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Synthesis and Crystal Structure of the Alkylbismuth Diiodides: A Family of Extended One-Dimensional Organometallic Compounds

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Crystals of the organometallic compounds $C_nH_{2n+1}BiI_2$ ($n = 2, 4$) have been grown under solvothermal conditions, using a reaction between R_3Bi ($R = C_2H_5$, C_4H_9) and BiI_3, in a diethyl ether solution. Both compounds crystallize in the orthorhombic space group *Pbam* with the unit cell parameters $a = 15.228(1)$ Å, $b = 10.964(1)$ Å, $c = 4.3505(2)$ Å, and $Z = 4$, for $C_2H_5BiI_2$, and $a = 25.515(2)$ Å, $b = 8.4192(6)$ Å, $c = 4.3467(2)$ Å, and $Z = 4$, for $C_4H_9BiI_2$. The solid state structures of these two compounds, when compared with the recently reported CH_3-BiI_2 ($n = 1$) structure, demonstrate that the alkylbismuth diiodides form a family of extended one-dimensional organic−inorganic materials. The framework of the $RBiI_2$ (R = alkyl) chains in each compound is virtually identical, with each bismuth having a square pyramidal coordination of four iodines in the basal plane and a covalently bonded terminal carbon from an alkyl group in the apical site. Each basal square shares trans edges with two nearest neighbors to form a one-dimensional BiI_2 chain, with the alkyl groups aligned on one side of the BiI_2 basal plane. The Bi(III) lone pair is stereochemically active and extends into the space trans to each alkyl group. The principle difference between the members of this family derives from the stacking of the $RBiI_2$ chains in the overall structure. This study demonstrates the flexibility to accommodate a range of different length organic constituents within a basic extended one-dimensional organometallic framework.

Introduction

Alkylbismuth dihalides were first synthesized over 100 years ago by Dünhaupt[1] and Marquardt.[2] A typical method of preparing the methyl- and ethylbismuth diiodides, for example, is to react trialkylbismuth with the corresponding alkyliodide at elevated temperatures (as high as 200 °C).[2] Interest in the alkyl- and the related arylbismuth halides has primarily focused on their usefulness as intermediates in synthetic chemistry. They have been used, for example, to produce asymmetric organobismuthines.[3,4] Bismuthines bearing three different ligands have a chiral bismuth center and may be optically active.[5] Potential thermochromic[6] and antibacterial/antifungal[7] properties of some organobismuth derivatives have provided further interest in these compounds. In addition, the reduced valence, highly-conducting, one-dimensional compound BiI, has been formed through the thermal decomposition of CH_3BiI_2.[8] While these compounds have been examined in numerous studies,[1−10] very little is known about their structure in the solid state.

Recently, the crystal structures of $PhBiBr_2$[9] and CH_3BiI_2[8] have been reported and demonstrate that in addition to their usefulness in synthetic organometallic chemistry, these materials also have interesting solid state structural features. $PhBiBr_2$, for example, consists[9] of $Ph_2Bi_2Br_6$ dimers in which bismuth adopts a square pyramidal local geometry, with the bromines forming the base and the phenyl bonding in the apical site. The two bismuths in the dimer are bonded through two bridging bromines, with an angle of 123.4° between the basal planes of the two edge-sharing $PhBiBr_4$ pyramids. The opposite sides of the the two basal planes are in fact not terminal, but rather bridge to an adjacent dimer on each corner, leading to an extended one-dimensional chain which zigzags along one axis, with the phenyls on each successive dimer alternating from side to side of the chain. In addition to the interactions within the chain, there is also a $\pi-\pi$ interaction between phenyls on adjacent chains, giving the structure a two-dimensional character.

CH_3BiI_2 crystallizes in the form of dark red needlelike crystals, with a simpler extended one-dimensional chainlike structure.[8] As for $PhBiBr_2$, the Bi atoms have a square pyramidal local geometry, with four iodine atoms forming the base and one methyl group in the apical site. In contrast to $PhBiBr_2$, however, each basal square shares two trans edges to form nominally straight one-dimensional BiI_2 chains along one axis, with the methyl groups all covalently bonded to bismuth on one side of the BiI_2 basal plane. Band structure calculations demonstrate that this material is electronically one-dimensional.[8]

Our interest in the organobismuth dihalides stems from a search for hybrid organic−inorganic systems in which both the organic and the inorganic components of the structure contribute either structurally or electronically to the creation of lower-dimensional systems with interesting physical properties. Inorganic materials offer the potential for high electrical mobility, a wide range of bandgaps (enabling the design of insulators, semiconductors, and metals), interesting magnetic interactions, a range of dielectric properties, and high thermal stability. On the other hand, organic materials provide the possibility for efficient luminescence, structural diversity, and a high degree of polarizability and they may also be conducting or even superconducting. One example of this type of organic−inorganic hybrid is the family of organic−inorganic layered

