

Synthesis and structure of bis(tetraphenyl- λ^5 -stibanyl)-1,7-carborane-1,7-dicarboxylate

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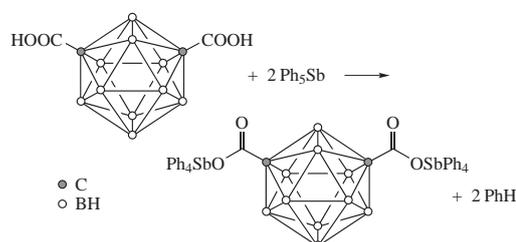
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DOI: 10.1016/j.mencom.2018.11.019

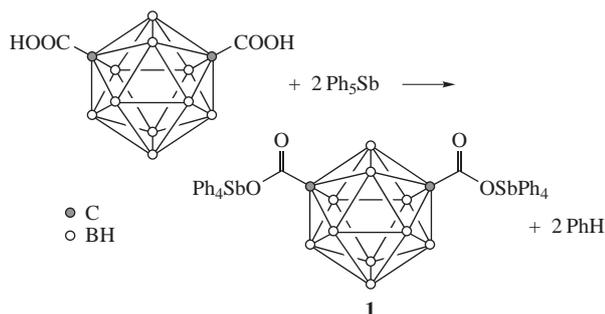
The reaction between pentaphenylantimony and *meta*-carboranedicarboxylic acid in benzene leads to the title compound that was characterized by X-ray diffraction data.



Some organoantimony compounds reveal a biological activity.^{1–3} At the same time, there are many publications on biological activity of carboranes^{4–8} and some organometallic compounds.⁹ Organotin carborane carboxylates possess anticancer activity.¹⁰ Therefore, synthesis of novel organoantimony carborane conjugates may have interest in view of biological activity. The purpose of this work was to synthesize bis(tetraphenyl- λ^5 -stibanyl)-1,7-carborane-1,7-dicarboxylate **1** and to study its structure.

Earlier it was shown that dicarboxylic acids react with pentaphenylantimony to give compounds of two types.^{11–14} Depending on molar ratio of the reactants, bis(tetraaryl- λ^5 -stibanyl)dicarboxylates or related monoesters were obtained. We found previously that the reaction of equimolar amounts of pentaphenylstiborane and *ortho*-carboranedicarboxylic acid in toluene led to tetraphenylstibanyl *ortho*-carboranedicarboxylate in high yield. When 2:1 molar ratio of the reactants was used, the related diester was obtained in 94% yield.¹⁴

In this work we show that reaction between pentaphenylantimony and *meta*-carboranedicarboxylic acid in benzene using both 2:1 and 1:1 molar ratios results only in diester **1** (Scheme 1).[†] The best yield (88%) of product **1** was achieved when 2 equiv. of Ph₅Sb were applied.



Scheme 1

Colourless crystals of compound **1** were grown by crystallization from DMF. According to X-ray data,[‡] the crystal unit cell contains two molecules where antimony atoms have distorted trigonal-bipyramidal environment (Figure 1).

Antimony atoms are out of the equatorial plane [C₃] towards axial carbon atoms by 0.313 and 0.236 Å, which leads to distortion of angles between axial and equatorial bonds: angles C_{ax}Sb(1)C_{eq} [97.34(8)°–100.28(8)°] and C_{ax}Sb(2)C_{eq} [94.62(8)°–98.93(8)°] are more than 90°, angles OSb(1)C_{eq} [78.09(6)°–83.97(6)°] and

[†] IR spectra were collected on a Shimadzu IR Presige 21 FT-IR spectrometer using KBr pellet. The ¹H NMR spectra were recorded at 400.13 MHz on a Bruker Avance-400 spectrometer, tetramethylsilane was used as a standard. Elemental analysis was performed at the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds by the methods developed in this laboratory.¹⁵ Contents of C and H were determined by express-gravimetry. Content of B was determined by spectrophotometry with azomethine, and Sb content – by nondestructive X-Ray fluorescence analysis.

Bis(tetraphenyl- λ^5 -stibanyl)-1,7-carborane-1,7-dicarboxylate 1. A mixture of pentaphenylantimony (249 mg, 0.491 mmol) and 1,7-carborane-1,7-dicarboxylic acid (51 mg, 0.245 mmol) in benzene (5 ml) was heated in glass ampoule in vacuum at 80 °C for 1 h. The mixture was cooled, the solvent was removed, and the residue was crystallized from DMF. The colourless crystals (0.212 g, 88% yield) were obtained, mp 219 °C (decomp.). IR (ν /cm⁻¹): 3055 (C–H), 2599 (B–H), 1653 (C=O), 1627 (C=O). ¹H NMR (CDCl₃) δ : 1.3–3.2 (br. s, 10H, BH), 7.43 (t, 16H, *m*-H_{Ph}, *J*_{CH} 7.3 Hz), 7.49 (t, 8H, *p*-H_{Ph}, *J*_{CH} 7.2 Hz), 7.65 (t, 16H, *o*-H_{Ph}, *J*_{CH} 7.2 Hz). Found (%): C, 57.39; H, 4.81; B, 9.79; Sb, 22.50. Calc. for C₅₂H₅₀O₄B₁₀Sb₂ (%): C, 57.27; H, 4.62; B, 9.91; Sb, 22.33.

