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Polymorphism in pentacene

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Pentacene, $C_{22}H_{14}$, crystallizes in different morphologies characterized by their $d(001)$-spacings of 14.1, 14.5, 15.0 and 15.4 Å. We have studied the crystal structure of the 14.1 and 14.5 Å d-spacing morphologies grown by vapour transport and from solution. We find a close correspondence between the 14.1 Å structure reported by Holmes, Kumaraswamy, Matzeger & Vollhardt [*Chem. Eur. J.* (1999), **5**, 3399–3412] and the 14.5 Å structure reported by Campbell, Monteath Robertson & Trotter [*Acta Cryst.* (1961), **14**, 705–711]. Single crystals commonly adopt the 14.1 Å d-spacing morphology with an inversion centre on both molecules in the unit cell. Thin films grown on SiO_2 substrates above 350 K preferentially adopt the 14.5 Å d-spacing morphology, with a slightly smaller unit-cell volume.

Comment

Recently, molecular organic conductors were shown to exhibit a number of physical phenomena that were previously reserved for inorganic materials. This new development was triggered by the growth of ultrapure single crystals. In these crystals, the electronic mobility is comparable with single-crystal silicon (Schön *et al.*, 2000*a*), which has been shown to be essential for phenomena such as electric-field-induced superconductivity (Schön *et al.*, 2000*b*), Quantum Hall oscillations (Schön, Berg *et al.*, 2000) and amplified spontaneous emission resulting in an injection laser (Schön, Kloc *et al.*, 2000). A number of molecular conductors were shown to exhibit these properties, such as C_{60}, thiophenes and the acenes. The acenes, from anthracene to hexacene, have been widely studied for electronic transport properties in the thin film as well as the single-crystal form.

(I)
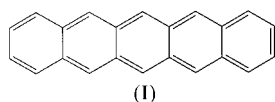
The crystal structure of pentacene, (I), was reported by Campbell *et al.* (1961) for crystals grown from solution. They constructed a triclinic crystal structure using $0kl$ and $h0l$ Weissenberg films. The molecules are detected along the c axis with a $d(001)$-spacing of 14.5 Å. Because this d-spacing is by far the largest in this structure, it becomes characteristic for the structure. A much smaller d-spacing of 14.1 Å was recently reported by Holmes *et al.* (1999), also for crystals grown from solution. For thin films, different values for the $d(001)$-spacing have been reported, although the unit cell is not known. For thin films evaporated on SiO_2 at temperatures above 350 K, a d-spacing of 14.5 Å has been reported (Minakata *et al.*, 1992; Bouchoms *et al.*, 1999). Lower substrate temperatures and different types of substrate result in thin films with d-spacings of 15.0 and 15.4 Å. We have studied the structure of single crystals, grown both from vapour transport and solution, in detail and report on the relationship between the 14.1 and 14.5 Å modifications.

We have grown single crystals of pentacene both by vapour transport and from a solution in trichlorobenzene. We found that both growth methods yield crystals with a d-spacing of 14.1 Å, in good agreement with Holmes *et al.* (1999). Despite the different d-spacings, the molecular ordering of the structures exhibit remarkable resemblances (Figs. 1 and 2). In order to compare the 14.1 Å morphology with the structure reported by Campbell *et al.* (1961), we transformed the 14.1 Å unit cell to yield a c axis that has approximately the length of the molecule of 16 Å. The three possible unit-cell transformations $(100, 010, 1\bar{1}1)$, $(100, 010, 101)$ and $(100, 010, \overline{1}1\overline{1})$ result in c-axis values of 16.01, 16.05 and 16.11 Å, respectively. Only for the last transformation does the long axis of the molecule runs approximately along the new c axis, which was also the guideline used by Campbell. This comparison shows that the 14.1 Å structure is very similar to the structure reported by Campbell *et al.* (1961) if we assume that their structure should be read in a left-handed coordinate system. We recall that the
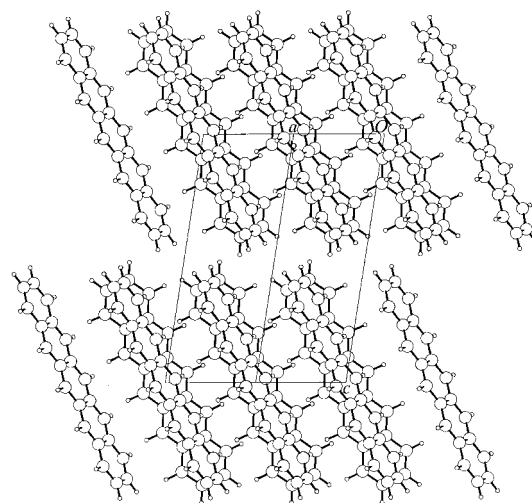

Figure 1
Stacking of the pentacene molecules in the unit cell, viewed along the $[1\bar{1}0]$ axis. The heart-lines of the pentacene molecules lie at angles of 25.17 (2) and 24.39 (2)°, respectively, with respect to the c^* axis. The $d(001)$-spacing is clearly visible.

determination of the handedness in triclinic systems was a very delicate problem at that time. Even with this identification, there remain discrepancies between the two solutions of almost $10°$ in the unit-cell angles, which is beyond standard deviations. These discrepancies concern the angles α and β, the two angles that are important in determining the $d(001)$-spacing and the discrepancies may have been the reason for a redetermination by Campbell *et al.* (1962), where the lattice parameters were revised, but not the angles.

