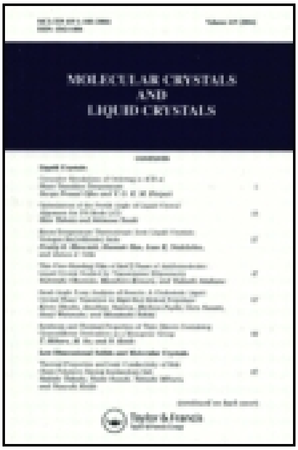

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Aspects of the Polymorphic Phase Transformation in p-Diiodobenzene

L. J. Soltzberg [a] , E. C. Armstrong [a] & P. A. Kelly [a]

[a] Department of Chemistry, Simmons College, Boston, Massachusetts, 02115, U.S.A.

Version of record first published: 21 Mar 2007.

To cite this article: L. J. Soltzberg , E. C. Armstrong & P. A. Kelly (1979): Aspects of the Polymorphic Phase Transformation in p-Diiodobenzene, Molecular Crystals and Liquid Crystals, 50:1, 179-181

To link to this article: http://dx.doi.org/10.1080/15421407908084425

Mol. Cryst. Liq. Cryst., 1979, Vol. 50, pp. 179–182

Printed in Holland

Aspects of the Polymorphic Phase Transformation in *p*-Diiodobenzene

L. J. SOLTZBERG, E. C. ARMSTRONG, and P. A. KELLY

Department of Chemistry, Simmons College, Boston, Massachusetts 02115, U.S.A.

(*Received June 16, 1978*)

Interest in solid *p*-diiodobenzene has focused on the characterization and properties of the material before and after the phase transformation at around 51 °C and, more recently, on the nature of the transformation itself. Our initial attention was drawn by the discovery by Schwartz. *et al.*,[1] that the hole carrier mobility of the photoconductive room temperature material drops sharply in the vicinity of 50°C.

In an earlier thermodynamic study, Ueberreiter and Orthmann[2] found a molar volume discontinuity at about this temperature but detected no specific heat anomaly. (A very small latent heat has been reported more recently.)[3] These authors also pointed out that the entropies of fusion of *p*-diiodobenzene (PDI), *p*-dibromobenzene (PDB), and *p*-dichlorobenzene (PDC) are identical, implying that the degree of order—if not the detailed crystal structure—is the same in each solid at the melting point. This observation suggests the existence of non-trivial one-component phase behavior here, since PDC and PDB are monoclinic at room temperature while PDI is orthorhombic; and PDC is triclinic above 30.8°C.[4]

Along other lines, Kitaigorodskii and coworkers[5] explored the phase behavior of the binary system PDI/PDB, seeking to interpret the fact that these two similar molecules do not form isomorphous solids and, thus, do not form a continuous series of solid solutions. These investigators assigned space groups to the various phases, based on room temperature x-ray diffraction photographs, as follows: 100 % to 96 % PDI–Pbca, 94.5 % to 51.9 % PDI–Pccn, 27 % to 0 % PDI–$P2_1/a$.

There seems to be no question that PDI crystallized at room temperature is orthorhombic, space group Pbca. The presence of the phase transformation can be detected in various ways, among them by measurement of the optical thickness of crystals for light vibrating along each of the three principal vibration directions.[6] While the change in optical properties is distinct, it is noteworthy that the effect is so small that it is not detected in ordinary fusion preparations. It is also interesting that the optical thickness changes discontinuously in two vibration directions but only changes slope in the third. Measurement of birefringence seems to suggest that the transformation is reversible with hysteresis, a crystal returning quite reproducibly to its room temperature birefringence over a period of hours;[7] as will be seen, this indication is at variance with recent x-ray diffraction results.

The foregoing observations would be consistent with a first order transformation between two energetically similar structures. Indeed, preliminary x-ray diffraction photographs seemed to indicate that the "high temperature form" of PDI was an orthorhombic lattice of space group Pccn. It is intriguing that perturbation of the PDI lattice by small to moderate amounts of PDB does result in a change to space group Pccn at room temperature.[5] A transformation between two well-defined structures is also suggested by the passage of a sharp phase boundary which we sometimes observe in PDI crystals undergoing the transformation.

