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High pressure phase transitions in organic solids I: $\alpha \rightarrow \beta$ transition in resorcinol

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Abstract. An experimental program has been started to study polymorphic phase transitions under pressure in organic solids using the Be gasketing technique developed by us. This allows us to obtain x-ray diffraction patterns of low symmetry organic solids with high resolution, employing CuK_α radiation. The first organic solid studied is α-resorcinol. At 0·5 GPa, it transforms to its high temperature and denser modification, β-resorcinol. The transformation mechanism is discussed with the help of molecular packing calculations.

Keywords. High pressure; organic compounds; resorcinol; phase transitions.

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1. Introduction

The pioneering work of Kitaigorodskii (1959) on the systematics of the structures of molecular organic solids has convincingly shown that organic crystals are built according to the principle of close packing. This assertion means that it is possible to select sufficiently universal intermolecular radii with the help of which a certain shape may be given to a molecule. Having done this, a crystal turns out to be a close-packing of these molecules *i.e.* the bumps in one molecule enter the hollows in another (*i.e.* the adjacent molecules dovetail). The packing coefficients for a majority of the organic crystals are within 0·65 to 0·77 *i.e.* of the same order as those of the spheres. Later quantitative calculations of lattice binding energies of molecular crystals by the atom-atom potential method, taking into account van-der-Waals and electrostatic interactions etc., showed that these closed-packed arrangements correspond to the minima in the potential energy surfaces and the deepest minimum usually corresponded to the actual structure (Kitaigorodskii and Mirskaya 1961; Kitaigorodskii 1970; Williams 1966). Of course, interactions like hydrogen bond interaction which have directed specificity can sometimes lead to more open arrangements.

For polymorphic transitions in organic solids, the above principles have the following implications: (a) Other deep minima in the potential energy surface lying above the lowest minimum may represent possible transitions and (b) under change of temperature or/and pressure the relative amounts of different interactions in the molecular force field may change. Then the molecule may adopt a different conformation or the rigidity of a molecule may breakdown and the crystal may go into another close-packed configuration.

In this context, we have started a series of x-ray diffraction studies on organic solids under pressure. It may be noted that very few such investigations have so far been carried out (see Adams and Martin 1981). This may be partly attributed to the fact that these organic solids mostly crystallize in low symmetry space groups. The Bragg peaks in the diffraction pattern then overlap strongly if one uses the conventional boron gasket as sample chamber and MoK_α radiation. Recently, it has been shown that this problem may be alleviated by the use of Be gaskets in a high pressure powder diffractometer (Vohra *et al* 1984). These, besides permitting the use of a liquid pressure transmitting medium in the sample chamber giving rise to hydrostatic pressure conditions, allow the use of softer x-ray radiations. For example, the use of CuK_α radiation gives a clear $2\theta = 0$–$50°$ range, *i.e.* without interference from Be gasket lines, for recording the diffraction pattern with much higher resolution.

The first organic solid chosen by us is resorcinol (p–$C_6H_4(OH)_2$) At ambient conditions, it crystallizes in the α-phase, space group $Pna2_1$ with $a = 10{\cdot}53$, $b = 9{\cdot}53$ and $c = 5{\cdot}66$ Å and $Z = 4$ (Robertson 1936).

2. Experimental

The present experimental studies were done using angle dispersive x-ray diffraction along with an opposed tungsten carbide (WC) anvils high pressure cell mounted on a diffractometer, employing a NaI(Tl) scintillation detector (Gupta *et al* 1981). The x-ray source is a rotating Cu anode (GX 20) ($\lambda = 1{\cdot}5418$) (Marconi Avionics, UK) of focal spot $0{\cdot}2 \times 0{\cdot}2$ mm with a total power loading of 2 kW.

