

phosphonium chloride obtained from single-crystal X-ray diffraction was compared with those obtained from DFT method in gas phase. The calculated geometric parameters were compared to the corresponding x-ray determination results of the compound. In addition, DFT calculations of the title compound, molecular electrostatic potential and Mulliken charge analysis were performed at B3LYP/6-31G(d) level of theory.

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Experimental and computational study of (E)-2-[(4-iodophenyl)iminomethyl]-6-methylphenol

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Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances [1], [2], [3].

In general, Schiff bases display two possible tautomeric forms, the phenol-imine (OH) and the keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O—H...N in phenol-imine and N—H...O in ketoamine tautomers. Another form of the Schiff base compounds is also known as zwitterion having an ionic intramolecular hydrogen bond (N+—H...O-) and this form is rarely seen in the solid state.

The investigations of the structural stability of the compounds by both experimental techniques and theoretical methods have been of interest for many years. The crystal and molecular structure of the title compound, C₁₄H₁₇O₂N₁I₁, has been synthesized and x-ray single-crystal structure determination has been performed. The compound crystallizes in the Orthorhombic, space group, P212121 with unit cell dimensions a=4.6773(4) b=11.6092(12), c=23.6751(4), Mr=337.15, V=1285.55(17), Z=4 and wR2=0.037. The molecular structure of the title compound shows that the molecule exists in the phenol-imine form. This conformation is stabilized by intramolecular N-H...O hydrogen bond and weak intermolecular C-H...O hydrogen bonds link the molecules forming a zig-zag chain parallel to the b axis.

Geometric optimization based on x-ray diffraction technique and quantum mechanical calculations were performed. The calculated geometric parameters were compared to the corresponding x-ray determination results of the compound.

To inform minimum energy conformation of the title compound, selected torsion angle are varied from -180 to +180 in every 10° and then molecular energy profile is calculated by DFT calculations method. In addition, DFT calculations of the title compound, molecular electrostatic potential and frontier molecular orbitals were performed at B3LYP/6-31G(d) level of theory.

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On differences in electron densities of phenoxazine and phenothiazine derivatives

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The concept of excited-state intramolecular electron transfer in acceptor-donor (A-D) molecular fragments linked by formally single bond plays a central role in discussion of their photophysical properties [1,2].

High resolution X-ray studies for three single crystals of derivatives of phenoxazine and phenothiazine: 1-(4-phenothiazin-10-yl-phenyl)-ethanon (PAS), 1-(4-phenoxazin-10-yl-phenyl)-ethanon (PAO), and (4-phenoxazin-10-yl-phenyl)phenyl-methanon (PBO) have been carried out and experimental charge densities for these crystals have been established. The analysis of geometry of these compounds allowed to explain differences in the values of electronic coupling element V_0 obtained for these compounds. Three most important factors influencing the coupling element are the following: hybridization of the nitrogen atom, conformation of the heterocyclic ring and the torsion angle between acceptor and donor part of the molecules. A significant intramolecular charge transfer is observed for the studied moieties. The donor parts of the molecules studied in all three cases are negatively charged (-0.701, -0.362 and -0.218) and the acceptor fragments carry out significant positive charges (0.674, 0.375 and 0.224) for **PBO**, **PAS** and **PAO**, respectively.

Intramolecular charge transfer was investigated by topological analysis of estimated electron densities from the high resolution X-ray experiments. Separation of the charge between the donor and acceptor parts in the solid state is in the opposite direction in comparison to the molecule behaviour in the solution after the exposure on light. Commonly electron jumps take place from the donor to the acceptor part. However in the solid state, the charge transfer is from the formal acceptor to the donor. The acceptor part is positively charged and the donor negatively. The biggest difference between the acceptor and donor part is for benzoic derivative of phenoxazine which has the largest system of coupled double bonds. Two effects inductive and mesomeric one are resulting from intramolecular charge transfer. The first one is present between the two atoms connecting the acceptor and donor parts: the nitrogen atom N(8) and carbon atom C(5). The degree of charge transfer depends on the hybridization of nitrogen atom. The hybridisation of the N atom in phenoxazine derivatives is close to sp² and in phenothiazine close to sp³. Also hybridization of nitrogen atom close to sp² allows to form a coupled system of double bond in phenoxazine derivatives. Our experimental results are supported by DFT computations.

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DFT studies on stability and ordering of mixed dipnictide compounds

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