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Synthesis and structure of tetra- and triphenylbismuth arenesulfonates

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Tetraphenylbismuth arenesulfonates were synthesized by the reaction of pentaphenylantimony or -bismuth with triphenylbismuth bis(arenesulfonates). Triphenylbismuth bis(arenesulfonates) were synthesized by the reaction of triphenylbismuth with arenesulfonic acids in the presence of hydrogen peroxide. The crystal structures of the tetraphenylbismuth 2,5-dimethylbenzenesulfonate crystal hydrate (**1**), tetraphenylbismuth 3-carboxy-4-hydroxybenzenesulfonate (**2**), and triphenylbismuth bis(2,5-dimethylbenzenesulfonate) (**3**) were determined by X-ray diffraction analysis. The Bi atom in **1** has a tetrahedral coordination (bond angles vary from 106.6(6) to 111.9(10)°). The Bi coordination observed in **2** is intermediate between tetrahedral and trigonal-bipyramidal, and that in structure **3** is trigonal-bipyramidal, with the oxygen atoms in the axial positions. The Bi—O bond lengths are 2.19(2) and 2.27(2) Å. In the crystal of **2**, the anions form an infinite hydrogen-bonded chain.

Key words: pentaphenylbismuth, pentaphenylantimony, tetraphenyl- and triphenylbismuth arenesulfonates, synthesis, X-ray diffraction analysis, molecular structure.

Pentavalent bismuth compounds Ph_4BiX can be prepared[1—3] by treatment of pentaphenylbismuth with halogens or acids (HX). We showed that tetraphenylbismuth arenesulfonates can be successfully synthesized by disproportionation of pentaphenylbismuth with triphenylbismuth bis(arenesulfonates).

$$Ph_5Bi + Ph_3Bi(OSO_2Ar)_2 \longrightarrow 2\ Ph_4BiOSO_2Ar$$

$(Ar = 2,5\text{-}Me_2C_6H_3,\ 4\text{-}MeC_6H_4)$

Pentaphenylantimony reacts with triphenylbismuth bis(arenesulfonates) in a similar way.

$$Ph_5Sb + Ph_3Bi(OSO_2Ar)_2 \longrightarrow Ph_4SbOSO_2Ar + Ph_4BiOSO_2Ar$$

$(Ar = 2,5\text{-}Me_2C_6H_3,\ 4\text{-}MeC_6H_4)$

Tetraphenylbismuth arenesulfonates can also be synthesized from pentaphenylbismuth and arenesulfonic acids.

$$Ph_5Bi + HOSO_2Ar \longrightarrow Ph_4BiOSO_2Ar + PhH$$

$(Ar = 2,5\text{-}Me_2C_6H_3,\ 4\text{-}MeC_6H_4,\ 3\text{-}(HOC(O)C_6H_3(OH)\text{-}4))$

Triphenylbismuth bis(arenesulfonates) were prepared in up to 98% yields from triphenylbismuth and arenesulfonic acid in an ethereal solution in the presence of hydrogen peroxide.

$$Ph_3Bi + 2\ HOSO_2Ar + H_2O_2 \longrightarrow Ph_3Bi(OSO_2Ar)_2 + 2\ H_2O$$

$(Ar = 2,5\text{-}Me_2C_6H_3,\ 4\text{-}MeC_6H_4)$

The resulting Bi^{5+} compounds are colorless crystalline substances soluble in polar organic solvents and aromatic hydrocarbons.

