

High pressure phase transitions in organic solids II: X-ray diffraction study of *p*-dichlorobenzene at high pressures

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Abstract. X-ray diffraction experiments on *p*-dichlorobenzene at high pressures show a transition at ~ 0.3 GPa, to a new phase, the diffraction pattern of which cannot be indexed on the anticipated low temperature monoclinic crystal structure. We have instead found an orthorhombic cell, very closely related to the low temperature monoclinic cell, for this new phase. This structure, which also occurs in *p*-diiodobenzene at ambient conditions, has cell constants $a = 14.02$, $b = 6.06$, $c = 7.41 \text{ \AA}$ and $Z = 4$. The space group is *Pbca*. This new phase has a non- β herring-bone structure, in contrast with the initial α phase which has a β -structure with ribbon-like arrangement of molecules, with Cl-Cl contacts of $\sim 4 \text{ \AA}$ between adjacent molecules. This implies that with pressure the halogen-halogen interaction in this compound plays a less dominant role in crystal engineering.

Keywords. High pressure; organic compounds; *p*-dichlorobenzene; phase transitions; x-ray diffraction.

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1. Introduction

Halogen-substituted aromatic organic compounds show "steering effects" where the orientation and packing of molecules are largely governed by the strongly directional intermolecular forces. It is observed that the X-X ($X = \text{halogen}$) and the C-C forces tend to steer the crystal structures of these compounds to the β -form, with ribbon-like arrangement of molecules and short X-X bonds ($\sim 4 \text{ \AA}$) while non- β structures are characterized by short C-X contacts (Desiraju 1984; Sarma and Desiraju 1985). β -structures, where a structure stabilization is achieved by the interaction of a molecule with two of its translational neighbours, are usually triclinic or monoclinic. In non- β -structures the molecules are disposed more uniformly, often in a herring-bone arrangement, and higher coordination numbers, usually six or more, emerge naturally through the C-X bonds.

The compound *p*-dichlorobenzene ($p\text{-C}_6\text{H}_4\text{Cl}_2$) is known to exist in three phases and is an ideal system for studying the role of these intermolecular forces in determining the crystal structures. At ambient conditions, *p*-dichlorobenzene is in the monoclinic α -phase (Croatto *et al* 1952) while at higher temperatures ($\sim 304 \text{ K}$), it goes to the triclinic β phase* (Jeffrey and Mc Veagh 1955; Housty and Clastre 1957; Frasson *et al* 1959). A

* It may be noted that β -structure and β -phase do not mean the same thing, and to avoid this confusion we refer to the three phases α , β and γ as I, II and III respectively.

third phase was accidentally discovered in a NQR experiment when the crystal was subjected to strain at a low temperature and a sudden shift in resonance frequency observed (Dean 1952). Subsequent NQR experiments (Dean and Lindstrand 1956; Kushida *et al* 1956) under high pressure confirmed the existence of a new phase, referred to as the γ phase, stable at room temperature at pressures greater than 0.16 GPa. However, the structure of this new phase was not determined. The existence of a phase transformation ~ 0.1 GPa was also confirmed by compressibility measurements by Vaidya and Kennedy (1971). Later, a low temperature phase was detected (Buyle Bodin 1957; Kantimati 1966; Reynolds *et al* 1972; Figure and Szwarc 1974) and because the NQR frequency lay in the same region, it was assumed that it was the same as the high pressure phase. The structure of the low temperature phase was found to be monoclinic (Fourme *et al* 1974; Wheeler and Colson 1975). *p*-dichlorobenzene has also been investigated using Raman spectroscopy under high pressure by Adams and Ekejiuba (1981). They observed a first order discontinuity in the Raman frequencies at ~ 0.15 GPa and a second order one at 0.9 GPa. The former was attributed to the I \rightarrow III* phase transition and the latter to a phase of unknown crystal structure.

