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$Bi_{16}I_4$ – A New Bismuth Subiodide: An Analysis of Molecular Packing and Electronic Structures of the Compounds in the Bi_mI_4 (m = 14, 16, 18) Family

Martin Lindsjö,[a] Lars Kloo,*[a] Alexei Kuznetzov,[b] and Boris Popovkin[b][†]

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A new bismuth subiodide $Bi_{16}I_4$ was synthesized by high-temperature synthesis. Its structure was determined by single-crystal X-ray diffraction analysis [$C2/m$ (No. 12), a = 25.948(6) Å, b = 4.354(1) Å, c = 13.259(3) Å, β = 104.48(2)°, Z = 2, R_1 = 0.041, $wR_{all}(F^2)$ = 0.109]. The compound belongs to the Bi_mI_4 (m = 14, 16, 18) family of low-dimensional subhalides that feature one-dimensional bismuth stripes of varying width, terminated by iodine atoms. Ab initio calculations at the DFT level were performed on 3D structures of all three Bi_mI_4 compounds of the family. According to the computational data all three compounds are expected to exhibit metallic behavior and Pauli paramagnetism, with a directional anisotropy of the properties indicated by the calculated band structures. The molecular packing in bismuth subiodides has been analyzed in detail and two homologous series – $Bi_{8+4n}I_4$ and $Bi_{10+4n}I_4$ (n = 0, 1, 2, ...) – are suggested to describe existing and possible structures of the compounds of the Bi_mI_4 family.

Introduction

The element bismuth has an extensive subvalent chemistry illustrated by the formation of naked, polyhedral, cationic clusters and low-dimensional extended structures.[1] The latter ones are exemplified by the subvalent bismuth iodides (bismuth in an oxidation state lower than +3) and their derivatives.[2–8] The existence of bismuth monoiodide, BiI, the first bismuth subiodide, was confirmed in 1970.[2] A few years later the crystal structures of BiI (or Bi_4I_4)[8] and the related bismuth monobromide, Bi_4Br_4,[4] were determined. Further work on the Bi–BiI_3 system produced two more bismuth subiodides, $Bi_{14}I_4$ and $Bi_{18}I_4$,[5–7] and different mixed bismuth monohalides, $Bi_4Br_xI_{4-x}$.[8] The main route has in all cases been solid-state synthesis from the elements.

The main elements of the structures of the existing bismuth subiodides are discrete, neutral ribbons of polymeric molecules in one crystallographic direction. The internal structure in the ribbons is constructed solely of bismuth–bismuth bonds, and iodine atoms are attached along the edges of the ribbons. These ribbons are then packed into the crystals. The similarities in topology between molecules of the bismuth subiodides and bismuth metal are well documented.[9] The molecules of all known subiodides can be viewed as slices of the 2D-bismuth metal layers, formed by the connection of corrugated Bi-atom hexagons into 1D stripes of varying width and terminated by iodine atoms. The width of the stripes determines the stoichiometry of the respective compound. Two different ways of slicing are realized: in Bi_4I_4 and other bismuth subhalides with a 1:1 ratio of the metal and halogen atoms the terminal Bi-atom hexagons are open, and terminal bismuth atoms are coordinated by one bismuth atom and four halogens. In $Bi_{14}I_4$ and $Bi_{18}I_4$ the terminal Bi-atom hexagons are closed, rendering terminal bismuth atoms coordinated by two bismuth and two iodine atoms.

The calculated electronic structures and physical properties of the single crystals of the compounds of this family have been investigated for Bi_4I_4 and Bi_4Br_4 only.[10] Both phases are diamagnetic and show rather complicated and interesting temperature dependences of the electrical resistance in the interval 4–300 K. As evident from both computational and experimental data both compounds predominantly (except below 55–60 K) exhibit semiconducting behavior. During our attempts to produce single crystals of bismuth-rich subiodides, suitable for measurements of various physical properties, a new bismuth subiodide, $Bi_{16}I_4$, was isolated. The crystal and electronic structures of this new compound are reported here. Furthermore, the crystal and electronic structures of $Bi_{14}I_4$ and $Bi_{18}I_4$ are compared and rationalized.

