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Synthesis and Characterization of the First Azastibatranes and Azabismatranes

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Syntheses of title compounds, viz. $N(CH_2CH_2NR)_3E$ (**1**, E = Sb, R = Me; **4**, E = Bi, R = Me; **6**, E = Sb, R = $SiMe_3$; **8**, E = Bi, R = $SiMe_3$), by the reaction of $E(NAlk_2)_3$ (**3**, E = Sb, Alk = Et; **5**, E = Bi, Alk = Me) with $N(CH_2CH_2NMeH)_3$ (**2**) or $N(CH_2CH_2NSiMe_3H)_3$ (**7**) are reported. The reactions of $SbCl_3$ with $N[CH_2CH_2N(Me)Li]_3$ or $N[CH_2CH_2N(SiMe_3)Li]_3$ and $BiCl_3$ with $N[CH_2CH_2N(SiMe_3)Li]_3$ resulted in compounds **1**, **6**, and **8**, respectively. Composition and structures of all novel compounds were established by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The X-ray structural study of **8** clearly indicated the presence of transannular interaction $Bi \leftarrow N_{dat}$ in this compound, while **6** possesses a long $Sb\cdots N_{dat}$ distance. The structural data obtained from geometry optimizations on **6** and **8** reproduce experimental trends, i.e., a decrease in the $E–N_{dat}$ distance from Sb to Bi. The values of electron density in $E–N_{dat}$ critical point and the Laplacian of charge density for **8** indicate that a closed-shell interaction exists between the metal atom and N_{dat} atom.

Introduction

The chemistry of metal derivatives of tripodal ligands such as trialkanolamines, $N(CH_2CHROH)_3$, tris(aminoethyl)amines, $N[CH_2CH_2N(R)H]_3$, etc., named metallatranes has attracted considerable interest in recent years.[1−4] The main focus is the nature of transannular N→M bond, which is strongly affected by the design of the atrane building block and the substituents at the metal atoms.[1,4−14] Although a lot of work has appeared on intramolecular nonbonding interactions between nitrogen atoms and atoms of the group 14 and 15 elements and its effect on structural and chemical properties of compounds containing a hypervalent bond,[15,16] to the best of our knowledge no atrane types of structure **A** containing antimony and bismuth as a central atom were

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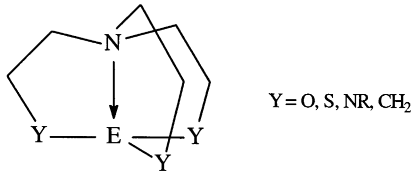
structurally characterized and only a few examples were prepared earlier.



A

Stibatrane (**A**, M = Sb, Y = O) was prepared by the reaction of 1-vinylsilatrane with SbF_3, but no evidence for a transannular bond was presented.[17] Bismatrane (**A**, M = Bi, Y = O) was formed in reaction between $Bi(OH)_3$ and triethanolamine in the presence of catalytic amounts of EtONa, but no structural characterization was reported.[18]

Compounds containing heavier group 15 elements (Sb, Bi) have attracted great attention over the past decade due to their application in heterogeneous catalysis,[19−21] as precursors for superconducting materials in MOCVD processes,[22,23] and due to the potential antimicrobial bioactivity of bismuth compounds in general.[24−29]

In this contribution we present the synthesis and X-ray characterization of the first azaatranes of the group 15 heavier elements **1**, **4**, **6**, and **8**. Our motivation was to prepare first azastibatranes and azabismatranes, to confirm and to characterize of the intramolecular N→E bond in these derivatives by X-ray crystallography and DFT calculations.

Experimental Section

General Procedures. All manipulations were performed under an dry, oxygen-free argon atmosphere using standard Schlenk techniques. All manipulations with Bi-containing compounds were carried out in brown glass equipment. Solvents were dried by standard methods and distilled prior to use. $BiCl_3$ (Aldrich) and $SbCl_3$ (Aldrich) were sublimed in vacuo (200 °C/5 $\times$ 10^{-3} Torr and 50 °C/5 $\times$ 10^{-3} Torr, respectively) prior to use. $N(CH_2CH_2NH_2)_3$ was distilled over $LiAlH_4$. Starting materials $Sb(NEt_2)_3$,[30] $Bi(NMe_2)_3$,[31] $N[CH_2CH_2N(Me)H]_3$,[32] and $N[CH_2CH_2N(SiMe_3)H]_3$[9] were prepared according to the literature. C_6D_6 was obtained from Deutero GmbH and dried over sodium.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer (in C_6D_6 at 23 °C). Chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm relative to internal Me_4Si. Assignments of the ^{13}C NMR data were supported by APT experiments. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes. Elemental analyses were carried out by the Fachbereich Chemie of the Philipps-University Marburg (Heraeus-Rapid-Analyzer).

