# Pressure-induced phase transition in $C_6O_2I_4$

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**Abstract**
Powder x-ray diffraction measurements on iodanil ($C_6O_2I_4$) have been carried out at pressures up to 39 GPa at room temperature with a diamond-anvil cell under the best hydrostatic conditions using helium as the pressure-transmitting medium. The diffraction patterns up to 23.3 GPa were fitted with a space group $P2_1/c$. New peaks appeared above 26.8 GPa and their intensities increased with increasing pressure while the original ones observed for the low-pressure phase were gradually depressed. This phase transition was accompanied with a mixed state of low- and high-pressure phases over the wide pressure range between 26.8 and at least 39 GPa.

## 1. Introduction

Tetraiodo-p-benzoquinone (iodanil, $C_6O_2I_4$) shows pressure-induced metallization at pressures above 33 GPa and superconductivity at 52 GPa and 2 K [1]. According to the observation of a reversible pressure change in the infrared absorption spectrum, $C_6O_2I_4$ has a metallic molecular phase over a very wide pressure range from 33 to at least 48 GPa [2]. In addition, it has been found that hexaiodobenzene ($C_6I_6$) also shows the insulator-to-metal transition at 35 GPa and superconductivity at 58 GPa at 2 K [3].

We previously investigated the crystal structure of $C_6O_2I_4$ up to 10.3 GPa by means of powder x-ray diffraction measurements using a mixed pressure-transmitting medium (PTM) of n- and i-pentane (1:1 by volume) [4]. Solidification of this PTM at pressure higher than 7.4 GP leads to poor quality of the powder x-ray diffraction rings; we could not obtain the crystal structures in the metallic phase. Recently we have obtained good powder x-ray diffraction patterns of $C_6I_6$ up to 22 GPa at room temperature under the best hydrostatic conditions using helium as the PTM [5]; 35% reduction in volume, no phase transition and no molecular dissociation were consequently confirmed [6]. On the other hand, there had been no results for powder x-ray diffraction measurements of $C_6O_2I_4$ using helium PTM.

The crystal structures of $C_6O_2I_4$ and $C_6I_6$ at pressures below 10 GPa are isomorphous with monoclinic $P2_1/c$ [4, 7]. The molecular structure of $C_6O_2I_4$ is similar to that of $C_6I_6$, which is obtained by substituting oxygen atoms for iodine atoms of $C_6I_6$. The structural data on $C_6O_2I_4$ at pressures above 10 GPa are comparable to those for $C_6I_6$ [7] and indispensable for discussing the origin of the pressure-induced metallization.

Powder x-ray diffraction measurement of $C_6O_2I_4$ using helium PTM, which supplies the best hydrostatic conditions [6], has been carried out at pressures up to 39 GPa at room temperature with a diamond-anvil cell (DAC). We report an observation of a new phase of $C_6O_2I_4$ and pressure changes in the crystal and molecular structures in the low-pressure (LP) phase.

## 2. Experimental details

Reddish-black prismatic needles were obtained by synthesis through replacement reactions of $C_6O_2Br_4$ with iodine [8]. The purity of the sample was checked by mass spectroscopy and a four-circle single-crystal diffraction measurement at 1 atm. We regarded the above impurity as not having affected the result on the crystal structure.

The powdered sample was prepared by the following arrangement for obtaining ideal smooth Debye–Scherrer rings that we could use for analysing. The crystals were ground into fine powder in an agate mortar for more than 5 h. This ground sample was heat treated at 80 °C for 2 h. Large grains in the powder sample were carefully removed.

Diffraction patterns were measured by using a DAC with 0.3 mm culet diameter and 1.5 mm thick diamond anvils. The gasket was made of stainless steel with a 47 $\mu$m thick dent, in which a 120 $\mu$m hole was drilled. A small amount of the powdered sample was put in the gasket hole mounted on the culet of the anvil. Helium gas was used to fill the DAC at room temperature using a high-pressure (HP) gas-loading system operating at a gas pressure of 180 MPa [5]. The sample pressure was determined on the basis of the ruby pressure scale [9].

