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Tetraphenylphosphonium Carboxylates and Sulfonates. Synthesis and Structure

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Abstract—The reaction of the pentaphenyphosphorus solvate $Ph_5P\cdot 1/2PhH$ (**I**) with carboxylic and sulfonic acids was used to synthesize tetraphenylphosphonium carboxylates $Ph_4POC(O)R$, R = C_6H_4(2-OH) (**II**), C_6H_4(2-COOH) (**III**), H (**IV**), Me (**V**), CCl_3 (**VI**), Ph (**VII**), PhCH=CH (**VIII**), $CH_2CH_2C(O)OH$ (**IX**), CH=CHC(O)OH (**X**), and $CH_2C(O)OH$ (**XI**) and tetraphenylphosphonium sulfonates Ph_4POSO_2Ar, Ar = Ph (**XII**), C_6H_4Me-4 (**XIII**), and C_6H_3(-COOH)(4-OH) (**XIV**). Compound **XII** was also prepared from compound **I** and SO_3 in benzene. According to X-ray diffraction data, the crystals of **I** contain two types of crystallographically independent molecules with a slightly distorted trigonal-bipyramidal configuration [**Ia**, $C_{ax}PC_{ax}$ 178.44(8)°, P–C_{ax} 1.985(2), 1.987(2) Å, P–C_{eq} 1.854(2), 1.846(2), 1.840(2) Å; **Ib**, $C_{ax}PC_{ax}$ 178.45(9)°, P–C_{ax} 1.980(2), 1.975(2) Å, P–C_{eq} 1.840(2), 1.846(2), 1.854(2) Å]. In the cations of compounds **II, III** and **XIV,** the coordination of the phosphorus atom is tetrahedral [CPC angle: **II**, 106.2(2)–111.6(1)°; **III**, 104.01(6)–113.03(6)°; **XIV**, 107.54(6)–112.79(6)°]; the anions contain intramolecular O–H···O hydrogen bonds between the hydroxyl hydrogen atom and carboxyl oxygen atom (**II**, 1.34; **III**, 1.23; and **XIV**, 1.83 Å).

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Pentaphenylphosphorus is known to crystallize from organic solutions as solvates, e.g., $Ph_5P\cdot 1/2$*cyclo*-C_6H_{12} [1].

We synthesized pentaphenylphosphorus from tetraphenylphosphonium iodide and phenyllithium and extracted it from the reaction mixture with benzene, where its solubility is higher than in cyclohexane. After filtration and removal of the solvent we obtained colorless crystals which, by X-ray diffraction data, are pentaphenylphosphorus solvate with benzene, $Ph_5P\cdot 1/2PhH$ (**I**) (Fig. 1). In the crystals of **I,** there are two types of crystallographically independent pentaphenylphosphorus molecules with a trigonal-bipyramidal central atom. The slight coordination distortion is evidenced by the values of the $C_{ax}PC_{ax}$ axial angles [178.44(8)° and 178.45(9)° in **Ia** and **Ib**, respectively] and bond angles $C_{ax}PC_{eq}$ between the axial and equatorial substituents [86.53(8)°–92.44(8)° and 86.34(8)°–92.68(8)° in **Ia** and **Ib**, respectively], that are close to the theoretical values 180° and 90°. The sums of the equatorial bond angles are 359.99(9)° (**Ia**) and 359.91° (**Ib**); therewith, the individual $C_{eq}PC_{eq}$ angles span the ranges 118.73(9)–120.73(9)° (**Ia**) and 119.67(9)°–120.24(9)° (**Ib**). In agreement with the valence-shell electron-pair repulsion (VSEPR) theory, the axial P–C_{ax} distances [1.985(2), 1.987(2) Å (**Ia**) and 1.975(2), 1.980(2) Å (**Ib**)] are longer than equatorial P–C_{eq} [1.840(2), 1.848(2), 1.854(2) Å (**Ia**) and 1.840(2), 1.846(2), 1.854(2) Å (**Ib**)].

The overall conformation of the phenyl rings in the equatorial plane in both **Ia** and **Ib** is not propeller. The C^{111}–C^{116} and C^{121}–C^{126} phenyl rings in **Ia** are turned around the equatorial bonds by large torsion angles, while the C^{141}–C^{146} plane of the third ring practically coincides with the equatorial plane; therewith, one of the rings (C^{121}–C^{126}) is turned to a direction opposite to that of the other two rings. The corresponding torsion angles are as follows: $C^{131}P^1C^{111}C^{116}$ –39.44°; $C^{151}P^1C^{111}C^{112}$ –41.98°; $C^{131}P^1C^{121}C^{126}$ 55.74°; $C^{151}P^1C^{121}C^{122}$ 58.11°; $C^{131}P^1C^{141}C^{166}$ –93.45°; and $C^{151}P^1C^{141}C^{142}$ –93.82°). The angle between the axial phenyl planes is about 80°. Similar positions but with slightly different torsion angles are occupied by equatorial and axial substituents in **Ib**.

Analysis of intermolecular contacts in the crystal of **I** showed that the molecular packing is defined mainly by van der Waals interactions. Parallel orientation of the aromatic rings is not realized. Weak interactions of the C–H···π type are possible. The shortest C···H distances between the benzene and pentaphenylphosphorus molecules are 2.41 and 2.90 Å.

Reactions of pentaphenylphosphorus with hydrohalic acids are known to afford tetraphenylphosphonium halides [1]. We found that dephenylation of pentaphenylphosphorus with carboxylic acids (1:1 molar ratio; benzene) results in quantitative formation of tetraphenylphosphonium carboxylates:

Tetraphenylphosphonium carboxylates are colorless crystalline substances readily soluble in aromatic hydrocarbons, THF, and dioxane. The IR spectra of the obtained compounds contain strong absorption bands in the region of stretching vibrations of ionized carboxy groups. The yields, melting points, and elemental analyses of tetraphenylphosphonium carboxylates are listed in Table 1.

According to X-ray diffraction data, tetraphenylphosphonium salicylate (**II**) and hydrogen phthalate (**III**) are ionic compounds. The tetraphenylphosphonium cations have a slightly distorted tetrahedral configuration (Figs. 2 and 3). The CPC bond angles vary within the ranges 106.2(1)°–111.6(1)° (**II**) and 104.01(6)°–113.03(6)° (**III**). The P–C distances are 1.798(3)–1.809(3) and 1.786(1)–1.795(1) Å for **II** and **III**, respectively. Their average values (1.802 and 1.790 Å) are smaller than the average P–C bond lengths in **Ia** and **Ib** (1.895 and 1.902 Å, respectively).

