

X-ray structures of the tris(2,4-xylyl)phosphane and its trisulfonated derivative: Molecular architecture of a water-soluble sulfonated phosphane with propeller chirality

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Received 9 September 2006; received in revised form 17 October 2006; accepted 17 October 2006

Available online 24 October 2006

Professor Gyula Pályi on the occasion of his 70th birthday.

Abstract

The structure of tris(2,4-xylyl)phosphane (**1**) is reported and supramolecular assembly of gua^+ salt of tris(2,4-dimethyl-5-sulfonatophenyl)phosphane co-crystal with guanidine chloride (**2**) is analyzed in detail. Weaving hydrogen bond ribbons with polar and apolar stabilizing pillars as well as stacking interaction of phenyl rings resulting sixfold phenyl embraces interpenetrating with the polar networks were found. Both compounds are racemate, show propeller chirality and **2** crystallizes in non-centrosymmetric space group (C_3 symmetry) with the *ortho*-methyl groups outside of the molecular cone. According to the DFT calculations on the anion of **2**, the high barrier of concerted ring rotation opens the possibility of resolving the enantiomers through hydrogen bonds to chiral donors.
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Keywords: Sulfonated phosphane; Propeller chirality; X-ray analysis; Guanidium; Supramolecular chemistry

1. Introduction

Aqueous organometallic catalysis (AOC) is one of the most important areas of green chemistry. Although usually ligand tailoring is a somewhat more complex task than in the case of non-aqueous homogenous catalytic systems, the chance to recover and reuse the catalyst is frequently considered worth of the synthetic efforts. This fact is confirmed by the million tonscale industrial applications of AOC [1].

The monosulfonated and trisulfonated derivatives of triphenylphosphanes (TPPMS = (3-diphenylphosphanyl)-

benzenesulfonic acid, TPPTS = 3,3',3''phosphanetriyltrisbenzenesulfonic acid) are probably the most commonly used hydrophilic ligands in both the industry and the academic research. Over the last few years we have introduced a synthetic approach, which provides easy access to a wide range of sulfonated triphenylphosphane derivatives with tuneable steric bulk, electronic properties and hydrophilic character [2]. One of the developed hydrophilic ligands is the trisulfonated derivative of tris(2,4-xylyl)phosphane (TXPTS), which has provided very efficient catalysts for aqueous-phase Heck- and Suzuki-coupling reactions [3], and has quickly become commercially available. Using rhodium and iridium complexes of this ligand as catalysts we have observed drastic steric effects in the course of biphasic hydrogenation of aldehydes [4]. In order to explain the

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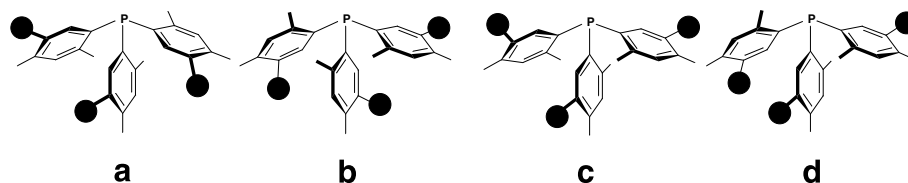


Fig. 3. Possible diastereomeric arrangements of TXPTS.

Table 1

Natural bond orbital (NBO) properties and Tolman's cone angles of triphenylphosphane (TPP), tris(3-sulphonatophenyl)phosphane (TPPTS), tris(2,4-xylyl)phosphane (TXP) and tris(2,4-dimethyl-5-sulphonatophenyl)phosphane (TXPTS)

Ligand	Q_P^a	NEC (valence) ^b	NHO _{P,lp} ^c	WBI ^d	θ (°) ^e
TPP	0.881	(3s) ^{1.39} (3p) ^{2.69}	sp ^{1.00}	0.916	165
TPPTS ^{f,g}	0.873	(3s) ^{1.40} (3p) ^{2.69}	sp ^{0.98}	0.916	184
TPPTS ^{f,h}	0.856	(3s) ^{1.40} (3p) ^{2.71}	sp ^{1.00}	0.912	
TXP (1)	0.866	(3s) ^{1.37} (3p) ^{2.73}	sp ^{1.06}	0.924	210
TXPTS (2) ^{f,g}	0.846	(3s) ^{1.33} (3p) ^{2.79}	sp ^{1.27}	0.944	192
TXPTS (2) ^{f,h}	0.858	(3s) ^{1.33} (3p) ^{2.78}	sp ^{1.25}	0.943	

^a NBO charge on the phosphorus atom.

