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Ring strain in boroxine rings: computational and experimental considerations

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Abstract

B3LYP/6-311 + G(d) calculations indicate that $(HBO)_3$ (**4**) and $(HBO)_4$ (**5**) possess (zero-point energy corrected) strain enthalpies of 11.4 and 31.6 kJ mol^{-1}, respectively. The absence of eight-membered $(RBO)_4$ rings is attributed to a combination of ring strain and the lability of the B–O bond. The synthesis, characterization and molecular structure of $(PhBO)_3$·pyridine (**1**) are described and chemical phenomena related to the addition of amines to triorganoboroxine rings are rationalized in terms of relief of ring strain in **4**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: DFT analysis; Boroxine rings; Ring strain

1. Introduction

The dehydration of organoboronic acids, $RB(OH)_2$ (R = alkyl, aryl), exclusively produces six-membered triorganoboroxine rings, $(RBO)_3$, regardless of the nature of the organic substituents [1]. There is one report describing the synthesis of a four-membered ring (2,4,6-*t*-Bu_3–C_6H_3–$BO)_2$ [2], however, the product was not completely characterized. It has also been suggested that hydrolysis of triorganoboroxine rings by trace amounts of water may lead to erroneously low molecular weight determinations [3]. The preference for six-membered rings was attributed to resonance stabilization of a conjugated six π-electron system by Snyder et al. in 1938 [4] and since then, the degree of aromaticity in triorganoboroxines has been the subject of vigorous debate [5–19].

Recent work on the magnetic properties of triorganoboroxines and the results of DFT calculations suggest that the lone pair electrons are mostly localized at the oxygen atoms and consequently, triorganoboroxines possess very little aromatic character [15–19]. In a recent publication, Gillespie et al. demonstrated that the boron–oxygen bonds in boron oxides are predominantly ionic in nature and therefore, the geometries of these molecules would not be satisfactorily understood using a covalent model [20].

In 1958, Snyder et al. reported the synthesis of a 1:1 complex between triphenylboroxine and pyridine, $(PhBO)_3$·pyridine (**1**), and proposed that the coordination of the pyridine occurs at one boron atom within the B_3O_3 ring (Chart 1) [21].

Over the years, a diverse range of other 1:1 complexes between triorganotriboroxines and nitrogen donors, $(RBO)_3$·L (R = alkyl, aryl; L = amines, hydrazines), have been prepared and some examples were investigated by X-ray diffraction [22–31]. It is worth

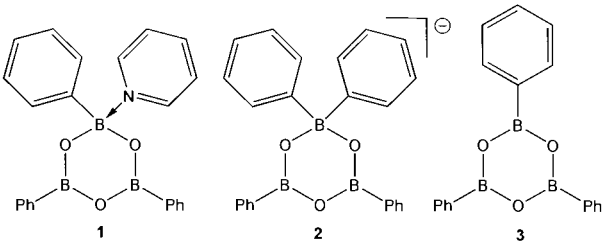

Chart 1.

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mentioning that most attempts to prepare such complexes with a stoichiometry other than 1:1 have failed, the only notable exception being tris(2-(*N*,*N*-dimethylhydrazo)phenyl)boroxine, in which coordination of two out of three potentially intramolecular coordinating ligands is found [32]. However, the coordination in the latter compound is weaker than in the aforementioned 1:1 adducts. According to NMR studies, complexes between triorganoboroxines and amines undergo a dissociation–recombination process that is fast on the NMR time scale at room temperature. The activation energies associated with this effect range from 39 to 54 kJ mol^{-1} [24].

Moreover, the reaction of oxybis(diphenylborane), Ph_2BOBPh_2, with four equivalents of phenylboronic acid, $PhB(OH)_2$, in the presence of tetramethylammonium hydroxide, NMe_4OH, provides the anion $[Ph_2B(OBPh)_2O]^-$ (**2**) (counterion $[NMe_4]^+$) [33], which is isoelectronic with the amine complex $(PhBO)_3$·pyridine (**1**) (Chart 1). The same anion is formed serendipitously by the hydrolysis of the tetraphenylborate anion, Ph_4B^-, in the presence of the tetrakis[(tri - *tert* - butylphosphine)gold(I)]phosphonium cation $[\{(t\text{-}Bu)_3PAu\}_4P]^+$ [34]. In a similar manner, the analogous anion $[F_2B(OBF)_2O]^-$ is formed by the hydrolysis of BF_3 in the presence of the hexakis[(tri-*iso*-propylphosphane)gold(I)]methanium dication $[(i\text{-}Pr_3PAu)_6C]^{2+}$ [35].

