Water-soluble non-ionic triarylbismuthanes. First synthesis and properties

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The synthesis and properties of some new water-soluble non-ionic triarylbismuthanes are described. *o*-, *m*- and *p*-Tris(methoxymethoxyphenyl)bismuthanes 1a–c are prepared from $BiCl_3$ and the corresponding organolithium or Grignard reagents. Oxidative chlorination of 1a–c with SO_2Cl_2 affords tris(methoxymethoxyphenyl)bismuth dichlorides 2a–c, which are deprotected by aqueous HCl to give tris(hydroxyphenyl)bismuth dichlorides 3a–c. Treatment of tris(3-hydroxyphenyl)bismuth dichloride 3b with NH_2NH_2 yields tris(3-hydroxyphenyl)bismuthane 5, which dissolves in dilute aqueous NaOH. *N*,*N*-Bis(2-*tert*-butyldimethylsiloxyethyl)benzenesulfonamide, prepared from benzenesulfonyl chloride and silyl-protected diethanolamine, is *ortho*-lithiated and reacted with $\frac{1}{3}$ equiv. of $BiCl_3$ to give Ar_3Bi 9a {Ar = 2-[*N*,*N*-bis(2-*tert*-butyldimethylsiloxyethyl)sulfamoyl]phenyl}. *m*-Phenylene-bridged Bi_2- and Bi_3-polybismuthanes 12 and 13 are prepared by the reaction between *ortho*-lithiated 9a and Ar_2BiI 10. Desilylation of 9a, 12 and 13 by Bu_4NF or *p*-TsOH·H_2O in EtOH leads to the corresponding bismuthanepolyols 11, 14 and 15. The reaction between benzene-1,3-disulfonamide 16 bearing the silyl-protected bis(2-hydroxyethyl)amino side chains and $\frac{1}{3}$ equiv. of $BiCl_3$ affords tris{2,4-bis[*N*,*N*-bis(2-*tert*-butyldimethylsiloxyethyl)sulfamoyl]phenyl}bismuthane 17, which is deprotected by *p*-TsOH·H_2O to yield tris{2,4-bis[*N*,*N*-bis(2-hydroxyethyl)sulfamoyl]phenyl}bismuthane 18. Compounds 11, 14 and 15 are only slightly soluble in water, but compound 18 is fairly soluble.

Introduction

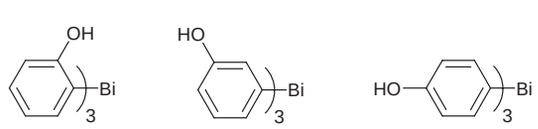
Bismuth differs considerably from other members of the Group 15 family in that it is non-toxic, therapeutic and radiopaque.[1,2] Due to their disinfective action and low toxicity, a variety of bismuth salts such as bismuth subnitrate, subgallate, subsalicylate and subcitrate have long been used as pharmaceuticals.[1] In addition, bismuth is an excellent shielding material for soft X-rays because of its high density and atomic number.[3] When appropriately incorporated into an organic molecular framework, it could lead to a novel type of contrast media for medical diagnosis by inhibiting the passage of X-rays and producing a shadow of positive contrast. However, this aspect of bismuth chemistry has apparently received little attention up to now. Most X-ray contrast media in current use are based on aromatic polyiodo compounds.[4] They produce good diagnostic shadows, but sometimes bring severe side effects, probably due to the intrinsic physiological nature of iodine as an essential trace element.

As part of our systematic study on organic bismuth chemistry,[5] we have investigated the potential of neutral organobismuth compounds as contrast media for X-rays. In designing such bismuth-derived contrast media, target compounds need to clear the following prerequisites: low toxicity, low osmotic activity, reasonable stability in body fluid and high water solubility. Taking all these into consideration, we have chosen water-soluble triarylbismuthanes as a fundamental molecular unit and synthesized two classes of polyol-type triarylbismuthanes; one bears phenolic hydroxy groups and the other alcoholic ones as side chains attached to the aromatic ring. To the best of our knowledge, the literature so far contains only a few reports on the synthesis of water-soluble bismuthanes, none of which meets the above requirements. In 1926, Supniewski and Adams reported that the oxidation of tris(methylphenyl)bismuth dichlorides with potassium permanganate or chromic acid gave tris(carboxyphenyl)bismuth dichlorides, which were soluble in aqueous alkali and gradually decomposed in the solution.[6] Attempted synthesis of water-soluble bismuthanes bearing phenolic or carboxylic groups from the reaction between alkali diphenylbismuthides and *p*-bromophenol or halobenzoic acids resulted in the formation of triphenylbismuthane as the major isolable product.[7] A triarylbismuthane-derived sulfonic acid salt, $(4\text{-}NaO_3SC_6H_4)_3Bi$, was patented as a supersensitizer for IR spectrally sensitized silver halide emulsions.[8] In the present paper, we report the first synthesis and properties of some water-soluble non-ionic triarylbismuthanes.

Results and discussion

Synthesis of triarylbismuth compounds bearing a hydroxyphenyl group as ligand

We chose tris(hydroxyphenyl)bismuthanes as the first model compound for water-soluble bismuthanes. The hydroxy group



on the benzene ring was expected to give rise to water solubility on alkaline media. Scheme 1 and eqn. (2) show the synthetic routes employed.

Treatment of *ortho*-lithiated methoxymethoxybenzene[9] with $\frac{1}{3}$ equiv. of $BiCl_3$ in THF afforded tris[2-(methoxymethoxy)-

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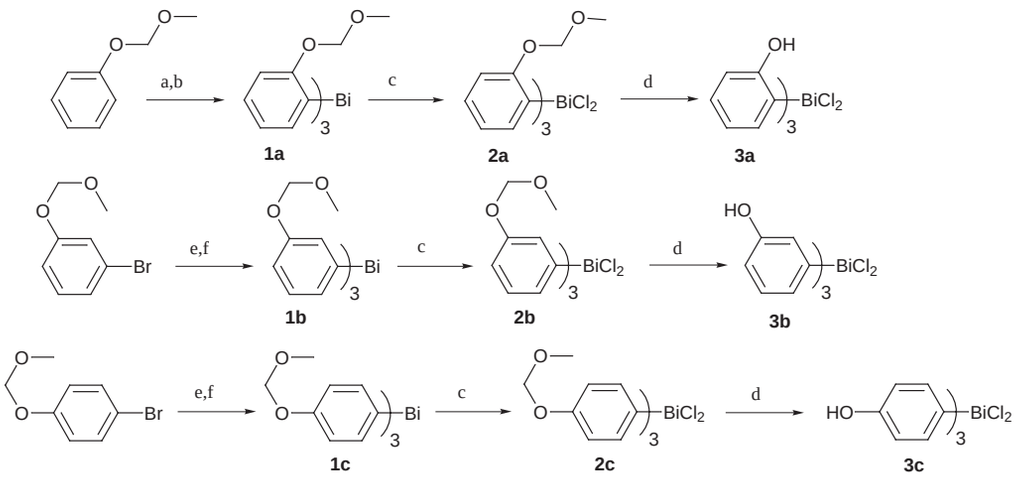
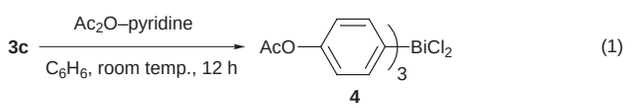