^b Natural electronic configuration on phosphorus.

^c Natural bond orbital hybridization on the phosphorus lone pair.

^d Wiberg bond indices of the P–C_{ipso} bonds.

^e Determined on the DFT-optimized structures.

^f Anionic forms of TPPTS and TXPTS.

^g In gas phase.

^h PCM calculation in water phase.

ment the phosphorus must be severely flattened to permit bonding. In order to attain this geometry, the hybridization of the phosphorus must change. Significant deviation from normal pyramidal configuration results in a change of geometry around phosphorus. While the hybridization at the “normal” phosphane sp³ in the special kind of propellers, one would expect, that the flattening of the phosphorus should result in a change to approximately sp² hybridization. However this assumption is not entirely supported by quantum chemical calculations (Table 1).

Some electronic properties characteristic for coordination to transition metals were determined using the natural bond orbital method. The natural charge (Q_P) describes the charge on the phosphorus atom obtained by natural population analysis i.e. the nuclear charge minus the total electron population. The natural electron configuration (NEC), which is evaluated by summing NAO occupancies over subshells, gives the effective valence electron configuration for the phosphorus atom. The lone pair of the phosphorus is composed entirely of a single normalized natural hybrid orbital (NHO).

While the partial charges of the substituted triphenylphosphanes show little difference, the P–C_{ipso} bond strength slightly increases when increasing the cone angle. Interestingly the natural hybridization of phosphorus is somewhat closer to sp³ in the much more flattened TXP than in triphenylphosphane. The bulky substituents in TXPTS result in even stronger p-character of both the phosphorus atom and the lone pair of phosphorus.

Our preliminary density functional calculations with respect to TXP and TXPTS reveal that the rotation of aryl-rings create a tightly coupled system, i.e. due to bulky substituents displacing one of the rings around the P–C_{ipso} axis results in a rotary motion of the neighboring ring which forces to rotate the third ring.

Both in TXP and TXPTS the concerted rotation of aryl rings in one direction takes place through a transition state with rings perpendicular to the C_{ipso}–C_{ipso}–C_{ipso} plane. The free energy barrier of rotation is significantly higher at TXPTS, namely 27.7 kcal/mol, indicating this process only realistic at very harsh reaction condition. However, the concerted rotation in **1** needs considerably lower free energy of activation (11.1 kcal/mol) due to the lack of powerful repulsion between sulfonic groups bearing threefold negative charge in the molecule.

Also the steric and electronic repulsion is responsible for the significantly higher barrier of rotation in TXPTS, when one of the aryl groups constrains the concerted rotation of one of the rings while the third ring rotates in the opposite direction. This intramolecular rearrangement breaking the chiral C₃-symmetry needs 14.4 kcal/mol free energy of acti-

Table 2

Data of hydrogen bonds in structure of **2** (alphabetized atom labels indicate symmetry generated atoms)

D–H...A	H...A (Å)	D...A (Å)	D–H...A (°)
N11–H11A...O23a	2.23	2.967(13)	143.6
N11–H11B...O12b	2.08	2.878(14)	153.3
N12–H12A...O23a	2.04	2.827(15)	150.8
N12–H12B...Cl1c	2.51	3.232(15)	141.8
N12–H12B...Cl1	2.76	3.468(14)	140.7
N13–H13A...O21d	2.03	2.881(17)	172.4
N13–H13B...Cl1	2.17	3.014(16)	165.3
N21–H21A...O12e	2.27	3.087(13)	158.2
N21–N21B...O13f	2.17	2.968(13)	154.3
N31–H31A...O11g	1.96	2.71(2)	145.3
N31–H31B...Cl1h	2.18	2.98(2)	156.2
N32–H32A...O22	2.29	3.004(16)	140.8
N32–H32B...O13i	2.08	2.879(15)	154.0
N33–H33A...Cl1h	2.29	3.11(3)	158.4
N33–H33A...Cl1k	2.97	3.66(3)	138.4
N41–H41A...O21b	2.29	3.061(13)	149.0
N41–H41A...O12l	2.49	3.089(12)	127.1
N41–H41B...O22m	2.21	3.057(12)	168.4
N51–H51A...O22n	2.49	3.27(2)	150.0
N51–H51B...N32b	2.39	2.97(3)	125.1