We recall that the d-spacing of 14.5 Å reported by Campbell *et al.* (1961) is in fact observed in thin films. We deposited pentacene thin films on thermally oxidized Si wafers. The pentacene layer of 2 μm thickness was then mechanically removed from the substrate and made into a powder. The diffraction pattern was measured in Bragg–Brentano and Guinier geometry and showed preferential orientation along the [001] axis. Besides the 14.5 Å phase, (00l) lines of the 14.1 and 15.4 Å phases were clearly observable. The 15.4 Å phase was transformed into the 14.5 Å phase by exposure to ethanol (Gundlach *et al.*, 1999). The diffraction pattern could be indexed with $a = 6.485$ (1), $b = 7.407$ (2), $c = 14.745$ (4) Å, $\alpha = 77.25$ (2), $\beta = 85.72$ (2), $\gamma = 80.92$ (2)$°$ and $V = 681.6$ Å^3, yielding $d(001) = 14.37$ Å. This is in good agreement with
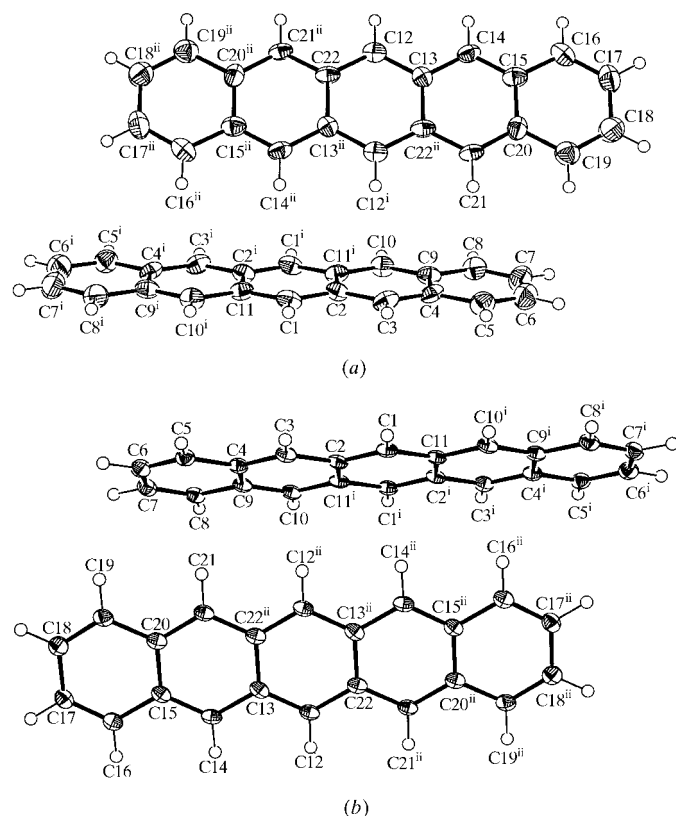
reports on the 14.5 Å d-spacing, but the unit-cell parameters are distinctly different from the values reported by Campbell *et al.* (1961, 1962). We will report this unit-cell determination separately. We conclude that pentacene exhibits at least four morphologies, which can be identified by their $d(00l)$-spacings. Single crystals commonly adopt the smallest $d(001)$-spacing of 14.1 Å. Thin films grown above 350 K adopt preferentially the 14.5 Å $d(001)$-spacing with a slightly smaller unit-cell volume.

Experimental

The source material, 99.9% pure pentacene, was purchased from Aldrich and not purified further. Single crystals of pentacene were grown using physical vapour transport in a horizontal glass tube (Laudise *et al.*, 1998). A temperature gradient was applied over the tube. The source material was sublimed at 550 K and crystallized at the other end of the tube at approximately 490 K. The growth was performed under a stream of N_2 (99.999% purity, AGA gas) and H_2 gases (99.995% purity, AGA gas), with a volume percentage of 5.1 (1)% H_2 [for (I) at 293 K]. This yielded almost centimetre-sized violet crystals in the form of platelets and needles. The c^* axis was normal to the plane of the very thin platelets (typically 10 to 100 μm) and the growth of the needles was along the [1$\bar{1}$0] direction. Also, at a different part of the tube, a small amount of hydrogenated pentacene crystals (red needles) was found. Lowering the flow rate yielded a larger fraction of hydrogenated pentacene. At lower hydrogen content or if no ultrapure inert transport gas is used, the pentacene oxidizes, forming 6,13-pentacenequinone, and small brown needles crystallize (Dzyabchenko *et al.*, 1979). The crystal structure of hydrogenated pentacene will be reported separately. Crystals were also grown from solution in trichlorobenzene by slowly evaporating the solvent over a period of four weeks at 450 K, under a stream of ultrapure N_2 gas. Crystals thus obtained [(I) at 90 K] exhibit the same crystal structure as the crystals grown by vapour transport. Pentacene thin films have been deposited using high-vacuum sublimation (10^{-8} mbar; 1 mbar = 100 Pa). The source material was heated in a crucible and evaporated onto a thermally oxidized Si wafer heated to 370 K. A low evaporation rate of 0.1 nm s^{-1} was used to ensure crystallinity and the sample was cooled rapidly afterwards. The layer thickness was 2 μm.

