Crystal Structure of a Metastable Anthracene Modification, Grown from the Vapor Phase

B. Marciniak [a] & V. Pavlyuk [a]

[a] Institute of Chemistry and Environment Protection, Pedagogical University, Cze̜stochowa, Poland

PLEASE SCROLL DOWN FOR ARTICLE

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.

Crystal Structure of a Metastable Anthracene Modification, Grown from the Vapor Phase

B. MARCINIAK and V. PAVLYUK

Institute of Chemistry and Environment Protection, Pedagogical University, Częstochowa, Poland

The crystal structure of a new monoclinic metastable phase of anthracene formed during vapor growth has been determined from single crystal X-ray data (DARCH-1 automatic diffractometer, Mo K_α radiation). This metastable anthracene phase crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.553(2)$, $b = 6.021(1)$, $c = 22.334(4)$, Å and $\beta = 124.54(3)°$, and four molecules per unit cell. All carbon and hydrogen atom positions have been determined and refined to R = 0.044 for 330 unique reflections.

INTRODUCTION

The aromatic hydrocarbon anthracene ($C_{14}H_{10}$) is commonly treated as the arch-type of molecular crystals; it is a material whose properties are known best in all aspects of crystal physics [1–3].

Crystals of anthracene have been used in scintillation counting [4]. Due to relatively low (5–100 kJ/mol) lattice energies, which are the result of weak van der Waals intermolecular interactions, a strong tendency to defect formation is generally observed. A lattice energy of 96.14 kJ/mol of anthracene means only 40 meV per atom [5].

The nature and concentration of defects are very important features of molecular crystals, as they usually strongly influence the electrical and optical properties, which are promising in low-cost applications of these crystals as photoconductors and scintillators [4–6].

In previous works [7, 8] the facile production of a triclinic metastable phase of anthracene was reported, which was discovered from analysis of the electron diffraction patterns of the thermodynamically stable parent phase ($P2_1/a$) that had suffered stress at room temperature. This triclinic form was generated by the application of compressive force or shear stress approximately perpendicular to the basal plane of the stable parent phase.

This triclinic metastable phase, only 2 kJ/mol less stable than the above monoclinic parent phase of anthracene, crystallizes in the space group $P\bar{1}$ with two molecules per unit cell of dimensions: $a = 8.342$, $b = 5.890$, and $c = 11.282$ Å and with $\alpha = 123.34°$, $\beta = 96.70°$ and $\gamma = 85.91°$.

Apart from this phase, two monoclinic $P2_1/c$ and $P2_1/n$ phases close in energy may be expected for anthracene, as was shown by an "atom-atom" calculation by Craig et al. [9]. Only small differences between unit cell parameters calculated in this work for parent anthracene and experimental values [10, 11] prove that the prediction of Craig et al. is very precise.

Results of the above calculation are also in accordance with data determined by Ramdas et al. [8] for a triclinic metastable phase of anthracene discovered by them, differing significantly only in the values of the lattice constant *a*.

The existence of that metastable phase of anthracene, predicted theoretically by Craig et al. [9] to crystallize 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.

In the present paper the crystal structure of this new metastable phase has been solved and refined from the X-ray data obtained by using an automatic single crystal diffractometer.

EXPERIMENTAL

Purity and Purification

We started with "analytically pure," commercially available anthracene (Naftochem, Poland) in which fourteen contaminants of 0.93% total contents have been determined by gas chromatography. Gas chromatographic (GC) 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.

The starting material was prepurified, first by crystallization from dimethylsulfoxide to remove the main contaminant carbazole (0.75%) and then by vacuum sublimation. Alternatively, column chromatography and vacuum sublimation were used to obtain a material of comparable purity.

Next the material was extensively zone refined by using a multistage zone refiner as described previously [12] (two-fold passage of 100 molten zones with the rate of 10 mm/h in the first, and 5 mm/h in the second stage; spectrally pure nitrogen as an inert gas). A material of total purity of 99.97% was so obtained [13].

Crystal Growth Apparatus

The crystals were grown in an apparatus as shown schematically in Figure 1 (cf. Lipset [14]).

A glass ampoule containing the material to be sublimed, of an approximately 1:1 ratio of its diameter to its length was placed in a specially 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.

X-ray Crystal Structure Examination

A preliminary examination of the crystal structure of the grown anthracene crystals was carried out using photographic data obtained from traditional Laue, rotation (RKD-86 camera, Mo radiation), and Weissenberg (RGNS-2 camera, Cu radiation) X-ray single crystal methods.

The X-ray powder diffraction patterns were obtained using a DRON-3 powder diffractometer with CuK_α radiation. The data that enabled an ultimate solution of the structure of the metastable anthracene phase were collected on an automatic DARCH-1 single crystal diffractometer using MoK_α radiation. The SHELX package programs [15, 16] were used for all structure calculations and for the refinement.

