Salts of 4-(2,4,6-Triphenyl-1-pyridinio)phenolate with *p*-Toluenesulfonic Acid in Molar Ratio 1:1 and 2:1 − Crystal and Molecular Structure

Piotr Milart*[a] and Katarzyna Stadnicka[a]

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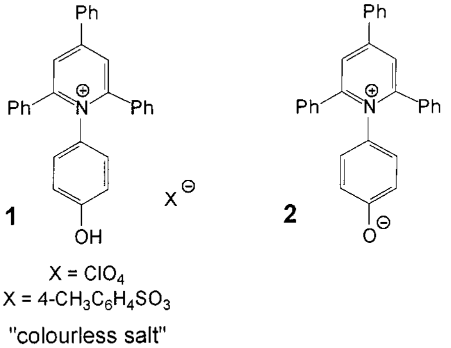
Two new salts of 4-(2,4,6-Triphenyl-1-pyridinio)phenolate with *p*-toluenesulfonic acid in molar ratio 2:1 ("red salt") and 1:1 ("colourless salt") were synthesised. The solvatochromic effect, ^{1}H NMR spectra and crystal structure of the salts were investigated. In the crystalline "red salt" two molecules of the betaine dye are joined by a strong, asymmetric hydrogen bond contrary to previous suggestions. Similar behaviour is observed in polar solvents, but the hydrogen bond is symmetric. In solvents of low polarity an additional intermolecular charge-transfer interaction is possible.

Introduction

In 1935 Dilthey and Dierichs[1] described the condensation of 2,4,6-triphenylpyrylium perchlorate with *p*-aminophenol leading to a colourless product 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium perchlorate (**1**; X = ClO_4). In the presence of a strong base, for example potassium methoxide used in excess, the red betaine dye 4-(2,4,6-triphenyl-1-pyridinio)phenolate (**2**) is obtained (Scheme 1).



Scheme 1

Compound **2** shows a very strong negative solvatochromism [Dimroth−Reichardt betaine dye no. 1, $E_T(1)$].[2] According to Dilthey and Dierichs, **2** crystallises from aqueous solutions as a dodecahydrate but it loses water of crystallisation very rapidly, changing its colour to dark blue. Schneider et al.[3] claimed that the betaine dye **2** forms a hexahydrate. Dilthey and Dierichs observed that when a small amount of potassium methoxide is added to the methanolic solution of the pyridinium salt **1**, another red product, different from betaine dye **2**, is obtained. Elemental analysis has shown that the new red product contains two molecules of **2** and one molecule of perchloric acid. The same compound can be obtained from the mixture of equimolar solutions of pyridinium salt **1** and betaine **2**. Similarly, "red salts" with other anions, like nitrate, picrate, chloride, bromide and iodide are formed and crystallise as hydrates containing between one and four molecules of H_2O.[1] Addition of a strong base to the solution of the "red salt" gives betaine **2**, whereas addition of an acid gives pyridinium salts of type **1**. The authors also speculated about the possible structure of the "red salt". They suggested that a covalent bond is formed between the pyridinium ring of the betaine molecule and the pyridinium ring of the salt, with the simultaneous opening of the betaine pyridinium ring and loss of aromaticity of the pyridinium ring of the salt (Figure 1).

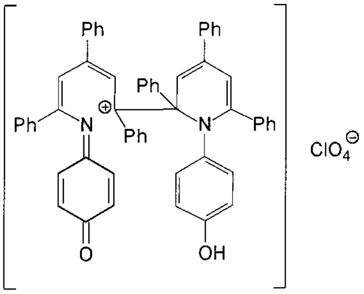


Figure 1. The structure of the red perchlorate as suggested by Dilthey and Dierichs in 1935[1]

Recently, Neiland et al.[4] reported solvatochromic and acid-base properties of 4-(1-pyridinio)pyrocatecholate and its salts. In the case of perchlorate, they were able to isolate a complex compound containing one molecule of the pyridinium salt and one molecule of the betaine dye. The character of its IR spectrum in the range of 3500−3000 cm^{-1} indicated, that the molecules are joined together with an −O−H···O− hydrogen bond.