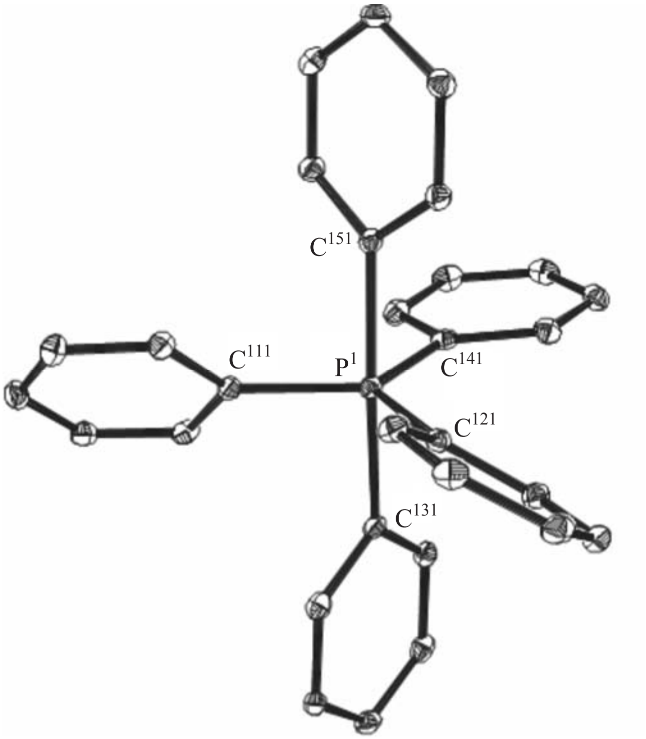

Fig. 1. Structure of pentaphenylphosphorus benzene solvate (**I**) (the benzene molecule is omitted).

In the salicylate anion, the hydroxy and carboxy groups are *ortho* to each other, and this allows formation of an intramolecular hydrogen bond with the following parameters: O^3–H^1 1.11 Å, H^1···O^2 1.34 Å, O^3···O^2 2.424 Å; $O^3H^1O^2$ angle 161°. The aromatic ring and the six-membered ring formed due to hydrogen bonding are almost coplanar. The C^{317}–O^1 and C^{317}–O^2 distances in the carboxy group are almost

Table 1. Yields, melting points, and elemental analyses of tetraphenylphosphonium carboxylates $Ph_4PO(O)CR$ prepared from pentaphenylphosphorus (**I**) and carboxylic acids (benzene, 80°C, 10 min)

Comp. no.	R	mp, °C	Yield, %	Found, %		Formula	Calculated, %	
				C	H		C	H
II	$C_6H_4(OH\text{-}2)\cdot PhH$	142	83	77.83	5.34	$C_{31}H_{25}O_3P$	78.15	5.26
III	$C_6H_4(COOH\text{-}2)$	180	98	75.76	5.17	$C_{32}H_{25}O_4P$	76.19	4.96
IV	H	152	87	77.75	5.68	$C_{25}H_{21}O_2P$	78.12	5.47
V	Me	98	72	78.11	5.92	$C_{26}H_{23}O_2P$	78.39	5.78
VI	CCl_3	112	97	62.03	4.14	$C_{26}H_{20}O_2PCl_3$	62.21	3.99
VII	Ph	131	96	80.47	5.68	$C_{31}H_{25}O_2P$	80.87	5.43
VIII	PhCH=CH	116	97	81.09	5.66	$C_{33}H_{27}O_2P$	81.48	5.56
IX	CH_2CH_2COOH	212	92	73.27	5.69	$C_{28}H_{25}O_4P$	73.68	5.48
X	CH=CHCOOH	202	78	73.86	5.18	$C_{28}H_{23}O_4P$	74.01	5.06
XI	CH_2COOH	230	96	72.97	5.46	$C_{27}H_{23}O_4P$	73.30	5.20

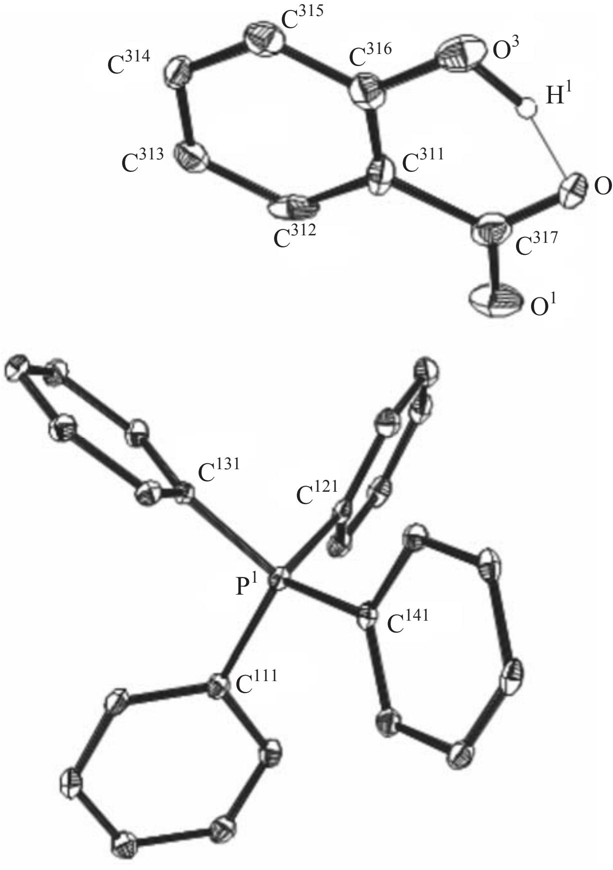

Fig. 2. Structure of tetraphenylphosphonium salicylate benzene solvate (**II**) (the benzene molecule is omitted).

equal to each other: 1.228(4) and 1.274(4) Å, respectively. By reference data, the delocalized bond length in the carboxylate anion is 1.26±0.01 Å [2]. The $O^1C^{317}O^2$ bond angle is 126.5(3)°. The $C^{316}–O^3$ bond length of 1.414(4) Å) is larger than the standard C–O bond length in compounds of the ArOH type (1.36±0.01 Å [2]), which is explained by the redistribution of electron density due to hydrogen bond formation.

In the crystal we found no intermolecular hydrogen bonds between the anions. The cation and anion packings in the crystal are defined by numerous C–H···O interactions (the H···O distances vary in the range 2.41–2.51 Å). Solvate benzene molecules are involved in C–H···π bonding.