A summary of the measurement parameters is presented in Table 1.
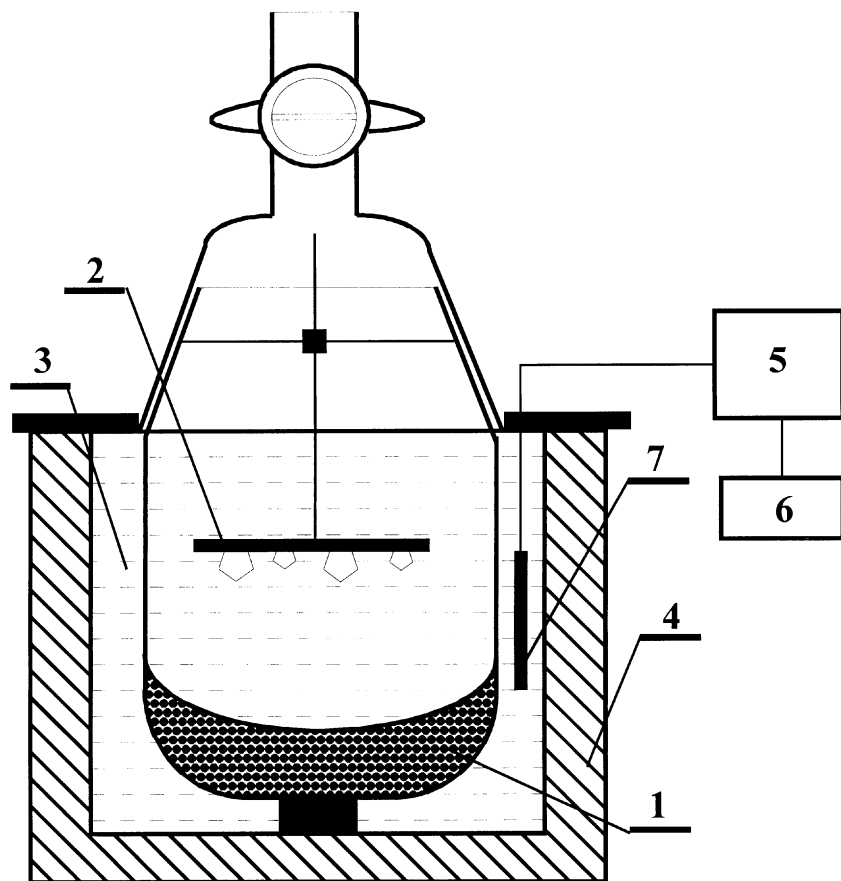
FIGURE 1   Schematic diagram of crystal growth apparatus: 1, subliming material; 2, copper plate; 3, silicon oil; 4, Peltier thermostat; 5, Peltier temperature regulator; 6, AC power supply; 7, Pt 100 thermometer.

RESULTS AND DISCUSSION

Crystal Growth

Previous experience [2, 4, 5] of crystal growth of some aromatic hydro-carbons from the vapor phase has indicated that the plate sublimation technique usually leads to several crystals, grown simultaneously, often in the form of thin (0.01–0.5 mm) *ab* platelets and/or needles, elongated in the crystallographic *c*-direction. However, for anthracene and a number of

TABLE 1   Crystal data and structure refinement for the monoclinic (P2$_1$/n) metastable phase of anthracene

Empirical formula	$C_{14}H_{10}$
Formula weight	712.88
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions	$a = 8.553(2)$ Å, $b = 6.021(1)$ Å, $c = 22.333(4)$ Å $\beta = 124.54(3)$ deg.
Volume	947.4(3) Å^3
Z Calculated density	4, 1.250 g/cm^3
Absorption coefficient	0.071 mm^{-1}
F(000)	376
Crystal size	plate, $0.17 \times 0.13 \times 0.01$ mm
Theta range for data collection	4.04–21.33°
Index ranges	$0 \leq h \leq 8,\ 0 \leq k \leq 5,\ -18 \leq 1 \leq 18$
Reflections collected/unique	352/330 [R(int) = 0.0280]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	330/0/168
Goodness-of-fit on F^2	0.989
Final R indices [$I > 2\sigma(I)$]	R$_1$ = 0.0444, wR$_2$ = 0.1004
R indices (all data)	R$_1$ = 0.0665, wR$_2$ = 0.1124
Extinction coefficient	0.000(5)
Difference electron density (max. and min.)	0.101 and -0.100 e. Å^{-3}

other compounds grown under high vacuum conditions, bulky crystals of a size of the order of $10 \times 10 \times 5$ mm^3 have been obtained [5].

Crystals grown in this way often show much higher crystallographic and optical perfection than crystals grown by other techniques, especially by the most popular Bridgman method, in which strain and stress problems arising from different thermal expansion/contraction of the ampoule with respect to the growing crystal take place.

Due to the fact that the samples of such crystals may be prepared without any mechanical treatment, they are often useful for many optical measurements as well as for crystal structure examination.

As a result of our growth experiments, a number of anthracene crystals of various size, having generally a platelike shape with two major faces {001}, has been obtained. The largest of crystals of a rhomboidal tabular habit, with additional small {110} and {$\bar{1}$11} side faces, were about $8 \times 8 \times 3$ mm^3. It was observed that the growth of these individual crystals often occurred such that they contacted the copper plate with a small face only; therefore they came off from it very easily.

