

X-ray Diffraction Study of Organic Mixed Crystals

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Pyrene doped anthracene organoluminophors formed solid solutions. Pyrene in anthracene shows point defects and can be analysed by X-ray studies. Study of these defects is very significant in solid state devices.

Key words: XRD, organic mixed crystals, pyrene, anthracene.

INTRODUCTION

The indexing of X-ray diffraction patterns of monoclinic system is a very difficult job. The present paper reports the approximate method for indexing a monoclinic organic system, pyrene doped anthracene and also the effect of addition of pyrene impurity on the X-ray diffraction (XRD) patterns of anthracene. X-ray diffraction patterns of pure anthracene and anthracene with varying amounts of pyrene show the formation of mixed crystals. The intensity of peaks was found to decrease by the addition of guest impurity pyrene.

The addition of pyrene as an impurity in anthracene creates point defects in the crystal and the system is described as solid solution. The evidence for defect structure has been provided by X-ray diffraction studies of pyrene doped anthracene luminophors. The XRD patterns of luminophors are taken and indexed on the basis of monoclinic unit cell. The decrease in intensity of reflections and presence of additional lines on the XRD pattern indicate that the equivalent positions in the anthracene lattice are occupied by pyrene molecules.

EXPERIMENTAL

Polycrystalline crystals of anthracene and pyrene doped anthracene have been prepared. An increase in intensity of anthracene fluorescence by the addition of pyrene was reported by Patil and Kulkarni.¹ The present paper reports the structural studies of anthracene and pyrene doped anthracene mixed crystals.

Anthracene and pyrene were purified separately by the process of adsorption column chromatography. Mixed powder systems containing 10^{-2} and 10^{-1} mole of pyrene per mole of anthracene were prepared. The calculated amounts of anthracene and pyrene were intimately mixed and heated in silica crucibles at 217°C to get melt.² The melt was cooled slowly in an evacuated chamber. The mixed crystals were crushed to fine powder. Powder X-ray diffraction patterns were registered at the rate of 0.1 (2 θ) min⁻¹ by means of Philips PW 1710 diffractometer with PW 1725 generator using Cu LFF $k\alpha$ radiation in University Science Instrumentation Centre at Kolhapur (M.S.), India.

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RESULTS AND DISCUSSION

Optical properties are related with the structure of compounds. Pyrene and anthracene are crystallographically similar and are monoclinic space lattices. The molecular packings in these crystals are governed by atom-atom potentials and sandwich pairs of molecules are formed. Thus, if impurity and basic compound possess similar structures, the impurity may be incorporated in the basic compound to form mixed crystals.³ Figs. 1 (a), (b) and (c) shows the X-ray diffraction patterns of pure anthracene and pyrene doped anthracene mixed crystals. The patterns show many more reflections indicating that mixed crystal systems formed by cooling melt of two components have more regular arrangement of molecules in the unit cell. The lines on the XRD patterns were indexed on the basis of monoclinic unit cell for which the values of lattice constants are available in literature.⁴

For anthracene, the cell data are $a = 8.58$, $b = 6.02$, $c = 11.18$ Å and $\beta = 125^\circ$.

Pyrene is a low symmetry monoclinic crystal and the cell data are $a = 13.649$, $b = 9.256$, $c = 8.470$ Å and $\beta = 100.28^\circ$.

The expected values of $\sin^2 \theta$ for the various reflections are calculated from

$$\sin^2 \theta = \frac{\lambda^2}{4 \sin^2 \beta} \left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \right]$$

(where h , k , l are the miller indices) were compared with the observed values. The expected values of $\sin^2 \theta$ and the observed values (XRD) are listed in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA OF ANTHRACENE

Peak No.	2 θ (deg)	d-values (Å)	$\sin^2 \theta$ (XRD)	$\sin^2 \theta$ (calculated)	hkl	Relative intensity (I/I _{max})
1.	21.325	4.1633	—	—	(100)	55.69
2.	25.990	3.4256	0.0505	0.0540	(111)	70.85
3.	29.155	3.0605	0.0633	0.0620	(102)	54.20
4.	29.420	3.0336	0.0644	0.0644	(320)	88.30
5.	31.260	2.8591	0.0725	0.0729	(210)	6.06
6.	32.370	2.7635	0.0776	0.0775	(201)	6.70
7.	36.810	2.4397	0.0996	0.0996	(421)	20.91
8.	39.220	2.2952	0.1126	0.1101	(120)	19.70
9.	42.120	2.1436	0.1291	0.1208	(202)	4.56
10.	43.200	2.0925	0.1355	0.1334	(310)	3.36
11.	44.655	2.0276	0.1443	0.1460	(220)	24.25
12.	45.395	1.9963	0.1488	0.1490	(301)	8.06
13.	51.965	1.7583	0.1919	0.1936	(400)	4.14
14.	53.192	1.7023	0.1999	0.1992	(314)	15.05
15.	54.315	1.6876	0.2083	0.2069	(320)	6.31
16.	56.375	1.6308	0.2231	0.2188	(222)	5.34

