THE MORPHOLOGY OF CRYSTALS OF A METASTABLE ANTHRACENE PHASE, FORMED DURING THEIR GROWTH FROM THE VAPOUR PHASE

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INTRODUCTION

In the recent papers [1,2], the existence of a new metastable modification of anthracene, which as Craig et al. [3] predicted earlier crystallises in the monoclinic space group $P2_1/n$, has been confirmed experimentally as a result of our structure examination of several selected anthracene crystals grown by sublimation.

The crystal structure of this new metastable phase was solved and refined from the X-ray data obtained with the help of an automatic DARCH-1 single diffractometer using MoK_α radiation. For the structure solution and the refinement the SHELX package programs [4,5] were used. The refined cell parameters of this metastable anthracene phase are a=8.553(2), b=6.021(1), c=22.333(4)Å and β=124.54(3)°. In the obtained intensities data file there exist 23 observable reflections with odd indexes I which do not allow to reduce the parameter c by a factor of two to arrive at the monoclinic unit cell of the stable parent phase of anthracene with a=8.562(6), b=6.038(8), c=11.184(8)Å and β=124.42(6)° [6,7]. At the present stage of our study we suppose that the main reason why the metastable phase was formed only in a few anthracene crystals was their considerably faster growth than that of the stable parent phase $P2_1/a$.

By analogy to the previous works [8,9] in which the triclinic metastable phase ($P\bar{1}$) was discovered in its parent phase that had suffered stress at room temperature, we think that the excessive stress and mechanical deformations resulting from this fast growth were large enough to generate the observed monoclinic metastable phase of anthracene. This assumption is also probable in view of the fact that, according to the Craig et al. [3] calculation, the lattice energy of this new form should only slightly differ from that of the stable anthracene modification. Although no considerable differences of crystal shape were observed during the selection of samples for crystal structure examination, a further more precise investigation has shown that the crystals of the metastable anthracene phase have faces with forms different from those of the stable parent phase $P2_1/a$. The morphology of these crystals is the subject of this paper.

First, we report the growth conditions and the experimental morphology of these crystals which results from the X-ray orientation data and from the optical reflection goniometry measurements. Then, we compare this morphology with that predicted on the basis of the structure of this new metastable phase. The program HABIT [10,11] and the crystal drawing program SHAPE [12] were used to calculate the lattice (E_{latt}), slice (E_{slice}) and attachment (E_{att}) energies and to give the predicted morphology. For comparative purposes, the structures of the metastable phase ($P2_1/n$) and the parent anthracene ($P2_1/a$) have been standardised to space group $P2_1/c$ using the STRUCTURE TIDY program [13].

EXPERIMENTAL

Purity and purification
The starting material was analytically pure anthracene purchased from Polish Chemical reagents in which fourteen contaminants of 0.93% total contents have been determined by gas chromatography. Analyses were performed on a Jeol 1100 (capillary column with liquid stationary phase) and a Hewlett Packard 6890 GC System (fused silica capillary column with HP1 methyl silicone as a stationary phase) both equipped with FID detectors.
To remove the main contaminant carbazole (0.75%), the starting material was recrystallized from DMSO [14], then, it was extensively chromatographed on column filled with Al_2O_3, sublimed under vacuum and zone refined (two-fold passage of 100 molten zones with the rate of 10mm/h in the first, and 5mm/h in the second stage; spectrally pure nitrogen as an inert gas). A material of total purity of 99.97mass% was so obtained.

Crystal growth
The crystals were grown in an apparatus shown schematically in Fig.1.
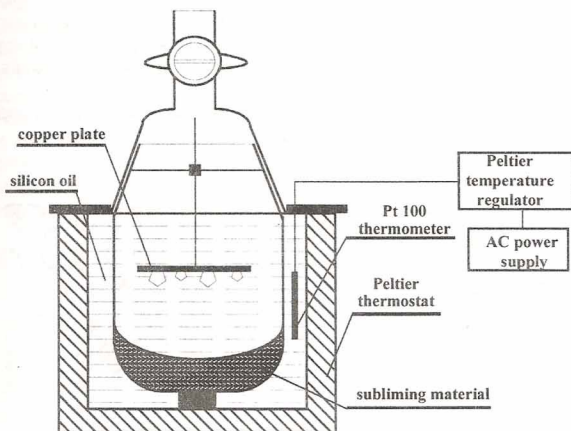
Fig. 1. Schematic diagram of crystal growth apparatus

A glass ampoule containing the material to be sublimed, of an approximately 1:1 ratio of its diameter to its length was placed in an especially constructed Peltier thermostat, equipped with a temperature controlling system. The proper perpendicular temperature gradient could be chosen by manual regulation of the position of a copper plate in relation to the surface of the subliming starting material. Based on spontaneous nucleation, several crystals were usually obtained on this plate in one run.

