A Tetranuclear Arylstibonic Acid with an Adamantane Type Structure

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Supplementary Material

Content

- Experimental section including the synthesis and characterization of 2 and 3.
- Topological bond paths motifs of 2 and 3,
- ELI-D representations of bonding and core basins,
- ED mapped on the Sb atom of **3** and bond topological properties of **1**, **2**, and **3**.

Experimental Section. Reagents were obtained commercially (Sigma-Aldrich, Germany) and were used as received. Dry Solvents were collected from a SPS800 mBraun solvent system. (6-(diphenylphosphino)acenaphth-5-yl)antimony dichloride (1)⁷ was prepared according to aliterature procedure. ¹H-, ¹³C-, ³¹P-NMR spectra were recorded at r.t. using a Bruker Avance-360 spectrometer and are referenced to tetramethylsilane (¹H, ¹³C) and phosphoric acid (85% in water) (³¹P). Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). The ESI MS spectra were obtained with a Bruker Esquire-LC MS. Dichloromethane/acetonitrile solutions (or otherwise stated, c = $1 \cdot 10^{-6}$ mol L⁻¹) were injected directly into the spectrometer at a flow rate of 3 µL min⁻¹. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 5 L min⁻¹ and a pressure of 5 psi, respectively. Pressure in the mass analyzer region was usually about $1 \cdot 10^{-5}$ mbar. Spectra were collected for one minute and averaged. The nozzle-skimmer voltage was adjusted individually for each measurement.

Synthesis of 6-(diphenylphosphino)-acenaphth-5-yl-antimony tetrachloride (2). Sulfuryl chloride (0.65 mL, 7.92 mmol) was added dropwise to a suspension of 1 (3.50 g, 6.60 mmol) in CH_2Cl_2 (20 mL). The volatiles were removed in vacuo. The solid residue was recrystallized from THF to give orange crystals of 2 (2.66 g, 4.43 mmol, 67%, Mp. 159°C).

¹H-NMR (CDCl₃): $\delta = 8.52$ (dd, ³*J*(¹H-¹H) = 7.2 Hz, *J*(³¹P-¹H) = 3.4 Hz, 1H, H-4 or H-7), 7.95-7.89 (m, 5H), 7.66-7.58 (m, 4H), 7.54-7.49 (m, 4H), 3.61-3.53 ppm (m, 4H, H-1,2). ¹³C{¹H}-NMR (CDCl₃): $\delta = 155.0$ (d, ⁴*J*(³¹P-¹³C) = 2.1 Hz, C_c or C_d), 151.1 (d, ³*J*(³¹P-¹³C) = 75.0 Hz, C₅), 150.2 (d, ⁴*J*(³¹P-¹³C) = 0.7 Hz, C_d or C_c), 139.1 (d, *J*(³¹P-¹³C) = 8.5 Hz, C_a or C_b), 137.4 (s, C₄), 134.6 (d, ²*J*(³¹P-¹³C) = 9.4 Hz, C_o), 132.9 (d, ⁴*J*(³¹P-¹³C) = 3.6 Hz, C_p), 129.9 (d, *J*(³¹P-¹³C) = 13.0 Hz, C_b or C_a), 129.3 (d, ³*J*(³¹P-¹³C) = 12.4 Hz, C_m), 129.1 (d, ²*J*(³¹P-¹³C) = 8.7 Hz, C₇), 122.3 (d, ¹*J*(³¹P-¹³C) = 55.1 Hz, C_i or C₆), 121.7 (d, *J*(³¹P-¹³C) = 7.2 Hz, C₃ or C₈), 120.7 (d, *J*(³¹P-¹³C) = 8.8 Hz, C₈ or C₃), 110.2 (d, ¹*J*(³¹P-¹³C) = 56.1 Hz, C₆ or C_i), 31.5 (s, C₁ or C₂), 30.4 ppm (s, C₂ or C₁). ³¹P{¹H}-NMR (CDCl₃): $\delta = -33.1$ ppm. ESI MS (CH₂Cl₂/MeCN 1:10, positive mode): *m/z* = 621.0 (C₂₄H₁₈PCl₄SbNa) for [**2** + Na⁺], 637.0 (C₂₄H₁₈PCl₄SbK) for [**2** + K⁺]. Anal. Calcd for C₂₄H₁₈PCl₄Sb (600.94): C, 47.97; H, 3.02. Found: C, 48.24; H, 3.25. Synthesis of $(ArSb)_4O_6(OH)_4$ (3). A solution of sodium hydroxide (0.13 g, 3.33 mmol) in water (5 mL) was added to a suspension of 2 (0.50 g, 0.83 mmol) in diethyl ether (15 mL). The reaction was vigorously stirred at r.t. overnight to give a clear two layer solution. After extracting the organic layer with water (3 × 5 mL) the solvent was removed in vacuo. The solid residue was obtained by recrystallization from CH_2Cl_2 to give colorless crystals of 3 (300 mg, 0.15 mmol, 72%, Mp. 153°C).