The chemistry of triorganoboroxines is dominated by ring-cleavage reactions [36]. On the other hand, 1:1 triorganoboroxine–amine complexes are so stable and easily formed that a convenient literature preparation of $(MeBO)_3$ from $B(OMe)_3$ involves the initial formation of $(MeBO)_3$·pyridine followed by removal of pyridine [37].

In this paper, DFT calculations are applied to investigate the following questions: (i) Given that triorganoboroxines possess very little aromatic character, what is the real reason for the exclusive preference of six-membered $(RBO)_3$ rings over eight-membered $(RBO)_4$ rings? (ii) Why does the addition of amines to triorganoboroxines rarely proceed beyond 1:1 stoichiometry? (iii) Why are triorganoboroxines more susceptible to ring cleavage compared to their 1:1 amine adducts?

We propose that all three questions may be addressed using ring strain considerations. To the best of our knowledge, there are no experimental or computational reports in the literature concerning ring strain in boron–oxygen rings. The cubic form of the tetramer $(HBO)_4$ has been studied computationally [38], however, we have been unable to locate any computational studies concerning the eight-membered ring form of $(HBO)_4$.

We also revisit the synthesis of $(PhBO)_3$·pyridine (**1**) and report full details of its molecular structure and compare it with those of the isoelectronic anion $[Ph_2B(OBPh)_2O]^-$ (**2**) [33,34] and the parent triphenylboroxine $(PhBO)_3$ (**3**) [39,40] (Chart 1).

2. Discussion

*2.1. Differences in reactivity between $(PhBO)_3$·pyridine (**1**) and $(PhBO)_3$ (**3**): experimental evidence of ring strain?*

The reaction of phenylboronic acid, $PhB(OH)_2$, with pyridine in a 3:1 molar ratio proceeds via complete condensation and provides the 1:1 complex between triphenylboroxine and pyridine, $(PhBO)_3$·pyridine (**1**), in an almost quantitative yield (Eq. (1)).

$$3\ PhB(OH)_2 + \text{pyridine} \xrightarrow[-\ 3\ H_2O]{\text{ether, reflux}} \underset{\mathbf{1}}{(PhBO)_3\cdot\text{pyridine}} \quad (1)$$

It is important to note that the reaction temperature during the preparation of $(PhBO)_3$·pyridine (**1**) never exceeded 35 °C (reflux temperature of ether). In sharp contrast, the condensation of phenylboronic acid, $PhB(OH)_2$, to give triphenylboroxine, $(PhBO)_3$ (**3**), in the absence of pyridine requires strong desiccants or prolonged heating in a high-boiling solvent, such as toluene or xylene, in a Dean–Stark apparatus. Evidently, formation of the six-membered triorganoboroxine ring is more facile in the presence of pyridine. Repeating the reaction between $PhB(OH)_2$ and pyridine in an equimolar ratio under the same reaction conditions also resulted in the isolation of $(PhBO)_3$·pyridine (**1**) as the sole product.

The hydrolysis of triphenylboroxine, $(PhBO)_3$ (**3**), which can be considered to be the reverse reaction to the aforementioned condensation, occurs readily in organic solvents at room temperature with (traces of) water to give phenylboronic acid, $PhB(OH)_2$ [41,42]. Triorganoboroxines containing small substituents such as the methyl group show an even higher reactivity toward hydrolysis [43]. However, solutions of the complex $(PhBO)_3$·pyridine (**1**) remain unchanged under the same conditions. These observations suggest that the complex $(PhBO)_3$·pyridine (**1**) possesses a higher stability towards ring-opening compared to its parent compound $(PhBO)_3$ (**3**). One possible explanation is the assumption that ring strain is present in the parent compound **1**. The geometry change of one boron centre from trigonal planar to tetrahedral upon complexation may relieve this ring strain. This postulate will be examined in detail in the following sections.