In the phthalate monoanion, an intramolecular hydrogen bond involving the hydrogen atom of the $O^2–H^2···O^3$ carboxy group (the $O^2–H^2$ and $H^2···O^3$ distances are 1.16 and 1.23 Å, respectively). The distance between the oxygen involved in hydrogen bonding ($O^2···O^3$) is 2.394 Å. The $O^2H^2O^3$ angle equals 174°. The seven-membered ring formed due to hydrogen bonding is nonplanar. The dihedral angle between the $C^{26}C^{28}C^{27}C^{24}$ and $C^{24}O^2···O^3O^{26}$ fragments is 159°. The $O^1C^{24}O^2$ and $O^3C^{26}O^4$ carboxylate planes form an angle of 30°. The geometric parameters of the carboxylate groups practically coincide: $O^1–C^{25}$ 1.228(2) Å, $O^2–C^{25}$ 1.293(2) Å, $O^1C^{25}O^2$ 122.4(1)°; $O^4–$

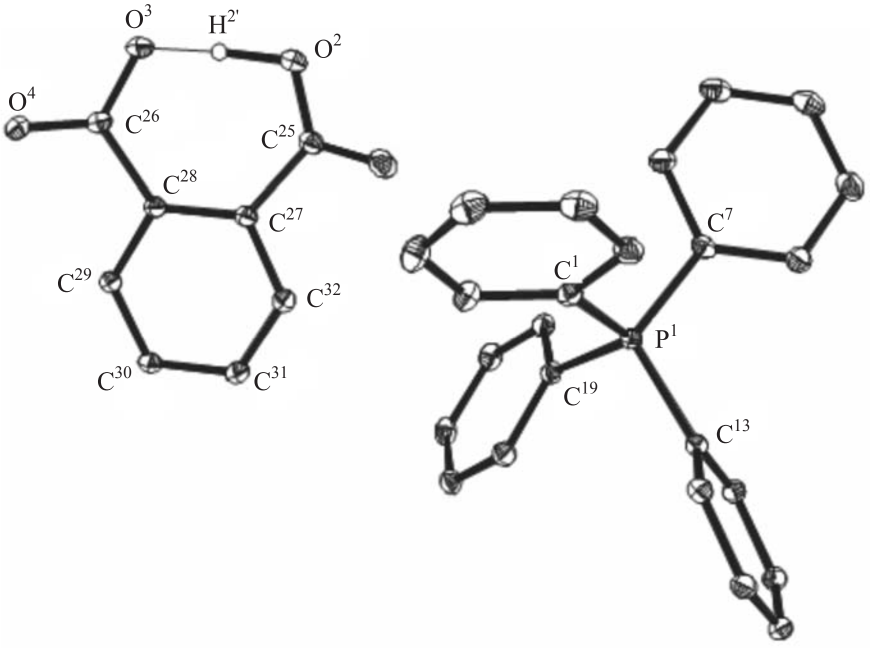

Fig. 3. Structure of tetraphenylphosphonium hydrogen phthalate (**III**).

Table 2. Yields, melting points, and elemental analyses of tetraphenylphosphonium arenesulfonates Ph_4POSO_2Ar prepared from pentaphenylphosphorus **I** and arenesulfonic acids (benzene, 80°C, 10 min)

Comp. no.	Ar	mp, °C	Yield, %	Found, %		Formula	Calculated, %	
				C	H		C	H
XII	$C_6H_5 \cdot H_2O$	176	85	69.97	5.43	$C_{30}H_{27}O_4PS$	70.04	5.25
XIII	C_6H_4Me-4	172	89	72.68	5.39	$C_{31}H_{27}O_3PS$	72.94	5.29
XIV	C_6H_3(COOH-3)(OH-4)	222	93	66.67	4.37	$C_{31}H_{25}O_6PS$	66.91	4.50

C^{26} 1.227 Å, O^3–C^{26} 1.292(2) Å, $O^4C^{25}O^3$ 122.4(1)°. The symmetrical phthalate monoanion in the structurally characterized tetramethylstibonium phthalate is planar; the O···O distance in the seven-membered ring is 2.322 Å, and the C–O bonds lengths are 1.136 and 1.259 Å [3].

In the crystal, phthalate monoanions form infinite zig-zag chains by means of weak intermolecular hydrogen bonds $O^2 \cdots H^{31}$–C^{31} (2.69 Å) and $O^3 \cdots H^{30}$–C^{30} (2.66 Å) (Fig. 4). The $O^2H^{31}C^{31}$ and $O^3H^{30}C^{30}$ angles are 130.7° and 137.9°, respectively. Besides, a lot of intermolecular C–H···O hydrogen bonds between cations and anions were found in the crystal. The O···H distances vary in the range 2.36–2.71 Å. Noteworthy is that there is no anion–phosphorus coordination, unlike what is observed in tetramethylstibonium phthalate, where each anion coordinates with two antimony atoms via oxygens.

We found that pentaphenylphosphorus reacts with arenesulfonic acids (1:1 molar ratio, benzene) to form tetraphenylphosphonium arenesulfonates:

$$Ph_5P + HOSO_2Ar \rightarrow Ph_4POSO_2Ar + PhH,$$

Ar = C_6H_5 (**XII**), C_6H_4Me-4 (**XIII**), C_6H_3(COOH-3)OH-4) (**XIV**).

Tetraphenylphosphonium arenesulfonates are colorless crystalline substances readily soluble in polar organic solvents and water. The yields, melting points, and elemental analyses of tetraphenylphosphonium arenesulfonates are listed in Table 2.

We also synthesized tetraphenylphosphonium benzenesulfonate from pentaphenylphosphorus and sulfur trioxide:

$$Ph_5P + SO_3 \rightarrow Ph_4POSO_2Ph.$$

After passing sulfur trioxide through a solution of pentaphenylphosphorus in benzene followed by removal of the solvent and recrystallization of the residue from water we obtained tetraphenylphosphonium benzenesulfonate hydrate. The reaction proceeds at room temperature, like the reaction of sulfur trioxide with pentaphenyl derivatives of antimony or bismuth [4, 5].

