Synthesis and First X-Ray Structure Analysis of a Stabilized Chiral Chlorobismuthine: Fixation of Molecular Geometry Induced by the Intramolecular Coordination of a Sulfonyl Group

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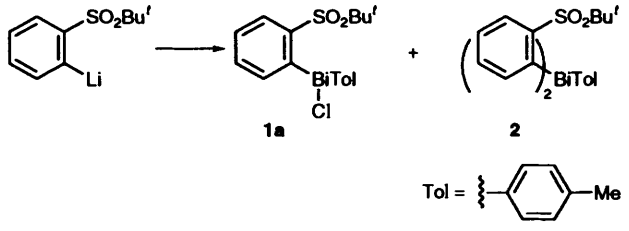
A sulfonyl-stabilized chiral chlorobismuthine **1a** was synthesized by the selective fluorodearylation of compound **3a** with boron trifluoride–diethyl ether, followed by halogen exchange of the resulting fluorobismuthine **4a** with brine. The ^{1}H NMR spectrum of compound **1a** showed an unusually large downfield shift of a proton signal (δ 9.16), and X-ray structure analysis revealed that this unique shift was due to the anisotropic deshielding of the proton adjacent to the bismuth atom by the chlorine atom in close proximity. The bismuth centre of compound **1a** was found to adopt a distorted pseudotrigonal bipyramidal geometry, probably through the formation of a hypervalent 3-centre 4-electron bond with the oxygen and chlorine atoms at apical positions. This is in marked contrast to the bismuthine **3a** which has a pyramidal configuration characteristic of trivalent organobismuth compounds. A quite short Bi–O distance [2.592(5) Å] of compound **1a**, compared with that [2.914(6) Å] of the bismuthine **3a**, indicates that the introduction of an electronegative chlorine atom onto the bismuth atom enhances the Lewis acidity of the metal centre, leading to the pronounced intramolecular Bi–O interaction.

Many chlorobismuthines have so far been reported,[1] but the structure of this class of compounds was characterized only recently for chlorobis[2,4,6-tris(trifluoromethyl)phenyl]-bismuthine.[2]† The reason may be attributed to the difficulty in obtaining these compounds in a high state of purity, because they are quite sensitive to moisture, which readily leads to an insoluble bismuth-containing polymeric species due to the reactive nature of the bismuth–chlorine bond.[1] In our recent study on the heterocyclic bismuth compounds,[3] we have revealed by X-ray structure analysis that the introduction of a sulfonyl group at an appropriate ring position spatially capable of interacting with the bismuth atom leads to the special stabilization of weak bismuth–aliphatic carbon and bismuth–chlorine bonds, and we have applied this unique property to the synthesis of several new chiral bismuthines.[4] As an extension of this work, we now report the synthesis and full structure characterization of a new chiral chlorobismuthine **1a** stabilized by the intramolecular coordination of a sulfonyl group. Only a few stable chlorobismuthines have hitherto been prepared,[5] and no chiral ones have been reported as yet.‡

Results and Discussion

Compound **1a** was not easily accessible by the reaction of dichloro(4-methylphenyl)bismuthine and 2-(*tert*-butylsulfonyl)phenyllithium[7] because of the favoured formation of compound **2** as the main product (Scheme 1).

After many attempts, we were successful in developing a new efficient method for the synthesis of chlorobismuthine **1a**. The reaction of compound **3a**[4] with boron trifluoride–diethyl ether resulted in the selective cleavage of an aryl–bismuth bond to give unstable diarylfluorobismuthine **4a**§ and subsequent treatment of the crude product with brine led to compound **1a** in 90% isolated yield (Scheme 2). This strategy has many advantages over the previous synthetic methods based on the comproportionation between triarylbismuthine and bismuth(III) chloride and the Pd^0-catalysed ligand exchange of triarylbismuthine with benzoyl chloride[3,8] in terms of the simplicity of manipulation, mild conditions and rapid completion of the reaction (within 1 min). The use of aq. sodium bromide or iodide similarly led to the corresponding halogenobismuthines **5** and **6** in high yields. The mode of aryl–bismuth cleavage was found to be dependent on the nature of the aryl groups attached to the bismuth atom. When mixed triarylbismuthine **3b**[4] was allowed to react with boron trifluoride–diethyl ether under the above conditions, the 4-methoxyphenyl group was preferentially replaced by fluorine atom to produce fluorobismuthine **4a** together with anisole. A

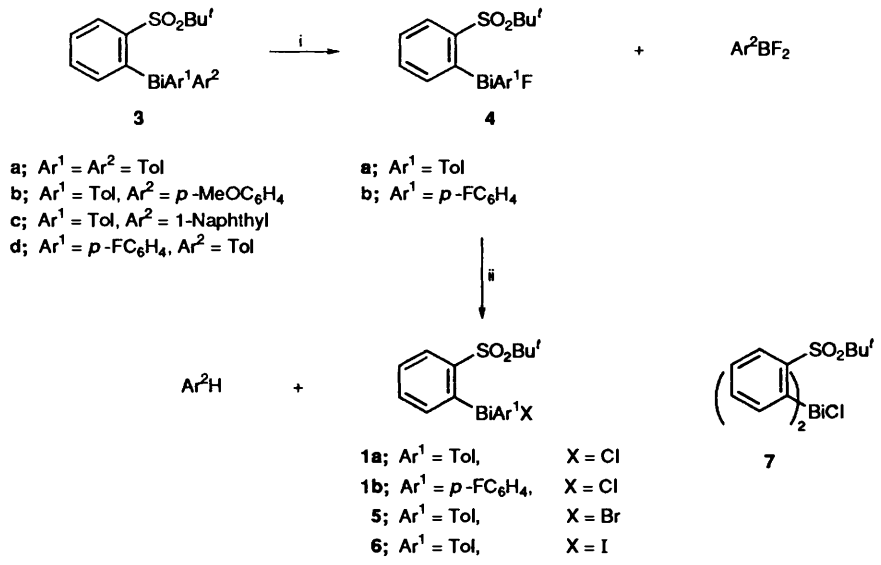


Scheme 1 *Reagents:* $TolBiCl_2$, Et_2O

† The crystal structure of this chlorobismuthine shows a pyramidal geometry about the bismuth atom.[2]

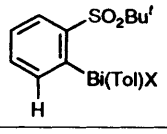
‡ Chiral bromo-[6] and iodo-bismuthines[4] have been reported recently.