Scheme 1 *Reagents and conditions*: a, BuLi, TMEDA, THF, 0 °C, 6 h; b, $BiCl_3$ ($\frac{1}{3}$ equiv.), THF, −35 °C to room temp.; c, SO_2Cl_2, CH_2Cl_2, −35 °C to room temp.; d, aq. HCl, CH_2Cl_2, room temp.; e, Mg, THF, room temp.; f, $BiCl_3$ ($\frac{1}{3}$ equiv.), THF, 0 °C to room temp.

phenyl]bismuthane **1a** in 46% yield, while the reaction of 3- and 4-(methoxymethoxy)phenylmagnesium bromide with $\frac{1}{3}$ equiv. of $BiCl_3$ gave the corresponding *meta*- and *para*-substituted triarylbismuthanes **1b**,**c** in 78–86% yields (Scheme 1). Bismuthanes **1a**–**c** were oxidatively chlorinated to the corresponding tris[(methoxymethoxy)phenyl]bismuth dichlorides **2a**–**c** by treatment with SO_2Cl_2 in CH_2Cl_2. As expected, attempts to deprotect the MOM group by protonic acid only led to the fission of the Bi–C bond of the bismuthanes.[4,10] For instance, treatment of **1b** with aqueous HCl in CH_2Cl_2 resulted in the cleavage of both O–C and Bi–C bonds, affording a complex mixture of phenol and polymeric bismuth-containing substances. In contrast, the Bi–C bonds in triarylbismuth dichlorides are known to be more stable toward acids compared to the corresponding bonds in triarylbismuthanes. Thus, MOM dichlorides **2a**–**c** were successfully deprotected to tris(hydroxyphenyl)bismuth dichlorides **3a**–**c** by treatment with aqueous HCl in CH_2Cl_2.

Dichlorides **3** were soluble in MeOH, but not in H_2O. Esterification of **3c** by a mixture of Ac_2O and pyridine gave tris(4-acetoxyphenyl)bismuth dichloride **4** in 61% yield [eqn. (1)].



(1)

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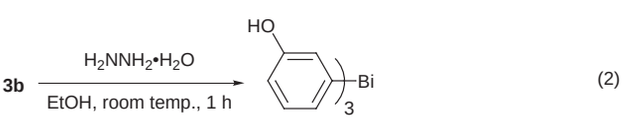
Although compounds **3a**–**c** did not show any signs of decomposition in MeOH over three days, they readily decomposed in the presence of NaOH.

Reduction of **3b** with hydrazine hydrate[11] in EtOH yielded tris(3-hydroxyphenyl)bismuthane **5** [eqn. (2)], while similar



(2)

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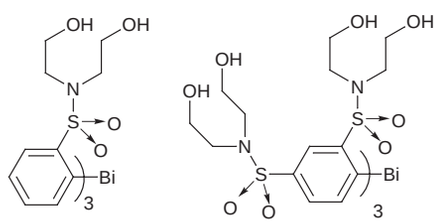
treatment of **3a**,**c** afforded a complex mixture containing free phenol. Although the reason is not clear at present, the difference in behaviour may probably be ascribed to the facilitation of cleavage of the Bi–C bond due to conjugative electron release from the hydroxy group at the *ortho*- or *para*-position.

meta-Substituted bismuthane **5** is a white solid, soluble in MeOH and insoluble in H_2O. It dissolved in H_2O without decomposition in the presence of NaOH. The ^1H NMR spectrum (in D_2O) of a white solid formed from **5** and one equiv. NaOH showed proton peaks at relatively high-field δ 6.5 (m, 3H), 6.95 (d, 3H), 7.13 (s, 3H) and 7.18 (t, 3H). This suggested that the white solid obtained was a phenolic salt of **5** and we may regard it as an additional example of a water-soluble ionic bismuthane.‡

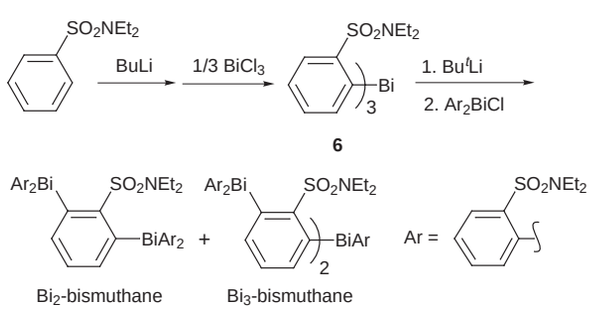
Synthesis of triarylbismuthanes bearing hydroxylated alkyl side chains

All reported water-soluble organobismuth compounds are ionic in nature and dissolve in alkaline media through salt formation. For practical use as an X-ray contrast agent, however, it is prerequisite to design non-ionic water-soluble bismuthanes to avoid the change in osmotic pressure of body fluid on administration. As an approach to this type of bismuthanes, we next undertook the synthesis of triarylbismuthanes bearing hydroxylated alkyl side chains. These bismuthanes have multiple non-



ionic hydroxy groups on the alkyl chains bound to the benzene ring *via* the sulfonamide moieties, both of these functionalities being expected to promote water solubility.

During a preliminary study on the synthesis of model compound **6**,[12] we have found that the *ortho*-lithiation directed by a sulfamoyl group[13] was quite effective for the preparation of **6** and polybismuth derivatives (Scheme 2).[14] It seemed to be

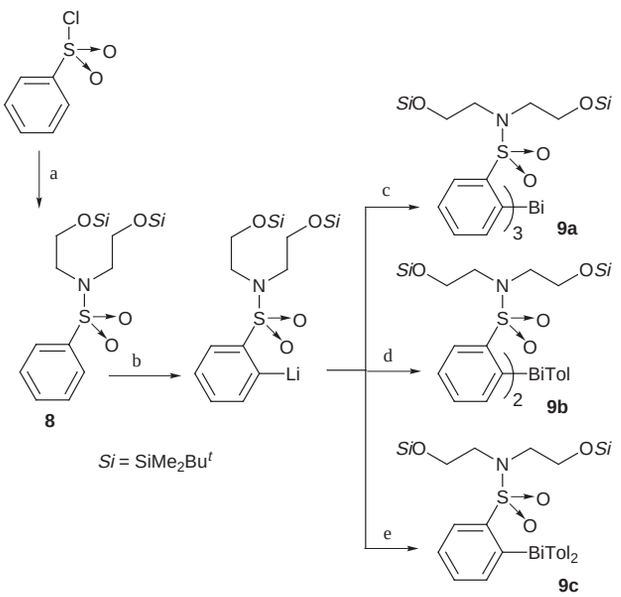


Scheme 2

‡ The simple resonance pattern observed suggests a rapid interconversion between free and ionized phenolic hydroxy groups on the NMR time scale.

appropriate to construct an oligobismuth network in a water-soluble molecule in order to obtain the high bismuth content necessary for X-ray imaging.§ Thus, oligomeric Bi_2- and Bi_3-bismuthanes bearing *N*,*N*-bis(2-hydroxyethyl)sulfamoyl groups were also prepared by this methodology.

