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Crystal and molecular structure of 3-methyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate salts with *o*-arsanilic and perchloric acids

Łukasz Wojtas*, Piotr Milart, Katarzyna Stadnicka

Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

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Abstract

The crystal structure for two salts of 3-methyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (**1**) with *o*-arsanilic (2-aminobenzene-arsonic) and perchloric acids were determined by X-ray diffraction. **1** was synthesized in order to break the symmetry of 4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (**2**) and to overcome a tendency of the molecule for centrosymmetrical arrangement in a crystalline state. The structure of $\mathbf{1}\cdot HClO_4$ (space group Pbca) is governed by an antiparallel arrangement of pyridinium cations, connected to perchlorate anions through hydrogen bonds of O–H···O type. The crystals of $\mathbf{1}\cdot H_2NC_6H_4AsO_3H_2\cdot H_2O$ belong to tetragonal space group $I\bar{4}$. Due to strong O–H···O$^-$ and moderate N–H···O$^-$ interactions, hydrogen *o*-arsaniliate counterions form aggregates to which the cations of **1** are connected via O–H···O=As hydrogen bonds. The anionic aggregates are linked together by the crystallization water molecules through the system of hydrogen bonds.

The comparison of the 1-(4-hydroxy-2-methylphenyl)-2,4,6-triphenylpyridinium hydrogen *o*-arsanilate and perchlorate structures reveals the importance of choosing the appropriate acids in order to obtain desired structure properties.

Keywords: Pyridinium betaine dye; o-Arsanilic acid; Perchloric acid; Crystal engineering; Crystal structure; Intermolecular interactions

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1. Introduction

An application of crystals in non-linear optics (e.g. SHG) demands non-centrosymmetric, polar solids. Among many of the investigated compounds the push–pull chromophore systems were found to be important for NLO properties [1]. The studied compound 3-methyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (**1**), a methyl derivative of 4-(2,4,6-triphenylpyridinium-1-yl)-phenolate (**2**), Scheme 1, can be considered as such a push-pull system. **2** shows substantial negative solvatochromic effect [2] but unfortunately it has tendency to form antiparallel dipole–dipole arrangements and subsequently its salts crystallize in centrosymmetrical space groups [3]. Because the non-centrosymmetric crystals with push–pull chromophores could be utilized as NLO materials, the modification of **2** by introducing the methyl group to the phenolate ring was designed to break the symmetry of **2** without loosing its solvatochromic properties.

o-Arsanilic acid was used to build the stable hydrogen-bond network, to which betaine dye cations could be linked to. It was expected that hydrogen *o*-arsanilate anions would prevent the betaine dye cations to form an antiparallel arrangement observed in the salt of **1** with perchloric acid. The strategy appeared to be successful and let us to obtain non-centrosymmetric crystals ($I\bar{4}$) potentially useful in NLO application.

In the present paper the structures of 1-(4-hydroxy-2-methylphenyl)-2,4,6-triphenyl-pyridinium hydrogen *o*-arsanilate ($\mathbf{1}\cdot H_2NC_6H_4AsO_3H_2\cdot H_2O$) and 1-(4-hydroxy-2-methylphenyl)-2,4,6-triphenylpyridinium perchlorate ($\mathbf{1}\cdot HClO_4$) are analyzed, and the utilization of 1-(4-hydroxy-2-methylphenyl)-2,4,6-triphenylpyridinium cation in designing of NLO materials was discussed.

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* Corresponding author. Tel.: +48 12 6632059; fax: +48 12 6340515.
E-mail address: wojtas@chemia.uj.edu.pl (Ł. Wojtas).

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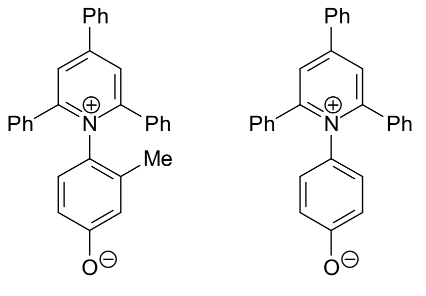

1 **2**

Scheme 1.

2. Experimental

2.1. Materials and methods

The pale yellow crystals of $\mathbf{1}\cdot H_2NC_6H_4AsO_3H_2\cdot H_2O$ (Mp. 204–206 °C) and the colourless crystals of $\mathbf{1}\cdot HClO_4$ (Mp. 300–301 °C), suitable for X-ray analysis, were grown from water and acetonitrile solutions, respectively, by slow evaporation of the mixture containing 3-methyl-4-(2,4,6-triphenylpyridinium-1-yl)-phenolate and the appropriate acid in molar ratio 1:1.

