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2,2'-Bi[benzo[b]thiophene]: an unexpected isolation of the benzo[b]thiophene dimer

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The crystal structure of 2,2'-bi[benzo[b]thiophene], $C_{16}H_{10}S_2$, at 173 K has triclinic ($P\overline{1}$) symmetry. It is of interest with respect to its apparent mode of synthesis, as it is a by-product of a Stille cross-coupling reaction in which it was not explicitly detected by spectroscopic methods. It was upon crystal structure analysis of a specimen isolated from the mother liquor that this reaction was determined to give rise to the title compound, which is a dimer arising from the starting material. Two independent half-molecules of this dimer comprise the asymmetric unit, and the full molecules are generated *via* inversion centers. Both molecules in the unit cell exhibit ring disorder, and they are essentially identical because of their rigidity and planarity.

Keywords: crystal structures; chemical reactions and mechanisms; computational chemistry; pharmaceutical compounds; structure and spectroscopy; by-products.

1. Introduction

This account of the structural chemistry of 2,2'-bi[benzo-[b]thiophene], (I), is of a rather serendipitous nature. The original intent was to utilize (benzo[b]thiophen-2-yl)tributylstannane in a Stille cross-coupling reaction (Espinet & Echavarren, 2004) with 2-chloro-3-methylpyridine to yield 2-(benzo[b]thiophen-2-yl)-3-methylpyridine. Surprisingly, analysis of the crystals that were grown and harvested after the reaction did not support the structure of the desired compound, but rather that of (I), which is a by-product formed during the cross-coupling reaction. The generalized crosscoupling reaction involves a halogenated sp^2 -hybridized species R reacting with an sp^2 -hybridized species R' that is bonded to a sterically hindered metal core. In order for homodimer (I) to form, the species benzo[b]thiophene–Pd– benzo[b]thiophene must have formed during the Pd^{II} to Pd⁰ catalyst-reduction step of the cross-coupling. Reductive elimination would then give rise to the observed dimer. Although only a minor impurity in the isolated desired product, by-product (I) was the sole species identified during single-crystal structure determination. Whilst impurities from cross-coupling reactions can occur, this study demonstrates the importance of reconciling the crystal structures from crosscoupling reactions with the identity of the material in the bulk product.



2. Experimental

2.1. Synthesis and crystallization

Compound (I) was synthesized using a one-step procedure starting from (benzo[*b*]thiophen-2-yl)tributylstannane (3.0 g, 7.1 mmol) and dichloridobis(triphenylphosphane)palladium(II) (0.33 g, 0.47 mmol). 2-Chloro-3-methylpyridine (0.60 g, 4.7 mmol), while present in the reaction mixture (9.4 ml tetrahydrofuran, reflux, 43 h), did not participate in the dimerization reaction.

After completion of the cross-coupling reaction, as determined by high-performance liquid chromatography-mass spectroscopy (HPLC-MS), the reaction mixture was adsorbed onto silica gel and subjected to flash chromatography (19:1 hexane-ethyl acetate). The isolated material was re-subjected to silica-gel flash chromatography (19:1 hexane-ethyl acetate) to remove residual undesired by-products (e.g. Bu₃SnX residues). A portion of the purified material (48 mg of 1.0 g, 94% yield, >95% purity by HPLC-MS and ¹H NMR) was dissolved in diisopropyl ether (1.0 ml) and the resulting solution was filtered through a 0.45 µm Teflon filter into an uncapped small vial, which was then placed into a large vial containing hexane (4.0 ml). Vapor diffusion led to the crystallization of a cluster of solid, of which one crystal appeared to be suitable for single-crystal X-ray diffraction analysis. Although the solid was colorless, the selected crystal was clearer than its surroundings.

With regard to the ¹H NMR spectroscopic data, a very small aberrant singlet was noted in the aromatic region, and if this tiny peak is assumed to be that of a single proton of compound (I), then (I) was present at less than 3 mol% in solution, perhaps even as low as 2 mol%. The elusiveness of (I) in solution is further established by its total lack of appearance in the HPLC–MS data. However, once the unexpected X-ray crystal structure was obtained, re-evaluation of the bulk material in a deliberate search for this by-product by thinlayer chromatography (TLC) revealed traces of it.

