Synthesis and Properties of a Series of Phenylene-Bridged Bi$_n$-Bismuthanes

Yoshihiro Matano,*,[†] Haruto Kurata,[†] Toshihiro Murafuji,[†,‡] Nagao Azuma,[§] and Hitomi Suzuki*,[†]

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan, and Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan

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A series of *meta*- and *para*-phenylene-bridged Bi(III)$_n$ and Bi(V)$_n$ compounds ($n \geq 2$) have been synthesized. Reaction of Ph_2BiX (X = Cl, OSO_2CF_3) with *p*-$Li_2C_6H_4$, *p*-$(BrMg)_2C_6H_4$, or *p*- and *m*-$(Me_2S{\cdot}Cu)_2C_6H_4$ generated in situ from dibromobenzenes gave the corresponding *para*- and *meta*-phenylene-bridged Bi$_n$−bismuthanes, $Ph_2BiC_6H_4BiPh_2$ (**2**), $Ph_2BiC_6H_4Bi(Ph)C_6H_4BiPh_2$ (**3**), and $Ph_2BiC_6H_4Bi(Ph)C_6H_4Bi(Ph)C_6H_4BiPh_2$ (**4**), in 2−30% yields. Bi$_n$-bismuthanes **2**−**4** were oxidatively chlorinated by SO_2Cl_2 to yield the Bi$_n$-bismuth polychlorides **5**−**7**, in which all pentavalent bismuth atoms bore three aryl groups and two chlorine atoms. Compounds **2**−**7** showed λ_{max} at around 244−249 and 285−290 nm in the UV−vis spectra, suggesting that the phenylene bridges did not perturb significantly the σ- and π-transitions of the aromatic systems in these bismuth oligomers. *Ortho*-lithiation directed by the sulfonyl group was employed for the one-pot preparation of highly branched Bi$_n$-bismuthanes; successive treatment of Ar_3Bi **9a** with 3 equiv of *t*-BuLi and Ar_2BiI (**10b**) (Ar = 2-$Et_2NSO_2C_6H_4$) afforded *m*-phenylene-bridged Bi$_n$-bismuthanes, $Ar_2Ar'Bi$ (**11a**), $ArAr'_2Bi$ (**12a**), and Ar'_3Bi (**13a**) in 2−49% yields (Ar′ = 3-Ar_2Bi-2-$Et_2NSO_2C_6H_3$). Treatment of *ortho*-lithiated (2-*t*-$BuSO_2C_6H_4$)(*p*-Tol)$_2$Bi (**14**) with *p*-Tol_2BiCl gave sulfone-substituted Bi$_2$-bismuthane **15**, which was converted to the corresponding Bi$_2$-chlorodiarylbismuthane (**16**) by the Bi−C cleavage reaction. An X-ray diffraction analysis of **16** showed that both bismuth centers have a distorted trigonal pyramidal geometry weakly coordinated by the neighboring sulfonyl-oxygen atoms. The symmetrically branched Bi$_4$-bismuthane **13a** was successfully converted to a dendritic Bi$_{10}$-bismuthane **17** in 20% isolated yield by successive treatment with *t*-BuLi and **10b**. The reaction between *ortho*-lithiated **9a** and $ArBiI_2$ (**10c**) followed by GPC separation afforded two fractions of oligomeric Bi$_n$-bismuthanes, the vapor depression measurement of which revealed that the average numbers of the bismuth atoms present therein were 7 and 16, respectively. UV−vis spectra of **9a, 11a**, **12a**, **13a**, and **17** exhibited no bathochromic shift; the inefficient π-electron delocalization would probably be due to the twisted geometry between aromatic rings, as inferred from the X-ray structure of the related Bi$_2$-bismuthane **16**. The extinction coefficients of these phenylene-bridged Bi$_n$-bismuthanes were found to increase with increasing number of bismuth atoms.

Introduction

Synthesis of oligomeric heavy heteroatom-containing organic compounds has recently been receiving growing interest owing to their uniqueness in property arising from a combination of multiple heavy heteroatoms involved therein. However, little or no information is available at present for the bismuth counterparts due to the lack of convenient methodology for the synthesis of this class of compounds.[1] Most known organopolybismuth compounds bear two bismuth atoms in a molecule, as shown by $R_2Bi{-}BiR_2$,[2] $ArBi{=}BiAr$,[3] $R_2BiC{\equiv}CBiR_2$,[4] *p*-$Ph_2BiC_6H_4BiPh_2$,[5] $Ph_2BiS(CH_2)_5SBiPh_2$,[6] $R_2Bi(CH_2)_nBiR_2$,[2d,7] $R_2BiEBiR_2$ (E = O, S, Se, Te),[2h,8] *p*-$Ph_2BiOC_6H_4OBiPh_2$,[2d] triptycene-like Bi$_2$-bismuthanes,[9] polysilylated Bi$_2$-bismuthanes,[10] a biphenylene-bridged Bi$_2$-bismuthane,[11] *p*-$Ph_2Bi(Br)_2C_6H_4Bi(Br)_2Ph_2$,[5] and $(Ph_3BiX)_2O$[12] (hereafter *n* in Bi$_n$ denotes the number of bismuth atoms present in a molecule). From practical as well as theoretical points of view, syntheses of a series of thermally and kinetically stabilized oligomeric

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[†] Kyoto University: matano@kuchem.kyoto-u.ac.jp.

[‡] Present address: Department of Chemistry, Faculty of Science, Yamaguchi University, Yoshida, Yamaguchi 753-8512, Japan.

[§] Ehime University.

(1) For survey of organobismuth compounds, see: (a) *Gmelin Handbuch der Anorganischen Chemie, Bisumut-Organische Verbindungen*; Wieber, M., Ed.; Springer-Verlag: Berlin, 1977; Band 47. (b) Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982**, *82*, 15. (c) Abramovitch, R. A.; Barton, D. H. R.; Finet, J.-P. *Tetrahedron* **l988**, *44*, 3039. (d) Finet, J.-P. *Chem. Rev.* **1989**, *89*, 1487. (e) Wardell, J. L. *Organomet. Chem.* **l994**, *23*, 138, and previous reviews in the series. (f) Akiba, K.-y.; Yamamoto, Y. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley; New York, l994; Chapter 20, pp 761−812. (g) Doak, G. O.; Freedman, L. D. *J. Organomet. Chem.* **l995**, *496*, 1, and previous reviews in the series. (h) Matano, Y.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2673. (i) Postel, M.; Duñach, E. *Coord. Chem. Rev.* **1996**, *155*, 127. (j) Suzuki, H.; Matano, Y. In *Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie Academic and Professional: London, 1997; Chapter 6, pp 283−343.

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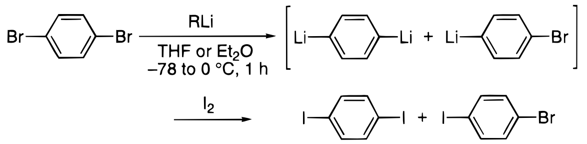
bismuth compounds bearing more than two bismuth atoms are of interest, since they would provide key information regarding the basic property of the bismuth-containing polymers.[13] On the basis of this consideration, we have recently reported a preliminary work on the synthesis of Bi_2-, Bi_3-, and the dendritic Bi_n-bismuthanes ($n = 4$, 10) bearing a sulfonamide group on the respective aromatic rings.[14] Since the phenylene unit works as a useful connector for the construction of the stabilized oligobismuth network, we undertook the synthesis of several oligomeric arylbismuth compounds with unsubstituted or sulfonyl-substituted phenylene bridges. Herein we report the synthesis and properties of a series of *meta*- and *para*-phenylene-bridged $Bi(III)_n$ and $Bi(V)_n$ compounds bearing two or more bismuth atoms in the framework.

Results and Discussion

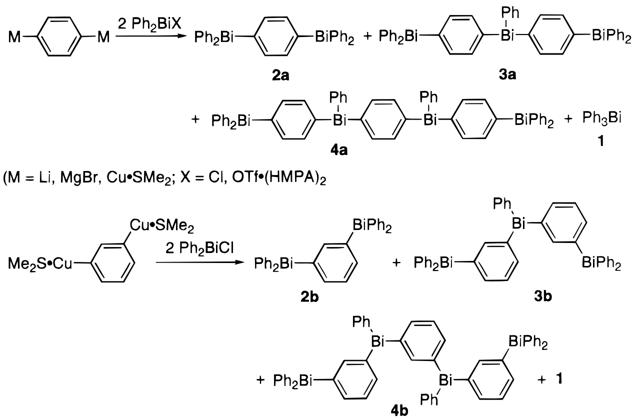
Synthesis of Unsubstituted Phenylene-Bridged Bi_n-Bismuth Compounds. As an entry to look into the basic property of oligomeric bismuth-containing compounds, we chose unsubstituted phenylene-bridged Bi_n-bismuthanes as the first target and compared their properties with those of triphenylbismuthane **1**. Thus, the synthesis of *p*-bis(diphenylbismuthino)benzene (**2a**) was first investigated. In the previous synthesis of **2a**, Zorn et al. reacted Ph_2BiCl with *p*-dilithiobenzene, in situ generated from *p*-dibromobenzene and *n*-BuLi in petroleum ether, and obtained the expected product in 14−20% yield.[5] Other products were not given in their report. Since the dilithiation seemed to us to be a key step for improving the efficiency of coupling,[15] we examined the alternative lithiation method proposed by Koo and Liebeskind for the high-yield synthesis of *p*-bis(tributylstannyl)benzene.[16] The iodolysis of *p*-dilithiobenzene, reportedly generated from *p*-dibromobenzene and *t*-BuLi, revealed that 4.4 equiv of *t*-BuLi was necessary for the exclusive formation of *p*-dilithiobenzene in a high yield; when 2.2 equiv of *t*-BuLi or *n*-BuLi was used under the same conditions (−78 to 0 °C, 1 h), the dilithiated benzene was produced at best in a 35% yield, together with a significant amount of monolithiated benzene (Scheme 1). *m*-Dilithiobenzene was similarly generated from *m*-dibromobenzene in a good yield by using 4.4 equiv of *t*-BuLi.[16]

Scheme 1



t-BuLi (4.4 equiv)	85–91%	0%
t-BuLi (2.2 equiv)	35%	35%
n-BuLi (2.2 equiv)	20%	67%

Scheme 2



(M = Li, MgBr, Cu•SMe$_2$; X = Cl, OTf•(HMPA)$_2$)

