Evidence for π Bonding in the Boron–Thiolate Compounds $(2,4,6\text{-}Me_3C_6H_2)_2B(SPh)$ and $(2,4,6\text{-}Pr^i{}_3C_6H_2)B(SPh)_2$†

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The use of the bulky aryl substituent groups $2,4,6\text{-}Me_3C_6H_2$ and $2,4,6\text{-}Pr^i{}_3C_6H_2$ has allowed the structural characterization of two monomeric boron–sulfur compounds $(2,4,6\text{-}Me_3C_6H_2)_2B(SPh)$ **1** and $(2,4,6\text{-}Pr^i{}_3C_6H_2)B(SPh)_2$ **2**. The crystal structures of **1** and **2** show a close alignment between the boron and sulfur p orbitals that is consistent with a π interaction. Furthermore, the B–S distances in **1** [1.790(6)] and **2** [1.801(6) Å] are slightly shorter than the sum of the covalent radii (with allowance made for ionic effects) of boron and sulfur. Variable-temperature ^1H and ^{13}C NMR data for **2** indicate an average barrier to rotation around the B–S bond of *ca.* 12 kcal mol^{-1}. This value is significantly less than the 18.4 kcal mol^{-1} reported earlier for **1**. The lower rotational barrier observed in **2** is consistent with the delocalization of the B–S π bond over the three atom BS_2 π system which has a similar electronic arrangement to that of an allyl anion. Crystal data at 130 K: **1**, triclinic, space group $P\bar{1}$, $a = 7.851(5)$, $b = 11.685(6)$, $c = 13.096(7)$ Å, $\alpha = 63.52(2)$, $\beta = 73.93(2)$, $\gamma = 74.54(2)°$, $Z = 2$, $R = 0.073$; **2**, monoclinic, space group $P2_1/c$, $a = 18.373(3)$, $b = 12.713(2)$, $c = 10.844(2)$ Å, $\beta = 99.96(1)°$, $Z = 4$, $R = 0.072$.

Compounds in which there is a multiple bond between boron and the heavier main-group elements phosphorus or arsenic have been the subject of considerable recent attention.[1,2] Quite substantial rotation barriers (*ca.* 20 kcal mol^{-1}) have been demonstrated for B–P[3] and B–As[4] bonds indicating that the π bond can be of comparable strength to those observed in similar B–N systems.[5] In contrast, there are little data available for corresponding B–S or B–Se bonds. More surprisingly, perhaps, there have also been few dynamic NMR investigations of the lighter B–O system. One study[6] has shown that the rotation barrier for compounds of the type $R_2B(OMe)$ ($R = 2,6\text{-}Me_2C_6H_3$ or $2,4,6\text{-}Me_3C_6H_2$) is *ca.* 12 kcal mol^{-1} and for $(2,4,6\text{-}Me_3C_6H_2)B(OMe)_2$ it is 9.4 kcal mol^{-1}. The presence of restricted rotation around a B–S bond has been experimentally demonstrated in the case of only one compound, $R_2B(SPh)$ ($R = 2,4,6\text{-}Me_3C_6H_2$), for which a barrier of 18.4 kcal mol^{-1} was measured.[7] For simple thioborates, *e.g.* $R_2B(SR')$, no structural data in conjunction with B–S rotational barrier measurements have appeared although a gas-phase electron-diffraction study of $Me_2B(SMe)$[8] [B–S 1.779(5) Å] has been published.‡ In this paper we report a structural determination for the compound $(2,4,6\text{-}Me_3C_6H_2)_2B(SPh)$ **1** and the synthesis, spectroscopic and structural characterization of $(2,4,6\text{-}Pr^i{}_3C_6H_2)B(SPh)_2$ **2**. The data obtained are consistent with the presence of significant π bonding in the B–S bonds in these compounds.

Experimental

General.—All experiments were performed either by using modified Schlenk techniques or in a Vacuum Atmospheres HE43-2 dry box under nitrogen. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. Proton, ^{13}C, ^{11}B NMR spectra were recorded in C_6D_6 or C_7D_8 solutions using a General Electric QE-300 spectrometer. ^{11}B NMR chemical shifts were referenced to a $BF_3{\cdot}OEt_2$ solution in $CDCl_3$ as external standard. The compounds $2,4,6\text{-}Me_3C_6H_2Br$, $BF_3{\cdot}OEt_2$, PhSH, $2,4,6\text{-}Pr^i{}_3C_6H_3$ and $BH_2Cl{\cdot}SMe_2$ were purchased commercially and used as received, and $2,4,6\text{-}Pr^i{}_3C_6H_2Br$,[10] $(2,4,6\text{-}Me_3C_6H_2)_2BF$[11] and $[(2,4,6\text{-}Pr^i{}_3C_6H_2)Li{\cdot}OEt_2]_2$[12] were synthesized according to literature methods.

