

**s9.m3.p1** **Molecular Interactions in the Crystal Structures of 4-(2,4,6-triphenyl-1-pyridinio)phenolate and its Salts.** K. Stadnicka, P. Milart, *Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland.*

Keywords: betaine dye, pyridinium salts, solvatochromism.

Crystal structures of 4-(2,4,6-triphenyl-1-pyridinio)phenolate and its salts with a variety of strong inorganic and organic acids were determined. The salts are of two types depending on the cation to anion molar ratio in solution. At molar ratio 2:1 the crystals of "red" salts can be obtained, whereas for molar ratio 1:1 usually "colourless" crystals are grown.

The title compound belongs to the family of the pyridinium  $N^+O^-$  betaine dyes, which are known for their very large negative solvatochromism. The structure of the betaine dye crystals, grown and kept in appropriate conditions, is noncentrosymmetric and contains some amount of water (space group either  $P2_1$  or  $C222_1$  - the assignment of space group will be discussed). Due to their relatively high ground-state dipole moment, the betaine dye molecules form anti-parallel arrangements leaving channels for disordered water molecules. Between the betaine dye and neighbouring water molecules there is an interaction via  $O^{\cdots}HOH$  hydrogen bonds.

Crystals of the "colourless" salts, especially those of strong inorganic acids ( $HNO_3$ ,  $HF$ ,  $HClO_4$ ,  $HClO_3$  etc.) are, in general, centrosymmetric (Pbca). The same is true for crystals of the salts of organic acids (e.g. picrate:  $P-1$ , naphthalenesulfonate: Pbca). To prevent the crystal structure from centrosymmetry, the cations of such organic acids as *p*-toluenesulfonic ( $P2_12_12_1$ ) or chiral (1S)-(+)-10-camphorsulfonic ( $P2_12_12_1$ ) should be considered.

The "red" salts of the betaine dye form in solution a fully symmetric complex cation  $betaine^{\cdots}H^{\cdots}betaine$ , as it was found by using  $^1H$  NMR spectroscopy. In solvents of relatively high polarity the shape of absorption spectra of "red" tosylate in the visible range is almost the same as for the betaine dye itself. It means that free betaine must be present in such solutions and quick proton exchange with pyridinium salt is observed. In solvents of low polarity an additional broad band at 26000 - 22000  $cm^{-1}$  is observed. Thus, it is possible that there is an intermolecular CT interaction in addition to the strong hydrogen bond. The strong, almost symmetric hydrogen bond between two betaine molecules is also found in the crystal structures of its "red" salts: (1S)-(+)-10-camphorsulfonate ( $P2_1$ ) and tosylate ( $P2_1/c$ ). Intermolecular interactions in the crystal structures will be discussed in relation to properties of the molecules in solutions.

**s9.m3.p2** **Intermolecular Interactions in the Crystal Structures of Some Diaryl Telluride Antioxidants.** L. Engman<sup>\*)</sup>, I. Kania<sup>\*\*)</sup>, A. Kurtyka<sup>\*\*)</sup>, B.J. Oleksyn<sup>\*\*)</sup> and J. Sliwinski<sup>\*\*)</sup>, *Uppsala Univ., Institute of Chemistry, Box 531, S-75121 Uppsala, Sweden; Faculty of Chemistry, Jagiellonian Univ., ul. R. Ingardena 3, 30-060 Kraków, Poland.*

Keywords: diaryl tellurides, antioxidants, crystal structures.

The antioxidative properties of diaryl tellurides result from the ability of tellurium to easily change its oxidation states between +II and +IV. They act as catalytic decomposers of hydrogen peroxide and organic hydroperoxides in the presence of thiols. Thus, they mimic the properties of glutathione peroxidase. The thiol peroxidase-like activity of 4,4'-disubstituted diphenyl tellurides was investigated by Engman *et al.*<sup>1,2</sup>. It was shown that the higher is the electron-donating ability of a substituent in the aromatic part of the molecule the more active is the diaryl telluride.

We have determined the crystal structure of three compounds: bis(4-aminophenyl)telluride (1), bis[4-(N,N-dimethylamino)phenyl]telluride (2) and bis(4-hydroxyphenyl)telluride monohydrate (3) in order to study the 3D-aspects of their activity. For comparison also the structure of 2-(dimethylaminomethyl)phenyl-chlorotellurium crystals was investigated.

The most interesting intermolecular interactions in (1) and (2) are relatively close contacts between methyl and phenyl moieties. These contacts can be classified as p-hydrogen bonds<sup>3</sup>. The packing in (3) is dominated by intermolecular hydrogen bonds between hydroxyl groups with contribution of water molecules. In (4) a short intermolecular contact between the tellurium atom and the phenyl moiety of the nearest molecule occurs.

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