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Tetraphenylphosphorus and Tetraphenylantimony (2-Carboxy)benzenesulfonates: Synthesis and Structures

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Abstract—The reactions of pentaphenylphosphorus and pentaphenylantimony with 2-sulfobenzoic acid in benzene afford tetraphenylphosphonium $[Ph_4P]^+[OSO_2C_6H_4(COOH\text{-}2)]^-$ (**I**) and tetraphenylstibonium $[Ph_4Sb]^+[OSO_2C_6H_4(COOH\text{-}2)]^-$ (**II**) (2-carboxy)benzenesulfonates in the yield up to 90%. Compounds **I** and **II** are also synthesized from tetraphenylphosphonium and tetraphenylstibonium chlorides and 2-sulfobenzoic acid in water in the yield up to 89%. The complexes are characterized by X-ray diffraction (XRD) (CIF files CCDC nos. 2144288 (**I**) and 2123516 (**II**)) and IR spectroscopy.

Keywords: tetraphenylphosphonium (2-carboxy)benzenesulfonate, tetraphenylstibonium (2-carboxy)benzenesulfonate, synthesis, structure, XRD

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INTRODUCTION

Pentaphenyl compounds of phosphorus, antimony, and bismuth have attracted attention since the moment of their discovery by the laureate of the Nobel Prize G. Wittig [1] in the middle of the 20th century and to the present time [2–31]. Along with classical substitution reactions for pentaphenylphosphorus (PPP), unusual reactions are known among which the following processes can be distinguished: preparation of esters by using PPP in organic synthesis [32], formaldehyde insertion at the phosphorus–carbon bond [33], and addition of carbon dioxide to PPP with the formation of oxaphospholane [34]. The reactions of pentaphenylantimony (PPA) are also interesting [3], among which the reactions of PPA with arenesulfonic acids should be emphasized [35–38], especially those with polyfunctional arenesulfonic acids [39]. The methods for the preparation of two bifunctional derivatives of tetraphenylphosphonium and tetraphenylstibonium are described in this work.

Continuing the studies in this field, we carried out the reactions of PPP and PPA with (2-carboxy)benzenesulfonic acid and established structural features of the formed compounds.

EXPERIMENTAL

Prior to synthesis, solvents (reagent grade) were dried over calcium chloride and distilled.

Synthesis of tetraphenylphosphorus (2-carboxy)benzenesulfonate $[Ph_4P]^+[OSO_2C_6H_4(COOH\text{-}2)]^-$ (I). (a) A mixture of pentaphenylphosphorus solvate (247 mg, 0.5 mmol) and 2-sulfobenzoic acid (101 mg, 0.5 mmol) in benzene (10 mL) was hold at 80°C for 1 min. The reaction mixture was cooled to room temperature, octane (1 mL) was added, and the solvent was slowly removed. The yield of colorless crystals with T_m = 202°C was 260 mg (96%).

For $C_{31}H_{25}O_5SP$

Anal. calcd., %	C, 68.82	H, 4.26
Found, %	C, 68.68	H, 4.37

IR (ν, cm^{-1}): 3080, 3062, 2956, 2384, 2256, 1822, 1705, 1587, 1566, 1483, 1463, 1436, 1340, 1296, 1261, 1170, 1157, 1139, 1122, 1109, 1072, 1028, 995, 950, 802, 763, 752, 723, 702, 690, 619, 572, 528, 455, 426, 410.

(b) A mixture of tetraphenylphosphonium chloride (187 mg, 0.5 mmol) and 2-sulfobenzoic acid (101 mg, 0.5 mmol) in water (10 mL) was heated to the formation of a transparent solution, and the solvent was slowly evaporated. After solvent evaporation, compound **I** was obtained in a yield of 265 mg (98%).

Synthesis of tetraphenylantimony (2-carboxy)benzenesulfonate (II) was carried out similarly to the procedure for compound **I**, but $Ph_5Sb{\cdot}PhH$ was used instead of $Ph_5P{\cdot}PhH$. Colorless crystals with T_m = 160°C were obtained in yields of 93 and 97%.

