

Molecular Structure of Tri(2-thienyl)borane

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Tri(2-thienyl)borane, X-Ray, ¹³C NMR Spectra, Solid-state ¹³C CP/MAS NMR

The molecular structure of tri(2-thienyl)borane (**1**) was determined [monoclinic, space group P2₁/c; *a* = 12.216(2), *b* = 7.765(2), *c* = 12.605(2) Å, β = 93.13(2)°]; two of the three thienyl groups are disordered, as is also indicated by the solid-state ¹³C CP/MAS NMR spectrum of **1**. The ¹³C NMR spectra of **1** were measured at variable temperature in solution and the barrier to rotation about the B-C bonds was found to be <35 kJ/mol. Thus, CB(pp) π interactions must be regarded as rather weak, in spite of suggestive $\delta^{11}\text{B}$, $\delta^{13}\text{C}$ data and structural parameters.

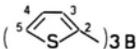
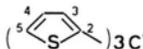
The dynamic and structural properties of triarylboranes have attracted considerable interest [1–3]. In this context, we have recently determined the molecular structures of triferrocenylborane [4] and two tri(N-pyrrolyl)boranes [5]. So far, all structural data and the low activation energy of the rotation about the B-C or B-N bonds point towards negligible or very weak (pp) π interactions between boron and the aromatic or heteroaromatic systems. In contrast, changes in the chemical shifts $\delta^{11}\text{B}$ and $\delta^{13}\text{C}$ seem to suggest significant (pp) π interactions, when compared with appropriate data, e.g. of trialkylboranes, unsubstituted aromatic compounds or triaminoboranes.

The ¹¹B nuclear magnetic shielding in tri(2-thienyl)borane (**1**) ($\delta^{11}\text{B}$ +47.3 [6]) is markedly increased with respect to triphenylborane ($\delta^{11}\text{B}$ +68.0 [7]). The same is true for $\delta^{13}\text{C}(\text{C}^+)$ of the tri(2-thienyl)carbocation ($\delta^{13}\text{C}$ 153.3 [8]) when compared with the triphenylcarbocation ($\delta^{13}\text{C}(\text{C}^+) = 210.9$ [9]). In a search for potential CB(pp) π interactions we have studied the ¹³C

NMR spectra of **1** in solution (see [7] for $\delta^{13}\text{C}$ data of other 2-thienylboranes) and in the solid state, and have determined the molecular structure of tri(2-thienyl)borane by X-ray structural analysis.

NMR spectroscopic data

The $\delta^{13}\text{C}$ data of **1** and the corresponding carbocation [8] are compared in Scheme 1. In addition to the deshielding of ¹³C(2), there is a marked deshielding of the ¹³C(3,5) nuclei in **1** and only a minor change in $\delta^{13}\text{C}(4)$. This reminds of the $\Delta^{13}\text{C}$ values of triphenylborane [7,10] with respect to benzene [$\Delta^{13}\text{C}(\text{i}) +16.4$, $\Delta^{13}\text{C}(\text{o}) +11.3$, $\Delta^{13}\text{C}(\text{m}) -0.9$, $\Delta^{13}\text{C}(\text{p}) +3.0$]. In solid triphenylborane, the phenyl rings are twisted against the C₃B plane by 54.4° [2]. Since it can be expected that this conformation will also be adopted on average in solution, CB(pp) π bonding will be very weak, and therefore changes in the $\delta^{11}\text{B}$ or $\delta^{13}\text{C}(\text{o,p})$ values are not directly related to such bonding. In the case of **1** there is little steric hindrance and the thienyl rings can adopt a conformation almost ideal for CB(pp) π interactions. However, as mentioned above the changes in the $\delta^{13}\text{C}$ data are not really dramatic when compared with $\Delta\delta$ values for triphenylborane. Therefore, it must be assumed that CB(pp) π interactions in **1** are rather weak, and that the increased ¹¹B nuclear shielding arises mainly from σ bonding effects. In contrast, the $\delta^{13}\text{C}$ values of the tri(2-thienyl)-carbocation indicate strong C⁺ C(pp) π interactions, and it has been suggested [8] that the $\delta^{13}\text{C}$ data, in particular $\delta^{13}\text{C}(5)$, indicate localisation of positive charge on the sulfur atoms.