The present synthesis of **2a** was carried out under optimized conditions using *p*-dibromobenzene and 4.4 equiv of *t*-BuLi in THF or Et_2O. Treatment of *p*-dilithiobenzene with 2 equiv of Ph_2BiCl,[17] prepared in situ from a 2:1 mixture of **1** and $BiCl_3$, gave a complex mixture, from which Bi_2-bismuthane **2a** was isolated by gel permeation chromatography (GPC) in 9% yield. To our surprise, however, triphenylbismuthane **1**, Bi_3-bismuthane **3a**, and Bi_4-bismuthane **4a** were obtained as byproducts in 37, 2, and 2% yields, respectively (Scheme 2 and Table 1). All efforts to improve the yield of **2a** by varying the reaction time, temperature, and order of addition of the reagents have met with unfruitful results. Although the reason is not clear at present, the low yields of **2a** and other oligomeric products in the present reaction may partly be ascribed to the

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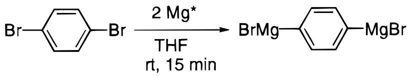
Table 1. Yields of Bi_n-Bismuthanes 1−4[a]

entry no.	MC_6H_4M	X	Bi_1 (**1**)	Bi_2 (**2**)	Bi_3 (**3**)	Bi_4 (**4**)
1	*p*-LiC_6H_4Li	Cl	37	9 (**2a**)	2 (**3a**)	2 (**4a**)
2	*p*-$BrMgC_6H_4MgBr$	OTf	21	28 (**2a**)	7 (**3a**)	3 (**4a**)
3	*p*-$Me_2S{\cdot}CuC_6H_4Cu{\cdot}SMe_2$	Cl	30	27 (**2a**)	13 (**3a**)	9 (**4a**)
4	*m*-$Me_2S{\cdot}CuC_6H_4Cu{\cdot}SMe_2$	Cl	27	26 (**2b**)	8 (**3b**)	2 (**4b**)

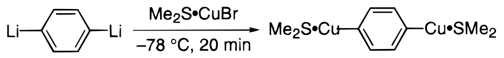
[a] Isolated yields based on the total bismuth.

disproportionation of the initial product via an ate complex of the type $[Ar_3Ar'Bi^-][Li^+]$, formed from the lithium reagent $Ar'Li$ and triarylbismuthane (Ar_3Bi).[18]

To circumvent this complexity, we next used the Grignard and organocopper reagents in place of dilithiobenzenes because these soft organometallic reagents were expected to suppress the disproportionation via the ate complex formation. The Grignard reagent was prepared by using Rieke's activated magnesium,[19] and the organocopper reagent was generated in situ through the transmetalation between *p*-dilithiobenzene and 2 equiv of $CuBr{\cdot}SMe_2$[20] (eqs 1 and 2).



(1)



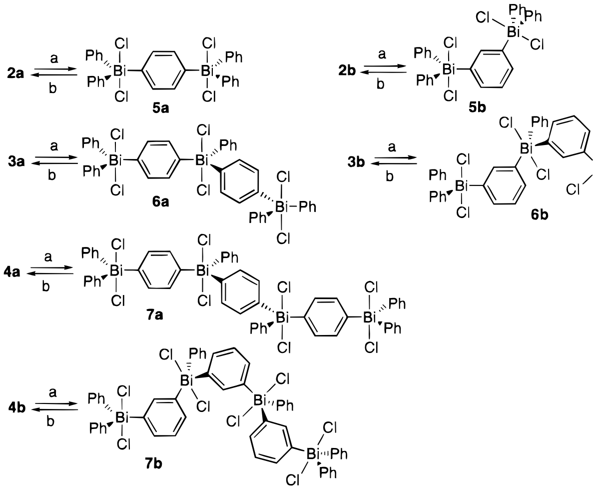
(2)

Both *p*-dimetallobenzenes thus obtained reacted smoothly with Ph_2BiOTf[21] and Ph_2BiCl under ambient conditions to give a mixture of Bi_n-bismuthanes (Table 1). Although the formation of higher oligomers could not be excluded completely, the isolated yields of **2a**, **3a**, and **4a** were higher as compared to those from the reaction with *p*-dilithiobenzene (entries 2, 3). A similar reaction of Ph_2BiCl with *m*-phenylene biscopper reagent, prepared from *m*-dilithiobenzene and $CuBr{\cdot}SMe_2$, afforded *meta*-phenylene-bridged Bi_n-bismuthanes **2b** (26%), **3b** (8%), and **4b** (2%) after GPC separation (entry 4). Although the methodology based on the use of dimetallobenzene proved to be inadequate for the exclusive synthesis of Bi_2-bismuthanes **2**, it still appears to be useful for the *one-pot* synthesis of oligomeric Bi_n-bismuthanes such as **3** and **4** from Ph_2BiX type bismuth compounds.

Para- and *meta*-phenylene-bridged Bi_n-bismuthanes **2−4** were oxidatively chlorinated by SO_2Cl_2 to afford the corresponding pentavalent bismuth polychlorides **5−7** (Scheme 3). By treatment with aqueous $Na_2S_2O_3$, compounds **5−7** were reductively dechlorinated to the original bismuthanes **2−4**.

All isolated products were fully characterized by NMR, IR, and MS spectroscopies as well as by elemental analysis. In the ^1H NMR spectra, protons of the phenylene bridges were always observed at lower field than those of the terminal phenyl groups irrespective of the valency of the bismuth atoms. In the *meta* isomers, for instance, the protons *ortho* to two bismuth atoms were observed at δ 8.03−8.10 for **2−4** and δ 9.90−9.93 for **5−7**, respectively. The lower chemical shifts of protons *ortho* to the pentavalent bismuth indicate that each bismuth center in **5−7** possesses a trigonal bipyramidal structure with two chlorine atoms at apical sites. Fast atom bombardment (FAB) mass spectra of bismuthanes **2−4** showed strong fragment peaks due to $[M-Ph]^+$ ions, while those of pentavalent bismuth compounds **5−7** displayed fragment peaks due to $[M-Cl]^+$ ions.

Scheme 3



Reagents and conditions: a, SO_2Cl_2 (*n* equiv), CH_2Cl_2, 0 °C to r.t. (*n* = 2 for **2**, *n* = 3 for **3**, *n* = 4 for **4**); b, $Na_2S_2O_3$ aq (excess), CH_2Cl_2, r.t.

To look into the basic optical property, UV−vis spectra of compounds **1−7** and Ph_3BiCl_2 (**8**)[22] were measured (Table 2).[23] Zorn et al. reported that the absorption maxima of **2a** in EtOH was not so different from those of triphenylbismuthane **1**,[5] although their extinction coefficients were considerably different.[24] In accord with this, the increase in number of bismuth atoms from two to four did not change the absorption maxima so much for a series of *para*- and *meta*-phenylene-bridged bismuthanes **2−4**, indicating that

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[18] Disproportionation via an ate complex of the type $[R_3BiR'^-][M^+]$ has been suggested for some reactions of triorganylbismuthanes with Grignard and lithium reagents: (a) Gilman, H.; Yablunkly, H. L.; Svigoon, A. C. *J. Am. Chem. Soc.* **1939**, *61*, 1170. (b) Gilman, H.; Yale, H. L. *J. Am. Chem. Soc.* **1950**, *72*, 8. (c) Kauffmann, T.; Steinseifer, F. *Chem. Ber.* **1985**, *118*, 1031. However, we cannot exclude the possibility that a trace amount of $PhBiCl_2$ induced the oligomeric coupling to form **3a** and **4a**.

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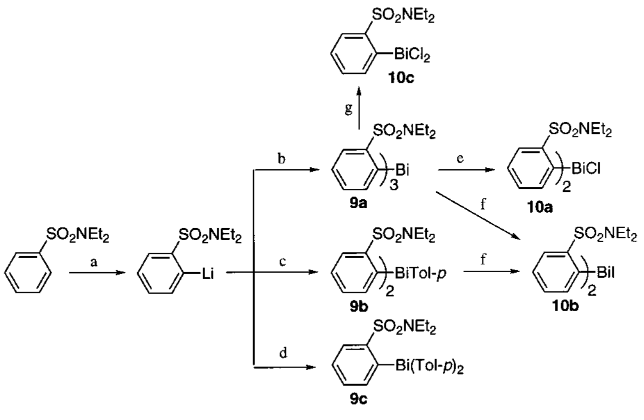
[24] The extinction coefficients of two characteristic bands at λ_{max} 248 and 280 nm for **1** (in EtOH) were $\epsilon = 1.29 \times 10^4$ and 0.42×10^4,[23c] while those at λ_{max} 248 and 279 nm for **2a** (in EtOH) were $\epsilon = 4.0 \times 10^4$ and 2.1×10^4, respectively.[5]

Table 2. UV−Vis Spectra of Bi_n-Bismuth Compounds 1−8[a]

1−4 (n)	λ_{max}/nm ($\epsilon \times 10^{-4}$/M^{-1} cm^{-1})	**5−8**[b](n)	λ_{max}/nm ($\epsilon \times 10^{-4}$/M^{-1} cm^{-1})
1 (1)	244 (1.5), 285 (0.4)	**8** (1)	244 (1.9)
2a (2)	246 (3.6), 285 (1.3)	**5a** (2)	246 (4.8)
3a (3)	247 (6.0), 285 (2.4)	**6a** (3)	246 (8.2)
4a (4)	249 (9.2), 285 (4.1)	**7a** (4)	246 (12)
2b (2)	244 (3.3), 285 (1.0)	**5b** (2)	244 (3.8), 260 (3.1)
3b (3)	246 (5.4), 285 (1.7)	**6b** (3)	244 (5.5), 260 (4.9)
4b (4)	247 (7.1), 285 (2.4)	**7b** (4)	244 (7.2), 260 (6.2)

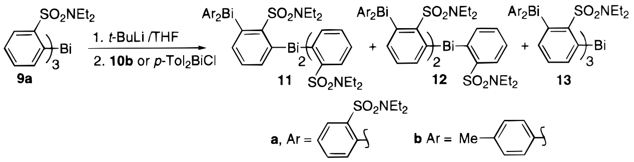
[a] Measured in chloroform at room temperature. [b] A shoulder was observed at around 285−290 nm. Its extinction coefficient was not estimated due to the broad nature of the absorption band.