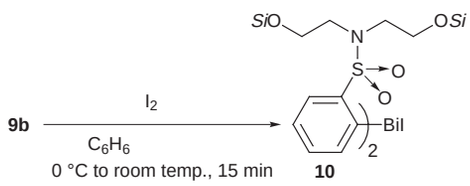
Syntheses of the desired triarylbismuthanes are depicted in Schemes 3, 4 and 5. Both hydroxy groups of diethanolamine



Scheme 3 *Reagents and conditions*: a, $HN(CH_2CH_2OSiMe_2Bu^t)_2$ **7**, NEt_3, C_6H_6, room temp., 5 h; b, BuLi, Et_2O, −78 °C, 1.5 h; c, $BiCl_3$ ($\frac{1}{3}$ equiv.), Et_2O, −60 °C to room temp.; d, $TolBiCl_2$ ($\frac{1}{2}$ equiv.), Et_2O, −78 °C to room temp.; e, Tol_2BiCl, Et_2O, −78 °C to room temp.

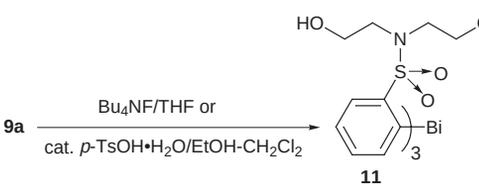
were protected by the *tert*-butyldimethylsilyl group according to the reported method.[15] *N*,*N*-Bis[2-(*tert*-butyldimethylsiloxy)-ethyl]amine **7** readily coupled with benzenesulfonyl chloride in the presence of triethylamine to afford *N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]benzenesulfonamide **8**. The sulfonamide moiety is known to be a good directing group for *ortho*-lithiation.[13] Thus, treatment of amide **8** with BuLi followed by reaction with $\frac{1}{3}$ equiv. of $BiCl_3$ gave Ar_3Bi **9a** (Ar = 2-{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]sulfamoyl}phenyl) in 63% yield. The lithiated benzenesulfonamide **8** also coupled with $TolBiCl_2$ or Tol_2BiCl (Tol = 4-methylphenyl) in Et_2O to give $TolBiAr_2$ **9b** in 69% and Tol_2BiAr **9c** in 54% yield, respectively. The Bi–C(Tol) bond of **9b** was selectively cleaved by iodine in benzene to afford Ar_2BiI **10** in 93% yield [eqn. (3)].

§ The high bismuth content (m/m%) is a prerequisite for obtaining a clear image, since the use of a dilute test solution is preferred in order to minimize the osmotic pressure change of body fluid.



(3)

Deprotection of the silyl groups in **9a** was carried out by two different methods [eqn. (4)]; treatment of **9a** with tetrabutyl-



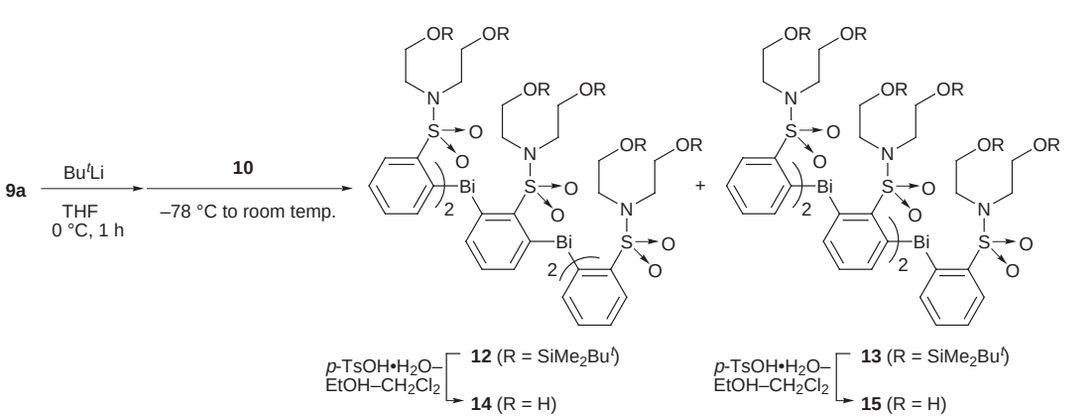
(4)

ammonium fluoride in THF gave deprotected bismuthane **11** in 61% yield, while toluene-*p*-sulfonic acid (*p*-TsOH)-catalysed desilylation of **9a** in EtOH–CH_2Cl_2 afforded **11** in 43% yield.

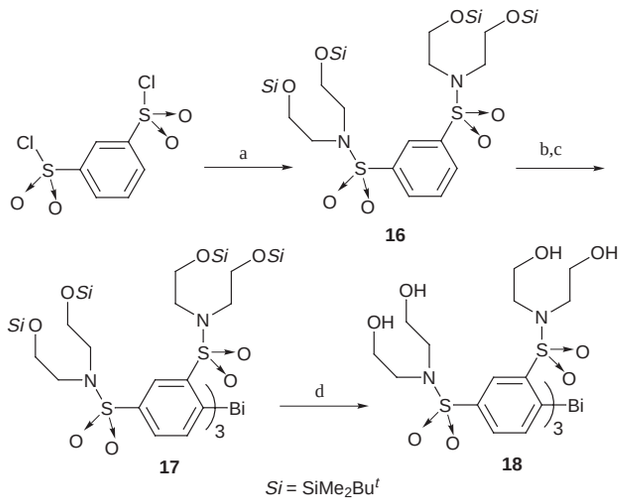
Bismuthane **9a** has three acidic aromatic protons adjacent to the sulfonamide moiety. Reaction of **9a** with 3 equiv. of Bu^{t}Li at 0 °C followed by treatment with 3 equiv. of **10** resulted in the formation of Bi_2-bismuthane **12**, Bi_3-bismuthane **13** and unchanged **9a** in 7, 37 and 10% yields, respectively (Scheme 4). Bismuthanes **12** and **13** were subsequently deprotected by *p*-TsOH·H_2O in EtOH–CH_2Cl_2 to give the corresponding poly-bismuthanes **14** and **15** bearing the *N*,*N*-bis(2-hydroxyethyl)-sulfamoyl moieties.

Compounds **11**, **14** and **15** were characterized by NMR, IR and mass spectroscopies as well as by elemental analysis. They showed the hydroxy protons at around δ 3–4 in the ^{1}H NMR spectra and broadened O–H stretching absorptions at 3600–3000 cm^{-1} in the IR spectra. MALDI-TOFMS spectra of these compounds gave a characteristic peak due to $[M^+ + Na]$ ion. Bismuthanes **11**, **14** and **15** are colourless solids, soluble in MeOH and acetone and insoluble in CH_2Cl_2. In spite of the presence of six to fourteen hydroxy groups and three to seven sulfonamide functions in the molecule, they are only slightly soluble in H_2O. For example, the solubility of **11** in H_2O was below a level of 0.5 mmol dm^{-3}.