Figure 2
Perspective *ORTEP*-3 (Farrugia, 1997) drawing of the pentacene molecules at (*a*) 293 K and (*b*) 90 K, showing the non-H atom-numbering scheme. All C atoms are represented by displacement ellipsoids at the 50% probability level and the H atoms are drawn with arbitrary radii. Both molecules have a crystallographically imposed centre of inversion: C1—C11^i at ($\frac{1}{2}$,$\frac{1}{2}$,0) and C12—C22^{ii} at (0,0,0) [symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $-x$, $-y$, $-z$].

Compound (I) at 293 K

Crystal data

$C_{22}H_{14}$	$Z = 2$
$M_r = 278.35$	$D_x = 1.349$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.266$ (1) Å	Cell parameters from 23
$b = 7.775$ (1) Å	reflections
$c = 14.530$ (1) Å	$\theta = 17.9$–21.7$°$
$\alpha = 76.475$ (4)$°$	$\mu = 0.08$ mm^{-1}
$\beta = 87.682$ (4)$°$	$T = 293$ K
$\gamma = 84.684$ (4)$°$	Needle–block, violet
$V = 685.15$ (15) Å^3	$0.10 \times 0.08 \times 0.08$ mm

Data collection

Enraf–Nonius CAD-4F diffractometer	$\theta_{max} = 26.0°$
	$h = -7 \rightarrow 6$
$\omega/2\theta$ scans	$k = -6 \rightarrow 9$
2856 measured reflections	$l = -17 \rightarrow 17$
2684 independent reflections	3 standard reflections
843 reflections with $I > 2\sigma(I)$	frequency: 180 min
$R_{int} = 0.034$	

Refinement

Refinement on F^2
$R(F) = 0.069$
$wR(F^2) = 0.179$
$S = 0.94$
2684 reflections
199 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Compound (I) at 90 K

Crystal data

$C_{22}H_{14}$
$M_r = 278.35$
Triclinic, $P\bar{1}$
$a = 6.239 (1)$ Å
$b = 7.636 (1)$ Å
$c = 14.330 (2)$ Å
$\alpha = 76.978 (3)°$
$\beta = 88.136 (3)°$
$\gamma = 84.415 (3)°$
$V = 661.94 (17)$ Å^3

$Z = 2$
$D_x = 1.396$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1062
  reflections
$\theta = 2.8–26.1°$
$\mu = 0.08$ mm^{-1}
$T = 90$ K
Platelet, violet–blue
$0.25 \times 0.24 \times 0.01$ mm

Data collection

Bruker SMART APEX diffrac-
  tometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Bruker, 2000)
  $T_{min} = 0.981$, $T_{max} = 0.999$
5619 measured reflections

2584 independent reflections
1252 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 26.1°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 17$

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.145$
$S = 0.97$
2584 reflections
255 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

The needle axis appeared to be along the $[1\bar{1}0]$ vector (9.52 Å) in the chosen (standard) unit-cell setting. The studied plate-shaped crystals were all twinned and the plane normal is along the c^* axis (meaning the a and b axes in the plate). The relation between the twin orientations is a 180° rotation around the $[1\bar{1}0]$ axis (rotation matrix: $0\bar{1}0$, $\bar{1}00$, $00\bar{1}$). Although an X-ray structure determination was thwarted by persistent crystal twinning and the weak scattering power of the crystals, we ultimately found a single crystal (needle-shaped) fit to the X-ray diffraction experiment.

For compound (I) at 293 K, data collection: *CAD-4-UNIX Software* (Enraf–Nonius, 1994); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *PLUTO* (Meetsma, 2000) and *PLATON* (Spek, 1994); software used to prepare material for publication: *PLATON* (Spek, 1990).

For compound (I) at 90 K, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *XPREP* (Bruker, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTO* (Meetsma, 2000), *ORTEP-3* (Farrugia, 1997; Johnson *et al.*, 2000) and *PLATON* (Spek, 1994); software used to prepare material for publication: *PLATON* (Spek, 1990) and *SHELXL*97.

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