The Be gaskets (3 mm diameter, 0·25 mm thickness with a 0·65 to 0·7 mm hole at the centre for the sample) employed as sample containers were fabricated by the spark erosion technique from a 99·9 % pure Be foil. Powdered resorcinol (> 99 % purity) was packed into the hole and the anvil then loaded onto the high pressure cell. However, a liquid pressure transmitting medium could not be used, as resorcinol is soluble in 4 : 1 methanol-ethanol mixture or water. The non-hydrostatic effects are however, expected to be small in organic samples. The diffraction patterns were recorded using a conventional step scan method with 0·1° step. The pressure corresponding to a given press load (oil pressure) was read from a calibration curve obtained from NaCl diffraction runs at different oil pressures along with Decker's equation of state (Decker 1966).

3. Results and discussion

Figure 1 shows the diffraction pattern at room pressure. All the peaks could be assigned to the unit cell for the α-phase. At 0·5 GPa, the diffraction pattern changed completely (see figure 2). The diffraction lines could now be indexed according to the high temperature form β-resorcinol cell (space group $Pna2_1$, $Z = 4$) with $a = 7{\cdot}75(3)$, $b = 12{\cdot}43(5)$ and $c = 5{\cdot}44(2)$ ($V = 524$ A^3/cell). These unit cell parameters may be compared with those obtained by Robertson and Ubbelhode (1938) at ambient conditions: $a = 7{\cdot}91$A, $b = 12{\cdot}57$A, $c = 5{\cdot}50$A ($V = 547$ A^3). The phase change $\alpha \rightarrow \beta$ is a first order transition with $\Delta V/V_0 \sim 2\,\%$. Further compression up to 2 GPa, revealed no further phase transitions from the β-resorcinol structure. On release of pressure,

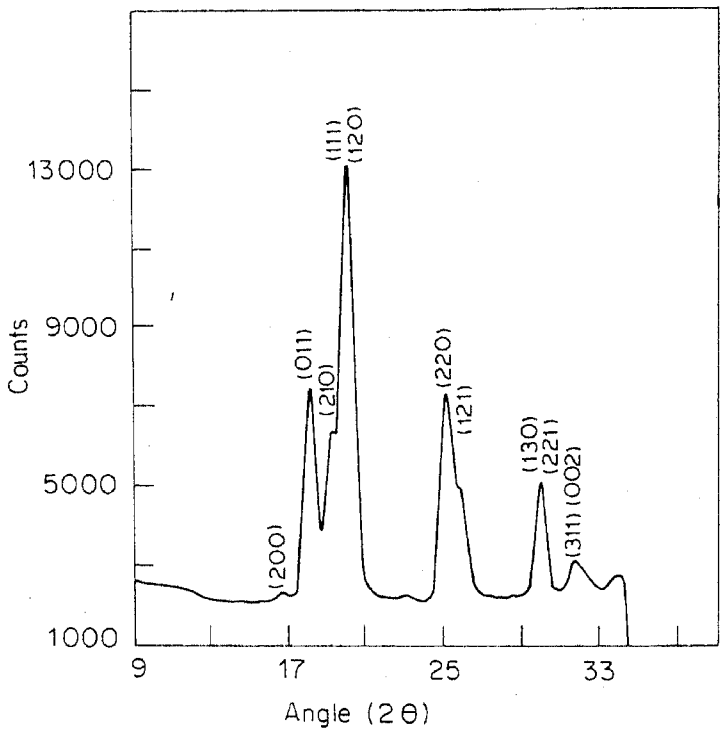

Figure 1. The diffraction pattern of α-resorcinol at ambient conditions (λ = 1·5418 Å).

