

First Introduction of an Azulenyl Group into the Bismuth and Antimony Center. Synthesis and Structure of Azulenylbismuthanes and Their Difluorides

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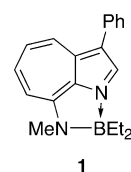
A nonalternant organyl ligand derived from azulene, a 1,3-dichloro-2-azulenyl group, is introduced for the first time into the bismuth and antimony center. Conversion of the azulenylbismuthanes into the pentacoordinated difluorides by xenon difluoride promotes the π -polarization of the azulene nucleus, which is detected as a color change in solution as well as changes in the chemical shifts of the ^{13}C NMR spectra. A similar tendency is observed in the antimony congeners. The X-ray crystallographic study of (1,3-dichloro-2-azulenyl)-diphenylbismuth difluoride (**20b**) reveals that intermolecular π - π stacking takes place between the azulenyl groups through the interaction of the five-membered ring with the seven-membered ring. This may reflect the more polarized azulenyl group of the difluorides, which strengthens the stacking interaction.

Introduction

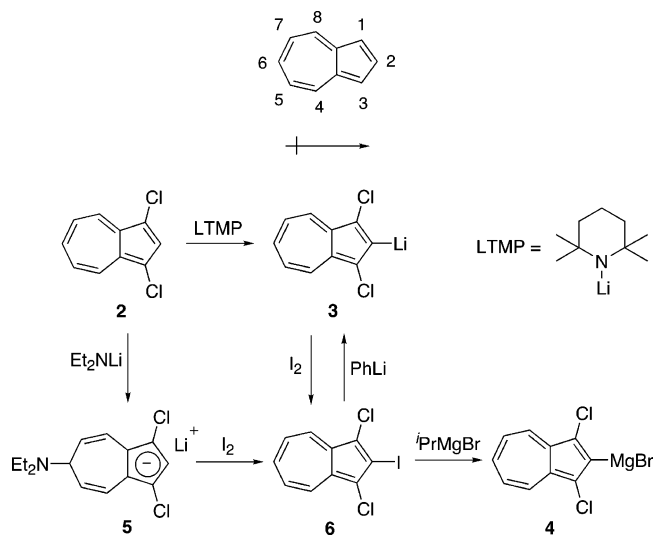
Construction of organometallics based on nonalternant conjugation has been receiving increasing interest.¹ Formation of a σ - or π -type coordinate bond between a metal center and nonalternant ligands is considered to endow molecules with a significant change of the properties that are markedly different from those given by the coordination of alternant ligands since the resonance stabilization of nonalternant conjugation is smaller than that of alternant conjugation.² Thus, we have revealed a unique structure of boron complex **1** comprised of nonalternant 8-methylamino-3-phenyl-1-azaazulene, in which the nonalternant conjugation in the 1-azaazulene skeleton is destroyed through the intramolecular boron–nitrogen coordinate bond.^{1d}

Azulene, a nonalternant hydrocarbon and isomer of alternant naphthalene, is physicochemically characterized by high electron affinity, low ionization potential, and low aromatic resonance energy, together with the dipole moment vector whose negative end is toward its five-membered ring (Scheme 1). Despite such uniqueness of the electronic structure, the organometallic species bearing an azulenyl group as a ligand of the metal center have been very limited. In particular, there

Chart 1



Scheme 1

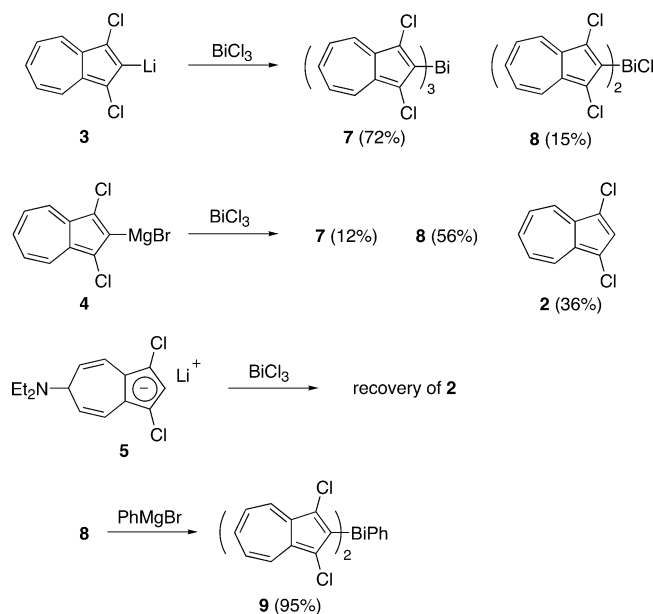


(1) (a) Matsubara, K.; Ryu, K.; Maki, T.; Iura, T.; Nagashima, H. *Organometallics* **2002**, 21, 3023. (b) Arce, A. J.; De Sanctis, Y.; Galarza, E.; Garland, M. T.; Gobetto, R.; Machado, R.; Manzur, J.; Russo, A.; Spodine, E.; Stchedroff, M. J. *Organometallics* **2001**, 20, 359. (c) Nitta, M.; Mitsumoto, Y.; Yamamoto, H. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1901. (d) Sugihara, Y.; Murafuji, T.; Abe, N.; Takeda, M.; Kakehi, A. *New J. Chem.* **1998**, 1031.