Table 1
Selected geometric parameters of the B3LYP/6-311+G(d)-optimized geometries of **4**–**9**

Molecule	B–H (Å)	B–O (Å)	B–O–B (°)	O–B–O (°)
4	1.187	1.377	120.6	119.4
expt. [a]	1.192(7)	1.375(2)	120.0(6)	120.0(6)
5	1.189	1.366	138.7	122.5
6	1.193, 1.199	1.352	–	–
7	1.190 (B1)	1.352 (B1–OH)	126.8	117.0 (O–B2–O)
	1.193 (B2)	1.366 (B2–O) 1.380 (B1–O)		119.0 (O–B1–O)
8	1.193, 1.196	1.370	125.9	–
9	1.190 (B1)	1.351 (B1–OH)	126.4 (B2–O2–B2)	116.9 (O–B2–O)
	1.193 (B2)	1.364 (B2–O1) 1.368 (B2–O2) 1.381 (B1–O1)	127.0 (B1–O1–B2)	119.0 (O–B1–O)

[a] Experimental values from C.H. Chang, R.F. Porter, S.H. Bauer, Inorg. Chem. 8 (1969) 1689.

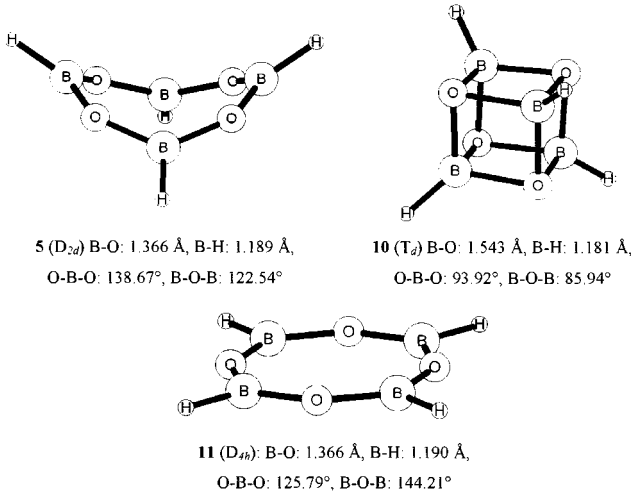

Fig. 1. Structures and selected geometric parameters of the B3LYP/6-311+G(d)-optimized geometries of the $(HBO)_4$ isomers **5**, **10** and **11**.

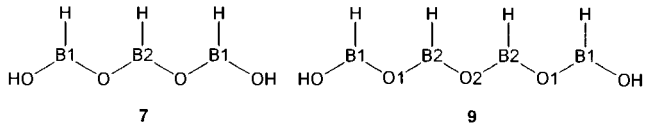

Chart 2.

2.2. DFT study on ring strain in $(HBO)_3$ (4) and $(HBO)_4$ (5)

The ring strain in the model compounds $(HBO)_3$ (**4**) and $(HBO)_4$ (**5**) was evaluated using the following group-equivalent reactions at the B3LYP/6-311+G(d) level of theory (Eqs. (2) and (3)).

$$\underset{\mathbf{4}}{(HBO)_3} + \underset{\mathbf{6}}{2\,H_2BOH} \longrightarrow \underset{\mathbf{7}}{HO(BHO)_3H} + \underset{\mathbf{8}}{H_2BOBH_2} \quad (2)$$

$$\underset{\mathbf{5}}{(HBO)_4} + \underset{\mathbf{6}}{2\,H_2BOH} \longrightarrow \underset{\mathbf{9}}{HO(BHO)_4H} + \underset{\mathbf{8}}{H_2BOBH_2} \quad (3)$$

Eqs. (2) and (3) were formed using the group-equivalent procedure of Bachrach [44] in order to minimize contributions from other chemical changes not associated with the ring strain.

Selected geometric parameters of the optimized model compounds **4**–**9** are listed in Table 1. The calculated geometric parameters for **4** are found to be in excellent agreement with experimental values. The atom numbering scheme for **7** and **9** used in Table 1 is shown in Chart 2. Comparing the various B–O–B and O–B–O angles between the rings **4** and **5** and the open-chain compounds **7**–**9** reveals that while all the O–B–O angles remain in a reasonably narrow range, the B–O–B angles in **4** and **5** are 5.9° lower and 12.2° higher, respectively, than the average B–O–B angle of the open-chain compounds **7**–**9**. This indicates that angular strain may be present in **4** and **5**. The calculated B–O bond lengths for all six model compounds lie in the narrow range between 1.351 and 1.381 Å, regardless of whether they are open-chain or cyclic.