In this work, the nonempirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew et al. was employed.[33,34] Calculations were performed using the program "PRIRODA" developed by Laikov, which implements an economical computational procedure.[35] Large orbital basis sets of contracted Gaussian-type functions of the size (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, (11s6p2d):[4s3p2d] for N, (16s12p2d):[5s4p2d] for Si, (22s19p12d):[7s6p4d] for Sb, and (24s22p15d9f): [8s7p5d1f] for Bi were used. Full geometry optimization was performed for a number of structures followed by vibrational frequency calculation using analytical first and second derivatives. Each structure has been characterized by the vibrational analysis. The present theoretical method has been used and has given very useful results in the organometallic chemistry of Cr, Ti, and Zr.[36,37] The chemical bonds were analyzed by using the topological analysis of the wave function. The MOLDEN program was used in this case.[38]

Synthesis of *N,N′,N″*-Trimethylazastibatrane, $N(CH_2CH_2NMe)_3Sb$ (1). Method A. A solution of tetramine **2** (0.65 g, 3.5 mmol) in toluene (15 mL) was added dropwise via cannula at −78 °C to a stirred solution of the tris(diethylamino)stibane (**3**) (1.19 g, 3.5 mmol) in toluene (10 mL). The reaction mixture was stirred for 14 h at room temperature, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The solvent was evaporated in vacuo to give a colorless oil, **1** (yield 1.01 g, 95%). NMR spectra: ^1H, δ 2.27 (t, 6H, NCH_2), 2.83 (t, 6H, NCH_2), 2.90 (s, 9H, NCH_3); $^{13}C\{^1H\}$, δ 38.94 (NCH_2), 48.09 (NMe), 50.10 (NCH_2). Mass spectrum (EI-MS) [*m/e* (rel int)]: 306 (12, M^+), 207 (15, $M^+ - CH_3NCH_2CH_2NCH_2CH_2$).

Method B. A 1.6 M *n*-butyllithium solution (10.32 mL, 16.5 mmol) in hexane was added dropwise to a stirred solution of the tetramine **2** (1.03 g, 5.5 mmol) in toluene (40 mL) at room temperature, and the resulting mixture was stirred for 5 h. Then a solution of $SbCl_3$ (1.25 g, 5.5 mmol) in toluene (20 mL) was added dropwise to the reaction mixture at −78 °C. The reaction mixture was stirred at room temperature for 24 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The solvent was evaporated in vacuo to give a colorless oil, **1** (yield 1.47 g, 87%).

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Table 1. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for **6** and **8**

	6	**8**
formula	$C_{15}H_{39}N_4SbSi_3$	$C_{15}H_{39}BiN_4Si_3$
fw	481.52	568.75
cryst system	rhombohedral	rhombohedral
space group	$R\bar{3}$	$R\bar{3}$
a, Å	16.2434(7)	16.306(2)
c, Å	15.482(1)	15.460(2)
V, Å^3	3537.7(3)	3559.8(8)
Z	6	6
d(calcd), g·cm^{-3}	1.356	1.592
abs coeff, mm^{-1}	1.327	7.585
F(000)	1500	1692
θ range, deg	1.96−27.44	2.50−26.33
index ranges	$21 \leq h \leq 21$ $20 \leq k \leq 21$ $20 \leq l \leq 20$	$20 \leq h \leq 0$ $0 \leq k \leq 20$ $19 \leq l \leq 2$
reflcns collcd	17 246	1986
indpdt reflcns	1790	1623
R_{int}	0.0277	0.0531
data/restrs/params	1790/0/123	1623/0/73
GOF on F^2	1.287	1.024
R_1 [$I > 2\sigma(I)$]	0.0176	0.0335
wR_2 (all data)	0.0598	0.0800
Largest diff peak/hole (e·Å^{-3})	0.573/−0.518	2.027/−1.137