By X-ray diffraction data, the crystal of **XIV** consists of tetrahedral tetraphenylphosphonium cations [its CPC angles and P–C bond lengths span the ranges 107.54(6)°–112.79(6)° and 1.789(1)–1.801(1) Å, respectively, with an average bond length of 1.796 Å] and sulfosalicylate anions (Fig. 5). In the anions, there is an intramolecular hydrogen bond formed by the hydroxyl hydrogen atom and the carbonyl oxygen atom (O^4–$H^{40}O^6$=C^7), having the following parameters: O^4–H^{40} 0.87 Å, $H^{40} \cdots O^6$ 1.83 Å, O···O 2.619 Å, and $O^4H^{40}O^6$ angle 152°. (The hydrogen bond in tetraphenylstibonium sulfosalicylate has similar parameters: O–H 0.91 Å, H···O 1.72 Å, O···O 2.572 Å, and OHO angle 156° [6]). Note that the respective hydrogen bond in the anion of **II** is stronger. The angle between the formed six-membered ring (including hydrogen atom) and benzene ring planes is as small as 2.5°. Besides,

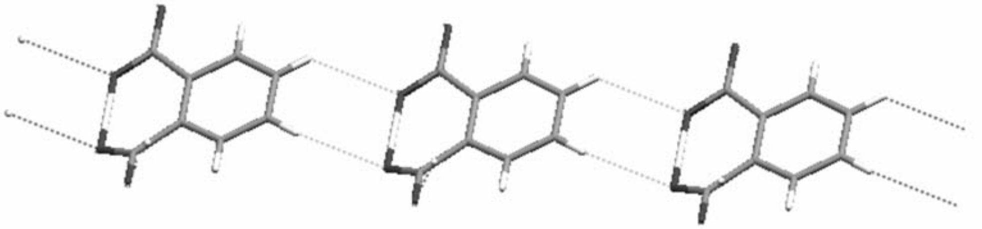

Fig. 4. View of the polymeric chain of hydrogen phthalate anions in the crystal of **III**.

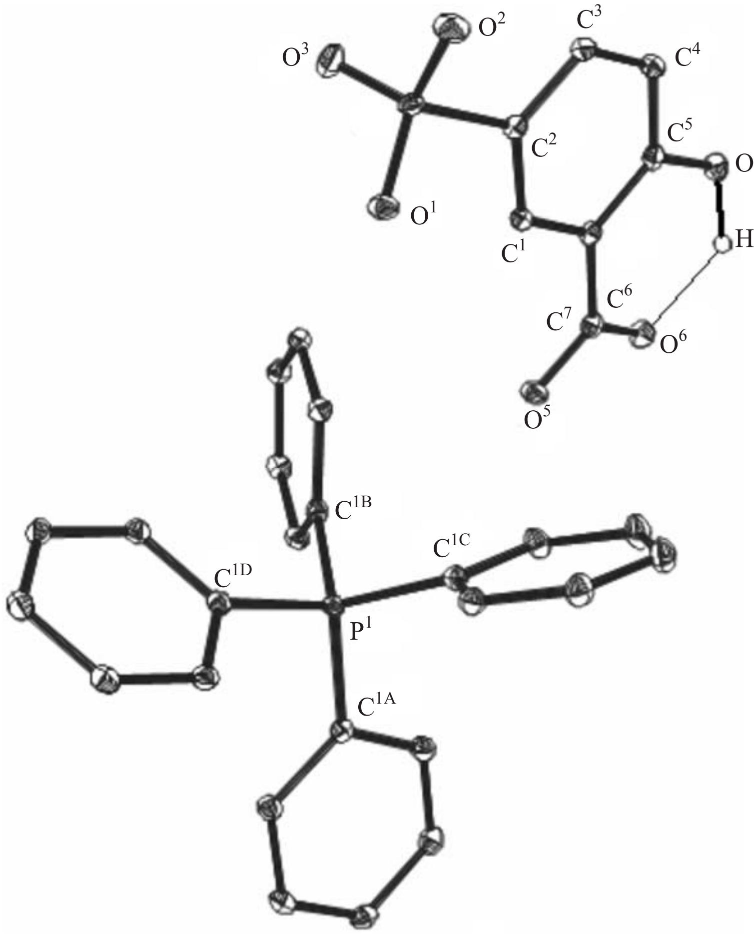

Fig. 5. Structure of tetraphenylphosphonium sulfosalicylate (**XIV**).

there are intermolecular hydrogen bonds between the carboxy group and one of the oxygen atoms of the sulfonate group, $O^4–H^{40}\cdots O^2=S$, with the following parameters: $O^4–H^{40}$ 0.92 Å, $H^{40}\cdots O^2$ 1.67 Å, $O^4\cdots O^2$ 2.579 Å, and $O^4H^{40}O^2$ angle 171°. This hydrogen bond binds the anions into an infinite one-dimensional chain (Fig. 6).

The $C^7–O^4$ and $C^7–O^6$ distances in the carboxy group are equal to 1.314(2) and 1.231(2) Å, respectively, that fall to the respective ranges for single (C–O, 1.293–1.308 Å) and double (C=O, 1.214–1.229 Å) bonds in carboxylic acids [7]. The $O^4C^7O^6$ angle [123.6(1)°] has its normal value. The $C^5–O^4$ distance [1.355(2) Å] is smaller than the respective distance in the anion of **II** [1.414(4) Å], which correlates with a lower strength of the hydrogen bond in **XIV**.

The sulfur atom in the sulfonate group is four-coordinated [the OSO bond angles falls to the range 105.51(6)°–113.30(6)°]. The $S^1=O^1$ and $S^1=O^3$ bond lengths are equal [1.450(1) and 1.451(1) Å], and the $S^1=O^2$ bond is longer [1.468(1) Å], on account of the involvement of O^2 to the intermolecular hydrogen bond. The reference value for the S=O bond length is 1.43±0.01 Å [2].

In the crystal of **XIV,** the chains of anions are parallel. Therewith, the benzene ring planes are shifted

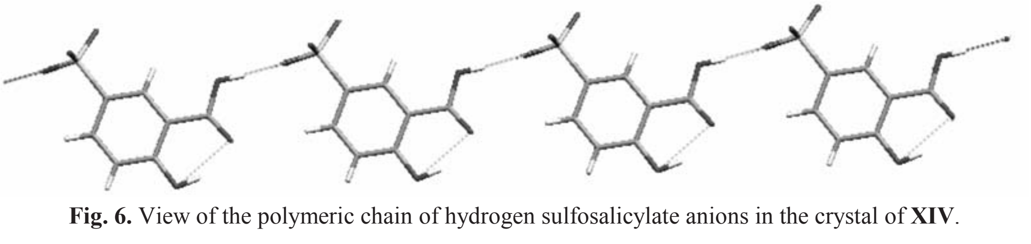

Fig. 6. View of the polymeric chain of hydrogen sulfosalicylate anions in the crystal of **XIV**.