IR (ν, cm^{-1}): 3145, 3072, 3049, 2951, 2544, 1977, 1899, 1832, 1766, 1718, 1620, 1589, 1568, 1479, 1433, 1361, 1336, 1296, 1251, 1170, 1157, 1138, 1120, 1066, 1018, 1002, 995, 974, 925, 900, 879, 860, 837, 800, 758,

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{31}H_{25}O_5PS$	$C_{31}H_{25}O_5SSb$
FW	512.64	631.32
Crystal system	Tetragonal	Triclinic
Space group	$I\bar{4}$	$P\bar{1}$
a, Å	18.319(17)	9.529(3)
b, Å	18.319(17)	10.584(3)
c, Å	16.067(17)	13.745(5)
α, deg	90.00	94.619(17)
β, deg	99.00	97.731(18)
γ, deg	90.00	90.336(16)
V, Å^3	5392(8)	1369.0(7)
Z	8	2
ρ_{calc}, g/cm^3	1.332	1.531
μ_{Mo}, mm^{-1}	0.219	1.123
F(000)	2256.0	636.0
Crystal size, mm	0.16 × 0.16 × 0.12	0.36 × 0.28 × 0.26
2θ, deg	5.58–55.98	5.74–54.32
Ranges of reflection indices	$-24 \le h \le 24$, $-21 \le k \le 24$, $-21 \le l \le 21$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-17 \le l \le 17$
Total number of reflections	49841	34082
Independent reflections (R_{int})	6496 (0.1110)	6043 (0.0213)
Number of refined parameters	431	344
GOOF	0.863	1.122
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0492$, $wR_2 = 0.0988$	$R_1 = 0.0201$, $wR_2 = 0.0509$
R factors for all reflections	$R_1 = 0.1606$, $wR_2 = 0.1192$	$R_1 = 0.0221$, $wR_2 = 0.0520$
Residual electron density (max/min), e/Å^3	0.16/–0.19	0.20/–0.65

738, 729, 702, 688, 644, 619, 570, 526, 495, 455, 447, 424.

For $C_{31}H_{25}O_5SSb$

Anal. calcd., %	C, 58.95	H, 3.96
Found, %	C, 58.86	H, 4.02

IR spectra were recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer in a range of 4000–400 cm^{-1} (KBr pellets).

XRD of crystals of complexes **I** and **II** was conducted on a D8 Quest diffractometer (Bruker, MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293 K. Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [40]. All calculations on structure determination and refinement were performed using the SHELXL/PC [41] and OLEX2 [42] programs. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement results for compounds **I** and **II** are given in Table 1. Selected bond lengths and bond lengths are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2144288 (**I**) and 2123516 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 2. Selected bond lengths and bond angles in the structures of compounds **I** and **II**

Bond	d, Å	Angle	ω, deg
		I	
S(1)–O(1)	1.441(9)	O(1)S(1)O(2)	114.4(10)
S(1)–O(2)	1.450(9)	O(1)S(1)O(3)	118.8(8)
S(1)–O(3)	1.467(7)	O(1)S(1)C(1)	105.7(8)
S(1)–C(1)	1.788(6)	O(2)S(1)O(3)	110.9(8)
S(1')–O(1')	1.443(9)	O(2)S(1)C(1)	101.5(7)
S(1')–O(2')	1.477(7)	O(3)S(1)C(1)	103.1(5)
S(1')–O(3')	1.435(7)	O(1')S(1')O(2')	112.7(10)
S(1')–C(1')	1.774(5)	O(1')S(1')C(1')	106.9(10)
P(1A)–C(1A')^1	1.811(5)	O(2')S(1')C(1')	105.5(5)
P(1A)–C(1A)	1.811(5)	O(3')S(1')O(1')	111.1(11)
P(1A)–C(7A)	1.793(5)	O(3')S(1')O(2')	112.8(7)
P(1A)–C(7A)^1	1.793(5)	O(3')S(1')C(1')	107.3(6)
P(1B)–C(1B)	1.792(6)	C(1A)^{1}P(1A)C(1A)	103.8(3)
P(1B)–C(1B)^2	1.792(6)	C(7A)P(1A)C(1A)^1	112.5(3)
P(1B)–C(1B)^3	1.792(6)	C(7A)P(1A)C(1A)	111.3(3)
P(1B)–C(1B)^4	1.792(6)	C(7A)P(1A)C(7A)^1	105.6(3)
P(1C)–C(1C)^5	1.792(6)	C(1B)^{2}P(1B)C(1B)^3	111.4(2)
P(1C)–C(1C)^6	1.792(6)	C(1B)P(1B)C(1B)^4	111.4(2)
P(1C)–C(1C)^7	1.792(6)	C(1C)^{5}P(1C)C(1C)^6	111.4(2)
Symmetry transforms: $^1\,-x, 1-y, z$; $^2\,1-x, 1-y, z$; $^3\,1-x, y, 1-z$; $^4\,x, 1-y, 1-z$; $^5\,-x, 2-y, z$; $^6\,1-x, -1+y, 1-z$; $^7\,1+x, 1-y, 1-z$.			
		II	
Sb(1)–C(1)	2.0811(17)	C(1)Sb(1)C(21)	106.77(7)
Sb(1)–C(21)	2.1081(17)	C(1)Sb(1)C(11)	108.20(6)
Sb(1)–C(11)	2.1027(17)	C(1)Sb(1)C(31)	111.21(6)
Sb(1)–C(31)	2.1010(17)	C(11)Sb(1)C(21)	108.21(6)
S(1)–O(3)	1.4707(15)	C(31)Sb(1)C(21)	109.42(7)
S(1)–O(2)	1.4461(14)	C(31)Sb(1)C(11)	112.80(6)
S(1)–O(1)	1.4399(14)	O(3)S(1)C(41)	104.33(8)
S(1)–C(41)	1.7854(17)	O(2)S(1)O(3)	112.87(9)