To make the aryl ligand more hydrophilic, an additional *N*,*N*-bis(2-hydroxyethyl)sulfamoyl group was introduced onto each benzene ring of **11**. Benzene-1,3-disulfonamide **16** was prepared in 78% yield by the base-promoted reaction between benzene-1,3-disulfonyl dichloride and two equiv. of silyl-protected amine **7** (Scheme 5). Reaction of **16** with BuLi in THF followed by treatment with $\frac{1}{3}$ equiv. of $BiCl_3$ yielded tris-(2,4-bis{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]sulfamoyl}-phenyl)bismuthane **17** in 70% yield. An isomeric 2,6-disub-



Scheme 4



Scheme 5 *Reagents and conditions*: a, $HN(CH_2CH_2OSiMe_2Bu^t)_2$ **7**, NEt_3, THF, room temp., 23 h; b, BuLi, THF, −78 °C, 30 min; c, $BiCl_3$ ($\frac{1}{3}$ equiv.), THF, −78 °C to room temp.; d, *p*-TsOH·H_2O (0.3 equiv.), EtOH, CH_2Cl_2, 50 °C, 6 h

stituted derivative was not formed at all. The silyl groups of **17** were deprotected by *p*-TsOH·H_2O in EtOH–CH_2Cl_2 at 50 °C to yield tris{2,4-bis[*N*,*N*-bis(2-hydroxyethyl)sulfamoyl]phenyl}-bismuthane **18** as a colourless solid. Compound **18** was fully characterized by NMR, IR and mass spectroscopies as well as by elemental analysis. In the IR spectrum, the broad O–H stretching absorption was observed at 3700–3000 cm^{-1}. The fragment ion [M^+ + Na] was detected in the MALDI-TOFMS spectrum. Bismuthane **18** bearing twelve hydroxy groups was soluble in H_2O without any additives. The solubility of this compound in H_2O was estimated to be around 280 mmol dm^{-3}.

In summary, the combination of sulfonamide function and neutral hydroxy groups seems to be adequate for the construction of non-ionic water-soluble triarylbismuthanes, in that (1) a variety of water-soluble amino alcohols are readily available, (2) the sulfonamide bond is easy to prepare and (3) multiple arylbismuth units can be readily incorporated into the aryl ligands *via* multiple *ortho*-lithiation. Although much further study is needed to provide promising bismuth-based contrast media, we have now reached the first example of a water-soluble non-ionic bismuthane.

Experimental

All reactions with air-sensitive compounds were carried out under an atmosphere of argon. All mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H (200 MHz) and ^{13}C NMR (50 MHz) were recorded on a Varian Gemini-200 spectrometer. Chemical shifts are reported as the relative value *vs.* tetramethylsilane ($CDCl_3$ and CD_3OD) or 3-(trimethylsilyl)[2,2,3,3-$^2H_4$]propionic acid sodium salt (D_2O) and coupling constants *J* are given in Hz. IR spectra were observed on a Shimadzu FTIR-8100S spectrometer using a KBr pellet unless otherwise noted. EI, FAB and MALDI-TOF mass spectra were obtained on a Shimadzu GCMS-QP2000A, a JEOL JMS-HS110 or a Shimadzu MALDI-II-TOF spectrometer, respectively. 3-Nitrobenzyl alcohol was used as the matrix for FAB, and CHCA (α-cyano-4-hydroxycinnamic acid) or DHBA (2,5-dihydroxybenzoic acid) for MALDI-TOF, respectively. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University.

Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under argon before use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine was distilled from CaH_2 and stored over NaOH. Methoxymethoxybenzene and the corresponding bromo derivatives were prepared from phenol, NaH and chloromethyl methyl ether, or from phenol, dimethoxymethane and a catalytic amount of *p*-TsOH according to the reported methods.[16,17] *N*,*N*-Diethylbenzenesulfonamide was prepared from benzenesulfonyl chloride and diethylamine.[18] *N*,*N*-Bis-[2-(*tert*-butyldimethylsiloxy)ethyl]amine **7** was obtained by the base-promoted reaction of diethanolamine with *tert*-butyldimethylsilyl chloride.[15] Benzene-1,3-disulfonyl dichloride was prepared from disodium benzene-1,3-disulfonate and PCl_5.[19] Other reagents were used as commercially received. Column chromatography was performed on silica gel (Wakogel C200).

Synthesis of tris(methoxymethoxyphenyl)bismuthanes 1

Tris[2-(methoxymethoxy)phenyl]bismuthane 1a. To a mixture of BuLi (hexane solution; 21 cm^3, 33 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5.0 cm^3, 33 mmol) was added dropwise methoxymethoxybenzene (4.23 g, 30.6 mmol) at 0 °C. After stirring for 6 h at this temperature, a THF solution (50 cm^3) of $BiCl_3$ (3.16 g, 10.0 mmol) was added slowly at −35 °C. The mixture was allowed to warm to room temperature with vigorous stirring and then poured into water (*ca.* 100 cm^3). The insoluble substances were filtered off and the filtrate was extracted with ethyl acetate (50 $cm^3 \times 3$). The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to leave an oily residue, which was recrystallized from MeOH to yield bismuthane **1a** (2.85 g, 46%) as a colourless solid, mp 95 °C (Found: C, 46.5; H, 4.4. $C_{24}H_{27}BiO_6$ requires C, 46.5; H, 4.4%); $\delta_H(CDCl_3)$ 3.33 (9H, s, Me), 5.14 (6H, s, CH_2), 6.93 (3H, t, *J* 7, ArH), 7.27 (6H, m, ArH) and 7.53 (3H, d, *J* 6, ArH); ν_{max}/cm^{-1} 3050, 2901, 1570, 1456, 1435, 1225, 1186, 1150, 1113, 1073, 1044, 1007, 918 and 749.

Tris[3-(methoxymethoxy)phenyl]bismuthane 1b. To a THF solution (10 cm^3) of 3-(methoxymethoxy)phenylmagnesium bromide, prepared from Mg (875 mg, 36.5 mmol) and 3-bromo-1-methoxymethoxybenzene (7.16 g, 33.0 mmol), was added a THF solution (20 cm^3) of $BiCl_3$ (3.16 g, 10.0 mmol) at 0 °C. The mixture was allowed to warm to room temperature with vigorous stirring and then poured into water (*ca.* 100 cm^3). Usual work-up as described above left an oily residue, which was purified by column chromatography on silica gel using hexane–ethyl acetate as the eluent to give bismuthane **1b** (4.81 g, 78%) as a colourless oil (Found: C, 46.7; H, 4.45. $C_{24}H_{27}BiO_6$ requires C, 46.5; H, 4.4%); $\delta_H(CDCl_3)$ 3.42 (9H, s, Me), 5.10 (6H, s, CH_2), 6.98 (3H, dt, *J* 7 and 2, ArH), 7.29–7.40 (6H, m, ArH) and 7.48 (3H, d, *J* 2, ArH); *m*/*z* (EI) 346 ($ArBi^+$) and 209.

Tris[4-(methoxymethoxy)phenyl]bismuthane 1c. This compound was similarly prepared in 86% yield from Mg, 4-bromo-1-methoxymethoxybenzene and $BiCl_3$, mp 60–61 °C (Found: C, 46.5; H, 4.4. $C_{24}H_{27}BiO_6$ requires C, 46.5; H, 4.4%); $\delta_H(CDCl_3)$ 3.47 (9H, s, Me), 5.26 (6H, s, CH_2), 7.03 (6H, d, *J* 8.6, ArH) and 7.62 (6H, d, *J* 8.6, ArH); *m*/*z* (EI) 483 (Ar_2Bi^+), 346 ($ArBi^+$) and 209.

