Solid State Structures of Trialkylbismuthanes BiR_3

(R = Me, *i*-Pr)

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Dedicated to Prof. Gerald Henkel on the occasion of his 65th birthday

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ABSTRACT. Two trialkylbismuthines BiR_3 (R = Me **1**, *i*-Pr **2**) were structurally characterized by single crystal X-ray diffraction. Single crystals were grown using an IR-laser-assisted technique. **1** forms short intermolecular $\text{Bi}\cdots\text{Bi}$ interactions in the solid state, which were further investigated through quantum chemical computations with *ab initio* coupled cluster and dispersion-corrected density functional methods.

Introduction

Trialkylbismuthines BiR_3 have initially been reported by Marquardt in 1887, who synthesized Me_3Bi and Et_3Bi by reaction of BiBr_3 and ZnR_2 .^[1] Since then, alternate synthetic pathways were established and several trialkylbismuthines were synthesized. They were found to be weak Lewis bases, since their electron lone pair exhibits high s-character. As a consequence, the number of transition metal and main group metal complexes of bismuthines is much smaller compared to the corresponding amine and phosphine complexes.^[2] Most of them contain aryl-substituted bismuthines, whereas trialkylbismuthine complexes are still rare and, to the best of our knowledge, only ten of them have been structurally characterized, to date.^[3] In addition, trialkylbismuthines have been used as Bi-source in MOCVD reactions for the deposition of bismuth-containing films, in particular Me_3Bi due to its high volatility.^[4]

Even though 38 homo- and heteroleptic triarylbismuthines are found in the CCDC database,^[5] only two trialkylbismuthines, $\text{Bi}[\text{CH}(\text{SiMe}_3)_2]_3$ and $\text{Bi}(\text{CH}_2\text{SiMe}_3)_3$, have been structurally characterized in the solid state.^[6] In addition, the solid state structure of Me_5Bi was reported.^[7] The lack of structural data can be explained by the fact, that most trialkylbismuthines are liquid at ambient temperature, hence complicating the growth of suitable single crystals. Due to our long term interest in the structure and reactivity of divalent (E_2R_4) and trivalent organoantimony and -bismuth compounds (ER_3),^[3a-c,8] we started to investigate the solid state structures of trialkylstibines and bismuthines and report herein on the solid state structures of Me_3Bi **1** and *i*- Pr_3Bi **2**. In addition, based on quantum chemical calculations we present an assessment of the energetic role of various intermolecular contacts for the crystal stability, such as contacts between Bi atoms or between a Bi atom and a neighboring methyl group.

Results and Discussion

Me_3Bi **1** and $i\text{-Pr}_3\text{Bi}$ **2** were synthesized by reaction of BiCl_3 and RMgX and purified by distillation at 110 °C and 1013 mbar (**1**) or 70 °C and 10 mbar (**2**), respectively.^[9] Single crystals of **1** and **2** were grown directly on the diffractometer using an IR-laser-assisted technique in a closed quartz glass capillary under an inert argon atmosphere. The IR-laser allowed a very controlled and focused heating of the sample, which is frozen in a nitrogen stream, hence resulting in optimized growth conditions, in which the sample recrystallizes without decomposition.^[10] Figures 1 and 2 show the crystal structures of **1** and **2**.

((Table 1 here))

Figure 1. Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

Figure 2. Solid state structure of **2** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

1 crystallizes as colorless needles in the triclinic space group $P\bar{1}$ and **2** as pale yellow crystals in the monoclinic space group Pn . Table 2 summarizes the central structural parameters of **1** and **2** as well as those of $\text{Bi}[\text{CH}(\text{SiMe}_3)_2]_3$ and $\text{Bi}(\text{CH}_2\text{SiMe}_3)_3$.^[6] The average Bi-C bond length (2.259(17) Å **1**; 2.287(9) Å **2**) and the sum of the C-Bi-C bond angles (276.6(24)° **1**; 290.6(9)° **2**) clearly reflect the different steric requirements of the alkyl groups. According to these parameters, the sterical size increases in the following order: $\text{Me} < \text{CH}_2\text{SiMe}_3 < \text{CHMe}_2$ (*i*-Pr) < $\text{CH}(\text{SiMe}_3)_2$. Comparable Bi-C bond lengths and C-Bi-C bond angles were observed for aryl-substituted bismuthines with sterically less demanding substituents such as C_6H_5 , 4-Me C_6H_4 , 4-Me $_2\text{NC}_6\text{H}_4$,^[11] whereas those containing sterically more demanding groups such as 2,4,6-(CH $_3$) $_3\text{C}_6\text{H}_2$ or 2,4,6-(CF $_3$) $_3\text{C}_6\text{H}_2$ show longer Bi-C bond lengths (> 2.30 Å) and wider C-Bi-C bond angles (100 – 107°).^[2a,12] In addition, the average Bi-C bond length of **1** (2.259(17) Å) as determined in the solid state compares very well with that from a gas phase structure determination by electron diffraction (Bi-C 2.263(4) Å), whereas the sum of the C-Bi-C bond

angles in the gas phase (291.3(18)°) is wider than that in the solid state (276.6(24)°).^[13]

