

1-[5-(4,5-Dimethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl]ethanone and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde

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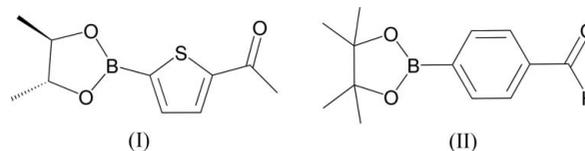
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In both title compounds, $C_{10}H_{13}BO_3S$, (I), and $C_{13}H_{17}BO_3$, (II), the molecules adopt nearly planar conformations. The crystal packing of (I) consists of a supramolecular two-dimensional network with a herringbone-like topology formed by self assembly of centrosymmetric pairs of molecules linked *via* dipole–dipole interactions. The crystal structure of (II) consists of a supramolecular two-dimensional network built up from centrosymmetric pairs of molecules *via* π – π interactions. These pairs of molecules are self-organized in an offset fashion related by a symmetry centre, generating supramolecular ribbons running along the [101] direction. Neighbouring ribbons are stacked *via* complementary van der Waals and hydrophobic methyl–methyl interactions.

Comment

Compounds containing boronate esters $[RB(OR)_2]$ represent valuable intermediates in organic synthesis, particularly in the Suzuki–Miyaura coupling reaction (Miyaura & Suzuki, 1995). They are also well established compounds for the detection of carbohydrates (Striegler, 2003), as a result of their ability to form cyclic esters with appropriate diols (Schnürch *et al.*, 2007). It has been found that some imines containing boronate ester groups display antifungal behaviour against both *Aspergillus niger* and *A. flavus* (Vogels *et al.*, 2001). Crystallographic studies related to the structure–property relationship of boronate esters remain largely unexplored and only a few crystal structures have been reported so far. In particular, there is a crystallographic report on the space group revision of 4-formylphenylboronic acid (Fronczek *et al.*, 2001), where both the formyl and $B(OH)_2$ groups were found ordered, in contrast with the previous report where these groups were disordered (Feulner *et al.*, 1990). In this contribution, as part

of our ongoing investigation of the synthesis and solid-state reactivity of unsaturated pyridyl compounds (Linares & Briceño, 2010; Hill *et al.*, 2012), we describe the molecular structures of the title compounds, (I) and (II), which are interesting precursors for the preparation of asymmetric olefins *via* a condensation process.



The molecule of (I) (Fig. 1) adopts a nearly planar conformation. The acetyl and boronate ester substituents make dihedral angles of 3.35 (6) and 2.96 (2)°, respectively, with the mean plane of the thiophene ring. The methyl groups are oriented in a *trans* configuration on the five-membered ring formed by atoms B1/O2/C1/C2/O1. The B–O distances are statistically similar, with B1–O1 = 1.363 (4) Å and B1–O2 = 1.347 (5) Å. Likewise, the C–S [1.711 (3) and 1.712 (3) Å] and C=C [C3–C4 = 1.373 (4) Å and C5–C6 = 1.362 (4) Å] distances from the thiophene ring are also similar, displaying bond lengths typical for C–S single and C=C double bonds, respectively [average C–S = 1.69 (8) Å and average C=C = 1.34 (3) Å (Cambridge structural Database, Version 5.32; Allen, 2002)]. The carbonyl group is oriented *cis* to the S atom of the thiophene ring, forming an S1–C6–C7–O3 torsion angle of –1.7 (5)°.

The crystal structure of (I) consists of supramolecular layers built up from centrosymmetric pairs of molecules linked by dipole–dipole interactions between carbonyl and B–O groups [B1ⁱ...O3 = 3.545 (5) Å and O1ⁱ...C7 = 3.699 (5) Å; symmetry code: (i) –x, –y, –z + 1] (Fig. 2b), generating a herringbone-like supramolecular two-dimensional network parallel to the *bc* plane (Fig. 2a). The three-dimensional array is achieved by stacking of the layers through van der Waals and hydrophobic methyl–methyl interactions.

The molecule of (II) (Fig. 3) deviates from planarity, with the boronate ester group forming a dihedral angle of 7.53 (2)° with the mean plane of the benzaldehyde group. The B–O [B1–O1 = 1.348 (3) Å and B1–O2 = 1.349 (3) Å] distances in (II) are similar.