RESULTS AND DISCUSSION

It was found that holding a mixture of PPP and (2-carboxy)benzenesulfonic acid in benzene resulted in the formation of tetraphenylphosphonium (2-carboxy)benzenesulfonate $[Ph_4P]^+[OSO_2C_6H_4(COOH\text{-}2)]^-$ (**I**) in a yield of 96%.

$$Ph_5P + HOSO_2C_6H_4(COOH\text{-}2) \rightarrow \underset{\textbf{(I)}}{[Ph_4P]^+[OSO_2C_6H_4(COOH\text{-}2)]^-} + PhH$$

Compound **I** was also isolated in a yield of 96% by concentrating an aqueous solution containing equimolar amounts of tetraphenylphosphonium chloride and (2-carboxy)benzenesulfonic acid.

$$Ph_4PCl + HOSO_2C_6H_4(COOH\text{-}2) \rightarrow [Ph_4P]^+[OSO_2C_6H_4(COOH\text{-}2)]^- + HCl$$

Analogous reactions were shown to be characteristic of similar antimony derivatives.

$$Ph_5Sb + HOSO_2C_6H_4(COOH\text{-}2) \rightarrow [Ph_4Sb]^+[OSO_2C_6H_4(COOH\text{-}2)]^- + PhH \ \textbf{(II)}$$

$$Ph_4SbCl + HOSO_2C_6H_4(COOH\text{-}2) \rightarrow [Ph_4Sb]^+[OSO_2C_6H_4(COOH\text{-}2)]^- + HCl$$

The formed colorless crystals are highly soluble in arenes and polar solvents and insoluble in aliphatic hydrocarbons.

The IR spectrum of complex **I** exhibits an absorption band at 763 cm^{-1} corresponding to the ν(P–C) stretching vibrations, and the spectrum of complex **II** contains a band at 447 cm^{-1} characteristic of the Sb–C bond. The presence of the carbonyl group is characterized by the high-intensity absorption band of the C=O stretching vibrations at 1705 (**I**) and 1718 (**II**) cm^{-1}. Stretching vibrations of the bound OH group appear at 3396 (**I**) and 3419 (**II**) cm^{-1}. The bands at 1261, 1170, 1157 (**I**) and 1251, 1170, 1157 cm^{-1} (**II**) belong to the $\nu(OSO_2)$ vibrations. The aromatic fragments are characterized by the bands at 1587, 1463, 1436 cm^{-1} (**I**) and 1589, 1479, 1433 cm^{-1} (**II**). The weak-intensity absorption bands at 3080, 3062 (**I**) and 3072, 3049 (**II**) cm^{-1} correspond to the stretching vibrations of the C_{Ar}–H bonds, and the out-of-plane bending vibrations of the same bonds are characterized by the high-intensity bands at 723, 690 cm^{-1} (**I**) and 738, 729 (**II**) cm^{-1}.