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Table 1

Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{10}S_2$
$M_{\rm r}$	266.36
Crystal system, space group	Triclinic, P1
Temperature (K)	173
a, b, c (Å)	5.8415 (1), 7.6197 (1), 14.2782 (2)
α, β, γ (°)	76.286 (1), 81.118 (1), 88.699 (1)
$V(\text{\AA}^3)$	609.94 (2)
Ζ	2
Radiation type	Cu Ka
$\mu \text{ (mm}^{-1})$	3.73
Crystal size (mm)	$0.36 \times 0.32 \times 0.04$
Data collection	
Diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (SADABS; Sheldrick, 1996)
T_{\min}, T_{\max}	0.348, 0.853
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	8960, 2313, 2129
R _{int}	0.036
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.112, 0.93
No. of reflections	2313
No. of parameters	177
H-atom treatment	H-atom parameters constrained
$\Delta ho_{ m max}, \Delta ho_{ m min} ({ m e} { m \AA}^{-3})$	0.29, -0.23

Computer programs: COSMO (Bruker, 2009), APEX2 (Bruker, 2010), SAINT (Bruker, 2010), SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008) and SHELXTL (Sheldrick, 2008).

The ¹H NMR spectra are available in the *Supporting information*. The 'aberrant singlet' is at δ 7.51 in the ¹H NMR expansion and integrates to 0.02 (2 mol% if it is one proton). ¹H NMR (400 MHz, chloroform-*d*): δ 8.54 (*d*, *J* = 4.3 Hz, 1H), 7.92–7.85 (*m*, 1H), 7.84–7.78 (*m*, 1H), 7.69 (*s*, 1H), 7.58 (*d*, *J* = 7.6 Hz, 1H), 7.41–7.31 (*m*, 2H), 7.16 (*dd*, *J* = 4.7, 7.6 Hz, 1H), 2.67 (*s*, 3H).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. C-bound H atoms were placed in calculated positions and constrained as riding atoms, with C-H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

The additional atoms arising from the disorder of (I) (see §3 for more details) were located in Fourier difference maps. The disorder was modeled by refining the occupancies of the C and S atoms involved in the disorder. The geometries from the refinement were found to be reasonable without the application of restraints, but the atomic displacement parameters of the two positions for each disordered atom were constrained to be equal.

3. Results and discussion

The crystal structure of (I) obtained from the present structure determination was found to contain two independent half-molecules of (I) in the asymmetric unit (Fig. 1). The proximity of each half-molecule to an inversion center results in the



Figure 1

The asymmetric unit of (I), showing the two molecules in the unit cell. S1AA and S1BA are generated by the inversion center. Displacement ellipsoids are drawn at the 50% probability level.

generation of the rest of the molecule by symmetry. The C–C bond distances between the two halves of each molecule across the inversion center are 1.448 (3) and 1.447 (3) Å, suggestive of the fact that this C–C bond has double-bond or aromatic character, a conclusion which is reinforced by the planarity of the molecules.

During the course of the refinement, it became clear that there was disorder of the benzo[b]thiophene ring. The S atom was found to be disordered with the C atom at the 7-position, meaning that the entire molecule is flipped 180° over its long axis. The center of inversion makes it impossible for the disorder to arise from the presence of molecules with the *syn* geometry because the inversion center necessitates that a halfmolecule of (I) generates the other half of the molecule with the opposing conformation. As there are two independent half-molecules of (I) in the asymmetric unit, if we designate one molecule as A and the other as B, molecule A is 61% in its major orientation and 39% in its minor, whereas molecule B is 72% in its major orientation and 28% in its minor.



Initial assessment of the crystal structure of (I) suggested that there were two independent benzo[b]thiophene rings in the asymmetric unit. This would have been suggestive of their having become disengaged from the stannane starting material during the course of the reaction. However, their proximity to an inversion center imposes a symmetry equivalent that is 1.448 Å from the C atom at the 8-position, which could only be explained if dimerization had occurred (Fig. 1). The C-C bond length is similar to that observed for 2,2'-bithiophene, which was reported to be 1.448 Å (Ali-Adib *et al.*, 1984).