The structures of the tetraphenylbismuth 2,5-dimethylbenzenesulfonate crystal hydrate $Ph_4Bi^+[O_3SC_6H_3Me_2\text{-}2,5]^- \cdot 0.5H_2O$ (**1**), tetraphenylbismuth 3-carboxy-4-hydroxybenzenesulfonate $Ph_4Bi^+[O_3SC_6H_3(COOH)\text{-}3\text{-}(OH)\text{-}4]^-$ (**2**), and triphenylbismuth bis(2,5-dimethylbenzenesulfonate) $Ph_3Bi(OSO_2C_6H_3Me_2\text{-}2,5)_2$ (**3**) were established by X-ray diffraction analysis. The structure of **1** consists of tetraphenylbismuthonium cations, 2,5-dimethylbenzenesulfonate anions, and water molecules which are disordered over two positions in the crystal. The Bi atom in the cation of **1** (Fig. 1) has a tetrahedral coordination (the C(Ph)—Bi—C(Ph) angles vary from 106.6(9) to 111.9(10)°). No short contacts between the cation and the anion were detected. The geometries of the anion and the cation are normal in general (Table 1). Unfortu-

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Table 1. Principal bond lengths (*d*) and angles (ω) in the structure of **1**

Bond	*d*/Å	Bond	*d*/Å
Bi(1)—C(1)	2.111(8)	S(2)—O(1)	1.482(7)
Bi(1)—C(7)	2.115(8)	S(2)—O(2)	1.497(7)
Bi(1)—C(13)	2.119(7)	S(2)—O(3)	1.459(7)
Bi(1)—C(19)	2.098(8)	S(2)—C(25)	1.780(8)
Angle	ω/deg	Angle	ω/deg
C(1)—Bi(1)—C(7)	112.3(3)	O(1)—S(2)—O(2)	112.8(4)
C(1)—Bi(1)—C(13)	110.9(3)	O(1)—S(2)—O(3)	111.5(4)
C(1)—Bi(1)—C(19)	107.9(3)	O(1)—S(2)—C(25)	106.0(4)
C(7)—Bi(1)—C(13)	110.7(3)	O(2)—S(2)—O(3)	112.6(4)
C(7)—Bi(1)—C(19)	106.2(3)	O(2)—S(2)—C(25)	106.7(4)
C(13)—Bi(1)—C(19)	108.7(3)	O(3)—S(2)—C(25)	106.7(4)

Table 2. Principal bond lengths (*d*) and angles (ω) in the structure of **2**

Bond	*d*/Å	Angle	ω/deg
Bi(1)—C(1)	2.198(7)	C(1)—Bi(1)—C(7)	120.6(3)
Bi(1)—C(7)	2.207(7)	C(1)—Bi(1)—C(13)	98.7(3)
Bi(1)—C(13)	2.222(9)	C(1)—Bi(1)—C(19)	115.1(3)
Bi(1)—C(19)	2.222(6)	C(7)—Bi(1)—C(13)	102.6(3)
S(2)—O(3)	1.439(6)	C(7)—Bi(1)—C(19)	112.0(2)
S(2)—O(4)	1.450(5)	C(13)—Bi(1)—C(19)	104.3(3)
S(2)—O(5)	1.465(6)	O(5)—Bi(1)—C(1)	76.3(4)
S(2)—C(25)	1.778(8)	O(5)—Bi(1)—C(7)	78.1(4)
O(6)—C(31)	1.32(1)	O(5)—Bi(1)—C(13)	174.4(4)
O(6)—H(61)	1.18(8)	O(5)—Bi(1)—C(19)	80.3(4)
O(7)—C(31)	1.23(1)	O(3)—S(2)—O(4)	113.3(3)
O(41)—C(28)	1.36(1)	O(3)—S(2)—O(5)	114.4(3)
O(41)—H(41)	0.72(6)	O(3)—S(2)—C(25)	106.7(4)
Bi(1)...O(5)	2.830(7)	O(4)—S(2)—O(5)	110.2(3)
		O(4)—S(2)—C(25)	106.8(3)
		O(5)—S(2)—C(25)	104.7(3)
		C(31)—O(6)—H(61)	100.0(5)
		C(28)—O(41)—H(41)	108.0(6)