However, because of the structural parameter's rather high standard deviations the significance of these deviations cannot be assessed. For this reason, we performed quantum chemical geometry optimizations of the isolated monomers **1** and **2** using the Turbomole program^[14] with dispersion corrected density functional theory employing the B-P86 functional^[15] and a third generation dispersion correction^[16] in conjunction with a small core relativistic effective core potential for the Bi atom,^[17] a quadruple-zeta basis set for all atoms,^[18] and the resolution-of-the-identity approximation.^[19] This level of theory accounts for scalar relativistic effects neglecting spin-orbit coupling, an approximation which was found to work very well for the structural parameters of BiPh₃^[20]. The results of our geometry optimizations compare well with the experimental findings of the single crystal X-ray diffraction studies: the Bi-C distance for **1** (point group *C*_{3v}) is 2.289 Å, and the sum of the C-Bi-C bond angles is 277.2°, while the average Bi-C distance for **2** (point group *C*₁) is 2.321 Å and the sum of the C-Bi-C bond angles is 287.5°.

((Table 2 here))

Very few trialkylbismuthine-metal complexes of the type Me₃Bi-M(CO)₅ (M = Cr, W) and *i*-Pr₃Bi-M(*t*-Bu)₃ (M = Al, Ga) have been structurally characterized in the past (Table 3).^[3a,b,e] According to a model described by *Haaland and Frenking et al.*,^[21] the coordination of the Lewis base BiR₃ to a Lewis acid (metal complex) should increase the s-orbital contribution to the Bi-C bonding electron pairs, hence leading to shorter Bi-C bond lengths and wider C-Bi-C bond angles. The expected structural trends were observed for Ph₃Bi complexes and also reported for pentacarbonyl metal complexes of the type Me₃Bi-M(CO)₅ (M = Cr, W).^[22,3d] Pure *i*-Pr₃Bi **2** shows wider C-Bi-C bond angles and slightly shorter Bi-C bond lengths than the corresponding alane and gallane adducts *i*-Pr₃Bi-M(*t*-Bu)₃ (M = Al, Ga). These findings clearly illustrate the

high steric demand of the very bulky *tert*-butyl substituents attached to the group 13 metal atoms and their decided role on the structural parameters of the resulting complexes. Unfortunately, transition metal complexes of *i*-Pr₃Bi are unknown, to date, hence allowing no structural comparisons with *i*-Pr₃Bi **2**. In addition, numerous attempts to grow suitable single crystals of Et₃Bi, from which also two adducts with *t*-Bu₃M (M = Al, Ga) have been structurally characterized in our group in the past,^[3a,b] failed.

((Table 3 here))

Figure 3. Intermolecular Bi⋯Bi interactions in **1** lead to the formation of an inversion symmetric, weakly bound dimer in the solid state.

1 forms a centro-symmetric dimer via an intermolecular Bi $\cdots$ Bi contact (3.899(1) Å), that is shorter than the sum of the van-der-Waals radii (4.318(1) Å).^[23] However, the intermolecular distance is slightly longer than intermolecular Bi $\cdots$ Bi interactions as-observed in thermochromic dibismuthines Bi₂R₄, which typically range from 3.5 to 3.8 Å (3.582(7) Me₄Bi₂,^[24] 3.6595(5) ([HC=CMe]₂)₂Bi₂,^[25] 3.804(3) ((Me₃Si)₄Bi₂).^[26] Despite the fact that the next shorter intermolecular distances in **1** (Bi $\cdots$ C 3.905 Å; Bi $\cdots$ Bi 4.318(1) Å) clearly exceed the sum of the *van-der Waals* radii (Bi $\cdots$ C 3.77 Å),^[23] additional attractive interactions cannot be neglected as is later shown by quantum chemical calculations. According to these calculations, the interaction **8** (Figure 5) combined with the Bi $\cdots$ Bi interaction results in a packing of **1** that can best described as a stacking of zig-zag-chains parallel to [111]. In contrast, **2** forms isolated molecules in the solid state without short Bi $\cdots$ Bi contacts to neighboring molecules. Obviously, the sterically less demanding Me substituents in **1** favor the formation of attractive intermolecular Bi $\cdots$ Bi interactions.