Results and Discussion

Synthesis and Crystal Structure of $Bi_{16}I_4$

Attempts to synthesize larger single crystals of $Bi_{18}I_4$, following a slight modification of the procedure described in

[a] Inorganic Chemistry, School of Chemical Science and Engeneering, Royal Institute of Technology,
10044, Stockholm, Sweden
[b] Department of Chemistry, M. V. Lomonosov Moscow State University,
119992 Moscow, Russia
[†] This article is dedicated to the memory of our colleague and friend Boris Popovkin, who tragically passed away in March 2008.

the literature,[11] did not produce the expected needle-shaped crystals of sufficient size. Instead, the new subhalide $Bi_{16}I_4$ was isolated as small, cone-shaped crystals. The three attempts to repeat this experiment at identical conditions all resulted in different subiodides: $Bi_{14}I_4$, $Bi_{16}I_4$, and $Bi_{18}I_4$ in varying relative amounts.

The structure of $Bi_{16}I_4$ consists of packed polymeric molecules constructed from six-membered, bismuth-atom rings with iodine atoms at the terminals on the polymer edges; two attached to each edge-bismuth atom (Figure 1, a). The width of the molecular ribbon is 16 bismuth atoms, thus corresponding to the overall stiochiometry. These polymer molecules are packed into parallel two-dimensional blocks (Figure 1, b). Finally, the blocks are joined into a three-dimensional lattice (Figure 1, c).

The shortest cell parameter *b* ("molecular" parameter) corresponds to the translation along the molecule. The translation along the direction of the molecule packing in the block corresponds to the cell parameter *c* ("molecule packing" parameter), and along the direction of the block packing to the cell parameter *a* ("block packing" parameter). The polymeric molecules feature a twofold screw axis or mirror plane (hereafter denoted "molecular axis"), co-directional with the crystallographic *b* axis (Figure 1, a). Within the block, as well as in the whole structure, all the molecular axes are parallel and form a 17.5° angle with respect to the block borders, which may be defined as the planes going through all the terminal atoms of the I(2) block (Figure 1, b).