A puckered ring (**5**) (framework group D_{2d} [2SGD(B_2H_2), X(O_4)]) and 'cubic' structure (**10**) (T_d symmetry) were located as minima on the $(HBO)_4$ potential energy surface. The eight-membered ring (**5**) is calculated to be 314.2 kJ mol^{-1} more stable than **10**. The planar eight-membered ring (**11**) (D_{4h} symmetry) is calculated to be a first-order saddle-point located 21.3 kJ mol^{-1} above **5** with an imaginary frequency corresponding to deformation towards the puckered structure **5**. Optimization of a puckered eight-membered ring structure possessing the D_{2d} [2SGD(O_2), X(B_4H_4)] framework group leads to the planar conformation. The structures and selected geometric parameters of the optimized stationary points on the $(HBO)_4$ potential energy surface are shown in Fig. 1.

According to Eq. (2), the B3LYP/6-311+G(d)-calculated strain energy ($-\Delta E$) of the six-membered ring (**4**) is 13.1 kJ mol^{-1}. Incorporating zero-point energy corrections results in a slightly lower strain enthalpy of 11.4 kJ mol^{-1}. It is noteworthy that these values are within the range of the experimentally measured strain energy (8–17 kJ mol^{-1}) of the six-membered siloxane ring $(Me_2SiO)_3$ [45]. The dramatic differences in ring

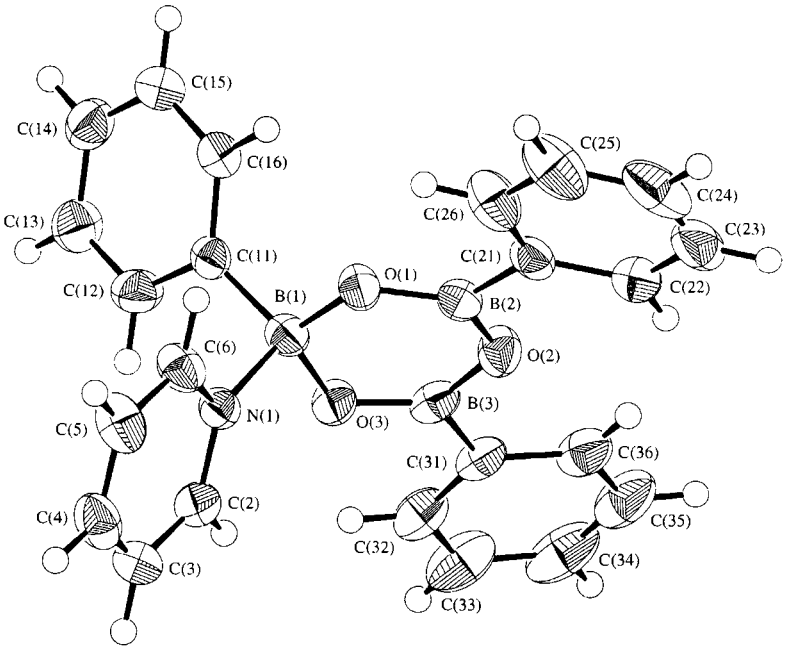

Fig. 2. Molecular structure and crystallographic numbering scheme for $(PhBO)_3$·pyridine (**1**).

opening polymerization (ROP) behaviour between $(Me_2SiO)_3$ and the practically strainless eight-membered siloxane ring, $(Me_2SiO)_4$ are attributed to this difference in ring strain [46]. Therefore, it would not be unreasonable to suggest that six-membered boroxine rings similarly possess a small but chemically significant amount of ring strain.

The strain energy of the eight-membered ring (**5**) according to Eq. (3) is calculated to be 34.6 kJ mol^{-1}. This value is reduced to 31.6 kJ mol^{-1} after zero-point energy corrections. Thus, the eight-membered ring $(HBO)_4$ (**5**) possesses significantly more ring strain than the six-membered ring $(HBO)_3$ (**4**). Given the lability of the B–O bond in solution [36], we suggest that the eight-membered rings, $(RBO)_4$, have not been observed experimentally to date owing to the fact that their ring strain would cause disproportionation to the corresponding six-membered triorganoboroxine rings, $(RBO)_3$, which possess less ring strain. The aforementioned disproportionation would also be favoured on entropic grounds.

2.3. Molecular structure of $(PhBO)_3$·pyridine (1)

The molecular structure of $(PhBO)_3$·pyridine (**1**) is shown in Fig. 2 and selected bond lengths and angles are listed in Table 2. The structure is essentially molecular with the closest intermolecular contact in crystal lattice indicated by the separation (3.80 Å) and superimposition (dihedral angle 2.6°) of the pyridine and a symmetry-related C(31)–C(36) phenyl ring. This arrangement is indicative of a $\pi-\pi$ interaction; symmetry operation: $x, 1/2-y, -1/2+z$.