Table 3. Crystallographic data and experimental and structure refinement parameters of compounds **I–III** and **XIV**

Parameter	Values			
	I	**II**	**III**	**XIV**
M	455.52	554.59	504.49	556.54
T, K	100.0(2)	90.0(2)	100(2)	100(2)
Syngony	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\overline{1}$	$P2_1/n$	$P\overline{1}$	$P\overline{1}$
a, Å	12.7040(4)	11.8526(3)	7.8354(2)	8.8278(2)
b, Å	14.0778(4)	9.4053(3)	12.1713(3)	10.8649(3)
c, Å	14.7550(5)	26.1375(9)	13.3766(3)	14.4034(4)
α, deg	89.3000(10)		90.0320(10)	76.9920(10)
β, deg	67.5880(10)	98.8790(10)	90.7320(10)	82.1540(10)
γ, deg	86.3440(10)		98.6820(10)	72.0720(10)
V, Å^3	2434.35(13)	2878.82(15)	1260.96(5)	1277.30(6)
Z	4	4	2	2
P_{calc}, g cm^{-3}	1.243	1.280	1.329	1.447
μ, mm^{-1}	0.133	0.132	0.146	0.236
F(000)	964	1168	528	580
Crystal shape (size, mm)	Prism (0.35×0.29×0.23)	Prism (0.30×0.29×0.18)	Prism (0.40×0.35×0.20)	Prism (0.69×0.45×0.42)
θ range, deg	1.49–31.53	2.02–25.0	2.63–30.04	2.24–27.00
Range of reflexion indices	$-18 \leq h \leq 14$, $-16 \leq k \leq 19$, $-19 \leq l \leq 20$	$-14 \leq h \leq 11$, $-9 \leq k \leq 11$, $-30 \leq l \leq 31$	$-10 \leq h \leq 9$, $-16 \leq k \leq 16$, $-18 \leq l \leq 11$	$-10 \leq h \leq 11$, $-13 \leq k \leq 10$, $-18 \leq l \leq 18$
Measured reflections	28814	12287	9742	8317
Unique reflection	13155 (R_{int} 0.0436)	5051 (R_{int} 0.0305)	6746 (R_{int} 0.0152)	5508 (R_{int} 0.0114)
Refinement parameters	613	373	434	452
GOOF	1.024	1.039	1.024	1.033
R factors on $F^2 > 2\sigma(F^2)$	R_1 0.0555, wR_2 0.1120	R_1 0.0564, wR_2 0.0953	R_1 0.0459, wR_2 0.1155	R_1 0.0346, wR_2 0.0893
R factors on all reflections	R_1 0.1090, wR_2 0.1321	R_1 0.0607, wR_2 0.1476	R_1 0.0558, wR_2 0.1241	R_1 0.0370, wR_2 0.0914
Extinction coefficient	–	0.00012(8)	–	–
Residual electron density (min/max), e Å^{-3}	–0.389/0.420	–0.620/1.319	–0.263/0.476	–0.429/0.420

with respect to each other, which excludes stacking π–π interaction. Probably, the key role in this case belongs to dipole–dipole interaction. The intermolecular interactions of anions and cations are defined by numerous C–H···O contacts. The cations and anions in the crystal of tetraphenylstibonium sulfosalicylate form tight ion pairs. The anion coordinated with the antimony atom via one of the sulfonate oxygen atoms, the Sb···O distance (2.691 Å) is much shorter than the sum of the van der Waals radii of antimony and oxygen [8]).

Thus, we reacted pentaphenylphosphorus with carboxylic and sulfonic acids to synthesize tetraphenylphosphonium salts. In the crystals, coordination between phosphorus and potential coordination centers (oxygen atoms) of the anions is absent.

EXPERIMENTAL

The X-ray structural analysis of the crystals of **I** and **II** was carried out on a Bruker AXS Smart Apex automatic diffractometer and of the crystals of **III** and **XIV,** on a Bruker–Nonius X8Apex automatic four-circle diffractometer. The structures were decoded by the direct method and refined by the least-squares method in anisotropic approximation for all non-hydrogen atoms. Positions of H atoms were calculated geometrically and refined in the ride-on model.

Acquisition and edition of data, refinement of unit cell parameters, and introduction of absorption corrections were performed using the SMART and SMART Plus programs [9]. The structures were decoded and refined using the SHELXTL/PC programs [10].

The principal crystallographic data and details of structure refinement are listed in Table 3, the atomic coordinates and temperature factors, in Table 4, and the principal bond lengths and bond angles, in Table 5.

The IR spectra of the complexes were registered on an FSM 1201 FT–IR spectrometer from KBr pellets.

Table 4. Atomic coordinates ($\times10^4$) and equivalent thermal parameters ($\times10^3$) in structures **I–III** and **XIV**