¹**H-NMR (CDCl₃):** $\delta = 8.35$ (d, ³*J*(¹H-¹H) = 7.2 Hz, 4H, H-4), 7.72-7.68 (m, 5H), 7.49 (d, ³*J*(¹H-¹H) = 7.0 Hz, 6H), 7.38 (d, ³*J*(¹H-¹H) = 7.0 Hz, 5H), 7.21-7.17 (m, 11H), 7.12-7.08 (m, 11H), 7.01 (t, ³*J*(¹H-¹H) = 7.5 Hz, 7H), 6.56 (t, ³*J*(¹H-¹H) = 7.3 Hz, 7H), 3.55-3.44 ppm (m, 16H, H-1,2). ¹³C{¹H}-NMR (CDCl₃): $\delta = 151.2$, 145.9, 138.8, 136.1, 133.5, 132.7, 129.8, 129.1, 128.3, 127.5, 121.3, 119.3, 30.9 (C₁ or C₂), 30.2 ppm (C₂ or C₁). The ¹³C-NMR spectra showed only broad signals which prevent the assignment of any *J*(P-C)-coupling information. ³¹P{¹H}-NMR (CDCl₃): $\delta = -44.7$ ppm. Anal. Calcd for C₉₇H₇₈Cl₂O₁₀P₄Sb₄ (2085.49): C, 55.86; H, 3.77. Found: C, 55.76; H, 3.74.

X-ray crystallography. Intensity data of **2** and **3** were collected on a Bruker Venture D8 diffractometer at 173 K with graphite-monochromated Mo-K α (0.7107 Å) radiation. Both structures were solved by direct methods and refined based on F² by use of the SHELX program package as implemented in OLEX2.^{S1} All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Diffuse electron density related to the presence of heavily disordered solvent molecules (THF for **1** and CH₂Cl₂ for **2**) was taken in account by solvent masking.^{S1} Crystal and refinement data are collected in Table S1. Selected bond parameters are listed in Table S2. Figures were created using DIAMOND.^{S2} Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)

	2·THF	$3 \cdot 4 \operatorname{CH}_2\operatorname{Cl}_2$
Formula	C ₂₈ H ₂₆ Cl ₄ OPSb	$C_{100}H_{84}Cl_8O_{10}P_4Sb_4$
Formula weight, g mol ⁻¹	673.01	2340.15
Crystal system	triclinic	monoclinic
Crystal size, mm	$0.30 \times 0.20 \times 0.20$	$0.25 \times 0.20 \times 0.15$
Space group	P-1	C2/c
<i>a</i> , Å	9.6541(5)	21.2249(10)
b, Å	10.0084(5)	20.2061(9)
<i>c</i> , Å	16.5724(8)	26.9813(13)
<i>α</i> , °	101.464(2)	90
<i>β</i> , °	106.588(2)	108.7330(10)
γ, °	90.666(2)	90
<i>V</i> , Å ³	1500.01(13)	10958.5(9)
Ζ	2	4
$ ho_{ m calcd},{ m Mg}~{ m m}^{-3}$	1.348	1.418
μ (Mo K α), mm ⁻¹	1.490	1.280
<i>F</i> (000)	672	4656
θ range, deg	2.62 to 25.50	2.37 to 25.50
Index ranges	$-11 \le h \le 11$	$-25 \le h \le 25$
	$-12 \leq h \leq 12$	$-24 \leq h \leq 24$
	$-19 \leq h \leq 20$	$-32 \le h \le 32$
No. of reflns collected	71631	69016
Completeness to $\theta_{\rm max}$	99.9%	99.8%
No. indep. Reflns	5570	10206
No. obsd reflns with $(I \ge 2\sigma(I))$	5264	7074
No. refined params	334	617
GooF (F^2)	1.060	1.035
$R_1(F)(I > 2\sigma(I))$	0.0211	0.0624
$wR_2(F^2)$ (all data)	0.0552	0.1542
Largest diff peak/hole, e Å ⁻³	0.717 / -0.529	1.512 / -1.234
CCDC number	1045474	1045475