Scheme 4



Reagents and conditions: a, n-BuLi, Et_2O or THF, –78 °C, 1.5 h; b, $BiCl_3$ (1/3 equiv), Et_2O or THF, –78 °C~r.t.; c, p-$TolBiCl_2$ (1/2 equiv), Et_2O, –78 °C~r.t.; d, p-Tol_2BiCl, Et_2O, –78 °C~r.t.; e, SO_2Cl_2, CH_2Cl_2, –40 °C~r.t.; f, I_2, acetone, r.t., 1.5 h.; g, $BiCl_3$ (2 equiv), C_6H_6, reflux, 1.5 h

Scheme 5

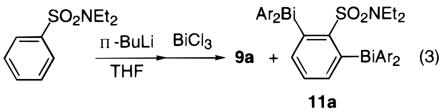


the introduction of the phenylene bridges did not affect significantly the strength of the Bi−C bond nor the extent of delocalization of π electrons over the molecules. Hypervalent compounds **5**−**8** showed similar trends, the absorption maxima appearing in almost the same region with no bathochromic shift as those of trivalent bismuthanes **1**−**4**. This suggests that the phenylene bridge placed at equatorial position causes little effect on the delocalization of electrons over the molecule. The extinction coefficients of **1**−**8** at λ_{max} 244−246 nm increased with increasing number of bismuth atoms according to simple amplification. The observed UV−vis spectra suggest that the unsubstituted phenylene units do not perturb significantly the σ- and π-transitions of the aromatic systems in polyarylated bismuth oligomers both in the tri- and pentavalent states of the bismuth.

Synthesis of *Meta*-Phenylene-Bridged Bi_n-Bismuth Compounds. We next employed an alternative strategy to construct the phenylene-bridged oligobismuth framework by using *ortho*-lithiation of aromatic sulfonamides.[25] The sulfonamide moiety is recognized as a good directing group in the *ortho*-lithiation[26] and has recently been applied to the synthesis of highly branched bismuthanes having the *m*-phenylene network.[14]

Reaction of $BiCl_3$ with 3 equiv of *ortho*-lithiated benzenesulfonamide, generated from *N*,*N*-diethylbenzenesulfonamide and *n*-BuLi in THF at −78 °C, gave tris[2-(*N*,*N*-diethylsulfamoyl)phenyl]bismuthane (**9a**) in 63% yield (Scheme 4). Unsymmetrical triarylbismuthanes were similarly prepared; the reaction between p-$Tol_{3-n}BiCl_n$ and n equiv of ArLi [n = 1 or 2, Ar = 2-(*N*,*N*-diethylsulfamoyl)phenyl] yielded p-$TolBiAr_2$ (**9b**) (64%) and p-Tol_2BiAr (**9c**) (62%). Reaction of **9a** with 1 equiv of SO_2Cl_2 in CH_2Cl_2 afforded Ar_2BiCl (**10a**) in 78% yield, whereas treatment of **9a** or **9b** with iodine gave Ar_2BiI (**10b**) in 83 and 78% yields, respectively. Metathesis between **9a** and 2 equiv of $BiCl_3$ yielded $ArBiCl_2$ (**10c**) in 85% yield.

During the course of optimizing the formation of **9a**, we observed that Bi_2-bismuthane **11a** was formed as a byproduct depending on the conditions (eq 3).



(3)

Compound **11a** was likely to be formed via the *ortho*-lithiation of one aryl ring of **9a**, followed by coupling with **10a** present as a precursor to **9a** in the reaction system. This was confirmed by the independent synthesis of **11a** from **9a**, *t*-BuLi, and **10b**, as shown in Scheme 5; the *ortho*-lithiation of **9a** with 1.1 equiv of *t*-BuLi followed by treatment with 1 equiv of **10b** at −78 °C yielded **11a**, Bi_3-bismuthane **12a**, and unchanged **9a**, in 37, 18, and 25% yields, respectively (Table 3, run 1). These compounds were separated by column chromatography on silica gel.

A *tert*-butyl sulfone-substituted Bi_2-bismuthane **15** was also prepared using the similar *ortho*-lithiation methodology (Scheme 6). Thus, the reaction of p-Tol_2-BiCl with the lithiated bismuthane generated from a sulfone-substituted bismuthane **14**[25b] and lithium 2,2,6,6-tetramethylpiperidide gave **15** in 40% yield. Cleavage of two Bi−C bonds in **15** with $BF_3{\cdot}OEt_2$ followed by treatment with brine gave Bi_2-chlorobismuthane **16** in 59% yield.

The crystal structure of Bi_2-chlorobismuthane **16** was successfully determined by an X-ray diffraction analysis. The ORTEP diagram is depicted in Figure 1, and the

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(25) *Ortho*-lithiated arenes have successfully been used for the preparation of *ortho*-sulfonyl-substituted triarylbismuthanes; see ref 14 and (a) Suzuki, H.; Murafuji, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1593. (b) Suzuki, H.; Murafuji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1143. (c) Suzuki, H.; Murafuji, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1169.

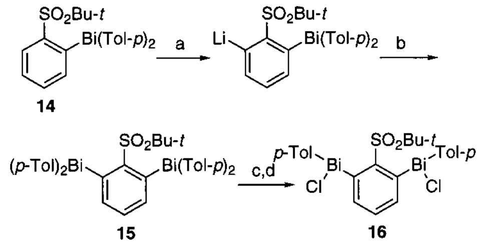
(26) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. *Ortho*-lithiation of benzenesulfonamide, see: Watanabe, H.; Schwarz, R. A.; Hauser, C. R.; Lewis, J.; Slocum, D. W. *Can. J. Chem.* **1969**, *47*, 1543.

Table 3. Yields of Bi_n-Bismuthanes[a]

				isolated yield (%)			
run	*t*-BuLi (equiv)	Ar_2BiX (equiv)	temp[b] (°C)	Bi_1	Bi_2	Bi_3	Bi_4
1	1.1	**10b** (1.0)	−78	**9a** (25)	**11a** (37)	**12a** (18)	**13a** (0)
2	3.3	**10b** (3.0)	−78	**9a** (9)	**11a** (7)	**12a** (31)	**13a** (0)
3	3.3	**10b** (3.0)	−78 to −20	**9a** (4)	**11a** (9)	**12a** (11)	**13a** (13)
4	3.3	**10b** (3.0)	−78 to 0	**9a** (6)	**11a** (2)	**12a** (8)	**13a** (49)
5[c]	3.3	*p*-Tol_2BiCl (3.0)	−78 to −30	**9a** (2)	**11b** (2)	**12b** (6)	**13b** (11)

[a] Isolated yields based on the total bismuth. [b] Temperature for *ortho*-lithiation. [c] *p*-Tol_3Bi was obtained in 13% yield.

Scheme 6



Reagents and conditions: a, *N*-lithio-2,2,6,6-tetramethylpiperidine, THF, –50 °C, 1 h; b, *p*-Tol_2BiCl (2 equiv), Et_2O, –78 °C~r.t.; c, BF_3•OEt_2 (6 equiv), C_6H_6, 10 °C; d, $NaCl_{aq}$ (excess).

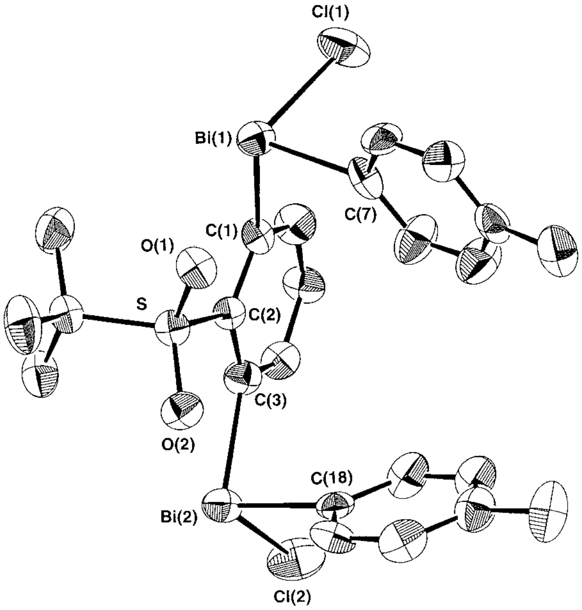


Figure 1. ORTEP drawing of compound **16** with the atom-numbering scheme.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of Compound 16 with Estimated Standard Deviations in Parentheses

	Bond Lengths		
Bi(1)−C(1)	2.285(9)	Bi(2)−Cl(2)	2.546(3)
Bi(1)−C(7)	2.235(9)	S−O(1)	1.455(6)
Bi(1)−Cl(1)	2.559(3)	S−O(2)	1.453(6)
Bi(2)−C(3)	2.285(9)	Bi(1)−O(1)	2.666(6)
Bi(2)−C(18)	2.230(9)	Bi(2)−O(2)	2.693(6)
	Bond Angles		
C(1)−Bi(1)−C(7)	96.0(3)	Cl(2)−Bi(2)−C(18)	91.3(3)
Cl(1)−Bi−C(1)	92.2(2)	O(1)−S−C(2)	107.7(4)
Cl(1)−Bi−C(7)	89.7(2)	O(2)−S−C(2)	107.6(4)
C(3)−Bi(2)−C(18)	91.8(3)	O(1)−Bi(1)−Cl(1)	161.1(2)
Cl(2)−Bi(2)−C(3)	91.5(3)	O(2)−Bi(2)−Cl(2)	160.4(2)

selected bond parameters are summarized in Table 4. Two bismuth atoms essentially possess a trigonal pyramidal geometry with the C−Bi−X (X = C, Cl) angles of 89.7(2)−96.0(3)°. Two tolyl groups are oriented perpendicular to the *m*-phenylene unit, suggesting that the effective $\pi-\pi$ interaction is not likely to operate among the aromatic rings. The sulfonyl oxygen atoms were found to coordinate weakly to each bismuth center with the Bi−O bond distances of 2.666(6) and 2.693(6) Å. If we take this finding into consideration, the geometry of the bismuth centers may also be regarded as a pseudo-trigonal bipyramid with two aryl carbon atoms and one lone pair at equatorial sites and the oxygen and chlorine atoms at apical sites. The Bi−O bond distances are nearly identical with those observed for the related sulfonyl-substituted diarylbismuth chlorides.[25a,b] The relatively longer Bi−Cl bonds of 2.546(3)−2.559(3) Å as well as the O−Bi−Cl bond angles of 160.4(2)−161.1(2)° may be taken to support the hypervalent state of **16**. Attempts to elucidate the molecular structure of other Bi_n-bismuthanes have so far met with failure.