§ The fact that the ^{19}F NMR spectrum of an oily product obtained from the reaction of compound **3a** and boron trifluoride–diethyl ether showed an intense sharp signal (δ_F − 148 ppm relative to the internal standard $CFCl_3$) is indicative of the formation of the fluorobismuthine **4a** as an initial product. However, attempted purification of the crude product by recrystallization from organic solvents failed due to its low stability. Treatment of the partially decomposed product with brine gave bis[2-*tert*-(butylsulfonyl)phenyl]chlorobismuthine **7** besides other unidentified products; m.p. 218–221 °C; δ_H 1.33 (18 H, s, Me), 7.62 (2 H, t, *J* 7.6, ArH), 7.89 (2 H, t, *J* 7.5, ArH), 8.04 (2 H, d, *J* 7.9, ArH) and 8.95 (2 H, d, *J* 7.4, ArH); ν_{max}(KBr)/cm^{-1} 1480, 1440, 1420, 1370, 1270, 1190, 1130, 1100, 1070, 770, 760, 740, 710, 640, 630, 570, 520 and 460; *m*/*z* 603 (8%, M − Cl), 547 (5), 443 (14, $Bu^tSO_2C_6H_4BiCl$), 441 (38, $Bu^tSO_2C_6H_4BiCl$), 387 (34, $SO_2C_6H_4BiCl$), 385 (89, $SO_2C_6H_4BiCl$), 350 (25, $SO_2C_6H_4Bi$ + H), 349 (57, $SO_2C_6H_4Bi$), 333 (20), 285 (24, C_6H_4Bi) and 209 (100, Bi) (Found: C, 37.5; H, 4.1. $C_{20}H_{26}BiClO_4S_2$ requires C, 37.6; H, 4.1%).



Scheme 2 *Reagents and conditions:* i, BF_3-Et_2O, benzene, room temp.; ii, aq. NaX

Table 1 Chemical shift (δ) of a proton *ortho* to bismuth atom



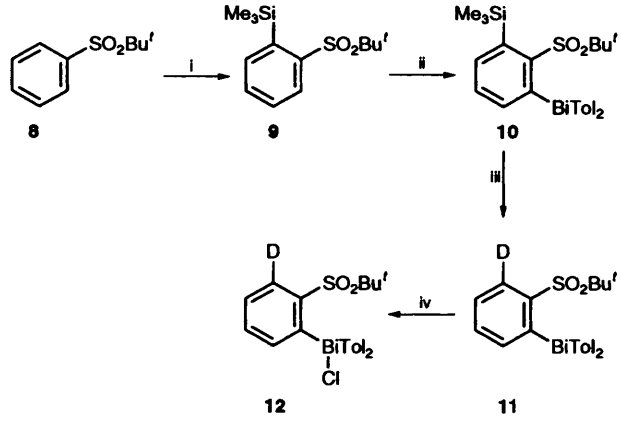
	X	δ
3a	Tol	8.10
4a	F	8.44
1a	Cl	9.16
5	Br	9.33
6	I	9.58

Table 2 Selected bond lengths (Å) and angles (°) for the chlorobismuthine **1a** with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi–C(1)	2.288(7)	O(1)–Bi–Cl	163.9(1)
Bi–C(11)	2.247(7)	C(1)–Bi–C(11)	94.4(2)
Bi–Cl	2.556(2)	C(1)–Bi–Cl	91.0(2)
S–O(1)	1.461(5)	C(11)–Bi–Cl	94.3(2)
S–O(2)	1.435(5)	C(1)–Bi–O(1)	73.0(2)
Bi···O(1)	2.592(5)	C(11)–Bi–O(1)	87.4(2)
H(6)···Cl	2.699		
H(12)···Cl	2.803		

similar reaction of compound **3c**[4] afforded fluoride **4a** and naphthalene, while the reaction of compound **3d** gave compound **4b** along with toluene. Thus, bismuthines **3** undergo ligand exchange with boron trifluoride to give a mixture of a fluorobismuthine **4** and an arylboron difluoride; the former is transformed into compounds **1**, **5** and **6**, respectively, by halogen exchange with sodium halides, while the latter would suffer simple hydrolysis, due to its high oxophilicity, to afford aryl hydrocarbon and boronic acid eventually.[9] The observed tendency that the more electron-donating aryl group is preferentially transferred from bismuth to boron is in accord with the Lewis acid character of the boron atom.

As shown in Table 1, ^{1}H NMR spectra of halogenobismuthines **1**, **5** and **6** showed a large downfield shift for a signal due to one aromatic proton, which was identified as the proton *ortho* to the bismuth atom on the sulfonyl-bearing ring by comparison of ^{1}H NMR spectra between chlorobismuthine **1a** and its deuteriated counterpart **12** (Scheme 3).* In



Scheme 3 *Reagents and conditions:* i, BuLi, THF, −78 °C, Me_3SiCl; ii, BuLi, Et_2O, −78 °C; Tol_2BiCl; iii, CsF, D_2O DMF, room temp.; iv, BF_3-OEt_2 benzene, room temp., brine

order to know the reason why the *ortho* proton showed such unique behaviour, an X-ray structure analysis was carried out on compound **1a** and the results are shown in Fig. 1. Interestingly, the bismuth atom was found to have a distorted pseudotrigonal bipyramidal configuration,[10] where the apical positions are occupied by the O(1) and chlorine atoms with the O(1)–Bi–Cl angle of 163.9(1)° (Table 2). The equatorial plane is considered to be occupied by two carbon atoms C(1) and C(11) and a lone pair of electrons with the C(1)–Bi–C(11) angle of 94.4(2)°. Four atoms, S, O(1), Bi and Cl, are all coplanar with one of the phenyl rings [C(1)–C(6)]. The intramolecular Bi–O(1) distance of 2.592(5) Å is longer than the sum of the covalent radii (2.10 Å) but remarkably shortened as compared with that of the van der Waals radii (3.72 Å).[3] The Bi–Cl bond