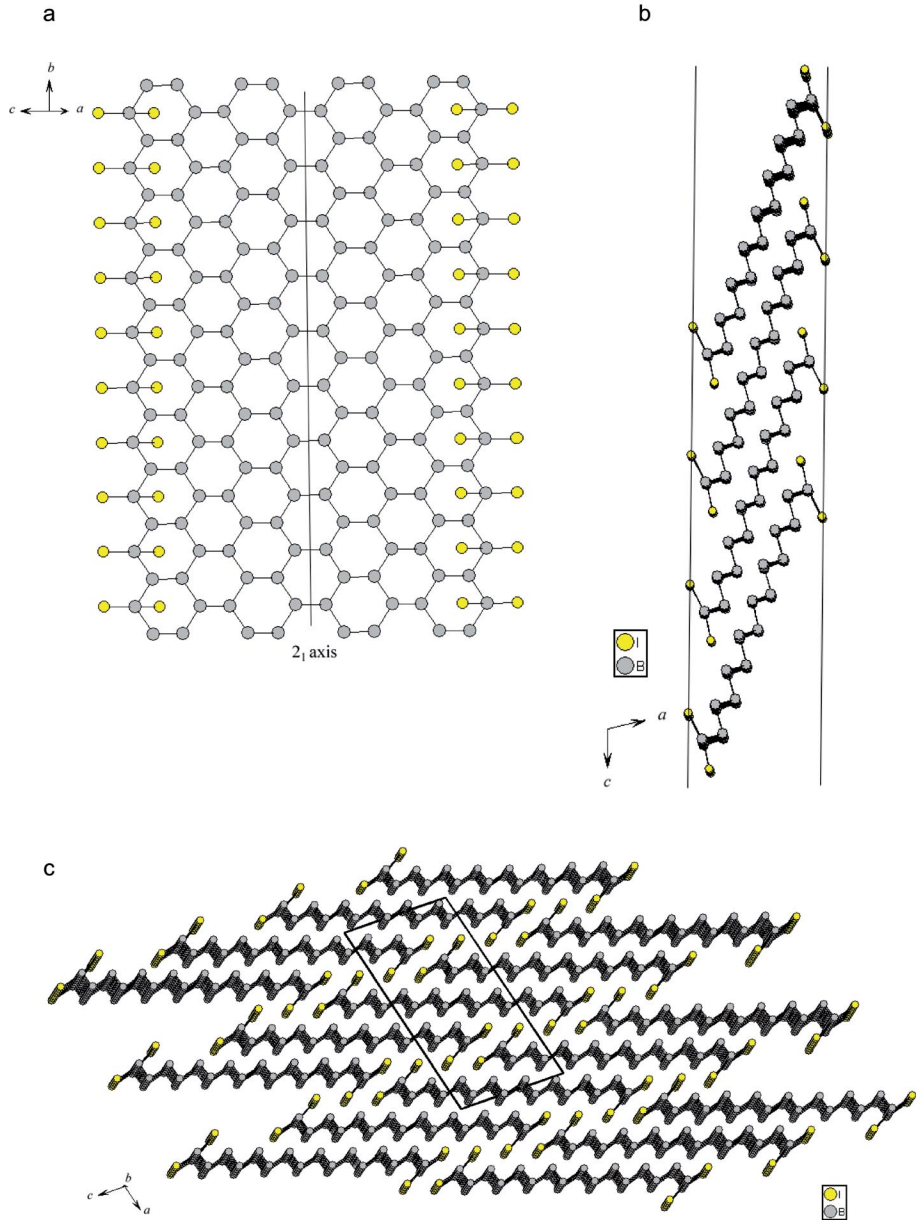

Figure 1. (a) A "molecule" in the structure of $Bi_{16}I_4$ with mirror-plane symmetry. (b) A single block in the packing of $Bi_{16}I_4$. (c) 3D packing in $Bi_{16}I_4$.

Atomic parameters and the shortest inter-atomic distances for $Bi_{16}I_4$ are given in Table 1 and Table 2, respectively. As seen from Table 2, the bonding of the molecules within the same blocks is based on bismuth–bismuth or bismuth–iodine interactions at distances far exceeding the shortest intra-molecular distances. Similar shortest distances are observed between the molecules belonging to different neighboring blocks; these are exclusively bismuth–iodine contacts. Evidently, upon the formation of the blocks and 3D structure, the weak nature of each single contact at distances of about 3.6–3.7 Å is to a certain extent compensated by the large number of such contacts (Figure 2).

The structure of $Bi_{16}I_4$, described above, displays the same structural motif as in $Bi_{14}I_4$ and $Bi_{18}I_4$ as well as the same structural features.[5–7] No significant differences can be observed in the bond lengths of $Bi_{16}I_4$ when compared to those of $Bi_{14}I_4$ or $Bi_{18}I_4$, although the interval of the molecular bismuth–bismuth bonds, 3.03–3.07 Å, is narrower in this new compound. The main difference is the width of the bismuth ribbons, where the latter two have 14 and 18 atoms, respectively. Besides this, the lattice of $Bi_{16}I_4$ features a slightly different style of packing of the blocks into the 3D structure. In this compound the neighboring blocks are shifted by ½ of the *b* translation (Figure 1, c), while in its analogues all the blocks are placed in identical positions with no translational shift. Such a disposition of the blocks should in all cases guarantee maximal contact. This difference arises from the fact that, unlike $Bi_{14}I_4$ and $Bi_{18}I_4$, the $Bi_{16}I_4$ compound contains single molecules with a mirror-plane symmetry element, rather than a 2_1 screw axis. As a consequence, the *c* parameter of the $Bi_{16}I_4$ unit cell is twice as large as the corresponding "block packing" parameters for the $Bi_{14}I_4$ and $Bi_{18}I_4$ structures (see Table 3), and the number of formula units for the former compound is 2 rather than 1.