Atom	*x*	*y*	*z*	U_{eq}, Å^2	Atom	*x*	*y*	*z*	U_{eq}, Å^2
					I				
P^1	7806.0(4)	494.1(3)	8096.9(4)	14.98(11)	C^{143}	8897.4(16)	979.4(15)	5130.9(15)	25.4(5)
C^{111}	7665.7(15)	–810.4(13)	8143.5(14)	16.6(4)	C^{144}	8962.0(16)	1958.9(15)	5069.1(15)	24.9(5)
C^{112}	6667.8(16)	–1193.9(14)	8778.2(14)	20.3(4)	C^{145}	8680.7(16)	2499.0(15)	5913.9(15)	23.4(5)
C^{113}	6578.5(17)	–2170.8(14)	8844.1(15)	23.0(4)	C^{146}	8321.1(16)	2062.0(14)	6821.5(15)	21.0(4)
C^{114}	7468.5(17)	–2784.6(14)	8267.0(15)	23.2(4)	C^{151}	6222.7(15)	747.6(13)	8160.6(13)	16.0(4)
C^{115}	8456.0(16)	–2419.5(14)	7620.1(14)	20.7(4)	C^{152}	5462.6(15)	1490.5(13)	8689.6(14)	18.2(4)
C^{116}	8561.9(16)	–1442.1(14)	7568.5(14)	20.0(4)	C^{153}	4396.6(16)	1675.5(14)	8642.6(14)	21.4(4)
C^{121}	7508.3(15)	1188.8(13)	9232.0(14)	16.3(4)	C^{154}	4057.2(16)	1130.6(14)	8046.3(14)	20.8(4)
C^{122}	6647.9(16)	961.9(14)	10119.6(14)	20.5(4)	C^{155}	4800.8(16)	408.6(14)	7479.1(14)	21.5(4)
C^{123}	6432.0(17)	1498.9(14)	10962.8(15)	22.9(4)	C^{156}	5860.8(15)	227.6(14)	7537.8(14)	19.8(4)
C^{124}	7056.9(17)	2274.1(14)	10933.1(15)	22.8(4)	P^2	2058.3(4)	4307.9(3)	6895.7(4)	16.24(12)
C^{125}	7922.5(16)	2503.2(14)	10065.7(15)	21.7(4)	C^{211}	2112.3(15)	5611.1(13)	6833.9(14)	17.3(4)
C^{126}	8155.9(16)	1956.3(13)	9226.2(14)	18.9(4)	C^{212}	2862.4(17)	6049.0(14)	6007.4(15)	23.3(4)
C^{131}	9398.7(15)	274.4(13)	8014.8(14)	16.2(4)	C^{213}	2893.2(19)	7030.7(14)	5971.0(16)	28.4(5)
C^{132}	10374.8(16)	583.8(13)	7280.2(14)	18.8(4)	C^{214}	2196.5(18)	7591.6(14)	6763.5(16)	26.9(5)
C^{133}	11458.7(16)	388.2(13)	7293.4(15)	21.3(4)	C^{215}	1444.4(17)	7171.4(14)	7585.2(16)	24.6(5)
C^{134}	11593.4(16)	–138.2(13)	8042.6(15)	21.5(4)	C^{216}	1385.8(16)	6185.8(14)	7616.4(15)	21.1(4)
C^{135}	10638.3(16)	–452.2(13)	8791.8(15)	19.4(4)	C^{221}	1691.1(15)	3714.2(13)	8090.1(14)	17.4(4)
C^{136}	9563.6(16)	–240.9(13)	8780.6(14)	18.8(4)	C^{222}	1779.3(17)	4178.5(15)	8884.3(15)	25.4(5)
C^{141}	8269.9(15)	1078.7(13)	6897.6(14)	17.0(4)	C^{223}	1536.4(18)	3721.1(16)	9775.1(15)	30.0(5)
C^{142}	8572.5(16)	540.0(15)	6035.1(14)	21.9(4)	C^{224}	1215.4(17)	2791.2(15)	9880.7(15)	27.7(5)

Table 4. (Contd.)

Atom	*x*	*y*	*z*	U_{eq}, Å^2	Atom	*x*	*y*	*z*	U_{eq}, Å^2
				I					
C^{225}	1129.0(16)	2321.9(14)	9100.0(15)	24.1(5)	C^{246}	222.7(19)	4990.4(15)	6303.4(17)	30.5(5)
C^{226}	1357.8(16)	2781.2(14)	8210.9(15)	21.8(4)	C^{251}	3662.2(15)	4130.5(13)	6771.7(13)	16.2(4)
C^{231}	2372.0(16)	3593.1(13)	5765.3(14)	18.0(4)	C^{252}	4268.6(16)	4834.7(14)	6969.9(16)	24.0(5)
C^{232}	1612.1(16)	2941.0(13)	5707.6(15)	20.9(4)	C^{253}	5343.7(17)	4639.1(15)	6988.1(18)	32.6(6)
C^{233}	1863.7(17)	2386.2(14)	4871.4(16)	25.7(5)	C^{254}	5851.8(17)	3726.5(15)	6811.7(16)	28.2(5)
C^{234}	2852.9(18)	2491.7(14)	4064.9(16)	27.1(5)	C^{255}	5268.0(16)	3008.4(14)	6627.4(14)	23.3(5)
C^{235}	3603.9(18)	3147.3(14)	4093.6(15)	26.3(5)	C^{256}	4191.9(16)	3208.9(14)	6616.9(14)	21.3(4)
C^{236}	3376.0(17)	3683.8(14)	4942.2(14)	22.5(4)	C^{1S}	5734(2)	4740.4(17)	10450(2)	45.8(7)
C^{241}	438.9(16)	4501.6(13)	7055.8(15)	21.1(4)	C^{2S}	5268(2)	5665.9(16)	10540.2(18)	40.5(6)
C^{242}	–510.3(17)	4260.4(14)	7869.2(17)	28.8(5)	C^{3S}	4532.6(18)	5922.3(16)	10090.8(17)	31.8(5)
C^{243}	–1618.2(18)	4478.2(16)	7922(2)	42.0(7)	C^{4S}	5081(2)	9028.2(15)	5110.3(16)	32.4(5)
C^{244}	–1800(2)	4952.7(17)	7166(2)	46.9(8)	C^{5S}	5986.2(19)	9556.5(16)	5025.6(16)	32.3(5)
C^{245}	–878(2)	5217.0(16)	6359(2)	40.1(7)	C^{6S}	5907.6(19)	10532.3(16)	4915.1(16)	33.1(5)
				II					
P^1	7872.1(6)	5408.6(7)	1340.8(3)	14.61(19)	C^{135}	5429(2)	7072(3)	235.4(10)	20.2(6)
O^1	4700.0(19)	2060(3)	1347.5(10)	51.5(7)	C^{136}	6282(2)	6195(3)	483.6(10)	17.9(6)
O^2	3346.1(18)	599(2)	959.6(9)	31.3(5)	C^{141}	7962(2)	3719(3)	1026.1(10)	15.3(6)
O^3	1699.9(19)	1450(3)	372.7(9)	40.2(6)	C^{142}	6990(2)	2866(3)	931.2(10)	18.5(6)
H^1	2360(30)	890(30)	649(14)	50	C^{143}	7039(2)	1572(3)	678.8(10)	19.3(6)
C^{111}	9150(2)	6420(3)	1318.8(10)	16.9(6)	C^{144}	8049(2)	1148(3)	518.7(10)	20.9(6)
C^{112}	10194(2)	6023(3)	1616.3(10)	19.4(6)	C^{145}	9015(2)	1982(3)	617.0(11)	22.1(6)
C^{113}	11160(2)	6825(3)	1594.9(11)	23.1(6)	C^{146}	8976(2)	3278(3)	873.2(10)	19.6(6)
C^{114}	11112(2)	8008(3)	1272.6(12)	24.5(7)	C^{211}	2171(3)	4072(4)	2548.5(12)	35.3(8)
C^{115}	10095(2)	8375(3)	966.4(12)	25.2(7)	C^{212}	1194(3)	3796(4)	2761.0(12)	38.7(9)
C^{116}	9110(2)	7594(3)	990.7(11)	21.2(6)	C^{213}	408(3)	2824(4)	2522.1(13)	36.9(8)
C^{121}	7604(2)	5195(3)	1999.1(10)	17.0(6)	C^{214}	588(3)	2152(3)	2073.1(13)	33.2(8)
C^{122}	8338(2)	5757(3)	2420.2(10)	20.1(6)	C^{215}	1563(3)	2430(3)	1863.6(13)	32.5(8)
C^{123}	8062(3)	5653(3)	2915.9(11)	24.5(7)	C^{216}	2359(3)	3384(4)	2104.3(12)	33.2(8)
C^{124}	7057(3)	5004(3)	2994.3(11)	24.9(7)	C^{311}	3097(3)	3070(3)	816.3(12)	33.9(8)
C^{125}	6325(3)	4439(3)	2577.1(11)	24.8(7)	C^{312}	3492(3)	4465(4)	927.1(12)	39.0(9)
C^{126}	6596(2)	4521(3)	2082.1(11)	21.4(6)	C^{313}	2838(3)	5640(3)	712.0(12)	31.2(7)
C^{131}	6681(2)	6399(3)	1006.6(10)	15.3(6)	C^{314}	1824(3)	5348(3)	394.0(12)	27.6(7)
C^{132}	6233(2)	7478(3)	1281.8(10)	19.0(6)	C^{315}	1471(3)	3976(4)	282.5(12)	32.7(8)
C^{133}	5385(2)	8360(3)	1029.3(11)	20.9(6)	C^{316}	2099(3)	2846(3)	490.4(13)	32.5(8)
C^{134}	4988(2)	8151(3)	508.5(11)	20.3(6)	C^{317}	3793(3)	1816(4)	1065.8(13)	38.0(8)