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perovskites,[11-19] which consist of alternating layers of metal halide-based perovskite sheets and organic ammonium cations, held together through ionic/hydrogen bonding. The inorganic sheets can be made magnetic,[11,12] conducting,[13-15] thermochromic,[16] or luminescent,[17-19] whereas the organic layers can make the structures more two- or three-dimensional (depending on the molecular length),[11,13] can control the crystallographic orientation of the inorganic sheets,[15] and can more generally be used to tune the physical properties arising in the inorganic sheets.[11,17]

In the layered perovskites, however, the organic component of the system is interacting with the extended inorganic sheets primarily through hydrogen bonding. Of particular interest to us are systems where the organic component of the structure is covalently bonded to an extended inorganic framework, thereby hopefully providing more significant electronic coupling between the two components. Whereas the majority of known organometallic structures consist of isolated molecules, several examples of organometallic structures with an extended inorganic framework have recently appeared in the literature. The proposed structure of polymeric CH_3ReO_3 is an interesting example[20] of a two-dimensional, extended organometallic oxide consisting of methyl-deficient, corner-sharing CH_3ReO_5 octahedra, which form electrically-conducting sheets. Among the halides, CH_3BiI_2 is a particularly attractive example because it structurally consists of simple, well-defined chains which are electronically one-dimensional.[8] This study was undertaken to see whether the structural characteristics found in CH_3BiI_2 could be generalized to the longer alkyl group analogs, and if so, to see how the incorporation of these longer alkyl side groups would affect the $C_nH_{2n+1}BiI_2$ chain structure and the packing of these chains within the full three-dimensional material.

Experimental Section

Synthesis. Red needlelike crystals of CH_3BiI_2 have been recently grown using a one-step reaction between Bi metal and CH_3I in an acid digestion bomb under solvothermal conditions.[8] The optimal temperature for the reaction was found to be approximately 125 °C. At temperatures below 100 °C, very little reaction was observed, while above 150 °C, BiI_3 was formed. Preliminary studies, in which methyl iodide was replaced with ethyl iodide, did not produce suitable crystals of ethylbismuth diiodide under the range of conditions examined.

Instead, crystals of the compounds $C_2H_5BiI_2$ and $C_4H_9BiI_2$ were grown using the two-step process (in a diethyl ether solution)

$$3RMgCl + BiCl_3 \rightarrow R_3Bi + 3MgCl_2 \quad (1)$$

$$R_3Bi + 2BiI_3 \rightarrow 3RBiI_2, \quad (2)$$

where $R = C_nH_{2n+1}$. This is similar to the process described earlier by Marquardt[2] for the synthesis of CH_3BiCl_2 and CH_3BiBr_2. However, we make use of an acid digestion bomb in step 2 to facilitate single crystal growth. It should be noted that the Grignard reagents used during step 1 react vigorously with oxygen and water. Consequently, all operations must be carried out in an inert atmosphere, and all solvents should be anhydrous and oxygen-free. In addition, concentrated triethylbismuth is self-igniting when exposed to air and may explode when heated.[21] During this synthesis we do not distill the trialkylbismuths from the ether solution. Nevertheless, care should be taken and adequate shielding should be used when heating the acid digestion bomb containing the diluted trialkylbismuth in step 2.

For $C_4H_9BiI_2$, 0.315 g of $BiCl_3$ (1.0 mmol; ultradry/anhydrous, 99.999%, Johnson Matthey) was dissolved in 8 mL of anhydrous diethyl ether at room temperature. Given the air/moisture sensitivity of the Grignard reagents used during the synthesis, the $BiCl_3$ was weighed in an argon-filled drybox (<1 ppm O_2 and H_2O) and sealed in a test tube using a septum. A syringe was used to introduce solvents. After the $BiCl_3$ was dissolved, the solution was cooled to 0 °C and 1.5 mL of C_4H_9MgCl (2 M in diethyl ether, Aldrich) was slowly added while agitating the test tube vigorously. A white precipitate of primarily $MgCl_2$ formed immediately, while $(C_4H_9)_3Bi$ remained in solution. The reaction tube was slowly heated to 30 °C and held at this temperature for 4 h, before being cooled to room temperature and centrifuged to separate the $MgCl_2$.

In the drybox, 0.621 g of BiI_3 (1.05 mmol; ultradry/anhydrous, 99.999%, Johnson Matthey) was loaded into a quartz cup, which fit into the teflon liner of an acid digestion bomb (23 mL, Parr 4749). Approximately 5 mL of the $(C_4H_9)_3Bi$ solution (0.53 mmol) was transferred into the quartz cup through a small hole in the top cover using a syringe. This process was performed outside the drybox under flowing nitrogen, with care taken to avoid introducing air into the reaction chamber. The acid digestion bomb was sealed and slowly heated to 95 °C over a 3-day period. After the bomb was maintained at 95 °C for 9 days, the oven was shut off and allowed to cool overnight to room temperature. The reaction vessel was opened and the yellow solution was removed from the quartz cup with a syringe. The remainder of the solvent was removed by drying the product for several hours in the evacuated antichamber of a drybox. Inside the quartz cup a mass of orange $C_4H_9BiI_2$ crystals formed (approximately 0.4 g, or 50% yield), primarily as small sheetlike crystals, a small number of very long (up to 1 cm) hairlike fibers, and a few larger slablike crystals which tended to grow at the top of the quartz cup. Each of these crystal types easily frayed into thin fibers and exhibited similar lattice constants. In addition, a small amount (several percent from powder X-ray diffraction) of fine Bi powder was also present in the quartz cup.