Synthesis of Highly Branched and Dendritic Bi_n-Bismuth Compounds. The formation of Bi_3-bismuthane **12a** implies that the ease of *ortho*-lithiation of the aryl rings in **9a** and **11a** is not very different, which suggested to us the idea of preparing highly branched oligomeric bismuth compounds. After several trials, efficient *one-pot* introduction of three diarylbismuthino groups into each aryl ring of **9a** was accomplished by using *t*-BuLi and **10b** (Scheme 5 and Table 3). The lithiation of **9a** with 3.3 equiv of *t*-BuLi for 1 h at 0 °C followed by treatment with 3 equiv of **10b** at −78 °C afforded Bi_4-bismuthane **13a** in 49% yield, together with small amounts of **9a**, **11a**, and **12a** (run 4). When the lithiation was performed at temperatures below −20 °C, the yield of **13a** was low or nearly zero (runs 2, 3). These results showed that the *ortho*-lithiation of all aryl rings of **9a** efficiently took place above 0 °C. When *p*-Tol_2BiCl was used in place of **10b**, *p*-tolyl-substituted Bi_n-bismuthanes **11b**, **12b**, and **13b** were obtained in 2, 6, and 11% yields, respectively (run 5).

Since the first discovery in early 1980s by Tomalia[27] and Newkome,[28] the dendritic compounds have attracted many researchers in polymer and material science fields due to their unique properties arising from the structural symmetry, shape, and branching patterns.[29] The present *ortho*-lithiation methodology for

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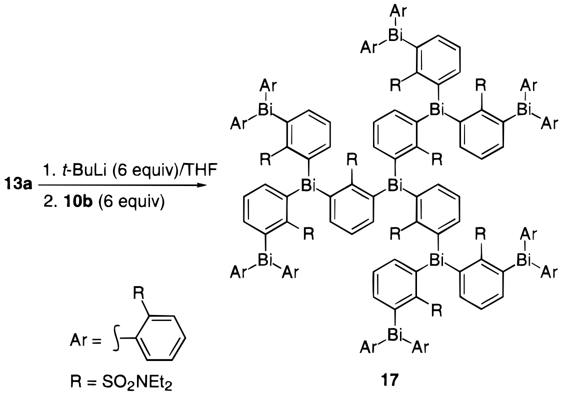
(27) Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117.

(28) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003.

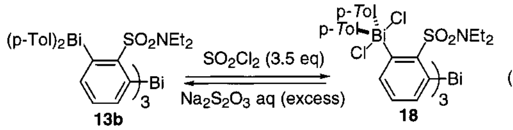
(29) For example, see: (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Mekelburger, H.-B.; Jaworek, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1571. (c) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (d) Hawker, C. J.; Fréchet, J. M. J. In *New Methods in Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, Scotland, 1995; pp 290−330.

introducing multiple diarylbismuthino moieties directly into the aromatic rings has enabled us to synthesize a dendritic Bi_{10}-bismuthane **17** from **13a**; the lithiation of **13a** with 6 equiv of *t*-BuLi at 0 °C followed by treatment with 6 equiv of **10b** at lower temperatures gave a mixture of oligobismuth compounds, from which the Bi_{10}-dendrimer **17** was isolated in 20% yield after GPC and column chromatography on silica gel (eq 4).



(4)

When treated with 3.5 equiv of SO_2Cl_2, Bi_4−bismuthane **13b** underwent oxidative chlorination to give Bi_4-bismuth hexachloride **18** in 55% yield (eq 5). Compound **18** possesses three pentavalent bismuth atoms on the outer side and one trivalent bismuth at the core. Treatment of **18** with $Na_2S_2O_3$ regenerated the parent Bi_4-bismuthane **13b** in 92% yield (eq 5). These findings imply that the molecular geometry and physical property of this type of bismuth-derived dendritic compounds can be reversibly interchangeable according to the change of oxidation state from Bi(III) to Bi(V) and vice versa by simple oxidation−reduction processes.



(5)

Meta-phenylene-bridged Bi_n-bismuthanes **11**−**17** were characterized by NMR, MS, and IR as well as by elemental analysis. The spectral features of Bi_{10}-bismuthane **17** are as follows: in the ^{13}C NMR spectrum, three distinct sets of resonances were observed for three nonequivalent ethyl groupings at δ 41.8, 40.3, and 40.0 for the methylene carbons and at δ 14.1, 13.0, and 12.7 for the methyl carbons, respectively. Judging from the relative strength of the peaks, we assigned these sets to the ethyl groups attached to the outermost, middle, and core benzene rings in this order. Simple NMR peak patterns observed suggested a high molecular symmetry in accord with the dendritic structure of this compound. In the MALDI-TOF mass spectrum, a $[M+Na]^+$ peak was detected at *m*/*z* 6558.1 (calc 6561.9). In the sense of atomic weight of a key element involved, compound **17** represents the *heaviest* example of dendrimers so far reported.

The UV−vis spectra of a series of Bi_n−bismuthanes bearing sulfamoyl groups, **9a, 11a**, **12a**, **13a**, and **17**, exhibited no bathochromic shift of λ_{max} (Table 5 and Figure 2). The inefficient π-electron delocalization would probably be due to the twisted geometry between the aromatic rings, as inferred from the X-ray structure of the related Bi_2-chlorobismuthane **16**. Similarly to the unsubstituted phenylene-bridged Bi_n-bismuthanes, the extinction coefficients at λ_{max} increased with increasing number of bismuth atoms. One interesting feature of the UV−vis spectra was that the skirt of the absorptions considerably broadened in the branched bismuthanes; bismuthane **9a** did not absorb light above 350 nm, but Bi_{10}-dendrimer **17** absorbed it weakly.

Table 5. UV−Vis Spectra of Bi_n-Bismuthanes 9a, 11a, 12a, 13a, and 17[a]

compd (*n*)	λ_{max}/nm ($\epsilon \times 10^{-4}$/M^{-1} cm^{-1})
9a (1)	244 (2.0), 274 (0.9), 281 (0.8)
11a (2)	244 (4.3), 275 (2.0), 281 (2.0)
12a (3)	244 (6.3), 275 (2.8), 282 (3.0)
13a (4)	244 (9.0), 274 (4.1), 281 (4.3)
17 (10)	244 (25.1), 274 (11.4), 281 (12.2)

[a] Measured in chloroform at room temperature.

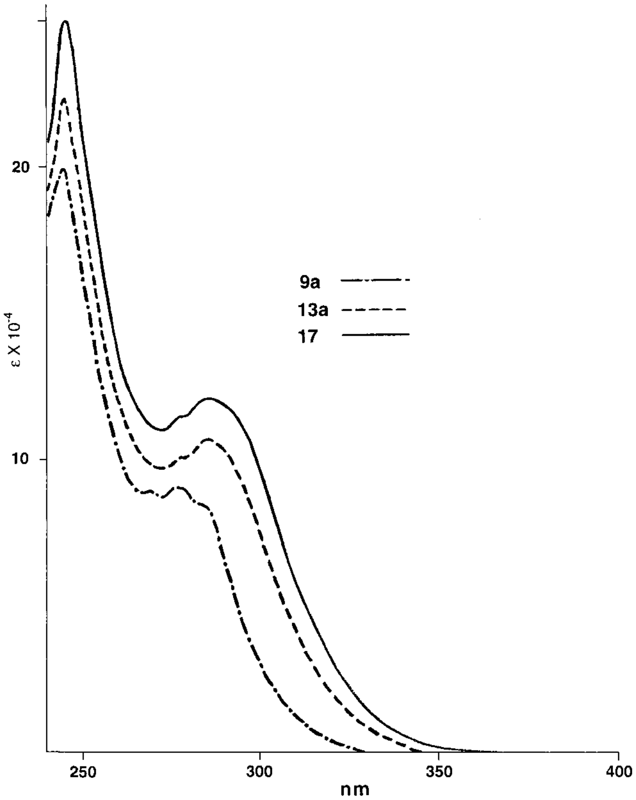
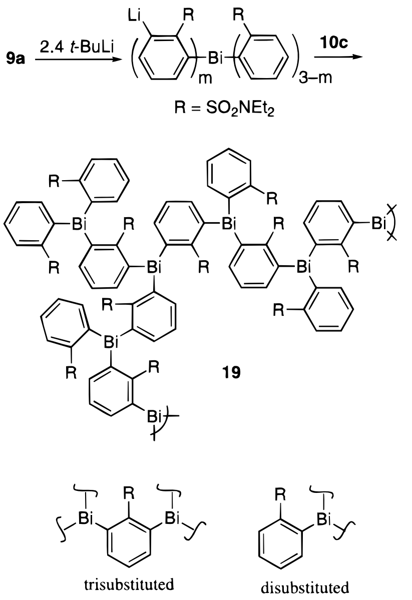


Figure 2. Comparison of UV−vis absorbance per Bi atom of **9a** (1 Bi; × 10), **13a** (4 Bi; × 2.5), and **17** (10 Bi; × 1) in chloroform at room temperature.

The present *ortho*-lithiation methodology was extended to the synthesis of hyperbranched bismuthane oligomers; successive treatment of **9a** with 2.4 equiv of *t*-BuLi and 1 equiv of **10c** in THF produced a pale yellow polar solid after usual workup, which was separated into two main fractions **19a,b** by fractional recrystallization from CH_2Cl_2/MeOH (Scheme 7). GPC analyses of these fractions by using a JEIGEL-3H column (critical molecular weight ~7 × 10^4) showed that they were a mixture of highly branched oligobismuthanes of different size. They melted around 260 °C with partial decomposition, at temperature much higher as compared with **9a** (mp 122−124 °C).

Proton NMR spectra of these solids were rather complicated owing to the broadened nature of peak

Scheme 7



patterns that did not change significantly between −55 °C (in $CDCl_3$) and 150 °C (in DMSO-d_6), while ^{13}C NMR spectra showed two sets of broad peaks attributable to two kinds of nonequivalent ethyl carbons at δ 12.9 and 40.3 and δ 14.1 and 41.8, respectively. On the basis of the spectral features, the former set was assigned to the ethyl groups of trisubstituted aromatic rings and the latter to those of disubstituted aromatic rings (Scheme 7). MALDI-TOF mass spectra of these fractions showed several peaks at 2529.4, 1896.8, 1246.6, and 633.0 with a regular interval of 633, indicating that they are composed of the $Ar^IAr^{II}Bi$ network (Ar^I = 2-$Et_2NSO_2C_6H_4$; Ar^{II} = 3-**Bi**-2-$Et_2NSO_2C_6H_3$, **Bi** = diarylbismuthino unit; $Ar^IAr^{II}Bi$ (excluding **Bi** = 633)). Elemental analysis also supported this interpretation. The mean molecular weights of fractions **19a,b** determined by vapor depression measurement were 10240 and 4360, respectively, indicating that the average numbers of bismuth atoms present were 16 for fraction **19a** and 7 for fraction **19b**. They were found to absorb UV light around 350−400 nm more effectively as compared to simple bismuthanes, suggesting that the higher bismuthane oligomers can cut a short wave region from sun light.

