The effects of P–T changes on intermolecular interactions in crystal structure of iodoform

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HIGHLIGHTS

- Room condition and high pressure crystal structures of iodoform are determined.
- A comparison between room and low temperature structures is done.
- A disorder–order phase transition occurs between room and high pressure conditions.
- Two types of halogen bondings determine the packing motif of the crystal structure.
- DFT calculations show how the strength of intermolecular bonds varies with pressure.

ARTICLE INFO

ABSTRACT

The structural transition at different pressures of a halogen and hydrogen bonded molecular structure (iodoform, CHI_3) is described. The pressures analyzed up to sample decomposition are 0.85 GPa (**P1RT**) and 2.15 GPa (**P2RT**); also room conditions (**P0RT**) and low temperature (106 K, **P0LT**) structures have been reported for comparison. The observed disorder–order phase transition, from $P6_3/m$ to $P6_3$ space group, can be rationalized by the intermolecular interaction analysis. The shortening of the distances among iodoform planes, observed during the compression and the temperature decreasing, determines an ordering of molecular dipoles in a parallel arrangement: this phase transition causes a shortening of I···I halogen bondings. The *BSSE* corrected cohesive energies have been calculated for all structures at DFT/B3LYP level of theory using a periodic boundary condition code and the Grimme dispersion correction. Hirshfeld surfaces and electrostatic potential mapped on charge density isosurfaces have been computed and their features have been analyzed, in order to better understand the halogen intermolecular interactions that control the structural modification of iodoform crystal.

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1. Introduction

Polar and/or non-centrosymmetric crystals of organic materials are highly requested because they can be used as optoelectronic transducers, actuators, ferro-, piezo and pyroelectric materials and for technological applications [1].

Iodoform (CHI_3) is a good molecule in this sense, with permanent dipole moment and a rigid molecular arrangement [2]. As well as many crystals characterized by charge transfer interactions, it has well known non-linear optical properties and it shows a wide range of applications in the synthesis of novel chemical products and polymers [3].

The applicability of this powerful material is strongly connected to the range of thermodynamic stability of its chiral crystal struc-

ture; about this peculiar property a lot of work has been done: the early X-ray diffraction studies at room temperature and pressure have suggested that it belongs to the chiral space group $P6_3$ [4], although a neutron diffraction experiment has shown a disordered structure refined in the $P6_3/m$ space group [5]. Almost all solid state spectroscopic studies of CHI_3 have been interpreted in term of polar structure; reports showing the anomalous behavior of lattice modes intensities have suggested a phase transition at 260 K [6]. About the behavior of iodoform crystal structure under pressure, recently X-ray powder diffraction experiments indicate no phase transitions up to 40 GPa [3]. First-principles pseudopotential plane-wave calculations based on the density-functional theory shown a new high pressure polar monoclinic structure with space group *Cc*, becoming thermodynamic stable at 40.1 GPa [1].

A recent X-ray single crystal study at 106 K has shown a $P6_3$ structure [7]. At our knowledge no attempts have been made to study CHI_3 crystal structure at variable pressure using single

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crystal X-ray diffraction techniques and diamond anvil cell (DAC) as a tool to freeze the structure at different pressures.

The crystal is built up of layers of molecules perpendicular to [001] direction; the halogen···halogen interactions form intra- and inter-layers bondings and hydrogen bonds contribute to the links among planes. Fig. 1 shows the antiparallel/parallel molecules of the disordered P6$_3$/m structure and the parallel packing of molecules in the P6$_3$ space group.

Pressure is well-known for suppressing structural disorder [8] and the aim of our study is to analyze the trend of structural changes in the title compound. The main effects of pressure on a chemical system involve changes in the interatomic distances (elastic- reversible or plastic-irreversible) and in the phenomena related to the redistribution of electron density. Since organic mol-ecules are usually not spherically symmetric, their rotations in the structure and the changes in the bond lengths and in bond and torsion angles increase the number of possible variants of pres-sure-induced structural changes; the weak bondings are more influenced by pressure changes. As a result, one can observe either a structural reconstruction (a phase transition) or a continuous distortion within the limits of stability of the same phase [9].

Our structural approach allows to deepen the CHI$_3$ crystal struc-ture in order to explore the behavior of its intermolecular interac-tions, as well as their stability and compressibility under different pressure and temperature conditions. The changing of hydrogen bond in CHI$_3$ under pressure has already been analyzed using pow-der XRD [3], but further information on halogen and hydrogen bonds can be achieved using the experimental approach of the present work.