There are two reports on the molecular structure of the parent triphenylboroxine $(PhBO)_3$ (**3**) [39,40]. The more precisely determined structure was reported to have average O–B–O and B–O–B angles of 119.3 and 120.3°, respectively, so as to give an overall sum of internal angles of 719.0°, which indicates that the ring is nearly planar (sum = 720°). The average B–O bond distance was reported to be 1.382 Å. In the structure of $(PhBO)_3$·pyridine (**1**), one boron atom, B(1) reveals a tetrahedral environment as a result of the coordination by pyridine. Compared to the parent compound, the corresponding O–B(1)–O bond angle decreases by 6.0° to 113.3(3)°. In turn, the O–B–O bond angles of the

Table 2
Selected bond lengths (Å) and bond angles (°) for $(PhBO)_3$·pyridine (**1**)

Bond lengths			
B(1)–O(1)	1.454(4)	B(1)–O(3)	1.462(4)
B(2)–O(1)	1.346(4)	B(2)–O(2)	1.388(4)
B(3)–O(2)	1.381(5)	B(3)–O(3)	1.348(5)
B(1)–N(1)	1.635(4)	B(1)–C(11)	1.602(5)
B(2)–C(21)	1.562(5)	B(3)–C(31)	1.561(5)
Bond angles			
O(1)–B(1)–O(3)	113.3(3)	O(1)–B(1)–N(1)	104.8(3)
O(1)–B(1)–C(11)	113.6(3)	O(3)–B(1)–N(1)	105.7(3)
O(3)–B(1)–C(11)	111.4(3)	N(1)–B(1)–C(11)	107.3(3)
O(1)–B(2)–O(2)	120.7(4)	O(1)–B(2)–C(21)	119.7(3)
O(2)–B(2)–C(21)	119.6(3)	O(2)–B(3)–O(3)	121.4(3)
O(2)–B(3)–C(31)	118.5(4)	O(3)–B(3)–C(31)	120.0(4)
B(1)–O(1)–B(2)	122.4(3)	B(2)–O(2)–B(3)	119.2(3)
B(1)–O(3)–B(3)	121.3(3)	C(2)–N(1)–C(6)	118.8(3)
C(2)–N(1)–B(1)	123.3(3)	C(6)–N(1)–B(1)	117.9(3)

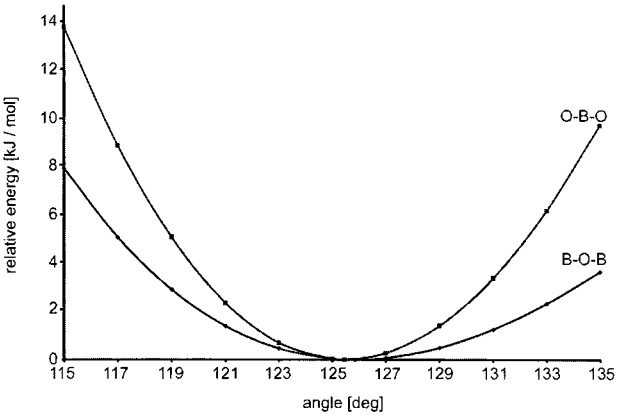

Fig. 3. Energy profiles for **8** and **12** with respect to deformation of the B–O–B and O–B–O angles, respectively.

