Organic Electronic Materials 2025 Exercise 3 (submit on 28.03.25)

Introduction: The goal of this exercise is to help you visualize the 3D structures of common organic molecules using the Cambridge Structural Database (CSD). The Cambridge Structural Database (CSD) is a highly curated and comprehensive repository for small-molecule organic and organometallic crystal structures, containing over one million structures from X-ray and neutron diffraction analyses. Each structure undergoes automated checking and manual curation by an in-house scientific editor, and is enriched with bibliographic, chemical, and physical property information.

1. Go to https://www.ccdc.cam.ac.uk/structures/ and look up an organic molecule of your interest (if you have no ideas, try out cubane or penguinone). Familiarize yourself with the 3D viewer and look at the molecule alone, in its unit cell, and then in a lattice (3x3x3). Then, use the following identifiers to look at the crystal structures of some common molecules in organic electronics.

    198723 – 233928 – 1108753 – 117770 – 2040902 – 1129883 – 114447 – 172476

    In each case, give the name of the molecule and identify the packing type (herringbone, sandwich herringbone, etc.).

2. Between two aromatic rings, there are three boundary stacking geometries. Name and draw each them for naphthalene molecule, and briefly explain which one of these stacking geometries is never observed for regular polycyclic aromatic hydrocarbons.

3. Describe the three basic crystal structure types that most polycyclic hydrocarbons adopt. Discuss with an example for each of these types, why the specific structure is adopted.

4. **Homework** – Answer the following question after reading "Week 4 Desiraju 1989 Molecular Structure and Packing": The two molecules A and B are planar aromatic hydrocarbons; the third molecule C is a derivative of B functionalized with 4 alcohol and 2 cyano groups. Molecule A has S_g = 135 A^2 and S_{st} = 65 A^2, and molecules B and C have S_g = 180 A^2 and S_{st} = 120A^2. Use the model proposed in the paper to predict the packing motif observed in each case.

5. Halogen atoms are introduced into conjugated molecules to tune the packing and resulting optoelectronic properties.

    i)   For perfluoropentacene compared to pentacene (Figure 1), do we observe a mesomeric (M) or inductive (I) effect? Give an example of a molecule that shows the other effect.

    ii) For perfluoropentacene compared to pentacene (Figure 1), describe in a comparative way the typical features that you recognize from the solid-state organization of both compounds.

    iii) For 5,11-dicholorotetracene (Figure 2), describe typical features that you recognize in the molecular packing.

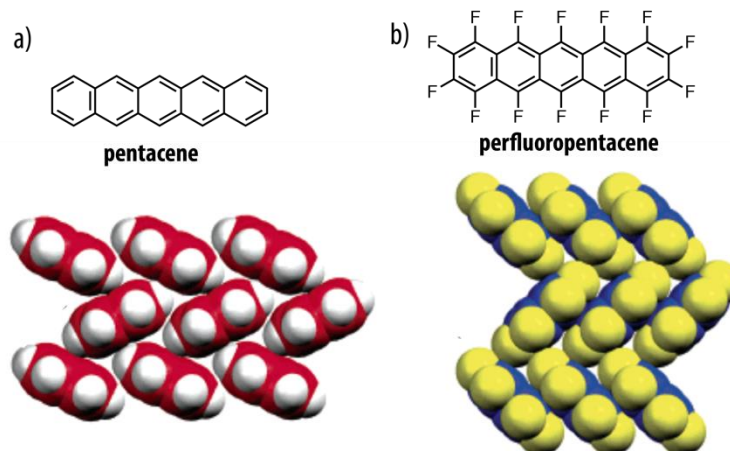   iv) What kind of molecular packing would be expected in tetracene without chlorine substitution and why?

Figure 1 : Molecular structure and packing of a) pentacene and b) perfluoropentacene
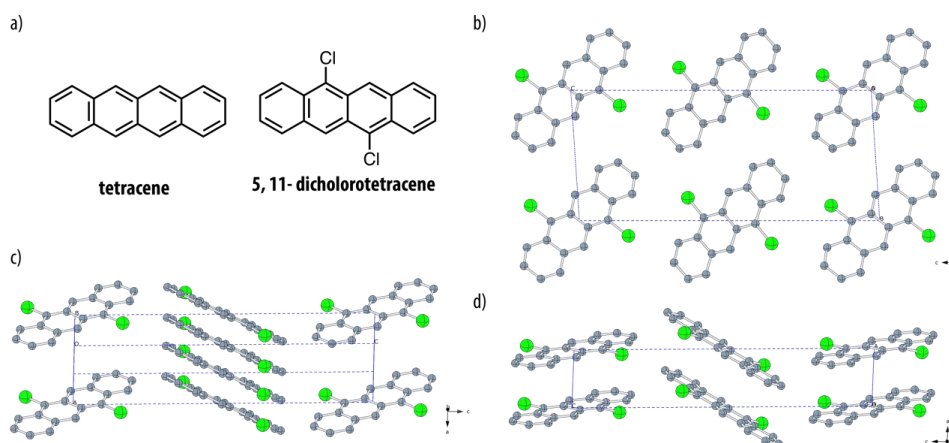

Figure 2: a) Molecular structure of tetracene and its dichloro derivative b–d) Molecular packing of 5,11-dichlorotetracene viewed along different crystallographic axes.

Reading suggestions:

[1]   Desiraju, G. R.; Gavezzotti, A. Crystal Structures of Polynuclear Aromatic Hydrocarbons. Classification, Rationalization and Prediction from Molecular Structure. *Acta Crystallogr. B* **1989**, *45* (5), 473–482.

[2]   Thakuria, R.; Nath, N. K.; Saha, B. K. The Nature and Applications of π–π Interactions: A Perspective. *Cryst. Growth Des.* **2019**, *19* (2), 523–528.

[3]   Martinez, C. R.; Iverson, B. L. Rethinking the Term "Pi-Stacking." *Chem. Sci.* **2012**, *3* (7), 2191.