Additional solvothermal reactions were carried out at both lower and higher temperatures to test the effect of temperature on phase purity and crystal quality. For the 70 °C run, better phase purity was achieved (i.e. virtually no Bi metal powder was detected visually or in the powder X-ray diffraction pattern). However, the crystals were very small and not of sufficient quality for single-crystal structural characterization. Reactions carried out at 120 °C produced significantly larger and thicker rod- or platelike crystals than in the lower temperature reactions. There was a more substantial volume of Bi powder generated, however, making it difficult to isolate clean single crystals. The growth of reasonable single crystals using this technique is therefore a compromise between crystal size and quality on one hand, and decomposition into Bi metal on the other.

The $C_2H_5BiI_2$ crystals were grown using a very similar process with, however, C_2H_5MgCl replacing C_4H_9MgCl in step 1 of the synthesis. Resulting crystals were red and generally more needlelike than for the $C_4H_9BiI_2$ crystals—more analogous to those observed for CH_3BiI_2. In addition, more Bi metal powder was generated during the solvothermal synthesis of $C_2H_5BiI_2$ compared with the butyl analog. Finally, while both of the alkylbismuth diiodides discussed here were reasonably air stable, some degradation in the powder X-ray patterns was noted after the samples remained in air for 24 h. All products were therefore stored and handled in the drybox after synthesis.

X-ray Crystallography. Suitable single crystals were selected in an argon-filled drybox, under a microscope, and sealed in glass capillaries. For $C_2H_5BiI_2$, a needlelike crystal (which had been grown at 100 °C) was chosen, with approximate dimensions 0.05 × 0.10 × 1.0 mm. For $C_4H_9BiI_2$, an approximately rectangular slab (0.10 × 0.15 × 0.30 mm), from the 95 °C reaction, was used. Data for each of the

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Table 1. Crystallographic Data for $C_nH_{2n+1}BiI_2$ (n = 2, 4)

formula	$C_2H_5BiI_2$	$C_4H_9BiI_2$
fw	491.851	519.904
space group	*Pbam* (No. 55)	*Pbam* (No. 55)
a, Å	15.228(1)	25.515(2)
b, Å	10.964(1)	8.4192(6)
c, Å	4.3505(2)	4.3467(2)
V, Å^3	726.353	933.740
Z	4	4
ρ_{calcd}, g/cm^3	4.498	3.698
T, °C	20(2)	20(2)
radiation (λ), Å	Mo Kα (0.7107)	Mo Kα (0.7107)
abs coeff (μ), cm^{-1}	325.06	252.96
$R_F{}^a$	0.047	0.044
$R_w{}^b$	0.063	0.058

^{a} $R_F = \sum(F_o - F_c)/\sum(F_o)$. ^{b} $R_w = \{\sum w(F_o - F_c)^2/\sum(wF_o{}^2)\}^{1/2}$.

title compounds were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell parameters and the crystal orientation matrix were obtained by least-squares fit of 25 reflections with 18° < 2θ < 30°. Data were collected in the range 3.0° < 2θ < 56.0° ($\pm h,+k,\pm l$) using the $\omega-2\theta$ scan technique. A summary of the crystal structure and structure refinement results is found in Table 1. Intensity control reflections were monitored every 5000 seconds during the data collection. For $C_2H_5BiI_2$, the control reflections decreased by 6.3% in intensity over the 67 h of X-ray exposure, while for $C_4H_9BiI_2$, a 9.9% drop was noted over 91 h. In each case, the decay was fitted and accounted for during data analysis. Empirical absorption corrections based on several azimuthal ψ scans were also applied. The NRCVAX 386 PC version[22] program was used for the structural solution and refinement.

The space group *Pbam* (No. 55) was chosen for both compounds based on the observation of the systematic reflection conditions—$0kl$ ($k = 2n$) and $h0l$ ($h = 2n$)—and the successful structural refinements. While both the $C_nH_{2n+1}BiI_2$ (n = 2, 4) structures could also be successfully refined in the non-centrosymmetric space group *Pba*2 (No. 32), with slight reductions in R-factors, the centrosymmetric space group was ultimately adopted because (a) the refinement in the centrosymmetric space group was well-behaved, (b) the thermal ellipsoids for the heavy atoms in the centrosymmetric space group were small and in fact almost identical with those from the noncentrosymmetric solution, (c) the atomic positions for the heavy atoms were very similar (after shift in origin) in both space groups, (d) using the program MISSYM[23] to check for missing symmetry, an inversion center was detected for the configuration of atoms refined in the non-centrosymmetric space group, (e) analysis of the E-statistics favored this choice (for example, for $C_4H_9BiI_2$, $|E^2 - 1| = 1.067$, experimental; 0.968, theoretical centric; 0.736, theoretical acentric).

