X-RAY EXAMINATIONS OF ACENAPHTHENE, FLUORANTHENE AND PYRENE CRYSTALS GROWN FROM SOLUTIONS

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ABSTRACT

Orientation and morphology of acenaphthene, fluoranthene and pyrene crystals grown from six-halogen derivative solvents have been determined by X-ray methods and optical goniometry. Rietveld analysis showed a good agreement between experimental and theoretical structural data. It was found that the quality of intrinsic structure of these crystals is dependent on the solvent from which they are grown.

INTRODUCTION

Policyclic aromatic hydrocarbons which contain rigid aromatic molecules belong to the most intensively investigated class of organic crystals, both in aspect of preparation materials of high purity and growth of perfect crystals [1].

Increasing interest in this class of crystals arose from their potential applicability as low cost photoconductors and scintillators, and, on the other hand, from their importance in understanding of the basic physical processes such as, for example, charge carrier transport properties.

It has been well known for some time that the habit and the intrinsic structure of molecular crystals depend on the solvent from which they are grown. As it was observed for other molecular crystals, solvent may often

incorporate on a molecular and on a macroscopic scale, forming inclusions.

This work is concerned with characterization by X-ray diffraction of the intrinsic structure of three typical representatives of organic molecular crystals, the aromatic hydrocarbons acenaphthene, fluoranthene and pyrene, grown from solutions in same halogen derivative solvents.

The investigations presented here are part of larger studies dedicated to the problems of growth and characterization of homologous series of aromatic hydrocarbons, which are carried out in our laboratory.

EXPERIMENTAL

Acenaphthene, fluoranthene and pyrene (Sigma Aldrich) were prepurified by recrystallization from benzene and ethyl alcohol and then vacuum sublimation was used to remove solvent contaminants.

After vacuum sublimation, the major part of the impurities was removed by an initial zone refining step, consisting of 100 zones passed across the material tubes at a speed of 10mm/h. Then the upper portions of the ingots were mixed and further zone refined for another 100 passages with the rate of zone passes 2.3mm/h.

The solvents, *i.e.* chloroform (CHL), 1,1-dichloroethane (1,1-dCHLE), 1,2-dichloroethane (1,2-dCHLE), trichloroethylene (tri-CHLE), tetrachloroethylene (tetra-CHLE) and tetrachloromethane (CCl_4) were all dehydrated with anhydrous sodium sulfate and then distilled in a packed column of 1m height at large reflux ratio.

The crystals were grown using the method worked out particularly for easily evaporating solution described previously [2].

First stage of X-ray examinations of obtained crystals comprising their lattice constants, symmetry and quality, was carried out by means of Laue and the rotation methods (camera RKD-86, Mo) radiation and using Weissenberg method (camera RGNS-2, Cu - radiation).

Further examinations were performed on polycrystalline samples using powder diffractometer DRON-3 (Cu k_α - radiation). Difraction data were collected in the 2Θ range 8 - 60° with 2Θ steps of 0.02° and step times 8 – 20 s.

Furthermore, crystallographic orientation and identification of faces as well as growth direction of crystals were determined from X-ray examinations and by optical goniometry, using optical reflection goniometer ZRG-3.

RESULTS AND DISCUSSION

The X-ray powder patterns of acenaphthene, fluoranthene and pyrene samples were in good agreement with theoretical profiles, calculated using atom coordinates from literature data [3-5]. The lattice parameters of these crystals were refined by Rietveld full profile analysis. All calculations were performed using Crystal Structure Determination (CSD) software.

Examplar experimental, calculated and difference diffraction profiles after the Rietveld refinement of acenaphthene crystal grown from 1,2-dCHLE are shown in Fig.1.
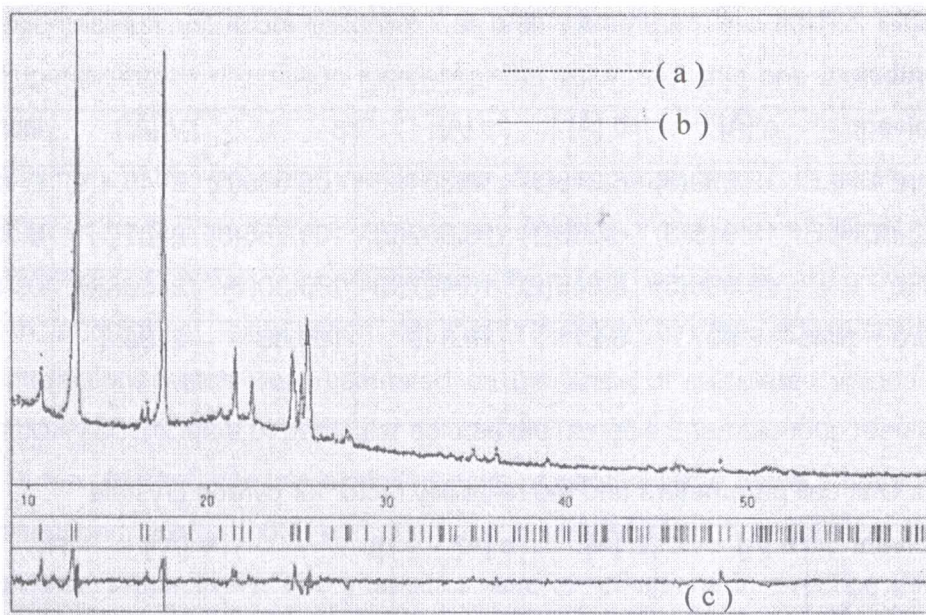
Fig.1 Diffractograms of acenaphthene crystals;
(a) experimental, (b) theoretical, (c) differential

The refine unit cell parameters and the reliability factor R for acenaphthene, fluoranthene and pyrene crystals are summarised in Tables 1, 2 and 3, respectively.