Table 1. Final coordinates and anisotropic thermal parameters [$U_{12} = U_{23} = 0$ Å^2] for $Bi_{16}I_4$. All atoms are in a 4*i* Wycoff position (*m* site symmetry).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{11} [Å^2]	U_{22} [Å^2]	U_{33} [Å^2]	U_{13} [Å^2]
Bi(l)	0.29029(3)	1/2	0.37236(5)	0.0206(4)	0.0205(4)	0.0140(4)	0.0049(3)
Bi(2)	0.37183(3)	0	0.36456(5)	0.0163(4)	0.0216(4)	0.0113(3)	0.0021(3)
Bi(3)	0.34041(3)	0	0.12824(5)	0.0187(4)	0.0198(4)	0.0105(3)	0.0030(3)
Bi(4)	0.42083(3)	1/2	0.11761(5)	0.0174(4)	0.0207(4)	0.0110(4)	0.0029(3)
Bi(5)	0.38526(3)	1/2	–0.11969(5)	0.0187(4)	0.0187(4)	0.0104(4)	0.0034(3)
Bi(6)	0.46523(3)	0	–0.13141(5)	0.0172(4)	0.0195(4)	0.0108(4)	0.0019(3)
Bi(7)	0.43458(3)	0	–0.37008(5)	0.0192(4)	0.0195(5)	0.0106(4)	0.0028(3)
Bi(8)	0.51444(3)	1/2	–0.38081(5)	0.0172(5)	0.0198(5)	0.0118(4)	0.0032(3)
I(1)	0.23017(5)	1/2	0.13404(9)	0.0199(7)	0.0271(8)	0.0163(6)	–0.0003(5)
I(2)	0.31981(5)	1/2	0.61387(9)	0.0201(7)	0.0232(8)	0.0121(6)	0.0038(5)

Table 2. Shortest atomic distances in $Bi_{16}I_4$.

Inside molecules		Between molecules inside the block		Between molecules in different blocks	
Atoms	Distance [Å]	Atoms	Distance [Å]	Atom	Distance [Å]
Bi(l)–Bi(2)	3.0556(9)	Bi(2)–Bi(8)	3.630	Bi(5)–I(1)	3.669
Bi(2)–Bi(3)	3.0423(12)	Bi(2)–Bi(7)	3.488	Bi(3)–I(1)	3.510
Bi(3)–Bi(4)	3.0432(9)	Bi(4)–Bi(6)	3.639	Bi(1)–I(2)	3.632
Bi(4)–Bi(5)	3.0577(13)	Bi(6)–Bi(6)	3.501		
Bi(5)–Bi(6)	3.0383(9)	Bi(7)–I(2)	3.652		
Bi(6)–Bi(7)	3.0722(12)	Bi(5)–I(2)	3.516		
Bi(7)–Bi(8)	3.0334(9)				
Bi(8)–Bi(8)	3.069(2)				
Bi(l)–I(l)	3.109(2)				
Bi(l)–I(2)	3.162(2)				
Bi(3)–I(1)	3.610				

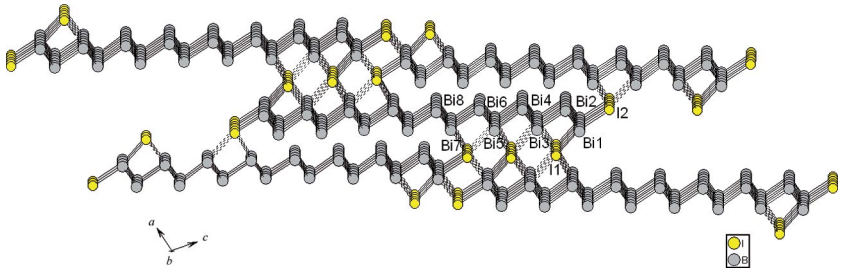

Figure 2. Inter-molecular Bi–I interactions in the structure of $Bi_{16}I_4$.

Table 3. Crystallographic parameters of bismuth subiodides.