The aim of our work was to find out the real structure of the "red salt" in the solid state, to discuss its molecular structure in solution and to compare some properties of the appropriate colourless and red salts. For that purpose we synthesised a new "red salt" **3** with *p*-toluenesulfonic acid by treating equimolar amounts of 1-(4-hydroxyphenyl)-

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[a] Faculty of Chemistry, Jagiellonian University,
R. Ingardena 3, 30-060 Kraków, Poland
Fax: (internat.) + 48-12/6340515
E-mail: milart@chemia.uj.edu.pl

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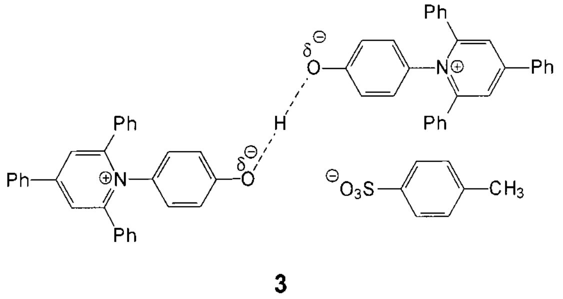
2,4,6-triphenylpyridinium *p*-toluenesulfonate (**1**; X = 4-Me-$C_6H_4SO_3$) and the betaine dye **2**. Greater solubility of the *p*-toluenesulfonate than that of the other salts mentioned above, made it possible to perform ^{1}H NMR measurements in different solvents, to study the solvatochromic effect and to grow crystals suitable for X-ray analysis.

Results and Discussion

^{1}H NMR Spectra

Measurements have been made for pyridinium salts **1** and **3** (colourless and red *p*-toluenesulfonates, respectively) and for betaine **2** itself in three different solvents: $CDCl_3$, CD_3OD and [D$_6$]DMSO. As can be seen from Table 1, the chemical shifts of the H signals of the pyridinium and phenolate ring depend strongly on the type of solvent. The protonation of the phenolate oxygen atom has very little influence on the chemical shifts of the pyridinium-ring H signals in all of the solvents used, whereas it strongly influences the chemical shifts of the protons of the phenolate moiety. The H signals of the "red salt" **3** are shifted upfield against those of the colourless *p*-toluenesulfonate and downfield against those of the betaine dye **2**. This behaviour suggests that the oxygen atom in the "red salt" is engaged in hydrogen bonding between two betaine molecules (a partial protonation of the oxygen atom) and supports the conclusion of Neiland et al.[4] Both betaine molecules give one set of ^{1}H NMR signals, which means that the complex cation [betaine···H^+···betaine] is fully symmetrical in solution. Moreover, the hydrogen bond is the only relatively strong bond between the betaine molecules in the "red salt" (Scheme 2).



3

"red salt"

Scheme 2

Solvatochromic Measurements

The negative charge of the phenolate oxygen atom in the red *p*-toluenesulfonate **3** is only partially compensated for by the hydrogen bonding. If part of the uncompensated charge is transferred to the pyridinium ring in the electronically excited CT state, the "red salts" should show, to some extent, a solvatochromic effect. Our results of absorption measurements in the visible range of wavelengths for **3** and **2** in several solvents are compared in Table 2.

Table 2. Solvatochromic properties of the red *p*-toluenesulfonate **3**; the data for anhydrous betaine dye **2** are taken from Stadnicka et al.[6]; $\Delta\tilde{\nu}_{max}$ is defined as $\tilde{\nu}_{max}(\mathbf{2}) - \tilde{\nu}_{max}(\mathbf{3})$

Solvent	Betaine dye **2** $\tilde{\nu}_{max}$ [cm^{-1}]	"Red salt" **3** $\tilde{\nu}_{max}$ [cm^{-1}]	$\Delta\tilde{\nu}_{max}$ [cm^{-1}]
Methanol	22120	22040	+80
Ethanol	20880	20800	+80
2-Propanol	19240	19280	−40
DMSO	17880	17920	−40
1,2-Dichloroethane	16280	20320	−4040
Chloroform	15160	16920	−1760
Anisole	14440	17920	−3480