The formation of a metal-metal bonded dimer is unusual for main group metal-methyl complexes. For instance, Lewis acidic group 13 metal trialkyls MMe₃ form Me-bridged dimers (AlMe₃), ladder-like pseudo-polymers or pseudo tetramers (GaMe₃, InMe₃, TlMe₃) due to the formation of 2-electron-3-center bonds.^[27] The same is true for BeMe₂,^[28] which adopts a polymeric chain-like structure, and even ZnMe₂ shows weak intermolecular Zn $\cdots$ Me contacts in the solid state.^[29] Unfortunately, the solid state structures of SeMe₂ and TeMe₂, even though frequently used in coordination chemistry,^[30] are unknown, to date, but weak intermolecular Te $\cdots$ Te interactions have been observed for [tmpTeI]₂ (tmp = 2,3,5,6-tetramethylphenyl), which forms a dimer,^[31] and PhTeI, which adopts a tetrameric structure in the solid state.^[32] Moreover,

dialkyl dichalcogenanes such as Se_2Me_2 and Te_2Me_2 as well as dialkyl dichalcogen cations also show intermolecular $\text{E} \cdots \text{E}$ interactions in the solid state.^[33,34]

In order to assess the energy of interaction between the bismuth atoms for the short (2.899(1) Å) and the long (4.318(1) Å) $\text{Bi} \cdots \text{Bi}$ -contact in the crystal structure of **1**, we carried out ab initio quantum chemical calculations with the Molpro program on the coupled cluster level (CCSD(T)) with extrapolation to the complete basis set limit^[35] for model systems composed of two BiH_3 molecules. The positions of the Bi atoms and the orientations of the Bi-H bonds were kept fixed to those of the Bi atoms and Bi-C bonds of the BiMe_3 crystal structure. Yet, each of the Bi-C bond lengths as found in the crystal was scaled by a factor of 0.8 so that the resulting average Bi-H bond length of 1.808 Å nearly reproduces the optimized value of 1.804 Å as obtained with DFT+D (using the same methodology as in the geometry optimizations of **1** and **2**, *vide supra*). Note that this value is close to the experimental and theoretical equilibrium bond distances of 1.7783 Å^[36] and 1.7814 Å^[37] for BiH_3 in the gas phase.

The resulting dimer-structures for the short and the long $\text{Bi} \cdots \text{Bi}$ -contacts are shown in figure 4, they are denoted as dimer **3** and **4**, respectively. For each bismuth atom a small core scalar relativistic effective core potential was employed,^[17] correlating 18 electrons per monomer. With an aug-cc-pwVTZ basis set^[38] for Bi and aug-cc-pVTZ for H we obtain counterpoise-corrected^[39] interaction energies of -3.72 and -3.07 kJ/mol for **3** and **4**, respectively, while with aug-cc-pwVQZ/aug-cc-pVQZ^[38] the interaction energy for **3** was -4.69 kJ/mol and -3.54 kJ/mol for **4**. Our final CCSD(T) interaction energies for **3** and **4** as obtained with a two-point extrapolation scheme for the correlation energy contribution are -5.39 and -3.89 kJ/mol, respectively.^[40]

Figure 4. BiH₃-Dimer structures **3** and **4** with short and long Bi···Bi interactions

((Table 4 here))

While CCSD(T) calculations with augmented quadruple-zeta quality basis sets become fairly demanding for the dimer of BiMe₃, they are feasible with second-order Møller-Plesset perturbation theory (MP2; calculations with seven frozen core orbitals including C(1s), thus correlating 36 electrons per monomer; aug-cc-pVXZ with X=T,Q for C, for Bi and H as above). Yet, as shown in Table 4, MP2 significantly overestimates the magnitude of the interaction energy of **3** and **4**, as it is often observed for dispersion-dominated weakly bound systems. With the spin-component-scaled variant of MP2 (SCS-MP2)^[41] on the other hand, one obtains interaction energies in good agreement with the "gold standard" CCSD(T), as also often observed in dispersion-dominated dimers (cf. Table 4). Klinkhammer and Pyykkö reported comparable results concerning the intermolecular dispersion interaction in H₂Bi-BiH₂ as obtained on the MP2 level of theory.^[42] In addition, a recent study on dimers of trivalent pnictogen halides comes to very similar conclusions as concerning the performance of MP2 and SCS-MP2 to reproduce CCSD(T) interaction energies^[43]. For the trimethylbismuthine dimer structures **5** and **6**, which were directly extracted from the crystal structure (cf. Fig. 5), we thus also expect SCS-MP2 interaction energies to be close to CCSD(T).