* Transformation of tris(4-methylphenyl)bismuthine into iodobis(4-methylphenyl)bismuthine did not bring about such a dramatic downfield shift of the *ortho* proton signal in the ^{1}H NMR spectrum; Tol_3Bi: δ_H 2.31 (9 H, s, Me), 7.20 (6 H, d, J_{AB} 7.8, ArH) and 7.62 (6 H, d, J_{AB} 7.8, ArH); Tol_2BiI: δ_H 2.36 (6 H, s, Me), 7.38 (4 H, d, J_{AB} 8.0, ArH) and 8.12 (4 H, d, J_{AB} 8.0, ArH).

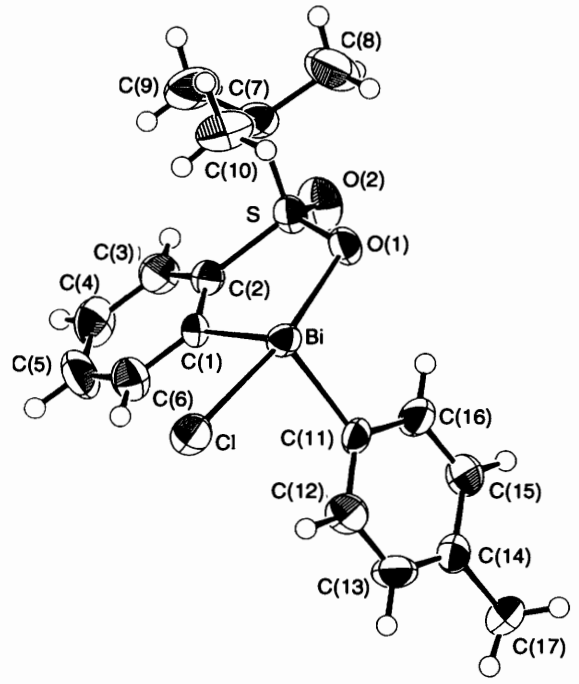


Fig. 1 An ORTEP perspective view of the chlorobismuthine **1a** with the atomic numbering scheme

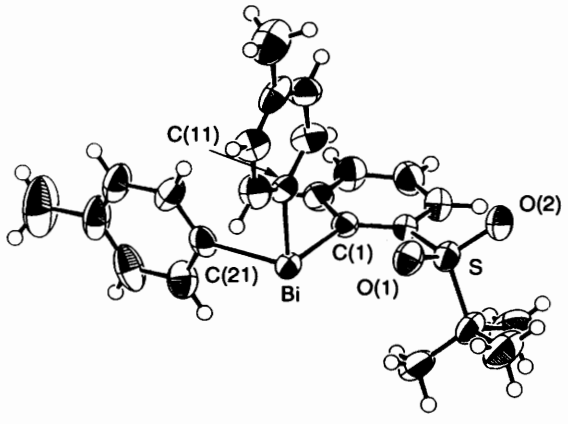


Fig. 2 An ORTEP perspective view of the chlorobismuthine **3a** with the atomic numbering scheme

2.556(2) Å is longer than that [2.463(3) Å] in chlorobis[2,4,6-tris(trifluoromethyl)phenyl]bismuthine.[2] These observations are suggestive of the formation of a hypervalent 3-centre 4-electron bond over the O(1), Bi and Cl atoms,[10] which will result in the enhanced stability of the bismuth–chlorine bond. This is also reflected by the extended S–O(1) bond length 1.461(5) Å relative to the S–O(2) 1.435(5) Å, as well as by the much restricted thermal vibration [B_{eq} 3.4(2)] of O(1) as compared with that [B_{eq} 5.1(3)] of O(2).* The distance between the *ortho* proton [attached to C(6)] and chlorine atom is 2.699 Å, which falls within the sum (2.81 Å) of the van der Waals radii of these atoms.[11] This fact may suggest the existence of a weak H–Cl interaction caused by the fixation of molecular geometry† into the distorted pseudotrigonal bipyramidal

* In a structurally related analogue **3a**, both of the S–O bonds are similar in length [1.434(7) and 1.444(7) Å] and the thermal vibration [B_{eq} 4.6(3)] observed for O(1) is not much different from that [B_{eq} 5.0(4)] for O(2), in accord with a too-weak Bi–O interaction to affect the normal geometry of the bismuth centre (Fig. 2).

Table 3 Selected bond lengths (Å) and angles (°) for the bismuthine **3a** with estimated standard deviations in parentheses

Bond length		Bond angle	
Bi–C(1)	2.312(9)	C(1)–Bi–C(11)	96.3(4)
B–C(11)	2.26(1)	C(1)–Bi–C(21)	92.8(3)
Bi–C(21)	2.307(9)	C(11)–Bi–C(21)	93.0(4)
S–O(1)	1.434(7)		
S–O(2)	1.444(7)		
Bi···O(1)	2.914(6)		

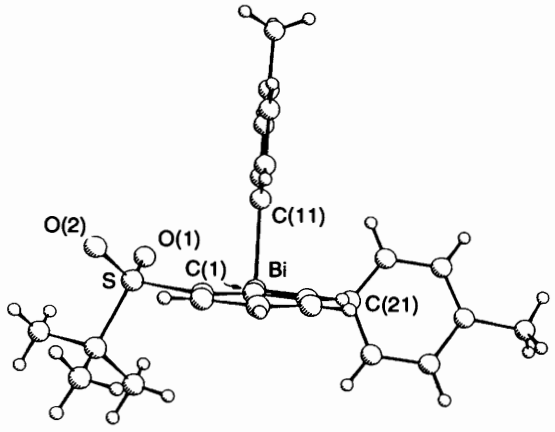


Fig. 3 A PLUTO perspective view of the bismuthine **3a** along the C(1)–Bi axis

structure. The unique ^{1}H NMR behaviour of the *ortho* proton can be attributed to the anisotropic deshielding due to its close proximity to the chlorine atom, as has been suggested by J. C. Martin in his study on sulfurane systems.[12] A similar observation has also been made for dibenz[*c*,*f*]azabismocines.[5b] The tolyl group has a geometry *trans* to the *tert*-butyl group to avoid steric congestion and constitutes one apical plane perpendicular to the phenyl group.‡ Unlike the reported heterocyclic bismuth system,[3] definite evidence for the existence of the intermolecular Bi–O interaction was not observed.