Preparations.—$[(2,4,6\text{-}Pr^i{}_3C_6H_2)BH_2]_2$. At 0 °C a solution of $Me_2S{\cdot}BH_2Cl$ (1.10 g, 10 mmol) in Et_2O (20 cm^3) was treated with a solution of $[(2,4,6\text{-}Pr^i{}_3C_6H_2)Li{\cdot}OEt_2]_2$ (2.84 g, 5 mmol) in Et_2O (30 cm^3) and stirred for 12 h at room temperature. Filtration, evaporation of all volatile materials and recrystallization from *n*-hexane yielded $[(2,4,6\text{-}Pr^i{}_3C_6H_2)BH_2]_2$ (1.09 g, 2.4 mmol, 48%) as colourless crystals. NMR: ^1H (C_6D_6), δ 7.18 (s, *m*-H), 3.14 (spt, *o*-CH, $^3J_{HH} = 6.3$), 2.87 (spt, *p*-CH, $^3J_{HH} = 6.9$ Hz), 2.66 (br s, μ-H), 1.33 (d, *o*-CH_3), 1.29 (d, *p*-CH_3); ^{11}B (C_6D_6), δ 22.9 (br s, $\Delta\nu_{\frac{1}{2}} = 670$ Hz).

$(2,4,6\text{-}Me_3C_2H_2)_2B(SPh)$ **1**. The synthesis is different from the published one by Davidson and Wilson[7] (LiSPh is used here instead of 'BrMgSPh'). A solution of $(2,4,6\text{-}Me_3C_6H_2)_2BF$ (0.38 g, 1.42 mmol) in *n*-hexane (30 cm^3) was slowly added to a slurry of LiSPh [generated *in situ* by reaction of PhSH (0.145 cm^3, 1.42 mmol) with *n*-BuLi solution (0.885 cm^3, 1.42 mmol) in *n*-hexane (30 cm^3) at 0 °C] in *n*-hexane (30 cm^3) at 0 °C. The mixture was warmed to room temperature, stirred for 24 h and filtered through a Celite-padded frit. Concentration and crystallization at −20 °C resulted in 0.37 g (1.0 mmol, 73%) of **1** as colourless plates.

$(2,4,6\text{-}Pr^i{}_3C_6H_2)B(SPh)_2$ **2**. A solution of PhSH (0.66 g, 6.0 mmol) in *n*-hexane (10 cm^3) was added slowly to a solution of $[(2,4,6\text{-}Pr^i{}_3C_6H_2)BH_2]_2$ (0.65 g, 1.5 mmol) in *n*-hexane (30 cm^3) at ambient temperature, whereupon a slight H_2 evolution was observed. After 4 h the mixture was filtered through a Celite-padded frit. Concentration to *ca.* 5 cm^3 and crystallization at −20 °C resulted in 1.02 g (2.36 mmol, 73%) of **2** in the form of colourless plates. Crystals suitable for X-ray crystallography were obtained by recrystallization from the minimum amount of *n*-pentane at *ca.* 5 °C, m.p. 117–119 °C. NMR: ^1H (C_7D_8), δ 7.31 (br s, *o*-H), 6.93 (s, *m*-H), 6.87 (br s, *m*-, *p*-H), 3.25 (spt,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: cal = 4.184 J.

‡ The structures of numerous other B–S compounds have also been determined;[9] however, the crystal structures of **1** and **2** are distinct in the sense that B–S π bonding is not compromised by other π interactions between the boron p orbital and π-donor substituents (*e.g.* NR_2 groups).

o-CH, $^3J_{HH}$ = 6.9), 2.70 (spt, *p*-CH, $^3J_{HH}$ = 6.9 Hz), 1.31 (d, *o*-CH_3), 1.15 (d, *p*-CH_3); ^{11}B (C_7D_8), δ 68.4 (br s, $\Delta\nu_{\frac{1}{2}}$ = 870 Hz); ^{13}C-{^1H} (C_7D_8, 60 °C), δ 150.4 [C(16)], 150.0 [C(14, 18)], 133.9 [C(13), C(2, 6), C(8, 12)], 132.4 [C(1, 7)], 128.8 [C(3, 5), C(9, 11)], 127.8 [C(4, 10)], 120.5 [C(15, 17)], 35.0 [C(19, 25)], 34.7 [C(22)], 24.9 [C(20, 21, 26, 27)], 24.1 [C(23, 24)] (for numbering scheme see Fig. 2).