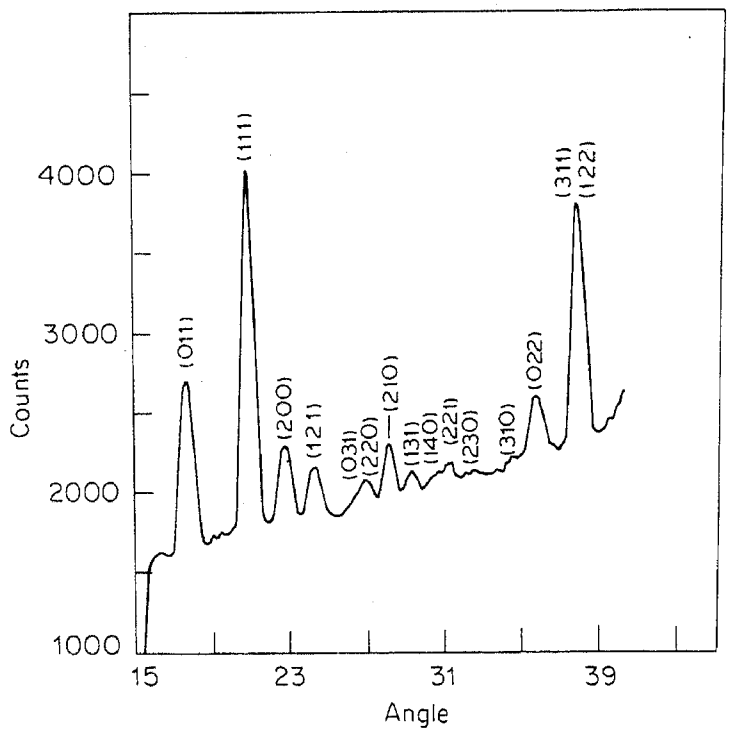

Figure 2. The diffraction pattern of resorcinol at 0·5 GPa, indexed as β-resorcinol.

Table 1. Molecular orientation parameters and energies of α and β resorcinol at $T = 0$ K and zero pressure.

	α-resorcinol	β-resorcinol
E^*_{NB}	−10·43 kcal/mole	−11·12 kcal/mole
E_{HB}	−10·51	−10·07
Euler angles† ϕ, θ and ψ at predicted energy minimum	140, 58, −103	106, 53, −117
Experimental	140, 62, −103	99, 51, −116

* E_{NB} = non-bonded energy due to van-der-Waals interactions, E_{HB} = energy for hydrogen bonds. These were calculated as described in the text.
† ϕ, θ and ψ are Euler angles to bring the molecular axes into coincidence with the crystal axes *a*, *b* and *c*. When $\phi = \theta = \psi = 0$, the resorcinol carbon skelton lies in the *ab* plane.

hysterises was observed. The β-phase remained stable for two days at room pressure before back-transforming to the α-phase. The diffraction patterns during the pressure release were highly effected by texture in the sample compared to the ones during the pressure increase.

The $\alpha \rightarrow \beta$ transition under pressure was not entirely unexpected as the high temperature β-phase was known to be denser. At high pressure, resorcinol adopted another closed-packed structure whose packing fraction is a little higher (0·665 and 0·678 for the α and β phases according to Kitaigorodskii 1959). The structural relationship between α and β forms of resorcinol has been described by Robertson and Ubbelhode (1938). The resorcinol molecule which is planar in the α-phase, distorts, so that the oxygen atoms deviate from this plane and rotates as a whole about the *c*-axis. This rotation about the *c*-axis is more transparent from the values of Euler angles ϕ, θ and ψ, given in table 1 for the resorcinol molecule configurations in the two forms. Robertson and Ubbelohde (1938) found a small heat of transition 0·22 kcal/mole, for the $\alpha \rightarrow \beta$ change. They speculated that the more open structure in α-resorcinol had a lower van-der-Waals energy but a larger hydrogen bond energy contribution than the β-form. This is supported (table 1) by molecular packing calculations using the PACK program (Sikka and Chidambaram 1972) where van-der-Waals interactions were summed up to distances of 15Å using Kitaigorodskii type of non-bonded potential functions and the hydrogen bonds were taken care of by the modified form of the Lippincott-Schroeder potential function for bent hydrogen bonds (Chidambaram and Sikka 1968). It may also be noted that the calculated molecular orientation angles are in excellent agreement with the experimental ones for the two cases.

To summarise, pressure distorts and rotates the resorcinol molecule so as to increase the van-der-Waals energy and decrease the hydrogen bond energy contribution to the total energy, culminating in the $\alpha \rightarrow \beta$ transition.

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