The positions of the heavy atoms (Bi and I) were determined by direct methods, while the remaining non-hydrogen atomic positions were picked up from Fourier difference maps. Locating the hydrogen atoms was not attempted. All the heavy atoms were refined anisotropically, while the carbon atoms were refined isotropically. The minimum and maximum electron densities in the final difference Fourier syntheses were −3.920, −2.820 e/Å^3 and +2.190, +2.840 e/Å^3 for the ethyl and butyl compounds, respectively. The atomic positions and isotropic thermal parameters for $C_2H_5BiI_2$ and $C_4H_9BiI_2$ are tabulated in Tables 2 and 3, respectively. The anisotropic temperature factors for each title compound are supplied as Supporting Information (Tables S2 and S3).

Results and Discussions

As recently reported,[8] CH_3BiI_2 crystallizes as dark red needles in the monoclinic space group $C2/m$, adopting an unusual one-dimensional organic-inorganic chain-like structure (Figure 1a) with the cell parameters a = 15.611(1) Å, b = 4.3485(4) Å, c = 19.297(2) Å, β = 106.395(6)°, and Z = 8. Locally, the two independent Bi atoms in the asymmetric unit have a square pyramidal coordination, with four I atoms forming the base and one covalently bonded methyl group occupying an apical site. Bi atoms bond to the four iodines with the bond lengths 3.087(1) (2×) and 3.128(1) Å (2×) for Bi(1) and 3.086(1) (2×) and 3.122(1) Å (2×) for Bi(2). The average Bi−I bond length, 3.106 Å, is smaller than the sum of ionic radii[24] for $Bi^{3+}I^-$ (d_{ion} = 3.16 Å), but is similar to the Bi−I bond length reported for BiI_3, 3.1 Å.[25] Other potentially important interactions within the unit cell include Bi(1)−Bi(2), Bi(1)−I(3), and Bi(2)−I(1), all approximately trans to a Bi−C bond, with the corresponding interatomic distances 4.437(1), 4.155(1), and 4.380(1) Å, respectively. These distances are all considerably greater than covalent or ionic bond lengths and are approximately equal to (or greater than) the sum of the van der Waals radii for these atoms.

Table 2. Positional and Thermal Parameters^a for $C_2H_5BiI_2$

atom	position	x	y	z	U_{eq},^{b} Å^2
Bi	4g	0.98716(7)	0.1954(1)	0.00	0.0300(5)
I(1)	4h	0.8692(1)	0.0764(2)	0.50	0.034(1)
I(2)	4h	0.1029(1)	0.3183(2)	0.50	0.035(1)
C(1)	4g	0.902(2)	0.371(3)	0.00	0.043(8)
C(2)	4g	0.815(4)	0.362(5)	0.00	0.08(2)

^{a} Heavy atoms (Bi and I) are refiend anisotropically; Anisotropic thermal parameters are found in Supplementary Table S2. ^{b} $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Positional and Thermal Parameters^a for $C_4H_9BiI_2$

atom	position	x	y	z	U_{eq},^{b} Å^2
Bi	4h	0.81596(4)	0.2602(1)	0.50	0.0360(5)
I(1)	4g	0.73406(7)	0.1583(2)	0.00	0.036(1)
I(2)	4g	0.89681(7)	0.3490(2)	0.00	0.040(1)
C(1)	4h	0.844(1)	0.999(4)	0.50	0.047(7)
C(2)	4h	0.902(1)	0.973(4)	0.50	0.048(7)
C(3)	4h	0.910(1)	0.783(4)	0.50	0.050(7)
C(4)	4h	0.971(2)	0.743(6)	0.50	0.10(2)

^{a} Heavy atoms (Bi and I) are refined anisotropically; Anisotropic thermal parameters are found in Supplementary Table S3. ^{b} $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

In BiI_3, the Bi(III) atoms adopt an octahedral coordination of six iodines (i.e. Bi(III) lone pair is “stereochemically inactive” or “inert”). Molecular orbital considerations suggest that the square pyramidal Bi coordination in CH_3BiI_2 arises primarily to reduce Bi−C antibonding character in the HOMO.[8] The resulting Bi 6s and 6p hybridization in the valence band (HOMO) leads to a stereochemically active lone pair oriented trans to each methyl group. A similar square pyramidal (or pseudo square pyramidal) local geometry has also been observed in several other alkyl- and arylantimony(III)/bismuth(III) dihalides and aryltellurium(IV) triiodides, including $PhBiBr_2$[9], $PhSbX_2$ (X = Cl, Br, I),[26] CH_3SbX_2 (X = Cl, Br, I),[27] $(4\text{-}CH_3C_6H_4)SbX_2$ (X = Cl, Br),[28] and $PhTeX_3$ (X = Cl, Br, I).[29]