Phases I and II have a β -structure, i.e., these two phases acquire stability mainly by the strong Cl-Cl bonds. In phase III, however, the C-Cl bonds are more important, and the structure is a non- β one (Sarma and Desiraju 1985). A decrease in the intermolecular distances may cause increased Cl-Cl repulsion, resulting in a change in the molecular packing from the ambient condition β -structure (phase I) to possibly a non- β -structure, with the Cl atoms of neighbouring molecules not adjacent to one another. With the possibility of altering the role of relative intermolecular forces with pressure and to clarify the structure of the high pressure phase, we studied polycrystalline *p*-dichlorobenzene under high pressure, employing x-ray diffraction technique. To our knowledge, so far, no x-ray investigation has been carried out on *p*-dichlorobenzene at high pressures.

2. Experimental

p-dichlorobenzene is the second of the series of organic compounds we have taken up for study under high pressure, using the Be gasketing technique (Vohra *et al* 1984) which has made possible the use of soft x-rays for the determination of structures of low symmetry compounds.

The sample was prepared by sublimation of commercially available 99.9% pure *p*-dichlorobenzene. The high volatility of the sample made it necessary to load it into the Be gasket and enclose it between the opposed tungsten carbide anvils very swiftly. Pressure was applied by means of a hydraulic ram (Gupta *et al* 1981) and the diffraction patterns were recorded on a diffractometer with a scan step of 0.1° using filtered Cu $K\alpha$ x-rays from rotating anode generator operating at 2 kW. The pressure-load calibration curve was determined using NaCl.

3. Results and discussion

At room pressure the diffraction pattern corresponded to phase-I ($p2_1/a$, $Z = 2$) and could be indexed on a cell with $a = 14.745$, $b = 5.84$, $c = 4.025$ Å, $\beta = 112.5^\circ$. On

