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# A new polymorph of tri(*p*-tolyl)boroxine

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A new orthorhombic polymorph of tri(*p*-tolyl)boroxine ($Pmn2_1$) with relatively short intermolecular B—O distances of 3.321 Å was crystallized from $CDCl_3$ at ambient temperature. The crystal structure of the orthorhombic polymorph of tri(*p*-tolyl)boroxine shows the shortest intermolecular B—O contact yet found in boroxines. The cell dimensions of the orthorhombic polymorph of tri(*p*-tolyl)boroxine are $a = 21.888(4)$ Å, $b = 9.304(2)$ Å, and $c = 4.7804(10)$ Å. The structural features of the orthorhombic polymorph of tri(*p*-tolyl)boroxine are quite different from a previously reported monoclinic (Beckett *et al., J. Organomet. Chem.* **1997**, *535*, 33–41) but similar to that of tri(*p*-bromophenyl)boroxine (Avent *et al.*, *Coll. Czech. Chem. Commun.* **2002**, *67*, 1051–1060). Obviously, electronic effects of substituents on the boron centers influence the structural features of substituted boroxines less than discussed in earlier reports (Boese *et al.*, *Angew. Chem.* **1987**, *99*, 239–241).

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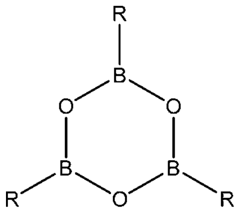
**KEY WORDS:** Boroxine; Lewis acidity; polymorphism; intermolecular B—O distances.

## Introduction

In the last two decades the extent of B—O $\pi$ bonding in boroxines was the topic of several articles.[1,2] In 1999, Beckett *et al.*[2] estimated the Lewis acidity of boron centers in boroxines in comparison to that of the related borazenes. Generally the boron atoms in boroxines possess a higher Lewis acidity than those in borazenes and therefore the related boroxines show a much lower aromatic character. Nevertheless, X-ray structure analysis of boroxines gives evidence for the existence of a $\pi$-ring system. Theoretical studies from Alcarez *et al.*[3] show that boroxines should possess interesting NLO properties.



**1** R = *p*-tolyl
**2** R = *p*-bromophenyl
**3** R = ethyl
**4** R = phenyl
**5** R = methoxy
**6** R = mesityl
**7** R = ferrocenyl

In 1987, Boese *et al.* discussed the different crystal packing in the boroxines **3** and **4**.[4] In the crystal structure of **3** the boroxine molecules form columns in which the boroxine rings stack on each other with each boron being surrounded by the oxygen atoms of the two neighboring layers (Fig. 1). Between these layers

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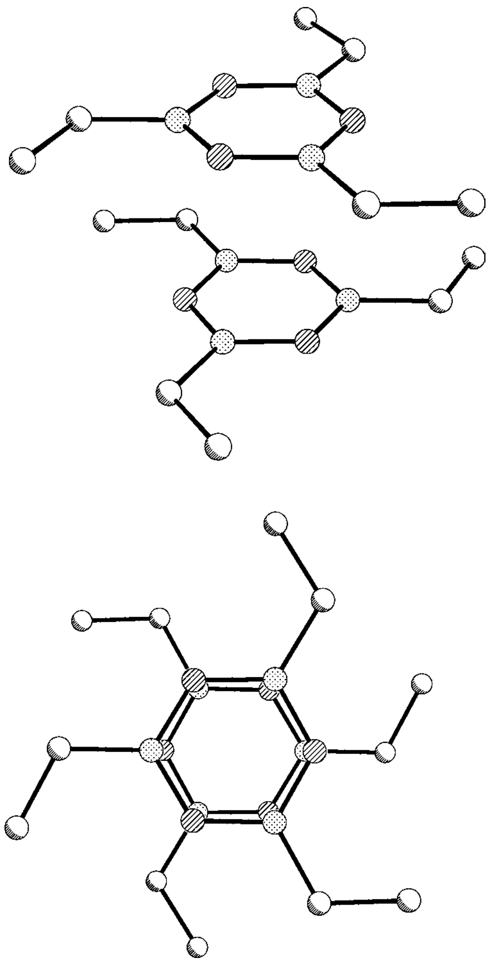