Figure 2

A packing diagram for (I), viewed along the c axis. H atoms have been omitted for clarity. Only one configuration of the disordered molecules is shown.

Owing to the planarity of each half-molecule and their relationship with the inversion center, the conformations of both independent molecules of (I) are essentially identical. The five- and six-membered rings are both planar, which was also reported for the crystal structure of the monomer benzo[b]thiophene (Pelletier & Brisse, 1994; Chaloner *et al.*, 1994). In (I), the S-C-C-S torsion angle that separates the two halves of each molecule is 180° (as depicted in Scheme 2). A 0° torsion angle occurs when the S atoms are *syn* to one another and a 180° torsion angle occurs when they are *anti* to each other.

The geometric results of this crystal structure determination complement the computational study performed by Hayashi & Higuchi (2009). In their work, the calculations predicted that (I) would have two minima in its energy landscape. The global minimum is the *anti* conformation at an S-C-C-S torsion angle of 157°. A local minimum exists at 44°, which represents an offset *syn* conformation. A fully planar *syn* conformation at an S-C-C-S torsion angle of 0° is calculated to be an energy maximum. Neither *syn* conformation is observed in the present crystal structure.

The molecular packing arrangement of (I) shows that the molecules do not have strong intermolecular contacts with each other (Fig. 2). The centroid-to-centroid distance between the closest neighboring benzene rings of (I) is 4.72 Å, and noncovalent interactions such as π - π are not present in this crystal structure, although possible C-H··· π contacts may be identified (*e.g.* C5B-H5BA and C5A-H5AA to neighboring intermolecular π -systems). Without stronger interactions to lock the orientations of the molecules in the solid state, the existence of disorder for this planar and symmetric molecule seems sensible.

In conclusion, while the cross-coupling reaction of (benzo-[b]thiophen-2-yl)tributylstannane and 2-chloro-3-methylpyridine using dichloridobis(triphenylphosphane)palladium(II) as the pre-catalyst resulted in almost exclusively the desired compound as analyzed by spectroscopic methods (>95%), dimer (I) formed in sufficient amounts to crystallize and become the dominant species in the specimen as analyzed by single-crystal X-ray diffraction. Because the prospect of dimerization is general to cross-coupling reactions, the results of single-crystal analysis of a specimen arising from such a reaction mixture should be carefully compared with spectroscopic data in order to determine how representative the crystal structure is of the surrounding solid product.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: UK3096).

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supplementary materials

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Computing details

Data collection: COSMO (Bruker, 2009); cell refinement: *APEX2* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2,2'-Bi[benzo[b]thiophene]

Crystal data

C₁₆H₁₀S₂ $M_r = 266.36$ Triclinic, *P*1 Hall symbol: -P 1 a = 5.8415 (1) Å b = 7.6197 (1) Å c = 14.2782 (2) Å a = 76.286 (1)° $\beta = 81.118$ (1)° $\gamma = 88.699$ (1)° V = 609.94 (2) Å³

Data collection

Bruker APEXII CCD area-detector diffractometer Radiation source: fine-focus sealed tube Graphite monochromator Detector resolution: 836.6 pixels mm⁻¹ ω and/f 0.5° scans Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min} = 0.348$, $T_{\max} = 0.853$

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.112$ S = 0.932313 reflections 177 parameters 0 restraints Z = 2 F(000) = 276 $D_x = 1.450 \text{ Mg m}^{-3}$ Cu K\alpha radiation, \lambda = 1.54178 \mathbf{A} Cell parameters from 5762 reflections $\theta = 3.2-72.2^{\circ}$ $\mu = 3.73 \text{ mm}^{-1}$ T = 173 KPlate, colourless $0.36 \times 0.32 \times 0.04 \text{ mm}$

8960 measured reflections 2313 independent reflections 2129 reflections with $I > 2\sigma(I)$ $R_{int} = 0.036$ $\theta_{max} = 72.2^\circ, \theta_{min} = 3.2^\circ$ $h = -5 \rightarrow 7$ $k = -9 \rightarrow 9$ $l = -16 \rightarrow 17$