Angle-dispersive powder patterns were taken using synchrotron radiation (SR) from the bending magnet on the beamline BL-18C at the Photon Factory, High Energy Accelerator Research Organization (KEK). The SR beam was monochromatized to a wavelength of 0.6198 Å and introduced to the specimen through a pin-hole collimator (40 $\mu$m diameter). Each pattern was obtained by exposing the sample to x-rays for 40 min at room temperature. An imaging plate and BAS2000 scanner supplied by Fuji Photo Film Co. Ltd were used to obtain two-dimensional powder diffraction images. Each image has $2000 \times 2560$ pixels with a resolution of $100 \times 100$ $\mu$m$^2$ per pixel.

## 3. Results and discussion

The Debye–Scherrer rings above 7.4 GPa were improved using helium PTM, which made the rings smooth, with sufficient quality for carrying out the Rietveld analysis. Two-dimensional diffraction images were integrated along the Debye–Scherrer ring directions with 0.02° as the $2\theta$ step. The iodine atom has higher x-ray scattering activity than the carbon atom. The atomic parameters of carbon were fixed at the atmospheric values, which had no influence on the analyses. The lattice and atomic parameters of iodine at each pressure were determined through the Rietveld analysis.

The diffraction patterns up to 23.3 GPa were explained with the space group $P2_1/c$. The lattice parameters were determined as $a = 6.698$, $b = 4.464$, $c = 12.16$ Å, which were shorter than the atmospheric values by 13.5, 16.6 and 13.4%, respectively, and $\beta = 112.8°$ at
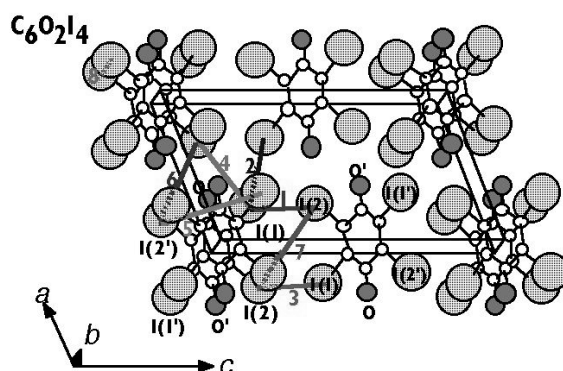
**Figure 1.** The crystal structure of $C_6O_2I_4$ and the atomic configuration of iodine atoms in the unit cell. The intermolecular I–I distances, which are shorter than twice the van der Waals radius of iodine, are numbered in the order of the lengths observed at 1 atm.
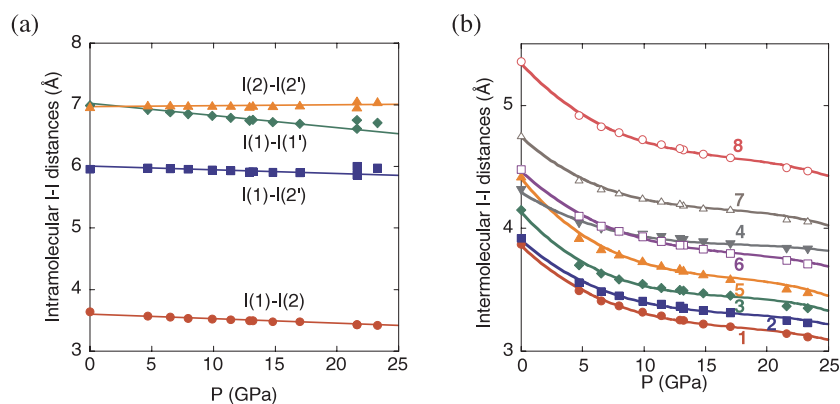


**Figure 2.** Pressure changes in intramolecular and intermolecular I–I distances up to 23.3 GPa at room temperature. Symbols I(1), I(1′), I(2) and I(2′), which are present in (a), and the numbers given in (b) correspond to those in figure 1. The solid curves are to guide the eye.