Table 4. (Contd.)

Atom	x	y	z	U_{eq}, Å^2	Atom	x	y	z	U_{eq}, Å^2
					III				
P^1	376(1)	2494(1)	7503(1)	17(1)	C^{19}	–1085(2)	1977(1)	6508(1)	19(1)
C^1	1951(2)	3616(1)	7091(1)	20(1)	C^{20}	–1082(2)	934(1)	6077(1)	21(1)
C^2	1901(2)	4041(1)	6127(1)	24(1)	C^{21}	–2321(2)	555(1)	5348(1)	25(1)
C^3	3194(2)	4888(1)	5834(1)	33(1)	C^{22}	–3540(2)	1210(1)	5058(1)	25(1)
C^4	4510(2)	5300(1)	6493(1)	32(1)	C^{23}	–3560(2)	2246(1)	5496(1)	24(1)
C^5	4560(2)	4881(1)	7454(1)	30(1)	C^{24}	–2335(2)	2633(1)	6221(1)	22(1)
C^6	3284(2)	4033(1)	7762(1)	24(1)	O^1	2578(2)	2205(1)	4462(1)	31(1)
C^7	1547(2)	1441(1)	7954(1)	19(1)	O^2	3875(1)	1668(1)	3131(1)	31(1)
C^8	2787(2)	1096(1)	7324(1)	24(1)	O^3	3859(2)	2009(1)	1369(1)	35(1)
C^9	3749(2)	295(1)	7658(1)	30(1)	O^4	2561(1)	3015(1)	313(1)	26(1)
C^{10}	3504(2)	–141(1)	8610(1)	31(1)	C^{25}	2637(2)	2077(1)	3553(1)	23(1)
C^{11}	2302(2)	213(1)	9238(1)	30(1)	C^{26}	2621(2)	2550(1)	1124(1)	22(1)
C^{12}	1310(2)	1004(1)	8915(1)	24(1)	C^{27}	1167(2)	2380(1)	2902(1)	19(1)
C^{13}	–989(2)	2958(1)	8427(1)	17(1)	C^{28}	1153(2)	2580(1)	1859(1)	18(1)
C^{14}	–2443(2)	2217(1)	8730(1)	20(1)	C^{29}	–356(2)	2844(1)	1414(1)	20(1)
C^{15}	–3646(2)	2585(1)	9346(1)	22(1)	C^{30}	–1842(2)	2888(1)	1954(1)	24(1)
C^{16}	–3417(2)	3693(1)	9654(1)	23(1)	C^{31}	–1832(2)	2688(1)	2973(1)	25(1)
C^{17}	–1989(2)	4428(1)	9358(1)	22(1)	C^{32}	–337(2)	2453(1)	3433(1)	23(1)
C^{18}	–764(2)	4066(1)	8741(1)	20(1)					
					XIV				
P^1	3735(1)	–322(1)	2037(1)	13(1)	O^4	–1200(1)	6737(1)	4499(1)	23(1)
S^1	–3509(1)	3517(1)	2517(1)	18(1)	C^{4A}	9173(2)	–1768(1)	2102(1)	20(1)
O^1	–2221(1)	2328(1)	2437(1)	21(1)	C^{4B}	1805(2)	3968(1)	581(1)	20(1)
C^{1D}	3107(2)	–1244(1)	1347(1)	15(1)	C^4	–3318(2)	6060(1)	4148(1)	21(1)
C^{1B}	3031(2)	1389(1)	1508(1)	15(1)	C^{4D}	2297(2)	–2660(1)	196(1)	20(1)
C^1	–1194(2)	4255(1)	3138(1)	16(1)	C^{4C}	2037(2)	–906(2)	5200(1)	26(1)
C^{1C}	2921(2)	–523(1)	3256(1)	16(1)	O^5	2014(1)	3959(1)	3049(1)	22(1)
C^{1A}	5881(2)	–868(1)	2024(1)	16(1)	C^{5B}	3444(2)	3390(1)	543(1)	20(1)
O^2	–4920(1)	3233(1)	3081(1)	30(1)	C^{5A}	8426(2)	–2299(1)	1568(1)	20(1)
C^2	–2813(2)	4402(1)	3184(1)	17(1)	C^{5D}	1877(2)	–1293(1)	–39(1)	19(1)
C^{2D}	3523(2)	–2626(1)	1583(1)	17(1)	C^5	–1688(2)	5953(1)	4068(1)	19(1)
C^{2A}	6635(2)	–320(1)	2552(1)	20(1)	C^{5C}	2090(2)	–1858(1)	4687(1)	23(1)
C^{2B}	1381(2)	1980(1)	1560(1)	17(1)	O^6	1666(1)	5655(1)	3779(1)	22(1)
C^{2C}	2842(2)	449(1)	3770(1)	22(1)	C^6	–608(2)	5035(1)	3567(1)	17(1)
O^3	–3878(1)	4398(1)	1606(1)	30(1)	C^{6C}	2530(2)	–1675(1)	3712(1)	18(1)
C^3	–3879(2)	5296(1)	3702(1)	19(1)	C^{6D}	2275(2)	–579(1)	534(1)	17(1)
C^{3B}	770(2)	3272(1)	1091(1)	18(1)	C^{6A}	6781(2)	–1847(1)	1521(1)	18(1)
C^{3D}	3103(2)	–3324(1)	1013(1)	20(1)	C^{6B}	4067(2)	2094(1)	1006(1)	18(1)
C^{3A}	8283(2)	–774(1)	2582(1)	21(1)	C^7	1127(2)	4909(1)	3482(1)	18(1)
C^{3C}	2395(2)	254(2)	4741(1)	27(1)					