Crystal Data Collection and Solution and Refinement of the Structures.—Crystallographic data for compounds **1**[13] and **2** are given in Table 1. Crystals of **1** and **2** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fibre by silicon grease and immediately placed in the low-temperature N_2 stream.[14] Crystal data were collected with Siemens R3 m/V (**1**) and Syntex P2_1 (**2**) diffractometers equipped with a graphite monochromator and a locally modified Enraf–Nonius (**1**) or Syntex LT-1 (**2**) low-temperature apparatus. Calculations were carried out on a MicroVax 3200 computer using the SHELXL 93 (**2**)[15] and the SHELXTL PLUS (**1**)[16] programs. Neutral atom-scattering factors and the correction for anomalous dispersion were from ref. 17. The structures of all molecules were solved by direct methods. The isopropyl group C(23) and C(24) atoms in compound **2** displayed disorder and were modelled using two sets of atoms with relative occupancies of 0.51(2) and 0.49(2). Atomic coordinates and selected bond distances and angles are given in Tables 2 and 3.

Table 1 Selected crystallographic data and structural parameters for compounds **1** and **2** *

Compound	**1**	**2**
Formula	$C_{24}H_{27}BS$	$C_{27}H_{33}BS_2$
M	358.3	432.5
Wavelength/Å	0.710 69 (Mo-Kα)	1.541 78 (Cu-Kα)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	7.851(5)	18.373(3)
b/Å	11.685(6)	12.713(2)
c/Å	13.096(7)	10.844(2)
α/°	63.52(2)	
β/°	73.93(2)	99.96(1)
γ/°	74.54(2)	
U/Å^3	1019(1)	2494.7(7)
Z	2	4
D_c/g cm^{-3}	1.168	1.151
F(000)	384	928
μ/mm^{-1}	0.163	1.993
2θ Range/°	0–55	4.8–114
Number of observed reflections	3217 [$I > 3\sigma(I)$]	3355 [$I > 2\sigma(I)$]
Number of variables	236	273
R, *R′*	0.073, 0.083	0.072, 0.165

* All data were collected at 130 K.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Structural Descriptions.—The structure of compound **1**, shown in Fig. 1, consists of monomeric units of formula (2,4,6-$Me_3C_6H_2)_2B(SPh)$ and there are no close interactions between these molecules. The co-ordination geometry at boron is planar with the widest angle, 125.5(4°) observed between the two mesityl substituents. The planarity almost extends to the sulfur and *ipso* carbon C(1) where there is a small angle (5.4°) between the perpendiculars to the planes at boron and sulfur. The planes of the mesityl rings are inclined at an angle of *ca.* 60° with respect to the boron co-ordination plane. The two C–B–S angles are quite different, 121.6(3) and 112.9(3)° with the wider angle associated with the mesityl group that is *Z* with respect to the SPh substituent. The B–S distance is 1.790(6) Å and the B–S–C(1) angle is 107.0(2)°.