(2) (a) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, 91, 789. (b) Sugihara, Y.; Hashimoto, R.; Fujita, H.; Abe, N.; Yamamoto, H.; Sugimura, T.; Murata, I. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2813.

are few examples of the σ -type species,³ although azulenes are known to coordinate with transition metal centers to form a π -complex.^{1a,b,4} The reason is attributed to the lack of suitable methods for preparing σ -anions such as azulenyllithium or azulenyl-Grignard

Scheme 2

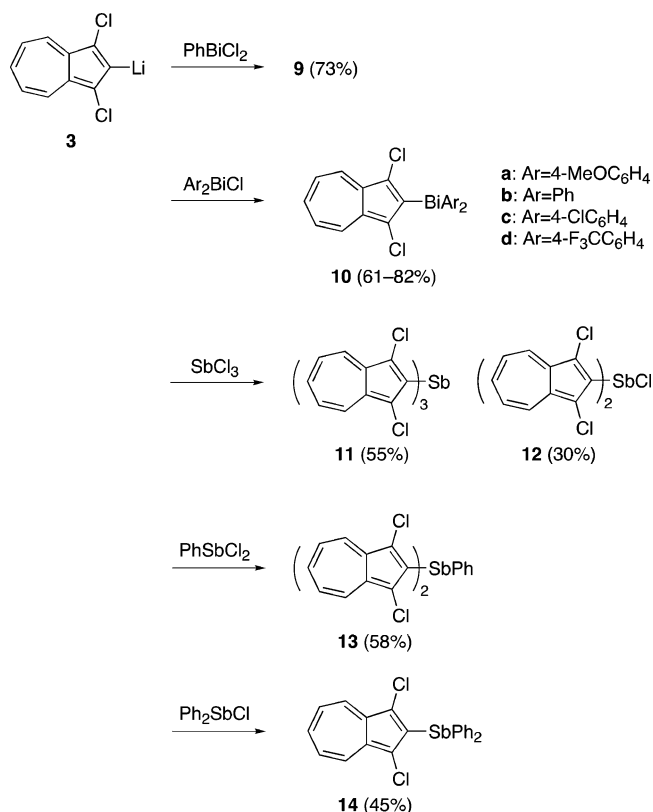


reagents, the generation of which has so far not been achieved. Very recently, we were successful for the first time in generating σ -anions **3** and **4**, starting from 1,3-dichloroazulene **2** (Scheme 1).⁵ Herein, we report the first introduction of an azulenyl group into the bismuth center, that is, the synthesis and structural characterization of azulenylylbismuthanes **7–10** and their difluorides **18–20**, together with their antimony congeners.

Results and Discussion

Synthesis of Azulenylbismuthanes and their Homologues of Antimony. To know the difference in reactivity among anionic species **3–5**, we initially tried the reaction of the respective anions (ca. 3 equiv) with bismuth(III) chloride (1 equiv). When azulenyllithium **3** was allowed to react with bismuth(III) chloride, bismuthane **7** preferentially formed together with minor chlorobismuthane **8** in 72 and 15% yields [based on bismuth(III) chloride], respectively (Scheme 2). In contrast, the distribution of **7** and **8** was reversed when azulenyl-Grignard **4** was used. Thus, **8** formed as a main product (56%) along with **7** (12%), and in addition, **2** was obtained in 36% yield (based on **6**), reflecting the lowered nucleophilicity of **4**. An attempted reaction of π -anion **5** resulted in the complete recovery of **2**. The diethylamino group of **5** seems to coordinate with Lewis acidic bismuth(III) chloride to promote the elimination of this group from the azulene nucleus since the π -anion reacts with iodine to produce **6** in moderate yield. These results clarify the efficiency of **3** for the bismuth–carbon bond formation. Despite the reactive bismuth–chlorine bond, **8** is resistant to aqueous workup, although chlorobismuthanes are usually sensitive toward hydrolysis

Scheme 3



at the bismuth atom. The structure of **8** was confirmed by the reaction with phenylmagnesium bromide giving **9**.

Dichloro- and chlorobismuthanes underwent substitution smoothly with **3** to afford the corresponding mixed bismuthanes **9** and **10**, respectively (Scheme 3). Next, azulenyllithium **3** was applied to the reaction with an electrophile of the group 15 homologue. When antimony(III) chloride was allowed to react with **3**, unlike the case of bismuth(III) chloride, the ratio of chlorostibine **12** relative to **11** considerably increased, reflecting the difference of the Lewis acidity between the bismuth and antimony atoms. Similar reaction with dichloro- and chlorostibines⁶ afforded the corresponding stibines **13** and **14**.

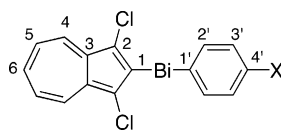
Halogenation. Triaryl bismuthanes undergo preferential halogenation at the bismuth atom with sulfuryl chloride or xenon difluoride to give triaryl bismuth dihalides in high yields. Unlike the aryl groups of benzenoid hydrocarbon, the azulenyl groups of **7** are considered to be reactive toward halogenation since the azulene nucleus undergoes electrophilic substitution at the five-membered ring (1- and 3-positions) and suffers from nucleophilic addition at the seven-membered ring (4-, 6-, and 8-positions) owing to the π -polarization. A preliminary reaction of **2** with sulfuryl chloride (1 equiv) in THF at 0 °C immediately produced brown, intractable substances and a small amount of **2** remained (confirmed by TLC), suggesting destruction of the conjugation in the azulene nucleus by sequential chlorination. When **7** was allowed to react with sulfuryl chloride under the same conditions, however, no such tendency

(3) (a) Kurotobi, K.; Tabata, H.; Miyauchi, M.; Murafuji, T.; Sugihara, Y. *Synthesis* **2002**, 1013. (b) Kurotobi, K.; Miyauchi, M.; Takakura, K.; Murafuji, T.; Sugihara, Y. *Eur. J. Org. Chem.* **2003**, 3663. (c) Ito, S.; Okujima, T.; Morita, N. *J. Chem. Soc., Perkin Trans. I* **2002**, 1896.

(4) Edelmann, F.; Behrens, U. *Chem. Ber.* **1978**, *111*, 3001.

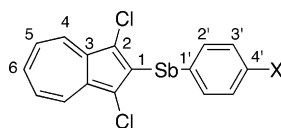
(5) Kurotobi, K.; Tabata, H.; Miyauchi, M.; Mustafizur Rahman, A. F. M.; Migita, K.; Murafuji, T.; Sugihara, Y.; Shimoyama, H.; Fujimori, K. *Synthesis* **2003**, 30.