trigonal boron atoms and the B–O–B bond angles increase by an average of 1.8 and 0.7° to average values of 121.1(2) and 121.0(2)°, respectively, maintaining approximately the same sum of internal angles (718.3°). Indeed, like the parent compound $(PhBO)_3$ (**3**), the complex $(PhBO)_3$·pyridine (**1**) is nearly planar with the largest deviation being 0.093 Å for B(2). The average B–O bond lengths to the tetrahedral (d_4) and trigonal (d_3) boron atoms amount to 1.458(3) and 1.366(3) Å, respectively. The increase in the B–O bond distances upon increasing the coordination number at boron from three to four is well known, having being reported previously for many other boroxine–Lewis base adducts [22,24–29,31]. This observed increase has been attributed to 'loss of π-bonding in the two B–O bonds involving this boron and a redistribution of the π-electron density around the remaining atoms of the ring' [23]. However, Gillespie et al. have demonstrated that this increase can be rationalized in terms of the close packing of anion-like ligands about a cation-like central atom [20]. Indeed, for $(PhBO)_3$·pyridine (**1**), the ratio d_4/d_3 is calculated to be 1.067, which is close to the theoretical ratio of 1.061 for 4- and 3-coordinate close packing. The molecular structure of the related boroxine anion, $[Ph_2B(OBPh)_2O]^-$ (**2**) has been investigated twice (counterions $[NMe_4]^+$ and $[\{(t\text{-}Bu)_3PAu\}_4P]^+$) [33,34]. A comparison of the more precisely determined structure with the parent triphenylboroxine, $(PhBO)_3$ (**3**), produces a similar result. The O–B–O bond angle related to the tetrahedral boron atom is decreased by 10.2° to 109.1(8)° as compared to the parent compound $(PhBO)_3$ (**3**). In contrast, the average trigonal O–B–O bond angles and the mean B–O–B angles increase by 2.6 and 1.5° to 121.9(9) and 121.8(8)°, respectively. We suggest that these observations are fully consistent with the relief of ring strain upon going from $(PhBO)_3$ (**3**) to $(PhBO)_3$·pyridine (**1**) and $[Ph_2B(OBPh)_2O]^-$ (**2**) and examine these claims more closely in the following section.

2.4. Computational estimation of the angular strain components in $(PhBO)_3$ (3) and $(PhBO)_3$·pyridine (1)

Owing to the strong evidence present that B–O bonds are predominantly ionic in nature and little delocalization of electron density from O to B occurs in boroxines, it should be possible to qualitatively assess ring strain in boroxines by decomposing it into its angular strain components. Direct comparison of the sums of angular strain components of $(PhBO)_3$ (**3**) and $(PhBO)_3$·pyridine (**1**) is possible since both rings are nearly planar and any torsional contributions to the ring strain in both molecules will be essentially identical.

The compounds H_2BOBH_2 (**8**) and $HB(OH)_2$ (**12**) were selected as model compounds for the B–O–B and O–B–O linkages in $(PhBO)_3$ (**3**). The conformer of **12** where the two O–H bonds are parallel was selected for study in order to minimize errors resulting from torsional contributions as the two B–O bonds flanking any O–B–O linkage in $(PhBO)_3$ (**3**) are also parallel. The equilibrium B–O–B angle in **8** was calculated to be 125.9°, whereas the equilibrium O–B–O angle in **12** was calculated to be 125.4°.

Both of these equilibrium angles are larger than those observed in $(PhBO)_3$ (**3**), providing an explanation to why the ring does not pucker to reduce ring strain. Three-dimensional geometry requires that the sum of endocyclic angles of any six-membered ring should be less than or equal to 720°, where the maximum sum corresponds to a planar ring. Puckering would therefore necessitate a reduction of the average endocyclic angle and force both the B–O–B and O–B–O linkages even further away from their preferred values.

Relaxed potential energy scans by varying the B–O–B and O–B–O angles between 115 and 135° were performed for **8** and **12**, respectively; the resulting potential energy curves are plotted in Fig. 3. Fitting the curves to polynomials and substituting the experimental B–O–B and O–B–O angles from $(PhBO)_3$ (**3**) indicate that the B–O–B and O–B–O linkages have angular strains of 1.9 and 4.6 kJ mol^{-1}, respectively, giving a total angular strain value of 19.5 kJ mol^{-1}. Upon complexation of pyridine to one boron atom in **3** to afford **1**, one O–B–O angle decreases, and the concomitant increases in the remaining five endocyclic angles cause the sum of angular strain components of the remaining five linkages to decrease by 6.0 kJ mol^{-1} from 14.7 to 8.7 kJ mol^{-1}, therefore supporting our postulate that relief of ring strain occurs upon going from $(PhBO)_3$ (**3**) to $(PhBO)_3$·pyridine (**1**) and $[Ph_2B(OBPh)_2O]^-$ (**2**) via widening of the endocyclic angles. The reduced ring strain of the adduct would also contribute towards lowering the reactivity of the boroxine ring towards hydrolysis.

Adduct formation of Lewis bases with the remaining boron atoms to form 2:1 and 3:1 adducts would necessitate a decrease in the corresponding O–B–O angles and may not be feasible as it would force an unfavourable widening of the B–O–B angles.