**Fig. 1.** Crystal packing diagram[4] for **3**.

short intermolecular B—O contacts of 3.462 Å were found. Contrary to **3**, boroxine **4** forms a layer structure in the solid state (monoclinic space group $P2_1/c$) in which the boroxine rings are located between two phenyl rings of the neighboring layers.[1] The shortest B—O distance found in the crystal structure of **4** was 4.441 Å. The monoclinic polymorph of tri(*p*-tolyl)boroxine **1** features the same structural motif as **4** (depicted in Fig. 2).[5]

The structural differences between aryl and alkyl substituted boroxines have been explained with the possibility of electronic interactions between the aryl substituents and the boron atoms. The aromatic substituents in boroxines are able to deliver $\pi$ electron density to the empty orbitals on the boron atoms. Consequently, the Lewis-acidity on the boron centers of **4** is decreased in comparison to **3**. Therefore, the intermolecular B—O interactions in **3** are stronger than in **4**. These interactions in **3** lead to a column type crystal packing. By contrast, the boron centers in the phenyl derivative **4** have a lower Lewis acidity and therefore intermolecular B—O interactions are no longer favored. Moreover, nonpolar stacking interactions between boroxine and phenyl rings become more attractive leading to the layer-type structure as shown in Fig. 2.

## Experimental

### *General considerations*

All experiments were carried out under dry argon or nitrogen using standard Schlenk techniques. Diethylether and toluene were distilled from sodium/benzophenone. $CDCl_3$ was dried over molecular sieves and stored under dry nitrogen. 4-(Dibromoboryl)toluene was prepared according to a published procedure.[6]

### *Synthesis of 4-(bromoethoxyboryl)toluene*

4-(Dibromoboryl)toluene (9.55 mmol, 2.50 g) was dissolved in 20 mL of toluene and diethylether (9.55 mmol, 0.71 g) was added via syringe at ambient temperature. The solution became cloudy immediately. After stirring for 5 d at RT the solution was clear again. The solvent was evaporated in vacuo to yield 4-(bromoethoxyboryl)toluene as a oily residue (2.15 g, 99.2%). $^{1}$H-NMR (250.1 MHz, $CDCl_3$): ( 8.16 (d, 2H, $^{3}J$(H,H) = 7.8 Hz, Ar-*H*), 7.13 (d, 2H, $^{3}J$(H,H) = 7.8 Hz, Ar-*H*), 4.18 (qa, 2H, $^{3}J$(H,H) = 7.1 Hz, $OCH_2CH_3$), 2.16 (s, 3H, $CH_3$), 1.13 (t, 3H, $^{3}J$(H,H) = 7.1 Hz, $OCH_2CH_3$); $^{13}$C-NMR (62.9 MHz, $CDCl_3$): (137.9, 135.9, 128.9 (Ar-*C*), n.o. (*C*B), 66.0 ($OCH_2CH_3$), 21.4 (Ar-$CH_3$), 16.1 ($OCH_2CH_3$); $^{11}$B-NMR (128.4 MHz, $CDCl_3$): (38.4 ($h_{1/2}$ = 200 Hz).