(6) Nunn, M.; Sowerby, D. B.; Wesolek, D. M. *J. Organomet. Chem.* **1983**, *251*, C45.

Table 1. ^{13}C NMR Spectral Data of Azulenylbismuthanes and Difluorides in $\text{DMSO}-d_6$ 

	C1	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'
2	132.56	113.16	132.56	135.73	124.69	141.73				
7	<i>a</i>	122.88	133.00	134.62	124.51	141.23				
8	<i>a</i>	121.50	133.68	133.87	124.04	140.30				
9	165.10	122.42	133.23	134.21	124.38	140.89	156.58	139.80	130.23	127.94
10a^b	164.08	122.64	133.33	134.01	124.27	140.76	147.12	139.73	116.29	159.07
10b	165.40	122.64	133.39	134.13	124.29	140.81	157.45	138.39	130.36	127.68
10c	167.22	122.44	133.49	134.25	124.27	140.98	157.11	140.35	130.30	132.84
10d^c	168.81	122.40	133.60	134.40	124.50	141.09	165.20	139.24	126.50	128.23
19^d	<i>a</i>	116.50	132.40	139.01	126.67	144.97	<i>a</i>	135.26	132.20	132.98
20a^{b,d}	158.57	116.35	132.30	138.49	126.41	144.47	144.08	135.25	117.21	162.27
20b^d	159.22	116.42	132.39	138.60	126.54	144.57	154.59	133.93	132.01	132.50
20c^d	158.88	116.56	132.37	138.57	126.48	144.61	154.62	135.35	131.53	137.32
20d^{c,d}	159.80	116.84	132.48	138.45	126.43	144.55	162.80	134.47	128.25	131.98

^a Not observed. ^b The chemical shift of the methyl carbon: δ 54.98 (**10a**) and 55.97 (**20a**). ^c J_{CF} = around 3.7(q), 32(q), and 273(q) for C3', C4', and CF₃, respectively. The chemical shift of the CF₃ carbon: δ 124.72 (**10d**) and 123.81 (**20d**). ^d The $^2J_{\text{CF}}$ and $^3J_{\text{CF}}$ couplings of the fluorine atoms attached to the bismuth atom were not detected in the azulenyl and phenyl ring carbons.

Table 2. ^{13}C NMR Spectral Data of Azulenylstibines and Difluorides in $\text{DMSO}-d_6$ 

	C1	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'
11	140.18	121.48	132.46	135.20	124.88	142.16				
13	141.88	120.94	132.62	134.91	124.81	142.78	134.30	137.46	128.78	129.26
14	141.95	121.25	132.84	135.02	124.82	143.64	136.49	136.39	128.95	128.89
21^a	137.19	117.42	132.65	138.80	126.29	145.02				
23^b	139.43	116.22	132.45	138.26	126.16	144.48	133.10	135.25	130.25	133.03

^a The $^2J_{\text{CF}}$ and $^3J_{\text{CF}}$ couplings of the fluorine atoms attached to the antimony atom were not detected in the azulenyl and phenyl ring carbons. ^b $^2J_{\text{CF}}$ = 13.9(t) for the C1' and $^3J_{\text{CF}}$ = 4.6(t) for the C2'.

X-ray Structure Analysis of Bismuthane 7 and Difluoride 20b. To know how the azulenyl group attached to the bismuth(III) and -(V) centers behaves in solid, X-ray structure analysis was carried out for **7** and **20b** (Tables 3 and 4 and Figures 1–3). The bismuth center of **7** has a pyramidal configuration (Figure 1) and is surrounded by the six chlorine atoms with distances of 3.493(6)–4.033(5) Å, which are all within the sum of the van der Waals radii (4.04 Å). The partially larger bond angles around the bismuth center are due to the steric bulkiness of the azulenyl groups. The enhanced stability of chlorobismuthane **8** may be mainly attributed to the intramolecular interaction and kinetic stabilization by these chlorine atoms. The bismuth center of **20b** possesses a trigonal bipyramidal geometry with the fluorine atoms and the carbon atoms of the azulenyl and phenyl groups in the apical and equatorial positions, respectively (Figure 2). An outstanding structural feature is seen in the crystal structure of **20b**. An intermolecular π - π stacking is observed between the azulenyl groups⁹ through the interaction of the five-membered ring with the seven-membered ring, with the

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **7** and **20b**

	7		20b
Bi–C(1)	2.23(2)	Bi–C(1)	2.15(2)
Bi–C(11)	2.27(2)	Bi–C(11)	2.19(2)
Bi–C(21)	2.26(2)	Bi–C(17)	2.19(2)
		Bi–F(1)	2.27(1)
		Bi–F(2)	2.189(9)
C(1)–C(2)	1.38(2)	C(1)–C(2)	1.40(2)
C(2)–C(3)	1.41(3)	C(2)–C(3)	1.40(2)
C(3)–C(4)	1.41(3)	C(3)–C(4)	1.42(2)
C(3)–C(9)	1.50(3)	C(3)–C(9)	1.47(2)
C(4)–C(5)	1.39(3)	C(4)–C(5)	1.31(2)
C(5)–C(6)	1.33(3)	C(5)–C(6)	1.32(3)
C(6)–C(7)	1.33(3)	C(6)–C(7)	1.44(3)
C(7)–C(8)	1.38(3)	C(7)–C(8)	1.41(2)
C(8)–C(9)	1.39(3)	C(8)–C(9)	1.36(2)
C(9)–C(10)	1.38(3)	C(9)–C(10)	1.39(2)
C(1)–C(10)	1.42(2)	C(1)–C(10)	1.37(2)
C(1)–Bi–C(11)	92.6(6)	C(1)–Bi–C(11)	115.5(6)
C(1)–Bi–C(21)	99.2(7)	C(1)–Bi–C(17)	117.4(6)
C(11)–Bi–C(21)	100.6(6)	C(11)–Bi–C(17)	127.1(6)
		F(1)–Bi–F(2)	178.5(4)

shortest interatomic distance of 3.54(2) Å between the C4 and C9 atoms (Figure 3). While the azulenyl group is approximately coplanar with the equatorial plane [C2–C1–Bi–C17 = 166(1)°], the two phenyl groups lie perpendicular to this plane as if they surround the azulenyl groups of the neighboring molecules. This