The $\tilde{\nu}_{max}$ values of the betaine dye **2**[6] correlate very well with the solvent polarity parameter $E_T(30)$ of Dimroth and Reichardt, but the case of the "red salt" is more complicated. In solvents of higher polarity the shape of the absorption band in the visible region is almost the same for compounds **2** and **3**. This suggests that in such solutions both the molecule of a free betaine dye **2** and that of the pyridinium salt **1** must be present as products of a dissociation of the complex salt **3**. ^{1}H NMR spectra show that there is a very quick proton exchange between betaine **2** and pyridinium salt **1**. In solvents of low polarity a distinguished difference in the VIS spectra for betaine **2** and salt **3** is observed. In the case of **3** an additional broad absorption band appears between 26000 and 22000 cm^{-1} and the long-wavelength band shows a hypsochromic shift in relation to the free betaine. It is possible that in "red salts" two betaine molecules are joined together not only by a strong hydrogen bond, but there is also an intermolecular charge-transfer interaction.

Table 1. ^{1}H NMR chemical shifts (δ/ppm) observed for the H signals of the pyridinium and phenolate rings of **1−3** in different solvents

Solvent	Protons[a]	"Colourless salt" **1**	"Red salt" **3**	Betaine dye **2**	Betaine dye **2**[5]
$CDCl_3$	H_A	6.77 (d)	6.45 (d)	6.31 (d)	
	H_B	7.00 (d)	6.63 (d)	6.38 (d)	
	H_C	7.95 (s)	8.05 (s)	8.07 (s)	
CD_3OD	H_A	6.56 (d)	6.44 (d)	6.34 (d)	
	H_B	7.19 (d)	7.03 (d)	6.89 (d)	
	H_C	8.55 (s)	8.52 (s)	8.51 (s)	
[D$_6$]DMSO	H_A	6.51 (d)	6.11 (d)	5.87 (d)	5.9 (d)
	H_B	7.20 (d)	6.88 (d)	6.69 (d)	6.7 (d)
	H_C	8.65 (s)	8.58 (s)	8.53 (s)	8.5 (s)

[a] H_A: H atoms *ortho* to OH or O^- group; H_B: H atoms *meta* to OH or O^- group; H_C: H atoms of pyridinium ring.

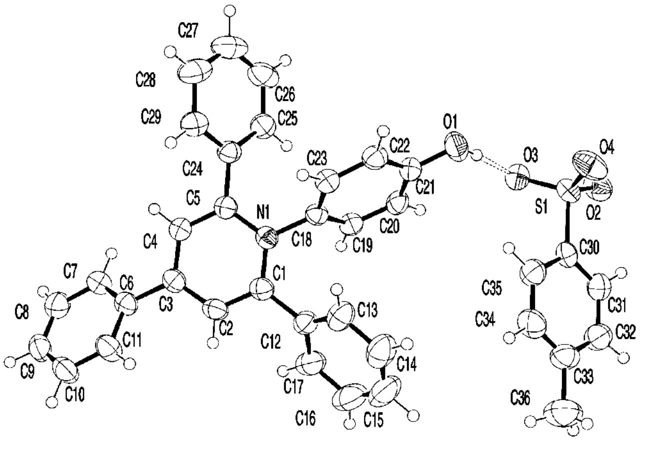


Figure 2. Colourless *p*-toluenesulfonate **1**; ORTEP-3[7] drawing of the structural moiety containing $[\mathbf{2}\cdot\mathrm{H}]^+$ and 4-$CH_3C_6H_4SO_3^-$ ions with the atom numbering scheme; the thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level, hydrogen atoms are given at an arbitrary scale; the hydrogen bond between the hydroxy group O(1)−H(1) and the *p*-toluenesulfonate oxygen atom O(3) is marked by a dotted line