nately, due to the low quality of the crystals, the H atoms of the hydrate water molecule were not identified in the structure of **1**; therefore, the pattern of hydrogen bonds was not determined. The structure of **2** (Fig. 2) consists of the tetraphenylbismuthonium cation and the 3-carboxy-4-hydroxyphenylsulfonate anion forming a contact ion pair. As indicated by analysis of the geometric parameters of the cation (Table 2), the coordination polyhedron of Bi in this compound is intermediate between a tetrahedron and a trigonal bipyramid and is similar to that in the structure of tetraphenylbismuth tosylate (**4**) described previously.[2] The O(5) atom of the sulfonate group is located opposite to the C(13)—C(18) phenyl substituent (the O(5)—Bi—C(13) angle is 174.4(2)°) at a distance of 2.830(6) Å from the Bi atom. Thus, the C(13)—C(18) phenyl group occupies a pseudoaxial position, while the C(1)—C(6), C(7)—C(12), and C(19)—C(24) phenyl groups occupy pseudoequatorial positions. The angles between the pseudoaxial Bi—C(13) bond and pseudoequatorial bonds are 98—104°, whereas the bond angles between the pseudoequatorial Bi—C bonds vary in the 112—120° range. The deviation of the Bi atom from the C(1)C(7)C(19) plane amounts to 0.4523(3) Å, which differs from the values of 0.78 and 0.41(2) Å found in the crystals of tetraphenylbismuth perchlorate having a classical tetrahedral coordination[4] and compound **4**,[2] respectively. The Bi—O(5) distance (2.830(6) Å) in the structure of **2** differs somewhat from the corresponding distance in the molecule of tetraphenylbismuth tosylate (2.77(3) Å)[2] and markedly exceeds the Bi—O distances in bismuth organic com-

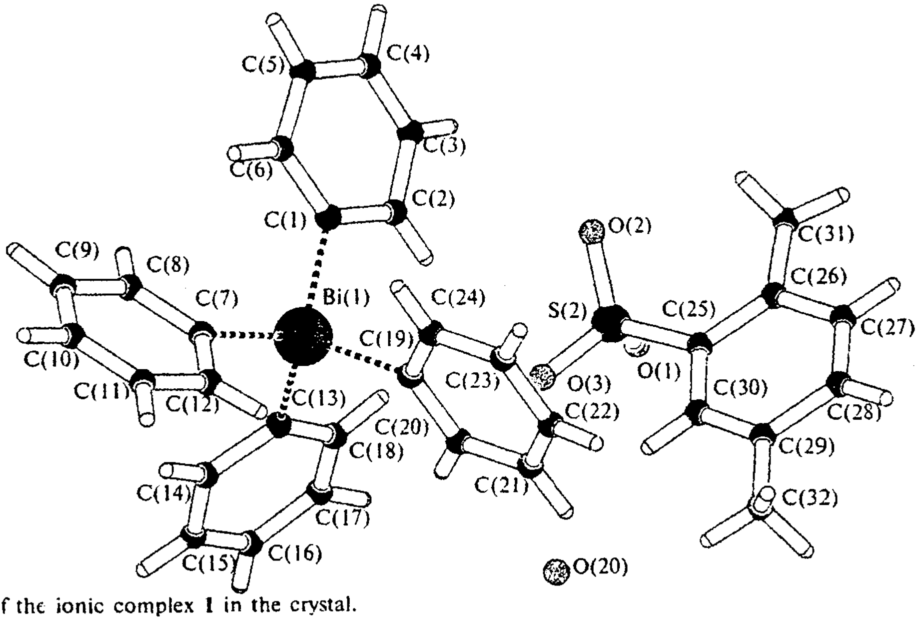

Fig. 1. Geometry of the ionic complex **1** in the crystal.

