



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

Transmission Electron Microscopic Study of the Low Temperature Phase Transformation in Pyrene

William Jones^a

^a Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel

Version of record first published: 20 Apr 2011.

To cite this article: William Jones (1977): Transmission Electron Microscopic Study of the Low Temperature Phase Transformation in Pyrene, *Molecular Crystals and Liquid Crystals*, 41:4, 103-107

To link to this article: <http://dx.doi.org/10.1080/01406567708071962>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

TRANSMISSION ELECTRON MICROSCOPIC STUDY OF THE LOW TEMPERATURE PHASE TRANSFORMATION IN PYRENE

WILLIAM JONES^{†*} and MENDEL D. COHEN
 Department of Structural Chemistry,
 The Weizmann Institute of Science,
 Rehovot, Israel.

(Submitted for Publication November 14, 1977)

Transmission electron microscopy has been utilized to study the low temperature phase transformation in pyrene. The transformation proceeds via an interface, lying on approximately (110) planes, and is similar to the martensitic-like transformation seen in other organic crystals. Domains of the room temperature phase are still present at temperatures 100 K below the transition temperature.

It has now been firmly established that pyrene undergoes a phase transformation when either cooled to temperatures close to 120 K or subjected to pressures of 4.0 K bar at room temperature (1).

Despite the importance attached to pyrene as a model for studying various spectroscopic phenomena, little is known about the low temperature phase or of the structural aspects of the phase transformation. The determination of the low temperature structure by X-ray analysis is complicated by the extensive cracking that occurs when single crystals are cooled to temperatures below the transition temperature. Renaud (2), however, has recently established the unit cell parameters of the low temperature structure (see Table 1).

TABLE 1: Cell parameters for the high and low temperature phases of pyrene.

	a (Å)	b (Å)	c (Å)	α	β	γ	v (Å ³)
293 K	13.63	9.25	8.48	89.92	100.42	89.99	1052
98 K	12.31	10.02	8.26	90.02	96.69	89.93	1013

[†] Jacob London Fellow

* Present address: Edward Davies Chemical Laboratories
 University College of Wales, Aberystwyth SY23 1NE, U.K.

We have already shown that transmission electron microscopy (TEM) may be used (despite the inherent instability of these organic specimens in the electron beam (3)) to great advantage as a technique for studying a variety of phenomena in organic molecular crystals (4). In particular, phase transformations, hitherto unsuspected, have been observed and fully characterized by utilizing the powerful combination of transmission microscopy and electron diffraction (5,6). Because of this proven success we were lead to believe that direct information on the phase transformation in pyrene might be obtained by TEM..

Thin crystals, (001) dominant, were grown by the floatation method, the solvent used in this instance being ether. Suitable samples (thickness less than ca 5000 Å) were examined in a Philips EM300, which has facilities for cooling the specimen to approximately 100 K.

On cooling the specimen to temperatures close to 110 K, faults, the traces of which ran approximately along $[110]$, were seen to appear (Figure 1a). These faults disappear when the foil is warmed to temperatures estimated to be near 140 K. They reappear on cooling (but not always in the same position) and provided the critical radiation dose has not been exceeded the process may be repeated several times. Selected area diffraction patterns taken over one of these faulted regions reveals two overlapping diffraction meshes (Figure 1b), one of which is interpretable in terms of the room temperature structure. The second mesh, rotated relative to the first by an angle of 4° , has the values of 12.4 and 10.2 Å for the dimensions of the most probable unit cell. These values are in good agreement with the values for d_{100} and d_{010} calculated using the unit cell parameter given by Renaud (see Table 1). In order to ascertain whether the transformation would be complete at much lower temperatures we were granted access to a liquid helium cooled microscope (courtesy of Dr.M.J. Goringe, Oxford University) which allows cooling of the specimen to near 10 K. It was found that even at these low temperatures domains of the room temperature structure were still present.