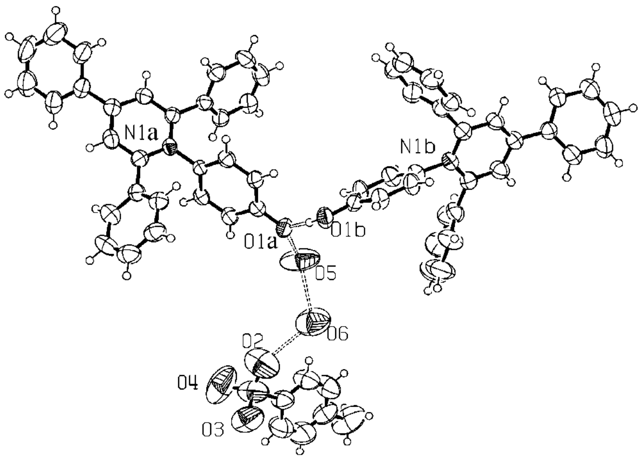


Figure 3. Red *p*-toluenesulfonate **3**; ORTEP-3[7] drawing of the asymmetric unit, which contains molecule **2** (A), $[\mathbf{2}\cdot\mathrm{H}]^+$ (B) and *p*-$CH_3C_6H_4SO_3^-$ ions and two water molecules, O(5) and O(6); the numbering scheme is the same as for the "colourless salt"; the thermal ellipsoids of non-hydrogen atoms are drawn at the 40% probability level, hydrogen atoms are given at an arbitrary scale; a hydrogen bond chain from the hydroxy group of B, through the oxygen atom of A and water molecules O(5) and O(6), to oxygen atom O(2) of *p*-$CH_3C_6H_4SO_3^-$ is expected (yet, the hydrogen atoms of water molecules have not been localised)

Crystal Structure Description

The main moiety of the crystal structure of the colourless *p*-toluenesulfonate containing betaine dye **2** and *p*-toluenesulfonic acid in the molar ratio 1:1, is shown in Figure 2.

Phenolate **2** is protonated at the oxygen atom by the H(1) atom which is found at a distance of 85(4) pm from O(1) and at the angle C(21)−O(1)−H(1) of 115(2)°. The protonation is supported by a significant elongation of the C(21)−O(1) bond to 135.3(3) pm, when compared to the value observed for the betaine **2** molecule in its crystal structure,[6] and by the endocyclic angle at C(21) close to 120° [C(20)−C(21)−C(22) 119.5(3)°]. The conformation of the cation is described by the following torsion angles: N(1)−C(1)−C(12)−C(13) 47.9(4), N(1)−C(5)−C(24)−C(25) 54.3(4), C(1)−N(1)−C(18)−C(19) 62.7(3) and C(2)−C(3)−C(6)−C(11) 37.6(4)°. The bond lengths: S(1)−O(2) 144.4(2), S(1)−O(3) 145.6(2), S(1)−O(4) 143.7(2) and S(1)−C(30) 177.4(3) pm, as well as the appropriate angles (average value of O−S−O angle is 112.6° and that of O−S−C is 105.7°) are typical for the sulfonate group. The pyridinium cation of the "colourless salt" **1**, is joined to the *p*-toluenesulfonate anion by a relatively strong hydrogen bond of geometry: O(1)···O(3) 268.5(3), O(1)−H(1) 85(4), H(1)···O(3) 183(4) pm and O(1)−H(1)···O(3) 176(3)°. Such a moiety forms a three-dimensional structure by an intermolecular interaction of the π-electron system of the pyridinium ring with the oxygen atoms O(2) and O(4) of the adjacent sulfonate group. The essential distances are N(1)···O(2) ($-x$, $y + 1/2$, $-z + 1/2$) 312.9(3) and N(1)···O(4) ($-x + 1$, $y + 1/2$, $-z + 1/2$) 315.9(3) pm. Other intermolecular interactions are weakly dispersive and the shortest intermolecular distance of 238(5) pm is observed between hydrogen atoms H(11)···H(22) ($-x + 1$, $y + 1/2$, $-z + 1/2$) and H(23)···H(26) ($x + 1/2$, $-y + 3/2$, $-z$). In the crystal structure of red *p*-toluenesulfonate **3,** the asymmetric part of the unit cell shown in Figure 3 consists of the betaine dye **2** and *p*-toluenesulfonic acid in the molar ratio 2:1.