Table 2 Atomic coordinates (× 10^4) for compounds **1** and **2**

Atom	*x*	*y*	*z*
Compound **1**			
S	3 934(1)	8 996(1)	6 608(1)
B	4 767(5)	9 612(4)	7 372(3)
C(1)	4 904(5)	7 329(3)	7 026(3)
C(2)	4 536(5)	6 457(3)	8 173(3)
C(3)	5 214(5)	5 149(3)	8 473(3)
C(4)	6 237(5)	4 708(3)	7 645(3)
C(5)	6 623(5)	5 572(4)	6 506(3)
C(6)	5 943(5)	6 880(3)	6 192(3)
C(7)	6 262(4)	8 758(3)	8 136(3)
C(8)	8 015(4)	8 278(3)	7 655(3)
C(9)	9 242(5)	7 490(3)	8 384(3)
C(10)	8 843(5)	7 163(3)	9 560(3)
C(11)	7 131(5)	7 646(3)	10 033(3)
C(12)	5 853(4)	8 430(3)	9 340(3)
C(13)	8 656(5)	8 626(3)	6 372(3)
C(14)	10 208(5)	6 306(4)	10 331(3)
C(15)	4 009(4)	8 861(3)	9 931(3)
C(16)	3 882(5)	11 065(3)	7 173(3)
C(17)	4 994(5)	12 035(3)	6 646(3)
C(18)	4 224(5)	13 324(3)	6 416(3)
C(19)	2 389(6)	13 715(3)	6 671(3)
C(20)	1 323(5)	12 765(3)	7 188(3)
C(21)	2 007(5)	11 458(3)	7 445(3)
C(22)	6 987(5)	11 724(3)	6 274(3)
C(23)	1 623(6)	15 130(3)	6 406(3)
C(24)	686(5)	10 521(4)	8 054(4)
Compound **2**			
S(1)	7 440(1)	7 967(1)	1 117(2)
S(2)	8 750(1)	9 445(1)	999(2)
C(1)	8 219(3)	7 117(4)	1 231(5)
C(2)	8 303(3)	6 510(4)	210(5)
C(3)	8 870(3)	5 787(4)	289(6)
C(4)	9 377(3)	5 705(4)	1 379(6)
C(5)	9 305(3)	6 308(4)	2 398(6)
C(6)	8 726(3)	7 020(4)	2 346(5)
C(7)	8 891(3)	10 790(4)	627(5)
C(8)	8 687(3)	11 616(4)	1 334(5)
C(9)	8 870(3)	12 630(4)	1 064(6)
C(10)	9 268(3)	12 833(5)	120(5)
C(11)	9 473(3)	12 013(4)	−578(5)
C(12)	9 282(3)	10 988(4)	−330(5)
C(13)	7 147(3)	10 138(4)	622(5)
C(14)	6 839(3)	10 607(4)	1 584(5)
C(15)	6 245(3)	11 312(4)	1 298(5)
C(16)	5 955(3)	11 558(4)	50(5)
C(17)	6 269(3)	11 093(4)	−887(5)
C(18)	6 855(3)	10 390(4)	−627(5)
C(19)	7 113(3)	10 329(5)	2 966(5)
C(20)	7 283(4)	11 297(5)	3 796(5)
C(21)	6 551(4)	9 614(5)	3 453(6)
C(22)	5 285(3)	12 261(5)	−291(6)
C(23)	4 386(7)	11 684(11)	98(18)
C(24)	5 382(9)	13 347(13)	294(16)
C(23b)	5 245(9)	13 170(13)	540(16)
C(24b)	4 621(8)	11 634(11)	−597(18)
C(25)	7 151(3)	9 880(5)	−1 714(5)
C(26)	6 550(4)	9 240(5)	−2 536(6)
C(27)	7 478(3)	10 692(5)	−2 489(6)
B	7 770(3)	9 279(5)	908(6)

Table 3 Selected bond distances (Å) and angles (°) for compounds **1** and **2**

Compound	1	2
B–S	1.790(6)	1.802(6) 1.799(6)
B–C	1.584(5) 1.584(5)	1.574(8)
S–C	1.773(4)	1.782(5) 1.786(5)
S(1)–B–S(2)		117.2(4)
S(1)–B–C(13)		114.7(4)
S(2)–B–C(13)		128.1(4)
S–B–C(7)	121.6(3)	
S–B–C(16)	112.9(3)	
C(7)–B–C(16)	125.5(4)	
C(1)–S(1)–B		106.6(3)
C(7)–S(2)–B		106.4(3)
C(1)–S–B	107.0(2)	