Table 1. Unit cell parameters and the reliability factor for acenaphthene crystals

No	Solvent	a [Å]	b [Å]	c [Å]	V [Å³]	R
1	tri-CHLE	8.286(1)	13.990(3)	7.222(1)	837.2(4)	0.111
2	1,1-dCHLE	8.289(2)	14.004(5)	7.223(2)	838.5(7)	-
3	1,2-dCHLE	8.291(1)	14.009(3)	7.231(1)	839.9(5)	0.139
5	CCl₄	8.287(2)	14.027(4)	7.230(1)	840.5(5)	0.127
6	CHL	8.292(2)	14.013(3)	7.239(1)	841.1(5)	0.121
Literature data [3]		8.290	14.000	7.225	838.5	-

Table 2. Unit cell parameters and the reliability factor for fluoranthene crystals

No	Solvent	a [Å]	b [Å]	c [Å]	β	V [Å³]	R
1	tetra-CHLE	19.899(3)	6.246(1)	18.364(2)	109.665(6)	2149.4(9)	0.133
2	1,2-dCHLE	19.915(3)	6.238(1)	18.397(2)	109.755(8)	2151(1)	0.138
3	CHL	19.936(5)	6.245(2)	18.407(3)	109.80(1)	2156(2)	0.150
Literature data [4]		19.907	6.211	18.349	109.86	2133.8	-

Table 3. Unit cell parameters and the reliability factor for pyrene crystals

No	Solvent	a [Å]	b [Å]	c [Å]	β	V [Å³]	R
1	$\sigma = 34\%$, T = 311K	13.645(2)	9.253(1)	8.469(1)	100.244(8)	1052.3(4)	0.104
2	$\sigma = 41\%$, T = 313K	13.656(2)	9.268(1)	8.467(1)	100.335(9)	1053.1(5)	0.108
3	$\sigma = 41\%$, T = 311K	13.652(2)	9.258(1)	8.479(1)	100.338(9)	1054.2(5)	0.130
Literature data [5]		13,6490	9.2560	8.4700	100.280	1052.9	-

One can notice from Table 1 and 2 that the unit cell dimensions increase in the following order of solvents: tri-CHLE, 1,1-dCHLE, 1,2-dCHLE, CCl₄ and CHL for acenaphthene and tetra-CHLE, 1,2-dCHLE and CHL for fluoranthene. The width half-value of reflections and their asymmetry increase in the same order, what was observed on registered diffractograms of both substances.

In the case of pyrene the crystals were obtained only from tri-CHLE solution, because other investigated solvents did not yield good crystals . As it can be seen from Table 3, the least volume of unit cell are exhibited

by pyrene crystal obtained at less supersaturation $\sigma = 34\%$. When supersaturation of solution increases, the volume of this one increases, too.

Basing on the obtained results one can suppose that the quality of intrinsic crystal structure expressing by volume of the unit cell for all the investigated crystals depends on the solvent from which they are grown.

An attempt of explanation of this influence by the solute-solvent interactions which were estimated on the basis of calculated values of activity coefficients of particular solutes did not give unambiguous results.

All the obtained crystals exhibited pairs of parallel large faces oriented in directions: [0k0], [h00] and [00l] for acenaphthene, fluoranthene and pyrene, respectively. The intensities ratio of reflections in direction [0k0] with $k = 2n$ were the following: $I_{020} : I_{040} : I_{080} : I_{0100} : I_{0120} = 1000 : 150 : 50 : 4 : 25$. For pyrene in direction [00l] this ratio was $I_{001} : I_{002} : I_{003} : I_{006} : I_{007} = 1000 : 150 : 2 : 1 : 5$. The growth directions gathered in Table 4 were also confirmed by texture analysis as a preferred orientation of crystallites at the Rietveld refinement. Texture parameters were 0.538(8) for acenaphthene and 0.661(7) for pyrene.

A typical morphology of acenaphthene, fluoranthene and pyrene crystals and their orientation are shown in Table 4.

Table 4. Morphological characterization of crystals

Crystal	Solvent	Growth direction	Miller indices		Habit	Space group
			Major face	Side face		
Acenaphthene	CHL	[010]	(010), $(0\bar{1}0)$	$\{110\},\{100\}, \{11\bar{1}\}$	Columnar	$Pcm2_1$
Fluoranthene	tetra-CHLE	[100]	(100), $(\bar{1}00)$	(001), $(\bar{1}0\bar{1})$, $(\bar{1}03)$, $\{\bar{1}12\}$	Columnar	$P2_1/n$
Pyrene	tri-CHLE	[001]	(001), $(00\bar{1})$	$\{110\}$, $\{20\bar{1}\}$	Tabular	$P2_1/a$

CONCLUSIONS

The reliability factor R determined by Rietveld method is insignificantly larger than 15% only in the case of fluoranthene crystal grown from CHL. Therefore, one can assume that for other crystals the structures were determined correctly. It may also be assumed from a comparison of the volume of unit cells that its increase is caused by influence of solvent; however, investigated hydrocarbons possessed the same purity and moreover, the presence of impurities was reduced by careful purification process including zone refining method.

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