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

6,13-Dihydropentacene and pentacene cocrystallize in a ratio of 2:1, i.e. $\text{C}_{22}\text{H}_{16}/0.5\text{C}_{22}\text{H}_{14}$, 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.

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.

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
slightly higher temperature, \( \sim 520 \text{ K} \). However, if hydrogen is present in the carrier gas either by dilution or by decomposition of the starting material, 6,13-dihydopentacene–pentacene cocrystals condense at a lower temperature, \( \sim 480 \text{ K} \). 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-Dihydopentacene–pentacene cocrystals were formed at the far end of the furnace, where the temperature of the reactor tube dropped to ambient temperature.

Crystal data

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\begin{align*}
&\text{C}_{22}\text{H}_{16}\cdot\text{C}_{22}\text{H}_{14} & D_\text{c} = 1.293 \text{ Mg m}^{-3} \\
&M_\text{r} = 839.02 & \text{Mo Kα radiation} \\
&\text{Monoclinic, } P2_1/n & \text{Cell parameters from 23} \\
&a = 6.163 (4) \text{ Å} & \text{reflections} \\
&b = 21.801 (5) \text{ Å} & \theta = 6.3–11.5^\circ \\
&c = 16.069 (3) \text{ Å} & \mu = 0.07 \text{ mm}^{-1} \\
&β = 93.73 (3)^\circ & T = 293 K \\
&V = 2154.5 (15) \text{ Å}^3 & \text{Needle, red} \\
&Z = 2 & 0.32 \times 0.07 \times 0.05 \text{ mm}
\end{align*}
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Data collection

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\begin{align*}
&\text{Enraf-Nonius CAD-4F} & \theta_{\text{max}} = 20.0^\circ \\
&\text{diffractometer} & k = 0 → 5 \\
&\omega/2θ scans & l = -15 → 15 \\
&4504 \text{ measured reflections} & \text{2 standard reflections} \\
&2001 \text{ independent reflections} & \text{frequency: 180 min} \\
&770 \text{ reflections with } I > 2σ(I) & \text{intensity decay: <0.1%} \\
&R_{\text{int}} = 0.123 & \text{Refinement}
\end{align*}
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Refinement

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\begin{align*}
&\text{Reefinement on } F^2 & H\text{-atom parameters constrained} \\
&R(F^2) > 2σ(F^2) = 0.064 & w = 1/\sigma^2(F^2) + 0.0453P^2 \\
&wR(F^2) = 0.151 & \text{where } P = (F^2 + 2F^2)/3 \\
&S = 0.93 & (Δθ)_{\text{max}} = 0.001 \\
&2001 \text{ reflections} & Δρ_{\text{max}} = 0.18 \text{ e Å}^{-3} \\
&299 \text{ parameters} & Δρ_{\text{min}} = -0.20 \text{ e Å}^{-3}
\end{align*}
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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 \( θ > 20^\circ \). 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.
Data collection: CAD-4-UNIX Software (Enraf-Nonius, 1994); cell refinement: SET4 (de Boer & Duijnenberg, 1984); data reduction: HELENA (Spek, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLUTO (Meetsma, 2002) and PLATON (Spek, 1994); software used to prepare material for publication: PLATON (Spek, 1990).

References