Each BiI_4 basal square shares trans edges with two nearest neighbors to form one-dimensional BiI_2 chains along the b-axis. The organic−inorganic chains are held together by a van der Waals interaction, thereby forming an extended solid state structural array. The two independent bismuth sites correspond to two symmetry-inequivalent CH_3BiI_2 chains which, however, are very similar in geometry. The two chains nominally form pairs—one chain with the methyl groups pointing roughly along the positive c-axis and one with these groups pointing along the negative c-axis—with the Bi(III) lone pairs occupying the space between the pair. The plane of the BiI_2 backbones of the chains lies approximately in the $a-b$ plane, with the nearest

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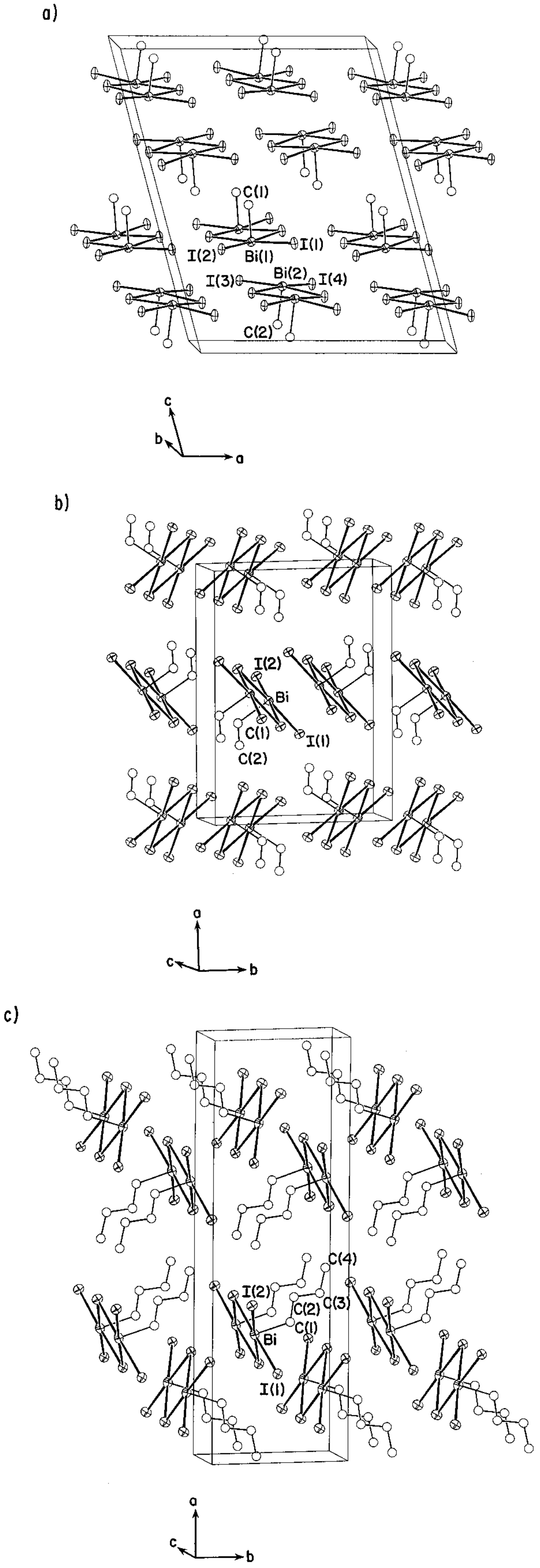

Figure 1. ORTEP drawings of the unit cells for $C_nH_{2n+1}BiI_2$ for (a) $n = 1$, (b) $n = 2$, and (c) $n = 4$, viewed approximately along the direction of chain propagation (*b*-axis for the methyl compound; *c*-axis for the ethyl and butyl compounds). The thermal ellipsoids for the bismuth and iodine atoms are drawn at 50% probability and represent their anisotropic thermal parameters. The carbon atoms are drawn as open circles and are drawn with an arbitrary scale factor. For each structure, the unit cell is outlined.