Small crystals with a size of about $0.17 \times 0.13 \times 0.01$ mm^3 were selected under a microscope for crystal structure examination. These crystals were

chosen from crystals obtained under a stable 2.5×10^{-2} mbar vacuum and at a constant temperature of the starting material of $93°C$. The rate of crystal growth was estimated as 1.44×10^{-2} mg/h.

Although no considerable differences of crystal shape were observed during this selection, a further, more precise examination [17] has shown that the crystals of the metastable anthracene phase had faces with forms different from those of the stable monoclinic phase $P2_1/a$ [10, 11].

Crystal Structure

Based on the data obtained from the single crystal photographic X-ray methods, we found that the symmetry and the unit cell parameters of the first selected anthracene crystal were in good agreement with the data given by Mason [10] and by Brock and Dunitz [11] for the monoclinic thermo-dynamically stable phase. A good accordance was also observed between an experimental powder diffraction pattern and a theoretical one, calculated for anthracene from this literature's data.

TABLE 2   Atomic coordinates (in unit of 10^4) and equivalent isotropic displacement coefficients (10^3 $\mathring{A}^2$) of refined atoms of metastable anthracene ($P2_1/n$) at 298 K

ATOM	x	y	z	$U(eq)^a$
C(1A)	920(5)	390(6)	1840(3)	182(18)
C(2A)	1050(3)	1590(4)	1365(15)	90(8)
C(3A)	540(4)	770(5)	720(18)	134(13)
C(4A)	880(3)	2040(4)	230(2)	121(13)
C(5A)	340(3)	1230(5)	9520(2)	121(14)
C(6A)	610(4)	2560(4)	9060(2)	98(10)
C(7A)	110(3)	1810(5)	8430(17)	98(8)
C(1B)	4370(3)	5840(4)	9320(9)	73(6)
C(2B)	5270(3)	3560(4)	9568(11)	97(8)
C(3B)	5070(4)	6750(7)	1604(19)	147(14)
C(4B)	5840(3)	4760(4)	1797(15)	92(9)
C(5B)	4430(3)	7570(4)	910(2)	126(11)
C(6B)	3650(3)	6530(5)	8584(15)	120(10)
C(7B)	5900(3)	2880(5)	246(13)	110(9)
H(1A)	1300(2)	200(3)	2360(10)	110(7)
H(2A)	2080(19)	2500(2)	1850(8)	110(5)
H(4A)	1000(2)	3100(3)	−30(8)	100(6)
H(6A)	1560(19)	3900(3)	9080(8)	140(6)
H(7A)	10,200(3)	3200(3)	8100(11)	140(6)
H(3B)	4500(4)	7800(5)	1870(17)	140(10)
H(4B)	6300(2)	4300(3)	2210(11)	100(7)
H(5B)	3650(10)	9260(14)	680(4)	30(2)
H(6B)	3070(10)	8040(13)	8500(4)	19(19)
H(7B)	6440(14)	1100(2)	500(6)	80(4)

$^a U(eq)$ is defined as one-third of the trace of the ortogonalized U_{ij} tensor.

In view of this, the automatic single crystal diffractometer was used for a more precise determination of the lattice parameters. However, during the measurements of the first selected sample it was observed that the unit cell

TABLE 3   Bond lengths and angles for metastable anthracene (P2$_1$/n) at 298 K

Bond lenghts[Å]		Angles [deg]	
C(1A)-C(2A)	1.35(5)	C(2A)-C(1A)-C(7A)#1	116(4)
C(1A)-C(7A)#1	1.52(4)	C(3A)-C(2A)-C(lA)	122(3)
C(2A)-C(3A)	1.34(3)	C(2A)-C(3A)-C(5A)#2	122(4)
C(3A)-C(5A)#2	1.36(4)	C(2A)-C(3A)-C(4A)	121(3)
C(3A)-C(4A)	1.50(4)	C(5A)#2-C(3A)-C(4A)	117(3)
C(4A)-C(5A)#3	1.45(4)	C(5A)#3-C(4A)-C(3A)	123(3)
C(5A)-C(3A)#2	1.36(4)	C(3A)#2-C(5A)-C(6A)	120(4)
C(5A)-C(6A)	1.41(4)	C(3A)#2-C(5A)-C(4A)#4	120(4)
C(5A)-C(4A)#4	1.45(4)	C(6A)-C(5A)-C(4A)#4	121(3)
C(6A)-C(7A)#5	1.31(4)	C(7A)#5-C(6A)-C(5A)	120(3)
C(7A)-C(6A)#6	1.31(4)	C(6A)#6-C(7A)-C(1A)#1	120(3)
C(7A)-C(1A)#1	1.52(5)	C(7B)#7-C(1B)-C(6B)	121(2)
C(1B)-C(7B)#7	1.35(3)	C(7B)#7-C(1B)-C(2B)	120(2)
C(lB)-C(6B)	1.45(3)	C(6B)-C(1B)-C(2B)	118(2)
C(1B)-C(2B)	1.52(3)	C(7B)#4-C(2B)-C(5B)#7	125(3)
C(2B)-C(7B)#4	1.35(3)	C(7B)#4-C(2B)-C(1B)	119(2)
C(2B)-C(5B)#7	1.41(4)	C(5B)#7-C(2B)-C(1B)	116(2)
C(3B)-C(4B)	1.32(5)	C(4B)-C(3B)-C(5B)	119(4)
C(3B)-C(5B)	1.40(5)	C(3B)-C(4B)-C(6B)#7	125(3)
C(4B)-C(6B)#7	1.39(4)	C(3B)-C(5B)-C(2B)#7	123(2)
C(5B)-C(2B)#7	1.41(4)	C(4B)#7-C(6B)-C(1B)	117(2)
C(6B)-C(4B)#7	1.39(4)	C(2B)#3-C(7B)-C(1B)#7	121(3)
C(7B)-C(2B)#3	1.35(3)		
C(7B)-C(1B)#7	1.35(3)		