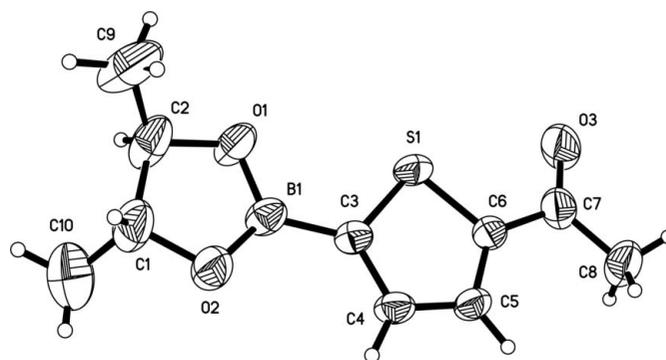
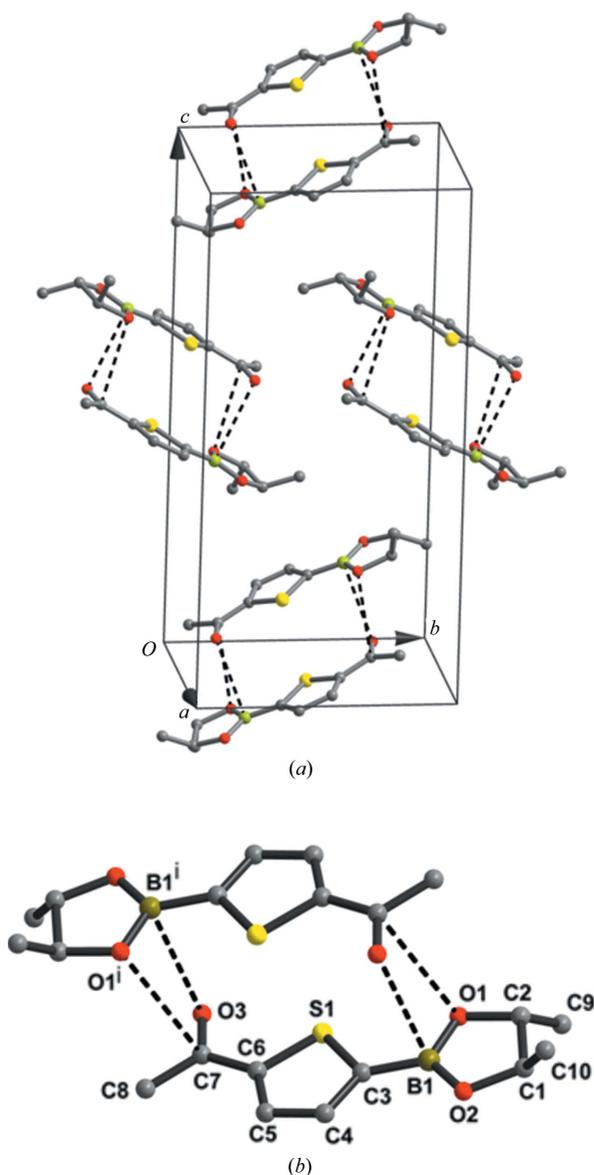


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

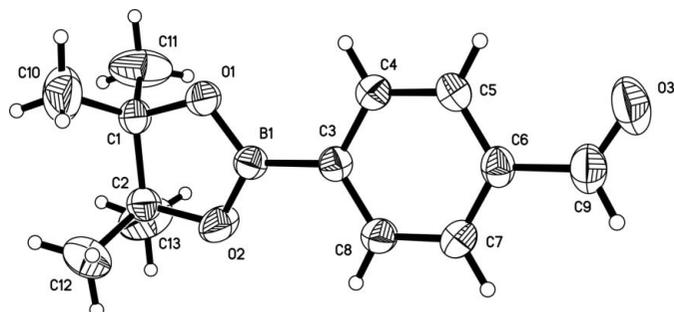

Figure 2

(a) A view of the herringbone array in the structure of (I). Dashed lines indicate dipole-dipole interactions. (b) Pairs of molecules of (I) linked by dipole-dipole interactions (dashed lines) between carbonyl and B–O groups. [Symmetry code: (i) $-x, -y, -z + 1$.]