Synthesis of tris(methoxymethoxyphenyl)bismuth dichlorides 2

Tris[2-(methoxymethoxy)phenyl]bismuth dichloride 2a. To a CH_2Cl_2 (50 cm^3) solution of **1a** (2.85 g, 4.59 mmol) was added SO_2Cl_2 (0.37 cm^3, 4.6 mmol) at −35 °C, and the resulting mixture was allowed gradually to warm to room temperature. Evaporation of the solvent under reduced pressure left a crystalline solid, which was recrystallized from hexane–ethyl acetate to give dichloride **2a** (1.39 g) together with small amounts of partially deprotected **2a**. Compound **2a** was used without further purification for subsequent reactions, $\delta_H(CDCl_3)$ 3.43 (9H, s, Me), 5.14 (6H, s, CH_2), 7.20–7.60 (9H, m, ArH) and 8.18 (3H, d, *J* 8, ArH); *m*/*z* (EI) 483 (Ar_2Bi^+), 346 and 209.

Tris[3-(methoxymethoxy)phenyl]bismuth dichloride 2b. This

compound was similarly prepared from **1b** and SO_2Cl_2 and used without further purification for subsequent reactions, $\delta_H(CDCl_3)$ 3.49 (9H, s, Me), 5.22 (6H, s, CH_2), 7.22 (3H, d, *J* 8, ArH), 7.57 (3H, t, *J* 8, ArH), 8.12 (3H, d, *J* 8, ArH) and 8.25 (3H, s, ArH).

Tris[4-(methoxymethoxy)phenyl]bismuth dichloride 2c. This compound was similarly prepared from **1c** and SO_2Cl_2 and recrystallized from hexane–ethyl acetate (49%), mp 74–79 °C (Found: C, 41.2; H, 3.9. $C_{24}H_{27}BiCl_2O_6$ requires C, 41.7; H, 3.9%); $\delta_H(CDCl_3)$ 3.47 (9H, s, Me), 5.20 (6H, s, CH_2), 7.27 (6H, d, *J* 9, ArH) and 8.41 (6H, d, *J* 9, ArH); $\delta_C(CDCl_3)$ 56.2, 94.2, 118.7, 136.0, 147.2 and 159.2; ν_{max}/cm^{-1} 1570, 1483, 1399, 1304, 1237, 1175, 1152, 1080, 982 and 922; *m*/*z* (EI) 483 ($M^+ - Ar$), 346 and 209.

Synthesis of tris(hydroxyphenyl)bismuth dichlorides 3 and an acetylated derivative 4

Tris(2-hydroxyphenyl)bismuth dichloride 3a. To a CH_2Cl_2 (10 cm^3) solution of **2a** (691 mg, *ca.* 1 mmol) was added 36% aq. HCl (1 cm^3) at room temperature. The resulting mixture was stirred for 7 h, during which time a white solid precipitated from the solution. The solid was filtered off, washed with a minimum amount of CH_2Cl_2 and dried *in vacuo* to give dichloride **3a** (559 mg, *ca.* 100%) as a white powder, mp 158–160 °C; $\delta_H(CDCl_3)$ 7.15–7.28 (6H, m), 7.48 (3H, t, *J* 8) and 8.16 (3H, d, *J* 8); ν_{max}/cm^{-1} 3331 (OH), 1595, 1565, 1483, 1443, 1339, 1296, 1262, 1204, 1001, 828 and 747; *m*/*z* (FAB) 523 ($M^+ - Cl$).

Tris(3-hydroxyphenyl)bismuth dichloride 3b. This compound was similarly obtained from **2b**, $\delta_H(CDCl_3)$ 6.99 (3H, d, *J* 8), 7.52 (3H, t, *J* 8), 7.90 (3H, d, *J* 8) and 7.95 (3H, s); ν_{max}/cm^{-1} 3405 (OH), 1590, 1576, 1470, 1449, 1310, 1254, 1202, 1163, 1080, 984, 837, 766 and 673; *m*/*z* (FAB) 523 ($M^+ - Cl$).

Tris(4-hydroxyphenyl)bismuth dichloride 3c. This compound was similarly obtained from **2c**, $\delta_H(CDCl_3)$ 7.05 (6H, d, *J* 8.3) and 8.23 (6H, d, *J* 8.3); $\delta_C(CD_3OD)$ 118.4, 135.9, 145.9 and 159.4; ν_{max}/cm^{-1} 3230 (OH), 1574, 1483, 1426, 1269, 1215, 1173 and 822. The OH resonances were not clearly observed in the ^1H NMR spectra of compounds **3a**–**c**. Although spectroscopic data supported a high state of purity, we were not successful in obtaining satisfactory elemental analysis data within ±0.3%.

Tris(4-acetoxyphenyl)bismuth dichloride 4. A mixture of **3c** (1.41 g, 2.52 mmol), acetic anhydride (1.42 cm^3, 15.1 mmol), pyridine (1.22 cm^3, 15.1 mmol) and benzene (20 cm^3) was stirred for 12 h at room temperature. The mixture was poured into water and the organic phase was separated, dried over Na_2SO_4 and concentrated under reduced pressure to leave an oily residue, which was crystallized from hexane–ethyl acetate to give dichloride **4** (1.06 g, 61%) as a colourless solid, mp 161 °C (Found: C, 42.15; H, 3.2. $C_{24}H_{21}BiCl_2O_6$ requires C, 42.1; H, 3.1%); $\delta_H(CDCl_3)$ 2.32 (9H, s, Me), 7.48 (6H, d, *J* 9.0, ArH) and 8.57 (6H, d, *J* 9.0, ArH); $\delta_C(CDCl_3)$ 21.1, 124.7, 134.9, 135.8, 153.0 and 168.7; *m*/*z* (EI) 479 (Ar_2Bi^+), 344 and 209.

Synthesis of tris(3-hydroxyphenyl)bismuthane 5

To an EtOH solution (12 cm^3) of **3b** (559 mg, 1.0 mmol) was added $H_2NNH_2{\cdot}H_2O$ (0.19 cm^3, 4.0 mmol) at room temperature and the resulting mixture was stirred for 1 h. The insoluble substances were filtered off and the filtrate was diluted with water (100 cm^3) and extracted with ethyl acetate (40 $cm^3 \times 4$). The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to leave a crystalline residue, which was washed with CH_2Cl_2 and dried *in vacuo* to give bismuthane **5** (118 mg, 24%) as a colourless solid. On heating, compound **5** decomposed without showing a definite melting range (Found: C, 44.5; H, 3.3. $C_{18}H_{15}BiO_3$ requires C, 44.3; H, 3.1%); $\delta_H(CD_3OD)$ 6.70 (3H, m) and 7.18–7.28 (9H, m); ν_{max}/cm^{-1} 3212 (OH), 1591, 1574, 1431, 1240, 1173, 841, 777 and 693; *m*/*z* (FAB) 395 (Ar_2Bi^+). Although not soluble in H_2O, bismuthane **5** dissolved in H_2O in the presence of NaOH. A white solid formed from equimolar amounts of **5** and NaOH dissolved in D_2O and showed four ^1H NMR peaks due to aromatic protons at δ_H 6.5 (3H, m), 6.95 (3H, d), 7.13 (3H, s) and 7.18 (3H, t). The corresponding peaks in CD_3OD were observed at δ_H 6.5, 6.86, 6.98 and 7.20. The species in the solution was assigned to the partially ionized bismuthane **5**, although its exact nature has not been elucidated yet.