Symmetry codes: (a) 1 – y, x – y, z; (b) 1 – x, 1 – x + y, z – 1/2; (c) 1 – y, 1 + x – y, z; (d) x – 1, y, z; (e) x, y, z – 1; (f) 1 – y, x – y, z – 1; (g) x – y, – y, z – 1/2; (h) 1 – x, – x + y, z – 1/2; (i) 1 + y, x, z – 1/2; (k) 1 + x – y, 1 – y, z – 1/2; (l) x – 1, y, z – 1; (m) x – y – 1, – y, z – 1/2; (n) y, x, z – 1/2.

vation in aqueous phase for TXPTS, whereas the free energy barrier is 7.1 kcal/mol for TXP.

Most importantly, the calculations support the idea that the chiral C_3 conformation of TXPTS, which has been found in solid state, might be stable in solution *at room temperature* as well, and that the resolution of the enantiomers should be possible.

2.2. Supramolecular architecture of TXPTS guanidinium salt

TXPTS shows very complicated supramolecular architecture in the solid phase. Search of the Cambridge Structural Database [8] (CSD, Version 5.27, May 2006) had shown that by 2006 there were 34 structures of sulfonated

phosphanes or their complexes in the CSD and 11 of them were gua^+ salts. Five years ago the corresponding values were 12 and zero, respectively. In these early cases often disordered structures were found. This class of compounds tends to crystallize together with solvent water molecules and are sensitive to dehydration which results in the collapse of the crystal structure. Recently we managed to determine [9] the structure of cesium salt of (4-diphenylphosphino)benzenesulfonic acid and it contained water molecule in the lattice, too. A real breakthrough could be reached by applying the Ward [10]–Kathó [11] approach to utilize strong hydrogen donor cations especially gua^+ to stabilize the crystal lattice of sulfonated phosphanes and five new structures of various sulfonated phosphanes have been published. By this method we managed to crystallize **2**, too. The lattice in each case was stabilized by