Figure 5. BiMe₃-Dimer structures **5**, **6**, **7** and **8**

As in the case of **3** and **4**, the structure with the longer Bi $\cdots$ Bi distance has the smaller interaction energy, which, however, still amounts to roughly two thirds of that of the short Bi $\cdots$ Bi distance structure. The magnitude of the interaction energy in both cases is roughly twice that of the corresponding (BiH₃)₂ structures. This is likely due to additional attractive “far-distance” dispersion interactions between Bi and the methyl-groups of the neighboring molecule and similar Me $\cdots$ Me interactions: note that despite a slight increase of the partial charge of +0.34e as determined with a natural population analysis^[44] for BiH₃ on the DFT(BP86)/def2-QZVP level to the value of +0.89e for BiMe₃ the (dispersion free) Hartree Fock interaction energies for **3** and **5** are nearly the same. Table 4 also presents the interaction energies for the BiMe₃ dimer structures **7** and **8**, which also directly represent pairs of neighboring molecules of the crystal structure. Also for these structures there are significant differences between the MP2 and SCS-MP2 interaction energies - yet here we believe the MP2 results to be closer to CCSD(T): note that the MP2 interaction energies between two methane molecules at two

different distances and in orientations as found for neighboring methyl groups in the crystal structure, i.e., the methane dimer structures **9** and **10** (c.f. figure 6) are closer to the CCSD(T) benchmark values than SCS-MP2 (cf. Table 4).

Figure 6. Methane dimers **9** and **10**

Despite the approximations inherent in considering exclusively two-body interactions it is thus certainly save to conclude that the main factors for the formation of zig-zag chains of antiparallel BiMe₃ monomers in the crystal are Bi···Bi interactions at one end and the accumulation of Me···Me interactions at the other end of the molecule, as represented by structure **8**. Between the chains, there are somewhat weaker, yet still significant interactions, exemplified by dimer structures **6** and **7**. All of these interactions should be classified as dispersion-dominated, since (i) the (dispersion-free) Hartree-Fock interaction energies for all of them are positive, and (ii) the dispersion correction in DFT(BP86)+D/def2-QZVP very significantly contributes to the stabilization of the dimers, as shown by comparison with the (not entirely dispersion-free) "pure" DFT(BP86)/def2-QZVP interaction energies also listed up in Table 4.

Finally, it should be noted that DFT(BP86)+D/def2-QZVP without counterpoise correction (CPC) agrees quite well with the SCS-MP2 interaction energies for **5** and **6**, and with MP2 for **7** and **8**, which, as argued above, are likely to be the best results in each case. This opens the possibility to use the highly efficient DFT+D approach to determine interaction energies between neighboring molecules in the crystal of triisopropylbismuthine. Corresponding data for the two

symmetry inequivalent possibilities **11** and **12** (cf. figure 7) for finding pairs of closely neighboring Bi(*i*-Pr)₃ molecules in the crystal are also collected in Table 4. Again, dispersion interactions play the dominant role for crystal stability (cf. DFT and DFT+D interaction energies) even though short Bi⋯Bi contacts are missed.

Figure 7. The two symmetry inequivalent Bi(*i*-Pr)₃-dimers **11** and **12**

Experimental Section

Me₃Bi **1** and *i*-Pr₃Bi **2** were prepared according to literature methods.^[28]

Single crystal X-ray analyses. Crystallographic data of **1** and **2**, which were collected on a Bruker AXS SMART diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) at 150(1) K (**1**) and 141(2) K (**2**), are summarized in Table 1. The solid-state structures of **1** and **2** are shown in Figures 1 and 2. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97).^[45,46] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups.

Single crystals of **1** and **2** were formed by an *in-situ* zone melting process inside a quartz capillary using an IR-laser.^[8] The experimental setup does only allow for ω scans with χ set to

0°. Any other orientation would have partially removed the capillary from the cooling stream and thus led to a melting of the crystals. This limits the completeness of the data to 65% to 90% depending on the crystal system. The crystallographic data of **1** and **2** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-933627 (**1**) and CCDC-808073 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic details of **1** and **2**.