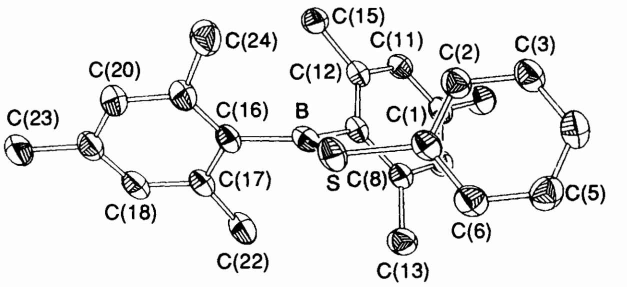

Fig. 1 Thermal ellipsoid (40%) plot of **1**. H atoms are not shown for clarity

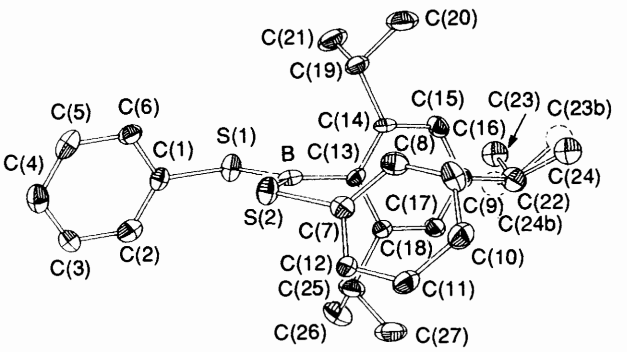

Fig. 2 Thermal ellipsoid (50%) plot of **2**. H atoms are not shown for clarity

The structure of **2** (Fig. 2) consists of well-separated molecules with no crystallographically imposed symmetry. The boron is surrounded in a planar fashion by two sulfurs and an *ipso* carbon, C(13), from the triisopropylphenyl group. The B–S distances are identical within experimental error and average 1.801 Å. The angle between the B–S bonds is 117.2(4)°. However, the two S–B–C angles differ considerably, 128.1(4) *vs.* 114.7(4)°, and the wider angle is associated with the *Z* oriented SPh group [S(2)]. The planes defined by B–S(1)–C(1) and B–S(2)–C(7) are almost coincident with the co-ordination plane at boron. The angles between the perpendiculars to the planes at S(1), S(2), the plane of the triisopropylphenyl ring and B are 6.2, 8.5 and 83.6°, respectively.

Variable-temperature ^{1}H *and* ^{13}C *NMR Studies*.—The temperature dependence of the ^{1}H NMR and ^{13}C NMR spectra of **2** in the range −100 to +100 °C was investigated in C_7D_8 solution. Energy barriers ($\Delta G^\ddagger$) for the observed dynamic processes were calculated by using an approximate formula as previously described.[18] In the ^{1}H NMR spectrum at 23 °C, a broadened doublet was observed for the *ortho*-isopropyl methyl groups which became a sharp doublet at 65 °C. Cooling the sample resulted in splitting of the *ortho*-isopropyl methyl peak into two well separated doublets. Taking a T_c of −20 °C and a maximum peak separation of 121 Hz at −99 °C gives a barrier of 11.9 kcal mol^{-1} for the dynamic process. Peak overlap in the aromatic region prevented an interpretation of the dynamic behaviour of the thiophenolate hydrogens. Therefore a ^{13}C-{^{1}H} variable-temperature NMR study was undertaken. As before, the room temperature spectrum showed a broadened *ortho*-isopropyl methyl carbon signal, which sharpened on warming to 60 °C. Upon cooling the solution, all thiophenolate signals broadened and separated into two sets of signals. Due to overlap of the *p*- and *m*-C (thiophenolate) peaks with the solvent, only three sets of signals were suitable for the calculation of the rotational barrier. For the isopropyl methyl group a T_c of −5 °C and a maximum peak separation of 250 Hz at −99 °C resulted in a barrier of 12.2 kcal mol^{-1}. Analogous calculation for the *ipso*- and *ortho*-thiophenolate carbon signals led to barriers of 11.9 and 12.1 kcal mol^{-1} respectively (*ipso*: T_c = −25 °C, maximum peak separation 77 Hz at −99 °C. *ortho*: T_c = −15 °C, maximum peak separation 124 Hz at −99 °C).

Discussion

The mono- and bis-thio-borate species **1** and **2** were synthesized by simple salt- or hydrogen-elimination procedures. The synthesis of compound **1** (by a different route) has been previously described, and dynamic ^{1}H NMR studies indicated that there was a barrier of 18.4 kcal mol^{-1} to a process that was interpreted to be rotation around the B–S bond.[7] Nonetheless, no detailed structural data for this compound have appeared. It was therefore felt that an X-ray structural characterization of this compound as well as a structural and spectroscopic investigation of a bis-thiolato derivative such as **2** would shed somewhat more light on the nature of any possible B–S π interactions.