Higher quality diffraction photographs, however, have revealed that the systematic absences required by space group Pccn are not rigorously observed. More surprising has been our observation that a variety of distinctly different diffraction patterns are obtained over a period of time, the rate of change depending on the temperature at which the crystal is held. What appeared initially to be a straightforward process now seems to be a much more involved sequence of events, characterized so far as follows. Starting from room temperature space group Pbca:

1) a crystal of PDI raised to the transition temperature initially undergoes a rapid transformation to another orthorhombic space group:
   a) an unambiguous structural effect of this first step is the loss of the b-glide plane normal to the a-axis;
   b) this step is also accompanied by a slight lengthening of the b-axis, approximately sufficient to account for the molar volume increment observed by Ueuberreiter and Orthmann.[2]

2) once transformed, a crystal held at room temperature for up to a month does not re-establish the lost glide plane

3) if held 1° to 3° above the transition temperature over a period of 20 hours, the crystal then
   a) loses the a-glide plane and b-screw axis;
   b) 0kl net loses mm diffraction symmetry; some reflections show doubling

c) doubling disappears, mm symmetry returns, b-axis is shorter by about 0.5 Å; this diffraction pattern remains stable over a period of eight hours at elevated temperature; space groups consistent with systematic absences are Pma2, $Pmc2_1$, Pmma

4) if the crystal, after the initial transformation, is held 10° below the transition temperature, the same sequence of events occurs as described in 3) above, but more slowly.

It seems unlikely that PDI would crystallize in a non-centrosymmetric space group. Thus, Pmma seems to be the probable candidate corresponding to the best defined of the high temperature diffraction patterns so far observed. For PDI to crystallize in this space group with the molecules occupying centers of symmetry would require disorder in the molecular orientation. This leads to a tentative model of the transformation processes in which room temperature PDI first undergoes a rapid displacive transformation to another ordered lattice (perhaps Pccn). This new lattice is then subject to a gradual disordering which, over a period of time, results in the disordered form characterized above.

In view of the foregoing, it seems unlikely, though not impossible, that PDI is in space group Pbca at the melting point. The transformation observed here might also take place in PDI/PDB mixed crystals containing predominantly PDI. Thus, it may be that the phase behavior of the PDI/PDB binary system is even richer than has been thought previously. Alternatively, if Kitaigorodskii is correct that lattice voids created by the presence of PDB molecules in the PDI lattice interfere with the propagation of thermal waves,[5] then it is possible that small amounts of PDB stabilize the Pbca lattice against destruction by a soft lattice vibration. While a recent examination of eleven Raman-active lattice modes in PDI did not show evidence of softening,[3] such a mechanism should not be ruled out of the complex of events associated with the PDI transformation.

Acknowledgments

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Simmons College Fund for Research for support of this work.

References

1. L. M. Schwartz, H. G. Ingersoll and J. F. Hornig, *Mol. Cryst.*, **2**, 379 (1967).
2. K. Ueberreiter and H. Orthmann, *Z. Naturforsch. Teil*, **A5**, 101 (1950).
3. S. P. Cramer, B. Hudson and D. M. Burland, *J. Chem. Phys.*, **64**, 1140 (1976).
4. J. Housty and J. Clastre, *Acta Cryst.*, **10**, 695 (1957).
5. A. I. Kitaigorodskii and L. Dun-Chai, *Kristallografia*, **5**, 238 (1960). See also "Molecular Crystals and Molecules," A. I. Kitaigorodskii, (Academic Press 1973), pp. 110–114.
6. L. J. Soltzberg, M. W. Athearn, J. E. Levy and E. L. Simpson, *Appl. Optics*, **16**, 3206 (1977).
7. L. J. Soltzberg, B. M. Ash and P. C. McKay, *Mol. Cryst. Liq. Cryst.*, **21**, 283 (1973).