

metal-hydrogen systems. To study structure of liquid transition metal hydrogen alloys, we have performed in-situ energy-dispersive x-ray diffraction measurements at high pressures and high temperatures using a cubic-type multi-anvil press on BL14B1 at SPring-8 synchrotron facility. Pure metal wire was used as a starting material and LiAlH<sub>4</sub> was used as a hydrogen source. The x-ray diffraction measurements on liquid pure metals were also performed for comparison.

FeH<sub>x</sub> is one of the most studied hydrides under high pressure. A solubility of hydrogen in iron is small at ambient conditions but iron and hydrogen react under high pressure and FeH<sub>x</sub> (x≈0.8) is formed at 6.7GPa and 250°C [1]. The melting temperature of FeH<sub>x</sub> has been reported by several groups and it is lower than that of pure iron by 500°C at 5 GPa [2], [3]. Our X-ray measurements confirmed the hydrogenation of iron and the decrease of the melting temperature. The pair correlation functions, which are obtained by Fourier transformation of structure factor, indicate that the Fe-Fe nearest neighbor distance in FeH<sub>x</sub> is slightly longer than that in pure Fe [4]. Similar amount of elongations of the atomic distance were observed also in NiH<sub>x</sub> and CoH<sub>x</sub>. In spite of a suggestion of a large decrease of melting temperature in VH<sub>x</sub> [5], we have not observed melting transition in our X-ray measurements for VH<sub>x</sub>.

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**Keywords: liquid, hydride, pressure**

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### Experimental and DFT studies of (E)-1-((3-iodophenylimino)methyl)naphthalene 2-ol

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The title compound, C<sub>17</sub>H<sub>12</sub>INO, crystallizes in a enol imine tautomeric form.

The title compound, (E)-1-((3-bromophenylimino)methyl)naphthalene-2-ol, has been synthesized and characterized by IR, UV, electronic spectroscopy, and X-ray single-crystal determination. The single crystal X-ray diffraction analysis of the title compound, C<sub>17</sub>H<sub>12</sub>BrNO, reveals that the crystal structure is stabilized in the solid state as an enol-imine tautomer, with a strong intramolecular O—H...N hydrogen bond. Molecular geometry from X-ray experiment of the title compound in the ground state have been compared using the density functional method (B3LYP) with 6-31G(d,p) basis set. To determine conformational flexibility, molecular energy profile of the title compound was obtained by DFT calculations with respect to two selected degrees of torsional freedom, which were varied from -180° to +180° in steps of 10°. Besides, molecular electrostatic potential (MEP), natural bond orbitals (NBO), frontier molecular orbitals (FMO), and thermodynamic properties were performed at B3LYP/6-31G(d,p) level of theory.

The C9-O1 and C7-N1 bond lengths verify the enol-imine tautomeric form. These distances agree with the literature [1]. The C1-I1 bond length in is also in a good agreement with the corresponding distances in the literature [2].

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**Keywords: density functional theory(DFT), crystal and molecular structure studies, tautomerism**

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### Experimental and DFT computational study on hexaaquamagnesium(II) acesulfamate

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The parameters of unit cell are a=6.9404, b=8.5775, c=8.7200 α=68.564, β=78.640, γ=81.260 and Z=1. The crystal structure of the title compound, [Mg(H<sub>2</sub>O)<sub>6</sub>](C<sub>4</sub>H<sub>4</sub>NO<sub>4</sub>S)<sub>2</sub>, was determined at 296 K. The complex crystallizes in centrosymmetric triclinic space group P-1 and Mg<sup>II</sup> atom is coordinated by six O atoms from six water molecules. The ligands in the Hexaaquamagnesium(II) Acesulfamate are linked with three dimension via O—H...O and O—H...N interactions. In this paper, the geometric parameters which are obtained from X-ray determination and theoretical parameters which are calculated by using density functional theory (B3LYP) with the 6-31G basis sets were compared. Experimental IR study, theoretical IR calculations, molecular electrostatic potential and frontier molecular orbital calculations were also put in this paper.

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

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### Experimental and DFT studies of (2-Hydroxyethyl) trihenylphosphoniumchloride

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Triphenylphosphonium compounds and their various derivatives are key reagents in the Wittig reactions and are used to convert aldehydes and ketones into alkenes [1], specifically in applications ranging from the synthesis of simple alkenes to the construction of complex biologically active molecules in the pharmaceutical research [2]. They are also an important class of isoaromatic compounds and have widespread applications for their antimicrobial and anticancer activities [3].

In the crystal structure of the title compound, C<sub>20</sub>H<sub>20</sub>OOP<sup>+</sup>CP<sup>-</sup>, the cations and anions are linked by intermolecular C—H...Cl and O—H...Cl hydrogen bonds into chains running parallel to the b axis. The compound crystallizes in the monoclinic, space group C2/c with unit cell dimensions a=14.1988(4), b=12.5743(3), c=19.7098(6), Mr=342.78 and Z=8.

The experimental geometry of (2-Hydroxyethyl)trihenyl

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

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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 wR<sub>2</sub>=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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### DFT studies on stability and ordering of mixed dipnictide compounds

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