Synthesis of *N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-benzenesulfonamide 8

A mixture of benzene (30 cm^3), benzenesulfonyl chloride (1.8 cm^3, 14 mmol), triethylamine (2.5 cm^3, 18 mmol) and silyl-protected diethanolamine **7** (4.67 g, 14.0 mmol) was stirred for 5 h at room temperature. The resulting suspension was poured into H_2O (20 cm^3) and the organic layer was separated. The aqueous phase was extracted with benzene (10 $cm^3 \times 3$) and the combined organic extracts were washed with saturated aq. $NaHCO_3$ (10 $cm^3 \times 2$) and brine (10 $cm^3 \times 2$), dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was purified by silica gel column chromatography using hexane–ethyl acetate as the eluent to give amide **8** (4.9 g, 74%) as a colourless oil, $\delta_H(CDCl_3)$ 0.03 (12H, s, Me), 0.87 (18H, s, Bu^t), 3.35 (4H, t, *J* 6.3, CH_2CH_2), 3.74 (4H, t, *J* 6.3, CH_2CH_2), 7.45–7.58 (3H, m, ArH) and 7.84 (2H, d, *J* 8, ArH).

Synthesis of tris(2-{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-sulfamoyl}phenyl)bismuthane 9a

To a suspension of **8** (870 mg, 1.84 mmol) in Et_2O (20 cm^3) was added BuLi (hexane solution; 1.4 cm^3, 2.0 mmol) at −78 °C. After stirring at this temperature for 90 min, the resulting pale yellow suspension was transferred to a suspension of $BiCl_3$ (157 mg, 0.50 mmol) in the same solvent (10 cm^3) at −60 °C and the resulting mixture was allowed gradually to warm to room temperature. After 3 h, saturated aq. NH_4Cl (20 cm^3) was added and the insoluble substances were removed by filtration. The organic phase was separated and the aqueous phase was extracted with Et_2O (20 $cm^3 \times 2$). The combined organic extracts were washed with brine (20 $cm^3 \times 2$), dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was purified by silica gel column chromatography using hexane–ethyl acetate as the eluent and further recrystallized from CH_2Cl_2–pentane to give bismuthane **9a** (510 mg, 63%) as a colourless solid, mp 106–108 °C (Found: C, 48.6; H, 8.0; N, 2.3. $C_{66}H_{126}BiN_3O_{12}S_3Si_6$ requires C, 48.7; H, 7.8; N, 2.6%); $\delta_H(CDCl_3)$ 0.01 (36H, s, Me), 0.87 (54H, s, Bu^t), 3.46 (12H, t, *J* 6, CH_2CH_2), 3.70 (12H, t, *J* 6, CH_2CH_2), 7.32 (3H, t, *J* 7, ArH), 7.48 (3H, t, *J* 7, ArH), 7.67 (3H, d, *J* 7, ArH) and 8.02 (3H, d, *J* 7, ArH); ν_{max}/cm^{-1} 2900, 1474, 1330, 1255, 1155, 1111, 1001, 837 and 777; *m*/*z* (FAB) 1570 ($M^+ - Bu^t$), 1249, 1153, 849, 536, 349, 333, 285 and 209.

Synthesis of bis(2-{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-sulfamoyl}phenyl)(4-methylphenyl)bismuthane 9b

A mixture of tris(4-methylphenyl)bismuthane (299 mg, 0.62 mmol), $BiCl_3$ (391 mg, 1.24 mmol) and Et_2O (10 cm^3) was stirred at room temperature for 2 h. To the resulting yellow suspension was added at −78 °C a suspension of 2-lithiobenzenesulfonamide, generated from **8** (1.76 g, 3.72 mmol), BuLi (hexane solution; 2.7 cm^3, 4.1 mmol) and Et_2O (20 cm^3), and the mixture was allowed to warm to room temperature with stirring. Usual work-up followed by silica gel column chromatography using hexane–ethyl acetate as the eluent yielded bismuthane **9b** (1.61 g, 69%) as a colourless oil (Found: C, 49.0; H, 7.55; N, 2.0. $C_{51}H_{91}BiN_2O_8S_2Si_4$ requires C, 49.2; H, 7.4; N, 2.25%); $\delta_H(CDCl_3)$ 0.01 (24H, s, $SiMe_2$), 0.87 (36H, s, Bu^t), 2.29 (3H, s, C_6H_4Me), 3.39 (8H, t, *J* 5.6, CH_2CH_2), 3.66 (8H, t, *J* 5.6,

CH_2CH_2), 7.20 (2H, d, *J* 7.6, ArH), 7.35 (2H, t, *J* 7.3, ArH), 7.47 (2H, t, *J* 7.3, ArH), 7.51 (2H, d, *J* 7.6, ArH), 7.85 (2H, d, *J* 7.3, ArH) and 8.00 (2H, d, *J* 7.3, ArH); ν_{max}/cm^{-1} 2900, 1472, 1330, 1255, 1155, 1110, 999, 837 and 777; *m*/*z* (FAB) 1153 (M^+ − Tol), 849, 772, 349, 333 and 209.

Synthesis of (2-{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-sulfamoyl}phenyl)bis(4-methylphenyl)bismuthane 9c

A mixture of tris(4-methylphenyl)bismuthane (482 mg, 1.0 mmol), $BiCl_3$ (158 mg, 0.50 mmol) and Et_2O (10 cm^3) was stirred at room temperature for 1 h. To the resulting white suspension was added at −78 °C a suspension of 2-lithiobenzenesulfonamide, generated from **8** (713 mg, 1.50 mmol), BuLi (hexane solution; 1.14 cm^3, 1.65 mmol) and Et_2O (10 cm^3), and the mixture was allowed to warm to room temperature with stirring. Usual work-up followed by recrystallization from MeOH–pentane yielded bismuthane **9c** (697 mg, 54%) as a colourless solid, mp 112–114 °C (Found: C, 49.9; H, 6.6; N, 1.4. $C_{36}H_{56}BiNO_4SSi_2$ requires C, 50.0; H, 6.5; N, 1.6%); δ_H($CDCl_3$) 0.00 (12H, s, SiMe_2), 0.86 (18H, s, Bu^t), 2.31 (6H, s, C_6H_4Me), 3.32 (4H, t, *J* 6.2, CH_2CH_2), 3.59 (4H, t, *J* 6.2, CH_2CH_2), 7.21 (4H, d, *J* 7.3, ArH), 7.35 (1H, t, *J* 7.2, ArH), 7.45 (1H, d, *J* 7.2, ArH), 7.60 (4H, d, *J* 7.3, ArH) and 7.96–8.04 (2H, m, ArH); ν_{max}/cm^{-1} 2900, 1472, 1335, 1250, 1155, 1105, 999, 835 and 777; *m*/*z* (FAB) 772 (M^+ − Ar), 680, 376, 349, 333, 300 and 209.