		$\Delta^{13}\text{C}$	 1	 3C⁺
$\delta^{13}\text{C}(2)$	125.6	+18.6	144.2	132.8
$\delta^{13}\text{C}(3)$	127.3	+14.2	141.5	137.9
$\delta^{13}\text{C}(4)$	127.3	+ 1.6	128.9	124.3
$\delta^{13}\text{C}(5)$	125.6	+10.8	136.4	143.7
				$\delta^{13}\text{C}(\text{C}^+)$ 153.3

Scheme 1. Comparison of $\delta^{13}\text{C}$ data of thiophene, **1** (in CDCl₃) and tri-2-thienylmethyl cation (in H₂SO₄) [8].

We have also determined the coupling constants $J(^{13}\text{C},^1\text{H})$ and $J(^{13}\text{C},^{13}\text{C})$ in **1**, in order to confirm the assignment of the ¹³C NMR signals (see experimental part). None of these data indicate a special bonding situation in **1**.

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^1H and ^{13}C NMR spectra of **1** were measured between room temperature and 183 K. There was no indication of restricted rotation about the B-C bonds which would give rise to the presence of two diastereomers [1,3,4]. Thus, it can be estimated [11] that the activation energy of the barrier to rotation about the B-C bonds is less than 35 kJ/mol, typical of very weak $\text{CB}(\text{pp})\pi$ bonding.

In the solid-state ^{13}C CP/MAS NMR spectra of **1**, only the signal at $\delta^{13}\text{C}(4) = 130$ is resolved as a single signal, whereas the other $^{13}\text{C}(2,3,5)$ NMR signals overlap to give a broad unresolved hump between 135 and 145 ppm. The $^{13}\text{C}(4)$ nuclear magnetic shielding is in general much less affected by substituent effects or by slight structural changes than that of $^{13}\text{C}(2,3,5)$. Considering the disorder of two thienyl groups in single crystals of **1** (vide infra), one expects indeed a much more complex ^{13}C resonance pattern than in solution, at least for the $^{13}\text{C}(2,3,5)$ NMR signals. Although the numerous $^{13}\text{C}(2,3,5)$ resonances are not resolved, the general pattern of the solid-state ^{13}C NMR spectrum agrees qualitatively with the disorder of thienyl groups.

X-Ray analysis of tri(2-thienyl)borane (**1**)

Crystals suitable for X-ray analysis were grown from hexane solution. Table I lists experimental data relevant to the X-ray analysis [12], the molecular structure is shown in Fig. 1. The disorder of two of the thienyl groups indicates the presence of

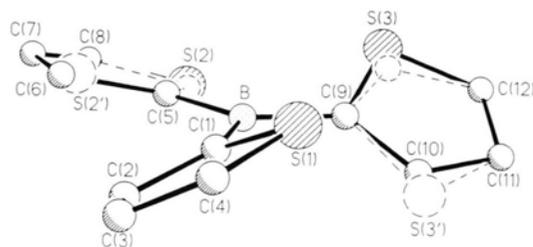


Fig. 1. Molecular structure of tri(2-thienyl)borane (**1**). Selected bond lengths [pm] and angles [$^\circ$]: B-C(1) 154.8(4), B-C(5) 154.1(3), B-C(9) 155.2(3), S(1)-C(1) 172.1(2), S(1)-C(4) 169.3(3), C(1)-C(2) 142.8(3), C(2)-C(3) 140.1(3), C(3)-C(4) 135.0(4); C(1)-B-C(5) 119.3(2), C(5)-B-C(9) 121.6(2), C(1)-B-C(9) 119.1(2), B-C(1)-S(1) 121.1(2), B-C(1)-C(2) 130.6(2), S(1)-C(1)-C(2) 108.3(2), S(1)-C(4)-C(3) 112.0(2), C(1)-S(1)-C(4) 93.6(1), C(1)-C(2)-C(3) 112.6(2), C(2)-C(3)-C(4) 113.5(2).