	$Bi_{14}I_4$	$Bi_{16}I_4$	$Bi_{18}I_4$
Parameter [Å]			
Molecular	4.342	4.354	4.383
Molecular packing	13.309	13.259	13.353
Block packing	11.447	25.948	15.184
Angle [°]			
β	92.08	104.48	115.06
Molecular axis with respect to block borders	18.5	17.5	16.5

In this context a few structural properties of $Bi_{16}I_4$ should be highlighted. As shown by the anisotropic thermal parameters in Table 1, all atoms, including the iodine ones, are only slightly distorted from spherical symmetry. Notably, the coordination of the terminal Bi(1) atoms is the same as in the previously characterized $Bi_{14}I_4$ and $Bi_{18}I_4$ compounds, where each terminal bismuth atom binds to four neighbors (2Bi + 2I). Such coordination is not typical for bismuth; however, it is supported by two important points of our structural analysis. Firstly, all occupancies obtained in the structural refinements are 1; thus, the introduction of split positions or disorder is not required for an accurate structural characterization. Secondly, no signs of diffuse scattering could be detected in the [*h*0*l*] planes generated from diffraction data.

A comparison of the unit-cell parameters for all three compounds (Table 3) clearly shows that while "molecular" and "molecular packing" parameters remain relatively constant, the "block packing" parameter, as well as the monoclinic angle β, increase considerably with the increase in the width of the polymeric molecules. It is interesting to note that the angle between the molecular axis and block borders simultaneously decreases, effectively compensating for the effect of increased molecular width.

Electronic Structure and Bonding in Bismuth Subiodides

Calculated densities of states (total and projected) for the three subiodides are shown in Figures 3, 4, and 5, and Mulliken charges for symmetry-unique atoms are given in Table 4. The computational results predict all the compounds to be metallic conductors and, considering the rather low density of states at the Fermi level, to exhibit Pauli paramagnetism.

As seen from Table 4, the distribution of atomic charges is essentially the same in all three compounds: iodine atoms are, as expected, negatively charged, approx. –0.75, and the coordinating bismuth atom [Bi(1)] correspondingly displays the highest positive charge of all the bismuth atoms. There is also a general trend over all the compounds with regard to the charges of the inner [i.e. all excluding the terminal Bi(1)] bismuth atoms: odd-numbered atoms [except Bi(9) in $Bi_{18}I_4$] have a higher positive charge (ca. +0.25 to +0.40), while all even-numbered ones are essentially uncharged. The reason for this situation is that all odd-numbered bis-

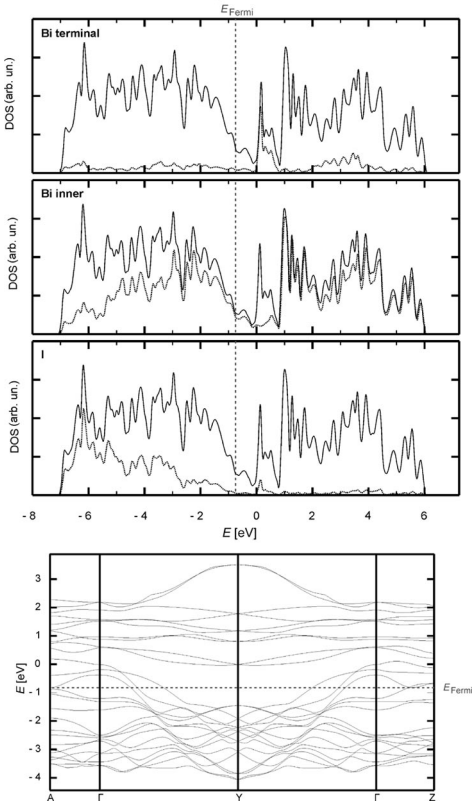

Figure 3. Calculated partial (dotted line) and total (solid line) density of states and band structure near the Fermi level for $Bi_{14}I_4$.