Table S1.Crystal data and structure refinement of 2 and 3.

	1 (Sb1)	2 (Sb1)	3 (Sb1)	3 (Sb2)	
	(X1 = C11) (X2 = C12)	(X1 = C11) (X1 = C12)	(X1 = O1) (X1 = O2)	(X1 = O2) (X1 = O1)	
	(X3 = null) (X4 = null)	(X3 = C13) (X4 = C14)	(X3 = O3) (X4 = O5)	(X3 = O4) (X4 = O6)	
	(X4 = null)	(X4 = C14)	(X4 = 05)	(X4 = 06)	
Bond Lengths and Angles					
Sb-X1	2.525(1)	2.3806(5)	1.981(5)	1.985(4)	
Sb-X2	2.396(1)	2.4041(5)	1.949(3)	1.946(4)	
Sb-X3		2.4244(5)	1.934(3)	1.935(3)	
Sb-X4		2.3964(5)	2.013(5)	2.001(5)	
Sb-C10	2.170(2)	2.136(2)	2.156(8)	2.141(6)	
C10-Sb-X1	93.16(7)	97.31(6)	86.2(2)	91.1(2)	
C10-Sb-X2	95.62(7)	172.94(5)	164.4(3)	163.8(2)	
C10-Sb-X3		90.85(5)	96.6(3)	96.5(2)	
C10-Sb-X4		92.63(5)	89.0(2)	84.7(2)	
X1-Sb-X2	87.58(3)	89.72(2)	93.1(2)	93.8(2)	
X1-Sb-X3		90.26(2)	97.1(2)	97.6(2)	
X1-Sb-X4		91.44(2)	169.0(2)	166.8(2)	
X2-Sb-X3		88.49(2)	98.9(2)	98.2(2)	
X2-Sb-X4		87.79(2)	88.9(2)	87.1(2)	
X3-Sb-X4		175.90(2)	93.4(2)	95.2(2)	
peri Region Distances					
P(1)···Sb	2.808(1)	2.5911(5)	2.717(2)	2.729(2)	
peri Region Bond Angles					
Sb-C(10)-C(19)	121.5(3)	114.4(2)	119.6(5)	119.7(5)	
C(10)-C(19)-C(18)	128.7(2)	128.4(2)	127.3(7)	127.9(6)	
P(1)-C(18)-C(19)	116.1(2)	117.0(2)	115.6(6)	116.0(5)	
Σ of bay angles	366.3(7)	359.8(6)	362.5(18)	363.6(16)	
Splay angle ^a	6.3(7)	0.2(6)	2.5(18)	3.6(16)	
C(20)-P(1)-C(30)	104.0(2)	111.11(9)	105.7(4)	104.4(3)	
Out-of-Plane Displacement*					
P(1)	0.1075(6)	0.1623(5)	0.071(2)	0.244(2)	
Sb	0.1799(3)	0.0794(1)	0.0333(4)	0.1152(4)	
Central Acenaphthene Ring Torsion Angles					
C:(13)-(14)-(19)-(18)	180.0(3)	180.7(2)	178.4(9)	175.6(8)	
C:(15)-(14)-(19)-(10)	176.1(3)	178.7(2)	178.1(9)	177.7(9)	

Table S2.Selected bond parameters [Å, °] of 1 - 3.