[‡] *Crystal data for 1*: C₅₂H₅₀B₁₀O₄Sb₂ (*M* = 1090.52), triclinic, space group *P* $\bar{1}$, at 100(10) K: *a* = 10.2522(3), *b* = 11.6319(3) and *c* = 20.2654(5) Å, α = 91.990(2)°, β = 92.193(2)°, γ = 92.965(2)°, *V* = 2410.07(11) Å³, *Z* = 2, *d*_{calc} = 1.503 g cm⁻³, μ (MoK α) = 1.167 mm⁻¹, *F*(000) = 1092. Total of 81376 reflections were collected (14689 independent reflections, *R*_{int} = 0.102) and used in refinement which converged to *wR*₂ = 0.0687, GOOF = 0.96 for all independent reflections [*R*₁ = 0.0334 was calculated for 11603 reflections with *I* > 2 σ (*I*)].

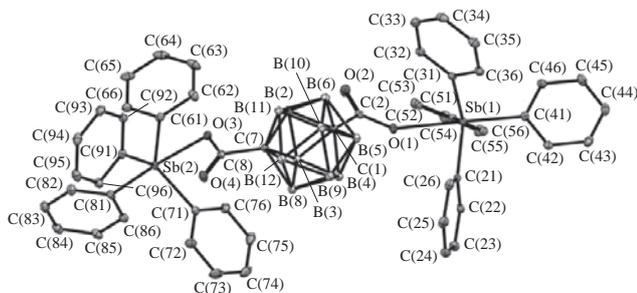


Figure 1 Molecular structure of compound 1.

$\text{OSb}(2)\text{C}_{\text{eq}}$ [$80.71(7)^\circ$ – $88.40(7)^\circ$] are less than 90° . The sum of $\text{C}_{\text{eq}}\text{Sb}(1)\text{C}_{\text{eq}}$ and $\text{C}_{\text{eq}}\text{Sb}(2)\text{C}_{\text{eq}}$ angles in equatorial planes is $353.50(8)^\circ$ and $356.27(8)^\circ$. Average values of equatorial bonds $\text{Sb}(1)\text{--C}_{\text{eq}}$ [$2.116(2) \text{ \AA}$] and $\text{Sb}(2)\text{--C}_{\text{eq}}$ [$2.111(2) \text{ \AA}$] are less than those of the corresponding axial bonds [$2.143(2)$ and $2.162(2) \text{ \AA}$]. The distances $\text{Sb}(1)\text{--O}(1)$ and $\text{Sb}(2)\text{--O}(3)$ are equal to $2.426(1)$ and $2.329(1) \text{ \AA}$, respectively. Thus, a distortion of trigonal–bipyramidal coordination of $\text{Sb}(1)$ atom to tetrahedral coordination manifests itself to a greater extent than that of $\text{Sb}(2)$. It is reflected in reducing sum of angles in equatorial plane, increasing angle $\text{C}_{\text{ax}}\text{Sb}(1)\text{C}_{\text{eq}}$ and convergence of average values of $\text{Sb}(1)\text{--C}_{\text{eq}}$ bonds with axial bond $\text{Sb}(1)\text{--C}_{\text{ax}}$. In carboxylate group linked with $\text{Ph}_4\text{Sb}(1)$ fragment, distances $\text{C}(2)\text{--O}(1)$ [$1.275(2) \text{ \AA}$] and $\text{C}(2)\text{--O}(2)$ [$1.234(2) \text{ \AA}$] are more levelled compared to carboxylate group linked with $\text{Ph}_4\text{Sb}(2)$ fragment where electron density is delocalized to a less extent [corresponding distances are $1.284(2)$ and $1.226(2) \text{ \AA}$]. Note that intramolecular distance between $\text{Sb}(2)$ atom and $\text{O}(4)$ of carboxylic group [$3.252(2) \text{ \AA}$] is less than sum of Van der Waals radii, while $\text{Sb}(1)\cdots\text{O}(2)$ [$4.262(2) \text{ \AA}$] distance is essentially higher than this value.

In summary, interaction of pentaphenylantimony with *meta*-carboranedicarboxylic acid in benzene using 2:1 or 1:1 molar ratio leads to bis(tetraphenyl- λ^5 -stibanyl)-1,7-carborane-1,7-di-

Single-crystal X-ray diffraction study was carried out with an XtaLAB Proof Rigaku diffractometer (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). Collection, data editing and refinement of elemental cell parameters, as well as absorption record were carried out using CrysAlisPro programs.¹⁶ Structure determination and definition calculations were performed using SHELXL/PC,¹⁷ ShelxLe¹⁸ and WinGX¹⁹ programs. The structure was solved by direct method and refined by least-squares method in anisotropic approximation for non-hydrogen atoms.²⁰

CCDC 1815215 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

carboxylate that was characterized by spectral and X-ray diffraction methods. The biological activity of the resulting compound will be studied.

Authors from South Ural State National Research University are grateful to the Ministry of Education and Science of the Russian Federation for financial support (state task no. 4.6151.2017/8.9).

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Received: 24th April 2018; Com. 18/5556