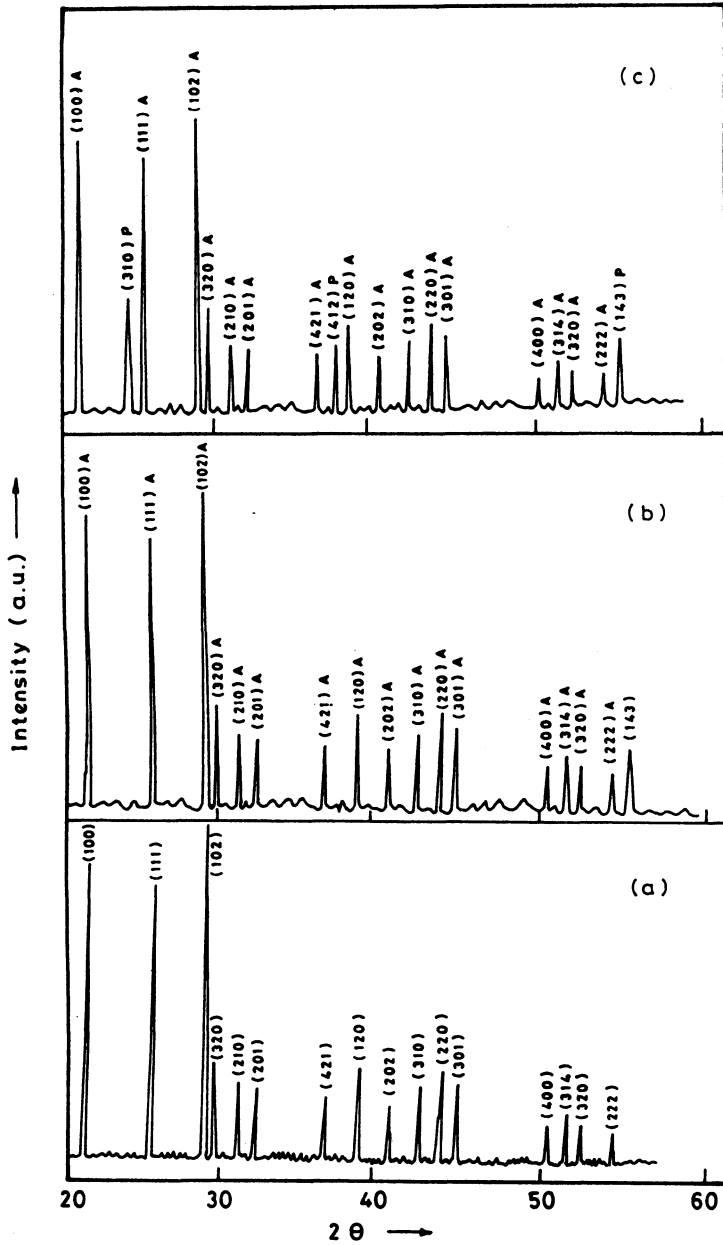


Fig. 1. X-ray powder diffraction patterns of anthracene and pyrene doped anthracene luminophors: (a) Pure anthracene; (b) 10^{-2} mole pyrene per mole of anthracene and (c) 10^{-1} mole pyrene per mole of anthracene

Observed and expected values for pyrene are shown in Table-2. The sufficient equivalence between the calculated and observed values permitted the indices of observed lines. The XRD pattern of pure anthracene was used as fingerprint to identify the reflections coming from guest pyrene molecule in the mixed crystal. Thus, the XRD patterns of mixed crystals [Figs. 1 (b) and (c)] were compared with those of pure anthracene [Fig. 1(a)].

TABLE-2
CRYSTALLOGRAPHIC DATA OF PYRENE

Line No.	2θ (deg)	d-value (Å)	$\sin^2 \theta$ (XRD)	$\sin^2 \theta$ (calculated)	hkl	Relative intensity (I/I_{\max}) (%)
1.	20.605	4.3031	–	–	(100)	4.27
2.	21.000	4.2270	0.0332	0.0318	(120)	5.74
3.	21.980	4.0407	0.0363	0.0367	(310)	6.50
4.	23.205	3.8300	0.0404	0.0417	(220)	100.00
5.	24.330	3.6554	0.0444	0.0438	(301)	34.69
6.	26.405	3.3727	0.0521	0.0526	(400)	7.55
7.	28.245	3.1570	0.0595	0.0597	(410)	51.33
8.	31.820	2.8100	0.0751	0.0751	(302)	4.45
9.	32.880	2.7218	0.0800	0.0812	(420)	7.79
10.	33.925	2.6403	0.0851	0.0834	(222)	4.00
11.	36.005	2.4924	0.0955	0.0939	(330)	1.51
12.	37.100	2.4213	0.1012	0.1019	(402)	2.04
13.	38.350	2.3452	0.1078	0.1090	(412)	2.30
14.	39.410	2.2846	0.1136	0.1169	(430)	1.07
15.	40.810	2.2094	0.1215	0.1234	(303)	1.51
16.	42.040	2.1475	0.1286	0.1305	(422)	7.55
17.	43.450	2.0810	0.1370	0.1398	(241)	4.64
18.	44.565	2.0315	0.1437	0.1521	(403)	12.83
19.	47.640	1.9073	0.1631	0.1593	(413)	10.44
20.	51.895	1.7605	0.1914	0.1878	(333)	3.09
21.	54.210	1.6907	0.2075	0.2002	(143)	3.09

Assumed that, evidently, first peak is due to the reflection of X-rays from (100) plane of system. The additional reflections (310), (412) and (143) are seen in the XRD pattern of the mixed crystals and may arise due to reflection of X-rays from pyrene molecule. No significant displacements in the diffraction peaks were observed in this interval of composition of impurity. The additional lines suggest the presence of impurity of pyrene and formation of the mixed crystals.⁵ One

significant observation noted is that the intensity of reflections decreases with increase in concentration of pyrene. The intensity of additional lines increases with pyrene concentration.

Hence it is highly probable that pyrene occupies lattice sites in anthracene for random distribution of impurity among the sites and is expected to exist in different regions of the crystal.

Most of the crystals are far from perfect crystals. The defects can be shown by X-ray analysis. Studies of these defects are significant in solid state devices.

ACKNOWLEDGEMENT

One of the authors (SBP) thanks the University Grants Commission, India, for financial assistance under Faculty Improvement Programme.

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(Received: 14 June 2001; Accepted: 26 September 2001)

AJC-2450