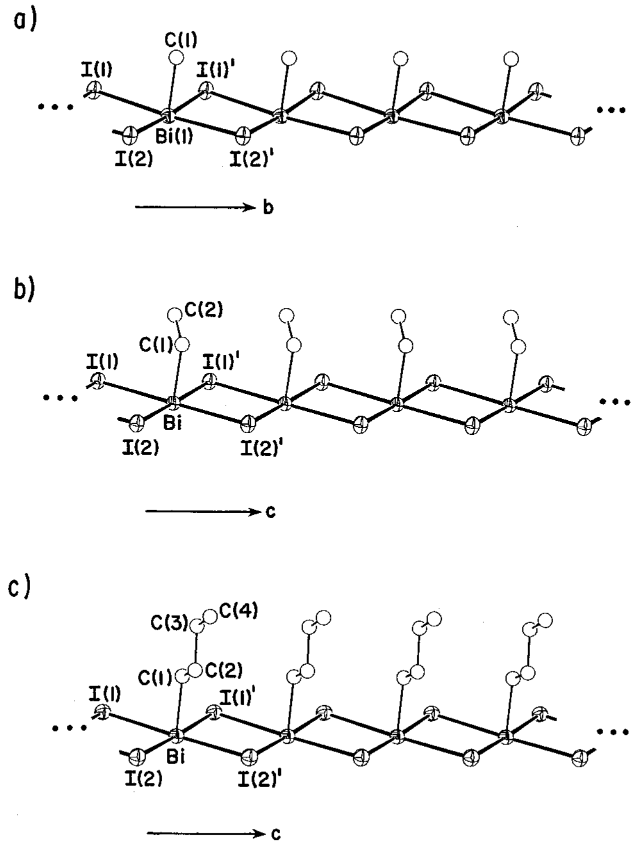

Figure 2. ORTEP drawings of $C_nH_{2n+1}BiI_2$ chain fragments for (a) $n = 1$, (b) $n = 2$, and (c) $n = 4$, showing the square pyramidal local bismuth coordination, the detailed chain structure, and the atom labeling. The thermal ellipsoids for the bismuth and iodine atoms are drawn at 50 percent probability and represent their anisotropic thermal parameters. The carbon atoms are drawn as open circles and are drawn with an arbitrary scale factor. Note that for CH_3BiI_2, only one of the two independent chains is shown.

neighbor chains on either side at the same point along the *c*-axis. Consequently, another way of looking at this structure is to consider it as consisting of bilayers of CH_3BiI_2 chains—one layer with the methyl groups pointing up and one with these groups pointing down along the *c*-axis. The methyl groups extend roughly perpendicular to the BiI_2 planes into the space between the bilayers. More details on the CH_3BiI_2 structure can be found in our earlier work.[8]

In $C_2H_5BiI_2$ and $C_4H_9BiI_2$ (Figure 1b,c), the internal structure of the organic−inorganic chains (Figure 2) is very similar to the methyl analog, with the longer alkyl groups covalently bonding to a single side of the BiI_2 backbone. However, since the chains are free to rotate around their direction of propagation, the packing of these chains is significantly different for each of the different length alkyl side groups, allowing each system to more adequately accommodate the different steric constraints of the longer side groups. In contrast to the methyl compound, the unit cells for the two longer alkyl side group compounds contain a single bismuth atom in the asymmetric unit, and the

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Table 4. Selected Bond Distances (Å) and Angles (deg) in $C_2H_5BiI_2$

Bi−I(1)	3.108(2)	Bi−C(1)	2.32(4)
Bi−I(1)^a	3.108(2)	I(1)−Bi^b	3.108(2)
Bi−I(2)	3.107(2)	I(2)−Bi^b	3.107(2)
Bi−I(2)^a	3.107(2)	C(1)−C(2)	1.33(6)
I(1)−Bi−I(1)^a	88.82(4)	I(2)−Bi−I(2)^a	88.86(4)
I(1)−Bi−I(2)	91.15(3)	I(2)−Bi−C(1)	87.4(6)
I(1)−Bi−I(2)^a	178.99(7)	I(2)^a−Bi−C(1)	87.4(6)
I(1)−Bi−C(1)	91.5(6)	Bi^b−I(1)−Bi	88.82(5)
I(1)^a−Bi−I(2)	178.99(7)	Bi^b−I(2)−Bi	88.86(5)
I(1)^a−Bi−I(2)^a	91.15(3)	Bi−C(1)−C(2)	119(3)
I(1)^a−Bi−C(1)	91.5(6)		

^{a} $x, y, -1 + z$. ^{b} $x, y, 1 + z$.

Table 5. Selected Bond Distances (Å) and Angles (deg) in $C_4H_9BiI_2$

Bi−I(1)	3.134(2)	I(1)−Bi^b	3.134(2)
Bi−I(1)^a	3.134(2)	I(2)−Bi^b	3.088(2)
Bi−I(2)	3.088(2)	C(1)−C(2)	1.51(4)
Bi−I(2)^a	3.088(2)	C(2)−C(3)	1.62(4)
Bi−C(1)	2.31(3)	C(3)−C(4)	1.59(6)
I(1)−Bi−I(1)^a	87.80(4)	I(2)−Bi−C(1)	91.6(5)
I(1)−Bi−I(2)	91.35(3)	I(2)^a−Bi−C(1)	91.6(5)
I(1)−Bi−I(2)^a	178.11(5)	Bi^b−I(1)−Bi	87.80(5)
I(1)−Bi−C(1)	86.7(5)	Bi^b−I(2)−Bi	89.45(5)
I(1)^a−Bi−I(2)	178.11(5)	Bi−C(1)−C(2)	116(2)
I(1)^a−Bi−I(2)^a	91.35(3)	C(1)−C(2)−C(3)	105(2)
I(1)^a−Bi−C(1)	86.7(5)	C(2)−C(3)−C(4)	109(3)
I(2)−Bi−I(2)^a	89.45(4)		

^{a} $x, y, -1 + z$. ^{b} $x, y, 1 + z$.