(This figure is in colour only in the electronic version)

23.3 GPa. The volume reduction by 37.5% had no molecular dissociation. The value of the bulk modulus $B_0$ was obtained as 9.3 GPa by fitting to a Vinet-type equation of state [10].

Iodine atoms in the $C_6O_2I_4$ crystal are arranged as shown in figure 1. Pressure changes in intramolecular and intermolecular I–I distances up to 23.3 GPa are shown in figure 2. The crystal structure of $C_6O_2I_4$ maintains the $P2_1/c$ symmetry at pressures lower than the insulator-to-metal transition point; four iodine atoms on the molecule remain at the same level while the intramolecular I–I distances shrink with increasing pressure. The intermolecular I–I distances of $C_6O_2I_4$ monotonically decrease upon pressurization up to 23.3 GPa. Such behaviours of intramolecular and intermolecular I–I distances are different from those of $C_6I_6$ [6, 7]. The molecular form of $C_6I_6$ is not planar even at 1 atm and pressurization causes six iodine atoms to be suspended from an average plane of the molecule. The intermolecular I–I distances indicate complicated pressure changes induced by the variation of the molecular orientation. Such differences are reflected in the dimension of each conductive network: a three-dimensional network of $C_6O_2I_4$ and a two-dimensional network of $C_6I_6$.

(a)

(b)
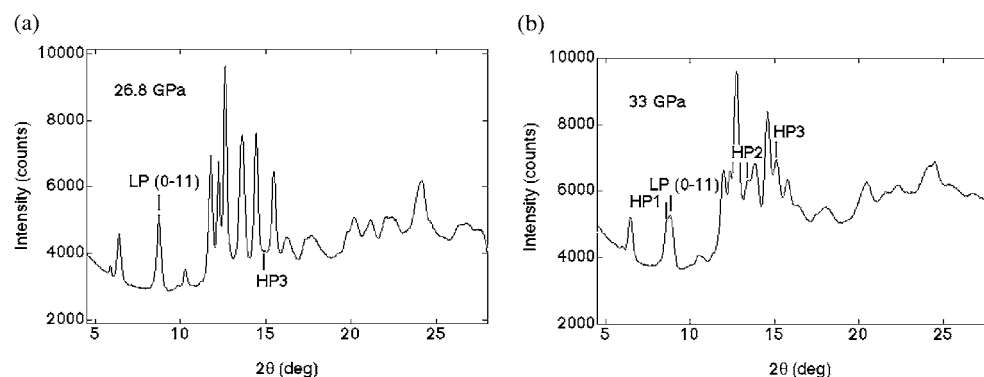


**Figure 3.** X-ray diffraction patterns of $C_6O_2I_4$ obtained at 26.8 (a) and 33 GPa (b) at room temperature. HP1, 2, and 3, labelled in (a) and (b), are the peaks observed in the HP phase.

X-ray diffraction patterns of $C_6O_2I_4$ obtained at 26.8 GPa and 33.0 GPa are shown in figure 3. New peaks appeared at pressures above 26.8 GPa, as shown in (a). LP phase reflections became weaker above 30 GPa and new reflections, which were observed in a HP phase and were marked as HP1, 2, and 3, appeared. The peak HP1 appeared at the shoulder of the peak coming from the $(0\bar{1}1)$ plane in the LP phase. The intensity of HP1 was enhanced with increasing pressure, and simultaneously the peak intensity of LP $(0\bar{1}1)$ decreased with increasing pressure. This indicates the existence of the mixed phase over a very wide pressure range between 26.8 and at least 39 GPa, where the insulator-to-metal transition is known to occur [1]. The crystal structure of the HP phase is unknown. Incidentally, the phase transition of $C_6I_6$ has not been confirmed yet.

The molecule of $C_6O_2I_4$ maintains its planar structure without molecular dissociation in the LP phase. The phase transition was first observed at around 26.8 GPa and room temperature.

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