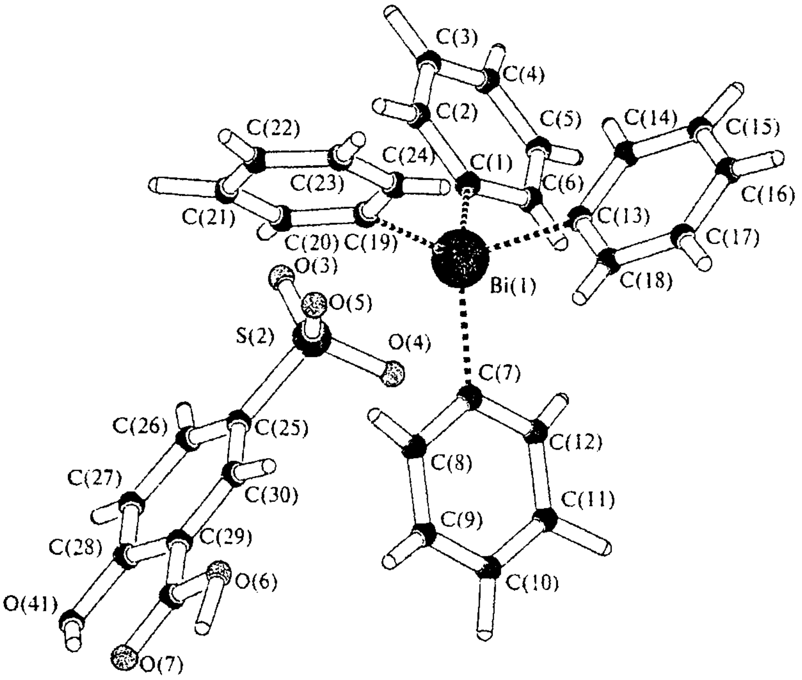

Fig. 2. Geometry of the ionic complex **2** in the crystal.

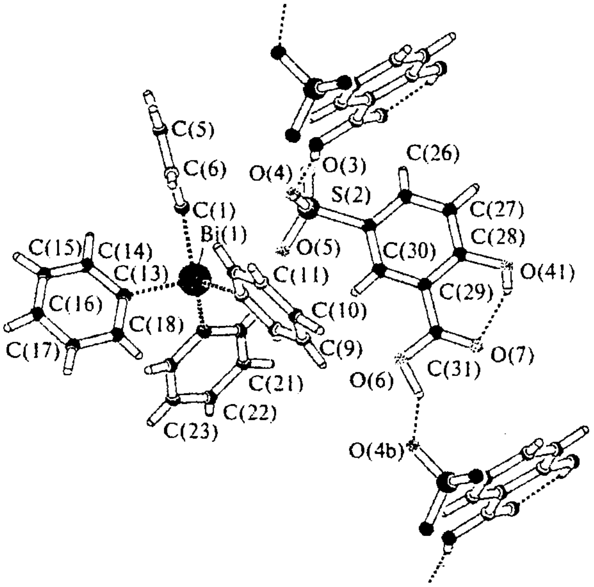

Fig. 3. System of hydrogen bonds in the crystal of **2**.

Table 3. Principal bond lengths (*d*) and angles (ω) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å
Bi(1)—C(1)	2.22(3)	S(1)—O(2)	1.43(2)
Bi(1)—C(7)	2.18(3)	S(1)—O(3)	1.53(2)
Bi(1)—C(13)	2.16(3)	S(1)—C(19)	1.77(3)
Bi(1)—O(3)	2.19(2)	S(2)—O(4)	1.38(2)
Bi(1)—O(6)	2.27(2)	S(2)—O(5)	1.46(2)
S(1)—O(1)	1.44(2)	S(2)—O(6)	1.50(2)
		S(2)—C(27)	1.83(3)

Angle	ω/deg	Angle	ω/deg
C(1)—Bi(1)—C(7)	118.0(1)	O(1)—S(1)—C(19)	108.0(1)
C(1)—Bi(1)—C(13)	130.0(1)	O(2)—S(1)—O(3)	110.0(1)
C(7)—Bi(1)—C(13)	112.0(1)	O(2)—S(1)—C(19)	106.0(1)
O(3)—Bi(1)—O(6)	176.6(7)	O(3)—S(1)—C(19)	104.0(1)
O(3)—Bi(1)—C(1)	82.5(9)	O(4)—S(2)—O(5)	117.0(2)
O(3)—Bi(1)—C(7)	95.0(1)	O(4)—S(2)—O(6)	110.0(1)
O(3)—Bi(1)—C(13)	91.0(1)	O(4)—S(2)—C(27)	112.0(1)
O(6)—Bi(1)—C(1)	94.6(9)	O(5)—S(2)—O(6)	106.0(1)
O(6)—Bi(1)—C(7)	85.0(1)	O(5)—S(2)—C(27)	108.0(1)
O(6)—Bi(1)—C(13)	92.0(1)	O(6)—S(2)—C(27)	103.0(1)
O(1)—S(1)—O(2)	120.0(1)	Bi(1)—O(3)—S(1)	141.0(1)
O(1)—S(1)—O(3)	108.0(1)	Bi(1)—O(6)—S(2)	128.0(1)