For the sake of comparison with chlorobismuthine **1a**, we also carried out an X-ray structure analysis of the bismuthine **3a** (Figs. 2 and 3). In contrast to compound **1a**, the bismuth atom of the latter compound has a pyramidal configuration characteristic of common organobismuth(III) compounds, with the bond angles C(1)–Bi–C(11) 96.3(4), C(1)–Bi–C(21) 92.8(3) and C(11)–Bi–C(21) 93.0(4)° (Table 3). These values are close to those of the angle C_{Ph}–Bi–C_{Ph} of triphenylbismuthine, 92–96°.[13] The intramolecular Bi–O distance 2.914(6) Å is comparable to that [2.979(7) Å] of a cyclic sulfonyl-bearing bismuthine recently reported by us,[3] but it is much longer than that [2.592(5) Å] of the chlorobismuthine **1a**, manifesting the operation of a strong intramolecular Bi–O interaction in

† Unlike ordinary triarylbismuthines, compound **3a** reacts with iodine to afford iodobismuthine **6** quantitatively without further iododearylation (see ref. 4). This may be accounted for by the fixation of the molecular geometry of compound **6** by the enhanced intramolecular Bi–O interaction, which suppresses the conformational transformation into a transition structure favourable for further iododearylation.

‡ Intramolecular distance between the chlorine atom and a proton on C(12) of the tolyl group is 2.803 Å, which is comparable to that (2.699 Å) between the chlorine atom and a proton on C(6) of another aromatic ring. However, the former proton (δ 8.09) did not suffer any significant magnetic deshielding as was observed for the latter (δ 9.16). This discrepancy may be explained in terms of the free rotation of the Bi–C(Tol) bond in solution.

compound **1a**.* The structural difference between compounds **1a** and **3a** is reflected in the fact that, unlike the situation in the chlorobismuthine **1a**, both O(1) and O(2) of the bismuthine **3a** are disposed out of the phenyl plane, defined by C(1)–C(6), toward the same side by 0.5968 and 0.9487 Å, respectively (Fig. 3.).

In summary, the present work has demonstrated that the introduction of an electronegative halogen atom onto the bismuth atom enhances the Lewis acidity of the metal centre to make the intramolecular Bi–O interaction more pronounced, resulting in the dramatic change of the molecular geometry of the bismuth(III) atom from the pyramidal bismuthine **3a** to the distorted pseudotrigonal bipyramidal chlorobismuthine **1a**.†

Experimental

General.—All reactions were carried out under argon unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether were distilled under argon from calcium hydride and sodium benzophenone ketyl, respectively, before use. Benzene and dimethylformamide (DMF) were distilled from calcium hydride and stored over molecular sieves 4 Å. Butyllithium was titrated against diphenylacetic acid. TLC was performed by using Merck precoated silica gel sheets 60F-254. Silica gel (Wakogel) of size 200 mesh was used for column chromatography. Bismuth(III) chloride was purified by refluxing with thionyl dichloride. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini-200 (200 MHz) spectrometer with tetramethylsilane as internal standard. Coupling constants J are given in Hz. IR spectra were obtained on a SHIMADZU FTIR-8100 spectrophotometer. Mass spectra were determined on a SHIMADZU GCMS-QP2000A spectrometer at an ionization potential 70 eV. Elemental analyses were performed at the Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

[2-(tert-*Butylsulfonyl*)*phenyl*]*bis*-(4-*methylphenyl*)*bismuthine* **3a**.—Chlorobis(4-methylphenyl)bismuthine (~10 mmol) was generated in a stirred solution of tris(4-methylphenyl)bismuthine (3.21 g, 6.66 mmol) and bismuth(III) chloride (1.05 g, 3.33 mmol) in diethyl ether (15 cm^3) for 1 h at room temperature. To a well stirred suspension of the chlorobismuthine cooled to −50 °C was added dropwise a suspension of lithiated *tert*-butyl phenyl sulfone[7] generated from butyllithium (10 mmol) and *tert*-butyl phenyl sulfone (1.98 g, 10 mmol) in the same solvent (20 cm^3), and the resulting mixture was stirred for 3 h during which time the temperature was gradually raised to ambient. The mixture was poured into cold brine (100 cm^3) and extracted with ethyl acetate (50 cm^3 × 3). After an insoluble bismuth-containing polymeric substance had been filtered off, the organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to leave a yellow oily residue. Recrystallization from MeOH–benzene (5:1) afforded pure *product* **3a** as crystals (3.65 g, 62%), m.p. 147–149 °C; δ_H 1.39 (9 H, s, Me), 2.31 (6 H, s, Me), 7.21 (4 H, d, J_{AB} 7.3, MeAr*H*), 7.42 (1 H, dt, J 1.5 and 7.3, SO_2ArH), 7.52 (1 H, dt, J 1.6 and 7.7, SO_2ArH), 7.58 (4 H, d, J_{AB} 7.3, MeAr*H*), 8.04 (1 H, dd, J 1.5 and 7.6, SO_2ArH) and 8.10 (1 H, dd, J 1.5 and 7.3, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1490, 1440, 1390, 1280, 1250, 1190, 1130, 1110, 1080, 790, 770, 730, 640, 570 and 480; m/z 497 (29%, M − C_6H_4Me), 441 (7, $SO_2C_6H_4BiC_6H_4Me$ + H), 406 (9, Bu^t$SO_2C_6H_4Bi$), 349 (100, $SO_2C_6H_4Bi$), 300 (11, MeC_6H_4Bi), 285 (26, C_6H_4Bi) and 209 (70, Bi) (Found: C, 48.9; H, 4.8. $C_{24}H_{27}BiO_2S$ requires C, 49.0; H, 4.6%).

