

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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**Keywords:** X-ray, triphenylphosphonium, DFT

## MS76.P04

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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, C<sub>14</sub>H<sub>17</sub>O<sub>2</sub>N<sub>1</sub>I<sub>1</sub>, 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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**Keywords:** X-ray diffraction, schiff bases, computational methods

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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 sp<sup>2</sup> and in phenothiazine close to sp<sup>3</sup>. Also hybridization of nitrogen atom close to sp<sup>2</sup> allows to form a coupled system of double bond in phenoxazine derivatives. Our experimental results are supported by DFT computations.

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**Keywords:** experimental, charge density, charge transfer

## MS76.P06

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### DFT studies on stability and ordering of mixed dipnictide compounds

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There is a big variety of structure types for  $MPn_2$  ( $Pn = N, P, As, Sb, Bi$ ) compounds with promising properties. Pyrite-type  $SiP_2$  served as a model compound for DFT calculations on electronic structure in both direct and momentum space as well as IR- and Raman spectra [1] [2]. The calculations were extended to the system  $SiP_{2-x}As_x$ , where P was successively substituted by As [3]. An ordering scheme derived from the pyrite structure type according to [4] resulted in hetero- and homoatomic dumbbells with the first clearly preferred over the latter due to dipole momentums from the charges of P (-0.8 e) and As (-0.3 e).

Here we present an extension of the calculations to different structure types not only with dumbbell but also with strand-like structures. In addition to the system  $SiP_{2-x}As_x$ , related compounds with either different metal or different pnictogen atoms were taken into consideration. New ordering schemes could be derived leading to the occurrence of distinct preferences and tendencies within the 5<sup>th</sup> main group. With a special focus on the 1:1:1 stoichiometry, the examined compounds were evaluated in terms of thermodynamic stability and hence the possibility of being capable of synthesis.

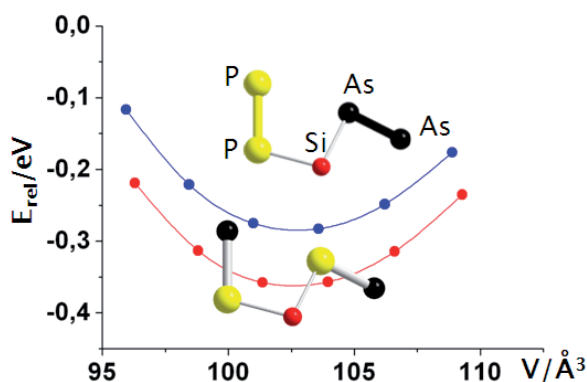


Fig. 1: Energy vs. volume plot of different structural variants of SiPAs derived from the marcasite structure type.

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### Mercury-ordering in $Hg_3S_2Cl_2$ polymorphs

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The crystal structures of different modifications of mercury chalcogenides  $Hg_3Ch_2X_2$  ( $Ch = S, Se, Te; X = F, Cl, Br, I$ ) were first investigated in the 1960s. All of these structures can be described in terms of cationic  $Hg_3Ch_2^{2+}$  partial structures. Different linking of  $ChHg_3$

trigonal pyramids leads from zero-dimensional clusters over one-dimensional polymers and two dimensional layers to three-dimensional networks [1], [2], [3], [4], [5], [6]. Another possibility to understand the structures of those ternary compounds is the description as ordered half-antiperovskites, where only  $\frac{1}{2}$  of perovskite O-sites is occupied with Hg-atoms [7]. The mercury ordering with respect to primitive  $X$ -supercells points out the structural relation to cubic perovskite  $SrTiO_3$  and allows for a systematical understanding of the whole family of the 3:2:2 mercury sulfo-, seleno- and tellurohalogenides which crystallize in a variety of different crystal systems.

There is a large amount of possibilities to synthesize  $Hg_3S_2Cl_2$ , but a specific reaction control is still missing.

The investigation of the relative and thermodynamic stabilities of those structures with DFT methods includes the newest polymorph ( $\delta$ ) [8] and leads to the prediction of more potential structures.

The chemical nature of the heavy element Hg requires calculations at a full relativistic level. To gain insight into the bonding situation, band structure calculations with the full potential local orbital method (FPLO) [9] have been performed and partial densities of states have been analysed.

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### Computational study with combined X-ray structure of dioxidomolybdenum(VI)Compound

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The geometry of Methanol {6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) complex optimized in the gas phase using density functional theory calculations. The agreement between theoretical and experimental data is for this metal complex. The electronic excitation energies and oscillator strengths  $f$  calculated by B3LYP/DZP method for this complex are summarized in this work. The longest wavelength transition is belonging to HOMO-LUMO with  $n \rightarrow \pi^*$  character [(the percentage composition of the lowest unoccupied and highest occupied molecular orbital levels for this compound are: For HOMO level, %Mo=0, %O=2.24( $p_x$ )+6.52( $p_y$ )+ 13.04 ( $p_z$ ), N=1.71( $p_y$ )+3.24( $p_z$ ) and %C=18.6( $p_y$ )+ 43.41( $p_z$ ). For LUMO level, %Mo=30.52( $d_{xz}$ ), %O=17.05( $p_x$ ), %N=2.22( $p_y$ )+8.46( $p_z$ ) and %C=8.73( $p_y$ )+ 22.22( $p_z$ )].

In the structure of the title compound, which was characterized by X-ray crystal analysis, and it has monoclinic space group  $p2_1/c$ , and  $a = 10.330(17) \text{ \AA}$ ,  $b = 9.397(15) \text{ \AA}$ ,  $c = 13.695(2) \text{ \AA}$ ,  $V = 1252.1(3) \text{ \AA}^3$ , and  $Z = 4$ . B3LYP theoretical method with DZP basis sets calculations nicely reproduces the X-ray experimental geometry, molecular orbital levels and the other structural properties for this complex.

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