both diastereomers (one with all sulfur atoms on one side of the C_3B plane and the other one with alternating positions of the sulfur atoms with respect to the C_3B plane) in the crystal. In contrast with tri(N-pyrrolyl)borane [5], intermolecular interaction between tri(2-thienyl)borane molecules are negligible (closest intermolecular contacts range from 420 to 580 pm). In the molecule, the thienyl groups are twisted by 27.0, 16.0 and 32.5 $^\circ$ against the C1-C5-C9-B plane. There is no indication of disorder for the third thienyl ring.

The changes in the structural parameters for the thienyl ring are rather large when compared with thiophene itself [13]. Table II lists structural data for **1**, thiophene and two 2-substituted thiophenes [14,15] for comparison. The bond lengths B-C in **1** [154.8(4), 154.1(3), 155.2(3) pm] are slightly shorter than in triferrocenylborane [4] [156.9(4), 155.2(4), 156.1(4) pm], and significantly shorter than in triphenylborane [2a] [158.5(1) pm]. The bond C(1)-C(2) = 142.8(3) pm is elongated as compared to C(3)-C(4) = 135.0(4) pm, and is even longer than C(2)-C(3) = 140.1(3) pm. The bond S(1)-C(4) = 169.3(3) pm is slightly shorter than S(1)-C(1) = 172.1(2) pm, and the bond angle S(1)-C(1)-C(2) = 108.3(2) $^\circ$ is more acute than S(1)-C(4)-C(3) = 112.0(2) $^\circ$.

The changes in bond lengths and angles in **1**, when compared with thiophene, are tempting to discuss mesomeric canonical structures with $\text{CB}(\text{pp})\pi$ interactions. Although, at a first glance, this would be in accordance with the $\delta^{11}\text{B}$ and $\delta^{13}\text{C}$ values of **1**, there is an apparent contradiction considering the low barrier to rotation about the B-C bonds in **1**. Indeed, if one inspects structural data of substituted thiophenes reported in

Table I. Experimental data related to the X-ray analysis of tri(2-thienyl)borane (**1**).

Formula (molecular mass)	$\text{C}_{12}\text{H}_9\text{BS}_3$ (260.2)
Colour; crystal size	Colourless; 0.40 x 0.25 x 0.20 mm ³
Crystal system; space group; Z	Monoclinic; $P2_1/c$; 4
Unit cell dimensions [Å]; $^\circ$	$a = 12.216(2)$, $b = 7.765(2)$, $c = 12.605(2)$; $\beta = 93.13(2)$
V [Å ³]; ρ (calcd.) [Mg/m ³]	1193.9(4); 1.436
Absorption coefficient [mm ⁻¹]	0.585
Diffractometer; temperature [K]	Siemens P4; 173
Radiation [Å]	$\text{MoK}\alpha$, $\lambda = 0.71073$ graphite-monochromator 173
Temperature [K]	173
2θ -range; scan type	2.0 to 55.0 $^\circ$; ω
Reflections collected	3717
Independent/observed reflections	2684 ($R_{\text{int}} = 2.98\%$)/2347 ($F > 2.0 \sigma(F)$)
Refined parameters	155
Solution	Direct methods (SHELXTL PLUS)
R -/ wR -value (against F)	4.85%/3.75%
Weighting scheme	$[w^1 = \sigma^2(F) + 0.0000F^2]$
Max./min. residual electron density [eÅ ⁻³]	0.59 / -0.47

Table II. Selected bond lengths [pm] and angles [°] in thiophene [11], tri(2-thienyl)borane (**1**), and two 2-substituted thiophene derivatives [14,15] for comparison.