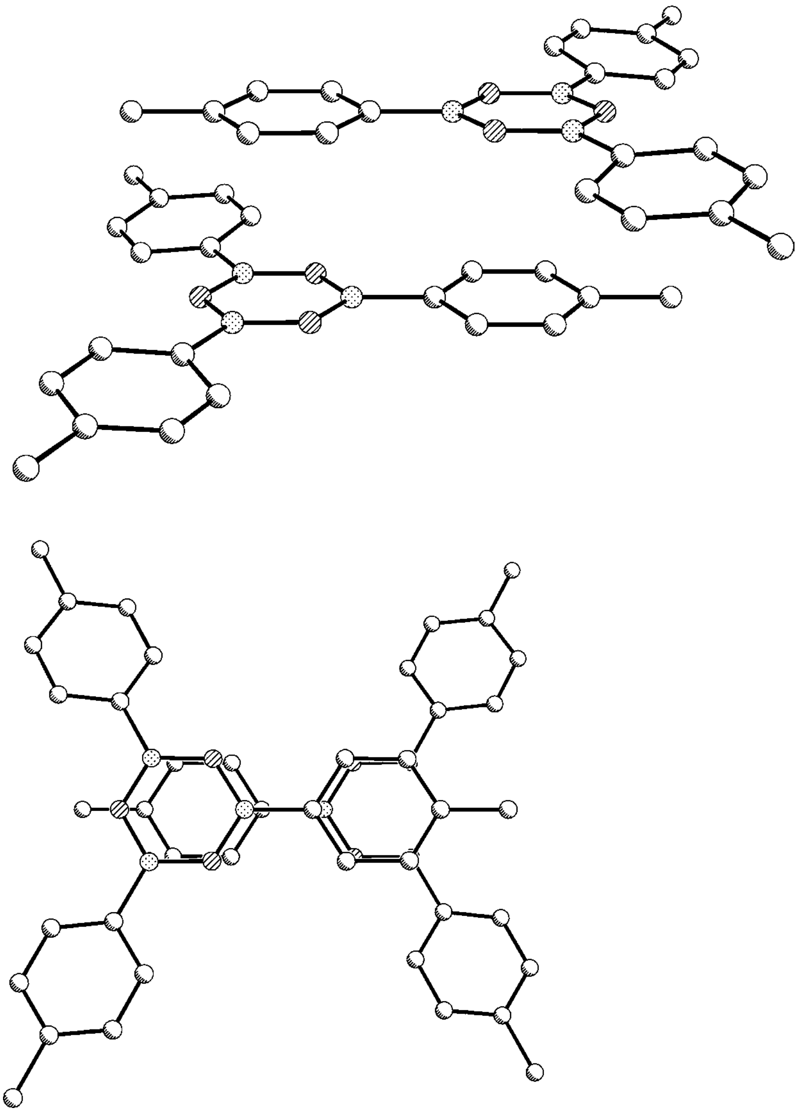


**Fig. 2.** Crystal packing diagram[5] for the monoclinic polymorph of **1**.

### *Synthesis of tri(tolyl)boroxine 1*

X-ray suitable single crystals of **1** were obtained on slow hydrolysis of a solution of 4-(bromoethoxyboryl)toluene in $CDCl_3$.

### *Crystal structure determination*

A suitable single crystal of **1** was selected and attached in a perfluoropolyether oil to a thin glass fiber. Intensity measurement was carried out using a STOE IPDS-II two circle diffractometer. The structure was solved with direct methods[7] and refined with full-matrix least-squares techniques.[8] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined using a riding model. The methyl groups were allowed to rotate but not to tip. The hydrogen atoms of one methyl group

