6,13-dihydropentacene and pentacene single co-crystals

Christine C. Mattheus a, Jakob Baas a, Auke Meetsma a, Jan L. de Boer a, Christian Kloc b, Theo Siegrist b c, and Thomas T. M. Palstra a∗

aSolid State Chemistry Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands
bBell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, NJ 07974, USA
cDepartment of Materials Chemistry, P.O. Box 124, Lund University, 221 00 Lund, Sweden

Abstract
6,13-dihydropentacene and pentacene co-crystallise in a ratio of 2:1 during vapour transport of commercial pentacene in a gas flow. The crystal structure is monoclinic P21/n and contains one dihydropentacene molecule, and half a pentacene molecule in the asymmetric unit.

Submitted to Acta Cryst. E. on 23 september 2002, accepted for publication on 7 october 2002.
The crystallographic information can be found at http://journals.iucr.org/e/or: Mattheus Ph. D. Thesis, available for download at: http://rugth30.phys.rug.nl/msc_newweb/ph_d.htm

1. Comment

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

The vapour transport of commercially available pentacene powder results in condensation of dark blue crystals of pentacene, either as platelets, lath or as dendritic needles. During the vapour transport growth, also crystals of 6,13-pentacenequinone and 6,13-dihydropentacene-pentacene were obtained. We have found that dihydropentacene co-crystallizes with pentacene to form long needle-like crystals. The colour of the crystals range from dark pink/red to reddish to white transparent, with the same structure. The 6,13-dihydropentacene molecules have two methylene groups at opposite sides of the central ring. The co-crystal structure is monoclinic, and crystallizes in space group P21/n. The unit cell consists of two planar pentacene molecules and four non-planar 6,13-dihydropentacene molecules, see Figure 1. The red needles were observed to grow along the a-axis. 6,13-pentacenequinone and 6,13-dihydropentacene molecules consist of 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.

2. Experimental

Two different crystal growth methods were used and both yielded the same 6,13-dihydropentacene-pentacene co-crystals. As source material for both methods pentacene powder (Aldrich) was used as supplied. X-ray powder diffraction spectra of this commercially available pentacene did not reveal any presence of contaminants, such as pentacenequinone.
or dihydropentacene. However, small amounts of contaminations cannot be detected by this method. Method I (Groningen): single crystals were grown using physical vapour transport in a horizontal glass tube. 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 the source material were placed at the end of the tube in a platinum crucible. The growth was either performed under a stream of nitrogen gas mixed with hydrogen gas or under a pure argon flow. The nitrogen and argon gasses were purified over activated copper and alumina columns, to remove any residual traces of H\textsubscript{2}O and oxygen. Gasses were obtained from AGA, with 5N purity for nitrogen and argon, and 4N5 for hydrogen. A temperature gradient was applied by resistive heating of two heater coils around the tube. The source material was sublimed at \( \sim 550 \) K. Depending on the exact temperature gradient, pentacene crystals condensed at \( \sim 300 \) mm from the sublimation point at a temperature of \( \sim 490 \) K. If the vapour transport is executed in a poorly sealed system or residual oxygen as e.g. H\textsubscript{2}O is present 6,13-pentacenequinone crystals are observed at a slightly higher temperature, \( \sim 520 \) K. However, if hydrogen is present in the carrier gas either by dilution of by decomposition of the starting material, 6,13-dihydropentacene-pentacene co-crystals condense at lower temperature, sim 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 red crystals.

Method II (Bell Labs): single crystals of pentacene were grown by physical vapor phase transport in a horizontal transparent furnace. A charge of a 10-30 milligrams of pentacene was placed in a high temperature (280 -320 °C) zone inside a two zone furnace and was exposed to either an Ar, He or H\textsubscript{2}O gas stream, flowing at a rate of 40-100 ml min\(^{-1}\). The pure gas, at a pressure of ca. 1 atm, 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 vapor pressure, gas flow will transport the smaller molecules from the hot zone to the cold zone of the furnace. Molecules with higher vapor pressure will remain in the hot zone and will not contaminate the growing pentacene crystals. For molecules with very similar vapor 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 center part of the cold zone was set to 220 °C, as measured by an external sensor in close proximity to the heater. Due to flow of hot gas, the temperature in the crystallization zone was spread from 320 °C to room temperature over the length of the tube. 6,13-dihydropentacene-pentacene co-crystals were formed at the far end of the furnace, where the temperature of the reactor tube drops down to ambient temperature.

3. Refinement

The X-ray structure determination was thwarted by persistent very weak scattering of the crystals. After many trials a crystal for the structure determination was obtained, but no observed reflections could be measured with \( \theta > 20^\circ \). Due to the low observation to param-
Figure 2. View of the 6,13-dihydropentacene molecule and a pentacene molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are shown as spheres of arbitrary radius. Symmetry code: (i) -x,-y,-z.

REFERENCEs
1. Boer, J.L. de and Duisenberg, A.J.M. (1984). Acta Cryst. A 40, C-410.
2. Dzyabchenko, A.V., Zavodnik, V.E. and Bel-sky, V.K. (1979). Acta Cryst. B35, 2250-2253.
3. Enraf-Nonius (1994). CAD4-UNIX Software. Version 5.1 Utrecht modified version October 1994. Enraf-Nonius, Delft, The Netherlands.
4. International Tables for Crystallography (1992). Vol. C. Edited by A.J.C Wilson, Kluwer Academic Publishers, Dordrecht, The Netherlands.
5. Laudise, R.A., Kloc, C., Simpkins, P., and Siegrist, T. (1998). J. Cryst. Growth 187, 449-454.
6. Sheldrick, G.M. SHELXL97. Program for crystal structure refinement. University of Göttingen, Germany, 1997.
7. Sheldrick, G.M. SHELXS97. Program for Crystal Structure solution. University of Göttingen, Germany, 1997.
8. Spek, A.L. (1990). Acta Cryst. A 46, C-34.
9. Spek, A.L. (1994). Am. Crystallogr. Assoc.-Abstracts, 22, 66.
10. Spek, A.L. (1997). HELENA, Program for Datareduction, Utrecht University, The Netherlands.

|   |   |
|---|---|
| Formula | 2(C_{22}H_{16})(C_{22}H_{14}) |
| Formula weight | 839.03 g mol^{-1} |
| Crystal system | monoclinic |
| Space group, no. | P21/n, 14 |
| a | 6.163(4) Å |
| b | 21.801(5) Å |
| c | 16.069(3) Å |
| β | 93.73(3)° |
| Volume | 2154.5(15) Å³ |
| Formula Z | 2 |
| Space group Z | 4 |
| ρ_{calc} | 1.293 g cm⁻³ |
| F(000) | 884 electrons |
| μ(Mo Kα) | 0.73 cm⁻¹ |
| Colour, habit | red, needle |
| Approx. crystal dimensions | 0.05 × 0.07 × 0.32 mm³ |

Table 1
Crystal data and details of the structure determination of 6,13-dihydropentacene and pentacene co-crystals