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A 2:1 cocrystal of 6,13-dihydropentacene and pentacene

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6,13-Dihydropentacene and pentacene cocrystallize in a ratio of 2:1, *i.e.* $C_{22}H_{16}\cdot0.5C_{22}H_{14}$, during vapour transport of commercial pentacene in a gas flow. The crystal structure is monoclinic, space group $P2_1/n$, and contains one dihydropentacene molecule and half a pentacene molecule in the asymmetric unit.

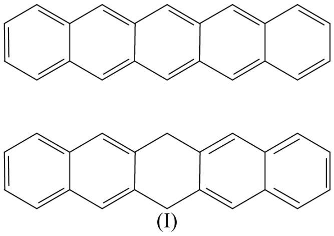
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.013 Å
R factor = 0.064
wR factor = 0.151
Data-to-parameter ratio = 6.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The growth of ultra-pure organic single crystals has recently attracted much attention. Such crystals are a prerequisite for the observation of high electronic mobilities and band conduction in these materials. We have studied single crystals of pentacene, a material that, due to its high carrier mobilities and body of published results, can be considered as a model system for the study of intermolecular interactions.


(I)

The vapour transport of commercially available pentacene powder results in the condensation of dark-blue crystals of pentacene, as either platelets, laths or dendritic needles. During the vapour transport growth, crystals of 6,13-pentacenequinone (Dzyabchenko *et al.*, 1979) and 6,13-dihydropentacene–pentacene were also obtained. We have found that dihydropentacene cocrystallizes with pentacene to form long needle-like crystals of the title cocrystal, (I). The colour of the crystals ranges from dark-pink/red to red to white transparent, with the same morphology. The 6,13-dihydropentacene molecules have two methylene groups on opposite sides of the central ring. The cocrystal structure is monoclinic, with space group $P2_1/n$. The unit cell contains two planar pentacene molecules and four non-planar 6,13-dihydropentacene molecules (see Figs. 1 and 2). The red needles were observed to grow along the a axis. 6,13–Pentacenequinone and 6,13-dihydropentacene molecules have two carbonyl groups and two methylene groups, respectively, at each side of the central ring. This indicates that the central ring of a pentacene molecule is the most reactive site.

Experimental

Two different crystal-growth methods were used and both yielded the same 6,13-dihydropentacene–pentacene (2/1) cocrystals. As source material for both methods, pentacene powder (Aldrich) was used as

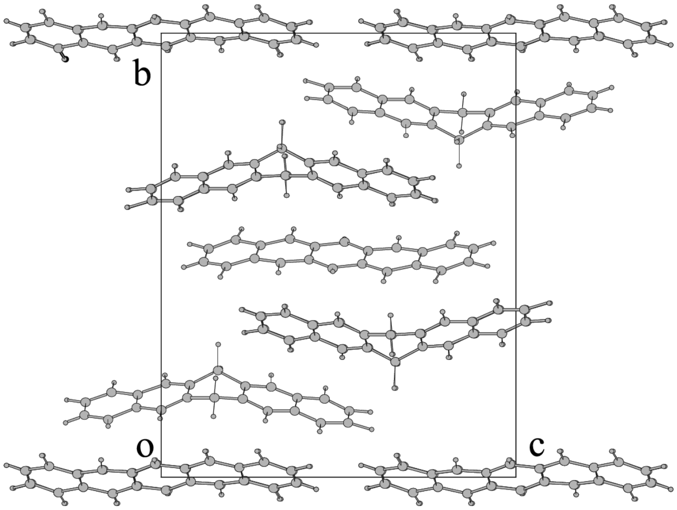


Figure 1
The unit-cell contents of the title 6,13-dihydropentacene-pentacene (2/1) cocrystal, viewed along the *a* axis.

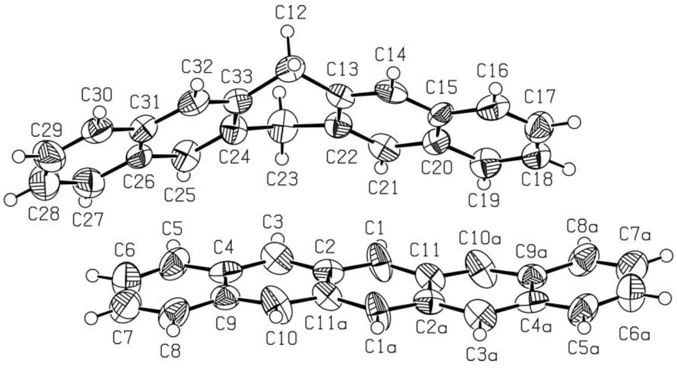


Figure 2
View of a 6,13-dihydropentacene molecule and a pentacene molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (*a*) $-x, -y, -z$.]

supplied. X-ray powder diffraction patterns of this commercially available pentacene did not reveal the presence of any contaminants, such as pentacenequinone or dihydropentacene. However, small amounts of contaminants cannot be detected by this method.

