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Orientational Disorder in Phenanthrene. Structure Determination at 248, 295, 339 and 344 K

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Abstract

Phenanthrene, $C_{14}H_{10}$, $M_r = 178{\cdot}2$, m.p. 374 K, shows a phase transition around 333–343 K. The structure is ordered at 295 K with $a = 8{\cdot}441\ (2)$, $b = 6{\cdot}140\ (1)$, $c = 9{\cdot}438\ (1)$ Å, $\beta = 97{\cdot}96\ (1)°$, $V = 484{\cdot}4\ (1)$ Å^3, monoclinic, $P2_1$, $Z = 2$, $D_x = 1{\cdot}221$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}064$ mm^{-1}, $F(000) = 188$, $R = 0{\cdot}043$ for 726 observed reflections. The high-temperature phase is orientationally disordered with the second possible position of the molecule related to the first by a center of symmetry. Two intensity data sets at 339 and 344 K were used in least-squares refinement. The occupancy of the second position was refined to 0·158 (5) and 0·446 (3) at 339 and 344 K, respectively. It is possible to quench the high-temperature phase by rapid cooling from 344 to below 260 K. The occupancy of the second position in the quenched phase was refined to 0·389 (3).

Introduction

Phenanthrene is one of the simple aromatic hydrocarbons which has been intensively studied. The structural phase transition in phenanthrene has been studied by measurement of several physical properties (Kroupa *et al.*, 1988; and references therein). The structure of the room-temperature phase was determined by Basak (1950), Trotter (1963) and Kay, Okaya & Cox (1971). An X-ray powder diffraction study of the phase transition and the structure of the high-temperature phase were reported by Matsumoto & Fukuda (1967). They suggested the same space group for both phases. The present diffraction study is the first attempt to solve and refine the structure of the high-temperature phase and the structure during the phase transition from X-ray diffraction single-crystal data.

Experimental

Colorless transparent monocrystals were grown by the Bridgman method. A spherical sample ($r = 0{\cdot}6$ mm), prepared by cutting and polishing, was mounted in a Lindeman-glass capillary to decrease sublimation. A Hilger & Watts diffractometer (Mo $K\alpha$, Nb filter) controlled by an M7000 computer was used to collect crystal and intensity data at different temperatures. The learnt-profile method (Diamond, 1969; Clegg, 1981) was used to obtain intensities and their e.s.d.'s. The scan speed was varied from 1 to 8° min^{-1}, determined from a rapid prescan. The intensities of three standard reflections ($41\bar{1}$, 132, 005) were measured every 30 reflections. Reflections with $I < 1{\cdot}96\sigma(I)$ were classified as unobserved, but were used in the refinement with $|F_{\text{unobs}}| = \frac{2}{3}|F_{\text{min}}|$ and $\sigma(|F_{\text{unobs}}|) = [1/(18)^{1/2}]|F_{\text{min}}|$ where $|F_{\text{min}}|$ is the minimum observed value of $|F|$. The data were corrected for Lorentz and polarization effects. Crystal data and details of the data collection are given in Table 1.

The sample was heated (cooled) by a nitrogen stream. The temperatures quoted were deduced by measuring the temperature of the nitrogen stream with a thermocouple. Four temperatures 248, 295, 339 and 344 K, at which the quenched, room-

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Table 1. *Crystal data, collection and reduction of intensity data and least-squares refinement details*

	248 K	295 K	339 K	344 K
a (Å)	8·436 (2)	8·441 (2)	8·489 (2)	8·506 (2)
b (Å)	6·127 (2)	6·140 (1)	6·204 (1)	6·215 (2)
c (Å)	9·449 (3)	9·438 (1)	9·526 (2)	9·525 (2)
β (°)	98·29 (3)	97·96 (1)	98·44 (2)	98·73 (2)
V (Å^3)	483·2 (2)	484·4 (1)	495·2 (20)	497·7 (2)
D_x (Mg m^{-3})	1·2246	1·2216	1·1949	1·1889
No. of reflections for cell determination	21	32	25	17
θ range (°)	10–17	8–18·5	10–17	10–14
μ (mm^{-1})	0·0644	0·0642	0·0628	0·0625
Data collection (θ–2θ scans)				
$\sin\theta/\lambda_{\max}$ (Å^{-1})	0·59463	0·59463	0·59463	0·59463
Min. *hkl*	0,0, −9	0,0, −11	0,0, −11	0,0, −11
Max. *hkl*	9,7,8	9,7,11	9,7,11	9,7,11
Independent reflections	914	944	961	968
No. with $I > 1{\cdot}96\sigma(I)$	595	726	572	377
Refinement				
Function minimized	$w(\lvert F_o\rvert - \lvert F_c\rvert)$; $w^{-1} = \sigma^2(\lvert F_o\rvert) + (0{\cdot}03\lvert F_o\rvert)^2$			
R	0·065	0·043	0·061	0·064
wR	0·105	0·059	0·092	0·088
S	1·9	1·4	1·7	1·5
No. of variables	92	166	92	92
$(\Delta/\sigma)_{\max}$	0·09	0·00	0·10	0·18
$\Delta\rho_{\max}$ (e Å^{-3})	0·16	0·17	0·12	0·15
$\Delta\rho_{\min}$ (e Å^{-3})	−0·15	−0·15	−0·16	−0·18