The present study has shown for the first time that the polybismuth network can be constructed by a simple one-pot polymetalation methodology. Especially, the *ortho*-lithiation directed by the sulfone moiety was found to be an efficient tool for the construction of dendritic and highly branched-chain oligomeric bismuthanes.

Experimental Section

General. All reactions with air-sensitive compounds were carried out under an atmosphere of argon. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR were recorded on a Varian Gemini-200 or a JEOL 400 spectrometer. $CDCl_3$ was used as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs tetramethylsilane, and coupling constants *J* are given in Hz. IR spectra were observed as a KBr pellet on a Shimadzu FTIR-8100S spectrophotometer and reported as cm^{-1} (see Supporting Information for full data of IR spectra). EI, FAB, and MALDI mass spectra were obtained on a Shimadzu GCMS-QP2000A, a JEOL JMS-HS110, and 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. GPC was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC. UV−vis measurements were performed in chloroform at room temperature on a Shimadzu UV-3000 spectrometer. The solvent did not interfere with the absorbance at λ_{max}, and the extinction coefficients were calculated according to the Lambert−Beer equation. Vapor pressure osmometry was carried out in chloroform at 35 °C by means of a Knauer digital vapor pressure osmometer with benzil as a standard. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University.

Materials. Column chromatography was performed on silica gel (Wakogel C200) or alumina (Merck aluminum oxide 90, neutral, activity I). Dichloromethane (CH_2Cl_2) was distilled from CaH_2 before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl before use. CuBr·SMe_2 was prepared according to the reported method.[20] *N,N*-Diethylbenzenesulfonamide was prepared from benzenesulfonyl chloride and diethylamine according to the reported procedure.[30] Other reagents were used as commercially received.

Synthesis of Phenylene-Bridged Bi$_n$-Bismuthanes 2−4. From *p*-Dilithiobenzene. To a solution of *p*-dibromobenzene (59 mg, 0.25 mmol) in THF (2 mL) was added dropwise a pentane solution of *t*-BuLi (1.67 M × 0.66 mL, 1.1 mmol) at −78 °C. The resulting yellow solution was allowed to warm to 0 °C and stirred for 1 h at this temperature, during which time the yellow solution changed to a white creamy suspension. Iodolysis of the resulting mixture produced *p*-diiodobenzene in 85% yield, showing that *p*-dilithiobenzene was generated at least in 85% yield. To the suspension of dilithiobenzene cooled to −78 °C was added Ph_2BiCl, generated in situ from triphenylbismuthane **1** (147 mg, 0.334 mmol) and $BiCl_3$ (53 mg, 0.17 mmol) in THF (2 mL). The resulting mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. Brine (5 mL) was poured into the mixture, and the organic phase was separated. The water phase was extracted with ethyl acetate (5 mL × 2), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent under reduced pressure left an oily residue, which was passed through an alumina column using hexanes/ethyl acetate as the eluent to remove insoluble and highly polar substances. GPC separation followed by recrystallization from MeOH yielded **1** (81 mg, 37%), Bi$_2$-bismuthane **2a** (17 mg, 9%), Bi$_3$-bismuthane **3a** (5 mg, 2%), and Bi$_4$-bismuthane **4a** (3 mg, 2%).

From *p*-Bis(bromomagnesio)benzene. A mixture of $MgCl_2$ (0.38 g, 4.0 mmol), potassium (0.31 g, 8.0 mmol), KI (0.33 g, 2.0 mmol), and THF (8 mL) was heated at reflux for 3 h. To the resulting black suspension of activated magnesium was added a solution of *p*-dibromobenzene (236 mg, 1.00 mmol) in THF (2 mL) at room temperature. After stirring for 3 h at this temperature, the suspension was treated with a solution of diphenylbismuth triflate−HMPA complex[21] (1.16 g, 1.33 mmol) in THF (13 mL) at 0 °C. The resulting mixture was allowed gradually to warm to room temperature and stirred for 3 h. Usual workup as described above afforded **1** (124 mg, 21%), **2a** (151 mg, 28%), **3a** (36 mg, 7%), and **4a** (15 mg, 3%).

From *p*-Dicuprobenzene−Bis(dimethyl sulfide) Complex. To a white creamy suspension of *p*-dilithiobenzene generated from *p*-dibromobenzene (472 mg, 2.0 mmol) and *t*-BuLi (pentane solution, 1.6 M × 5.2 mL, 8.3 mmol) in THF (14 mL) was added CuBr·SMe_2 (863 mg, 4.2 mmol) in one portion at −78 °C. The color changed to yellow. After stirring for 20 min, a THF solution (14 mL) of Ph_2BiCl prepared from

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(30) Ginzberg, A. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2703.

1 (1.174 g, 2.67 mmol) and $BiCl_3$ (420 mg, 1.33 mmol) was slowly added at the same temperature. The resulting mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. Brine (30 mL) was poured, and the organic phase was separated. The water phase was extracted with ethyl acetate (20 mL × 2), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent under reduced pressure left an oily residue, which was passed through a silica gel column with hexane/ethyl acetate as the eluent to remove insoluble and highly polar substances. GPC separation followed by recrystallization from MeOH yielded **1** (524 mg, 30%), **2a** (433 mg, 27%), **3a** (206 mg, 13%), and **4a** (139 mg, 9%). A similar reaction starting from *m*-dibromobenzene (472 mg, 2.0 mmol) yielded **1** (474 mg, 27%) and the corresponding *m*-phenylene-bridged Bi_n-bismuthanes **2b** (422 mg, 26%), **3b** (131 mg, 8%), and **4b** (36 mg, 2%).

Bi_2-Bismuthane 2a: mp 158−160 °C (lit.,[5] 160−162 °C); ^{1}H NMR δ 7.34 (m, 12H), 7.73 (dd, 8H, J = 1.5, 7.6), 7.75 (s, 4H); δ_C 127.7, 130.5, 137.6, 139.5, 154.5−155.5 (broad); FABMS m/z 803 ($[M + H]^+$), 725, 571, 495, 439, 307. Anal. Calcd for $C_{30}H_{24}Bi_2$: C, 44.90; H, 3.01. Found: C, 45.08; H, 2.99.

Bi_3-Bismuthane 3a: mp 55−58 °C; ^{1}H NMR δ 7.30−7.41 (m, 15H), 7.72 (dd, 10H, J = 1.5, 7.5), 7.74 (s, 8H); FABMS m/z 1087 ($[M - Ph]^+$), 725, 571, 418. Anal. Calcd for $C_{42}H_{33}Bi_3$: C, 43.31; H, 2.86. Found: C, 43.11; H, 2.75.

Bi_4-Bismuthane 4a: mp 75−79 °C; ^{1}H NMR δ 7.30−7.40 (m, 18H), 7.71−7.73 (m, 24H); FABMS m/z 1449 ($[M - Ph]^+$), 627, 495, 418. Anal. Calcd for $C_{54}H_{42}Bi_4$: C, 42.48; H, 2.77. Found: C, 42.71; H, 2.74.

Bi_2-Bismuthane 2b: mp 114−115 °C; ^{1}H NMR δ 7.25−7.42 (m, 13H), 7.64−7.76 (m, 10H), 8.10 (s, 1H); FABMS m/z 725 ($[M - Ph]^+$), 571, 495, 439. Anal. Calcd for $C_{30}H_{24}Bi_2$: C, 44.90; H, 3.01. Found: C, 44.58; H, 3.04.

Bi_3-Bismuthane 3b: mp 39−43 °C; ^{1}H NMR δ 7.21−7.36 (m, 17H), 7.58−7.69 (m, 14H), 8.07 (s, 2H); FABMS m/z 1087 ($[M - Ph]^+$), 801, 725, 627, 571, 495, 418. Anal. Calcd for $C_{42}H_{33}Bi_3$: C, 43.31; H, 2.86. Found: C, 43.04; H, 2.78.

Bi_4-Bismuthane 4b: mp 59−62 °C; ^{1}H NMR δ 7.25−7.35 (m, 21H), 7.59−7.68 (m, 18H), 8.03 (s, 1H), 8.06 (s, 2H); FABMS m/z 1449 ($[M - Ph]^+$), 1371, 1293, 1163, 1087, 1009, 725, 627, 571, 495, 418. Anal. Calcd for $C_{54}H_{42}Bi_4$: C, 42.48; H, 2.77. Found: C, 42.67; H, 2.72.

Bi_2-Bismuth Tetrachloride 5a. To a solution of Bi_2-bismuthane **2a** (48 mg, 0.060 mmol) in CH_2Cl_2 (1 mL) was added SO_2Cl_2 (9.6 μL, 0.12 mmol) at 0 °C. The mixture was stirred at room temperature for 30 min. Evaporation of the volatiles under reduced pressure gave Bi_2-bismuth tetrachloride **5a** as a white solid (57 mg, 100%). Other Bi_n-polychlorides **5b**, **6a**, **6b**, **7a**, and **7b** were obtained quantitatively by similar treatment of the corresponding Bi_n-bismuthanes **2b**, **3a**, **3b**, **4a**, and **4b** with a suitable amount of SO_2Cl_2 in CH_2Cl_2.

Bi_2-Bismuth Tetrachloride 5a: mp 180−185 °C (decomp); ^{1}H NMR δ 7.56 (t, 4H, J = 7.2), 7.69 (t, 8H, J = 7.6), 8.53 (d, 8H, J = 8.1), 8.78 (s, 4H); FABMS m/z 907 ($[M - Cl]^+$), 795. Anal. Calcd for $C_{30}H_{24}Bi_2Cl_4$: C, 38.16; H, 2.56. Found: C, 37.59; H, 2.64.

Bi_3-Bismuth Hexachloride 6a: mp 122−130 °C (decomp); ^{1}H NMR δ 7.52−7.60 (m, 5H), 7.69 (t, 10H, J = 7.6), 8.53 (d, 10H, J = 8.1), 8.79 (s, 8H); FABMS m/z 1339 ($[M - Cl]^+$), 1227, 1185, 795, 753, 391. Anal. Calcd for $C_{42}H_{33}Bi_3Cl_6$: C, 36.62; H, 2.41. Found: C, 36.67; H, 2.62.