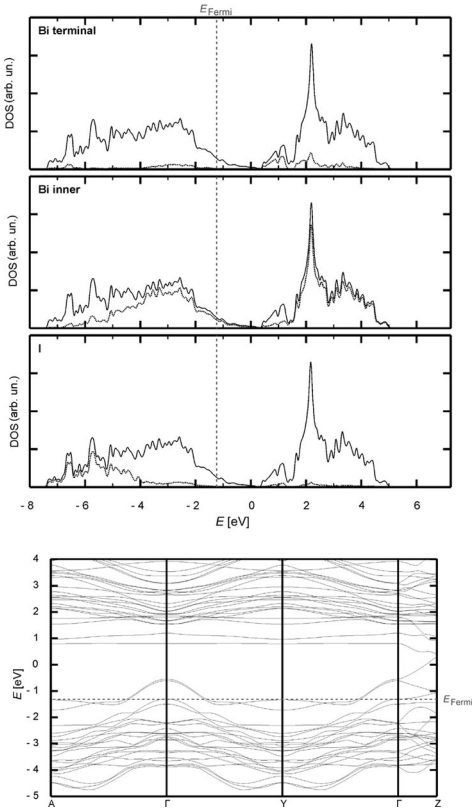

Figure 4. Calculated partial (dotted line) and total (solid line) density of states and band structure near the Fermi level for $Bi_{16}I_4$.

Table 4. Calculated atomic charges for $Bi_{14}I_4$, $Bi_{16}I_4$, and $Bi_{18}I_4$.

Compound	Bi(1)	Bi(2)	Bi(3)	Bi(4)	Bi(5)	Bi(6)	Bi(7)	Bi(8)	Bi(9)	I(1)	I(2)
$Bi_{14}I_4$	+0.59	+0.01	+0.41	–0.07	+0.38	–0.03	+0.25	–	–	–0.76	–0.77
$Bi_{16}I_4$	+0.68	–0.06	+0.37	–0.07	+0.38	–0.04	+0.23	–0.01	–	–0.74	–0.74
$Bi_{18}I_4$	+0.68	–0.06	+0.37	–0.08	+0.37	–0.04	+0.23	–0.02	+0.03	–0.75	–0.74

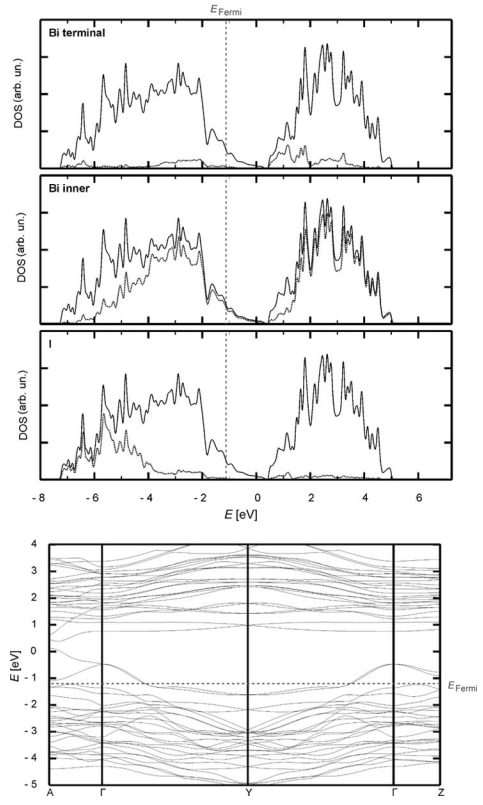

Figure 5. Calculated partial (dotted line) and total (solid line) density of states and band structure near the Fermi level for $Bi_{18}I_4$.

muth atoms [except Bi(9)] have iodine atoms from the neighboring molecule at a distance of about 3.6 Å, which evidently contribute a certain part of their electron density. Even-numbered bismuth atoms and Bi(9) are bonded only to other bismuth atoms. This inter-molecular Bi–I interaction is obviously not as strong as the bonding between terminal bismuth and iodine atoms. As illustrated by their respective charges this secondary interaction is considerably weaker (see Table 4). Nevertheless, this is the principal force that keeps the molecular strands together.