Additionally, the structure contains two water molecules in the asymmetric unit, O(5) and O(6). The conformation of the betaine molecules differs in the following torsion angles: N(1a)−C(1a)−C(12a)−C(13a), N(1a)−C(5a)−C(24a)−C(25a), C(1a)−N(1a)−C(18a)−C(19a), and C(2a)−C(3a)−C(6a)−C(11a). The torsion angles characteristic for the conformation of A are 49.4(9), 61.9(9), 65.0(8), and −40.8(11)°, and those characteristic for B are −68.1(9), −68.5(10), −65.3(9) and −32.5(11). The geometry of the sulfonate group is typical: S(1)−O(2) 137.2(8), S(1)−O(3) 138.5(7), S(1)−O(4) 157.6(11) and S(1)−C(30) 173.9(9) pm with O−S−O angles of 119.3(8), 108.0(7), 107.6(7) and the mean O−S(1)−C angle of 107°. The phenoxy groups of two betaine molecules are bridged by a very strong, almost linear hydrogen bond of geometry: O(1b)···O(1a) 248.7(7), O(1b)−H(01) 105(11), H(01)···O(1a) 144(11) pm and O(1b)−H(01)···O(1a) 171(9)°. The hydrogen bond seems to be asymmetric. This means that one of the betaine molecules (B) can be considered as protonated forming a pyridinium cation and acting as a proton donor, whereas the other one (A) is acting as a proton acceptor through its negatively charged oxygen atom. Inspection of the C(20)−C(21)−C(22) endocyclic angles of molecules A and B, which should be less affected by different sorts of experimental errors than bond lengths, revealed that in A the angle [117.5(6)°] is close to the value found in the crystal structure of betaine dye **2**[6] itself, whereas in B the angle [118.3(6)°] is somewhat different to the 120° observed for the "colourless salts" of **2**.[8] This observation suggests an intermediate state of the phenolate oxygen atom O(1a) when compared to the O^- and OH group. The geometry of the pyridinium ring of both molecules A and B is similar and thus, it seems to be uninfluenced by the state of the phenolate oxygen atom. All phenyl rings are planar within the limits of error. Significant differences in the conformations of A and B are mainly due to packing forces. Although we were unable to localise the hydrogen atoms of water molecules, O(5) and O(6), the distances O(1a)···O(5) 272.2(9), O(5)···O(6) 273.6(11), and O(6)···O(2) 272.8(14) pm, as well as the appropriate angles, indicate a relatively strong hydrogen bond chain between betaine molecule A and the sulfonate group of the anion. Oxygen atom O(5) is also close to N(1a) of an adjacent molecule [O(5)···N(1a) $(-x, y + 1/2, -z + 1/2)$ = 323.0(9) pm]. All other intermolecular interactions in the crystal structure of the red *p*-toluenesulfonate are weakly dispersive. The shortest intermolecular distance of 232.2(14) pm between the H(15) atoms related by the centre of symmetry is similar to the nonbonding contacts of the molecules A and B [H(4a)···H(7a) 236.2(10) and H(2b)···H(11b) 232.1(11) pm].

Experimental Section

General: Elemental analyses were performed by the Regional Laboratory of Physico-Chemical Analyses, Kraków. − IR spectra were recorded with a Bruker IFS-48 spectrometer as KBr pellets: − UV/Vis spectra were recorded with a Specord (Zeiss, Jena). − ^{1}H NMR spectra were taken at 500.13 MHz with a Bruker AMX-500 spectrometer using [D$_6$]DMSO, $CDCl_3$ and CD_3OD as solvents and TMS as an internal standard. Betaine **2** was prepared according to a literature procedure.[1,3] All solvents used for solvatochromic experiments were purified according to Riddick et al.[9] − Melting points (not corrected): Boetius apparatus. − X-ray data were collected with an automated four-circle diffractometer KM-4 (KUMA Diffraction) using a Mo fine-focus sealed tube and a graphite monochromator (Mo-K_α radiation).