[2-(tert-*Butylsulfonyl*)*phenyl*]*chloro*(4-*methylphenyl*)*bismuthine* **1a**.—To a well stirred solution of compound **3a** (588 mg, 1 mmol) in benzene (5 cm^3) was added dropwise boron trifluoride–diethyl ether (~3 mmol equiv.) at room temperature until substrate **3a** was completely consumed (checked by TLC). The mixture was diluted by the addition of brine (5 cm^3) and the organic phase was extracted with ethyl acetate (20 cm^3 × 3). The combined extracts were concentrated under reduced pressure to leave a pale yellow oily residue, which was recrystallized from MeOH–CH_2Cl_2 (5:1) to give *compound* **1a** as crystals (479 mg, 90%), m.p. 170–172 °C; δ_H 1.38 (9 H, s, Me), 2.25 (3 H, s, Me), 7.39 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.64 (1 H, t, J 6.7, SO_2ArH), 7.96 (2 H, t, SO_2ArH), 8.09 (2 H, d, J_{AB} 8.0, MeAr*H*) and 9.16 (1 H, d, J 7.4, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1480, 1420, 1400, 1370, 1270, 1250, 1190, 1130, 1100, 1070, 800, 770, 740, 640, 630, 570, 520, 480 and 460; m/z 497 (5%, M − Cl), 443 (3, M − C_6H_4Me), 441 (10, M − C_6H_4Me), 406 (39, Bu^t$SO_2C_6H_4Bi$), 387 (22, $SO_2C_6H_4BiCl$ + H), 385 (62, $SO_2C_6H_4BiCl$ + H), 349 (58, $SO_2C_6H_4Bi$), 300 (4, MeC_6H_4Bi), 285 (19, C_6H_4Bi) and 209 (100, Bi) (Found: C, 38.1; H, 3.9. $C_{17}H_{20}BiClO_2S$ requires C, 38.3; H, 3.8%).

[2-(tert-*Butylsulfonyl*)*phenyl*]*iodo*(4-*methylphenyl*)*bismuthine* **6**.—To a well stirred suspension of compound **3a** (588 mg, 1 mmol) in diethyl ether (10 cm^3) was added dropwise a solution of iodine (254 mg, 1 mmol) in the same solvent (10 cm^3) under ambient conditions until starting material was completely consumed (TLC). The resulting pale yellow solution was concentrated under reduced pressure to leave an oily residue, recrystallization of which from MeOH–benzene (5:1) afforded pure *compound* **6** quantitatively as pale yellow crystals (624 mg, 1 mmol), m.p. 142–144 °C; δ_H 1.38 (9 H, s, Me), 2.25 (3 H, s, Me), 7.31 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.70 (1 H, dt, J 1.3 and 7.4, SO_2ArH), 7.81 (1 H, dt, J 1.8 and 7.5, SO_2ArH), 7.94 (1 H, dd, J 1.4 and 7.3, SO_2ArH), 8.15 (2 H, d, J_{AB} 8.0, MeAr*H*) and 9.58 (1 H, dd, J 1.4 and 7.4, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1480, 1440, 1360, 1270, 1190, 1130, 1100, 1070, 1030, 1010, 800, 760, 740, 710, 640, 630, 570, 520, 480 and 460; m/z 497 (40%, M − I), 477 (8, $SO_2C_6H_4BiI$ + H), 441 (6, $SO_2C_6H_4BiC_6H_4Me$ + H), 349 (76, $SO_2C_6H_4Bi$), 336 (12, BiI), 300 (10, MeC_6H_4Bi), 285 (26, C_6H_4Bi) and 209 (100, Bi) (Found: C, 33.0; H, 3.15; I, 20.0. $C_{17}H_{20}BiIO_2S$ requires C, 32.7; H, 3.2; I, 20.3%).

[2-(tert-*Butylsulfonyl*)*phenyl*](4-*methoxyphenyl*)(4-*methylphenyl*)*bismuthine* **3b**.—To a solution of **6** (624 mg, 1 mmol) in THF (5 cm^3) was added dropwise a solution of 4-methoxyphenylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm^3) at room temperature until the pale yellow colour of compound **6** was completely lost, and the resulting mixture was stirred for 5 min. Quenching with brine, followed by concentration of the organic extract under reduced pressure, afforded an oily residue, which was recrystallized from MeOH to give pure *compound* **3b** as crystals (532 mg, 88%), m.p. 155–157 °C; δ_H 1.39 (9 H, s, Me), 2.31 (3 H, s, Me), 3.78 (3 H, s, OMe), 6.93 (2 H, d, J_{AB} 8.5, MeOAr*H*), 7.21 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.42 (1 H, dt, J 1.5 and 7.2, SO_2ArH), 7.52–7.61 (5 H, m, ArH) and 8.06 (2 H, t, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1580, 1490, 1280, 1240, 1180, 1130, 1100, 1080, 730, 640, 570 and 480; m/z 497 (10%, M − C_6H_4OMe), 457 (3, $SO_2C_6H_4BiC_6H_4OMe$ + H), 441 (4, $SO_2C_6H_4BiC_6H_4Me$ + H), 406 (11, Bu^t$SO_2C_6H_4Bi$),

* The IR spectrum of compound **1a** showed a lower frequency (shift by 12 cm^{-1}) relative to compound **3a** for the sulfonyl antisymmetric vibration. This observation is consistent with the extended S–O(1) bond length relative to the S–O(2) bond in compound **1a** as compared with compound **3a** (Tables 2 and 3). It is well known that the introduction of an electronegative atom onto the metal centre increases the Lewis acidity, leading to intramolecular coordination being more pronounced.[14]

† Conformational fixation induced by the Lewis base coordination has been reported for organohalogenostannanes (see ref. 14*a* and 14*b*).