We have attempted to rationalize the (nearly) exclusive formation of 1:1 triorganoboroxine–amine adducts and the lower propensity of such adducts towards ring-opening compared to their parent compounds using ring strain considerations; however, a contrasting argument is that both of these observations are made on simple steric grounds, i.e. increased steric crowding around the 1:1 adduct reduces its susceptibility to attack and there is insufficient space for a second amine to bind to the ring. While it is true that increased steric crowding around the boroxine ring would reduce its reactivity, the steric argument on its own is unconvincing as higher triorganoboroxine–amine adducts involving bases as small as ammonia are virtually unknown. The 1:2 complex $(CH_3BO)_3{\cdot}2NH_3$ has been previously reported, but it has been described as being far less stable than the corresponding 1:1 adduct [47]. Furthermore, instead of being a formal 1:2 adduct with both ammonia molecules coordinated to the boroxine ring, the second molecule of NH_3 in this adduct is believed to be hydrogen-bonded to the first ammonia molecule, which is coordinated to the ring.

A similar situation to that described above is found for the six-membered stannasiloxane rings *t*-$Bu_2Sn(OSiPh_2)_2O$ [48] and $[Me_2N(CH_2)_3]_2Sn(OSiPh_2)_2O$ [49]. The former possesses a considerable amount of ring strain and, consequently, undergoes an ROP upon crystallization. In contrast, the latter is practically strain-free due to stabilization by the intramolecular coordinating amine ligands. The complexation by amine ligands formally changes the coordination geometry at tin from a tetrahedral to an octahedral environment, and consequently the related O–Sn–O bond angle decreases significantly. We have suggested that as a result of the narrowing of one O–Sn–O angle, the concomitant widening of the remaining endocyclic angles causes a reduction in ring strain in a manner similar to $(PhBO)_3$·pyridine (**1**) [49].

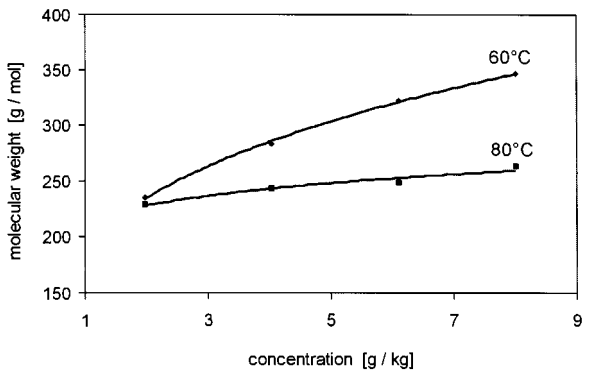

Fig. 4. Molecular weight determination of $(PhBO)_3$·pyridine (**1**) in toluene at 60 and 80 °C.

2.5. Thermodynamic and kinetic stability of $(PhBO)_3$·pyridine (1)

In order to evaluate how strongly the pyridine is bonded to the boroxine ring, a thermogravimetric analysis of **1** was carried out. Endothermic loss of pyridine was observed between a melting point of 152 and 200 °C.

It is well known that the B–N bond in triorganoboroxine amine complexes is kinetically labile in solution [22,23]. Thus, the ^{13}C-NMR spectrum in $CDCl_3$ of $(PhBO)_3$·pyridine (**1**) at room temperature exhibits seven signals implying the magnetic equivalence of all three boron centres. Only recently, an activation energy of 39 kJ mol^{-1} was reported for the dissociation–recombination process of $(PhBO)_3$·pyridine (**1**) in solution [22].

Molecular weight determinations of $(PhBO)_3$·pyridine (**1**) in toluene at 60 and 80 °C at four different concentrations further suggest that a dissociation process takes place and an equilibrium exists between **1** and $(PhBO)_3$ (**3**) and pyridine. Upon increasing the temperature or lowering the initial concentration of $(PhBO)_3$·pyridine (**1**), this equilibrium shifts from **1** towards $(PhBO)_3$ (**3**) and pyridine (Fig. 4, Eq. (4)).

$$\underset{\mathbf{1}}{(PhBO)_3{\cdot}\text{pyridine}} \rightleftharpoons \underset{\mathbf{3}}{(PhBO)_3} + \text{pyridine} \qquad (4)$$

This observation suggests that the pyridine is less strongly bonded in solution than in the solid state. A possible explanation for this might be the partial compensation of the ring strain in **3** by an increasing number of species upon the dissociation process. The increase of species would directly account to the entropy term of the Gibbs–Helmholtz equation ($\Delta G = \Delta H - T\Delta S$). A similar observation was made for the strained six-membered stannasiloxane ring *t*-$Bu_2Sn(OSiPh_2)_2O$ [48], which undergoes ring-opening polymerization upon crystallization. In solution, however, the ring strain is compensated by the entropic favour of a large number of molecular species [48].