^a Splay angle: Σ of the three bay region angles - 360. *Compounds 1 and 3 have a cisoid out-of-plane displacement, 2 shows a transoid out-of-plane displacement.

Computational Methodology. Starting from the X-ray single-crystal coordinates the gas-phase molecular geometries of **1** and **2** were fully optimized at the B3PW91 level of theory, ^{S3} using effective core potentials for Sb^{S4} along with the associated triple-zeta basis set^{S5} and 6-311+G(2df,p) basis set for all other atoms. The final geometries were confirmed to be minima by an analysis of harmonic vibrational frequencies. Geometry optimization of **3** was not feasible at the same level of theory. Therefore, the X-ray single-crystal coordinates were taken for a single point calculation, whereby the C-H distances were set to neutron diffraction data prior to processing.^{S6} All computations were performed using the Gaussian 09 program.^{S7} Subsequently, topological and integrated AIM and ELI-D parameters were derived using AIM2000^{S8} and DGID-4.6^{S9} based on wave function and checkpoint files, respectively. Bond topological properties are collected in Tables 1 and S3. For the grid calculations, a step size of 0.05 bohr was applied. The AIM-graphs (Figures S1 and S2) were displayed with AIMall.^{S10} ELI-D representations (Figures S3 and S3) were shown with MOLISO.^{S11}

		d [Å]	$ ho(r)_{bcp}$ [eÅ ⁻³]	$ abla^2 ho(r)_{bcp} $ [eÅ ⁻⁵]	d_1 [Å]	d_2 [Å]	3	$G/\rho(r)_{bcp}$ [he ⁻¹]	$H/\rho(r)_{bcp}$ [he ⁻¹]
1	Sb-P	2.924	0.27	0.7	1.401	1.528	0.08	0.38	-0.20
2	Sb-P	2.688	0.44	-0.1	1.268	1.419	0.02	0.32	-0.35
3	Sb-P	2.718	0.39	0.3	1.265	1.453	0.04	0.38	-0.32
1	Sb-Cl	2.560	0.41	2.0	1.218	1.342	0.08	0.84	-0.93
2	$Sb-Cl_{top}$	2.372	0.60	2.3	1.118	1.254	0.01	0.67	-0.40
2	Sb-Cl _{ax}	2.399	0.58	2.0	1.134	1.265	0.02	0.63	-0.39
2	Sb-Cl _{eq}	2.415	0.56	2.2	1.137	1.278	0.02	0.65	-0.38
2	Sb-Cl _{eq}	2.425	0.54	2.2	1.141	1.284	0.01	0.65	-0.37
3	Sb-O	1.982	0.80	10.3	1.006	0.976	0.02	1.26	-0.35
3	Sb-O	1.949	0.87	11.0	0.990	0.959	0.03	1.28	-0.39
3	Sb-O	1.934	0.88	12.4	0.980	0.954	0.02	1.37	-0.38
3	Sb-O(H)	2.011	0.78	8.8	1.016	0.995	0.09	1.15	-0.37
1	Sb-C	2.189	0.72	0.7	1.105	1.083	0.01	0.91	-0.28
2	Sb-C	2.158	0.77	0.3	1.098	1.060	0.03	0.53	-0.50
3	Sb-C	2.157	0.77	0.5	1.089	1.067	0.00	0.55	-0.50

Table S3.Bond topological properties of the Sb-Y bonds in 1, 2 and 3.



Figure S1. AIM bond paths motif for **2**.



Figure S2. AIM bond paths motif for **3**.



Figure S3. ELI-D distribution mapped on the Sb-Cl ELI-D basins in 2.



Figure S4. Left side: ELI-D distribution mapped on the ELI-D Sb core basins in **2**. Right side: Electron density distribution mapped on the AIM Sb atomic basin in **3**.

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