pounds (2.16 Å).[6] In the crystal of **2**, an intramolecular hydrogen bond, O(41)—H...O(7), was detected (O(41)...O(7) 2.573(8), O(41)—H 0.72(7), and H...O(7) 1.93(7) Å, the O(41)—H...O(7) angle is 149(8)°). An intermolecular hydrogen bond, O(6)—H...O(4′), was also found in this crystal ($x - 1/2$, $1/2 - y$, $x - 1/2$) (O(6)...O(4′) 2.564(8), O(6)—H 1.19(9) Å, and H...O(4′) 1.53(8) Å, the O(6)—H...O(4′) angle is 141(7)°); these bonds unite the anions into an infinite one-dimensional chain along the diagonal of the *xz* plane (Fig. 3).

The X-ray diffraction analysis of compound **3** showed that the Bi atom in this molecule has a trigonal-bipyramidal coordination; the three benzene rings occupy equatorial positions, while the 2,5-dimethylbenzenesulfonate substituents are in the axial positions (Fig. 4). The Bi atom deviates from the plane through the three atoms attached to it, C(1)C(7)C(13), by 0.028(2) Å; the O(3)—Bi—O(6) angle is 176.6(7)°. The Bi—O(3) and Bi—O(6) bonds are covalent (the bond lengths are 2.19(2) and 2.27(2) Å, respectively), which is also confirmed by the magnitudes of the O(1)—S(1)—O(2) (120(1)°) and O(4)—S(2)—O(5) (117(2)°) bond angles, which are typical of covalently bound sulfonate groups.[5] The Bi—C bond lengths (on the average, 2.19 Å, Table 3) correspond to those in other compounds with similar structures such as μ-oxobis(diphenylbismuth diperchlorate)[4] and triphenylbismuth bis(benzenesulfonate).[6]

Thus, we determined the spatial structures of compounds **1**—**3**, which are built as a tetraphenylbismuthonium salt, an intermediate structure with coordination of the Bi atom by the O atom of the sulfonate group, and a typical derivative of the five-coordinate Bi atom with a trigonal-bipyramidal configuration.

Experimental

The IR spectra were recorded on a Hitachi 215 spectrometer (a Vaseline oil mull).

Tetraphenylbismuth 2,5-dimethylbenzenesulfonate crystal hydrate (1). A mixture of pentaphenylbismuth (1.00 g, 1.68 mmol) and triphenylbismuth bis(2,5-dimethylbenzenesulfonate) (1.36 g, 1.68 mmol) in 30 mL of toluene was kept for 12 h at 20 °C. Slow evaporation of the solvent gave large crystals of compound **1**, yield 2.22 g (92%), decomp. point 177 °C. Found (%): C, 52.87; H, 4.12. $C_{32}H_{31}BiO_4S$. Calculated (%): C, 53.33; H, 4.31. IR, ν/cm^{-1}: 1260, 1155 (S=O); 1005 (S—O).

Tetraphenylbismuth 4-toluenesulfonate was prepared in a similar way (yield 70%).

Tetraphenylbismuth 3-carboxy-4-hydroxybenzenesulfonate (2). 5-Sulfosalicylic acid (0.37 g, 1.68 mmol) was added to a solution of pentaphenylbismuth (1.00 g, 1.68 mmol) in 20 mL of toluene, and the mixture was kept for 1 h at 20 °C. The solvent was evaporated, and the solid residue was washed with light petroleum and dried to give 0.65 g (60%) of compound **2**, decomp. point 199 °C. Found (%): C, 50.01; H, 3.65. $C_{31}H_{25}BiO_6S$. Calculated (%): C, 50.68; H, 3.41. IR, ν/cm^{-1}: 1675 (C=O); 1258, 1140 (S=O); 1025 (S—O).