2.6. Conclusions

The questions (i)–(iii) posed in Section 1 could be rationalized using the following ring strain considerations: (i) eight-membered tetraboroxine rings are calculated to possess significantly more ring strain than six-membered triboroxine rings; (ii) the addition of amines to triorganotriboroxines stops at 1:1 stoichiometry as maximum relief of ring strain occurs in 1:1

adducts; and (iii) triorganoboroxines are more susceptible towards ring-opening than their 1:1 amine adducts as they are more strained.

3. Computational methodology

DFT calculations were carried out using the GAUSSIAN-98 suite of programs [50]. Geometry optimizations were performed at the B3LYP/6-311 + G(d) level of theory using standard techniques. The nature of each stationary point was verified by vibrational frequency calculations. Unless otherwise stated, each structure is a minimum on its respective potential energy surface.

4. Experimental

Phenylboronic acid and pyridine were commercially obtained (Aldrich). All solvents were freshly distilled prior to use. NMR spectra were obtained using a Varian 300 MHz Unity Plus NMR spectrometer. ^{1}H- and ^{13}C-chemical shifts δ are given in ppm and are referenced against Me_4Si. Molecular weight determinations were performed on a Gonotec Osmomat 070 osmometer. The thermogravimetric analysis was made on a Perkin–Elmer TGA 7 thermogravimetric analyzer (with TAC 7/DX controller and gas selector). The elemental analysis was carried out on an instrument from Carlo Erba Strumentazione (Model 1106).

4.1. Synthesis of $(PhBO)_3$·pyridine (1)

To a solution of $PhB(OH)_2$ (1.10 g, 9.00 mmol) in Et_2O (100 ml), Py (237 mg, 3.00 mmol) was added at room temperature. The mixture was stirred for 15 min before the ether was removed by distillation at normal pressure. The crude product was recrystallized from hexane–CH_2Cl_2, providing colourless crystals of **1** (1.13 g, 2.89 mmol, 96%, m.p. 152 °C).

^{1}H-NMR ($CDCl_3$): δ 9.2–7.4. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 143.3, 140.9, 138.7 (broad), 133.6, 129.6, 127.5, 125.5. Anal. Found: C, 70.7; H, 5.1; N, 3.5. Calc. for $C_{23}H_{20}B_3NO_3$ (MW 390.9): C, 70.7; H, 5.2; N, 3.6%.

5. Crystallography

Intensity data for a colourless block (0.31 mm^3) were collected at 173 K on a Rigaku AFC7R diffractometer employing Mo–K_α radiation ($\lambda = 0.7107$ Å) and the ω–2θ scan technique such that θ_{max} was 27.5°. Corrections were made for Lorentz and polarization effects [51] but not for absorption. Of the 5275 reflections measured, 5062 were unique ($R_{int} = 0.041$) and of these, 1841 with $I \geq 3.0\sigma(I)$ were used in the subsequent analysis.

5.1. Crystal data

$C_{23}H_{20}B_3NO_3$, MW = 390.9, monoclinic, $P2_1/c$, a = 14.477(4), b = 11.507(4), c = 12.977(4) Å, β = 103.19(3)°, V = 2105(1) Å^3, $Z = 4$, $D_x = 1.233$ g cm^{-3}, μ(Mo–K_α) = 0.79 cm^{-1}, $F(000) = 816$, 271 refined parameters, $\rho_{max} = 0.14$ e Å^{-3}. The structure was solved by direct methods [52] and refined by a full-matrix least-squares procedure based on F [51]. The non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms were included in the model at their calculated positions. A weighting scheme of the form $w = 1/[\sigma^2(F) + 0.00001|F_o|^2]$ was employed and at convergence, final $R = 0.042$ and $R_w = 0.037$. Fig. 2 shows the crystallographic numbering scheme which was drawn with ORTEP at the 50% probability level [53].

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 150673 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Calculated energies and the Cartesian coordinates of the B3LYP/6-311 + G(d)-optimized structures of **4**–**12** are available upon request from the authors.

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