Synthesis of *N,N′,N″*-Trimethylazabismatrane, $N(CH_2CH_2NMe)_3Bi$ (4). Method A. A solution of tetramine **2** (0.76 g, 4.0 mmol) in toluene (15 mL) was added dropwise to a stirred solution of the tris(dimethylamino)bismuthane (**5**) (1.36 g, 4.0 mmol) in toluene (10 mL) at −78 °C. The reaction mixture was warmed to room temperature during 2 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The resulting solution was reduced in volume to 3 mL and stored at −30 °C to give yellow crystals, **4** (yield 1.20 g, 76%). NMR spectra: ^1H, δ 2.30 (t, 6H, NCH_2), 3.20 (s, 9H, NMe), 4.00 (t, 6H, NCH_2); $^{13}C\{^1H\}$, δ 40.72 (NCH_2), 52.82 (NMe), 53.92 (NCH_2). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: no M^+ was observed. Anal. Calcd for $C_9H_{21}N_4Bi$: C, 27.42; H, 5.37; N, 14.21. Found: C, 27.93; H, 5.58; N, 13.85.

Attempted Synthesis of 4 via $N[CH_2CH_2N(Me)Li]_3$. A 1.6 M *n*-Butyllithium solution (6.00 mL, 9.6 mmol) in hexane was added dropwise to a stirred solution of the tetramine **2** (0.60 g, 3.2 mmol) in THF (20 mL) at room temperature. The resulting solution was stirred for 5 h, and then a suspension of $BiCl_3$ (1.00 g, 3.2 mmol) in THF (20 mL) at −78 °C was added dropwise. The reaction mixture was warmed to room temperature during 3 h and stirred at room temperature for another 24 h; all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The solvent was evaporated in vacuo to give a solid residue which did not contain **4** (NMR data).

***N,N′,N″*-Tris(trimethylsilyl)azastibatrane, $N(CH_2CH_2NSiMe_3)_3Sb$ (6). Method A.** A solution of tetramine **7** (1.23 g, 3.4 mmol) in toluene (15 mL) was added dropwise to a stirred solution of the tris(diethylamino)stibane (**3**) (1.16 g, 3.4 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated at 90 °C during 110 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The resulting solution was reduced in volume to 3 mL and stored at −30 °C to give colorless crystals, **6** (yield 1.10 g, 67%). NMR spectra: ^1H, δ 0.23 (s, 27H, $SiMe_3$), 2.33 (t, 6H, NCH_2), 2.86 (t, 6H, NCH_2); $^{13}C\{^1H\}$, δ 1.94 ($SiMe_3$), 40.55 (NCH_2), 58.05 (NCH_2). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: 480 (1, M^+), 365 (15, $M^+ - Me_3SiNCH_2CH_2$).

Method B. A 1.6 M *n*-Butyllithium solution (10.34 mL, 16.5 mmol) in hexane was added dropwise to a stirred solution of the tetramine **7** (1.99 g, 5.5 mmol) in toluene (40 mL) at room temperature, and the resulting mixture was stirred for 5 h. Then a solution of $SbCl_3$ (1.26 g, 5.5 mmol) in toluene (20 mL) was added dropwise to the reaction mixture at −78 °C. The reaction mixture was refluxed for 1 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The resulting solution was reduced in volume to 5 mL and stored at −30 °C to give colorless crystals, **6** (yield 1.62 g, 61%).

***N,N′,N″*-Tris(trimethylsilyl)azabismuthatrane, $N(CH_2CH_2NSiMe_3)_3Bi$ (8). Method A.** A solution of tetramine **7** (0.58 g, 1.6 mmol) in toluene (10 mL) was added dropwise to a stirred solution of the tris(dimethylamino)bismuthane (**5**) (0.55 g, 1.6 mmol) in toluene (10 mL) at −78 °C. The reaction mixture was warmed to room temperature during 2 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The resulting solution was reduced in volume to 3 mL and stored at −30 °C to give pale-yellow crystals, **8** (yield 0.49 g, 54%). NMR spectra: ^1H, δ 0.22 (s, 27H, $SiMe_3$), 2.10 (t, 6H, NCH_2), 3.97 (t, 6H, NCH_2); $^{13}C\{^1H\}$, δ 2.01 ($SiMe_3$), 42.80 (NCH_2), 59.07 (NCH_2). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: 568 (1, M^+). Anal. Calcd for $C_{15}H_{39}N_4Si_3Bi$: C, 31.68; H, 6.91; N, 9.85. Found: C, 31.47; H, 6.94; N, 9.15.

