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

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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- 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 C2_2_2_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-H... HOH hydrogen bonds.

Crystals of the "colourless" salts, especially those of strong inorganic acids (HNO_3, HBF_4, HClO_4, HNCO etc.) are, in general, centrosymmetric (Pbcn). The same is true for crystals of the salts of organic acids (e.g. picrate: P-1, naphthalenesulfonate: Pbcn). To prevent the crystal structure from centrosymmetry, the cations of such organic acids as p-toluenesulfonic (P2_1_2_1_2_1) or chiral (1S)-(+)-10-camphorsulfonic (P2_1_2_1_2_1) should be considered.

The "red" salts of the betaine dye form in solution a fully symmetric complex cation betaine H^+ 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 the betaine dye itself. It means that free betaine must be present in such solutions and quick proton exchange with the betaine dye itself.

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