Synthesis of bis(2-{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-sulfamoyl}phenyl)bismuth iodide 10

To a benzene solution (12 cm^3) of **9b** (1.6 g, 1.3 mmol) was added a solution of iodine (0.33 g, 1.3 mmol) in the same solvent (9 cm^3) at 0 °C. After stirring for 15 min at room temperature, the solvent was evaporated to give a crude product, which was chromatographed on silica gel using hexane–ethyl acetate as the eluent to yield iodide **10** (1.54 g, 93%) as a yellow oil (Found: C, 41.8; H, 6.8; N, 2.3. $C_{44}H_{84}BiIN_2O_8S_2Si_4$ requires C, 41.2; H, 6.6; N, 2.2%); δ_H($CDCl_3$) 0.01 (24H, s, Me), 0.86 (36H, s, Bu^t), 3.33 (8H, t, *J* 5, CH_2CH_2), 3.59 (8H, t, *J* 5, CH_2CH_2), 7.53–7.69 (4H, m, ArH), 8.01 (2H, dd, *J* 1.5 and 7.5, ArH) and 9.18 (2H, dd, *J* 1.5 and 8, ArH); ν_{max}(neat)/cm^{-1} 2955–2857, 1472, 1464, 1362, 1312, 1256, 1001, 938, 837, 777, 739 and 662; *m*/*z* (MALDI; CHCA) 1154.8 (M^+ − I).

Synthesis of tris{2-[*N*,*N*-bis(2-hydroxyethyl)sulfamoyl]phenyl}-bismuthane 11

This compound was prepared by two different methods. Method A: to a THF solution (15 cm^3) of **9a** (355 mg, 0.218 mmol) was added Bu_4NF (THF solution; 1.35 cm^3, 1.35 mmol) at 0 °C and the resulting mixture was stirred at room temperature for 3 h. Saturated aq. NH_4Cl (15 cm^3) was added and the organic phase was removed by decantation. The aqueous phase was washed with Et_2O (10 cm^3 × 2) and then allowed to stand overnight. The deposit was filtered off, washed with H_2O and recrystallized from 6% EtOH–H_2O to yield bismuthane **11** (125 mg, 61%) as a colourless solid. Method B: to a solution of **9a** (0.65 g, 0.40 mmol) in EtOH (1 cm^3)–CH_2Cl_2 (2 cm^3) was added *p*-TsOH·H_2O (14 mg, 0.072 mmol) and the resulting mixture was heated under reflux for 6 h. The solvent was evaporated under reduced pressure and the solid residue was washed successively with acetone and CH_2Cl_2 to give compound **11** (0.16 g, 43%), mp 202–204 °C (Found: C, 37.85; H, 4.6; N, 4.2. $C_{30}H_{42}BiN_3O_{12}S_3$ requires C, 38.3; H, 4.5; N, 4.5%); δ_H([$^2H_6$]-acetone) 3.42 (12H, t, *J* 5.6, CH_2CH_2), 3.76 (12H, q, *J* 5.6, CH_2CH_2), 4.28 (6H, t, *J* 5.6, OH), 7.47 (3H, dt, *J* 1.3 and 7.4, ArH), 7.64 (3H, dt, *J* 1.5 and 7.7, ArH), 7.71 (3H, dd, *J* 1.3 and 7.4, ArH) and 8.12 (3H, dd, *J* 1.4 and 7.7, ArH); ν_{max}/cm^{-1} 3350 (OH), 1325, 1155, 1084, 991, 924, 737 and 710; *m*/*z* (FAB) 697 (M^+ − Ar), 501, 452, 361, 349, 333, 308, 289 and 209. The solubility of **11** (Bi content is 22.2 m/m%) in H_2O was *ca.* 0.5 g dm^{-3} (Bi: 0.5 mmol dm^{-3}).

Synthesis of Bi$_n$-bismuthanes 12 and 13

To a THF solution (7 cm^3) of **9a** (0.69 g, 0.43 mmol) was added dropwise Bu^{t}Li (pentane solution; 0.88 cm^3, 1.4 mmol) at −78 °C. After stirring for 1 h at 0 °C, a THF solution (7 cm^3) of **10** (1.6 g, 1.3 mmol) was added at −78 °C and the resulting mixture was allowed gradually to warm to room temperature with stirring. Usual work-up followed by silica gel column chromatography with hexane–ethyl acetate as the eluent yielded Bi$_n$-bismuthanes **12**, **13** and unchanged **9a** in 7, 37 and 10% yields (based on the total bismuth), respectively.

Bi$_2$-bismuthane 12. Mp 42–46 °C (Found: C, 47.4; H, 7.6; N, 2.5. $C_{110}H_{209}Bi_2N_5O_{20}S_5Si_{10}$ requires C, 47.5; H, 7.6; N, 2.5%); δ_H($CDCl_3$) 0.01 (60H, s, Me), 0.87 (90H, s, Bu^t), 3.45 (20H, br t, CH_2CH_2), 3.71 (20H, br t, CH_2CH_2), 7.11 (1H, t, *J* 8, ArH), 7.33 (4H, t, *J* 7, ArH), 7.47 (4H, t, *J* 7, ArH), 7.66 (4H, d, *J* 7, ArH), 7.79 (2H, d, *J* 7, ArH) and 8.01 (4H, d, *J* 8, ArH); ν_{max}/cm^{-1} 2955–2857, 1472, 1329, 1256, 1156, 1105, 999, 837, 777, 735 and 662; *m*/*z* (MALDI; CHCA) 2804.4 (M^+ + Na).

Bi$_3$-bismuthane 13. Mp 57–63 °C (Found: C, 47.2; H, 7.5; N, 2.45. $C_{154}H_{292}Bi_3N_7O_{28}S_7Si_{14}$ requires C, 47.0; H, 7.5; N, 2.5%); δ_H($CDCl_3$) −0.12–0.03 (84H, m, Me), 0.81–0.87 (126H, m, Bu^t), 3.3–3.5 (28H, br t, CH_2CH_2), 3.6–3.75 (28H, br t, CH_2CH_2), 7.1–7.2 (2H, m, ArH), 7.25–7.35 (5H, m, ArH), 7.43–7.51 (5H, m, ArH), 7.59–7.68 (5H, m, ArH), 7.73–7.82 (4H, m, ArH) and 7.91–8.06 (5H, m, ArH); ν_{max}/cm^{-1} 2957–2859, 1474, 1329, 1256, 1156, 1103, 999, 837, 777, 737 and 662; *m*/*z* (MALDI; CHCA) 3957.6 (M^+ + Na).

Synthesis of Bi$_n$-bismuthanepolyols 14 and 15

Bi$_2$-bismuthane 14. A mixture of Bi$_2$-bismuthane **12** (0.44 g, 0.16 mmol), *p*-TsOH·H_2O (9.0 mg, 0.047 mmol), EtOH (0.5 cm^3) and CH_2Cl_2 (1 cm^3) was heated at 50 °C for 6 h. Evaporation of the solvent gave an oily residue, which was chromatographed on deactivated silica gel using MeOH–CH_2Cl_2 as the eluent to give a crude product (60 mg). This was washed with H_2O (2 cm^3 × 4) and dried *in vacuo* to give Bi$_2$-bismuthane **14** (49 mg, 19%) as a colourless solid, mp 137–141 °C (Found: C, 36.7; H, 4.4; N, 4.15. $C_{50}H_{69}Bi_2N_5O_{20}S_5$ requires C, 36.65; H, 4.2; N, 4.3%); δ_H(CD_3OD) 3.29–3.32 (OH), 3.39 (16H, t, *J* 5.3, CH_2CH_2), 3.56 (4H, br t, CH_2CH_2), 3.71 (20H, t, *J* 5.3, CH_2CH_2), 7.17 (1H, t, *J* 7, ArH), 7.44 (4H, br t, ArH), 7.60 (4H, t, *J* 7.5, ArH), 7.69 (4H, d, *J* 7, ArH), 7.82 (2H, d, *J* 7, ArH) and 8.08 (4H, d, *J* 8, ArH); ν_{max}/cm^{-1} 3600–3000 (OH), 2930, 2882, 1443, 1420, 1312, 1248, 1152, 1082, 1042, 990, 916, 737 and 673; *m*/*z* (MALDI; CHCA) 1661.5 (M^+ + Na). The solubility of **14** (Bi content is 25.5 m/m%) in H_2O was *ca.* 0.5 g dm^{-3} (Bi: 0.6 mmol dm^{-3}).