Method B. A 1.6 M *n*-butyllithium solution (4.32 mL, 6.9 mmol) in hexane was added dropwise to a stirred solution of the tetramine **7** (0.84 g, 2.3 mmol) in THF (30 mL) at room temperature. The resulting mixture was stirred for 1 h and then added dropwise to a suspension of $BiCl_3$ (0.73 g, 2.3 mmol) in THF (10 mL) at −78 °C with stirring. The reaction mixture was warmed to room temperature during 3 h, and all volatiles were removed under reduced pressure. *n*-Pentane (10 mL) was added to the residue, and insoluble substances were separated by centrifugation. The resulting solution was reduced in volume to 3 mL and stored at −30 °C to give pale-yellow crystals, **8** (yield 0.60 g, 46%).

X-ray Crystallography. Crystal data, data collection, structure solution, and refinement parameters for compounds **6** and **8** are given in Table 1. Both experiments were performed at 193 K on an Stoe IPDS (for **6**) and on an Enraf Nonius CAD4 (for **8**) diffractometers using Mo Kα radiation (0.710 73 Å). The structures were solved by direct methods[39] and refined by full-matrix least-squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[40] All hydrogen atoms were placed in calculated positions and refined isotropically for **6** and using a riding model for **8**.

Results and Discussion

Transamination reactions of $X{-}E(NAlk_2)_3$ with tetramines $N[CH_2CH_2N(R)H]_3$ is usual method for preparation of main group element "azaatranes".[1,9,13] We used this reaction for the syntheses of azastibatranes and azabismatranes **1**, **4**, **6**, and **8**.

The parent tetramine **2** reacts in toluene at −78 °C with antimony and bismuth tris(dialkylamides) **3** and **5** to give the corresponding azaatranes **1** and **4**, which were isolated

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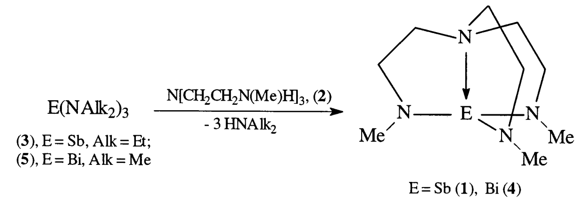
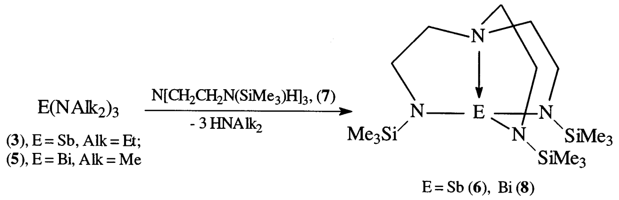
Scheme 1



Scheme 2



Scheme 3

$$\mathrm{SbCl_3} \xrightarrow[-\,3\,\mathrm{LiCl}]{\mathrm{N[CH_2CH_2N(Me)Li]_3}} \mathbf{1}$$

$$\mathrm{BiCl_3} \not\xrightarrow[-\,3\,\mathrm{LiCl}]{\mathrm{N[CH_2CH_2N(Me)Li]_3}} \mathbf{4}$$

Scheme 4

$$\mathrm{SbCl_3} \xrightarrow[-\,3\,\mathrm{LiCl}]{\mathrm{N[CH_2CH_2N(SiMe_3)Li]_3}} \mathbf{6}$$

$$\mathrm{BiCl_3} \xrightarrow[-\,3\,\mathrm{LiCl}]{\mathrm{N[CH_2CH_2N(SiMe_3)Li]_3}} \mathbf{8}$$

in 95 and 76% yields, respectively (Scheme 1). The bismuth complex **4** is light and temperature sensitive and should be stored preferably at −30 °C in the dark.