According to the XRD data, compounds **I** and **II** are ionic complexes with the tetrahedral coordination of the central atom in the cation and with the (2-carboxy)benzenesulfonate anion (Figs. 1 and 2). The crystal of compound **I** exhibits three types of centrosymmetric crystallographically independent tetraphenylphosphorus cations. The symmetry element (inversion rotation fourfold axis) passes directly through the phosphorus atoms. The anion in compound **I** is disordered over two positions with an atomic occupancy of 0.51/0.49.

The tetrahedral coordination of the phosphorus and antimony atoms in the cations of compounds **I** and **II** is insignificantly distorted. The CPC and CSbC angles deviate from the theoretical value and lie in ranges of 103.8(3)°–112.5(3)° (**I**) and 106.77(7)°–112.80(6)° (**II**). The average P–C bond length is 1.796(6) Å in the tetraphenylphosphorus cations. The Sb–C distances are close to each other and vary from 2.0811(17) to 2.1081(17) Å in the organostibium cations of complex **II**. The geometry of the anions correspond to the geometry of (2-carboxy)benzenesulfonic acid.

Spatial networks of crystals of compounds **I** and **II** are formed due to hydrogen bonds and CH···π interactions. Hydrogen bonds are observed between the aromatic protons of the cation and oxygen atoms of the anion and amount to 2.60 Å for C=O···H and 2.57, 2.53, 2.60, 2.70, and 2.49 Å for S=O···H in compound **I**; and 2.51, 2.60 Å for C=O···H and 2.68, 2.72, and 2.71 Å for S=O···H, and 2.71 Å for C–O···H in compound **II**. No contacts are observed between the cations, but the anions interact with each other due to hydrogen bonds of the types C–O···H (2.71 Å) in compound **I** and S=O···H (2.49 Å) in compound **II**. Interestingly, the intramolecular interaction S=O···HO(O)C is observed in the anions (1.70 and 1.75 Å for compounds **I** and **II**, respectively).

Thus, the reactions of pentaphenylphosphorus and pentaphenylantimony with (2-carboxy)benzenesulfonic acid afford tetraphenylphosphorus and tetraphenylantimony (2-carboxy)benzenesulfonates, which can also be synthesized from tetraphenylphosphorus and tetraphenylantimony chlorides and (2-carboxy)benzenesulfonic acid in water. The structures of the synthesized complexes were proved by XRD.

FUNDING

The study did not receive any funding.