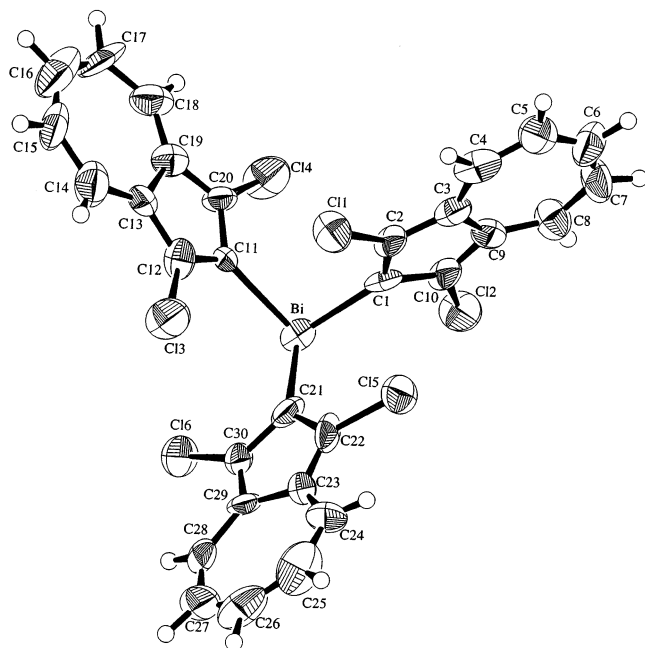
(8) π -Polarization is observed in diaryltrifluorosilicates. Thus, the ipso carbons attached to the pentacoordinate silicon appear more downfield compared to those of the parent tetracoordinate silanes. This is attributed to the π -inductive effect induced by the electronic fields of the charged substituents. The upfield shift of the ipso carbons in the pentacoordinate antimony and bismuth halides may be ascribed to this π -inductive effect. For the π -polarization of the silicates, see: Tamao, K.; Hayashi, T.; Ito, Y. *Organometallics* **1992**, *11*, 182.

(9) Sterically protected phosphathenes bearing an azulenyl group at the ethene carbon, see: Yasunami, M.; Ueno, T.; Yoshifuji, M.; Okamoto, A.; Hirotsu, K. *Chem. Lett.* **1992**, 1971.

Table 4. Crystallographic Parameters for 7 and 20b

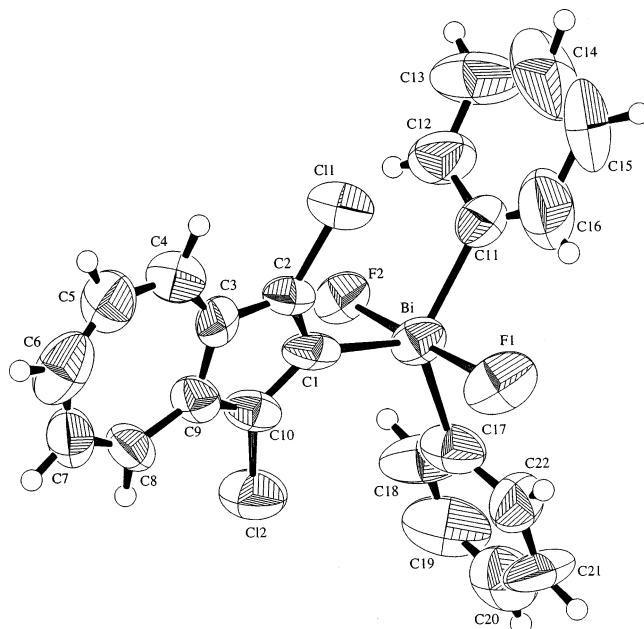
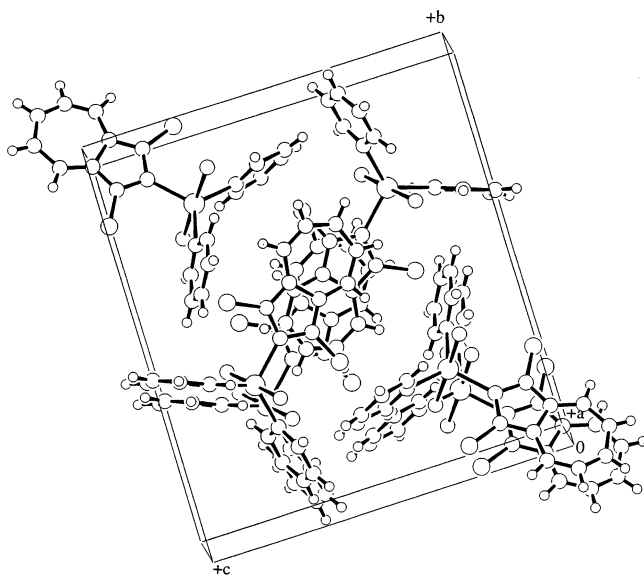
	7·THF	20b
empirical formula	C ₃₄ H ₂₃ BiCl ₆ O	C ₂₂ H ₁₅ BiCl ₂ F ₂
fw	869.25	597.24
color, habit	green, prismatic	green, prismatic
cryst dimens (mm)	0.33 × 0.28 × 0.18	0.25 × 0.13 × 0.13
cryst syst	monoclinic	monoclinic
<i>a</i> (Å)	12.063(6)	8.030(6)
<i>b</i> (Å)	21.085(7)	16.78(1)
<i>c</i> (Å)	12.721(7)	15.44(2)
β (deg)	92.81(4)	97.2(1)
<i>V</i> (Å ³)	3231(2)	2064(3)
space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.786	1.922
<i>F</i> ₀₀₀	1680.00	1128.00
μ(Mo Kα) (cm ⁻¹)	59.69	88.06
2θ _{max} (deg)	55.0	55.4
scan rate (deg min ⁻¹)	32.0	8.0
scan width (deg)	1.47 + 0.30 tan θ	1.52 + 0.30 tan θ
no. of rflns measd	7991; 7428	5263; 4749
total; unique		
no. of observns	5078 (<i>I</i> > 0.00σ(<i>I</i>))	2953 (<i>I</i> > 0.00σ(<i>I</i>))
no. of variables	369	244
residuals: <i>R</i> ; ^a <i>R</i> _w ^b	0.141; 0.191	0.096; 0.117
goodness of fit indicator	1.01	1.18
max. shift/error in final cycle	0.001	0.000
max. and min. peaks in final diff map (e ⁻ /Å ³)	4.01; -3.85	2.11; -2.19

^a $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. ^b $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(F_o^2)$.