Bi_4-Bismuth Octachloride 7a: mp 152−160 °C (decomp); ^{1}H NMR δ 7.52−7.60 (m, 6H), 7.69 (t, 12H, J = 7.2), 8.53 (d, 12H, J = 8.1), 8.79−8.80 (m, 12H); FABMS m/z 1771 ($[M - Cl]^+$), 1659, 391. Anal. Calcd for $C_{54}H_{42}Bi_4Cl_8$: C, 35.82; H, 2.34. Found: C, 35.87; H, 2.23.

Bi_2-Bismuth Tetrachloride 5b: mp 148−154 °C (decomp); ^{1}H NMR δ 7.54 (t, 4H, J = 7.2), 7.68 (t, 8H, J = 7.4), 7.91 (t, 1H, J = 8.0), 8.55 (d, 8H, J = 8.3), 8.73 (d, 2H, J = 7.8), 9.90 (s, 1H); FABMS m/z 907 ($[M - Cl]^+$), 795, 753, 474, 397, 321. Anal. Calcd for $C_{30}H_{24}Bi_2Cl_4$: C, 38.16; H, 2.56. Found: C, 37.95; H, 2.56.

Bi_3-Bismuth Hexachloride 6b: mp 87 °C (decomp); ^{1}H NMR δ 7.54 (t, 5H, J = 7.3), 7.68 (t, 10H, J = 7.5), 7.93 (t, 2H, J = 8.2), 8.54 (d, 10H, J = 8.0), 8.75 (br-d, 4H), 9.91 (s, 2H); FABMS m/z 1339 ($[M - Cl]^+$), 1227, 1185, 795, 753, 474, 391, 321. Anal. Calcd for $C_{42}H_{33}Bi_3Cl_6$: C, 36.62; H, 2.41. Found: C, 36.41; H, 2.40.

Bi_4-Bismuth Octachloride 7b: mp 103−106 °C (decomp); ^{1}H NMR δ 7.53 (t, 6H, J = 7.0), 7.67 (t, 12H, J = 7.5), 7.92 (t, 2H, J = 7.8), 7.94 (t, 1H, J = 7.9), 8.53 (d, 8H, J = 7.7), 8.56 (d, 4H, J = 7.3), 8.71−8.79 (m, 6H), 9.91 (s, 2H), 9.93 (s, 1H); FABMS m/z 1771 ($[M - Cl]^+$), 1659, 795, 391, 321. Anal. Calcd for $C_{54}H_{42}Bi_4Cl_8$: C, 35.82; H, 2.34. Found: C, 35.54; H, 2.48.

Reduction of Bi_n-Bismuth Polychlorides 5−7 to Bi_n-Bismuthanes 2−4. A typical example is as follows: a saturated aqueous $Na_2S_2O_3$ (5 mL) solution was added to a solution of **5a** (125 mg, 0.132 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After stirring for 8 h, the organic phase was separated and the water phase was extracted with CH_2Cl_2 (5 mL × 2). Evaporation of the combined organic phase under reduced pressure followed by recrystallization from MeOH yielded **2a** (83 mg, 78%). Other compounds **5b**, **6a**, **6b**, **7a**, and **7b** were similarly reduced by $Na_2S_2O_3$ to the corresponding Bi_n-bismuthanes **2b**, **3a**, **3b**, **4a**, and **4b** in 71, 70, 68, 45, and 61% yields, respectively. Alumina column chromatography and GPC separation were used for the isolation of respective Bi_n-bismuthanes.

Tris[2-(*N,N*-diethylsulfamoyl)phenyl]bismuthane (9a). To a THF solution (200 mL) of *N,N*-diethylbenzenesulfonamide (17.7 g, 83.0 mmol) was added *n*-BuLi (hexane solution, 1.5 M × 55 mL, 83 mmol) at −78 °C. After stirring at this temperature for 1 h, $BiCl_3$ (9.9 g, 31 mmol) was added, and the resulting yellow mixture was warmed gradually to room temperature with stirring. After 12 h, brine (100 mL) was added, and the insoluble substances were filtered off through Celite. The filtrate was separated, and the water phase was extracted with ethyl acetate (50 mL × 2). The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was crystallized from MeOH to give bismuthane **9a** (16.5 g, 63% based on $BiCl_3$) as a colorless solid: mp 122−124 °C; ^{1}H NMR δ 1.15 (t, 18H, J = 7.3, CH_2CH_3), 3.30 (q, 12H, J = 7.3, CH_2CH_3), 7.34 (t, 3H, J = 7.0), 7.48 (t, 3H, J = 7.4), 7.69 (d, 3H, J = 6.6), 7.99 (d, 3H, J = 7.6); ^{13}C NMR δ 13.9, 41.7, 127.8, 129.2, 135.2, 140.8, 144.4, 172.7; IR ν_{max} 1321 (SO_2), 1150 (SO_2); FABMS m/z 633 (Ar_2Bi^+), 421, 361, 333, 285, 209. Anal. Calcd for $C_{30}H_{42}BiN_3O_6S_3$: C, 42.60; H, 5.00; N, 4.97. Found: C, 42.86; H, 5.13; N, 4.77.

Bis[2-(*N,N*-diethylsulfamoyl)phenyl](4-methylphenyl)bismuthane (9b). A mixture of tris(4-methylphenyl)bismuthane (241 mg, 0.500 mmol), $BiCl_3$ (315 mg, 0.999 mmol), and Et_2O (10 mL) was stirred at room temperature for 1 h. To the resulting yellow suspension was added at −78 °C a Et_2O suspension (20 mL) of *ortho*-lithiated *N,N*-diethylbenzenesulfonamide, generated from *N,N*-diethylbenzenesulfonamide (639 mg, 3.00 mmol) and *n*-BuLi (hexane solution, 1.50 M × 2.1 mL, 3.2 mmol). The resulting mixture was warmed gradually to room temperature with stirring. Usual workup followed by silica gel column chromatography afforded bismuthane **9b** (696 mg, 64%) as a colorless glassy solid: ^{1}H NMR δ 1.08 (t, 12H, J = 7.1, CH_2CH_3), 2.28 (s, 3H, $C_6H_4CH_3$), 3.25 (q, 8H, J = 7.1, CH_2CH_3), 7.20 (d, 2H, J = 7.5), 7.34 (t, 2H, J = 7.3), 7.47 (t, 2H, J = 7.2), 7.51 (d, 2H, J = 7.5), 7.87 (d, 2H, J = 7.4), 7.98 (d, 2H, J = 7.3); IR ν_{max} 1321 (SO_2), 1150 (SO_2); EIMS m/z 633 (Ar_2Bi^+), 512, 421, 349, 300, 285, 209. Anal. Calcd for $C_{27}H_{35}BiN_2O_4S_2$: C, 44.75; H, 4.87; N, 3.87. Found: C, 44.46; H, 4.93; N, 3.78.

2-(*N,N*-Diethylsulfamoyl)phenylbis(4-methylphenyl)bismuthane (9c). A mixture of tris(4-methylphenyl)bismuthane (482 mg, 1.00 mmol), $BiCl_3$ (157 mg, 0.498 mmol), and Et_2O (10 mL) was stirred at room temperature for 1 h. To the resulting white suspension was added at −78 °C a Et_2O suspension (10 mL) of *ortho*-lithiated *N,N*-diethylbenzenesulfonamide, generated from *N,N*-diethylbenzenesulfonamide (320 mg, 1.50 mmol) and *n*-BuLi (hexane solution, 1.50 M × 1.1 mL, 1.7 mmol). The mixture was warmed gradually to room temperature with stirring. Usual workup gave bismuthane **9c** (561 mg, 62%) as a colorless glassy solid: ^{1}H NMR δ 1.01 (t, 6H, $J = 7.1$, CH_2CH_3), 2.30 (s, 6H, $C_6H_4CH_3$), 3.17 (q, 4H, $J = 7.1$, CH_2CH_3), 7.20 (d, 4H, $J = 7.5$), 7.34 (dt, 1H, $J = 1.6, 7.3$), 7.44 (dt, 1H, $J = 1.6, 7.5$), 7.61 (d, 4H, $J = 7.5$), 7.96 (dd, 1H, $J = 1.6, 7.5$), 8.02 (dd, 1H, $J = 1.6, 7.3$); IR ν_{max} 1322 (SO_2), 1152 (SO_2); EIMS *m/z* 512 ($ArTolBi^+$), 421, 391, 349, 333, 300, 285, 209. Anal. Calcd for $C_{24}H_{28}BiNO_2S$: C, 47.76; H, 4.68; N, 2.32. Found: C, 48.06; H, 4.76; N, 2.31.

Bis[2-(*N,N*-diethylsulfamoyl)phenyl]bismuth chloride (10a). To a solution of **9a** (0.28 g, 0.33 mmol) in CH_2Cl_2 (10 mL) was added SO_2Cl_2 (26 μL, 0.33 mmol) at −40 °C. The resulting yellow solution was allowed to warm to room temperature with stirring. After 1 h at room temperature, the volatiles were removed under reduced pressure to leave an oily residue, which was purified by column chromatography on silica gel with hexanes/ethyl acetate as the eluent, yielding chloride **10a** (173 mg, 78%), *N,N*-diethyl-2-chlorobenzenesulfonamide (70 mg, 86%), and *N,N*-diethylbenzenesulfonamide (15 mg, 21%). **10a:** mp 127−128 °C; ^{1}H NMR δ 1.04 (t, 12H, $J = 7.0$, CH_2CH_3), 3.16 (q, 8H, $J = 7.0$, CH_2CH_3), 7.57 (t, 2H, $J = 7.6$), 7.80 (t, 2H, $J = 7.5$), 7.95 (d, 2H, $J = 7.4$), 8.90 (d, 2H, $J = 7.5$); IR ν_{max} 1304 (SO_2), 1148 (SO_2); MALDIMS (CHCA) *m/z* 633.7 (Ar_2Bi^+). Anal. Calcd for $C_{20}H_{28}BiClN_2O_4S_2$: C, 35.91; H, 4.22; N, 4.19. Found: C, 35.88; H, 4.16; N, 4.16.