2.1.1. 1-(4-Hydroxy-2-methylphenyl)-2,4,6-triphenylpyridinium perchlorate

2,4,6-Triphenylpyrylium perchlorate (1.0 g, 2.5 mmol) was suspended in ethanol (15 cm^3). 4-Amino-3-methylphenol (0.62 g, 5.0 mmol) was added and the mixture was refluxed for 2 h with constant stirring. The precipitated colourless solid was collected by filtration and purified by re-crystallization from ethanol (ca. 60 cm^3) to afford 1.19 g (94%) of pyridinium salt. Mp 300–301 °C.

^1H NMR([D_6]DMSO/TMS); δ (ppm): 9.78 (s, 1H, OH), 8.66 (s, 2H, pyridinium-H), 8.35 (d, 2H, $J=8.0$ Hz, 2-and 6-H of aromatic ring 4), 7.64–7.70 (m, 3H, 3-, 4-and 5-H of

Table 1
Crystal data and structure refinement conditions for the salts of **1**

Identification code	Hydrogen *o*-arsanilate	Perchlorate (RT)	Perchlorate (LT)
Crystal data			
Chemical formula	$C_{30}H_{24}NO^+$, $C_6H_7NAsO_3^-$, H_2O	$C_{30}H_{24}NO^+$, ClO_4^-	$C_{30}H_{24}NO^+$, ClO_4^-
Mr	645.75	513.95	513.95
Temperature (K)	293(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Tetragonal, $I\bar{4}$	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*
Unit cell dimensions (Å, °)	$a=20.9886(4)$, $c=15.0478$ (5)	$a=16.4057(3)$, $b=17.3811(3)$, $c=18.1089$	$a=16.1333(3)$, $b=17.2841(3)$, $c=17.9208(3)$
V ($Å^3$)	6629.2(3)	5163.7(2)	4997.2(2)
Z, Dx (mg/m^3)	8, 1.294	8, 1.322	8, 1.366
μ (mm^{-1})	1.068	0.189	0.195
$F(000)$	2669	2144	2144
Crystal size (mm)	$0.25\times0.12\times0.12$	$0.57\times0.30\times0.07$	$0.57\times0.30\times0.07$
Crystal form, colour	Prisms, pale yellow	Plates, colourless	Plates, colourless
θ range (°)	3.04–25.01[a] (27.45)	2.57–27.50	2.60–31.02
Data collection			
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	ϕ scans$(\kappa=0)+\omega$ scans	ϕ scans$(\kappa=0)+\omega$ scans	ϕ scans$(\kappa=0)+\omega$ scans
Limiting indices	$0\le h\le 24$, $-17\le k\le 17$, $-17\le l\le 17$	$0\le h\le 21, 0\le k\le 22, -23\le l\le 23$	$0\le h\le 23, 0\le k\le 25, -25\le l\le 25$
Reflections collected, unique, R(int)	14494, 5806[a] (7536, 0.0595)	11181, 5914, 0.0390	15875, 7942, 0.0485
Reflections observed [$I>2\sigma(I)$]	5178	3895	5397
Completeness (%) to θ_{max}	99.3[a]	99.7	99.6
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.7760, 0.8825	0.8999, 0.9869	0.8968, 0.9865
Refinement			
Refinement method	On F^2	On F^2	On F^2
Data/restraints/parameters	5806/1/414	5914/2/346	7942/0/342
Goodness-of-fit parameter	$S=1.164$	1.054	1.025
Final R indices [$I>2\sigma(I)$]	$R1=0.0605$, $wR2=0.1112$	$R1=0.0696$, $wR2=0.1644$	$R1=0.0518$, $wR2=0.1193$
R indices (all data)	$R1=0.0746$, $wR2=0.1198$	$R1=0.1150$, $wR2=0.1893$	$R1=0.0890$, $wR2=0.1349$
Weighting scheme w: A, B	0.0619, 2.7630	0.0739, 4.5806	0.0566, 2.5100
Absolute structure parameter	0.003(14)	–	–
Extinction method, coefficient	SHELXL, 0.0042(5)	–	–
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($eÅ^{-3}$)	0.545, −0.270	0.563, −0.456	0.362, −0.670

$w=1/[\sigma^2(Fo^2)+(AP)^2+BP]$ where $P=(Fo^2+2Fc^2)/3$.

[a] Theta range diminished from 27.45° (7536 unique reflections) to 25.01° (5806 reflections) because of relatively high value of $K=\mathrm{Mean}(Fo^2)/\mathrm{Mean}(Fc^2)$ [7].