**Figure 1.** ORTEP drawing of **7** showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. A THF molecule is omitted for clarity.

stacking interaction was not observed in **7**, although the bismuth center possesses three azulenyl groups. The difference in the crystal structures of **7** and **20b** may reflect the enhanced polarization in the azulene nucleus of the latter, which strengthens the stacking interaction.

In conclusion, this work shows a potential utility of nonalternant azulenes not only as σ-ligands of the metal center but also as key building blocks for the construction of supramolecular systems composed of organometallics based on the π–π interaction.

**Figure 2.** ORTEP drawing of **20b** showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.**Figure 3.** Crystal structure of **20b**.

Experimental Section

General Comments. All reactions were carried out under argon unless otherwise noted. THF and diethyl ether were distilled from calcium hydride under nitrogen before use. Bismuth(III) chloride and antimony(III) chloride were purified by refluxing with thionyl chloride. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ on a Bruker AVANCE 400S spectrometer with TMS as an internal standard. ¹⁹F NMR spectra were measured in DMSO-*d*₆ on a Bruker AVANCE 400S spectrometer with benzotrifluoride (δ_F –64.0) as an internal standard. UV/vis spectra were measured in CHCl₃ by means of a Shimadzu UV-1600PC spectrophotometer. 1,3-Dichloroazulene **2** was synthesized by the chlorination of azulene with NCS.

1,3-Dichloroazulene (2): blue solids; yield 85%; mp 85–87 °C (lit.¹⁰ 85–87 °C); ¹H NMR (CDCl₃) δ 7.18 (2H, t, *J* 10.0),

(10) Anderson, A. G., Jr.; Nelson, J. A.; Tazuma, J. J. *J. Am. Chem. Soc.* **1953**, *75*, 4980.

7.64 (1H, t, J 9.9), 7.65 (1H, s), 8.32 (2H, d, J 9.3); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 241 (20420), 288 (34140), 294 (29410), 344 (3360), 352 (4520), 361 (3000), 369 (5030), 642 (380).

Generation of Azulenylithium 3 and the Reaction with Electrophiles. General Procedure. A typical example is exemplified by the reaction with bismuth(III) chloride. To a solution of lithium 2,2,6,6-tetramethylpiperidide (ca. 4.5 mmol) prepared from 2,2,6,6-tetramethylpiperidine (4.5 mmol) and BuLi (4.5 mmol) in THF (5 mL) at -70°C was added a solution of **2** (3.0 mmol) in THF (3 mL) at the same temperature. The color of the solution immediately turned from blue to dark green, showing the generation of **3**. To this solution thus obtained was added a solution of bismuth(III) chloride (1.0 mmol) in THF (5 mL), and the resulting solution was stirred for 5 min. The reaction was quenched at -70°C with brine (10 mL), and the green precipitate was separated by filtration. The filtrate was extracted with ethyl acetate (7 mL \times 3), and the combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was recrystallized from THF–MeOH (5:1) to give pure **7**. The precipitate was recrystallized from THF–MeOH (5:1) to give **8**. Yields are based on bismuth(III) chloride.

1,3-Dichloro-2-iodoazulene (6):⁵ blue solids; yield 95%; mp 102–103 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 7.22 (2H, t, J 10.0), 7.69 (1H, t, J 9.9), 8.35 (2H, d, J 10.2); ^{13}C NMR (CDCl_3) δ 103.78, 119.58, 124.60, 132.44, 134.66, 140.09. Anal. Calcd for $\text{C}_{10}\text{H}_5\text{Cl}_2\text{I}$: C, 37.19; H, 1.56. Found: C, 37.41; H, 1.50.

Tris(1,3-dichloro-2-azulenyl)bismuthane (7): green solids; yield 72%; mp 258–259 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.30 (6H, t, J 9.9), 7.77 (3H, t, J 9.9), 8.22 (6H, d, J 9.3); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (50 870), 313 (147 290), 348 (26 660), 365 (31 320), 645 (1210). Anal. Calcd for $\text{C}_{30}\text{H}_{15}\text{BiCl}_6$: C, 45.20; H, 1.90. Found: C, 45.44; H, 2.02.

Chlorobis(1,3-dichloro-2-azulenyl)bismuthane (8): green solids; yield 15%; mp 251–252 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.17 (4H, t, J 9.8), 7.66 (2H, t, J 9.8), 7.96 (4H, d, J 9.8); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (38 070), 295 (70 100), 300 (69 690), 315 (77 320), 345 (13 810), 352 (sh, 14 160), 361 (16 880), 645 (890). Elemental analysis of this compound failed due to its slow decomposition upon storage.

Bis(1,3-dichloro-2-azulenyl)phenylbismuthane (9): green solids; yield 73%; mp 206–207 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.27–7.32 (4H, m), 7.40 (2H, t, J 7.5, ArH), 7.77 (2H, t, J 9.8, AzH), 8.17 (2H, d, J 7.2, ArH), 8.20 (4H, d, J 9.8, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 241 (40 500), 309 (89 510), 349 (sh, 17 130), 365 (18 330), 642 (830). Anal. Calcd for $\text{C}_{26}\text{H}_{15}\text{BiCl}_4$: C, 46.05; H, 2.23. Found: C, 46.56; H, 1.94.