Primary atom site location: structure-invariant direct methods Secondary atom site location: difference Fourier map Hydrogen site location: inferred from neighbouring sites H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.070P)^2 + 0.3344P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\begin{array}{l} \Delta\rho_{\rm max}=0.29~{\rm e}~{\rm \AA}^{-3}\\ \Delta\rho_{\rm min}=-0.23~{\rm e}~{\rm \AA}^{-3} \end{array}$

Special details

Experimental. Data were collected using a Bruker CCD (charge-coupled device)-based diffractometer equipped with an Oxford low-temperature apparatus operating at 173 K. A suitable crystal was chosen and mounted on a nylon loop using mineral oil for copper radiation. Data were measured using ω and φ scans of 1.0° per frame for 30 s. The total number of images was based on results from the program COSMO, where redundancy was expected to be 4 and completeness to 0.83 to 100%. Cell parameters were retrieved using *APEX2* software and refined using *SAINT* on all observed reflections. Data reduction was performed using the *SAINT* software, which corrects for Lp and decay. Scaling and absorption corrections were performed by the *SADABS* program. The structures were solved by the direct method using the *SHELX90* program and refined by the least-squares method on F2 using *SHELXL93*, incorporated in *SHELXTL* version 6.1.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2 , conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger. The following atoms were constrained to having the same thermal values. eadp c7b c7bb eadp s1b s1bb eadp c7a c7ab eadp s1a s1ab

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	Occ. (<1)
S1A	-0.21435 (15)	0.36901 (11)	0.63774 (6)	0.0264 (2)	0.6131 (12)
C7A	0.1790 (7)	0.5360 (5)	0.5940 (3)	0.0281 (8)	0.6131 (12)
H7AB	0.3134	0.5998	0.5566	0.034*	0.6131 (12)
S1AB	0.2585 (3)	0.5707 (2)	0.58009 (12)	0.0264 (2)	0.3869 (12)
C7AB	-0.1321 (10)	0.4023 (8)	0.6306 (5)	0.0281 (8)	0.3869 (12)
H7AA	-0.2717	0.3466	0.6251	0.034*	0.3869 (12)
C1A	-0.0686 (3)	0.3982 (2)	0.72842 (13)	0.0297 (4)	
C2A	-0.1582 (3)	0.3364 (2)	0.82716 (14)	0.0354 (4)	
H2AA	-0.3037	0.2750	0.8465	0.042*	
C3A	-0.0319 (3)	0.3661 (3)	0.89592 (14)	0.0387 (4)	
H3AA	-0.0921	0.3259	0.9633	0.046*	
C4A	0.1830 (3)	0.4543 (2)	0.86815 (14)	0.0375 (4)	
H4AA	0.2681	0.4722	0.9168	0.045*	
C5A	0.2734 (3)	0.5157 (2)	0.77119 (14)	0.0339 (4)	
H5AA	0.4201	0.5755	0.7528	0.041*	
C6A	0.1472 (3)	0.4891 (2)	0.70008 (13)	0.0287 (4)	
C8A	0.0106 (3)	0.4855 (2)	0.55109 (12)	0.0238 (3)	
S1B	0.24675 (11)	0.11677 (9)	0.40529 (5)	0.0273 (2)	0.7234 (16)
C7B	0.6423 (7)	-0.0348 (4)	0.3769 (2)	0.0284 (7)	0.7234 (16)
H7BA	0.7830	-0.0949	0.3886	0.034*	0.7234 (16)
S1BB	0.7176 (4)	-0.0595 (3)	0.37345 (17)	0.0273 (2)	0.2766 (16)
C7BB	0.3217 (14)	0.0846 (11)	0.3997 (7)	0.0284 (7)	0.2766 (16)
H7BB	0.1844	0.1269	0.4319	0.034*	0.2766 (16)
C1B	0.3556 (3)	0.0977 (2)	0.29021 (13)	0.0277 (4)	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters $(Å^2)$

C2B	0.2467 (3)	0.1641 (2)	0.20905 (15)	0.0374 (4)
H2BA	0.0999	0.2199	0.2155	0.045*
C3B	0.3569 (4)	0.1470 (3)	0.11913 (15)	0.0449 (5)
H3BA	0.2853	0.1926	0.0630	0.054*
C4B	0.5712 (4)	0.0642 (3)	0.10913 (14)	0.0437 (5)
H4BA	0.6437	0.0542	0.0463	0.052*
C5B	0.6794 (3)	-0.0034 (2)	0.18894 (14)	0.0362 (4)
H5BA	0.8248	-0.0611	0.1817	0.043*
C6B	0.5729 (3)	0.0141 (2)	0.28060 (13)	0.0276 (4)
C8B	0.4907 (3)	0.0120 (2)	0.44888 (12)	0.0244 (3)