349 (100, $SO_2C_6H_4Bi$), 316 (5, $MeOC_6H_4Bi$), 300 (5, MeC_6H_4Bi), 285 (25, C_6H_4Bi) and 209 (63, Bi) (Found: C, 47.6; H, 4.5. $C_{24}H_{27}BiO_3S$ requires C, 47.7; H, 4.5%).

[2-(tert-*Butylsulfonyl*)*phenyl*](4-*methylphenyl*)(1-*naphthyl*)*bismuthine* **3c**.—To a solution of compound **6** (624 mg, 1 mmol) in THF (5 cm^3) was added dropwise a solution of 1-naphthylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm^3) at room temperature until the pale yellow colour of compound **6** was completely lost, and the resulting mixture was stirred for 5 min. Quenching with brine, followed by concentration of the organic extract under reduced pressure, afforded an oily residue, which was recrystallized from MeOH to give pure *compound* **3c** as crystals (612 mg, 98%), m.p. 182–184 °C; δ_H 1.42 (9 H, s, Me), 2.30 (3 H, s, Me), 7.19 (2 H, d, J_{AB} 7.3, MeAr*H*), 7.29–7.56 (7 H, m, ArH), 7.85–7.95 (4 H, m, ArH) and 8.00–8.08 (2 H, m, ArH); ν_{max}(KBr)/cm^{-1} 1500, 1480, 1440, 1420, 1290, 1250, 1190, 1140, 1110, 1080, 800, 790, 770, 730, 640, 570, 520, 480 and 470; *m/z* 497 (17%, M − $C_{10}H_7$), 406 (7, $Bu^tSO_2C_6H_4Bi$), 349 (84, $SO_2C_6H_4Bi$), 336 (41, $C_{10}H_7Bi$), 300 (14, MeC_6H_4Bi), 285 (23, C_6H_4Bi) and 209 (100, Bi) (Found: C, 51.7; H, 4.35. $C_{27}H_{27}BiO_2S$ requires C, 51.9; H, 4.4%).

[2-(tert-*Butylsulfonyl*)*phenyl*](4-*fluorophenyl*)(4-*methylphenyl*)*bismuthine* **3d**.—To a solution of compound **6** (624 mg, 1 mmol) in THF (5 cm^3) was added dropwise a solution of 4-fluorophenylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm^3) at room temperature until the pale yellow colour of substrate **6** was completely lost, and the resulting mixture was stirred for 5 min. Work-up with brine, followed by concentration of the organic extract under reduced pressure afforded an oily residue, which was recrystallized from MeOH to give pure *compound* **3d** as crystals (533 mg, 90%), m.p. 167–169 °C; δ_H 1.39 (9 H, s, Me), 2.32 (3 H, s, Me), 7.06 (2 H, t, *J* 8.6, ArH), 7.23 (2 H, d, J_{AB} 8.8, MeAr*H*), 7.40–7.68 (6 H, m, ArH) and 8.04 (2 H, d, J_{AB} 8.8, MeAr*H*); ν_{max}(KBr)/cm^{-1} 1650, 1480, 1290, 1280, 1250, 1220, 1160, 1130, 1080, 1010, 790, 730, 640, 570 and 480; *m/z* 497 (36%, M − C_6H_4F), 445 (5, $SO_2C_6H_4BiC_6H_4F$ + H), 441 (4, $SO_2C_6H_4BiC_6H_4Me$), 406 (6, $Bu^tSO_2C_6H_4Bi$), 349 (100, $SO_2C_6H_4Bi$), 304 (4, FC_6H_4Bi), 300 (3, MeC_6H_4Bi), 285 (28, C_6H_4Bi) and 209 (75, Bi) (Found: C, 46.5; H, 4.0. $C_{23}H_{24}BiFO_2S$ requires C, 46.6; H, 4.0%).

Reaction of Compounds **3b** *and* **3c** *with Boron Trifluoride–Diethyl Ether*.—To a well stirred solution of compound **3b** (604 mg, 1 mmol) in benzene (5 cm^3) was added dropwise boron trifluoride–diethyl ether (~3 mmol) at room temperature until substrate **3b** was completely consumed (TLC), and the resulting mixture was quenched by the addition of brine (5 cm^3). Extractive work-up with ethyl acetate, followed by recrystallization of the crude product from MeOH–CH_2Cl_2 (5:1), gave compound **1a** as crystals (426 mg, 80%), m.p. 170–172 °C. Compound **3c** (624 mg, 1 mmol) was similarly treated with boron trifluoride–diethyl ether in benzene (5 cm^3) at room temperature. Work-up of the reaction mixture as described above afforded compound **1a** (447 mg, 84%), m.p. 170–172 °C and naphthalene (102 mg, 80%).

