ data in Table 1 show that there is significant deshielding of C(3) (with respect to pyrrole) in the boranes **1a**–**e** ($\Delta(^{13}C(3))$ 5.6 to 6.4) and in the phosphorus compound **3b** ($\Delta(^{13}C(3))$ 5.2). Comparison of the $\delta(^{13}C(3))$ data for **1c** with those of the pyridine adduct, **1f**, clearly demonstrates that the three-coordinate boron atom in **1a**–**e** functions as a π-electron acceptor [13]. The changes in the shielding of C(3) are reminiscent of the changes in the shielding of C(*para*) in phenyl compounds [14], and in phenyl boranes [3], in particular, as shown in Table 2. The assessment of the (CH$_3$)$_2$P(S) group as a weak π-acceptor is more justified by the data presented here than by those reported for a large number of other *N*-pyrrolyl-phosphorus compounds [5]. Interestingly, the $\Delta(^{13}C(3))$ values for **2a** (3.6) and **3a** (3.5) are very similar, and their magnitudes appear to be indicative of weak π-interactions. These interactions must be much weaker in **2b, d**, as revealed by the very small shift differences $\Delta(^{13}C(3))$ (2.0, 1.0) with respect to pyrrole.

Comparison of $\Delta(^{13}C(2))$ values of **1** to **3** with $\Delta(^{13}C(\mathit{ortho}))$ values for corresponding phenyl compounds [3,14] (Table 2) reveals roughly the same features. In agreement with the large $\Delta(^{13}C(\mathit{ortho}))$ data this shows that changes in the $\delta(^{13}C(2))$ values cannot be related straightforwardly to π-interactions, because of the spatial proximity of C(2) to the *N*-substituent.

^{15}N NMR

The nitrogen NMR parameter should be particularly useful for the discussion of substituent effects on the pyrrole system in *N*-pyrrolyl derivatives, but interpretation of substituent induced changes of δ(N) values is still a formidable problem [15–17].

The π-electron charge density argument will also apply to the trigonal nitrogen atom, and this is certainly in agreement with the large $\Delta(^{15}N)$ values (33–50 ppm with respect to pyrrole) observed for the *N*-pyrrolyl boranes. There may be additional effects in the light of the appreciable $\Delta(^{15}N)$ values for **2a–c** (ca. 22 to 31 ppm) and **3a** (18.5 ppm), [the larger $\Delta(^{15}N)$ value for **3b** (25.2 ppm) is consistent with the picture which emerged from the $\delta(^{13}C)$data]. In alkylamines the replacement of hydrogen by a $(CH_3)_3Si$, $(CH_3)_3Sn$ or $(CH_3)_2P$ group increases the shielding of nitrogen between 5 to 20 ppm [16], whereas deshielding is observed in the case of the pyrrole-nitrogen atom.

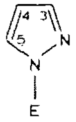
In the absence of additional significant π-interactions, the main change in the tensorial contributions to the shielding of trigonal planar nitrogen arises from B_0-induced paramagnetic circulations of the $\pi \leftrightarrow \sigma^\star$ or $\sigma \leftrightarrow \pi^\star$ type. Because of the latter, deshielding of the nitrogen atom can be predicted in the presence of electropositive substituents E with a strongly polarized N–E bond. Confirmation of this can be sought in the $\delta(^{13}C(ipso))$ values of corresponding phenyl compounds. These should show the same pattern as the $\delta(N)$ values, except for derivatives in which significant EN(*pp*) π-interaction is likely (a resonance structure such as **D** should be of minor importance in the phenyl compounds owing to the greater charge separation). That this is the case is shown by the values of $\Delta(^{15}N)$ and $\Delta(^{13}C(ipso))$ in Table 2.

We have also measured the ^{15}N NMR spectra of 1-trimethylsilylpyrazole (**4**) to obtain additional evidence [18]. The results, along with those for 1-methyl- and 1-phenylpyrazole, are given in Table 3. The data can be interpreted in the same way as for the pyrroles.

The spin–spin couplings $^1J(^{15}NX)$ ($X = {}^{11}B, {}^{29}Si, {}^{31}P, {}^{119}Sn, {}^{207}Pb$) are of interest since they involve a truly sp^2-hybridized nitrogen. The linewidth of the ^{15}N resonance in **1a** (~ 8 Hz) and the quadrupolar relaxation rate of the ^{11}B nucleus ($T_{Q(^{11}B)}$ 0.006 s) under the conditions used indicate that $|J(^{15}N^{11}B)| < 10$ Hz. This is

TABLE 3

NMR PARAMETERS OF SOME PYRAZOLES



E	$\delta(^{13}C)$			$\delta(^{15}N)$		$\delta(X)$
	C(3)	C(4)	C(5)	N(1)	N(2)	
CH_3 [a,b]	139.0	105.4	129.8	−180.8	−76.5	38.2 (^{13}C)
C_6H_5 [c]	141.1	107.6	126.8	−160.6	−78.6	140.5(*i*), 119.4(*o*), (^{13}C) 129.5(*m*), 126.5(*p*)
(**4**) $(CH_3)_3Si$ [d]	143.2	106.4	133.8	−158.7	−62.7	+14.2 (^{29}Si) −0.9 (^{13}C)

[a] In dioxane, data from H.-O. Kalinowski, S. Berger and S. Braun, ^{13}C-NMR Spektroskopie, Thieme Verlag, Stuttgart, 1984, p. 349. [b] In $CHCl_3$, B.C. Chen, W. von Philipsborn and K. Nagarajan, Helv. Chim. Acta, 66 (1983) 1537. [c] In $CDCl_3$, $\delta(^{15}N)$ converted to the external neat CH_3NO_2 scale by using the factor −359 [16]; G.E. Hawkes, E.W. Randall, J. Elguero and C.J. Marzin, J. Chem. Soc., Perkin Trans. II, (1977) 1024. [d] In C_6D_6, this work, $^1J(^{29}Si^{13}C)$ 58.0 Hz.