1-(4-Hydroxyphenyl)-2,4,6-triphenylpyridinium *p*-Toluenesulfonate (“Colourless Salt”, 1, X = *p*-$CH_3C_6H_4SO_3$): Betaine **2** hexahydrate (0.96 g, 2 mmol) was dissolved in aqueous ethanol (30 mL, 70%). A solution of *p*-toluenesulfonic acid monohydrate (0.66 g, 3.5 mmol) in water (5 mL) was added. The separated orange oil solidified within a few minutes. The yellowish product was filtered off, washed with cold water, and dried in air. The pyridinium salt was purified by recrystallization from either water or 2-propanol. Yield 1.0 g (87%), m.p. 219−220 °C. − IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (broad, OH involved in hydrogen bond), 3031 (CH), 1628 (intensive, H−O−H deformation), 1558, 1510 (aromatic rings), 1227, 1173 (intensive, S=O). − ^{1}H NMR ([D$_6$]DMSO/TMS): δ = 2.31 (s, 3 H, CH_3), 6.51 (d, 2 H, part of AA′BB′ system, J_{AB} = 8.0 Hz, 3-H and 5-H of phenolate ring), 7.19−7.54 (m, 16 H, 2-H and 6-H of phenolate ring, four H atoms of *p*-toluenesulfonate ring, and aromatic H of rings 2 and 6), 7.73 (m, 3 H, 3-, 4-, and 5-H of aromatic ring 4), 8.37 (m, 2 H, 2- and 6-H of aromatic ring 4), 8.65 (s, 2 H, pyridinium-H), 9.90 (s, 1 H, OH). − $C_{36}H_{29}NO_4S$ (571.66): calcd. C 75.62, H 5.12, N 2.68, S 5.61; found C 75.90, H 5.41, N 2.68, S 6.01.

1:1 Complex of 1-(4-Hydroxyphenyl)-2,4,6-triphenylpyridinium *p*-Toluenesulfonate and 4-(2,4,6-Triphenyl-1-pyridinio)phenolate (“Red Salt”, 3): A solution of betaine **2** hexahydrate (0.70 g, 1.5 mmol) in ethanol (5 mL) was added to a solution of pyridinium salt **1** (0.57 g, 1.0 mmol) in ethanol (10 mL). After 30 min, this mixture was added to water (70 mL). The red precipitate was filtered off, washed with water, and dried in air. Yield 0.7 g (70%), m.p. 258−259 °C. − IR (KBr): $\tilde{\nu}$ = 3648 cm^{-1} (narrow, free OH), 3439 (broad, OH involved in hydrogen bond), 3042 (CH), 1622 (intensive, H−O−H deformation), 1550, 1495 (aromatic rings), 1218, 1200 (S=O). − ^{1}H NMR ([D$_6$]DMSO/TMS): δ = 2.31 (s, 3 H, CH_3), 6.11 and 6.88 (2d, 8 H, AA′BB′ system, J_{AB} = 8.0 Hz, phenolate-H-atoms), 7.09−7.54 (m, 24 H, H-atoms of *p*-toluenesulfonate ring, and aromatic H of rings 2 and 6), 7.68 (m, 6 H, 3-, 4-, and 5-H of aromatic ring 4), 8.37 (m, 4 H, 2- and 6-H of aromatic ring 4), 8.58 (s, 4 H, pyridinium-H). − $C_{65}H_{50}N_2O_5S\cdot 2H_2O$ (1007.16): calcd. C 77.49, H 5.41, N 2.78, S 3.18; found C 77.71, H 5.73, N 2.84, S 3.26.