Atomic displacement parameters $(Å^2)$

	U^{11}	U ²²	U ³³	U^{12}	<i>U</i> ¹³	U^{23}
S1A	0.0193 (4)	0.0274 (4)	0.0304 (4)	-0.0038 (3)	-0.0013 (3)	-0.0039 (3)
C7A	0.0174 (16)	0.0246 (16)	0.0399 (17)	-0.0006 (13)	0.0000 (15)	-0.0056 (12)
S1AB	0.0193 (4)	0.0274 (4)	0.0304 (4)	-0.0038(3)	-0.0013 (3)	-0.0039 (3)
C7AB	0.0174 (16)	0.0246 (16)	0.0399 (17)	-0.0006 (13)	0.0000 (15)	-0.0056 (12)
C1A	0.0265 (8)	0.0232 (8)	0.0403 (10)	0.0048 (7)	-0.0077 (7)	-0.0084(7)
C2A	0.0266 (8)	0.0290 (9)	0.0450 (10)	0.0008 (7)	0.0030 (7)	-0.0033 (8)
C3A	0.0438 (10)	0.0350 (9)	0.0327 (9)	0.0082 (8)	0.0019 (8)	-0.0046 (8)
C4A	0.0432 (10)	0.0345 (9)	0.0402 (10)	0.0085 (8)	-0.0150 (8)	-0.0144 (8)
C5A	0.0264 (8)	0.0264 (8)	0.0490 (11)	0.0006 (7)	-0.0054 (7)	-0.0094 (8)
C6A	0.0271 (8)	0.0205 (7)	0.0354 (9)	0.0049 (6)	0.0003 (7)	-0.0043 (7)
C8A	0.0186 (7)	0.0174 (7)	0.0339 (9)	0.0020 (6)	-0.0012 (6)	-0.0047 (6)
S1B	0.0215 (4)	0.0283 (4)	0.0325 (3)	0.0069 (2)	-0.0049 (3)	-0.0078 (2)
C7B	0.0210 (14)	0.0254 (14)	0.0402 (15)	0.0067 (12)	-0.0076 (13)	-0.0096 (10)
S1BB	0.0215 (4)	0.0283 (4)	0.0325 (3)	0.0069 (2)	-0.0049 (3)	-0.0078(2)
C7BB	0.0210 (14)	0.0254 (14)	0.0402 (15)	0.0067 (12)	-0.0076 (13)	-0.0096 (10)
C1B	0.0246 (8)	0.0210 (7)	0.0374 (9)	-0.0013 (6)	-0.0034 (7)	-0.0075 (6)
C2B	0.0327 (9)	0.0272 (9)	0.0544 (12)	0.0045 (7)	-0.0181 (8)	-0.0072 (8)
C3B	0.0622 (13)	0.0337 (10)	0.0405 (11)	-0.0074 (9)	-0.0253 (10)	0.0000 (8)
C4B	0.0542 (12)	0.0448 (11)	0.0319 (9)	-0.0169 (10)	0.0018 (8)	-0.0125 (8)
C5B	0.0305 (9)	0.0346 (9)	0.0453 (11)	-0.0035 (7)	0.0017 (7)	-0.0176 (8)
C6B	0.0246 (8)	0.0211 (7)	0.0375 (9)	-0.0016 (6)	-0.0063 (7)	-0.0066 (7)
C8B	0.0202 (7)	0.0202 (7)	0.0331 (9)	0.0004 (6)	-0.0046 (6)	-0.0065 (6)

Geometric parameters (Å, °)