somewhat surprising since $|{}^1J({}^{15}N{}^{11}B)|$ in $(CH_3)_2BNH_2$ was found to be $\geq 30 \pm 3$ Hz [19b]. The small value of $|{}^1J({}^{119}Sn{}^{15}N)|$ in **2b** (6.4 Hz) is in agreement with the values of ${}^1J({}^{119}Sn{}^{15}N)$ in $(CH_3)_3SnNHC_6H_5$ [20] (-26.3 Hz) and in $(CH_3)_3SnN(CH_3)C_6H_5$ [21] ($+2.2$ Hz). Similarly in **2d** the value of ${}^1J({}^{207}Pb{}^{15}N)$ (290.0) is in the same range as that for $(CH_3)_3PbN(CH_3)C_6H_5$ [22] ($+261.0$), and it is likely that it has the same sign. From the various coupling constants ${}^1J({}^{119}Sn{}^{15}N)$ available [20–25], it can be assumed that there is a change of sign depending on the substituents at the tin or the nitrogen atom and on the coordination number of the tin atom, and this has been observed experimentally [20,21]. In contrast all the reduced coupling constants ${}^1K({}^{207}Pb{}^{15}N)$ available so far for lead with coordination number 4 [21,22,26] and 2 [25] appear to be large and negative. This can be attributed to the smaller *s*-overlap integral $\beta(PbN)$ with respect to $\beta(SnN)$, which gives rise to larger negative contributions to the Fermi contact energy term in the case of lead [21,22].

${}^{11}B$, ${}^{29}Si$, ${}^{119}Sn$ and ${}^{207}Pb$ NMR

The $\delta({}^{11}B)$ data for **1** have been discussed in detail previously [1,19]. They favour weak BN(*pp*) π-interactions. The other δ-values ($\delta({}^{29}Si)$, $\delta({}^{31}P)$, $\delta({}^{119}Sn)$, $\delta({}^{207}Pb)$) are less understandable, since either deshielding (${}^{29}Si$, **2a**, **4**; ${}^{119}Sn$, **2b**) or shielding (${}^{119}Sn$, **2c**; ${}^{207}Pb$, **2d**; ${}^{31}P$, **3a, b**) with respect to the corresponding diethylamino derivatives, $E{-}N(C_2H_5)_2$ [27] is observed. The values for the coupling constants ${}^1J({}^{13}CX)$ fall in the expected range (X = ${}^{11}B$ [19,30], ${}^{29}Si$ [28], ${}^{31}P$ [5], ${}^{119}Sn$ [23], ${}^{207}Pb$ [26]).

Experimental

NMR spectra (Table 1, 3) were recorded on a Bruker WP 200 spectrometer (${}^{11}B$: 64.21 MHz, ${}^{13}C$: 50.3 MHz, ${}^{14}N$: 14.4 MHz, ${}^{15}N$: 20.3 MHz, ${}^{29}Si$: 39.76 MHz, ${}^{31}P$: 81.02 MHz, ${}^{119}Sn$: 74.63 MHz, ${}^{207}Pb$: 41.8 MHz) using samples in 10 mm o.d. tubes as ca. 10 to 30% solutions. The following external references were used: $BF_3 \cdot OEt_2$ ($\delta({}^{11}B)$); $CDCl_3$ ($\delta({}^{13}C)$ 77.0); C_6D_6 ($\delta({}^{13}C)$ 128.0); neat CH_3NO_2 ($\delta({}^{14}N)$, $\delta({}^{15}N)$); $SiMe_4$ ($\delta({}^{29}Si)$); 80% H_3PO_4 ($\delta({}^{31}P)$); $SnMe_4$ ($\delta({}^{119}Sn)$), $PbMe_4$ ($\delta({}^{207}P)$); positive signs denote shifts to higher frequencies.

All compounds were handled under dry nitrogen, and dry deuterated solvents, saturated with nitrogen, were used. The *N*-pyrrolyl boranes **1a–1e** [1,7], the adduct **1f** [7] and the compounds **2a–2c** [6] and **3a, b** [5] were prepared by literature methods. The plumbane **2d** was obtained by the following method, which is typical of the method used for the other compounds (eq. 1).

N-Pyrrolyl-trimethylplumbane (**2d**)

A suspension of 11.84 g (37.2 mmol) $(CH_3)_3PbCl$ in 50 ml of benzene was prepared under N_2 in a 100-ml two-necked flask, equipped with a reflux condenser and a magnetic stirring bar, and cooled to −78°C. Then 4.21 g (40 mmol) potassium pyrrole was added as a powder, and the mixture was allowed to react at room temperature then refluxed for 12 h. (Reverse addition gave similar results) After cooling, undissolved material was filtered off and after removal of the benzene under vacuum the residue was fractionally distilled to give the air-sensitive **2d** as a colourless liquid (7.64 g, 63.5%), b.p. 106–108°C/10^{-2} mmHg which slowly turned into a colourless crystalline solid, m.p. 38–42°C. (Found: C, 24.8; H, 4.2; N, 4.5. $C_7H_{13}NPb$ calcd.: C, 26.4; H, 4.1; N, 4.4%). ^1H NMR (60 MHz), in CH_2Cl_2: $\delta(^1H)$ 1.30 (s, 9H) $PbCH_3$ $^2J(^{207}Pb^1H)$ 71.5 Hz; 6.68 (m, 2H) 2,5-H; 6.13 (m, 2H) 3,4-H.

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