The key structural parameters for **1** and **2** relate to the B–S bond lengths and the degree of coincidence of the co-ordination planes at boron and sulfur. The latter is often taken to be indicative of the efficiency of the overlap of the adjacent p orbitals. By this criterion, at least, the boron and sulfur p orbitals in **1** and **2** are correctly aligned for π overlap since the angles between the perpendiculars to the co-ordination planes at boron and sulfur do not exceed 8.5° in either molecule. The B–S bond lengths are also of major importance in indicating the presence of π bonding. In essence, shorter than predicted bond lengths are usually held to be indicative of the presence of a multiple interaction. The average B–S distance observed in **2** (1.80 Å) is slightly greater than, but not significantly different from, that in **1** (1.79 Å). The B–S bond length in **1** is close to the 1.779(5) Å observed in $Me_2B(SMe)$[8] (whose gas-phase structure was stated to have a 'probably planar' C_2BSC array) and may be compared to the sum of the covalent radii of boron* (0.85 Å) and sulfur (1.02 Å) which is 1.87 Å. Since the B–S bond has some polar character, this value can be corrected for ionic shortening according to the Schomaker–Stevenson formula.[20] This affords a corrected value of 1.83 Å for the B–S bond length. Thus, in the case of the simplest B–S compound **1**, the ionic correction accounts for about 0.04 Å, or half of the discrepancy between the observed and predicted values. It is possible to attribute the remaining 50% of the shortening to π bonding. For compound **1**, therefore, the coincidence of the co-ordination planes at boron and sulfur and the shorter than predicted B–S bond suggests the presence of a π interaction between the boron and

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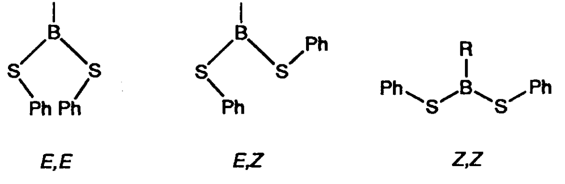
* The radius of boron used here is based upon B–B bond distances measured in diborane(4) compounds.[19]

sulfur p orbitals.* Furthermore these data are in agreement with the previously reported variable-temperature ^1H NMR studies for **1** which showed that there was a substantial barrier (18.4 kcal mol^{-1}) to rotation around the B–S bond.[7] It is unlikely that this barrier could be attributed to steric effects or ring flipping since the more crowded $B(C_6H_2Me_3\text{-}2,4,6)_3$ has a much lower barrier (*ca.* 12 kcal mol^{-1}) to the latter process. Compound **1** thus represents the simplest possible B–S p–p π bond since it involves the interaction of a single empty p orbital at boron with a p orbital on sulfur occupied by a lone pair of electrons. A slightly more complex p–p interaction is present in **2**. Here there are three adjacent p orbitals with two lone pairs of electrons provided by the sulfurs. An electronic analogy may thus be drawn with an allyl anion in which three π-molecular orbitals are possible. The most stable of these is strongly bonding affording, in effect, a delocalized three-centre two-electron π bond. The next highest molecular-orbital energy level is essentially non-bonding and thus accommodates the second pair of electrons. The remaining π orbital is antibonding. One consequence of the delocalized planar π system is that three distinct orientations of the thiolate groups are permitted. These are the *E,E*, the *E,Z* and the *Z,Z* configurations as illustrated in Scheme 1 (R = $2,4,6\text{-}Pr^i_3C_6H_2$). For steric reasons, the *E,E* isomer is the least favoured energetically and is unlikely to exist to a significant extent in solution. Of the two remaining possibilities, the *E,Z* isomer is observed in the solid and it can be easily converted to the *Z,Z* isomer by a simple rotation around a B–S bond. The average length of the B–S bonds in **2** is 1.801(6) Å, which is just slightly longer than the 1.796(7) Å observed in the gas phase structure of $MeB(SMe)_2$.[8] The near equivalence of the B–S bond lengths in **1** and **2** may be rationalized on the basis that **2** has a greater number of electronegative substituents which, in effect, contract the radius of boron and shorten the B–S distance. Apparently, this contraction is approximately equal to the lengthening arising from the weakening of the π bonding relative to that present in **1**.