Reaction of Compound **3d** *with Boron Trifluoride–Diethyl Ether*.—To a well stirred solution of compound **3d** (592 mg, 1 mmol) in benzene (5 cm^3) was added dropwise boron trifluoride–diethyl ether at room temperature until substrate **3d** was completely consumed (TLC), and the resulting mixture was quenched by the addition of brine (5 cm^3). Extractive work-up with ethyl acetate, followed by recrystallization of the crude product from MeOH–CH_2Cl_2 (5:1), gave *compound* **1b** as crystals (375 mg, 70%), m.p. 147–149 °C; δ_H 1.39 (9 H, s, Me), 7.18 (2 H, t, *J* 6.7, ArH), 7.40 (1 H, d, *J* 7.8, ArH), 7.60–7.72 (1 H, m, ArH), 7.88–8.28 (3 H, m, ArH) and 9.16 (1 H, d, *J* 7.2, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1490, 1470, 1270, 1250, 1220, 1180, 1160, 1130, 1100, 1070, 830, 800, 770, 740, 640, 630, 570, 520, 500, 480 and 460; *m/z* 501 (7%, M − Cl), 443 (5, M − C_6H_4F), 441 (12, M − C_6H_4F), 406 (19, M − $ClFC_6H_4$), 387 (14, $SO_2C_6H_4BiCl$ + H), 385 (37, $SO_2C_6H_4BiCl$ + H), 349 (51, $SO_2C_6H_4Bi$), 285 (17, C_6H_4Bi) and 209 (100, Bi) (Found: C, 35.95; H, 3.5. $C_{16}H_{17}ClFO_2S$ requires C, 35.8; H, 3.2).

Bromo[2-(tert-*Butylsulfonyl*)*phenyl*](4-*methylphenyl*)*bismuthine* **5**.—To a well stirred solution of compound **3a** (588 mg, 1 mmol) in benzene (5 cm^3) was added dropwise boron trifluoride–diethyl ether at room temperature until substrate **3a** was completely consumed (TLC), and the resulting mixture was quenched by the addition of saturated aq. NaBr (5 cm^3). The organic layer was extracted with ethyl acetate (20 cm^3 × 3) and the combined extracts were concentrated under reduced pressure to leave a pale yellow oily residue. Recrystallization from MeOH–CH_2Cl_2 (5:1) gave *compound* **5** as crystals (518 mg, 90%), m.p. 159–161 °C; δ_H 1.39 (9 H, s, Me), 2.25 (3 H, s, Me), 7.37 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.67 (1 H, t, *J* 7.5, SO_2ArH), 7.92 (2 H, t, SO_2ArH), 8.11 (2 H, d, J_{AB} 8.0, MeAr*H*) and 9.33 (1 H, d, *J* 7.3, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1470, 1390, 1270, 1250, 1190, 1130, 1100, 1070, 800, 770, 740, 640, 630, 570, 520, 480 and 460; *m/z* 497 (7%, M − Br), 487 (4, M − C_6H_4Me), 485 (4, M − C_6H_4Me), 431 (25, $SO_2C_6H_4BiBr$ + H), 429 (22, $SO_2C_6H_4BiBr$ + H), 406 (29, M − MeC_6H_4Br), 350 (31, $SO_2C_6H_4Bi$ + H), 349 (31, $SO_2C_6H_4Bi$), 300 (7, MeC_6H_4Bi), 290 (6, BiBr), 288 (6, BiBr), 285 (13, C_6H_4Bi) and 209 (100, Bi) (Found: C, 35.25; H, 3.5; Br, 13.8. $C_{17}H_{20}BiBrO_2S$ requires C, 35.4; H, 3.5; Br, 13.8%).

Treatment of the reaction mixture from compound **3a** and boron trifluoride with saturated aq. NaI gave compound **6** (87%), m.p. 142–144 °C.

tert-*Butyl* 2-(*Trimethylsilyl*)*phenyl Sulfone* **9**.—To a solution of lithiated *tert*-butyl phenyl sulfone[7] generated from butyllithium (10 mmol) and *tert*-butyl phenyl sulfone **8** (1.98 g, 10 mmol) in THF (20 cm^3) at −50 °C was added dropwise a solution of chlorotrimethylsilane (1.27 cm^3, 10 mmol) in the same solvent (5 cm^3) and the resulting mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient. The mixture was quenched by the addition of brine (5 cm^3) and extracted with ethyl acetate (20 cm^3 × 3). The combined extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to leave an oily residue, which was recrystallized from hexane–CH_2Cl_2 (5:1) to give compound **9** as crystals (2.19 g, 81%), m.p. 98–100 °C (lit.,[7] 100–101 °C); δ_H 0.40 (9 H, s, Me), 1.31 (9 H, s, Me), 7.48–7.62 (2 H, m, ArH) and 7.81–7.95 (2 H, m, ArH).

[2-tert-*Butylsulfonyl*-3-(*trimethylsilyl*)*phenyl*]*bis*(4-*methylphenyl*)*bismuthine* **10**.—Chlorobis(4-methylphenyl)bismuthine (~5 mmol) was prepared by stirring of tris(4-methylphenyl)-bismuthine (1.61 g, 3.33 mmol) and bismuth(III) chloride (526 mg, 1.67 mmol) in diethyl ether (15 cm^3) for 1 h at room temperature. An ethereal suspension of the chlorobismuthine thus obtained was cooled to −50 °C and a suspension of *tert*-butyl 2-lithio-6-(trimethylsilyl)phenyl sulfone generated from compound **9** (1.35 g, 5 mmol) and butyllithium (5 mmol) in the same solvent (20 cm^3) was added dropwise. The resulting mixture was stirred for 3 h, during which time the temperature was slowly raised to ambient. Extractive work-up with ethyl acetate, followed by purification of the crude product through column chromatography on silica gel with hexane–ethyl acetate (5:1) as eluent, afforded a viscous oil, which was recrystallized from MeOH–benzene (5:1) to give *compound* **10**

as crystals (2.05 g, 62%), m.p. 159–161 °C; δ_H 0.48 (9 H, s, Me), 1.32 (9 H, s, Me), 2.29 (3 H, s, Me), 2.39 (3 H, s, Me), 7.18 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.32 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.36–7.44 (3 H, m, ArH), 7.73 (2 H, d, J_{AB} 8.0, MeAr*H*), 7.91 (1 H, dd, *J* 1.2 and 7.4, SO_2ArH) and 8.23 (1 H, dd, *J* 1.3 and 7.3, SO_2ArH); ν_{max}(KBr)/cm^{-1} 1480, 1390, 1280, 1240, 1190, 1140, 1110, 1050, 1010, 850, 790, 740, 690, 640, 570, 480 and 420; *m/z* 569 (10%, M − C_6H_4Me), 497 (11, Bu^t$SO_2C_6H_4BiC_6H_4Me$), 421 (64, $SO_2C_6H_3SiMe_3Bi$), 300 (27, MeC_6H_4Bi) and 209 (100, Bi) (Found: C, 48.7; H, 5.35. $C_{27}H_{35}BiO_2SSi$ requires C, 49.1; H, 5.3%).