Method A (Groningen): single crystals were grown using physical vapour transport in a horizontal glass tube (Laudise *et al.*, 1998, Mattheus, 2002). A Pyrex glass tube (inner diameter of 16 mm) was cleaned by heating under a nitrogen gas flow and placed in a second tube. 200–400 mg of pentacene were placed at the end of the tube in a platinum crucible. The growth was performed either under a stream of nitrogen gas mixed with hydrogen gas or under a pure argon flow. The nitrogen and argon gases were purified over activated copper and alumina columns, to remove any residual traces of H_2O and oxygen. Gases were obtained from AGA, with 5*N* purity for nitrogen and argon, and 4*N*5 for hydrogen. A temperature gradient was applied by resistive heating of two heater coils around the tube. The source material was sublimed at ~550 K. Depending on the exact temperature gradient, pentacene crystals condensed at ~300 mm from the sublimation point at a temperature of ~490 K. If the vapour transport is executed in a poorly sealed system or residual oxygen, as *e.g.* H_2O, is present, 6,13-pentacenequinone crystals are observed at a slightly higher temperature, ~520 K. However, if hydrogen is present in the carrier gas either by dilution or by decomposition of the starting material, 6,13-dihydropentacene–pentacene cocrystals condense at a lower temperature, ~480 K. Increasing the amount of hydrogen in the carrier gas was observed to increase the amount of red crystals. The use of pure argon as transport gas yielded significantly less product.

Method B (Bell Labs): single crystals of pentacene were grown by physical vapour phase transport in a horizontal transparent furnace. A charge of 10–30 mg of pentacene was placed in a high temperature (553–593 K) zone inside a two-zone furnace and was exposed to either an Ar, He or H_2 gas stream; flow rate of 40–100 ml min^{-1}. The pure gas, pressure *ca* 1 atm (1 atm = 101325 Pa), was delivered to one end of the crystal-growth reactor and exited from the system through a bubbler, thus removing impurities and decomposition products. If the impurities in pentacene consist of larger and/or smaller molecules with either lower or higher vapour pressure, gas flow will transport the smaller molecules from the hot zone to the cold zone of the furnace. Molecules with higher vapour pressure will remain in the hot zone and will not contaminate the growing pentacene crystals. For molecules with very similar vapour pressures, the gas-transport mechanisms are expected to be alike. Pentacene crystals nucleated spontaneously on the reactor wall at the low-temperature region. The temperature of the central part of the cold zone was set to 493 K, as measured by an external sensor in close proximity to the heater. Due to flow of hot gas, the temperature gradient in the crystallization zone was from 593 K to room temperature over the length of the tube. 6,13-Dihydropentacene–pentacene cocrystals were formed at the far end of the furnace, where the temperature of the reactor tube dropped to ambient temperature.

Crystal data

$2C_{22}H_{16}\cdot C_{22}H_{14}$
$M_r = 839.02$
Monoclinic, $P2_1/n$
$a = 6.163$ (4) Å
$b = 21.801$ (5) Å
$c = 16.069$ (3) Å
$\beta = 93.73$ (3)°
$V = 2154.5$ (15) Å^3
$Z = 2$
$D_x = 1.293$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 6.3$–11.5°
$\mu = 0.07$ mm^{-1}
$T = 293$ K
Needle, red
0.32 × 0.07 × 0.05 mm

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
4504 measured reflections
2001 independent reflections
770 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.123$
$\theta_{\rm max} = 20.0°$
$h = 0 \rightarrow 5$
$k = -20 \rightarrow 20$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 180 min
intensity decay: <0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.151$
$S = 0.93$
2001 reflections
299 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

The X-ray structure determination was thwarted by persistent very weak scattering by the crystals. After many trials, a crystal for the structure determination was obtained, but no observed reflections could be measured with $\theta > 20°$. Due to the low observation-to-parameter ratio, the H atoms, which could be located from difference Fourier maps, were included in calculated positions and refined in the riding mode.

o1230 Christine C. Mattheus *et al.* • $C_{22}H_{16}\cdot 0.5C_{22}H_{14}$ *Acta Cryst.* (2002). E**58**, o1229–o1231

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, 2002) and *PLATON* (Spek, 1994); software used to prepare material for publication: *PLATON* (Spek, 1990).

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