In contrast to the high yields obtained for **1** and **4** in previous reactions, compounds **6** and **8**, containing three Me_3Si groups, are formed in transamination reactions in lower yields, 67% and 54%, respectively (Scheme 2). Probably the smaller yields obtained in the last reactions are due to the increased steric hindrance among the trimethylsilyl groups in **6** and **8**.

We also tested a new synthetic approach to azametallatranes of the main group elements: $SbCl_3$ reacts with $N[CH_2CH_2N(Me)Li]_3$ to give *N*,*N*′,*N*″-trimethylazastibatrane (**1**) which was isolated in a 87% yield (Scheme 3). The reaction proceeds smoothly after mixing the freshly prepared lithium salt with toluene solution of $SbCl_3$ at −78 °C, followed by keeping the reaction mixture for several hours at room temperature. $N[CH_2CH_2N(Me)Li]_3$ was generated in situ by treatment of **2** in toluene with 3 equiv of *n*-BuLi.

The metathetical exchange reaction between $BiCl_3$ and the lithiated parent amine **2** did not yield the expected product **4.**

Treatment of $SbCl_3$ and $BiCl_3$ with $N[CH_2CH_2N(SiMe_3)Li]_3$ leads to *N*,*N*′,*N*″-tris(trimethylsilyl)azastibatrane (**6**) and *N*,*N*′,*N*″-tris(trimethylsilyl)azabismatrane (**8**), which were isolated in a 61 and 46% yield, respectively (Scheme 4).

Compositions and structures of all novel compounds were established by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. However elemental analysis data for compounds **1** and **6** were not wholly satisfactory, probably due to partial hydrolysis. Analogous decomposition of chelating triamide complexes of antimony was recently found.[41]

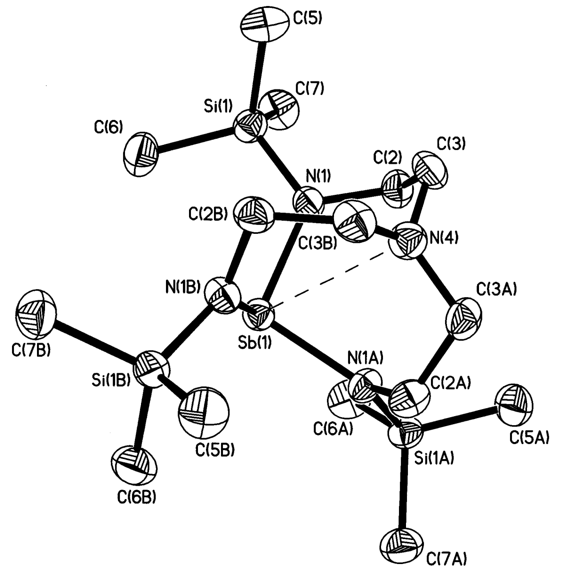


Figure 1. Molecular structure of **6**. Hydrogen atoms are omitted for clarity.

^1H and ^{13}C NMR spectra are in accord with the suggested structures. In the ^1H NMR spectra of **1**, **4**, **6**, and **8** the signals of the methylene protons of the azaatrane skeleton appear as a set of two pseudotriplets, forming an AA′BB′ spin system ($J = 5.2-5.8$ Hz). This pattern is a general feature of the "atrane" framework for a variety of metallatranes. In the ^{13}C NMR spectra of **1**, **4**, **6**, and **8** the signals of the carbon atoms of the azaatrane skeleton have standard values.[42,43]

To the best of our knowledge compounds **6** and **8** are the first derivatives of antimony and bismuth containing the "atrane" cage that have been structurally characterized. The molecular structures of **6** and **8** are shown in Figures 1 and 2. Table 2 summarizes significant geometrical parameters for these compounds. Compounds **6** and **8** are isostructural and possess a crystallographic 3-fold symmetry. The primary coordination environment of the group 15 elements Sb and Bi is formed by three covalent bonded nitrogen atoms (N_{cov}) and may be treated as a trigonal pyramid. The $E-N_{cov}$ distances (2.049(2) Å for Sb and 2.167(5) Å for Bi) are comparable with those found for closely related structures of the chelating triamide complexes $E[N(t\text{-}Bu)SiMe_2]_3CH$ (2.051(3)−2.062(3) Å for Sb and 2.149(7)−2.182(7) Å for Bi)[41] and lie within the values reported for $E[N(H)(C_6H_2\text{-}t\text{-}Bu_3)]_3$ (2.041(6)−2.064(6) Å for Sb and 2.14(2)−2.214(13) Å for Bi).[44] However, the $Bi-N_{cov}$ bond length in **8** is slightly shorter than it was observed for the simple triamide $Bi(NMe_2)_3$ (2.180(21), 2.189(18) Å).[31] It should be noticed that $N_{cov}-E-N_{cov}$ angles in **6** (100.91(7)°) and in **8** (103.5(2)°)