[2-tert-*Butylsulfonyl*-3-*deuteriophenyl*]*bis*(4-*methylphenyl*)-*bismuthine* **11**.—A mixture of silyl compound **10** (660 mg, 1 mmol), CsF (304 mg, 2 mmol), D_2O (40 mg, 2 mmol) and DMF (5 cm^3) was stirred at room temperature for 24 h. Extractive work-up with ethyl acetate, followed by recrystallization of the crude product from MeOH–benzene (5:1), gave compound **11** as crystals (518 mg, 88%), m.p. 148–150 °C; δ_H 1.39 (9 H, s, Me), 2.31 (6 H, s, Me), 7.21 (4 H, d, J_{AB} 7.9, MeAr*H*), 7.42 (1 H, t, *J* 7.4, SO_2ArH), 7.51 (1 H, dd, *J* 1.5 and 7.1, SO_2ArH), 7.58 (4 H, d, J_{AB} 7.9, MeAr*H*) and 8.10 (1 H, dd, *J* 1.5 and 7.3, SO_2ArH).

Chloro[2-tert-*butylsulfonyl*-3-*deuteriophenyl*](4-*methylphenyl*)*bismuthine* **12**.—To a well stirred solution of the bismuthine **11** (589 mg, 1 mmol) in benzene (5 cm^3) was added dropwise boron trifluoride–diethyl ether (~3 mmol) at room temperature until compound **11** was completely consumed (TLC), and the resulting mixture was quenched with brine (5 cm^3). Work-up gave product **12** as crystals (453 mg, 85%), m.p. 167–169 °C; δ_H 1.38 (9 H, s, Me), 2.25 (3 H, s, Me), 7.39 (2 H, d, J_{AB} 7.7, MeAr*H*), 7.64 (1 H, d, *J* 7.3, SO_2ArH), 7.97 (1 H, t, *J* 7.6, SO_2ArH), 8.09 (2 H, d, J_{AB} 7.7, MeAr*H*) and 9.16 (1 H, d, *J* 7.6, SO_2ArH).

X-Ray Crystallography of Compound **1a**.—A crystal of dimensions 0.180 × 0.320 × 0.430 mm was used for X-ray crystallography.

Crystal data: $C_{17}H_{20}O_2BiClS$, M = 532.84. Monoclinic, space group $P2_1/n$, a = 14.746(4), b = 7.578(4), c = 16.952(3) Å, β = 100.00(2)°, V = 1865(1) Å^3, Z = 4, D_c = 1.897 g cm^{-3}. Plates. μ(Mo-Kα, λ = 0.710 69 Å) = 96.79 cm^{-1}. Intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 12 KW rotating anode generator using the ω–2θ scan technique to a maximum 2θ-value of 55.0°. Scans of (0.73 + 0.30 tan θ)° were made at a speed of 16.0 deg min^{-1} (in omega). Of the 4780 reflections which were collected, 4608 were unique (R_{int} = 0.036). Data were corrected for Lorentz and polarization effects. Empirical correction for the absorption was made based on azimuthal or ψ scans [15] (transmission factors: 0.33–1.00). The correction for the secondary extinction was also made at the final stage of the refinement (coefficient: 10.8 × 10^{-7}). The structure was solved by the Patterson method.[16] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3031 observed reflections [$I > 3.00\ \sigma(I)$] and 200 variable parameters and converged with unweighted and weighted agreement factors of R = 0.034 and R_w = 0.038. The residual electron densities in the final difference Fourier map ranged from −1.91 to 1.25 e$^-$/Å^3. The weighting scheme, $w = 1/\sigma^2(F_0)$, was employed. Neutral-atom-scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ *and* $\Delta f''$ were those of Cromer.[19] All calculations were performed on a VAX station 3200 computer using the TEXSAN [20] crystallographic software package from the Molecular Structure Corporation. The ORTEP [21] program was used to obtain the drawing in Fig. 1. Selected bond lengths and bond angles are given in Table 2.

X-Ray Crystallography of **3a**.—A crystal of dimensions 0.400 × 0.330 × 0.150 mm was used for X-ray crystallography.

Crystal data: $C_{24}H_{27}BiO_2S$, M = 588.52. Monoclinic, space group $C2/c$, a = 25.256(6), b = 10.628(3), c = 18.133(4) Å, β = 102.36(2)°, V = 4754(2) Å^3, Z = 8, D_c = 1.644 g cm^{-3}. Prisms. μ(Mo-Kα, λ = 0.710 69 Å) = 74.93 cm^{-1}. Scans of (0.68 + 0.30 tan θ)° were made at a speed of 16.0 deg min^{-1} (in omega). Of the 5880 reflections which were collected, 5750 were unique (R_{int} = 0.160). The corrections for the intensity data were made in the same manner as those adopted for **1a**. Transmission factors: 0.43–1.00, secondary extinction coefficient: 0.403 × 10^{-7}. The final cycle of full-matrix least-squares refinement was based on 2982 observed reflections [$I > 3.00\ \sigma(I)$] and 254 variable parameters and converged with unweighted and weighted agreement factors of R = 0.038 and R_w = 0.041. The residual electron densities on the final difference Fourier map were in the range of −1.01 to 1.04 e$^-$/Å^3. The ORTEP [21] and PLUTO [22] programs were used to obtain the drawings. Selected bond lengths and bond angles are given in Table 3. Full details of crystal data, fractional atomic coordinates, bond lengths, bond angles, hydrogen coordinates, and thermal parameters of compounds **1a** and **3a** have been deposited at the Cambridge Crystallographic Data Centre.

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