**Table 1.** Crystal Data and Structure Refinement for the Orthorhombic Polymorph of **1**

| | |
|---|---|
| Formula | $C_{21}H_{21}B_3O_3$ |
| $F_w$ | 353.81 |
| Color, shape | Colorless, block |
| Crystal system | Orthorhombic |
| Space group | $Pmn2_1$ |
| Temperature (K) | 173(2) |
| Radiation (MoK$\alpha$) (Å) | 0.71073 |
| $a$ (Å) | 21.888(4) |
| $b$ (Å) | 9.304(2) |
| $c$ (Å) | 4.7804(10) |
| $V$(Å)$^3$ | 973.5(3) |
| Z | 2 |
| $D_{\text{calcd.}}$(g cm$^{-3}$) | 1.207 |
| $\mu$ (mm$^{-1}$) | 0.076 |
| $F$(000) | 372 |
| Crystal size (mm) | 0.24 × 0.14 × 0.12 |
| Theta range for data collection | 2.19–24.76° |
| Index ranges | $-25 \leq h \leq 24$, $-10 \leq k \leq 10$, $-5 \leq l \leq 5$ |
| no. of rflns. coll. | 5921 |
| no of indep. rflns. | 1679 |
| $R$(int) | 0.0512 |
| Completeness to $\theta = 24.76°$ | 99.8% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min transmission | 0.9909 and 0.9819 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data/restr./param. | 1679/1/133 |
| GOF on $F^2$ | 0.847 |
| $R1$, $wR2$ ($I > 2\sigma(I)$) | 0.0334, 0.0678 |
| $R1$, $wR2$ (all data) | 0.0697, 0.0782 |
| Absolute structure parameter | −0.1(15) |
| Extinction coefficient | 0.015(2) |
| Largest diff. Peak and hole (e Å$^{-3}$) | 0.116, −0.147 |
| CCDC | 248934 |

are equally disordered over two positions. Because of the kind of the radiation and the nature of the atoms the absolute structure could not be determined and was assigned arbitrarily. Crystal data, data collection parameters, and refinement statistics for **1** are listed in Table 1. Relevant geometric parameters are listed in Table 2.

### *Spectroscopic analysis*

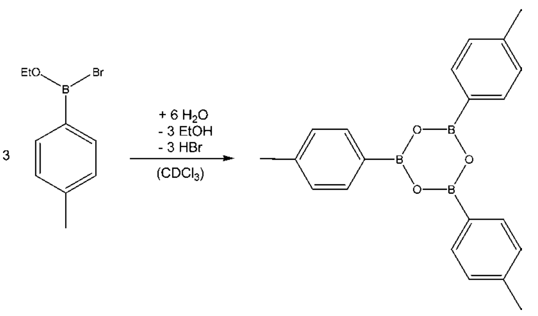
NMR spectra were recorded on a Bruker AM 250 ($^1$H/$^{13}$C: 250.133/62.895 MHz), and Bruker Avance 400 ($^1$H/$^{13}$C/$^{11}$B: 400.130/100.6/128.4 MHz) spectrometer.

**Table 2.** Bond Lengths (Å) and Angles (°) for **1** (Orthorhombic Polymorph)

| | |
|---|---|
| Bond lengths | |
| B(1)—O(1) | 1.381(3) |
| B(1)—O(2) | 1.386(3) |
| B(2)—O(2) | 1.384(2) |
| B(1)—C(11) | 1.542(3) |
| B(2)—C(21) | 1.545(5) |
| C(11)—C(16) | 1.385(3) |
| C(11)—C(12) | 1.401(3) |
| C(12)—C(13) | 1.392(3) |
| C(13)—C(14) | 1.382(3) |
| C(14)—C(15) | 1.381(4) |
| C(14)—C(17) | 1.507(3) |
| C(15)—C(16) | 1.395(3) |
| C(21)—C(22) | 1.400(3) |
| C(22)—C(23) | 1.390(3) |
| C(23)—C(24) | 1.385(3) |
| C(24)—C(25) | 1.503(5) |
| Bond angles | |
| B(1A)—O(1)—B(1) | 121.4(3) |
| O(1)—B(1)—O(2) | 118.7(3) |
| B(2)—O(2)—B(1) | 120.9(2) |
| O(2)—B(2)—O(2A) | 119.1(3) |
| O(1)—B(1)—C(11) | 120.3(2) |
| O(2)—B(1)—C(11) | 121.0(2) |
| O(2)—B(2)—C(21) | 120.44(15) |
| O(2A)—B(2)—C(21) | 120.44(15) |
| C(16)—C(11)—C(12) | 117.0(2) |
| C(13)—C(12)—C(11) | 120.8(3) |
| C(14)—C(13)—C(12) | 121.5(2) |
| C(15)—C(14)—C(13) | 118.1(2) |
| C(15)—C(14)—C(17) | 121.2(2) |
| C(13)—C(14)—C(17) | 120.7(3) |
| C(14)—C(15)—C(16) | 120.7(3) |
| C(11)—C(16)—C(15) | 121.9(3) |
| C(22A)—C(21)—C(22) | 116.4(3) |
| C(23)—C(22)—C(21) | 121.5(3) |
| C(24)—C(23)—C(22) | 121.7(3) |
| C(23)—C(24)—C(23A) | 117.1(3) |
| C(23)—C(24)—C(25) | 121.43(16) |
| C(23A)—C(24)—C(25) | 121.43(16) |
| C(22A)—C(21)—B(2) | 121.82(15) |
| C(22)—C(21)—B(2) | 121.82(15) |
| C(16)—C(11)—B(1) | 121.9(2) |
| C(12)—C(11)—B(1) | 121.1(2) |