Bis[2-(*N,N*-diethylsulfamoyl)phenyl]bismuth Iodide (10b). To a solution of **9b** (4.3 g, 5.9 mmol) in acetone (30 mL) was added a solution of iodine (1.5 g, 5.9 mmol) in the same solvent (20 mL) at room temperature. After stirring for 1.5 h, the solvent was evaporated to give a crude product, which was recrystallized from hexane/CH_2Cl_2 to yield iodide **10b** (3.5 g, 78%) as a yellow solid: mp 142−145 °C; ^{1}H NMR δ 1.04 (t, 12H, $J = 7.1$, CH_2CH_3), 3.16 (q, 8H, $J = 7.1$, CH_2CH_3), 7.55−7.7 (m, 4H), 7.92 (dd, 2H, $J = 1.7, 7.4$), 9.21 (dd, 2H, $J = 1.8, 7.0$); IR ν_{max} 1321 (SO_2), 1150 (SO_2); MALDIMS (CHCA) *m/z* 633.7 (Ar_2Bi^+). Anal. Calcd for $C_{20}H_{28}BiIN_2O_4S_2$: C, 31.59; H, 3.71; N, 3.68. Found: C, 31.52; H, 3.68; N, 3.72. Compound **10b** was similarly prepared by iodolysis of **9a** in 89% yield.

2-(*N,N*-Diethylsulfamoyl)phenylbismuth Dichloride (10c). To a solution of **9a** (1.23 g, 1.45 mmol) in benzene (10 mL) was added $BiCl_3$ (1.37 g, 4.34 mmol) in one portion at room temperature, and the resulting mixture was heated under reflux for 1.5 h. Brine (15 mL) was added, and the water phase was extracted with ethyl acetate (15 mL × 2). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure to leave a solid residue, which was recrystallized from CH_2Cl_2 to give dichloride **10c** (1.82 g, 85% based on **9a**) as a white solid: mp 177−181 °C; ^{1}H NMR δ 1.16 (t, 6H, $J = 7.1$, CH_2CH_3), 3.38 (q, 4H, $J = 7.1$, CH_2CH_3), 7.71 (t, 1H, $J = 7.2$), 8.04 (t, 1H, $J = 7.2$), 8.19 (d, 1H, $J = 7.2$), 9.74 (d, 1H, $J = 7.2$); IR ν_{max} 1308 (SO_2), 1102 (SO_2); MALDIMS (CHCA) *m/z* 457.7 ($ArBiCl^+$). Anal. Calcd for $C_{10}H_{14}BiCl_2NO_2S$: C, 24.40; H, 2.87; N, 2.85. Found: C, 24.71; H, 2.80; N, 2.87.

***m*-Phenylene-Bridged Bi$_n$-Bismuthanes Bearing Sulfamoyl Groups 11a, 12a, and 13a.** To a solution of **9a** (0.17 g, 0.20 mmol) in THF (3 mL) was added *t*-BuLi (pentane solution; 1.5 M × 0.43 mL, 0.65 mmol) dropwise at −78 °C. After 10 min, the solution was allowed to warm to 0 °C and stirred for 1 h. To the resulting yellow creamy suspension was added a THF solution (6 mL) of **10b** (0.46 g, 0.60 mmol) at −78 °C. The mixture was allowed gradually to warm to room temperature, during which time the suspension changed to a yellow solution. Water (10 mL) was poured, and the organic phase was separated. The water layer was extracted with CH_2Cl_2 (10 mL × 3), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent gave a crude product, which was separated by column chromatography on silica gel with hexanes/ethyl acetate as the eluent. Recrystallization of the respective eluates from ethanol yielded **9a** (0.04 g, 6%) and Bi$_n$-bismuthanes **11a** (0.03 g, 2%), **12a** (0.14 g, 8%), and **13a** (0.88 g, 49%). The yields were based on the total bismuth.

Bi$_2$-Bismuthane 11a: mp 143 °C; ^{1}H NMR δ 1.13 (t, 30H, $J = 7.2$, CH_2CH_3), 3.26 (q, 16H, $J = 7.2$, CH_2CH_3), 3.37 (q, 4H, $J = 7.3$, CH_2CH_3), 7.14 (t, 1H, $J = 7.3$), 7.35 (dt, 4H, $J = 1, 7.4$), 7.48 (dt, 4H, $J = 1, 7.5$), 7.73 (dd, 4H, $J = 1, 7.3$), 7.82 (d, 2H, $J = 7.3$), 7.98 (dd, 4H, $J = 1, 7.7$); ^{13}C NMR δ 12.8, 13.9, 40.2, 41.7, 127.7, 129.2, 135.1, 138.4, 140.0, 140.7, 144.5, 147.0, 174.3, 175.6; IR ν_{max} 1320 (SO_2), 1148 (SO_2); MALDIMS (CHCA) *m/z* 1500.9 ($[M + Na]^+$). Anal. Calcd for $C_{50}H_{69}Bi_2N_5O_{10}S_5$: C, 40.62; H, 4.70; N, 4.74. Found: C, 40.58; H, 4.61; N, 4.56.

Bi$_3$-Bismuthane 12a: mp 132 °C; ^{1}H NMR δ 1.07−1.20 (m, 42H, CH_2CH_3), 3.18−3.32 (m, 28H, CH_2CH_3), 7.15 (t, 2H, $J = 7.3$), 7.36 (t, 5H, $J = 7.3$), 7.47 (t, 5H, $J = 7.3$), 7.70 (d, 4H, $J = 7.3$), 7.74 (d, 1H, $J = 7.6$), 7.81 (d, 2H, $J = 7.2$), 7.86 (d, 2H, $J = 7.1$), 7.96 (d, 1H, $J = 7.6$), 7.97 (d, 4H, $J = 7.3$); ^{13}C NMR δ 12.8, 13.9, 40.1, 41.6, 127.7, 129.1, 134.8, 135.0, 138.2, 139.9, 140.6, 144.3, 144.4, 144.6, 146.9, 173−175, 175.5, 175.8, 176−177; IR ν_{max} 1320 (SO_2), 1148 (SO_2); MALDIMS (CHCA) *m/z* 2134.3 ($[M + Na]^+$). Anal. Calcd for $C_{70}H_{96}Bi_3N_7O_{14}S_7$: C, 39.83; H, 4.58; N, 4.64. Found: C, 39.64; H, 4.66; N, 4.53.

Bi$_4$-Bismuthane 13a: Melting point, ^{1}H NMR, MS, and analytical data were reported in ref 14. ^{13}C NMR: δ 13.0, 14.0, 40.3, 41.8, 127.7, 129.1, 135.1, 138.2, 139.9, 140.6, 140.7, 144.3, 146.8, 173.7, 174.7, 175.4, 178.5; IR ν_{max} 1320 (SO_2), 1148 (SO_2).

Tolyl-Substituted *m*-Phenylene-Bridged Bi$_n$-Bismuthanes Bearing Sulfamoyl Groups 11b, 12b, and 13b. To a solution of **9a** (0.42 g, 0.50 mmol) in THF (8 mL) was added *t*-BuLi (pentane solution; 1.8 M × 0.89 mL, 1.6 mmol) at −78 °C. After a few minutes, the solution was allowed to warm to −30 °C and stirred for 1 h at this temperature. To the resulting yellow creamy suspension was added a THF solution (12 mL) of bis(4-methylphenyl)bismuth chloride, generated from tris(4-methylphenyl)bismuthane (0.48 g, 1.0 mmol) and $BiCl_3$ (0.16 g, 0.51 mmol) at −78 °C. The suspension gradually changed to a yellow solution, which was allowed to warm to room temperature with stirring. Usual workup followed by column chromatography on silica gel with hexanes/ethyl acetate as the eluent yielded **9a** (38 mg, 2%), tris(4-methylphenyl)bismuthane (127 mg, 13%), and Bi$_n$-bismuthanes **11b** (22 mg, 2%), **12b** (65 mg, 6%), and **13b** (112 mg, 11%). The yields were based on the total bismuth.

Bi$_2$-Bismuthane 11b: mp 95−100 °C; ^{1}H NMR δ 1.05 (t, 6H, $J = 7.1$, CH_2CH_3), 1.14 (t, 12H, $J = 7.1$, CH_2CH_3), 2.31 (s, 6H, $C_6H_4CH_3$), 3.27 (m, 12H, $J = 7.2$, CH_2CH_3), 7.15 (t, 1H, $J = 7.2$), 7.21 (d, 4H, $J = 7.8$), 7.34 (dt, 2H, $J = 1, 7.3$), 7.48 (dt, 2H, $J = 1, 7.4$), 7.59 (d, 4H, $J = 7.7$), 7.72 (dd, 2H, $J = 1, 7.4$), 7.76 (dd, 1H, $J = 1, 7.3$), 7.98 (dd, 2H, $J = 1, 7.8$), 8.11 (dd, 1H, $J = 1, 7.2$); IR ν_{max} 1320 (SO_2), 1148 (SO_2); MALDIMS (CHCA) *m/z* 1259.9 ($[M + Na]^+$). Anal. Calcd for $C_{44}H_{55}Bi_2N_3O_6S_3$: C, 42.75; H, 4.48; N, 3.40. Found: C, 42.82; H, 4.49; N, 3.28.

Bi$_3$-Bismuthane 12b: mp 102−108 °C; ^{1}H NMR δ 1.03 (t, 12H, $J = 7.2$, CH_2CH_3), 1.12 (t, 6H, $J = 7.1$, CH_2CH_3), 2.31 (s, 12H, $C_6H_4CH_3$), 3.23 (q, 8H, $J = 7.2$, CH_2CH_3), 3.27 (q, 4H, $J = 7.1$, CH_2CH_3), 7.16 (t, 2H, $J = 7.3$), 7.20 (d, 8H, $J = 7.0$), 7.34 (dt, 1H, $J = 1, 7.1$), 7.47 (dt, 1H, $J = 1, 7.6$), 7.59 (d, 8H, $J = 7.0$), 7.76 (dd, 1H, $J = 1, 7.6$), 7.80 (d, 2H, $J = 7.4$), 7.96 (dd, 1H, $J = 1, 7.9$), 8.11 (d, 2H, $J = 7.3$); IR ν_{max} 1291 (SO_2), 1146 (SO_2); MALDIMS (CHCA) *m/z* 1649.2 ($[M + Na]^+$). Anal.

Calcd for $C_{58}H_{68}Bi_3N_3O_6S_3$: C, 42.83; H, 4.21; N, 2.58. Found: C, 42.97; H, 4.22; N, 2.52.

Bi_4-Bismuthane 13b: Melting point, ^1H NMR, MS, and analytical data were reported in ref 14. ^{13}C NMR: δ 12.5, 21.5, 39.8, 131.4, 137.1, 137.5, 137.8, 139.9, 140.2, 147.0, 157.8, 159−161, 179.5; IR ν_{max} 1293 (SO_2), 1146 (SO_2).