Table 5. Principal interatomic distances (*d*) and bond angles (ω) in structures **I–III** and **XIV**

Bond, Å		Angle, deg	
		I	
$P^1–C^{111}$	1.854(2)	$C^{121}P^1C^{111}$	120.53(8)
$P^1–C^{121}$	1.848(2)	$C^{141}P^1C^{111}$	118.73(9)
$P^1–C^{131}$	1.985(2)	$C^{141}P^1C^{121}$	120.73(9)
$P^1–C^{141}$	1.840(2)	$C^{131}P^1C^{151}$	178.3(8)
$P^1–C^{151}$	1.987(2)	$C^{211}P^2C^{221}$	119.67(9)
$P^2–C^{211}$	1.840(2)	$C^{211}P^2C^{231}$	120.24(9)
$P^2–C^{221}$	1.846(2)	$C^{221}P^2C^{231}$	120.09(9)
$P^2–C^{231}$	1.854(2)	$C^{251}P^2C^{241}$	178.45(9)
$P^2–C^{241}$	1.980(2)		
$P^2–C^{251}$	1.975(2)		
		II	
$P^1–C^{111}$	1.798(3)	$C^{111}P^1C^{121}$	111.22(12)
$P^1–C^{121}$	1.809(3)	$C^{111}P^1C^{131}$	108.20(12)
$P^1–C^{131}$	1.801(3)	$C^{111}P^1C^{141}$	110.07(12)
$P^1–C^{141}$	1.800(3)	$C^{131}P^1C^{121}$	106.21(12)
$O^1–C^{317}$	1.228(4)	$C^{141}P^1C^{121}$	111.60(12)
$O^2–C^{317}$	1.274(4)	$C^{141}P^1C^{131}$	109.39(12)
$O^3–C^{316}$	1.414(4)	$C^{112}C^{111}P^1$	121.0(2)
		III	
$P^1–C^7$	1.786(1)	$C^7P^1C^1$	106.46(7)
$P^1–C^1$	1.790(1)	$C^7P^1C^{13}$	113.03(6)
$P^1–C^{13}$	1.791(1)	$C^1P^1C^{13}$	110.89(6)
$P^1–C^{19}$	1.795(1)	$C^7P^1C^{19}$	111.18(6)
$O^1–C^{25}$	1.228(2)	$C^1P^1C^{19}$	111.38(6)
$O^2–C^{25}$	1.292(2)	$C^{13}P^1C^{19}$	104.01(6)
$O^2–H^{2'}$	1.16(3)	$C^{25}O^2H^{2'}$	112.4(14)
$O^3–C^{26}$	1.292(2)	$C^{26}O^3H^{2'}$	112.7(13)
$O^3–H^{2'}$	1.23(3)	$O^1C^{25}O^2$	122.38(14)
$O^4–C^{26}$	1.227(2)	$O^1C^{25}C^{27}$	118.79(13)
		IV	
$P^1–C^{1B}$	1.789(1)	$C^{1B}P^1C^{1C}$	107.54(6)
$P^1–C^{1C}$	1.796(1)	$C^{1B}P^1C^{1D}$	107.86(6)
$P^1–C^{1D}$	1.800(1)	$C^{1C}P^1C^{1D}$	112.79(6)
$P^1–C^{1A}$	1.801(1)	$C^{1B}P^1C^{1A}$	111.30(6)
$S^1–O^1$	1.450(1)	$C^{1C}P^1C^{1A}$	108.71(6)
$S^1–O^3$	1.451(1)	$C^{1D}P^1C^{1A}$	108.66(6)
$S^1–O^2$	1.468(1)	$O^1S^1O^3$	113.30(6)
$S^1–C^2$	1.778(1)	$O^1S^1O^2$	112.21(6)
$O^4–C^5$	1.355(2)	$O^6C^7O^5$	123.57(12)
$O^5–C^7$	1.314(2)	$O^6C^7C^6$	122.16(12)

Pentaphenylphosphorus solvate with benzene (**I**) was prepared by recrystallization of pentaphenylphosphorus [1] from benzene. The syntheses of tetraphenylhosphonium carboxylates and sulfonates were carried out by conventional procedures.

Tetraphenylphosphonium salicylate benzene solvate (II). A mixture of 0.17 g of salicylic acid, 0.55 g of **I,** and 5 ml of benzene in a glass ampule was heated at 80°C for 10 min. The solvent was slowly evaporated at room temperature to obtain 0.56 g (83%) of compound **II** as colorless crystals, mp 142°C.

Tetraphenylphosphonium benzenesulfonate hydrate (XII). Sulfur trioxide obtained from 0.25 g of sulfur was passed through a solution of 0.55 g (1.20 mmol) of **I** in 20 ml of benzene for 5 min. The reaction mixture became turbid and crystals formed. The solvent was removed, and the residue was recrystallized from water to obtain 0.42 g (81%) of compound **XII**, mp 176°C.

Tetraphenylphosphonium sulfosalicylate (XIV). A mixture of 0.22 g (1.01 mmol) of sulfosalicylic acid, 0.46 g (1.01 mmol) of **I,** and 15 ml of benzene was heated for 10 min at 80°C. The solvent was removed, and the residue was recrystallized from water to obtain 0.41 g (67%) of compound **XIV** as colorless crystals, mp 222°C.

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