The band structures of the three bismuth subiodides are also very similar (see Figures 3, 4, and 5). The main contribution to the valence band comes from the Bi atoms, while the states corresponding to the Bi(terminal)–I interactions lie far below the Fermi level. The local bonding can be rationalized in terms of hypervalency at the ribbon edges affecting the overall electronic state of the one-dimensional polymeric molecules.[12] Also, while all the compounds are predicted to be metallic conductors, some indications of directional anisotropy may be seen (Γ-Y direction features significantly lower densities than other directions). This feature is somewhat less pronounced for the $Bi_{16}I_4$ structure. Notably, the previously characterized electronic structure of the compound Bi_4I_4,[10] which contained much narrower ribbons, also gave both experimental and calculated indications for some anisotropy. However, this compound was found to be semiconducting.

Conclusions

The isolation of a new compound from the Bi–I system was rather surprising since no such phase had previously been identified in thermal analysis experiments.[5] Nevertheless, its characterization and the study of the molecular packing in all subiodides of the Bi_mI_4 family (m = 4, 14, 16, 18) allow a formulation of the general principles for the construction of a homologous series.

We can imagine the existence of other analogues of these subiodides, formed by polymeric molecules of different width. In such a case, the molecules with closed terminal hexagons and an even number of atoms may belong to either of two types: one with a mirror-plane symmetry and the other with a 2_1 screw axis. The corresponding compounds ought to have different block packing parameters. Since in the blocks of all three subiodides the stripes are stacked against each other with a shift of six bismuth atoms (Figure 2), it is easily deduced that the minimum molecular width for the formation of this type of structure is equal to eight bismuth atoms. Thus, two homologous series are possible: $Bi_{8+4n}I_4$ and $Bi_{10+4n}I_4$ (n is an integer, incl. zero) for the compounds formed by the molecules with a mirror plane or a 2_1 screw axis, respectively.

We foresee no principal limitations for the increase of the formula index n while retaining the structural type; however, it is likely that the stability of such compounds will decrease due to the decreased number of Bi–I inter-molecular contacts at about 3.6 Å and the increased number of Bi–Bi contacts. Adding to that, the enlargement of the blocks, while retaining the number of contacts, might cause an inherent instability of the structures.

Evidently, the energy difference between such compounds of different composition must be relatively small, which makes the selective synthesis of individual compounds problematic and dependent on arbitrary kinetic parameters. This might explain the lack of reproducibility we have experienced during the syntheses of $Bi_{14}I_4$, $Bi_{16}I_4$, and $Bi_{18}I_4$, as well as the fact that no other members of this series have been reported to the present day.

On the other hand, the formation of similar structures based on molecules with an odd number of bismuth atoms is highly unlikely. Such molecules will not have a twofold-screw axis since the terminal bismuth atoms on each side of the molecule, by necessity, would experience a different

coordination, corresponding to closed and open hexagons. This will make their packing into the blocks, as described above, rather unlikely. However, the possibility of the formation of different, more complex types of packing patterns for such molecules can of course not be ruled out.

We also believe it to be unlikely that another homologous series, formed by molecules with an even number of bismuth atoms but having a coordination of the terminal bismuth atoms identical to that in Bi_4I_4, exists. If we compare the effective charges on the iodine atoms in the Bi_4I_4 (ca. –0.2)[10] and in, for instance, the $Bi_{18}I_4$ (ca. –0.75, see Table 4) structures, it is clear that the former compound features a larger degree of covalent Bi–I interactions. This can be explained by the fact that, unlike in the $Bi_{18}I_4$ structure, the iodine atoms in Bi_4I_4 act like bridging atoms, coordinating two terminal bismuth atoms from the same polymeric molecule. As shown above, in the discussion of the molecular packing in bismuth subiodides, the stability of the structures with wider bismuth ribbons depends on the interactions between bismuth and iodine atoms from neighboring molecules. This, in turn, requires a rather high effective negative charge on iodine atoms, which has not been observed for iodides with a bridging coordination mode (and hence more covalent Bi–I bonding). In this case, it is highly unlikely that compounds with molecules more than six or eight bismuths wide will form, and even those are dubious at best. So far, no evidence of such compounds has been reported.