EXPERIMENTAL RESULTS

As a result of growth experiments, a number of anthracene crystals of various sizes, having generally a plate-like shape have been obtained under a stable 2.5×10^{-2} mbar vacuum and at a constant temperature of the starting material of 93^0C. The rate of crystal growth was estimated as 1.44×10^{-2} mg/h. The largest of crystals of a rhomboidal tabular habit, with additional small side faces, were ca $8 \times 8 \times 3$ mm^3.

The precise structure examination performed with the help of the automatic X-ray diffractometer showed that the crystals of the parent anthracene (P2$_1$/a) and of its metastable phase (P2$_1$/n) were present among the crystals grown as above.

The X-ray orientation data for single crystal (Dron 3.0 powder diffractometer) in combination with the results of the optical reflection goniometry measurements have shown, that the growth direction of the two largest faces present in the metastable phase anthracene crystals, was [00l].

The unit cells and the growth morphologies determined for parent and metastable modification anthracene crystals are shown in Fig. 2.

a)   b)
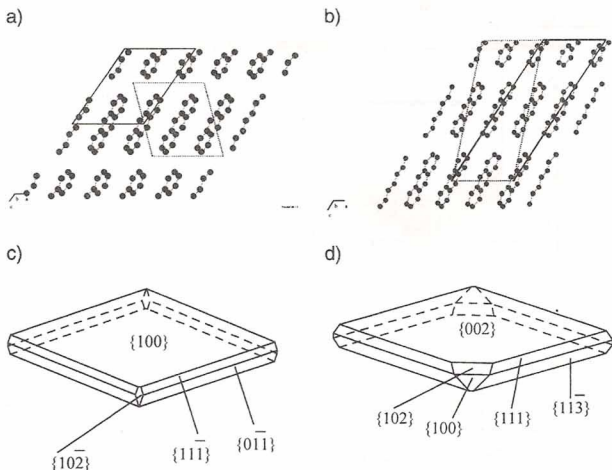

c)   d)

Fig. 2. Unit cells of the parent anthracene (a) in $P2_1/a$ (solid line) and in $P2_1/c$ (dashed line), and its metastable modification (b) in $P2_1/n$ (solid line) and $P2_1/c$ (dashed line), as well as growth morphologies of the parent anthracene (c) and its metastable modification (d) after transformation to $P2_1/c$ group

MODELLING CRYSTAL MORPHOLOGY

Morphological modelling techniques are based upon correlating the bulk structure in some way with the crystal morphology. The satisfying description of crystal morphology may be obtained using the geometrical and attachment energy models based on the Bravais-Friedel-Donnay-Harker (BFDH) law [15,16] and the Hartman-Perdok [17,18] theory of Periodic Bond Chain, respectively. These models are founded on the concepts that the growth rate R of a face (hkl) is related to the close-packing and interlayer spacing d_{hkl} of the molecular planes in different crystallographic direction $(R \propto 1/d_{hkl})$, and to the attachment

energy (E_{att}) of the molecule in the surface ($R \propto E_{att}$). The dominant solid-state intermolecular bonds were calculated from the crystal structure data for parent [6,7] and for metastable modification of anthracene obtained by us [1,2] using the mentioned already the computer program HABIT [10,11].

To calculate the lattice energy expressed as $E_{latt}=E_{slice}+E_{att}$, where E_{slice} is the intermolecular bonding energy contained within the surface growth slice of d_{hkl} thickness and E_{att} is the energy released on the addition of this slice to the surface of a growing crystal, the potential function given by Williams et al. [19] was used, Fig. 3.
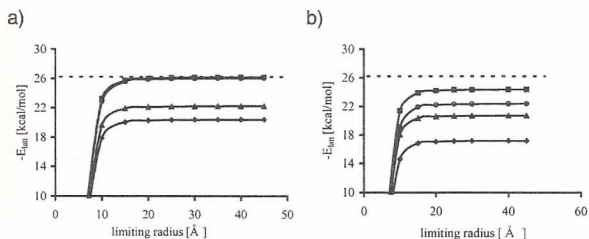
a)   b)

Fig. 3. Calculated lattice energy as a function of summation limit for parent (a) and metastable (b) anthracene using the potential functions given by Momany et al. [20] (♦), Williams (•) [19], Govers [21] (▲) and Nèmethy et al. [22] (○), and "experimental lattice energy" calculated from the sublimation enthalpy of anthracene [] (dashed line)

The reciprocal of the interplanar spacings ($1/d_{hkl}$), the attachment energies (E_{att}) and the morphological importance (MI) of the {hkl} forms predicted for the crystals of the parent anthracene and its metastable phase using the both theoretical models, are collected in Table I. The theoretical morphologies based on these models are shown in Fig. 4.