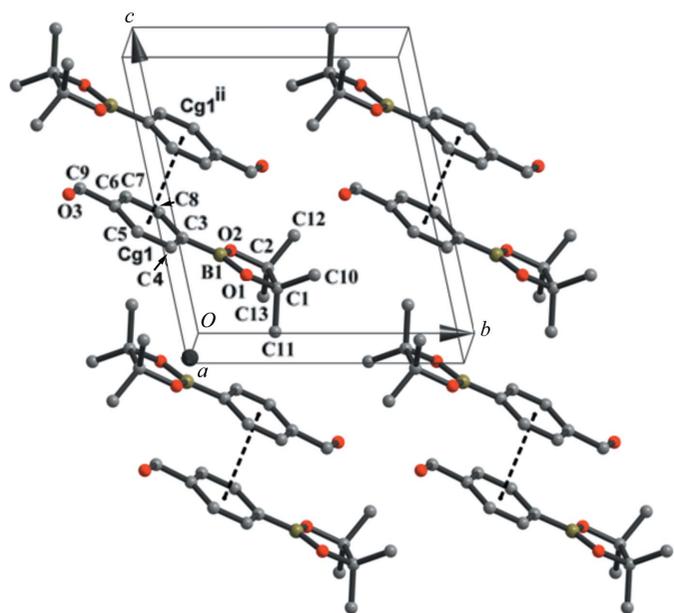
The crystal structure of (II) also consists of supramolecular layers, this time built up from centrosymmetric pairs of molecules *via* π – π interactions [$Cg1 \cdots Cg1^{ii} = 3.811(3) \text{ \AA}$; $Cg1$ is the centroid of the C3–C8 benzene ring; symmetry code: (ii) $-x + 2, -y, -z + 1$]. These pairs are self-organized in an offset fashion related by a symmetry centre, generating supramolecular ribbons running along the [101] direction. Neighbouring ribbons are stacked *via* complementary van der Waals and hydrophobic methyl–methyl interactions, generating a two-dimensional network (Fig. 4). The final three-dimensional array is stabilized *via* van der Waals interactions.

Experimental

Compounds (I) and (II) were synthesized from commercially available (5-acetylthiophen-2-yl)boronic acid and (4-formylphenyl)bor-


Figure 3

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.


Figure 4

A view of the two-dimensional network in (II), built from centrosymmetric pairs of molecules *via* π – π^{ii} interactions (dashed lines). [Symmetry code: (ii) $-x + 2, -y, -z + 1$.]

onic acid (Sigma–Aldrich Co.) by reaction with the corresponding diols (Schnürch *et al.*, 2007). Colourless crystals of both compounds were grown from a petroleum ether–tetrahydrofuran (1:2 *v/v*) solution kept at 277 K.

Compound (I)

Crystal data

$C_{10}H_{13}BO_3S$
 $M_r = 224.07$
 Monoclinic, $P2_1/c$
 $a = 6.038(3) \text{ \AA}$
 $b = 10.286(4) \text{ \AA}$
 $c = 20.096(8) \text{ \AA}$
 $\beta = 103.390(16)^\circ$

$V = 1214.2(9) \text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.25 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.42 \times 0.33 \times 0.22 \text{ mm}$

Data collection

Rigaku AFC-7S Mercury diffractometer
 Absorption correction: multi-scan (REQAB; Jacobson, 1998)
 $T_{\min} = 0.962, T_{\max} = 0.980$

13808 measured reflections
 2365 independent reflections
 1479 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.167$
 $S = 1.08$
 2365 reflections

139 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$\text{C}_{13}\text{H}_{17}\text{BO}_3$
 $M_r = 232.08$
 Triclinic, $P\bar{1}$
 $a = 6.664 (5) \text{ \AA}$
 $b = 9.537 (8) \text{ \AA}$
 $c = 10.771 (9) \text{ \AA}$
 $\alpha = 102.252 (19)^\circ$
 $\beta = 93.24 (3)^\circ$

$\gamma = 94.07 (3)^\circ$
 $V = 665.5 (9) \text{ \AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 $0.48 \times 0.37 \times 0.22 \text{ mm}$

Data collection

Rigaku AFC-7S Mercury
 diffractometer
 Absorption correction: multi-scan
 (REQAB; Jacobson, 1998)
 $T_{\min} = 0.962, T_{\max} = 0.980$

7390 measured reflections
 2388 independent reflections
 1639 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.203$
 $S = 1.06$
 2388 reflections

155 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$

C-bound H atoms were placed in idealized positions, with C–H = 0.93 and 0.98 Å for aromatic and methine groups, respectively, and 0.96 Å for methyl groups, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and methine groups, and $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

For both compounds, data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *CrystalStructure* (Rigaku/MS, 2005) and *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3242). Services for accessing these data are described at the back of the journal.

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