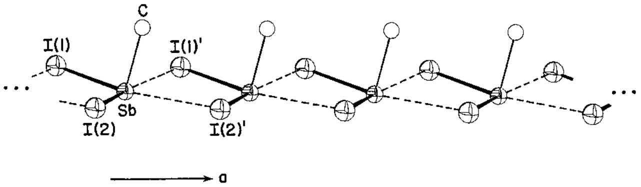

Figure 3. ORTEP drawing of a CH_3SbI_2 chain fragment using atomic coordinates from ref 27b, showing the pseudo-trigonal pyramidal primary antimony coordination and weak secondary bonds (shown as dashed lines) to two additional iodines. Note the similarity to the CH_3BiI_2 chain in Figure 2a. However, in this case, the long secondary Sb−I bonds interrupt the chain along its axis. The thermal ellipsoids for the antimony and iodine atoms are drawn at 50% probability and represent their isotropic thermal parameters. The carbon atoms are drawn as open circles and are drawn with an arbitrary scale factor.

cells adopt an orthorhombic *Pbam* symmetry rather than the monoclinic space group observed for CH_3BiI_2. As a result of the different choice of space groups, the $RBiI_2$ chains extend along the *b*-axis for the methyl compound, while they extend along the *c*-axis for the ethyl and butyl systems.

Within the $C_2H_5BiI_2$ chains, the Bi−I(1) and Bi−I(2) bond distances of 3.108(2) and 3.107(2) Å (see Table 4) are virtually the same, and the average of these two distances is very similar to the average value found in CH_3BiI_2. The Bi−C(1) bond distance of 2.32(4) is the same, within the experimental error, as the average distance observed for the methyl compound (2.28(2) Å). The bond angles $\angle$I(1)−Bi−I(1)^a = 88.82(4)°, $\angle$I(1)−Bi−I(2) = 91.15(3)°, and $\angle$I(1)−Bi−C(1) = 91.5(6)° are all close to 90°, indicating a nearly ideal square pyramidal local coordination for the bismuth atom and suggesting that the Bi(III) lone pair is stereochemically active in a similar manner to the methyl analog.

Despite the very similar bonding geometry within the chains for the ethyl- and methylbismuth diiodides, the different alkyl side group length leads to a significantly different stacking of the chains within the three-dimensional array. Although there is now only one independent chain in the structure (in this case running along the *c*-axis), by symmetry the chains still form pairs, with the ethyl groups pointing in opposite directions and with the Bi(III) lone pairs in the space between the pair. The Bi−Bi distance between chains, 4.302(2) Å, is slightly smaller than the corresponding Bi(1)−Bi(2) distance in CH_3BiI_2, and the interchain Bi−I(1) distance, 4.290(2) Å, is slightly larger than the average of the Bi(1)−I(3) and Bi(2)−I(1) distances (4.268 Å) in the methyl compound. For $C_2H_5BiI_2$, the pairs of chains are also rotated such that the basal plane of the BiI_2 backbone for each chain does not lie in the *b*−*c* plane. Rather, the backbones are now rotated approximately 50° with respect to this plane. The rotation is such that if we again consider this structure as consisting of layers of chains (this time in the *b*−*c* plane), the tails of the ethyl groups again extend perpendicular into the space between the layers.

In $C_4H_9BiI_2$, the Bi−I(1) and Bi−I(2) bond lengths within the chain are 3.134(2) and 3.088(2) Å, respectively, leading to an average Bi−I bond length of 3.111(2) Å. Other bond lengths and angles are similar to those found in the ethyl compound and are given in Table 5. Again, the major difference between the structures derives from how the chains pack into a three-dimensional structure. The plane of the BiI_2 backbones is now even more rotated out of the *b*−*c* plane (approximately 70°). Whereas for both the methyl and ethyl compounds the chains nominally form pairs with the alkyl groups pointing in opposite directions, in this case such pairs are not present. No significant (less than 5 Å) interchain Bi−Bi interactions are present. The Bi−I(1) distance between chains, 4.194(2) Å, is smaller than the interchain Bi−I(1) distance in the ethyl analog, but is still larger than the van der Waals distance for these atoms. For $C_4H_9BiI_2$, the packing of the chains is more layerlike (presumably accounting for the presence of more sheetlike crystals in the synthesis). Each layer consists of a bilayer of chains, made up of a layer containing nominally "up-pointing" and one with nominally "down-pointing" alkyl groups. There is, however, a significant tilting of the alkyl groups along the *b*-axis of the structure, with the tilt alternating in opposite senses as one progresses through successive layers down the *a*-axis.

For both the ethyl and butyl compounds, the bond angles at the bismuth end of the alkyl groups, $\angle$Bi−C(1)−C(2) (=119(3) and 116(2)°, respectively), are significantly larger than the 109.47° expected for sp^3 hybridization and also larger than the more terminal bond angles observed in the butyl group, $\angle$C(1)−C(2)−C(3) = 105(2)° and $\angle$C(2)−C(3)−C(4) = 109(3)°. The larger angles may arise from the steric effect of the large Bi atom adjacent to the end of the alkyl group or as a result of the difference in electronegativity between bismuth and carbon, which should lead to some shift in electron density in the Bi−C(1) bond toward the C(1) atom.