***tert*-Butylsulfonyl-Substituted Bi_2-Bismuthane (15).** To a solution of [2-(*tert*-butylsulfonyl)phenyl]bis(4-methylphenyl)bismuthane (**14**) (882 mg, 1.5 mmol) in THF (5 mL) was added at −50 °C lithium 2,2,6,6-tetramethylpiperidide, prepared from 2,2,6,6-tetramethylpiperidine (0.56 mL, 3.0 mmol) and *n*-BuLi (hexane solution, 1.6 M × 1.9 mL, 3.0 mmol), and the resulting mixture was stirred for 1 h at this temperature. To this mixture was then added at −50 °C a suspension of bis(4-methylphenyl)bismuth chloride, generated from tris(4-methylphenyl)bismuthane (964 mg, 2.0 mmol) and $BiCl_3$ (316 mg, 1.0 mmol) in Et_2O (10 mL), and the resulting suspension was allowed to warm to room temperature. Brine (5 mL) was added, and the water phase was extracted with ethyl acetate (20 mL × 3). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure to leave an oily residue, which was chromatographed on silica gel with hexanes/ethyl acetate as the eluent and recrystallized from MeOH to give Bi_2-bismuthane **15** (590 mg, 40% based on **14**) as a colorless solid: mp 218−220 °C; ^1H NMR δ 1.45 (s, 9H, $C(CH_3)_3$), 2.30 (s, 6H, $C_6H_4CH_3$), 2.34 (s, 6H, $C_6H_4CH_3$), 7.13−7.20 (m, 5H), 7.26 (d, 4H, $J = 7.3$), 7.41 (d, 4H, $J = 7.9$), 7.67 (d, 4H, $J = 7.9$), 8.18 (d, 2H, $J = 7.3$); IR ν_{max} 1210 (SO_2), 1034 (SO_2); MALDIMS (DHBA) m/z 739.8 ($[M - (2 \times Tol + t\text{-}Bu)]^+$). Anal. Calcd for $C_{38}H_{40}Bi_2O_2S$: C, 46.63; H, 4.12. Found: C, 46.51; H, 4.11.

***tert*-Butylsulfonyl-Substituted Bi_2-Chlorobismuthane (16).** To a solution of **15** (190 mg, 0.194 mmol) in benzene (5 mL) was slowly added $BF_3{\cdot}OEt_2$ at 10 °C (required 0.16 mL, 1.2 mmol) until the spot of **15** disappeared on TLC. Brine (3 mL) was added, and the water phase was extracted with ethyl acetate (20 mL × 3). The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure to leave an oily residue, which was recrystallized from MeOH to give Bi_2-chlorobismuthane **16** (100 mg, 59%) as a colorless crystalline solid: mp 185−190 °C (decomp); ^1H NMR δ 1.49 (s, 9H, $C(CH_3)_3$), 2.26 (s, 6H, $C_6H_4CH_3$), 7.25 (d, 4H, $J = 7.6$), 7.76 (d, 4H, $J = 7.6$), 8.24 (t, 1H, $J = 7.6$), 9.26 (d, 2H, $J = 7.6$); IR ν_{max} 1208 (SO_2), 1040 (SO_2); MALDIMS (DHBA) m/z 739.8 ($[M - (Cl \times 2 + t\text{-}Bu)]^+$). Anal. Calcd for $C_{24}H_{26}Bi_2Cl_2O_2S$: C, 33.23; H, 3.02. Found: C, 33.09; H, 2.96.

Dendritic Bi_{10}-Bismuthane (17). To a solution of **13a** (183 mg, 0.067 mmol) in THF (6 mL) was added *t*-BuLi (pentane solution, 1.5 M × 0.29 mL, 0.44 mmol) at −78 °C. The solution turned reddish brown within 5 min. The mixture was allowed to warm to 0 °C and stirred for an additional hour at this temperature, during which time the color changed to yellowish brown. The resulting solution was cooled to −78 °C, and a solution of **10b** (304 mg, 0.400 mmol) in THF (3 mL) was added. The resulting solution was gradually warmed to room temperature and further stirred for 1 h. Water (15 mL) was poured, and the aqueous phase was extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to leave a product mixture, which was separated by column chromatography on silica gel with hexanes/ethyl acetate as the eluent to afford crude Bi_{10}-bismuthane **17** (86 mg, ca. 20%) and a mixture of Bi_n-bismuthanes (87 mg; $n = 6-9$). The yields were based on the total bismuth. Analytically pure **17** was obtained after successive purification by GPC and silica gel column chromatography; mp 180−185 °C; ^1H NMR δ 1.12 (br-t, 126H, CH_2CH_3), 3.26 (br-q, 84H, CH_2CH_3), 7.1−7.2 (m, 9H), 7.2−7.5 (m, 24H), 7.6−7.7 (m, 12H), 7.7−7.8 (m, 9H), 7.8−8.0 (m, 21H); ^{13}C NMR δ 12.7, 13.0, 14.1, 40.0, 40.3, 41.8, 127.8, 129.3, 135.2, 138.3, 139.9, 140.8, 144.4, 147.1, 174.3, 175.5, 178.6; IR ν_{max} 1293 (SO_2), 1148 (SO_2); MALDIMS (CHCA) m/z 6558.1 ($[M + Na]^+$). Anal. Calcd for $C_{210}H_{285}Bi_{10}N_{21}O_{42}S_{21}$: C, 38.57; H, 4.39; N, 4.50. Found: C, 38.72; H, 4.40; N, 4.62.

Chlorination of Bi_4-Bismuthane 13b. To a solution of **13b** (117 mg, 0.058 mmol) in CH_2Cl_2 (5 mL) was added SO_2Cl_2 (16 μL, 0.20 mmol) at 0 °C, and the resulting pale yellow solution was stirred for 3 h at room temperature. The volatiles were removed under reduced pressure, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent. Further recrystallization from MeOH yielded Bi_4-bismuth hexachloride **18** as a pale yellow solid (72 mg, 55%). Melting point, ^1H NMR, MS, and analytical data were reported in ref 14. IR: ν_{max} 1304 (SO_2), 1150 (SO_2).

Reduction of Bi_4-Bismuth Hexachloride 18. A saturated aqueous $Na_2S_2O_3$ (3 mL) was added to a solution of **18** (46 mg, 0.021 mmol) in CH_2Cl_2 (3 mL) at room temperature, and the mixture was vigorously stirred for 1 h. The water layer was extracted with CH_2Cl_2 (3 mL × 3), and the combined extracts were dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yielded **13b** (38 mg, 92%).

Bi_n-Bismuthane Oligomers (19). To a solution of **9a** (4.65 g, 5.50 mmol) in THF (82 mL) was added *t*-BuLi (pentane solution, 1.6 M × 8.2 mL, 13 mmol) at −78 °C. After 20 min, the resulting yellow solution was allowed to warm to 0 °C within 10 min with stirring. The solution changed to a pale yellow suspension, which was again cooled to −78 °C. After 30 min, **10c** (2.71 g, 5.5 mmol) was added in one portion, and the mixture was warmed gradually to room temperature with stirring. Brine (80 mL) was added, and insoluble substances were filtered off through Celite. The organic phase of the filtrate was separated, and the water phase was extracted with ethyl acetate (30 mL × 2). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure to leave a pale yellow solid. Two fractions **19a** (2.48 g) and **19b** (2.87 g) were obtained by fractional recrystallization of the above solid from CH_2Cl_2/MeOH (1:10). The products **19a,b** were characterized by NMR, IR, and MS spectroscopies as well as by elemental analysis: mp 257−261 °C; ^1H NMR δ 0.8−1.4 (12H, CH_2CH_3), 3.0−3.5 (8H, CH_2CH_3), 7.0−7.6 (3H), 7.6−8.0 (4H) (proton number refers to the relative peak area ratio); ^{13}C NMR δ 12.9, 14.1, 40.3, 41.8, 127.8, 129.2, 135.1, 138.3, 140.1, 140.7, 144.6, 147.3, 175.9, 177.1; IR ν_{max} 1293 (SO_2), 1146 (SO_2); MALDIMS (DHBA) 2529.4 ($[Ar^IAr^{II}Bi \times 4]^+$), 1896.8 ($[Ar^IAr^{II}Bi \times 3]^+$), 1264.6 ($[Ar^IAr^{II}Bi \times 2]^+$), 633.0 ($Ar^IAr^{II}Bi^+$); Anal. Calcd for $C_{20}H_{27}BiN_2O_4S_2$ ($Ar^IAr^{II}Bi$): C, 37.98; H, 4.30; N, 4.43. Found: C, 37.99; H, 4.40; N, 4.44.

X-ray Diffraction Analysis of Compound 16. A crystal of dimensions 0.130 × 0.130 × 0.350 mm, grown from CH_2Cl_2/MeOH (1:5) at ambient temperature, was used for X-ray diffraction. $C_{24}H_{26}Bi_2Cl_2O_2S$: mw 867.40; monoclinic; space group $P2_1/c$; $a = 15.653(2)$ Å; $b = 10.076(2)$ Å; $c = 16.768(2)$ Å; $\beta = 99.70(1)°$; $V = 2606.9(7)$ Å^3 (by least-squares refinement on diffractometer angles for 24 carefully centered reflections in the range $29.65° < 2\theta < 30.00°$, 300 K, Mo K$\alpha$, $\lambda = 0.710\ 69$ Å); $Z = 4$; $D_c = 2.210$ g cm^{-3}; μ(Mo Kα, $\lambda = 0.710\ 69$ Å) = 137.46 cm^{-1}; $F(000) = 1608$. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo Kα radiation from a fine focus anode of 12 kW type rotating anode generator with the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.0°. Data were corrected for Lorentz and polarization effects. Scans of $(0.63 + 0.30 \tan \theta)°$ were made at a speed of 8.0° min^{-1} (in ω). The structure was solved by a combination of the Patterson and direct methods.[31] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3585 observed reflections ($I > 3.00\sigma(I)$) and 281 variable parameters and coverged with unweighted and weighted agreement factors of $R = 0.036$ and

$R_w = 0.034$. The weighting scheme $\omega = 1/\sigma^2(F_0)$ was employed. Neutral atom scattering factors were taken from Cromer and Waber.[32] Anomalous dispersion effects were included in F_c;[33] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[34] All calculations were performed using the TEXAN[35] crystallographic software package of Molecular Structure Corporation. The ORTEP[36] program was used to obtain Figure 1.

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Supporting Information Available: Tables of experimental details for the X-ray diffraction study, atomic coordinates, thermal parameters, bond distances and angles, torsion angles, intermolecular distances and angles, and least-squares planes and figures giving additional views and unit cell packing for **16**, and full IR data (ν_{max}) of all the new compounds (32 pages). See any current masthead page for ordering and Internet access instructions.

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