Symmetry transformations used to generate equivalent atoms:
#l: $-x, -y, -z + 1$; #2: $x, y, z - 1$; #3: $x, y, z + 1$; #4: $-x + 1, -y + 1, -z + 1$.

TABLE 4   Anisotropic displacement coefficients (10^3 Å^2) for metastable anthracene (P2$_1$/n)

	$U11$	$U22$	$U33$	$U23$	$U13$	$U12$
C(1A)	170(3)	170(3)	200(4)	70(3)	100(3)	0(2)
C(2A)	78(12)	55(15)	130(2)	−8(15)	51(13)	4(11)
C(3A)	83(14)	72(19)	190(3)	−80(2)	39(16)	−12(12)
C(4A)	108(14)	47(11)	260(4)	40(2)	140(2)	−4(11)
C(5A)	97(14)	100(2)	200(3)	−60(2)	99(17)	2(15)
C(6A)	104(17)	100(2)	140(2)	50(2)	96(19)	13(15)
C(7A)	97(15)	102(17)	120(3)	25(16)	81(17)	4(12)
C(1B)	51(9)	118(18)	51(12)	−17(13)	30(9)	−11(10)
C(2B)	70(11)	103(19)	80(16)	−28(13)	21(11)	7(11)
C(3B)	120(2)	150(3)	140(3)	20(2)	50(2)	26(19)
C(4B)	87(15)	90(17)	100(2)	36(16)	53(14)	−11(12)
C(5B)	84(17)	110(13)	150(3)	35(19)	46(17)	23(16)
C(6B)	93(14)	120(2)	140(2)	19(16)	58(15)	50(13)
C(7B)	106(14)	150(2)	47(10)	−10(14)	28(11)	−63(14)

The anisotropic displacement factor exponent takes the form $-2 \pi^2 [h^2 a^{*2} U11 + \ldots + 2hka^*b^*U12]$.

TABLE 5 Observed and calculated structure factors of metastable antracene ($P2_1/n$)

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	0	0	1289	1300	5	−4	1	6	79	82	4	0	0	12	50	49	8
4	0	0	50	48	7	−2	1	6	46	10	11	2	0	12	31	30	10
6	0	0	73	71	4	−1	1	6	213	207	3	−8	1	12	37	35	7
2	1	0	1008	939	5	1	1	6	73	73	5	−6	1	12	9	18	8
3	1	0	170	171	3	3	1	6	42	48	8	−2	1	12	29	27	15
4	1	0	298	315	3	4	1	6	44	41	6	0	1	12	20	10	20
5	1	0	41	46	8	−4	2	6	48	52	7	−8	2	12	19	5	18
6	1	0	48	42	6	−1	2	6	124	122	4	−6	2	12	43	44	6
7	1	0	20	26	19	0	2	6	60	61	4	−5	2	12	74	69	4
0	2	0	405	419	4	1	2	6	15	2	15	−3	2	12	95	99	4
1	2	0	313	308	3	−5	3	6	19	3	18	0	2	12	21	18	21
2	2	0	204	194	3	−3	3	6	24	26	24	−7	3	12	40	47	7
3	2	0	358	352	4	−2	3	6	39	41	10	−5	3	12	82	79	4
5	2	0	92	90	2	0	3	6	75	78	3	−4	3	12	35	32	9
1	3	0	266	274	9	1	3	6	124	122	3	−1	3	12	64	64	4
3	3	0	82	79	4	3	3	6	56	58	5	1	3	12	20	26	20
6	3	0	14	12	13	−5	4	6	15	14	15	−3	4	12	90	87	3
4	4	0	24	25	16	−4	4	6	57	59	5	−2	4	12	89	87	3
1	5	0	31	31	8	−3	4	6	45	54	8	−1	4	12	65	64	4
−8	0	1	17	20	17	−2	4	6	87	89	4	−5	1	13	14	19	14
−5	1	1	33	26	9	−1	4	6	54	53	6	−1	1	13	34	31	9
3	1	1	23	12	23	2	4	6	61	61	4	−8	2	13	18	18	18
−3	1	1	35	34	10	−2	5	6	81	79	4	0	2	13	10	17	9
6	1	1	15	16	15	−1	5	6	97	90	3	−7	3	13	17	11	16
−5	2	1	13	17	12	0	5	7	81	79	5	−2	3	13	14	5	14
−2	2	1	27	23	26	−7	1	7	5	10	5	−2	4	13	12	20	11
3	2	1	30	31	19	−3	1	7	36	36	12	−6	0	14	12	4	11
−4	4	1	34	28	10	−2	1	7	24	7	24	−4	0	14	56	57	5
−3	4	1	21	30	7	−1	1	7	42	42	10	−2	0	14	40	41	8
−2	4	1	27	31	15	0	1	7	6	3	6	0	0	14	28	4	14
−1	4	1	42	40	6	−2	2	7	15	19	14	−4	1	14	17	22	16
2	4	1	8	10	7	4	3	7	6	16	6	−2	1	14	60	61	5
						−4	4	7	27	23	14	−6	2	14	11	6	11