Bi$_3$-bismuthane 15. A mixture of Bi$_3$-bismuthane **13** (0.29 g, 0.074 mmol), *p*-TsOH·H_2O (5.8 mg, 0.030 mmol), EtOH (0.5 cm^3) and CH_2Cl_2 (1 cm^3) was heated at 50 °C for 7 h. Evaporation of the solvent gave an oily residue, which was chromatographed on deactivated silica gel using MeOH–CH_2Cl_2 as the eluent to yield Bi$_3$-bismuthane **15** (28 mg, 16%) as a colourless solid, mp 148–152 °C (Found: C, 35.75; H, 4.3; N, 4.1. $C_{70}H_{96}Bi_3N_7O_{28}S_7$ requires C, 36.0; H, 4.1; N, 4.2%); δ_H(CD_3OD) 3.25–3.35 (OH), 3.35–3.50 (20H, br t, CH_2CH_2), 3.50–3.60 (8H, br s, CH_2CH_2), 3.60–3.75 (28H, br s, CH_2CH_2), 7.1–7.3 (2H, m, ArH), 7.3–7.8 (15H, m, ArH), 7.8–7.9 (4H, m, ArH) and 8.0–8.1 (5H, m, ArH); ν_{max}/cm^{-1} 3600–3000 (OH), 2934, 2882, 1443, 1420, 1310, 1275, 1150, 1075, 1040, 990, 914 and 737; *m*/*z* (MALDI; CHCA) 2358.0 (M^+ + Na). The solubility of **15** (Bi content is 26.7 m/m%) in H_2O was *ca.* 0.7 g dm^{-3} (Bi: 0.9 mmol dm^{-3}).

Synthesis of 1,3-bis{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]-sulfamoyl}benzene 16

To a THF solution (20 cm^3) of *N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)ethyl]amine **7** (1.9 g, 5.7 mmol) and triethylamine (1.0 cm^3, 7.5 mmol) was added benzene-1,3-disulfonyl dichloride (0.74 g, 2.7 mmol) at 0 °C and the resulting suspension was

stirred at room temperature for 23 h. Water (20 cm^3) was added and the mixture was concentrated under reduced pressure to remove any organic volatiles. The aqueous residue was extracted with CH_2Cl_2 (15 cm^3 × 3) and the combined extracts were washed with H_2O (10 cm^3 × 2), dried over $MgSO_4$ and evaporated under reduced pressure to leave an oily residue, which was purified by silica gel column chromatography using hexane–ethyl acetate as the eluent to give compound **16** (1.83 g, 78%) as a colourless solid, mp 42–44 °C (Found: C, 52.5; H, 9.15; N, 3.1. $C_{38}H_{80}N_2O_8S_2Si_4$ requires C, 52.5; H, 9.3; N, 3.2%); $\delta_H(CDCl_3)$ 0.03 (24H, s, Me), 0.86 (36H, s, Bu^t), 3.37 (8H, t, *J* 6.1, CH_2CH_2), 3.75 (8H, t, *J* 6.1, CH_2CH_2), 7.64 (1H, t, *J* 7.9, ArH), 8.00 (2H, d, *J* 7.9, ArH) and 8.26 (1H, s, ArH).

Synthesis of tris(2,4-bis{*N*,*N*-bis[2-(*tert*-butyldimethylsiloxy)-ethyl]sulfamoyl}phenyl)bismuthane 17

To a THF solution (40 cm^3) of **16** (3.21 g, 3.69 mmol) was added BuLi (hexane solution; 2.8 cm^3, 4.0 mmol) at −78 °C. After stirring for 30 min at this temperature, a THF solution (10 cm^3) of $BiCl_3$ (316 mg, 1.0 mmol) was added and the resulting mixture was allowed gradually to warm to room temperature with stirring. The mixture was poured into H_2O (20 cm^3) and the aqueous phase was extracted with ethyl acetate (20 cm^3 × 2). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure to leave an oily residue, which was purified by silica gel column chromatography with hexane–ethyl acetate as the eluent to give bismuthane **17** (1.97 g, 70%) as a colourless solid, mp 115 °C (Found: C, 48.4; H, 8.5; N, 3.0. $C_{114}H_{237}BiN_6O_{24}S_6Si_{12}$ requires C, 48.65; H, 8.5; N, 3.0%); $\delta_H(CDCl_3)$ 0.02 (72H, s, Me), 0.87 (108H, s, Bu^t), 3.32 (12H, t, *J* 5.8, CH_2CH_2), 3.48 (12H, t, *J* 5.0, CH_2CH_2), 3.60–3.89 (24H, m, CH_2CH_2), 7.72 (3H, d, *J* 8, ArH), 7.78 (3H, d, *J* 8, ArH) and 8.36 (3H, s, ArH); ν_{max}/cm^{-1} 2957, 2930, 2859, 1474, 1362, 1337, 1258, 1171, 1105 and 1001.

Synthesis of tris{2,4-bis[*N*,*N*-bis(2-hydroxyethyl)sulfamoyl]-phenyl}bismuthane 18

A mixture of **17** (2.7 g, 0.97 mmol), *p*-TsOH·H_2O (54 mg, 0.28 mmol), EtOH (2.7 cm^3) and CH_2Cl_2 (5.4 cm^3) was heated at 50 °C for 6 h and, after cooling to room temperature, the resulting deposit was filtered off, washed with EtOH–CH_2Cl_2 (1 : 2, 1 cm^3) and dried *in vacuo* to give bismuthane **18** (0.60 g, 43%) as a colourless solid, mp 177–180 °C (Found: C, 34.9; H, 4.9; N, 5.6. $C_{42}H_{69}BiN_6O_{24}S_6$ requires C, 34.95; H, 4.8; N, 5.8%); $\delta_H(D_2O)$ 3.37 (12H, br t, CH_2CH_2), 3.52 (12H, br t, CH_2CH_2), 3.73 (24H, br t, CH_2CH_2), 6.91 (3H, d, *J* 8, ArH), 7.48 (3H, d, *J* 8, ArH) and 8.57 (3H, s, ArH); $\delta_C(D_2O)$ 53.0, 53.3, 62.0, 62.2, 130.8, 135.5, 142.8, 144.3, 148.7 and 182.0; ν_{max}/cm^{-1} 3700–3000 (OH), 2944–2884, 1638, 1565, 1445, 1358, 1302, 1167, 1150, 1132, 1076, 993, 949, 924, 843, 808, 715 and 691; *m*/*z* (MALDI; DHBA) 1467.0 (M^+ + Na). The solubility of **18** (Bi content is 21.1 m/m%) in H_2O was *ca.* 400 g dm^{-3} (Bi: 280 mmol dm^{-3}).

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