## Results and discussion

We obtained X-ray quality crystals of a new orthorhombic polymorph of **1** from $CDCl_3$ at ambient temperature. The boroxine **1** was synthesized by hydrolysis of ethoxy(p-tolyl)bromo borane at ambient temperature, as shown in Scheme 1.



**Scheme . 1.** Synthesis of tri(*p*-tolyl)boroxine.

The molecule possesses crystallographic $C_s$ symmetry. A mirror plane perpendicular to the molecular plane runs through O1, B2, C21, C24, and C25.

The boroxine ring of the orthorhombic polymorph of **1** adopts an almost planar conformation (rmsd 0.021 Å) as shown in Fig. 3. Except for the intermolecular B—O distance, the bond lengths and angles of the orthorhombic polymorph of **1** are similar to those of the monoclinic polymorph of **1** (see Table 3). The dihedral angles in 1 (orthorhombic) between the plane of the ring and the tolyl substituents are 5.7° and 4.2°, respectively. The B—O bond lengths average 1.384(3) Å and the B—C bond average 1.542(2) Å in **1** (orthorhombic). The B—O—B angles in the boroxine ring of **1** (orthorhombic) show an average size of 121.1(3)° and are wider than the O—B—O angles, which adopt an average value of 118.8°. The sums of all angles at the boron atoms are 360° in both polymorphs of **1**.

In the orthorhombic crystal structure the molecules of **1** form sloped columns. Along these columns all molecules adopt the same orientation. But in two neighboring layers the boroxine rings are shifted in such a way that the position of one boron atom is directly under that of the oxygen atom in the para position of the B—O ring as shown in Fig. 4. The intermolecular B—O contact between these two atoms is found to be 3.321 Å. This distance is shorter than that in the triethyl derivative.

A structural motive similar to **1** (orthorhombic) has also been found for tri(*p*-bromophenyl)boroxine (**2**) but the shortest intermolecular B—O distance in **2** is longer than in **1** (orthorhombic).[9]

Interestingly, the intermolecular B—O distances in the aryl substituted boroxines **1** (orthorhombic) and **2** are shorter than in the triethyl substituted boroxine **3** (3.462 Å). Otherwise, the crystal structure of the phenyl substituted boroxine **4** shows a structural motif with long intermolecular B—O distances which is different from **1** (orthorhombic) and **2** but identical