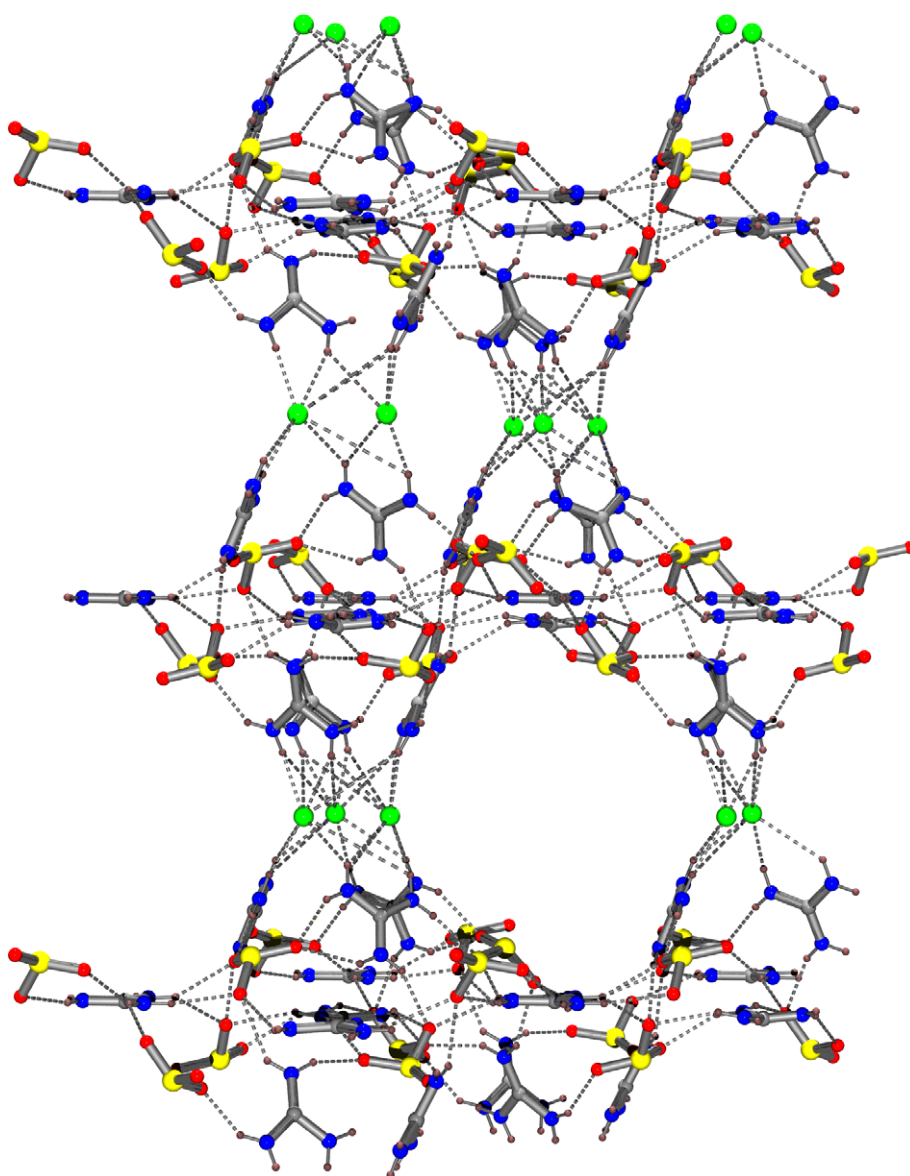


Fig. 4. Hydrogen bond network in structure **2**, view normal to (001). Atoms not participating in hydrogen bond web are omitted for clarity.

weaving ribbons and van der Waals interactions. Later other authors came to similar conclusion [12] by examining redetermined structures. A detailed database study [13] on the motifs of hydrogen bonds of organic sulfonates with various hydrogen donors was published.

Analysis of 3D network of strong hydrogen bonds (Table 2 and Figs. 4 and 5) helps to understand the role of these two kinds of gua^+ ions in building up the crystal.

For such networks the accepted graph set notation was developed [14] by Etter et al. In the case of $-\text{SO}_3^-$ - gua^+ networks the usually observed patterns are R_2^2 (8) and R_6^3 (12) rings. In such a basically 2D structure [10] weaving hydrogen bond sheets or ribbons are formed with apolar pillars between the sheets. Chains as well as R_2^2 (8), R_2^1 (6), R_3^3 (12) and R_4^3 (13) ring motifs are present in structure 2 (Fig. 5). Donor and acceptor atoms get close to each other because of restraints from the sigma bond network, too. The D–H...A angle is 125° and 127° for N51–H51B...N32 and N41–H41A...O12 bridges, respectively, and the distance of two neighbouring chloride ions is only 2.81 Å. The chloride ions form polar pillars between $-\text{SO}_3^-$ - gua^+ weaving ribbons. The base of this chloride column and the pillar-cap (Fig. 4) is formed by gua^+ ions which are in general position in the lattice and they are tilted by 70° to the main plane of gua^+ ions of special position i.e. to the $-\text{SO}_3^-$ - gua^+ ribbon. Bifurcated R_2^1 (6) pattern is formed when the chloride ion makes hydrogen bonds of two NH_2 groups of the same gua^+ ion in vertical direction. The packing of 2 shows the superposition of a polar (Fig. 4) and an apolar (Fig. 6) web as stacking interaction between phenyl rings which causes orientation of

two neighboring phosphanes in the lattice. Further studies are in progress to determine the structure of co-crystals with other gua^+ salts (nitrate, carbonate) as well as with chiral additives to resolve the enantiomers.