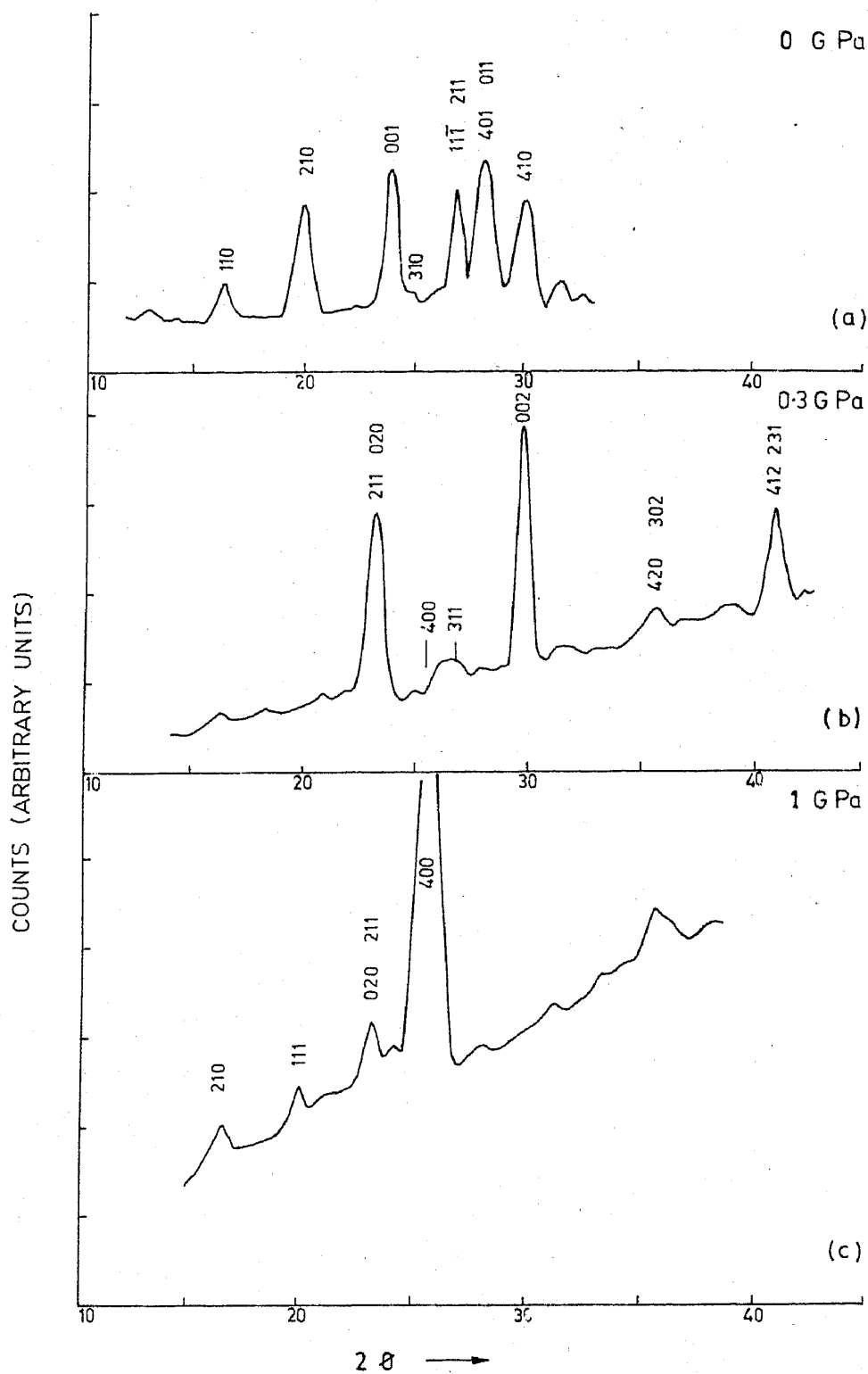


Figure 1. (a) Diffraction pattern for *p*-dichlorobenzene at room pressure (phase I) (b) at ~ 0.3 GPa (phase IV) (c) at ~ 0.9 GPa (phase IV).

applying pressure, a change was noticed in the diffraction pattern at ~ 0.3 GPa indicating a structural phase transition (figure 1). This, however, could not be indexed by any of the known phases I, II or III, or even by a mixture of these three phases. We next tried the orthorhombic structure of $p\text{-C}_6\text{H}_4\text{I}_2$, belonging to the space group $Pbca$ (Hendricks 1933). The pattern could be reasonably fitted with it. The lattice constants are $a = 14.02$, $b = 6.06$, $c = 7.41$ Å. We term this as phase IV (δ -phase). This cell is very closely related to the monoclinic phase III cell of $a = 8.624$, $b = 6.06$, $c = 7.414$ Å, $\beta = 127.51^\circ$. Figure 2 shows the (010) plane of the phase III cell. By choosing a and c axes along the dotted lines, we get $a = 14.02$, $b = 6.06$, $c = 7.41$ Å, $\beta = 102.7^\circ$. Slight distortion of the cell, possibly by shear, to get $\beta = 90^\circ$, produces the orthorhombic cell of phase IV, which contains 4 molecules (as against 2 molecules per cell in phases I and III). In view of the close relation between cells of phases III and IV, it is possible that indirect experiments like NQR and compressibility may find it difficult to discriminate between the two. The diffraction pattern changed once again at about 0.9 GPa. It contained one prominent reflection along with a few weak ones. This change was, however, found to be the effect of the texture of the sample as structure IV was adequate for indexing the pattern (Figure 1c).

It may be noted that p -diiodobenzene, has a non- β -structure. Thus under pressure we have a non- β -structure for p -dichlorobenzene which is not the same as the anticipated phase-III structure. Since isoelectronic substances have a similar sequence of structures, it is not surprising that p -dichlorobenzene also acquires the orthorhombic structure of p -diiodobenzene. The situation here is somewhat reminiscent of pressure-alloy homology rule (Kasper 1969). Further $p\text{-C}_6\text{H}_4\text{I}_2$, on application of pressure, becomes metallic at 14 GPa. Therefore the transformation in $p\text{-C}_6\text{H}_4\text{Cl}_2$ may be regarded as a first step towards metallization.