Compound	C ₄ H ₄ S ^[a]	1	Me ₂ In-2-C ₄ H ₃ S	H ₂ NC(O)-NHN=CH-2-C ₄ H ₃ S
S-C(1)	171.40(14)	172.1(2)	171.8(3)	171.6(5)
S-C(4)	171.40(14)	169.3(3)	169.4(4)	171.3(5)
C(1)-C(2)	136.96(17)	142.8(3)	136.8(5)	141.3(6)
C(2)-C(3)	142.43(23)	140.1(3)	140.2(6)	142.8(8)
C(3)-C(4)	136.96(17)	135.0(4)	134.4(8)	132.9(9)
C(1)-S-C(4)	92.16(10)	93.6(1)	94.1(2)	91.6(3)
S-C(1)-C(2)	111.5(3)	108.3(2)	107.5(3)	112.1(5)
S-C(4)-C(3)	111.5(3)	112.0(2)	110.7(3)	112.1(5)

^[a] Microwave study.

the literature [16], one finds a considerable range of bond lengths both for C(1)-C(2) and C(2)-C(3), also for cases with substituents for which mesomeric interactions are of minor importance. It should be noted here that disorder of 2-thienyl groups is frequently observed [17], but it may not have been always properly assigned. In contrast to the situation in phenyl derivatives, any substituent at the thiophene ring appears to distort significantly the ring geometry [18]. The data in Table II illustrate this situation, and also point out that changes in the bond lengths S-C(1) and S-C(4) and also in the bond angles may not be indicative of strong mesomeric interactions.

In conclusion, the interpretation of $\delta^{11}\text{B}$ and $\delta^{13}\text{C}$ data with regard to CB(pp) π bonding in **1** is ambiguous, even if seemingly conclusive direct structural information is available. Information on the barrier to rotation about the B-C bond is necessary in order to invoke or discard strong CB(pp) π interactions. This information should be obtained for systems with little steric hindrance as in the case of **1**.

Experimental

Tri(2-thienyl)borane (**1**) was prepared as described [6] (m.p. 101–103 °C), and samples of **1** were handled under an atmosphere of Ar or N₂,

observing all precautions to exclude moisture and oxygen. NMR spectra (¹H, ¹¹B, ¹³C) in solution were recorded using a Bruker ARX 250 instrument. Coupling constants [Hz]: $^1J(^{13}\text{C}(3),^1\text{H}(3)) = 167.5$; $^1J(^{13}\text{C}(4),^1\text{H}(4)) = 167.5$; $^1J(^{13}\text{C}(5),^1\text{H}(5)) = 183.5$; $^2J(^{13}\text{C}(3),^1\text{H}(4)) = 6.0$; $^3J(^{13}\text{C}(3),^1\text{H}(5)) = 10.8$; $^2J(^{13}\text{C}(4),^1\text{H}(3)) = 6.4$; $^2J(^{13}\text{C}(4),^1\text{H}(5)) = 4.4$; $^2J(^{13}\text{C}(5),^1\text{H}(4)) = 7.6$; $^3J(^{13}\text{C}(5),^1\text{H}(3)) = 9.6$; $^1J(^{13}\text{C}(2),^{13}\text{C}(3)) = 53.8$; $^1J(^{13}\text{C}(3),^{13}\text{C}(4)) = 55.8$; $^1J(^{13}\text{C}(4),^{13}\text{C}(5)) = 61.0$. Chemical shifts are given with respect to Me₄Si [$\delta^{13}\text{C}(\text{CD}_2\text{Cl}_2) = 53.8$] and Et₂O-BF₃ [$\delta^{11}\text{B} = 0$; $\Xi(^{11}\text{B}) = 32.083971$ MHz]. Solid-state ¹³C CP/MAS NMR spectra of **1** [packed under Ar into an air-tight insert [19], fitting exactly in the commercial 7 mm (o.d.) ZrO₂ rotor for the double bearing probe head] were recorded using a Bruker MSL 200 instrument (optimized contact time 3 ms, recycle delay 10 s, ¹H/¹³C 90° pulses 7 μs).

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