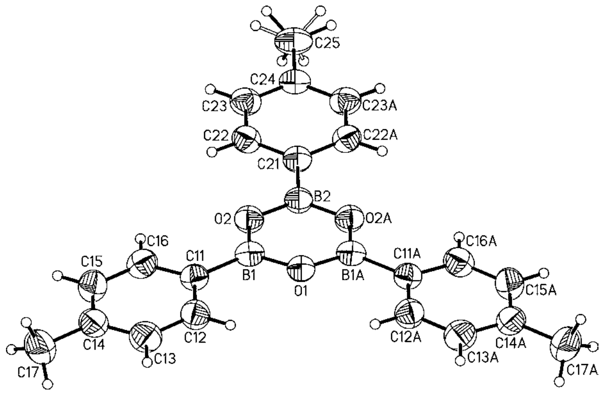


**Fig . 3.** ORTEP plot of the orthorhombic polymorph of **1** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

**Table 3.** The Average Bond Lengths (Å) and Angles (°) for Boroxines **1–7**

| | **1** (orthorhombic) | **1** (monoclinic) | **2** (orthorhombic) | **3** (hexagonal) | **4** (monoclinic) | **5** (monoclinic) | **6** (monoclinic) | **7** (orthorhombic) |
|---|---|---|---|---|---|---|---|---|
| space group | $Pmn2_1$ | $C2/c$ | $Pnma$ | $P6_3/m$ | $P2_1/c$ | $P2_1/n$ | $C2/c$ | $Cmc2_1$ |
| B—O | 1.384(3) | 1.384(1) | 1.390(20) | 1.384(4) | 1.386(8) | 1.378(4) | 1.377(2) | 1.383(6) |
| B—C | 1.543(2) | 1.536(15) | 1.524(4) | 1.565(1) | 1.546(3) | 1.544(3) | 1.552(12) | 1.529(5) |
| B—O—B | 121.1(3) | 121.5(7) | 121.9(11) | 121.6(1) | 121.7(4) | 121.1(2) | 122.7(9) | 120.5(8) |
| O—B—O | 118.8(3) | 118.5(6) | 118(1) | 118.4(1) | 118.0(8) | 118.9(3) | 117.3(9) | 119.2 (7) |

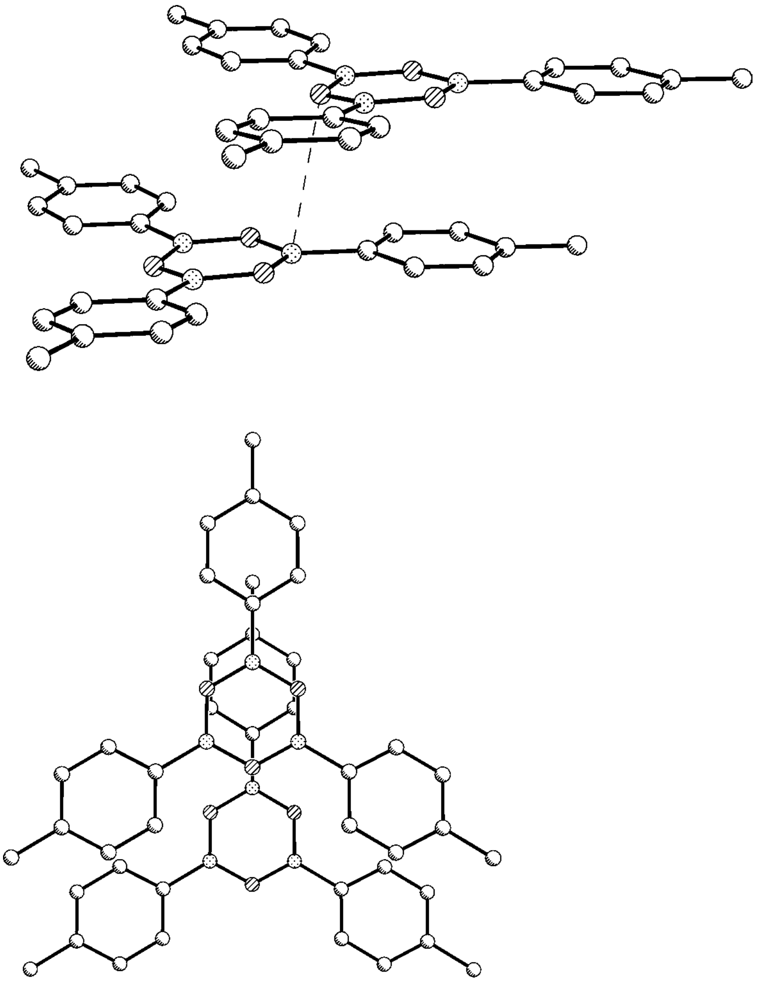


**Fig. 4.** Crystal packing diagram for the orthorhombic polymorph of **1**.

to **1** (monoclinic). Obviously, the Lewis acidity on the boron centers of boroxines is not the only driving force of crystal packing.