Tetraphenylbismuth 4-toluenesulfonate (86%) and tetraphenylbismuth 2,5-dimethylbenzenesulfonate (79%) were prepared in a similar way.

Triphenylbismuth bis(2,5-dimethylbenzenesulfonate) (3). 2,5-Dimethylbenzenesulfonic acid (1.01 g, 4.55 mmol) and a 27.5% aqueous solution of hydrogen peroxide (0.28 mL, 2.27 mmol) were added at 20 °C to a solution of triphenylbismuth (1.00 g, 2.27 mmol) in 50 mL of ether. After 12 h, the crystals that formed were filtered off, washed with ether, and dried to give 1.36 g (74%) of compound **3**, m.p. 163 °C. Found (%): C, 50.10; H, 4.14. $C_{34}H_{33}BiO_6S_2$. Calculated (%): C, 50.37; H, 4.07. IR, ν/cm^{-1}: 1290, 1155 (S=O); 925 (S—O).

Reaction of pentaphenylantimony with triphenylbismuth bis(2,5-dimethylbenzenesulfonate). A mixture of pentaphenylantimony (1.00 g, 1.97 mmol), triphenylbismuth bis(2,5-dimethylbenzenesulfonate) (1.60 g, 1.97 mmol), and 10 mL of toluene was heated for 1 h at 90 °C. Cooling the reaction mixture to 0 °C gave crystals, which were filtered off and dried to give 0.96 g (70%) of tetraphenylbismuth 2,5-dimethylbenzenesulfonate. Cooling the reaction mixture to −18 °C afforded 1.15 g (95%) of tetraphenylantimony 2,5-dimethylbenzenesulfonate crystals, whose melting point and IR spectrum did not differ from the corresponding characteristics of the tetraphenylantimony 2,5-dimethylbenzenesulfonate prepared from pentaphenylantimony and 2,5-dimethylbenzenesulfonic acid.[7] Removal of the solvent and recrystallization of the residue from ethanol gave 0.25 g (29%) of triphenylbismuth, m.p. 76 °C.

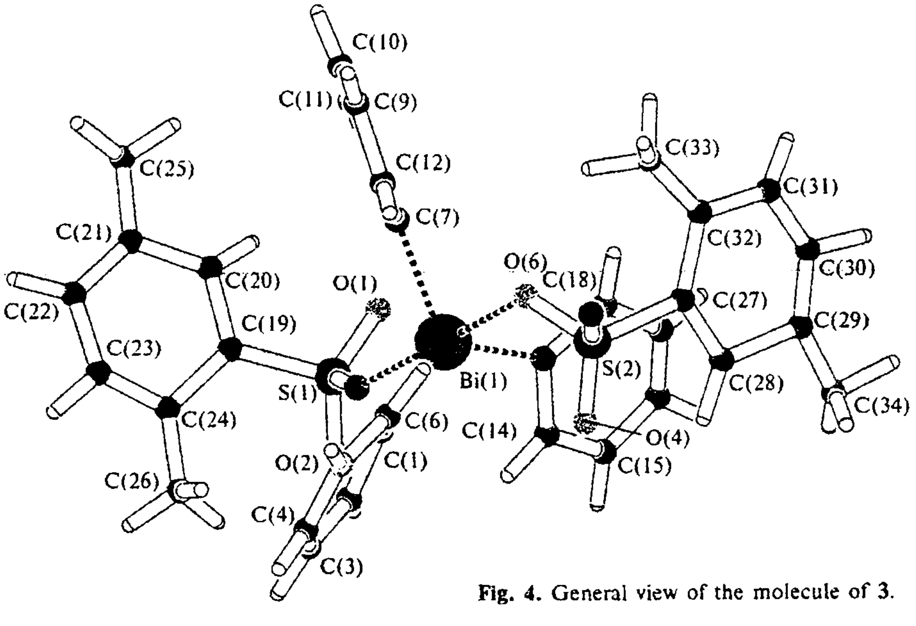

Fig. 4. General view of the molecule of **3**.