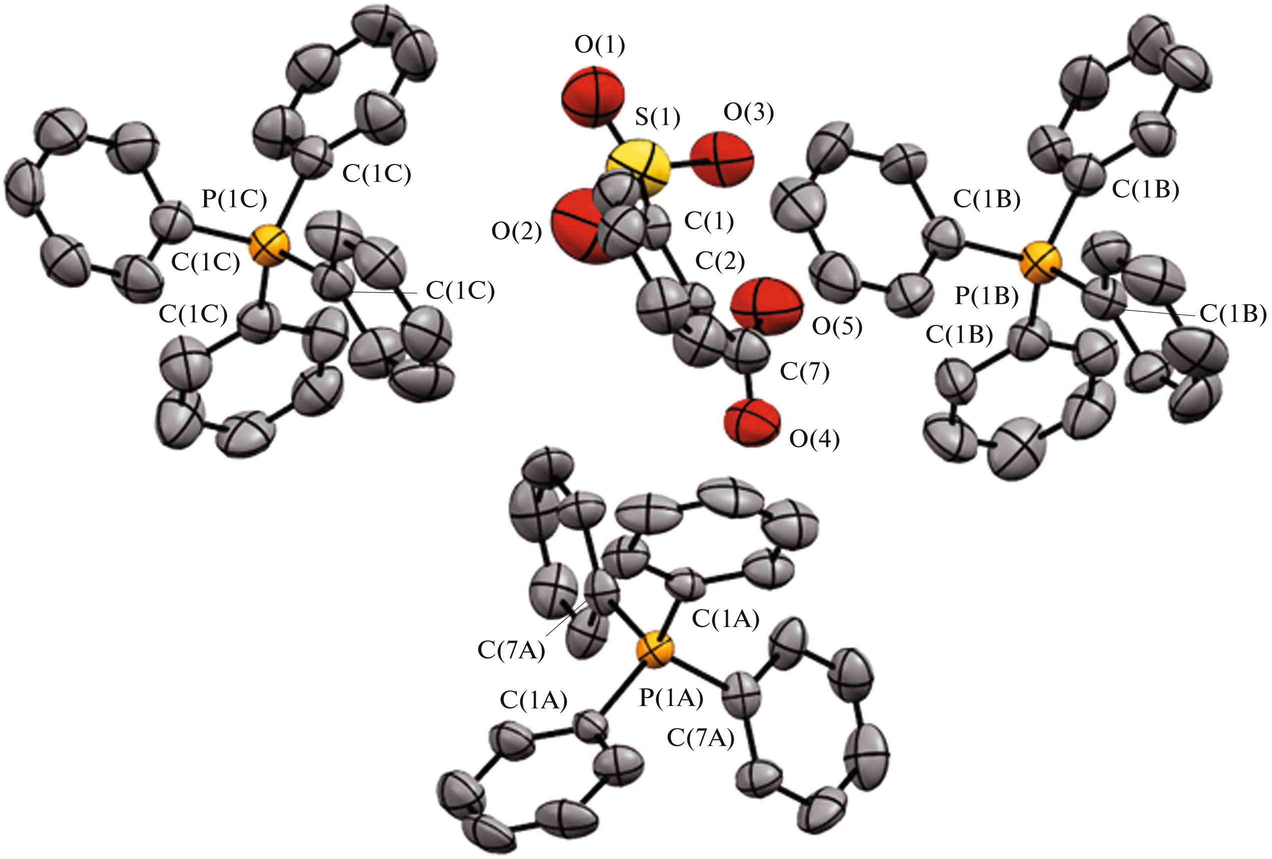

Fig. 1. Structure of tetraphenylphosphorus (2-carboxy)benzenesulfonate **I** (hydrogen atoms and disordered fragments are omitted).

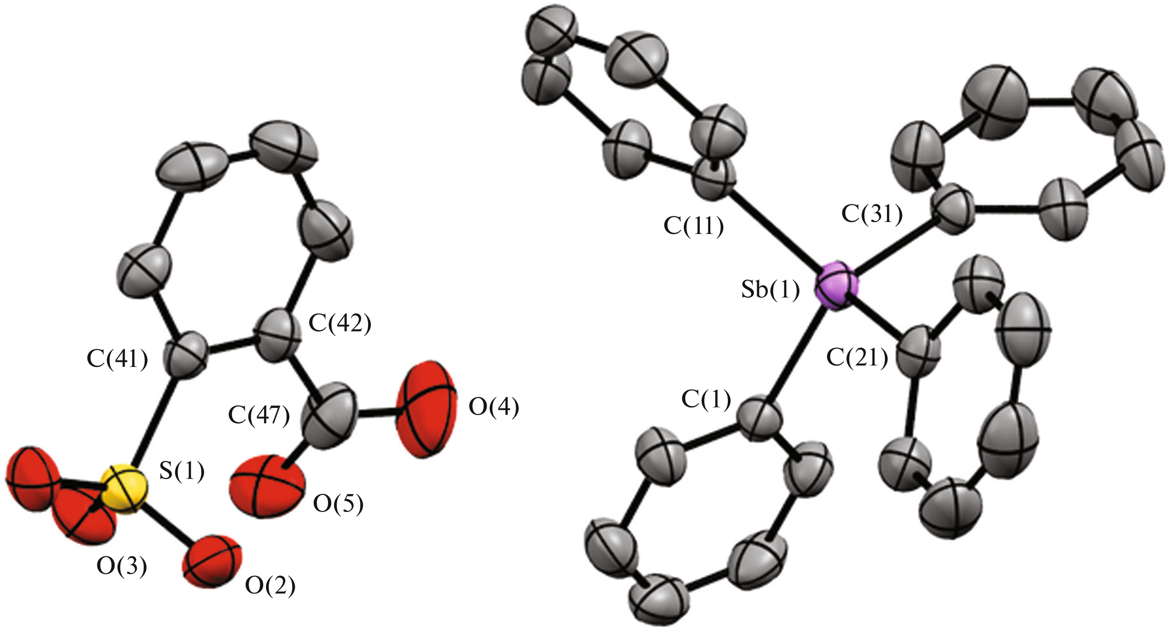

Fig. 2. Structure of tetraphenylantimony (2-carboxy)benzenesulfonate **II** (hydrogen atoms are omitted).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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