1,3-Dichloro-2-azulenylbis(4-methoxyphenyl)bismuthane (10a): green solids; yield 70%; mp 109–111 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 3.70 (6H, s), 6.95 (4H, d, J 8.4, ArH), 7.29 (2H, t, J 9.8, AzH), 7.76 (4H, d, J 8.4, ArH), 7.77 (1H, t, J 9.9, AzH), 8.21 (2H, d, J 9.7, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 243 (45 870), 300 (63 400), 307 (62 850), 349 (sh, 9420), 365 (8610), 642 (480). Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{BiCl}_2\text{O}_2$: C, 46.55; H, 3.09. Found: C, 47.08; H, 2.99.

(1,3-Dichloro-2-azulenyl)diphenylbismuthane (10b): green solids; yield 82%; mp 111–112 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.29 (2H, t, J 9.9, AzH), 7.29 (2H, t, J 7.3, ArH), 7.39 (4H, t, J 7.4, ArH), 7.78 (1H, t, J 9.9, AzH), 7.90 (4H, d, J 6.8, ArH), 8.21 (2H, d, J 9.5, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 240 (30 250), 299 (52 470), 307 (52 010), 364 (7620), 642 (400). Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{BiCl}_2$: C, 47.25; H, 2.70. Found: C, 47.15; H, 2.71.

1,3-Dichloro-2-azulenylbis(4-chlorophenyl)bismuthane (10c): green solids; yield 65%; mp 115–117 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.29 (2H, t, J 9.8, AzH), 7.42 (4H, d, J 8.3, ArH), 7.77 (1H, t, J 9.9, AzH), 7.89 (4H, d, J 8.3, ArH), 8.21 (2H, d, J 9.9, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 241 (38 110), 300 (sh, 52 060), 307 (52 860), 348 (sh, 7390), 363 (7930), 641 (420). Anal. Calcd for $\text{C}_{22}\text{H}_{13}\text{BiCl}_4$: C, 42.07; H, 2.09. Found: C, 42.36; H, 2.05.

1,3-Dichloro-2-azulenylbis(4-trifluoromethylphenyl)bismuthane (10d): green solids; yield 61%; mp 135–138 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.30 (2H, t, J 10.0, AzH), 7.71 (4H, d, J 7.9, ArH), 7.78 (1H, t, J 9.9, AzH), 8.15 (4H, d, J 7.9, ArH), 8.23 (2H, d, J 9.0, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 241 (25 820), 301 (43 360), 348 (5910), 362 (6710), 642 (380). Anal. Calcd for $\text{C}_{24}\text{H}_{13}\text{BiCl}_2\text{F}_6$: C, 41.46; H, 1.88. Found: C, 41.24; H, 1.97.

Tris(1,3-dichloro-2-azulenyl)stibine (11): green solids; yield 55%; mp 270–271 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.34 (6H, t, J 9.9), 7.82 (3H, t, J 9.9), 8.27 (6H, d, J 9.6); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (48 130), 310 (158 500), 367 (25 880), 648 (1250). Anal. Calcd for $\text{C}_{30}\text{H}_{15}\text{SbCl}_6$: C, 50.76; H, 2.13. Found: C, 50.72; H, 2.15.

Chlorobis(1,3-dichloro-2-azulenyl)stibine (12): green solids; yield 30%; mp 264–265 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 7.17 (4H, t, J 9.0), 7.63 (2H, t, J 9.8), 8.28 (4H, d, J 9.6); due to low solubility, measurement of ^{13}C NMR spectrum failed; UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (36 870), 308 (79 150), 364 (sh, 16 140), 648 (920). Anal. Calcd for $\text{C}_{20}\text{H}_{10}\text{SbCl}_5$: C, 43.73; H, 1.83. Found: C, 44.24; H, 1.85.

Bis(1,3-dichloro-2-azulenyl)phenylstibine (13): green solids; yield 58%; mp 195–198 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.31–7.36 (7H, m), 7.72 (2H, d, J 7.7, ArH), 7.81 (2H, t, J 9.8, AzH), 8.26 (4H, d, J 9.9, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (32 320), 306 (68 090), 367 (sh, 14 900), 644 (820). Anal. Calcd for $\text{C}_{26}\text{H}_{15}\text{SbCl}_4$: C, 52.48; H, 2.56. Found: C, 52.84; H, 2.50.

(1,3-Dichloro-2-azulenyl)diphenylstibine (14): green solids; yield 45%; mp 133–135 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.32–7.37 (8H, m), 7.50–7.52 (4H, m), 7.83 (1H, t, J 9.9, AzH), 8.28 (2H, d, J 9.4, AzH); UV/vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (ϵ) 242 (27 360), 299 (46 720), 329 (14 690), 645 (430). Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{SbCl}_2$: C, 55.98; H, 3.20. Found: C, 56.31; H, 3.19.

Generation of Azulenyl-Grignard 4 and the Reaction with Bismuth(III) Chloride. To a solution of **6** (3.0 mmol) in THF (5 mL) was added at -30°C a solution of *i*-PrMgBr (3.6 mmol) in THF (3 mL). The color of the solution turned from blue to bluish green, showing the generation of **4**. To this solution thus obtained was added a solution of bismuth(III) chloride (1.0 mmol) in THF (5 mL), and the resulting solution was stirred for 5 min. The reaction was quenched at -30°C with brine (10 mL), and the green precipitate was separated by filtration. The precipitate was recrystallized from THF–MeOH (5:1) to give **8** in 56% yield. The filtrate was extracted with ethyl acetate (7 mL \times 3), and the combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was recrystallized from THF–MeOH (5:1) to give pure **7** in 12% yield. Evaporation of the filtrate after filtration of **7** gave a residue, which was chromatographed (silica gel; hexane) to give **2** in 36% yield.