The reaction of pentaphenylantimony with triphenylbismuth bis(4-toluenesulfonate) was carried out in a similar manner.

The single crystal X-ray diffraction study of compounds 1—3 was carried out on a Enraf-Nonius CAD-4 four-circle automated diffractometer with K-geometry (20 °C, Mo-Kα-radiation, λ(Mo-Kα) = 0.71073 Å, graphite monochromator).

The crystals of $Ph_4Bi^+[O_3SC_6H_3Me_2\text{-}2,5]^- \cdot 0.5H_2O$ (**1**) are monoclinic, a = 14.183(5) Å, b = 22.144(10) Å, c = 18.463(11) Å, β = 100.29(4)°, V = 5705(5) Å^3, Z = 8, d_{calc} = 1.66 g cm^{-3}, space group $C2/c$.

The crystals of $C_{24}H_{20}Bi_1{}^+C_7H_5O_6S_1{}^-$ (**2**) are monoclinic, a = 11.177(1) Å, b = 21.762(3) Å, c = 12.2415(8) Å, β = 110.143(7)°, V = 2795.3(5) Å^3, Z = 4, d_{calc} = 1.75 g cm^{-3}, space group $P2_1/n$.

The crystals of $C_{34}H_{33}O_6S_2Bi_1$ (**3**) are monoclinic, a = 10.046(4) Å, b = 24.150(8) Å, c = 13.820(7) Å, β = 96.48(9)°, V = 3331.2(5) Å^3, Z = 4, d_{calc} = 1.62 g cm^{-3}, space group $P2_1/c$.

The absorption corrections were applied empirically (μ(Mo) = 62.61 (**1**), 64.00 (**2**), and 54.36 cm^{-1} (**3**), seven reflections with $\chi \geq 80°$ were scanned with rotation over the ψ vector with a step of 10°). The intensities of 10249 (**1**), 7211 (**2**), and 4852 (**3**) reflections were measured; for 4735 (**1**), 3210 (**2**), and 1220 (**3**) observed reflections, $I \geq 3\sigma$. The structures of **1** and **2** were studied using $\omega/2\theta$ scanning for $\theta \leq 29.96°$; for the structure of **3**, ω-scanning for $\theta \leq 23.36°$ was employed. The structures of **1** and **2** were solved by the direct method using the SIR program[6]; that of **3** was solved by the heavy-atom method. The refinement was first performed in the isotropic approximation; then all the nonhydrogen atoms in the structures of **1** and **2** and the Bi, S, and O atoms in the structure of **3** were refined in the anisotropic approximation. A disordered water molecule was found in the structure of **1**; its O atom was refined with an occupancy of 1/2. The C atoms in the structure of **3** were refined isotropically (due to the small number of measured reflections). The H atoms in structures **1** and **2** were revealed from the electron density difference series; those in structure **3** were placed in calculated positions. The contributions of the H atoms to the structural amplitudes in structures **1** and **3** were taken into account in the final stage of refinement with fixed positional and isotropic thermal parameters. The H atoms in structure **2** were refined isotropically. The final discrepancy factors were R = 0.065 and R_w = 0.074 over 4322 independent reflections with $F^2 \geq 3\sigma$ (**1**); R = 0.033 and R_w = 0.036 over 3011 independent reflections with $F^2 \geq 3\sigma$ (**2**); and R = 0.057, R_w = 0.054 over 1212 independent reflections with $F^2 \geq 3\sigma$ (**3**). The principal geometric parameters are listed in Tables 1—3. All the calculations were performed using the MolEN program package[8] on a DEC Alpha Station 200 computer. The intermolecular contacts in structures **1—3** were analyzed and the molecular models were drawn using the WINPL98 program package.[9] The atomic coordinates are deposited in the Cambridge Structural Data Bank and are available from the authors.

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