S1A—C1A	1.7136 (19)	S1B—C1B	1.7064 (18)	
S1A—C8A	1.7536 (18)	S1B—C8B	1.7442 (17)	
C7A—C8A	1.344 (4)	C7B—C8B	1.359 (4)	
C7A—C6A	1.454 (4)	C7B—C6B	1.455 (4)	
С7А—Н7АВ	0.9500	C7B—H7BA	0.9500	
S1AB—C6A	1.707 (2)	S1BB—C6B	1.661 (3)	
S1AB—C8A	1.745 (2)	S1BB—C8B	1.737 (3)	
C7AB—C8A	1.332 (6)	C7BB—C8B	1.334 (9)	
C7AB—C1A	1.493 (7)	C7BB—C1B	1.525 (9)	
С7АВ—Н7АА	0.9500	C7BB—H7BB	0.9500	
C1A—C2A	1.397 (3)	C1B—C2B	1.392 (3)	

C1A—C6A	1.408 (2)	C1B—C6B	1.410(2)
C2A—C3A	1.377 (3)	C2B—C3B	1.378 (3)
C2A—H2AA	0.9500	C2B—H2BA	0.9500
C3A—C4A	1.394 (3)	C3B—C4B	1.392 (3)
СЗА—НЗАА	0.9500	СЗВ—НЗВА	0.9500
C4A—C5A	1.376 (3)	C4B—C5B	1.376 (3)
С4А—Н4АА	0.9500	C4B—H4BA	0.9500
C5A—C6A	1.397 (3)	C5B—C6B	1.395 (3)
С5А—Н5АА	0.9500	C5B—H5BA	0.9500
C8A—C8A ⁱ	1.447 (3)	C8B—C8B ⁱⁱ	1.448 (3)
C1A—S1A—C8A	89.14 (9)	C1B—S1B—C8B	90.53 (8)
C8A—C7A—C6A	117.3 (3)	C8B—C7B—C6B	115.0 (3)
C8A—C7A—H7AB	121.3	C8B—C7B—H7BA	122.5
С6А—С7А—Н7АВ	121.3	С6В—С7В—Н7ВА	122.5
C6A—S1AB—C8A	87.65 (10)	C6B—S1BB—C8B	88.56 (13)
C8A—C7AB—C1A	118.8 (5)	C8B-C7BB-C1B	117.9 (6)
C8A—C7AB—H7AA	120.6	C8B—C7BB—H7BB	121.0
C1A - C7AB - H7AA	120.6	C1B - C7BB - H7BB	121.0
C^2A — C^1A — C^6A	120.37(17)	C2B-C1B-C6B	120.70(17)
C2A— $C1A$ — $C7AB$	139.6(3)	C2B— $C1B$ — $C7BB$	120.70(17) 140.6(3)
C6A - C1A - C7AB	100.1(3)	C6B-C1B-C7BB	98 7 (3)
C_{2A} C_{1A} S_{1A}	100.1(3) 122 15 (14)	$C^{2}B - C^{1}B - S^{1}B$	123 93 (14)
C6A - C1A - S1A	122.13(14) 117.48(14)	C6B-C1B-S1B	125.93(14) 115.33(14)
C7AB-C1A-S1A	1774(2)	C7BB-C1B-S1B	167(3)
$C_{AB} = C_{A} = C_{A}$	17.7(2)	C_{3B} C_{2B} C_{1B}	10.7(3) 118 48 (18)
$C_{3A} = C_{2A} = C_{1A}$	120.6	$C_{3B} = C_{2B} = H_{2BA}$	120.8
$C_{1A} = C_{2A} = H_{2AA}$	120.0	$C_{1B} = C_{2B} = H_{2BA}$	120.8
$C_{1A} = C_{2A} = \Pi_{2AA}$	120.0 120.03(18)	C_{1D} C_{2D} C_{1D} C_{2D} C_{4D}	120.8
$C_{2A} = C_{3A} = C_{4A}$	120.95 (16)	C2D - C3D - C4D	121.13 (18)
$C_{A} = C_{A} = H_{A}$	119.5	C2D—C3D—H3DA C4D—C2D—H2DA	119.4
$C_{4A} = C_{5A} = C_{5A}$	119.3	C4D - C3D - H3DA	119.4
$C_{5A} = C_{4A} = U_{4A} = C_{5A}$	120.82 (18)	C_{5D} C_{4D} U_{4DA}	120.90 (19)
$C_{A} = C_{A} = H_{A} A$	119.0	$C_{3}D_{-}C_{4}D_{-}H_{4}D_{A}$	119.0
C3A - C4A - H4AA	119.0	C_{3B} C_{4B} H_{4BA}	119.0
C4A - C5A - C6A	119.29 (17)	C4B - C5B - C6B	119.10 (18)
C4A—C5A—H5AA	120.4	C4B—C5B—H5BA	120.5
C6A—C5A—H5AA	120.4	COB-COB-HOBA	120.4
C5A - C6A - C1A	119.72 (17)	CSB—C6B—CIB	119.68 (17)
C5A - C6A - C/A	135.6 (2)	C5B—C6B—C7B	132.9 (2)
CIA - C6A - C/A	104.7 (2)	CIB-C6B-C/B	107.4 (2)
C5A—C6A—SIAB	118.74 (14)	C5B—C6B—S1BB	117.14 (16)
C1A—C6A—S1AB	121.54 (15)	C1B—C6B—S1BB	123.13 (16)
C/A—C6A—SIAB	16.86 (16)	C/B—C6B—SIBB	15.81 (15)
С/АВ—С8А—С7А	99.2 (3)	C ⁻ /BB—C8B—C7B	101.0 (4)
C/AB—C8A—C8A ¹	130.4 (3)	C'/BB—C8B—C8B ⁿ	129.9 (4)
C7A—C8A—C8A ¹	130.4 (2)	C7B—C8B—C8B"	129.1 (2)
C7AB—C8A—S1AB	111.9 (3)	C7BB—C8B—S1BB	111.6 (4)
C7A—C8A—S1AB	12.79 (19)	C7B—C8B—S1BB	10.69 (17)
C8A ⁱ —C8A—S1AB	117.62 (16)	C8B ⁱⁱ —C8B—S1BB	118.41 (17)