X-ray Structure Analysis of Colourless *p*-Toluenesulfonate (1): $C_{29}H_{22}NO^+\cdot C_7H_7SO_3^-$ (571.66), orthorhombic, space group $P2_12_12_1$, a = 852.24(6), b = 1801.1(2), c = 1937.7(2) pm, V = 2.9743(5) nm^3, Z = 4, λ(Mo-K_α) = 0.71073 Å, μ = 0.150 mm^{-1}, D_x = 1.277 Mg m^{-3}, F(000) = 1200, T = 293(2) K. A colourless prism of dimensions 0.32 × 0.20 × 0.16 mm was grown from an acetone/water solution by slow concentration. Unit cell parameters were refined from 44 reflections in the θ range 1.5−10.5 °. Range of θ angle for data collection 1.54−26.97 °, indices ranges $0 \leq h \leq 10$, $0 \leq k \leq 22$, $-24 \leq l \leq 24$; intensities of three standard reflections, monitored every 50 reflections, showed random variation less than 1.0%; 4338 intensities with $I \geq \sigma(I)$, from a total number of 7250 measured, were corrected for Lorentz and polarisation effects and 3975 unique reflections (R_{int} = 0.0215) were used for further analysis. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELX-97[10]) with anisotropic vibration displacements for non-hydrogen atoms. All hydrogen atoms were found from Fourier difference map and were included in the refinement with isotropic thermal parameters. The final $wR_2(F^2)$ for all reflections was 0.0814, a conventional $R_1(F)$ = 0.0375 for 496 refined parameters and $I \geq 2\sigma(I)$; weighting scheme $w = [\sigma^2(F_o^2) + (0.0432\,P)^2 + 0.0413\,P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$; extinction coefficient 0.0013(3); absolute structure parameter −0.15(8);[11] the largest difference electron density peak and hole at the final stage were 0.160 and −0.178 eÅ^{-3}.[12]

X-ray Structure Analysis of Red *p*-Toluenesulfonate (3): $[C_{29}H_{21}NO\cdot C_{29}H_{22}NO]^+\cdot C_7H_7SO_3^-\cdot 2H_2O$ (1007.16), monoclinic, space group $P2_1/c$, a = 2070.0(3), b = 1041.82(15), c = 2507.4(2) pm, β = 100.78(1)°, V = 5.3119(11) nm^3, Z = 4, λ(Mo-K_α) = 0.71073 Å, μ= 0.119 mm^{-1}, D_x = 1.259 Mg m^{-3}, F(000) = 2120, T = 296(2) K. A red prism of dimensions 0.20 × 0.18 × 0.13 mm was grown from a mixture of water/acetonitrile/acetone by slow concentration. Unit cell parameters were refined from forty reflections in the θ range 2.0−10.5°. Range of θ angle for data collection 1.65−25.06°, indices ranges $0 \leq h \leq 23$, $0 \leq k \leq 12$, $-29 \leq l \leq 29$; intensities of three standard reflections, monitored every 50 reflections, showed random variation less than 1.75%. From a total number of 10264 measured reflections, 3839 intensities with $I \geq \sigma(I)$ were corrected for Lorentz and polarisation effects, and 3822 unique reflections (R_{int} = 0.0205) were used for further analysis. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELX-97[10]) with anisotropic vibration displacements for non-hydrogen atoms. Positional parameters of hydrogen atoms at carbon atoms were calculated from geometric considerations. The position of the H(01) atom of a hydroxy group was found from Fourier difference synthesis. Hydrogen atoms of water molecules O(5) and O(6) have not been localised. Most of the H atoms were included in the refinement using isotropic thermal parameters within a riding model.

The final $wR_2(F^2)$ for all reflections was 0.1970 and a conventional $R_1(F) = 0.0680$ for 682 refined parameters and $I \geq 2\sigma(I)$; weighting scheme $w = [\sigma^2(F_o^2) + (0.1430\ P)^2 + 2.9475\ P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$; extinction coefficient 0.0033(8); largest difference electron density peak and hole at the final stage 0.89 (at close vicinity of the sulfur atom) and −0.32 eÅ^{-3}.[12] Very similar results have been obtained in independent experiments for two different crystals of the "red salt" **3**.

Acknowledgments

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[12] Crystallographic data (excluding structure factors) for structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no CCDC-151659 (**1**) and -151660 for (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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