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (*Hamilton*, 1959) *with e.s.d.'s in parentheses for the room-temperature phase* (295 K)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
C(1)	0·1668 (4)	0·992*	−0·3038 (3)	0·0759 (14)
C(2)	0·0751 (4)	−0·070 (1)	−0·3550 (4)	0·0842 (15)
C(3)	0·0368 (4)	−0·231 (1)	−0·2648 (4)	0·0785 (14)
C(4)	0·0945 (3)	−0·225 (1)	−0·1213 (3)	0·0643 (11)
C(5)	0·2289 (4)	−0·201 (1)	0·1860 (3)	0·0661 (11)
C(6)	0·2948 (5)	−0·181 (1)	0·3272 (3)	0·0852 (15)
C(7)	0·3867 (5)	−0·001 (1)	0·3754 (4)	0·0904 (18)
C(8)	0·4122 (4)	0·157 (1)	0·2813 (4)	0·0831 (15)
C(9)	0·3783 (4)	0·309 (1)	0·0364 (4)	0·0703 (13)
C(10)	0·3205 (3)	0·294 (1)	−0·1026 (4)	0·0661 (11)
C(11)	0·2263 (3)	0·113 (1)	−0·1562 (3)	0·0579 (10)
C(12)	0·1908 (3)	−0·055 (1)	−0·0639 (3)	0·0491 (9)
C(13)	0·2551 (3)	−0·0407 (8)	0·0869 (3)	0·0529 (10)
C(14)	0·3489 (3)	0·143 (1)	0·1351 (3)	0·0595 (11)

* Fixed.

Table 3. *Interatomic distances* (Å) *with e.s.d.'s in parentheses for the room-temperature phase* (295 K)

C(1)—C(2)	1·345 (7)	C(7)—C(8)	1·352 (8)
C(2)—C(11)	1·416 (4)	C(8)—C(14)	1·412 (4)
C(2)—C(3)	1·374 (8)	C(9)—C(10)	1·338 (5)
C(3)—C(4)	1·375 (4)	C(9)—C(14)	1·425 (7)
C(4)—C(12)	1·385 (7)	C(10)—C(11)	1·419 (7)
C(5)—C(6)	1·378 (4)	C(11)—C(12)	1·406 (7)
C(5)—C(13)	1·399 (7)	C(12)—C(13)	1·454 (6)
C(6)—C(7)	1·389 (9)	C(13)—C(14)	1·415 (7)

temperature, intermediate and high-temperature phases occur, respectively, were selected to investigate the structural changes during the phase transition. The intensity of the $10\bar{2}$ reflection was the most sensitive to change of temperature during the phase transition [$I_{339\,\rm K}(10\bar{2}) = 0{\cdot}41 \times I_{295\,\rm K}(10\bar{2})$, $I_{344\,\rm K}(10\bar{2}) = 0{\cdot}006 \times I_{295\,\rm K}(10\bar{2})$ and $I_{248\,\rm K}(10\bar{2}) = 0{\cdot}015 \times I_{295\,\rm K}(10\bar{2})$]. This reflection was monitored as a fourth standard reflection in order to check the stability of these phases. The quenched phase was prepared by rapid quenching (~1 s) from 344 K (the high-temperature phase) to 248 K. All characteristic intensities of this phase were much closer to those of the high-temperature phase than to those of the room-temperature phase. The intensity of the reflection $10\bar{2}$ increased slowly during data collection for this phase (37 h) from 1·5 to 6% of $I_{295\,\rm K}$ $(10\bar{2})$ but no correction to intensities was made for this effect.