244

h	k	l	Fo	Fc	σ	h	k	l	Fo	Fc	σ	h	k	l	Fo	Fc	σ	h	k	l	Fo	Fc	σ	h	k	l	Fo	Fc	σ
0	5	1	18	3	17	3	1	4	45	45	8	-1	4	8	7	11	7	-8	2	10	73	73	4	-3	2	14	39	36	8
-6	0	2	116	119	3	-7	2	4	61	57	4	-6	0	8	42	36	8	-7	2	10	66	68	5	-2	2	14	11	16	10
-4	0	2	53	47	6	-6	2	4	84	82	4	-2	0	8	58	59	8	-5	2	10	54	49	6	2	2	14	27	11	10
-2	0	2	1034	986	5	-5	2	4	66	67	5	0	0	8	278	289	4	-4	2	10	217	214	3	-5	3	14	18	2	18
2	0	2	73	71	6	-4	2	4	75	76	5	2	0	8	258	261	2	-3	2	10	74	77	5	-1	3	14	25	20	17
-7	1	2	34	35	9	-3	2	4	73	74	5	4	0	8	57	43	5	-2	2	10	235	231	2	0	3	14	19	27	19
-6	1	2	91	98	4	-1	2	4	91	91	5	-6	1	8	67	66	4	-1	2	10	51	52	6	-6	1	15	23	21	20
-5	1	2	61	69	5	0	2	4	110	109	3	-5	1	8	53	50	6	0	2	10	86	87	4	-5	2	15	19	21	19
-4	1	2	484	505	5	-7	3	4	76	75	4	-4	1	8	215	224	2	1	2	10	53	51	5	-7	2	15	19	11	19
-3	1	2	520	531	5	-2	3	4	63	58	4	-3	1	8	185	175	3	2	2	10	68	69	4	-5	2	15	22	29	18
-2	1	2	913	844	6	1	3	4	50	48	6	-2	1	8	106	104	4	3	2	10	135	138	3	0	0	15	32	24	21
-1	1	2	584	500	4	-4	4	4	47	46	7	-1	1	8	241	244	3	-7	3	10	105	107	3	-2	0	16	13	26	10
0	1	2	198	192	3	-2	4	4	82	78	4	0	1	8	142	141	2	-6	3	10	48	48	6	0	1	16	43	19	12
1	1	2	215	217	4	-1	4	4	57	60	5	1	1	8	158	155	3	-5	3	10	83	86	4	-7	0	16	20	34	5
2	1	2	42	35	4	0	4	4	19	16	18	2	1	8	39	28	3	-4	3	10	119	128	2	-6	0	16	38	1	20
3	1	2	93	87	3	-7	5	4	30	19	9	3	1	8	38	52	8	-3	3	10	134	131	3	-4	1	16	74	28	8
-7	2	2	62	59	2	-1	0	5	23	18	14	4	1	8	83	85	9	-2	3	10	90	85	3	-2	1	16	37	77	5
-6	2	2	124	118	2	0	0	5	13	20	13	-8	2	8	36	35	3	-1	3	10	54	57	5	-1	1	16	61	45	9
-5	2	2	247	254	2	-2	1	5	35	40	27	-6	2	8	51	48	6	0	3	10	39	44	9	0	1	16	20	58	3
-4	2	2	258	267	4	0	3	5	56	53	8	-5	2	8	40	27	6	1	3	10	97	90	3	-7	2	16	19	26	20
-3	2	2	316	330	6	3	3	5	21	17	21	-4	2	8	51	50	7	2	3	10	105	108	3	-6	2	16	66	25	18
-1	2	2	70	75	5	4	3	5	17	3	17	-3	2	8	141	144	7	3	3	10	100	105	7	-1	2	16	74	66	5
0	2	2	96	96	2	0	4	5	12	4	3	-2	2	8	328	314	3	4	3	10	20	6	19	0	2	16	51	73	4
1	2	2	281	290	3	-1	5	5	20	25	12	-1	2	8	148	153	3	-6	4	10	14	27	14	-1	2	16	35	53	5
2	2	2	159	155	3	-6	0	5	12	2	19	0	2	8	157	176	5	-5	4	10	24	21	23	-2	3	16	6	33	7
3	2	2	191	189	24	-4	0	6	37	40	11	1	2	8	35	42	10	-4	4	11	30	28	11	0	3	17	15	16	6
5	2	2	25	29	17	-2	0	6	49	48	7	2	2	8	96	89	3	-2	4	11	11	24	11	-7	2	17	33	14	14
6	2	2	24	7	10	0	0	6	88	89	6	3	2	8	53	57	5	-1	4	11	14	10	13	-4	3	17	21	20	7
-6	3	3	66	22	4	2	0	6	247	248	4	4	2	8	72	72	3	0	4	12	29	28	11	-1	3	18	29	1	20
-5	3	3	80	67	4	4	0	6	226	234	3	-6	3	8	100	98	3	2	4	12	63	61	5	0	3	18	37	24	8
-2	3	3	190	197	3	-8	1	6	53	55	2	-5	3	8	137	136	3	4	4	12	53	58	6	-6	3	18	28	36	11
-1	3	3	184	194	3	-6	2	6	66	62	6	-4	3	8	113	112	13	-8	5	12	46	49	8	-2	3	18	11	21	11