The results given here provide direct evidence for, and some information on, the solid-solid phase transformation in pyrene. Some interesting points arising are:

- a) The orientational character of the faults bears resemblances to those seen in the stress-induced phase transformation in 1,8-dichloro-10-methylantracene reported previously. It was shown that in this latter material the transformation is martensitic in character, being induced at high and low

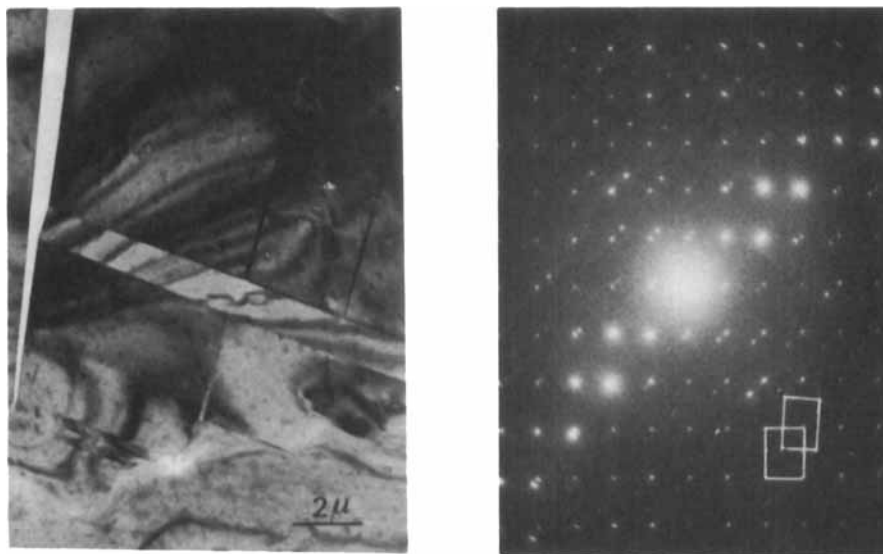


FIGURE 1: a) Electron micrograph taken at 110 K. A diffraction pattern (b) taken from such an area indicates the presence of both the high and low temperature forms.

temperatures. It is possible that in the case of pyrene the cooling of the sample may have produced sufficient stress to drive the transformation. This is in agreement with the observation that crystals of pyrene invariably crack upon cooling and also that the transformation may be induced upon application of pressures of 4.0 Kbar (1). Furthermore, close inspection of the diffraction pattern in Figure 1b shows coincidence of the 430 reflections from the two phases. This suggests similar interplanar spacings for the 430 planes in the low and high temperature structure and the calculated values using Renaud's results are in complete agreement with this: $d_{430} = 2.25 \text{ \AA}$ and 2.26 \AA for the room and low temperature structure respectively.

b) The changes in the cell parameters are quite small and suggest that the pairwise packing of the pyrene molecules is maintained through the transition. This is compatible with the knowledge that both forms give excimer emission. We are, at present, attempting to calculate, by atom-atom potential calculations (e.g. ref 7), the three dimensional structure of the low temperature phase.

c) It is interesting that even at temperatures well below the transition temperature small domains of the room temperature form are still present. The presence of such incipient phases may play an important role in the generation of deformation mechanisms and also in certain photophysical and photochemical effects not only in pyrene but also in other organic molecular crystals where similar phase changes occur.

Finally, it should be mentioned that a third crystal form of pyrene is frequently obtained from ether solution. This polymorph (which has a very different crystal structure to either of the excimer pyrene phases) exhibits monomer fluorescence similar to that observed by Mansour and Weinreb (8) and despite repeated attempts has not been found to undergo a similar phase transformation.

ACKNOWLEDGEMENTS

The authors are extremely grateful to Dr. M. Renaud for the information contained in Table 1 and W.J. is grateful to the Weizmann Institute for the award of a Weizmann Fellowship. Mr. Mansell Davies is thanked for the purification of the pyrene.

REFERENCES

1. R. Zallen, C.H. Griffiths, M.L. Slade, M. Hayek and O. Brafman, Chem.Phys.Letts., **39**, 85 (1976) and references therein.
2. M. Renaud, private communication.
3. W. Jones, Surface and Defect Properties of Solids, **5**, 65, (1976).
4. W. Jones, J.M. Thomas, J.O. Williams and L.W. Hobbs, J.C.S. Faraday II, **71**, 138 (1975)
5. W. Jones, J.M. Thomas and J.O. Williams, Phil.Mag., **32**, 1 (1975).

6. G.M. Parkinson, W. Rees, M.J. Goringe, W. Jones, S. Ramdas, J.M. Thomas and J.O. Williams, 50th Anniversary of the Discovery of Electron Diffraction, Institute of Physics, London, 1977.
7. S. Ramdas and J.M. Thomas, J.C.S. Faraday II, 72, 1251 (1976)
8. S. Mansour and A. Weinreb, Mol.Cryst. and Liq.Cryst., 27, 111 (1974).