Structure solution and refinement

Coordinates from Kay *et al.* (1971) were used as the starting point for our refinement of the room-temperature phase. All important characteristics and results are summarized in Tables 1–3. The packing of the molecules in the unit cell is illustrated in Fig. 1.* Difference electron density maps for 248, 339 and 344 K data based on the refined room-temperature data showed a second position of the molecule, related to the first by an inversion center close to (0·25, 0, 0). The y coordinate was set to zero by a suitable choice of origin in space group $P2_1$. The presence of the center of symmetry, *i.e.* equal occupancies of two molecular positions, leads to the centrosymmetric space group $P2_1/a$. Reflections $h0l$ with odd h (*e.g.* $10\bar{2}$) were very sensitive during the

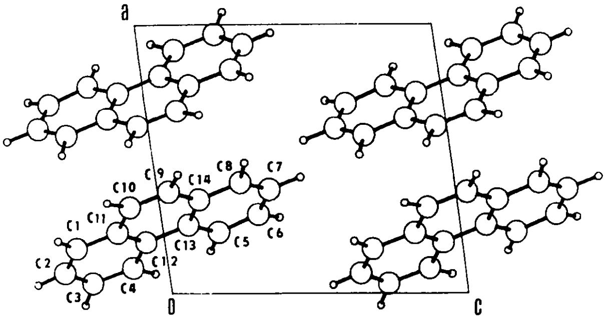

Fig. 1. Projection of the unit-cell contents (along the b axis) of the room-temperature phase.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and H-atom bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53351 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Occupation factors p, angles φ, χ, ψ (rotation along* **a**, **a** × **c***, **c*** *respectively) and translation x, y, z of the molecule of phenanthrene*

The second molecule is related to the first by an inversion point (0·25, 0, 0) and its occupation factor is $1 - p$.

T(K)	p	φ (°)	χ (°)	ψ (°)	x	y	z
244†	0·611 (3)	−0·25 (8)	−0·38 (5)	−0·57 (6)	0·1685 (4)	0·0864 (8)	−0·3089 (3)
295	1·000	0·0	0·0	0·0	0·1667 (4)	0·0992	−0·3038 (3)
339	0·842 (5)	−0·12 (6)	−0·63 (4)	−0·17 (5)	0·1696 (3)	0·086 (1)	−0·3060 (2)
344	0·554 (3)	−0·25 (7)	−1·01 (6)	−0·52 (7)	0·1710 (5)	0·0843 (7)	−0·3089 (4)

† Quenched phase.

phase transition and were practically all unobserved for the highest temperature data (344 K). The intermediate, high-temperature and quenched refinements were carried out under the assumption that the geometry of the molecules remains the same during the phase transition and anisotropic atomic displacement parameters for carbons, three rotation angles (along **a**, **a** × **c*** and **c***), three translations of the molecules and the occupancies of these positions were refined. The position of the inversion point was fixed at the position indicated above. Details of these refinements and the results are shown in Tables 1 and 4. The orientational disorder of the molecules is illustrated in Fig. 2. All calculations were performed by programs from our *SDS* package (Petříček & Malý, 1990) on a Siemens 7536 computer. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion

The phase transition can be described as an orientational disorder with a change of space group from $P2_1$ to $P2_1/a$. Similar disorder is not uncommon in crystals of related compounds (Hanson, 1960; Hazell, Hazel & Larsen, 1986; Prat, 1961; Robertson, Shearer, Sim & Watson, 1962; Welberry, 1973). The conclusion reached by Matsumoto & Fukuda (1967) that the space group does not change during the phase transition of phenanthrene does not seem convincing because only one reflection, $10\bar{2}$, from the set $h0l$ (h odd) from their powder diffraction data was indexed and this reflection disappeared during measurement. Our mesurements showed a drastic reduction of intensity for these reflections. However, we did not obtain a complete proof of space group $P2_1/a$, *i.e.* an occupation factor of 0·5, as the temperature could not be raised above 344 K (for full data collection) because of the risk of damage to the sample incurred by melting and/or sublimation. However, a rapid test of reflection $10\bar{2}$ at temperatures higher than 344 K resulted in its complete disappearance.

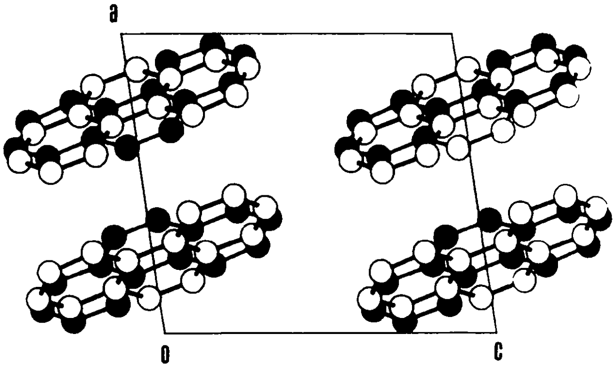

Fig. 2. Projection of the average unit cell of the high-temperature phase. The two possible positions of the molecules (white and black) are related by an inversion center at (0·250, 0, 0).

There are many ways to describe the orientational disorder. As the geometry of the molecule is close to local symmetry $mm2$, we can combine these symmetry elements with the inversion center and use different 'disorder elements'. Although we tried all combinations, such refinements resulted in slightly worse agreement factors.

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