245

TABLE 6   The standardized atomic positional parameters in P2$_1$/c space group

Atoms in P2$_1$/c		x	y	z	Atoms in P2$_1$/n (see Table 2)
Cl	4(e)	0.01831	0.57696	0.42796	C3A
H1	4(e)	0.02334	0.25412	0.18498	H2A
C2	4(e)	0.03156	0.65850	0.36350	C2A
C3	4(e)	0.06524	0.20406	0.02256	C4A
C4	4(e)	0.08216	0.37699	0.45211	C5A
C5	4(e)	0.09257	0.53945	0.31549	C1A
H2	4(e)	0.10078	0.52302	0.26408	H1A
H3	4(e)	0.10138	0.18545	0.49722	H4A
C6	4(e)	0.15456	0.24414	0.40647	C6A
C7	4(e)	0.16757	0.31898	0.34295	C7A
H4	4(e)	0.21042	0.17512	0.30958	H7A
H5	4(e)	0.24808	0.11108	0.40800	H6A
H6	4(e)	0.29719	0.57416	0.56802	H5B
C8	4(e)	0.40460	0.47590	0.17971	C4B
H7	4(e)	0.40729	0.43075	0.22149	H4B
C9	4(e)	0.49331	0.34747	0.14155	C6B
C10	4(e)	0.49507	0.41555	0.06801	C1B
H8	4(e)	0.54286	0.19571	0.14986	H6B
C11	4(e)	0.56529	0.28829	0.02459	C7B
C12	4(e)	0.57034	0.14369	0.45678	C2B
H9	4(e)	0.59339	0.10938	0.05031	H7B
C13	4(e)	0.64783	0.25688	0.40869	C5B
C14	4(e)	0.65316	0.17518	0.33955	C3B
Hl0	4(e)	0.73362	0.28243	0.31347	H3B

CELL $a = 8.5530$; $b = 6.0210$; $c = 18.8498$; $\beta = 102.592$.

parameters determined from the collected data displayed certain deviations from those expected. Therefore, we checked if the unit cell parameters were chosen correctly, and it appeared that there existed reflections, which indicated a two-fold larger unit cell.

Upon seeking further samples for confirmation of these X-ray results, we found that only a sixth of the selected crystals had unusual unit cell parameters like the first one.

For a selected crystal 352 observable reflections were collected, using an ω-2Θ scan technique, from which 330 had $|F| > 2\sigma|F|$ and were used for structure determination. The detailed information concerning data collection, processing, and structure calculation is given in Table 1.

The positional parameters of all carbon atoms were obtained by direct methods, and in the case of the hydrogen atoms by the difference Fourier synthesis. All atoms were found on 4e position. The atomic positions of the carbon atoms were refined anisotropically and the hydrogen atoms in the isotropic approximation, down to R = 0.044. The obtained atomic positional and equivalent isotropic displacement coefficients for both unique
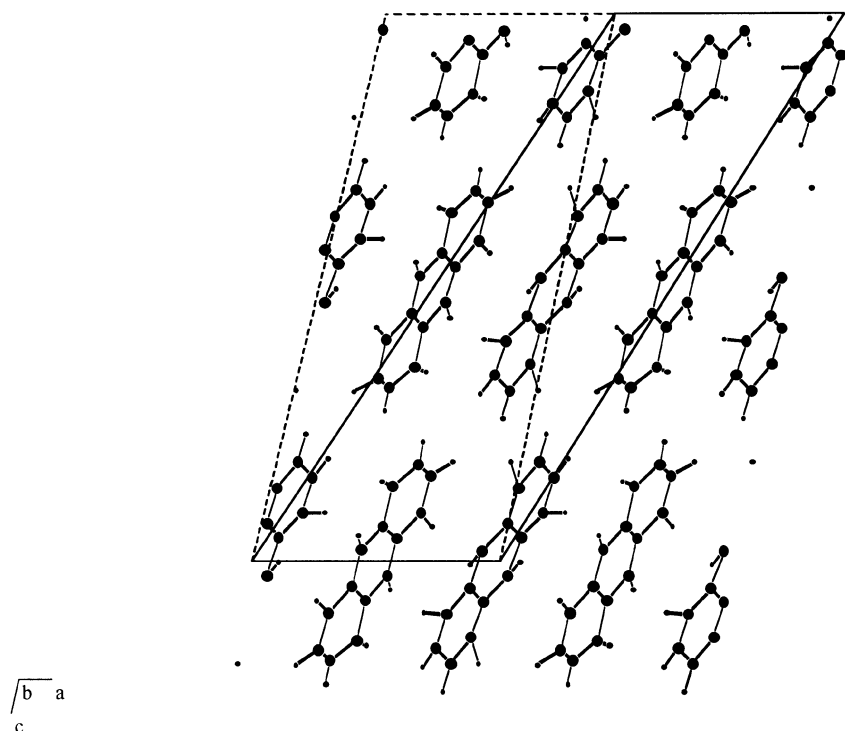
FIGURE 2   Unit cell of metastable anthracene in $P2_1/n$ (solid line) and $P2_1/c$ (dashed line) space groups.