C7AB—C8A—S1A	12.2 (3)	C7BB—C8B—S1B	10.9 (4)
C7A—C8A—S1A	111.4 (2)	C7B—C8B—S1B	111.80 (18)
C8A ⁱ —C8A—S1A	118.19 (16)	C8B ⁱⁱ —C8B—S1B	119.13 (16)
S1AB—C8A—S1A	124.18 (11)	S1BB—C8B—S1B	122.44 (12)
C8A—C7AB—C1A—C2A	177.7 (2)	C8B—C7BB—C1B—C2B	-176.4 (3)
C8A—C7AB—C1A—C6A	-1.8 (5)	C8B—C7BB—C1B—C6B	2.0 (6)
C8A—C7AB—C1A—S1A	178.0 (12)	C8B—C7BB—C1B—S1B	-174.9 (17)
C8A—S1A—C1A—C2A	178.43 (15)	C8B—S1B—C1B—C2B	-177.67 (16)
C8A—S1A—C1A—C6A	-1.08 (14)	C8B—S1B—C1B—C6B	0.09 (13)
C8A—S1A—C1A—C7AB	-1.3 (8)	C8B—S1B—C1B—C7BB	3.4 (11)
C6A—C1A—C2A—C3A	0.0 (3)	C6B—C1B—C2B—C3B	-0.3 (3)
C7AB—C1A—C2A—C3A	-179.4 (4)	C7BB—C1B—C2B—C3B	177.8 (5)
S1A—C1A—C2A—C3A	-179.48 (14)	S1B—C1B—C2B—C3B	177.30 (13)
C1A—C2A—C3A—C4A	-0.7 (3)	C1B—C2B—C3B—C4B	0.5 (3)
C2A—C3A—C4A—C5A	0.7 (3)	C2B—C3B—C4B—C5B	0.1 (3)
C3A—C4A—C5A—C6A	0.1 (3)	C3B—C4B—C5B—C6B	-0.8(3)
C4A—C5A—C6A—C1A	-0.8 (3)	C4B—C5B—C6B—C1B	1.0 (3)
C4A—C5A—C6A—C7A	178.2 (2)	C4B—C5B—C6B—C7B	-177.3 (2)
C4A—C5A—C6A—S1AB	178.48 (14)	C4B—C5B—C6B—S1BB	-176.67 (16)
C_{2A} C_{1A} C_{6A} C_{5A}	0.8 (2)	C2B-C1B-C6B-C5B	-0.4(3)
C7AB—C1A—C6A—C5A	-179.6(3)	C7BB—C1B—C6B—C5B	-179.2(3)
S1A-C1A-C6A-C5A	-17972(13)	S1B-C1B-C6B-C5B	-17824(12)
C_{2A} C_{1A} C_{6A} C_{7A}	-17854(19)	C2B-C1B-C6B-C7B	178 28 (18)
C7AB-C1A-C6A-C7A	11(3)	C7BB-C1B-C6B-C7B	-0.5(4)
S1A-C1A-C6A-C7A	1.0(2)	S1B-C1B-C6B-C7B	0.4(2)
C_{2A} C_{1A} C_{6A} S_{1AB}	-17852(14)	C2B-C1B-C6B-S1BB	177 11 (16)
C7AB-C1A-C6A-S1AB	11(3)	C7BB-C1B-C6B-S1BB	-1.7(3)
S1A - C1A - C6A - S1AB	1.1(3) 10(2)	S1B-C1B-C6B-S1BB	-0.7(2)
C8A - C7A - C6A - C5A	-1794(2)	C8B-C7B-C6B-C5B	17748(18)