The crystal structure of the orthorhombic polymorph of **1** with aryl substituents shows that the even more electronically saturated compound **1** possesses shorter intermolecular B—O contacts (3.321 Å) than the boroxine **3** with alkyl substituents. To the best of our knowledge the intermolecular B—O distance in **1** (orthorhombic) is the shortest yet reported for organyl-substituted boroxines.

Table 4 lists bond lengths and angles of X-ray characterized organyl-substituted boroxines.

**Table 4.** The Shortest Intermolecular B—O Distances (Å) in the Crystal Structures of **1**–**5**

| | **1** (orthorhombic) | **1** (monoclinic) | **2** (orthorhombic) | **3** (hexagonal) | **4** (monoclinic) | **5** (monoclinic) |
|---|---|---|---|---|---|---|
| B—O | 3.321 | 4.180 | 3.380 | 3.462 | 4.441 | 4.398 |

Boroxine **5** can also be crystallized in the monoclinic layer type structure as shown for **1** and **4** in Fig. 2.[3] Because of steric strain, the crystal structures of tri(mesityl)boroxine **6**[10] and tri(ferrocenyl)boroxine **7**[11] feature no columns.

The boroxines **1–7** possess quite similar B—O bond lengths in the solid (range of 1.377 Å for **6** and 1.390 Å for **2**). The average values for the B—O—B angles are found to be between 121.1 to 122.7° and are therefore larger than 120°, whereas the O—B—O angles are smaller than 120° with average sizes between 117.3° and 119.2°. Table 3 shows that the organic substituents on the boroxine ring do not substantially affect the geometry of the ring itself.

The degree of $\pi$ electron density transferred from the substituents on the boroxine core should be reflected in the length of the B—C bond. According to the literature, the calculated value for a B—C single bond is 1.61 Å, whereas the value for the B—C double bond is 1.40 Å.[12] The boron carbon bond lengths found of the boroxines **1–7** range between B—C single and B—C double bonds. With a length of 1.565 Å the triethyl derivative **3** possesses the longest B—C bond of all structurally characterized boroxines. Generally, the molecules bearing aromatic substituents possess shorter B—C bonds with the minimum of 1.542 Å found for **2**.

Obviously, the degree of B—C $\pi$ bonding is slightly higher in the aromatic substituted boroxines. The B—C bond in the monoclinic polymorph of **1** is shorter than that of **4** which might be due to tolyl being a better $\pi$ donor than phenyl.

The crystal structures of the monoclinic polymorph of **1**, and the boroxines **4** and **5**, show intermolecular B—O distances between 4.180 and 4.441 Å (Table 4).

## Summary and conclusion

The crystal structure of the orthorhombic polymorph of tri(*p*-tolyl)boroxine **1** presented here shows structural features which are different from those of the boroxines **3** and **4**. The orthorhombic polymorph of **1** possesses short intermolecular B—O contacts (3.321 Å) even though the boron centers in **1** are substituted with aromatic $\pi$ donor ligands. Obviously the degree of $\pi$ density the boron atoms receive from an aromatic substituent does not decrease their Lewis acidity to an amount where intermolecular B—O interactions generally become disfavored. Rather, two different structural motifs for the boroxines **1** with tolyl as aromatic substituent are possible: a monoclinic layer structure based on unpolar stacking interactions or an orthorhombic polymorph in which the molecules build sloped columns with short intermolecular B—O contacts. Thus we conclude that for boroxines bearing aromatic substituents as in **1** different intermolecular arrangements are attractive. Intermolecular B—O interactions are not necessarily responsible for the crystal packing but are still attractive. Moreover, they can be even shorter than in the aliphatic substituted boroxine **3**.

## Acknowledgment

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**Supplementary material** Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 248934. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax : +1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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