molecules, denoted as A and B, are listed in Table 2. The bond lengths and the valence angles in the unique molecules, calculated from their coordinates, are presented in Table 3. The anisotropic displacement coefficients and the observed and calculated structure factors are listed in Tables 2, 3, 4 and 5, respectively.

As shown in Table 1, the structure of selected anthracene crystal can be successfully solved in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The refined parameters of this cell are $a = 8.553(2)$, $b = 6.021(1)$, $c = 22.334(4)$ Å, and $\beta = 124.54(3)^{\circ}$. In the obtained intensities data file there exist 23 observable reflections with odd indexes l that do not allow the reduction of 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 $\beta = 124.42(6)^{\circ}$ [10, 11].

The determined structure has been standardized using the STRUCTURE TIDY program [18]. This implies transformation to space group $P2_1/c$ with
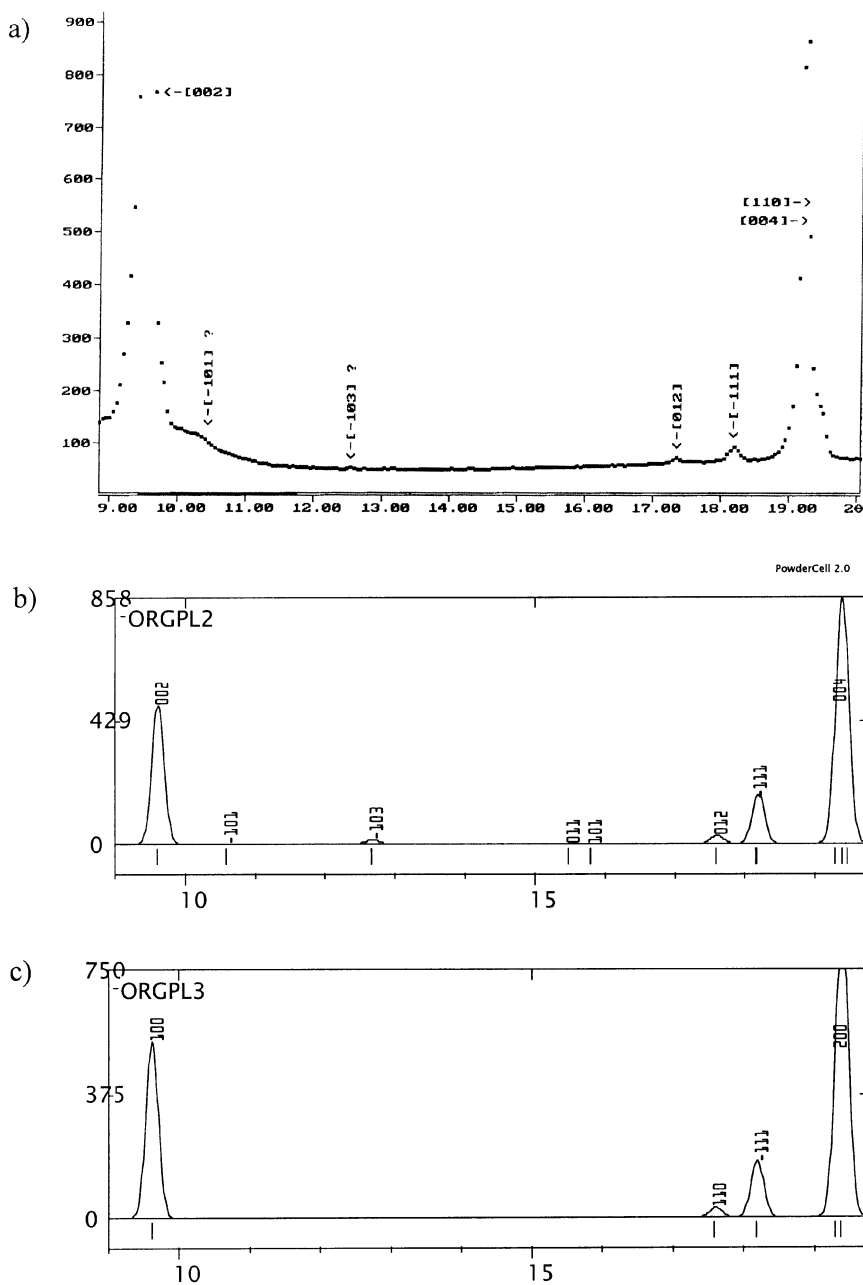
FIGURE 3   Experimental powder diffraction pattern of a sample containing metatastable and parent anthracene prepared from randomly selected crystals of both phases (a), and calculated profiles for this sample (b) and for parent anthracene (c).

the unit cell dimensions of $a = 8.553$, $b = 6.021$, $c = 18.849$ Å, and with $\beta = 102.59$. The standardized atomic positional parameters are given in Table 6, whereas the interrelation between both these unit cells is shown in Figure 2.