Table I. Results of the morphological calculations for the parent and for the metastable anthracene in standard space group $P2_1/c$

Form	Geometrical model		Attachment energy model	
	$1/d_{hkl}$ (Å^{-1})	MI	$|E_{att}|$ (kcal/mol)	MI
Parent anthracene				
{100}*	0.109	1	6.35	1
{01$\bar{1}$}*	0.205	2	16.52	3
{11$\bar{1}$}*	0.219	3	16.08	2
{10$\bar{2}$}*	0.240	4	17.86	4
{002}	0.241	5	20.56	9
{1$\bar{1}$1}	0.245	6	18.77	6
{2$\bar{1}\bar{1}$}	0.278	7	18.73	5
{20$\bar{2}$}	0.284	8	20.02	8
{102}	0.286	9	21.25	10
{2$\bar{1}$1}	0.319	10	19.00	7
{020}	0.332	11	24.11	13
{1$\bar{2}$0}	0.350	12	23.89	12
{202}	0.360	13	21.39	11
Metastable phase of anthracene				
{002}*	0.109	1	5.79	1
{100}*	0.120	2	9.00	3
{10$\bar{2}$}	0.143	3	9.14	4
{01$\bar{1}$}	0.175	4	11.29	5
{102}*	0.178	5	8.73	2
{1$\bar{1}\bar{1}$}	0.205	6	15.57	8
{1$\bar{1}$1}*	0.218	7	15.11	7
{01$\bar{3}$}	0.233	8	13.94	6
{200}	0.240	9	16.84	9
{20$\bar{2}$}	0.241	10	18.95	13
{11$\bar{3}$}*	0.245	11	17.53	11
{1$\bar{1}$3}	0.278	12	17.48	10
{202}	0.284	13	18.39	12

* the forms observed experimentally

a)   b)

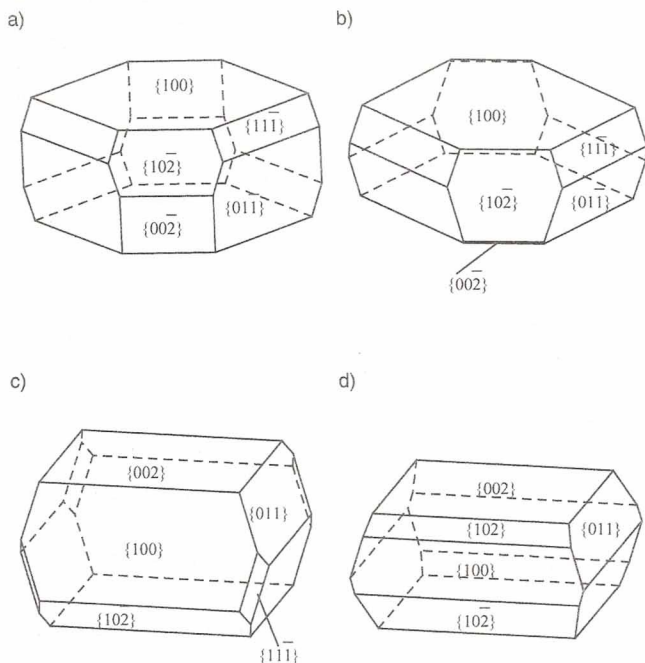c)   d)

Fig. 4. Theoretical morphologies of crystals of the parent anthracene (a, b) and its metastable phase (c, d); a, c and b, d correspond to the geometrical and attachment energy models, respectively

CONCLUSIONS

As mentioned in the introduction, at the present stage of our study we suppose that the main reason why the metastable phase was formed only in a few anthracene crystals was their considerably faster growth than that of the stable parent phase $P2_1/a$.

The crystals of the both phases of anthracene possessed the same tabular habit, their forms, however, showed significant differences. They have only one the same form of {100}; its observed morphological

importance is the largest in the crystals of the parent anthracene and the least in the crystals of its metastable modification.

Although the models used predict generally all the faces observed experimentally in the both crystals, they underestimate the {111} and {11$\bar{3}$} forms present in the crystals of the metastable anthracene phase, overestimating at the same time the MI of the {011} form which does not occur in the growth morphology of these crystals. Moreover, the higher MI of the {11$\bar{1}$} form in the crystals of the parent anthracene and the {102} form in the crystals of its metastable phase indicates that the morphology of both these crystals is more precisely predicted by the attachment energy model.

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