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Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

	6		**8**	
$E-N_{dat}$	Sb(1)−N(4)	3.200(2)	Bi(1)−N(2)	3.021(4)
$E-N_{cov}$	Sb(1)−N(1)	2.049(2)	Bi(1)−N(1)	2.167(5)
$N_{cov}-Si(1)$	N(1)−Si(1)	1.724(2)	N(1)−Si(1)	1.704(5)
$N_{cov}-E-N_{cov}$	N(1)#1−Sb(1)−N(1)	100.91(7)	N(1)#1−Bi(1)−N(1)	103.5(2)
$C-N_{dat}-C$	C(3)#1−N(4)−C(3)	118.51(8)	C(2)#1−N(2)−C(2)	115.5(3)

[a] Symmetry transformation used to generate equivalent atoms: #1, $-y$, $x - y$, z.

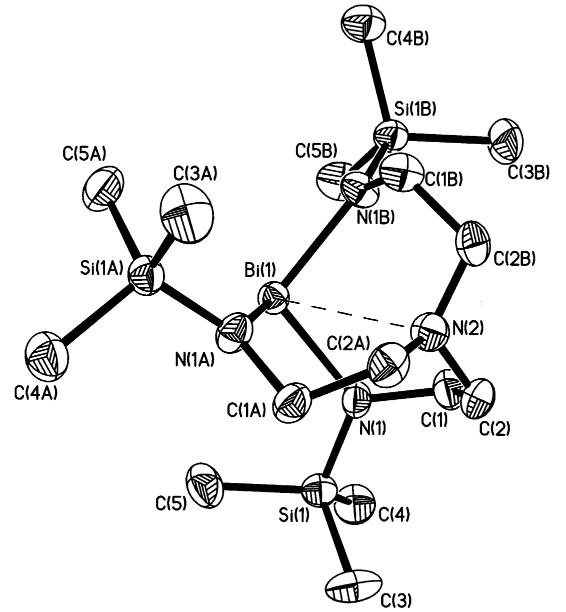

Figure 2. Molecular structure of **8**. Hydrogen atoms are omitted for clarity.

Table 3. Main Geometrical Parameters Calculated for $N(CH_2CH_2NSiMe_3)_3Sb$ (**6**), $N(CH_2CH_2NSiMe_3)_3Bi$ (**8**), and $N(CH_2CH_2NSiMe_3)_3P$ (**9**)[a] and Calculated $E-N_{dat}$ Bond Properties

compd	$E-N_{dat}$, Å	$E-N_{cov}$, Å	$N_{cov}-E-N_{cov}$, deg	$\rho(\mathbf{r}_b)$, au	$\nabla^2\rho(\mathbf{r}_b)$, au
6	3.067	2.098	103.34	0.018	0.0933
8	2.673	2.237	108.97	0.038	0.1260
9	3.415	1.761	102.96	0.007	0.0986

[a] X-ray data for **9** (two independent molecules):[47] $(E-N_{dat})_{average} = 3.360(7)°·$; $(E-N_{cov})_{average}$ = no data; $(N_{cov}-M-N_{cov})_{average} = 103.3(2)°$.