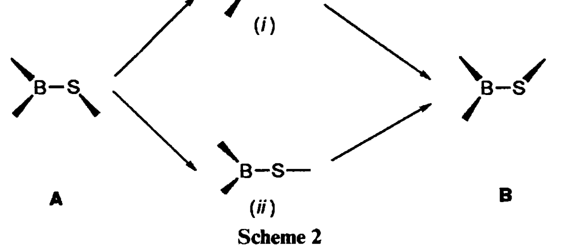
At room temperature, interconversion between the *E,Z* and *Z,Z* configurations is apparently still rapid in the case of **2** since only one, albeit broadened, set of phenyl peaks is observed in the ^{13}C NMR spectrum. Slight cooling, however, results in the observation of two separate sets of Ph resonances. The peaks are of equal intensity and are due presumably to the *E,Z* isomer. The average barrier to the dynamic process is 12.0 kcal mol^{-1} which is significantly less than the 18.4 kcal mol^{-1} measured for **1**.[7] The difference in values can be interpreted on the basis of the fact that in **1** the 1 : 1 B–S π interaction is stronger than the 1 : 2 B–S π interaction in **2** in which the π-molecular orbital is delocalized over three nuclei. Thus the much lower rotation barrier observed in **2** constitutes supporting evidence for the existence of B–S π bonding in both **1** and **2**.†



Scheme 1

The usual interpretation of the energy barriers in **1** and **2** and related species is that they are representative of the strength of the π bond. This interpretation is, however, based upon the assumption that the dynamic process is, in fact, a rotation around the B–S bond. It is apparent, however, that conversion of A into B (see Scheme 2) can proceed by two different pathways (*i*) or (*ii*) which involve different transition states.[†,21] During pathway (*i*) the co-ordination planes at boron and sulfur are perpendicular to each other, the angle at sulfur remains essentially unchanged and it is assumed that there is little or no π interaction between either lone pair on sulfur and the p orbital on boron. In pathway (*ii*), however, the thiolate sulfur is linearly co-ordinated in the transition state (*i.e.* a linear inversion process[7]) so that a lone-pair orbital may interact with the boron p orbital. In other words, there remains a significant π interaction in the transition state of pathway (*ii*), and an energy barrier involving this process would not necessarily give an accurate indication of the π-bond strength in the ground state. Recent calculations[21] on $H_2B(SH)$, however, have shown that the linear structure of pathway (*ii*) is 41.2 kcal mol^{-1} less stable than (*i*). In essence, pathway (*i*) is the operative one in the conversion A $\longrightarrow$ B and thus is representative of the strength of the B–S π interaction.

In summary, the variable-temperature ^1H NMR and crystal structural data for **1** and **2** indicate that the extent of B–S π bonding can be quite substantial and comparable in strength to B–O π bonding. Rotation about the latter type of π bond has been shown[21] to be complicated by the fact that the oxygen analogue of the linear transition state in pathway (*ii*) (Scheme 2) is just 4.5 kcal mol^{-1} less stable than transition state (*i*). Thus, rotation around the B–O bond involves a substantial participation by the linear transition state of pathway (*ii*) which retains a significant degree of π bonding. Accordingly, measurements of the B–O rotational barrier can substantially underestimate the strength of the π interaction in the ground state. Nonetheless, it appears that the strength of B–O and B–S π interactions in the ground states A and B are approximately equal, at least, in these compounds. This somewhat surprising result, in which similar π-bond strengths are observed for bonds that involve light or heavier main-group elements, has been explained on the basis of the polarities and relative sizes of the bonding atoms.[24] In effect the atom pair B–S [*cf.* Allred–Rochow electronegativity value of B (2.01) and S (2.44)] is significantly less polar than B–O [electronegativity value of O (3.5)]. In addition, the covalent radii of boron (0.85 Å) and sulfur (1.02 Å) are only slightly more disparate than those of oxygen (0.7 Å) and boron. Thus, the polarity and size compatibility of the B–O and B–S pairs is such that the B–O and B–S π bonding is of comparable magnitude with somewhat lower rotation barriers being observed in the B–O system owing to the differences in the structures of the transition states.[21] Further structural and spectroscopic measurements on a wider range of B–O compounds may be warranted in order to bear out this view.



Scheme 2

Acknowledgements

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* While the work described here was in progress, Professor M. T. Ashby informed us that he and his co-workers had studied the structures and performed theoretical calculations on the compounds $(2,4,6\text{-}Me_3C_6H_2)_2B(EMe)$ (E = O or S). They concluded that there was significant B–S π bonding in the compound $(2,4,6\text{-}Me_3C_6H_2)_2$-B(SMe). The measured B–S distance was 1.787(6) Å. These results have since been published (see ref. 21).

† The strength of B–S bonding had also been supported by earlier theoretical calculations[22] and has been inferred from experimental data.[23]

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