It should be noted that CH_3SbX_2 (X = Cl, Br, I) also forms a similar chainlike structure in the triclinic space group $P\bar{1}$,[27] with, in this case, highly distorted edge-sharing square pyramidally-coordinated CH_3SbX_4 units, and again methyl groups aligned on one side of each "chain." There are, however, two short and two long Sb−X bonds along the "chain" in CH_3SbX_2 (Figure 3), leading to an alternate description of this compound in terms of trigonal pyramidal CH_3SbX_2 molecular units, which weakly interact through long Sb-X secondary bonds. In CH_3SbBr_2, for example, the primary Sb−Br bonds have an average length of 2.57 Å, whereas the secondary bonds have an average length of 3.34 Å. As the secondary bonds are nearly 30% longer than the primary bonds, a molecular description of this structure, based on nearly isolated CH_3SbBr_2 trigonal units, seems at least as appropriate as the extended description with highly distorted square pyramidal Sb coordination. Even for the corresponding iodide, the two secondary Sb−I bonds (d_{av} = 3.43 Å) are over

20% longer than the two short bonds ($d_{av} = 2.78$ Å). This can be compared with the SbI_3 structure, which consists of three short (2.87 Å) and three long (3.32 Å) Sb−I bonds and is considered to be intermediate between a purely molecular structure (like AsI_3) and an extended structure (like BiI_3),[25] in which the primary and secondary bonds are the same length. For a purely molecular structure, we would expect the long interactions between trigonal pyramidal molecular units to be of a similar length as the sum of the van der Waals radii for Sb and I,[30] i.e. 4.03 Å.

In the $C_nH_{2n+1}BiI_2$ compounds, there are also nominally short and long Bi−I bond lengths. However, in this case, the differences between the two distances range from only 0.03% for the $n = 2$ compound (too small to be differentiated in the structure refinement), to 1.3% for $n = 1$, and 1.5% for $n = 4$. These Bi−I bond lengths are all substantially less than the expected van der Waals distance,[30] 4.13 Å. If we think about the alkyl bismuth and antimony dihalides as being based on molecular RMX_2 units (R = alkyl, M = Sb, Bi, X = Cl, Br, I), coupled through secondary bonding,[30] then the secondary interactions in the antimony compounds are moderately weak (i.e. the Sb−X bond lengths are substantially longer than the primary bond lengths, but still well below the expected van der Waals distance), whereas for bismuth, the secondary interactions are sufficiently strong that the distinction between primary and secondary bonding has become negligible, and the BiI_2 chains can be considered structurally and electronically[8] as truly extended one-dimensional units. This increase in secondary bond strength in the bismuth compounds is consistent with the expectation[30] that secondary bond strength should increase for more electropositive central atoms (A) in the system X−A···X, where A···X represents the secondary bond.

Conclusion

While alkylbismuth halides have been known for over 100 years, interest in them has primarily focused on their usefulness as intermediates in synthetic chemistry. The novel structures presented here demonstrate that, in addition, these materials are structurally interesting in their own right. Typically, organometallic compounds consist of isolated molecules or clusters. While not isostructural, the series $C_nH_{2n+1}BiI_2$ ($n = 1, 2, 4$) has been shown to form a family of one-dimensional chain-like compounds in which the alkyl groups are covalently bonded to one side of an extended, nominally straight, BiI_2 chain. Locally, the coordination around each bismuth(III) atom is square pyramidal, with four nearly equidistant iodines forming the base and an alkyl group bonded in the apical site. The extended chains are formed by edge-sharing between the bases of the square pyramids. While the structural framework for the $RBiI_2$ chains is virtually identical for the three members examined in this study, the packing of the chains is distinct for each compound, presumably to accommodate a sterically and more energetically favorable packing of the longer alkyl side groups.

Whereas we have presented results on the $n = 1$, 2, and 4 compounds, a similar chainlike structure would be expected for other (at least short and intermediate length) alkyl groups in the $C_nH_{2n+1}BiI_2$ family. The effect of longer ($n > 4$) alkyl groups on the packing of the chains is an interesting issue for future examination. It is clear from the present study that even for $n \leq 4$, the steric effects of the alkyl side groups play a critical role in determining the overall orientation and packing of the organometallic chains. In addition, it should also be possible to replace the saturated hydrocarbon groups with unsaturated groups, and perhaps even carefully designed aryl groups (although steric and electronic interactions between these groups would likely make it more difficult to maintain the simple chain-based structure). Consequently, although only three examples are given here, the unusual extended ("polymeric") chainlike structure observed in the title compounds provides an interesting model organic−inorganic system in which various organic components can be covalently bonded to an extended inorganic one-dimensional chain, perhaps providing a framework for designing organic−inorganic hybrid materials with interesting and potentially useful physical properties.

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Supporting Information Available: Listings of complete data collection and refinement parameters, and anisotropic temperature factors for the heavy atoms in the refinements for $C_2H_5BiI_2$ and C_4H_9-BiI_2 (2 pages). Ordering information is given on any current masthead page.

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