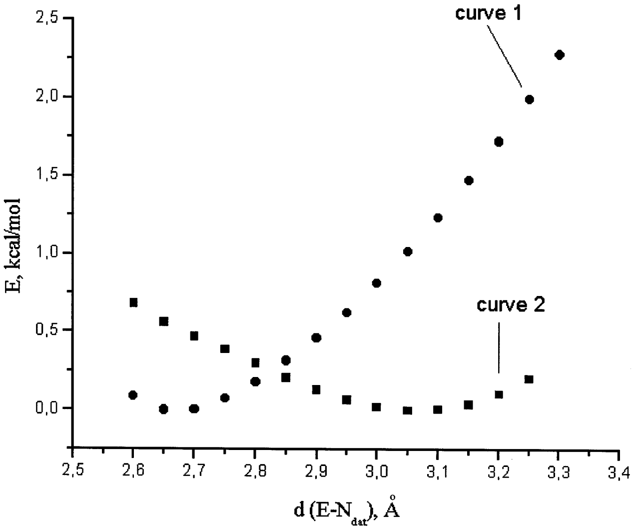

Figure 3. DFT variation of the molecule **8** (curve 1) and molecule **6** (curve 2) energy functions of $E-N_{dat}$ distance.

are somewhat greater than were observed for complexes $E[N(^tBu)SiMe_2]_3CH$ (98.8(1)−99.1(1)° for Sb and 97.1(3)−97.5(3)° for Bi).[41] The stereochemical active of the E(III) lone pair may be considered to occupy the vertex of the EN_3 pyramid.

The Sb−N(4) and Bi−N(2) (further denoted as $E-N_{dat}$) distances are 3.200(2) and 3.021(4) Å, respectively. These values are significantly smaller than the sum of the van der Waals radii of E and nitrogen (3.74 Å for Sb−N and 3.94 Å for Bi−N)[45] and are comparable with lengths of $E\leftarrow N_{dat}$ weak secondary interactions found in the structures of $E(C_6H_4CH_2NMe_2)_3$ (3.001(14)−3.16(2) Å for Sb and 2.97(2)−3.15(2) Å for Bi).[46] In both **6** and **8** N_{dat} atoms are shifted *toward* E atoms by 0.18 and 0.31 Å, respectively.

Consequently, the antimony and bismuth atoms can be regarded as [3+1]-coordinated in **6** and **8**. In contrast, the bridgehead nitrogen atom in the structure of $P[N(SiMe_3)CH_2CH_2]_3N$ (**9**) is shifted in the opposite direction and the P···N distance is 3.360(7) Å.[47] This value is slightly longer than the standard sum of phosphorus and nitrogen van der Waals radii (3.35 Å).[45] No short intermolecular contacts were observed in the structures of **6** and **8**.

Thus, the strengthening of intramolecular interaction E←N in *N,N′,N″*-tris(trimethylsilyl)azaatrane of group 15 elements increases as P···N < Sb←N < Bi←N. The latter may serve as an extra argument for the existence of $E\leftarrow N_{dat}$ secondary interaction; this conclusion is also confirmed by theoretical calculations.

We have carried out DFT calculations on compounds **6**, **8**, and **9** up to the PBE level of theory. The most important calculated geometry parameters of these compounds, the values of electron density in the $E-N_{dat}$ critical point [$\rho(\mathbf{r}_b)$], and the values of Laplacian of charge density in these points are listed in Table 3. The dependencies of compound **6** and **8** molecule energies on the $Sb-N_{dat}$ and $Bi-N_{dat}$ distances, respectively, are shown in Figure 3. There is a good agreement between geometry parameters of **6** and **9** for the solid phase (X-ray data) and for the free molecule (calculation data). The calculated value of the $Bi-N_{dat}$ distance for compound **8** is somewhat shorter than that in the solid state. Explanation of this disagreement is the weakness of the transannular bond in compounds **6**, **8**, and **9**. For example, only 0.75 kcal/mol is required to increase the calculated value of $Bi-N_{dat}$ distance in **8** to that of the solid-state value. The

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value of electron density in the Bi−N$_{dat}$ critical point and the Laplacian of charge density for **8** are close to the calculated data for 1-methylsilatrane, $N(CH_2CH_2O)_3SiCH_3$, −0.038 and 0.033 au, respectively.[48] The same values for compounds **6** and especially **9** are significantly smaller.

Thus, the strength of the Bi−N$_{dat}$ interaction in **8** is approximately corresponding to a strength of the transannular interaction in “usual” atranes (for example, silatranes) and significantly stronger than that in compounds **6** and **9**. Positive values of the Laplacian indicate that there is a closed-shell interaction between the metal atom and N$_{dat}$ atom.[49,50]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **6** and **8** and ^{1}H NMR spectra of **1** and **6** as well as calculation output files for **6**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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