2. Experimental

2.1. Single crystal X-ray diffraction

Yellow single crystals of iodoform (CHI$_3$) of suitable size have been grown from an ethylic ether solution. One crystal was used for data collection at standard conditions (**P0RT**). Two small crys-tals (**P1RT** and **P2RT**) were selected for high-pressure structural studies and loaded in an ETH-type diamond anvil cell (DAC) [10] for X-ray diffraction measurements. The unusual choice of using different crystals during a high pressure experiments derive from the well known low photo- and air-stability of iodoform crystals. These drawbacks have partially been avoided into the DAC hydro-static medium, but unfortunately not completely: for this reason the crystal has been changed after each data collection, in order to save the accuracy of the measurements. A foil of T301 steel 250 μm thick was used as a gasket to hold the crystals and it was pre-indented to a thickness of 100 μm (**P1RT**) and 80 μm (**P2RT**) before drilling a hole by spark-erosion (Ø 250 μm). The cell was loaded with an oil equivalent to one used previously in litera-ture [11] (SANTOVAC 5) as pressure-transmitting medium.

The ruby fluorescence method was used for *in situ* pressure measurement. The internal pressure was checked with Horiba–Jo-bin micro-Raman spectrometer [12] by the fluorescence line shift of three rubies scattered in the hole of the DAC cell. Uncertainty on P was estimated to be about 0.1 GPa [13]. The pressure of the experiments are: $P = 0.85$ GPa (**P1RT**) and $P = 2.15$ GPa (**P2RT**). The single crystal X-ray data have been collected on a Gemini R Ul-tra diffractometer [14] equipped with a Ruby CCD detector. A total of 2115 frames (width 0.2°, exposure time = 60 s per frame, detec-tor-sample distance 80 mm) were collected at each pressure in 4 φ-and 12 ω-scans, covering the whole accessible reciprocal space. The 171.35.21 version of CrysAlysPro software [15] has been used for data collection and reduction. Before integration the dia-monds reflections were rejected. Using Absorb-6.0 program [16] the absorption and gasket shadowing corrections have been per-formed. All structure have been solved by direct methods and re-fined by full-matrix least-squares on F^2 using SHELX-97 package [17]. The **P1RT** and **P2RT** refinements have given reliable results in P6$_3$ space group.

The data at standard conditions (**P0RT**) have been refined in the P6$_3$/m space group, owing to the disorder (50%) of the CH group with respect to the I$_3$ plane. The space group P6$_3$/m refinement leads to a significant decrease of R factors with respect to the P6$_3$ refinement (from 0.0254 to 0.0205) and agrees with previous neutron diffraction experiments [18]. The test proposed by Hamilton [19], in order to choose among different refinement models, has been used to strengthen the attribution of the space group of **P0RT**, **P1RT** and **P2RT**.
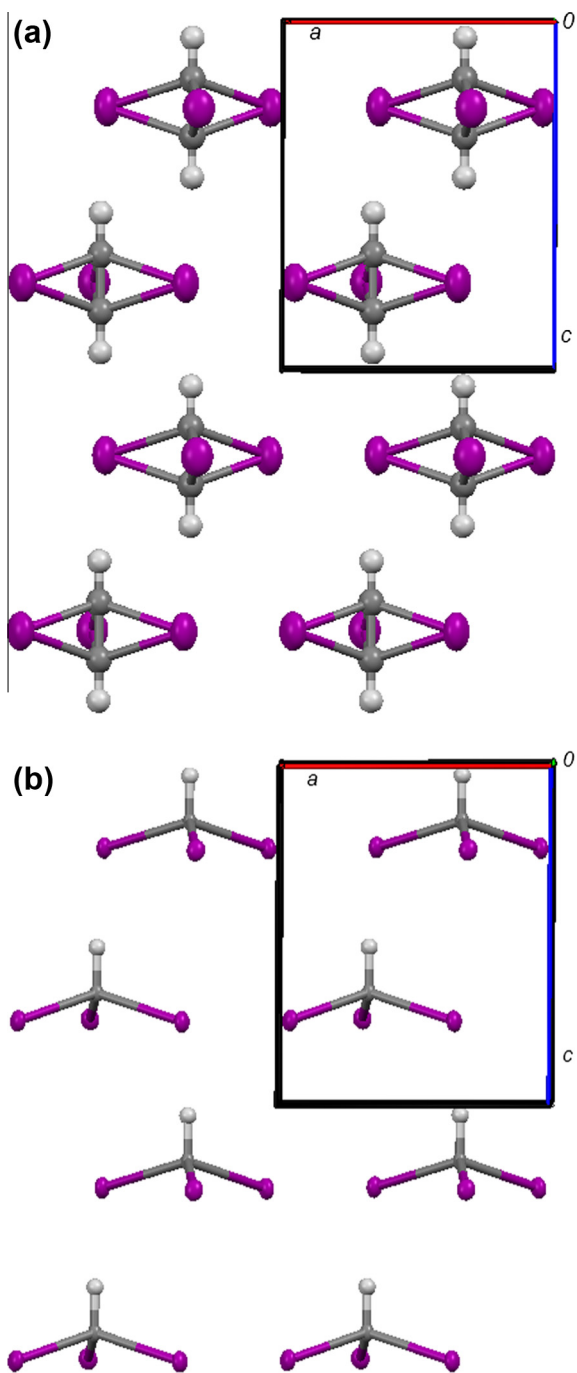

Fig. 1. Iodoform in P6$_3$/m (a) and P6$_3$ (b) packing.