	1	2
Empirical formula	C ₃ H ₉ Bi	C ₉ H ₂₁ Bi
Molecular mass	254.08	338.24
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>Pn</i>
a [Å]	6.1115(8)	7.7023(3)
b [Å]	6.6003(8)	10.0311(4)
c [Å]	8.7623(9)	7.8506(3)
α [°]	104.024(9)	90
β [°]	97.321(13)	109.833(2)
γ [°]	116.864(9)	90
V [Å ³]	294.22(6)	570.58(4)
Z	2	2
T [K]	150(1)	141(2)
μ [mm ⁻¹]	29.801	15.394
D _{calcd.} [g cm ⁻³]	2.868	1.969
2θ _{max} [°]	61.8	61.3
Crystal dim. [mm]	0.30 x 0.10 x 0.07	0.30 x 0.30 x 0.30

No. of reflections	5317	10969
No. of unique reflections	1324	2331
R_{int}	0.1447	0.0243
No. param. refined / restraints	41 / 0	97 / 2
Flack parameter ^[47]	-	0.083(18)
$R1^{[a]}$	0.0657	0.0233
$wR2^{[b]}$	0.1584	0.0627
Goodness of fit ^[c]	1.082	1.237
Max./min. Transmission	0.75 / 0.33	0.75 / 0.40
Final max/min. $\Delta\rho$, e Å ⁻³	3.809 (0.84 Å from Bi(1)) / - 5.269	1.058 / -2.533

^[a] $RI = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - ^[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. - ^[c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the program.

Table 2. Central structural parameter of trialkylbismuthines.

	Me ₃ Bi 1	<i>i</i> -Pr ₃ Bi 2	Bi(CH ₂ SiMe ₃) ₃	Bi[CH(SiMe ₃) ₂] ₃
Bi-C	2.23(2)	2.267(7)	2.2739(9)	2.331(14)
	2.26(2)	2.295(7)	2.2739(9)	2.347(13)
	2.288(16)	2.300(9)	2.2739(9)	2.306(13)
Bi···Bi	3.899(1); 4.318(1)	-	-	-
C-Bi-C	93.3(8)	96.1(3)	94.0(3)	102.9(5)
	90.7(7)	97.6(3)	94.0(3)	103.0(5)
	92.6(9)	96.9(3)	94.0(3)	102.7(5)
Σ∠C-Bi-C	276.6(24)	290.6(9)	282.0(9)	308.6(15)

Table 3. Central structural parameters of their metal complexes of **1** and **2**.

	Me ₃ Bi-Cr(CO) ₅	Me ₃ Bi-W(CO) ₅	<i>i</i> -Pr ₃ Bi-Al(<i>t</i> -Bu) ₃	<i>i</i> -Pr ₃ Bi-Ga(<i>t</i> -Bu) ₃
Bi-C	2.234(12)	2.236(16)	2.313(5)	2.278(9)
	2.208(12)	2.225(14)	2.246(5)	2.299(8)
	2.213(12)	2.252(16)	2.326(5)	2.300(6)
E-C (av.)	2.218(10)	2.238(11)	2.295(20)	2.292(7)
C-Bi-C	99.4(6)	100.6(7)	95.8(2)	95.9(4)
	99.4(6)	99.5(6)	93.1(2)	100.6(3)
	99.8(5)	97.0(7)	97.6(2)	90.6(3)
Σ∠C-Bi-C	298.6(17)	297.1(20)	286.4(6) ^o	286.1(10) ^o

Table 4. Calculated interaction energies (in kJ/mol) from various methods. CCSD(T), SCS-MP2, and MP2 interaction energies with CPC and triple/quadruple basis set extrapolation. HF interaction energies with CPC at aug-cc-pwVQZ/aug-cc-pVQZ basis set level. DFT and DFT+D without CPC at def2-QZVP basis set level.

	HF	CCSD(T)	SCS-MP2	MP2	DFT	DFT+D
3	9.46	-5.39	-5.34	-9.54	3.44	-3.37
4	5.87	-3.89	-3.83	-6.42	3.13	-3.16
5	8.89		-12.79	-19.06	3.27	-12.17
6	8.34		-7.62	-11.98	4.21	-8.51
7	3.20		-5.68	-8.23	3.21	-7.79
8	4.05		-7.41	-10.74	6.62	-11.00
9	0.05	-0.59	-0.42	-0.56	0.69	-0.35
10	0.64	-1.12	-0.64	-1.00	1.70	-0.97
11					8.83	-17.25
12					6.16	-8.10

Supporting Information. A CIF file giving X-ray crystallographic data of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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BiMe_3 **1** forms a weakly bonded dimer in the solid state due to attractive $\text{Bi}\cdots\text{Bi}$ dispersion interactions according to computational calculations. In contrast, $\text{Bi}(i\text{-Pr})_3$ **1**, which contains sterically more demanding *i*-Pr-substituents, is monomeric. Single crystals of **1** and **2** were grown using using an IR-laser-assisted technique.

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