Sixfold phenyl embraces i.e. concerted interaction of phenyl rings are interesting supramolecular motifs often found in XPh_n ($n = 2-4$) phosphane complexes. Database survey had discussed their occurrence [15] in various classes

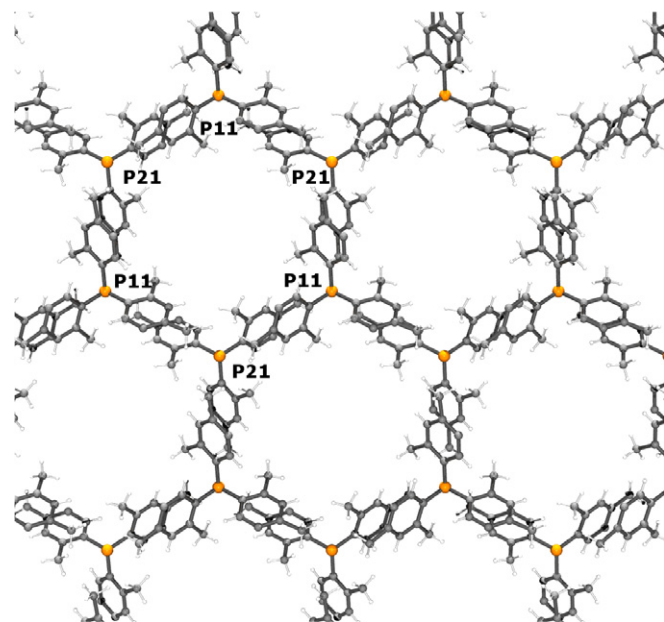


Fig. 6. Sixfold phenyl embraces in 2. The holes are occupied by gua^+ Cl^- pillars, shown in Fig. 4.

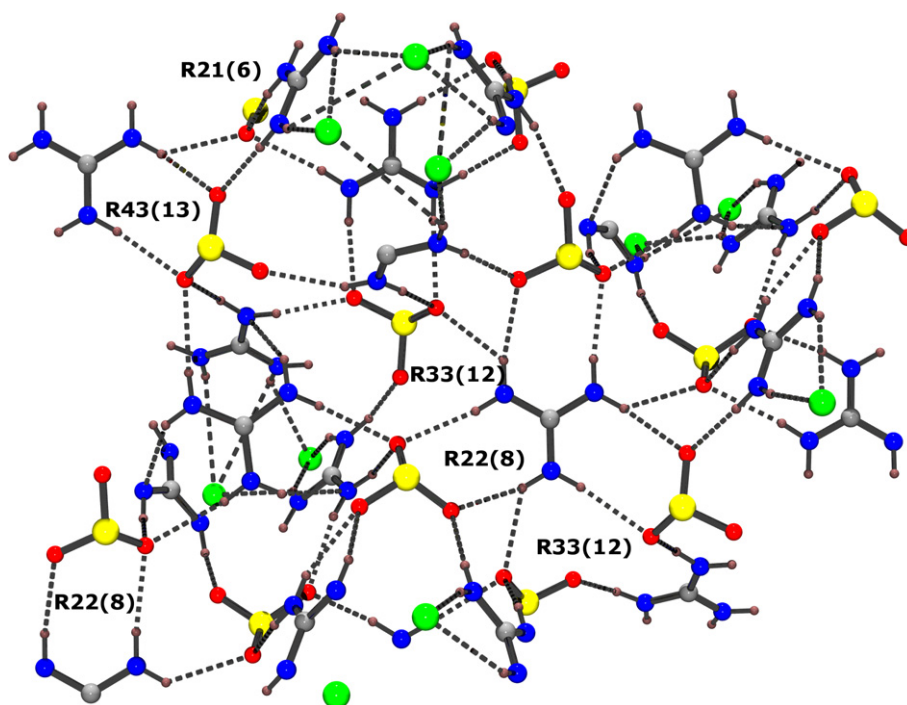


Fig. 5. Graph set analysis of hydrogen bond network in 2.