Reaction of 8 with Phenylmagnesium Bromide. To a solution of **8** (0.3 mmol) in THF (5 mL) was added at 0°C a solution of phenylmagnesium bromide (ca. 0.6 mmol) in the same solvent (1 mL), and the reaction mixture was stirred for 3 h, during which time the temperature was raised to ambient. The reaction was quenched with brine (3 mL), and the resulting mixture was extracted with ethyl acetate (5 mL \times 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was crystallized from MeOH to give **9** in 95% yield.

Generation of Lithium 6-*N,N*-Diethylamino-6*H*-azulenolate (5) and the Reaction with Bismuth(III) Chloride. To a solution of lithium diethylamide (ca. 3.0 mmol), prepared from diethylamine (3.0 mmol) and BuLi (3.0 mmol) in ether (10 mL) at -20°C , was added a solution of **2** (3.0 mmol) in ether (3 mL) at -70°C . The color of the solution turned from blue to yellow, showing the generation of **5**. Then a solution of bismuth(III) chloride (1.0 mmol) in THF (5 mL) was added at this temperature. After 5 min the reaction was quenched at -70°C with brine (10 mL) and the mixture was extracted

with ethyl acetate (7 mL \times 3). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, from which **2** was recovered intact.

Chlorination of 7 with Sulfuryl Chloride. To a solution of **7** (1.0 mmol) in THF (10 mL) was added sulfuryl chloride (1.0 mmol) in dichloromethane (1.0 mL) at 0 °C, and the reaction mixture was stirred for 3 h, during which time the temperature was raised to ambient. The mixture was evaporated to leave an oily residue containing insoluble substances, which was extracted with hexane (7 mL \times 3). The combined extracts were purified by silica gel column chromatography using hexane as eluent to give 1,3-dichloroazulene **2** (22%) and 1,2,3-trichloroazulene **16** (57%).

1,2,3-Trichloroazulene (16): blue solids; yield 57%; mp 136–137 °C (lit.¹¹ 137 °C); ¹H NMR (CDCl₃) δ 7.28 (2H, t, *J* 9.8), 7.66 (1H, t, *J* 9.6), 8.30 (2H, d, *J* 10.0); ¹³C NMR (CDCl₃) δ 112.38, 124.81, 131.86, 134.44 (\times 2), 139.58. Anal. Calcd for C₁₀H₅Cl₃: C, 51.88; H, 2.18. Found: C, 51.84; H, 2.25.

Chlorination of 11 with Sulfuryl Chloride. To a solution of **11** (1.0 mmol) in THF (10 mL) was added sulfuryl chloride (1.0 mmol) in dichloromethane (1.0 mL) at 0 °C, and the reaction mixture was stirred for 3 h, during which time the temperature was raised to ambient. The mixture was evaporated to leave solids, which were crystallized from hexane–AcOEt (5:1) to give pure **17**.

Tris(1,3-dichloro-2-azulenyl)antimony dichloride (17): green solids; yield 98%; mp 290–292 °C; ¹H NMR (DMSO-*d*₆) δ 7.58 (6H, t, *J* 9.9), 8.09 (3H, t, *J* 10.3), 8.66 (6H, d, *J* 9.6); due to low solubility, measurement of ¹³C NMR spectrum failed; UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (50 880), 313 (173 650), 355 (26 290), 371 (16 160), 648 (1610). Anal. Calcd for C₃₀H₁₅SbCl₈: C, 46.15; H, 1.94. Found: C, 46.16; H, 2.23.

Fluorination of Azulenylbismuthanes with Xenon Difluoride. General Procedure. A typical example is exemplified by the reaction of **7**. To a solution of **7** (1.0 mmol) in THF (15 mL) was added xenon difluoride (1.2 mmol) at 0 °C, and the mixture was stirred for 3 h. Evaporation of the resulting mixture gave a residue, which was crystallized from MeOH to give **18**.

Tris(1,3-dichloro-2-azulenyl)bismuth difluoride (18): green solids; yield 75%; mp 191–192 °C; ¹H NMR (DMSO-*d*₆) δ 7.36 (6H, t, *J* 9.9), 7.61 (3H, t, *J* 9.9), 8.64 (6H, d, *J* 9.3); ¹⁹F NMR (DMSO-*d*₆) δ –88.30 (s); due to low solubility, measurement of ¹³C NMR spectrum failed; UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (50 130), 311 (160 070), 346 (24 210), 351 (24 380), 368 (16 750), 645 (1540). Anal. Calcd for C₃₀H₁₅BiCl₆F₂: C, 43.15; H, 1.81. Found: C, 43.18; H, 1.76.

Bis(1,3-dichloro-2-azulenyl)phenylbismuth difluoride (19): green solids; yield 65%; mp 153–155 °C; ¹H NMR (DMSO-*d*₆) δ 7.57 (4H, t, *J* 10.0, AzH), 7.73 (1H, t, *J* 7.4, ArH), 7.79 (2H, t, *J* 9.6, AzH), 7.91 (2H, t, *J* 7.7, ArH), 8.38 (2H, d, *J* 7.5, ArH), 8.57 (4H, d, *J* 9.5, AzH); ¹⁹F NMR (DMSO-*d*₆) δ –117.95 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (34 700), 309 (92 700), 345 (15 300), 351 (15 100), 642 (950). Anal. Calcd for C₂₆H₁₅BiCl₄F₂: C, 43.60; H, 2.11. Found: C, 43.23; H, 2.46.

1,3-Dichloro-2-azulenylbis(4-methoxyphenyl)bismuth difluoride (20a): green solids; yield 75%; mp 124–126 °C; ¹H NMR (DMSO-*d*₆) δ 3.84 (6H, s), 7.37 (4H, d, *J* 8.9, ArH), 7.45 (2H, t, *J* 9.0, AzH), 7.93 (1H, t, *J* 9.9, AzH), 8.14 (4H, d, *J* 8.9, ArH), 8.40 (2H, d, *J* 9.6, AzH); ¹⁹F NMR (DMSO-*d*₆) δ –137.57 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 242 (57 950), 298 (54 750), 306 (55 810), 345 (7520), 351 (7640), 369 (5110), 642 (550). Anal. Calcd for C₂₄H₁₉BiCl₂F₂O₂: C, 43.86; H, 2.91. Found: C, 44.20; H, 3.01.