C8A - C7A - C6A - C1A	-0.3(3)	C8B - C7B - C6B - C1B	-10(3)
C8A - C7A - C6A - S1AB	179.8 (8)	C8B - C7B - C6B - S1BB	1.0(3) 175 4 (8)
C8A = S1AB = C6A = C5A	-179.53(14)	C8B $S1BB$ $C6B$ $C5B$	173.4(0) 178.44(14)
C8A = S1AB = C6A = C1A	-0.24(16)	C8B $S1BB$ $C6B$ $C1B$	1/0.44(14)
$C_{8A} = S_{1AB} = C_{6A} = C_{7A}$	-0.2(6)	C_{8B} S1BB C6B C7B	-3.2(6)
C_{0A} C_{7AB} C_{8A} C_{7A}	1.6(4)	$C_{1B} = C_{7B} = C_{8B} = C_{7B}$	-25(6)
$C_{1A} = C_{7AB} = C_{8A} = C_{7A}^{i}$	-177.8(3)	C1B = C7BB = C8B = C7B	2.3(0)
C1A C7AB C8A S1AB	177.8(5)	C1D = C7DD = C0D = C0D	-1.7(7)
C1A C7AB C8A S1A	1.0(3) -177.2(16)	C1D - C7DD - C0D - S1DD	-1.7(7)
CIA - C/AD - CoA - SIA	-177.2(10) -0.7(2)	CID - C/DD - COD - SID	1/2(3)
C6A C7A C8A C8Ai	0.7(3)	C6P $C7P$ $C9P$ $C9P$	2.1(4) -1782(2)
C6A = C7A = C8A = C8A	170.7(2)	$C_{0} = C_{0} = C_{0$	-170.2(2)
C6A = C7A = C8A = S1AB	-1/9.7(10)	$C_{0} = C_{0} = C_{0$	-1/5.0(11)
C(A = C/A = C A	-0.4(3)	COB - C/B - COB - SIB	1.1(3)
C_{0A} C_{1AB} C_{0A} C_{7AB}	-0.9(3)	COB = SIBB = COB = C7B	0.5 (4)
CA = SIAD = CA = CA	$0.2(\delta)$	COD = SIBB = CSB = CSB	J.I (9)
$CA = SIAB = C8A = C8A^{\circ}$	1/8.82(1/)	COB = SIBB = CSB = CSB	-1/9.00(18)
CIA = SIA = CSA = SIA	-0.01(13)	C_{1D} C_{1D} C_{2D} C_{2DD}	-0.81(16)
CIA - SIA - CAA - C/AB	2.1 (12)		-6 (2)
CIA—SIA—C8A—C7A	0.8 (2)	C1B—S1B—C8B—C7B	-0.65 (18)

C1A—S1A—C8A—C8A ⁱ	-178.41 (17)	C1B—S1B—C8B—C8B ⁱⁱ	178.71 (17)
C1A—S1A—C8A—S1AB	1.02 (12)	C1B—S1B—C8B—S1BB	0.53 (13)

Symmetry codes: (i) -*x*, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*, -*z*+1.

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