of compounds. In structure **2** P–P distance in the unit cell is 7.98 Å while phosphorus atoms of neighboring unit cells are significantly further away from each other, their distances are in the range of 12.77–16.27 Å. The π – π interactions are mirrored (Fig. 6) by the trigonal symmetry of the crystal lattice. Planes of contacting phenyl rings are almost parallel (7°), their distance is approximately 6 Å, while P11–P11–P11–P21 torsion angle in the hexagon is 12° . Honeycomb phenyl embraces can be found in structure **1**, too. There the P–P distances at the edges of the hexagon are 25 Å and in the middle of the hexagon another apolar phosphane pillar was found.

3. Summary

Crystal structure of **2** comprises extensive three dimensional hydrogen bond network with gua^+ ions and this web together with the stacking edge-to-edge hexagonal orientation of phenyl rings make highly ordered structure with both polar (Cl^- – gua^+) and apolar (phosphane) pillars between hydrogen bond ribbons forming interpenetrating nets. The molecule has a propeller symmetry crystallizing in non-centrosymmetric space group while in the hydrophobic analogous structure of **1** the mirror imaged propellers occupy alternating positions related by inversion. Interconversion of the C_3 -symmetry enantiomers of **2** requires 14.4 kcal/mol–27.7 kcal/mol free energy of activation depending on the suggested mechanism of rotation. The high energy barrier makes it plausible to try to isolate the compound in an optically pure form.

4. Experimental

4.1. Materials and general information

TXP [16] was prepared according to the literature. The analyzed crystals were obtained recrystallizing the compound from hot ethanol. TXPTS^{2a,b} and its guanidinium⁴ salt were prepared as described previously.

5. Computational details

Full geometry optimizations have been performed at the density functional level of theory without any symmetry constraints using the GAUSSIAN 03 program [17] and the 6-31G* basis set [18]. The stationary points were characterized by frequency calculations in order to verify that the minima have zero imaginary frequency. For all the calculations the gradient-corrected exchange functional developed by Perdew, Burke and Ernzerhof was utilised in combination with a correlation functional also developed by the same authors [19] and denoted as PBE. Solvation effects were estimated using the Polarizable Continuum Model (PCM) [20] with the dielectric constant $\epsilon = 78.4$ for water. In order to determine the Tolman's cone angles [21] the STERIC program [22] was used. Natu-

ral bond orbital (NBO) analyses were carried out on the stationary points at the same level of theory as used for geometry optimizations utilizing the NBO 3.1 program [23] as implemented in GAUSSIAN. The DFT calculations were based on the anionic forms of TPPTS and TXPTS, respectively.

6. Supplementary material

CCDC 618807 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Support from Hungarian National Science Foundation (OTKA Grants No. T046825, T043365 and OTKA F046959) is gratefully acknowledged. Use of SPring-8 and the theoretical calculation was supported by Japan Synchrotron Radiation Institute (JASRI/SPring-8) under Power User Priority Program (2005B6888-PU1-np, 2006A0095) and Supercomputer Center of the Hungarian National Information Infrastructure Development (NIIF) Program, respectively.

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- [5] Crystal data for **1**. A small colorless needle crystal ($0.06 \times 0.03 \times 0.03$ mm) was fixed to a glass fibre. Empirical formula: $\text{C}_{24}\text{H}_{27}\text{P}$, $M = 346.43$, crystal system: hexagonal, $a = 24.9150(8)$ Å, $c = 5.6590(8)$ Å, $V = 3042.23(15)$ Å³, $Z = 6$, space group: $P63/m$ (No. 176). Data were collected at 203(2) K at SPring-8, $\lambda = 0.5579$ Å, low temperature vacuum IP camera, $\theta_{\text{max}} = 23.48^\circ$, 3283 measured reflections of which 1953 were unique with $I > 2.00\sigma(I)$. $R(F) = 0.1057$ and $wR(F^2) = 0.2233$ for 3283 reflections,

- 191 parameters, goodness-of-fit: 1.386, residual electron density: 0.386/–0.427 e/Å⁻³.
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