(1,3-Dichloro-2-azulenyl)diphenylbismuth difluoride (20b): green solids; yield 70%; mp 152–154 °C; ¹H NMR (DMSO-*d*₆) δ 7.51 (2H, t, *J* 9.9, AzH), 7.65 (2H, t, *J* 7.4, ArH), 7.83 (4H, t, *J* 7.7, ArH), 7.99 (1H, t, *J* 9.9, AzH), 8.23 (4H, d, *J* 7.6, ArH), 8.47 (2H, d, *J* 9.7, AzH); ¹⁹F NMR (DMSO-*d*₆) δ

–139.85 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (23 300), 298 (49 700), 306 (49 700), 345 (sh, 6160), 351 (6400), 368 (4480), 642 (500). Anal. Calcd for C₂₂H₁₅BiCl₂F₂: C, 44.24; H, 2.53. Found: C, 44.36; H, 2.65.

1,3-Dichloro-2-azulenylbis(4-chlorophenyl)bismuth difluoride (20c): green solids; yield 68%; mp 144–146 °C; ¹H NMR (DMSO-*d*₆) δ 7.51 (2H, t, *J* 9.9, AzH), 7.90 (4H, d, *J* 8.6, ArH), 7.99 (1H, t, *J* 9.9, AzH), 8.25 (4H, d, *J* 8.6, ArH), 8.46 (2H, d, *J* 9.7, AzH); ¹⁹F NMR (DMSO-*d*₆) δ –138.98 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 240 (28 440), 298 (43 200), 306 (45 310), 345 (6370), 350 (6380), 367 (4410), 642 (500). Anal. Calcd for C₂₂H₁₃BiCl₄F₂: C, 39.67; H, 1.97. Found: C, 39.74; H, 2.15.

1,3-Dichloro-2-azulenylbis(4-trifluoromethylphenyl)bismuth difluoride (20d): green solids; yield 65%; mp 139–141 °C; ¹H NMR (DMSO-*d*₆) δ 7.50 (2H, t, *J* 9.8, AzH), 7.98 (1H, t, *J* 9.9, AzH), 8.19 (4H, d, *J* 8.4, ArH), 8.43 (2H, d, *J* 9.9, AzH), 8.49 (4H, d, *J* 8.4, ArH); ¹⁹F NMR (DMSO-*d*₆) δ 61.16 (s, 6F), –140.40 (s, 2F); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (20 430), 297 (39 160), 306 (40 080), 344 (5910), 349 (5880), 367 (4200), 644 (520). Anal. Calcd for C₂₄H₁₃BiCl₂F₈: C, 39.31; H, 1.79. Found: C, 39.65; H, 1.95.

Tris(1,3-dichloro-2-azulenyl)antimony difluoride (21): green solids; yield 94%; mp 238–240 °C; ¹H NMR (DMSO-*d*₆) δ 7.54 (6H, t, *J* 9.9), 8.06 (3H, t, *J* 9.9), 8.60 (6H, d, *J* 9.6); ¹⁹F NMR (DMSO-*d*₆) δ –97.98 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 241 (45 450), 310 (138 280), 347 (sh, 19 970), 353 (21 330), 370 (16 480), 650 (1500). Anal. Calcd for C₃₀H₁₅SbCl₆F₂: C, 48.18; H, 2.02. Found: C, 48.26; H, 2.14.

Bis(1,3-dichloro-2-azulenyl)phenylantimony difluoride (22): green solids; yield 93%; mp 248–250 °C (dec); ¹H NMR (DMSO-*d*₆) δ 7.51 (4H, t, *J* 9.9, AzH), 7.76–7.77 (3H, m), 8.03 (2H, t, *J* 9.9, AzH), 8.29–8.31 (2H, m), 8.54 (4H, d, *J* 9.6, AzH); ¹⁹F NMR (DMSO-*d*₆) δ –118.27 (s); due to low solubility, measurement of ¹³C NMR spectrum failed; UV/vis (CHCl₃) λ_{max} /nm (ϵ) 242 (27 600), 299 (65 830), 309 (79 170), 346 (sh, 10 640), 353 (11 650), 370 (9360), 645 (900). Anal. Calcd for C₂₆H₁₅SbCl₄F₂: C, 49.65; H, 2.41. Found: C, 50.08; H, 2.59.

(1,3-Dichloro-2-azulenyl)diphenylantimony difluoride (23): green solids; yield 91%; mp 220–222 °C; ¹H NMR (DMSO-*d*₆) δ 7.49 (2H, t, *J* 9.9, AzH), 7.69–7.70 (6H, m, ArH), 8.00 (1H, t, *J* 9.9, AzH), 8.16–8.18 (4H, m, ArH), 8.47 (2H, d, *J* 9.7, AzH); ¹⁹F NMR (DMSO-*d*₆) δ –134.31 (s); UV/vis (CHCl₃) λ_{max} /nm (ϵ) 240 (18 600), 290 (44 090), 305 (41 110), 353 (5750), 370 (4870), 641 (520). Anal. Calcd for C₂₂H₁₅SbCl₂F₂: C, 51.81; H, 2.96. Found: C, 51.85; H, 2.85.

X-ray Crystallography. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71069 Å) and a rotating anode generator. The data were collected at 298 K using the ω –2 θ scan technique. The data were corrected for Lorentz and polarization effects. The structures were solved by the Patterson method¹² and expanded using Fourier techniques.¹³ The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.¹⁴

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Anomalous dispersion effects were included in F_{calc} ,¹⁵ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁶ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁷ All calculations were performed using the teXsan¹⁸ crystallographic software package of Molecular Structure Corporation.

Supporting Information Available: Crystal data for compounds **7** and **20b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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