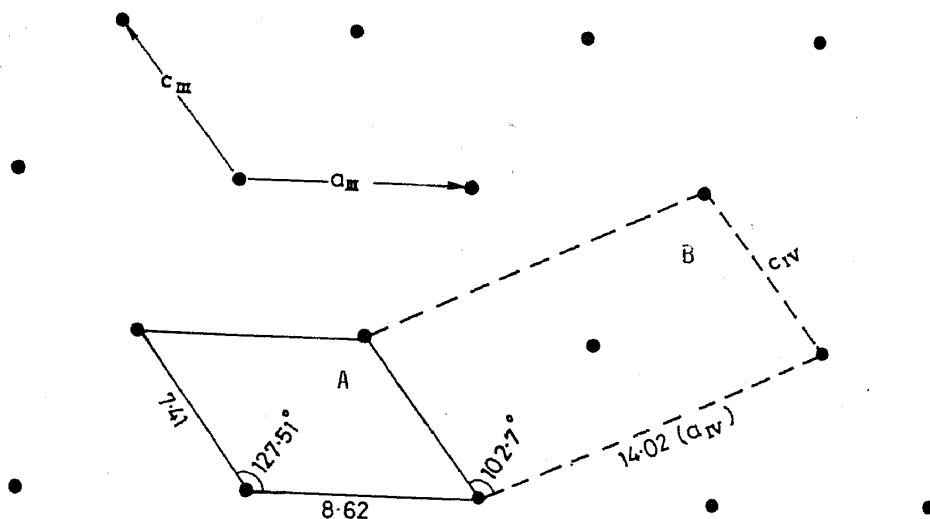


Figure 2. Relation between the cells of phases III and IV. The dots mark the lattice points in the 010 plane of the cell of III (cell A). The alternate cell (cell B) when sheared slightly gives the cell of phase IV.

References

- Adams D M and Ekejiuba I O C 1981 *J. Chem. Soc. Faraday Trans.* **77** 851
Buyle Bodin M 1957 *Geme Colloque Ampere* **10** 280
Croatto U, Bezzi S and Bua E 1952 *Acta Crystallogr.* **5** 825
Dean C 1952 Ph.D. thesis, Harvard University
Dean C and Lindstrand E 1956 *J. Chem. Phys.* **24** 1114
Desiraju G R 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 407
Figuire P and Szwarc H 1974 *Mol. Cryst. Liq. Cryst.* **27** 305
Fourme R, Clec H G, Figuire P, Ghelfenstein M and Szwarc H 1974 *Mol. Cryst. Liq. Cryst.* **27** 315
Frasson E, Garbuglio C and Bezzi S 1959 *Acta Crystallogr.* **12** 126
Gupta S C, Sikka S K, Wadhawan V K and Chidambaram R 1981 *Proc. Nucl. Phys. Solid State Phys. Symp. (DAE)* **24** 551
Hendricks 1933 *J. Chem. Phys.* **1** 549
Housty P J and Clastre J 1957 *Acta Crystallogr.* **10** 695
Jeffrey G A and Mc Veagh 1955 *J. Chem. Phys.* **23** 1165
Kantimati B 1966 *Indian. J. Pure Appl. Phys.* **4** 85
Kasper J S 1969 American Crystallographic Association **5** p. 1
Kushida T, Benedek G B and Bloembergen N 1956 *Phys. Rev.* **104** 1364
Reynolds P A, Kjems J K and White J W 1972 *J. Chem. Phys.* **56** 2928
Sarma J A R P and Desiraju G R 1985 *Chem. Phys. Lett.* **117**(2) 160
Vaidya S N and Kennedy G C 1971 *J. Chem. Phys.* **55** 987
Vohra Y K, Vijayakumar V, Godwal B K, Sikka S K and Chidambaram R 1984 *Rev. Sci. Instrum.* **55** 1593
Wheeler G L and Colson S D 1975 *Acta Crystallogr.* **B31** 911