Experimental Section

Synthesis of $Bi_{16}I_4$: Bismuth metal (0.295 g, 1.41 mmol; Baker, 99.99%) and BiI_3 (0.062 g, 0.105 mmol; Merck, 99.99%) were mixed and sealed in an 11 cm-long quartz ampoule (1 cm inner diameter). The ampoule was placed in a tube furnace at 270 °C. Because of the sublimation of BiI_3 at the cooler end of the ampoule, the ampoule was turned at intervals of 24 h to allow for the repeated passage of BiI_3 over the bismuth metal. After 72 h black, metallic, cone-shaped crystals could be observed growing from the bismuth metal grains like horns. Unreacted BiI_3 still remained at the cooler end of the ampoule. In order to be able to pick a suitable crystal for single-crystal X-ray diffraction analysis, the sample had to be ground in a mortar allowing mechanical separation of some crystals from the metal seeds.

Elemental Analysis: Energy dispersive X-ray analysis was performed on single crystals of $Bi_{16}I_4$, using a JEOL JSM-820 scanning electron microscope. Several points on different crystals were investigated. The average contents were found to be Bi, 78.9(6)% and I, 21.1(6)%. The corresponding theoretical values are 80.0 and 20.0%, respectively. Measurements were also made on crystals of $Bi_{18}I_4$ (the phase identification was based on the cell parameters of the crystals). The average contents in these crystals were found to be Bi, 81.4(6)% and I 18.6(6)%. The corresponding theoretical values are 81.1 and 18.9%, respectively.

X-ray Crystallographic Data and Refinement of $Bi_{16}I_4$: The crystallographic data for $Bi_{16}I_4$ are summarized in Table 5. Diffraction data were collected with a Bruker-Nonius KappaCCD diffractometer. The compound crystallizes in the monoclinic system, Laue group *2/m*. On the basis of the systematic absences the possible space groups were found to be *C*2/*m, C2*, and *Cm*. The *C*2/*m* space group (no. 12) was confirmed during the structure determination. The structure was solved with direct methods using the program SIR97[13] and refined with difference Fourier techniques using the SHELXL97 program.[14] All atoms were refined using anisotropic temperature parameters. Empirical absorption corrections were applied using the program SADABS.[15] Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (Fax: +49-7247-808-666; E-mail crysdata@fiz.karlsruhe.de) on quoting the depositary number CSD-418416. Band structures and densities of states were obtained for the three-dimensional structures of the Bi_mI_4 (m = 14, 16, 18) compounds using a hybrid density functional (B3LYP) method, employing the CRYSTAL98 program.[16] All calculations included a converged SCF run. Hay and Wadt large-core (HAYWLC) pseudopotentials were applied to both the iodine and bismuth atoms, and for the iodine atoms the original Hay and Wadt valence basis set, with a double-zeta quality, was used.[17] For the bismuth atoms a larger basis set was optimized (see Table 6) starting from the Hay and Wadt original set.

Table 5. Unit cell parameters and experimental crystal data for the structure of $Bi_{16}I_4$.

Compound	$Bi_{16}I_4$
Molecular mass [g mol^{-1}]	3851.28
Crystal system	monoclinic
Space group	*C*2/*m* (No. 12)
a [Å]	25.948(6)
b [Å]	4.354(1)
c [Å]	13.259(3)
β [°]	104.48(2)
V [Å^3]	1454.3(6)
Z	2
$d_{calcd.}$ [g cm^{-3}]	8.794
Crystal size [mm]	$0.08 \times 0.08 \times 0.25$
Temperature [K]	296
Radiation, λ [Å]	Mo-K_α, 0.71073
Monochromator	graphite
Scan range, 2θ [°]	9.24–55.00
Measured reflections	8551
Unique reflections	1877
Reflections, $I > 2\sigma(I)$	1335
Refined parameters	61
Max. Fourier peak/hole [e Å^{-3}]	2.20/–5.83
$R(\|F\|)$, $I > 2\sigma(I)$	0.041
$R(\|F\|)$, all	0.067
$wR(F^2)$, all	0.109
GoF	1.092

Table 6. Uncontracted bismuth basis set (used with HAYWLC pseudo-potential).

Shell type	Exponent
s	0.624
s	0.355
s	0.135
p	1.155
p	0.330

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