Since this new structure is closely connected with that of the long known structure of the stable parent anthracene, we have carried out comparative research using this parent anthracene crystal phase. With the use of the same diffractometer, we obtained the experimental intensity data of a unit cell with a twice smaller c parameter. Among the 272 collected reflections, 252 were unique. The refinement of the atomic positional and thermal parameters of the atoms resulted in R = 0.09 for $|F| > 2\sigma|F|$.

Having this result in mind as well as the fact that the reduction of the unit cell should require omitting as many as 23 reflections (printed bold in Table 5) which are 7% of the total number, it could be assumed that we really observed a new metastable phase of anthracene.

Moreover, further examinations showed that the traditional X-ray single crystal photograph and powder diffraction methods used at the preliminary stage were not sensitive enough for the detection of the metastable structure in this case. This fact is illustrated in Figure 3a, showing the experimental powder diffractogram obtained for the random sample containing crystals of metastable and of parent anthracene.

The intensities of the additional reflections indicating the presence of the metastable phase are very small and close to the level of the background. The difference between the diffraction profiles (Figs. 3b and 3c) calculated for the metastable and for parent anthracene is also insignificant. Only the weak reflection $\bar{1}03$ at $2\Theta = 12.6°$, indicating that the presence of a phase other than the parent one is visible.

CONCLUSIONS

At the present stage of our study we suppose that the main reason why the metastable phase was formed in only a few anthracene crystals was their considerably faster growth than that of the stable parent phase $P2_1/a$. As was previously mentioned, the fraction of crystals having the metastable structure is low; therefore, we could not detect these species in our preliminary examination.

By analogy to Ramdas et al. [8], we think that the excessive stresses and mechanical deformations resulting from this phase 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. [9] calculation, the lattice energy of this new form should only slightly differ from that of the stable anthracene modification.

REFERENCES

1. E. A. Silinsh, *Organic Molecular Crystals* (Springer-Verlag, Berlin, 1980).
2. K. Kojima, *Prog. Cryst. Growth and Charact.*, 23, 369–420 (1991). See also the references cited therein.
3. H. Bässler, Semiconducting and photoconducting organic solids, in *Organic Molecular Solids Properties and Applications*, W. Jones ed. (CRC Press Inc., Boca Raton, FL, 1997) pp. 267–308. See also the references cited therein.
4. B. J. McArdle, and J. N. Sherwood, The growing of organic crystals, in *Advanced Crystal Growth*, P. M. Dryburgh, B. Cockayne, and K. G. Barraclough eds. (Prentice Hall, New York, 1987) pp. 179–217.
5. N. Karl, High purity organic molecular crystals, in *Crystals Growth, Properties, and Applications*, Vol. 4, H. C. Freyhardt ed. (Springer-Verlag, Berlin, 1980), pp. 1–100. See also the references cited therein.
6. W. Warta, R. Stehle, and N. Karl, *Appl. Phys. A*, 36, 163–170 (1985).
7. G. M. Parkinson, M. J. Goringe, S. Ramdas, J. O. Williams, and J. M. Thomas, *JSC Chem. Commun.*, 134–135 (1978).
8. S. Ramdas, G. M. Parkinson, J. M. Thomas, C. M. Gramaccioli, G. Filipini, M. Simonetta, and M. J. Goringe, *Nature*, 284, 153–154 (1980).
9. D. P. Craig, J. F. Ogilvie, and P. A. Reynolds, *J. Chem. Soc. Faraday Trans. II*, 72, 1603–1612 (1976).
10. R. Mason, *Acta Crystallogr.*, 17, 547–555 (1964).
11. C. P. Brock, and J. D. Dunitz, *Acta Crystallogr. Sect. B*, 46, 795–806 (1990).
12. B. Marciniak, A novel multistage zone refiner for purification of organic materials, in *Solid State Crystals: Growth and Characterization Materials Science and Applications*, J. Żmija, A. Rogalski, J. Zieliñiski, eds. Proc. SPIE, 3178, 68 (1997).
13. B. Marciniak, *Mol. Cryst. Liq. Cryst.*, 162B, 301–313 (1988).
14. F. R. Lipsett, *Can. J. Phys.*, 35, 284–298 (1957).
15. G. M. Sheldrick, *SHELX 76:A program for crystal structure determination* (University of Cambridge, UK, 1976).
16. G. M. Sheldrick, *SHELX 86: A program for crystal structure solution* (University of Göttingen, FRG, 1986).
17. E. Różycka-Sokołowska, and B. Marciniak, in preparation.
18. E. Parthé, K. Cenzual, and R. Gladyshevskii, *J. Alloys Comp.*, 197, 291–301 (1993).