School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Organic Electronic Materials 2025 Exercise 3 Solutions

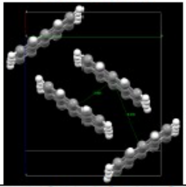
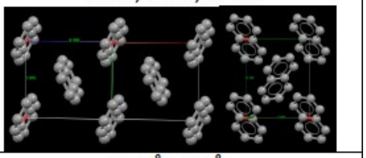
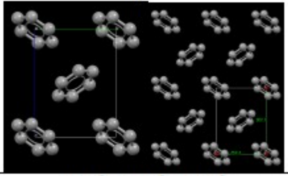
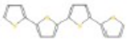
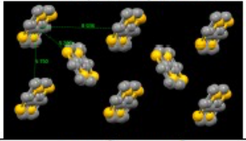
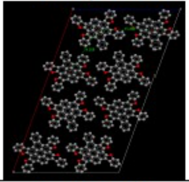
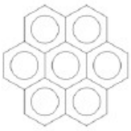
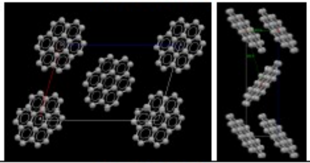
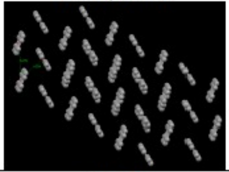
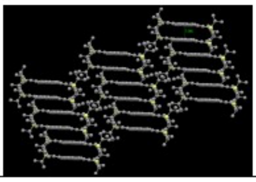
Solutions

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 visualizer 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.

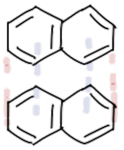
   198723 – 233928 – 1108753 – 117770 – 2040902 – 1129883 – 114447 – 172476

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

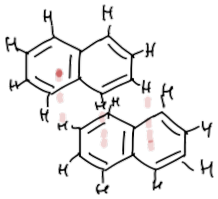
Identifier	Name	Packing type	Intermolecular distances
198723 PERLEN05	Perylene 	Sandwich herringbone	3.9 Å, 6.0 Å 
233928 NAPHTA15	Naphthalene 	Herringbone	6.0 Å, 7.8 Å, 8.1 Å 
1108753 BENZEN04	Benzene 	Herringbone	5.4 Å, 7.5 Å 
117770 PEWXAQ	α-Quaterthiophene 	Herringbone	5.3 Å, 5.8 Å, 8.9 Å 
2040902 IJOXAJ	contorted tetrabenzofuranylbenzocoronene (cTBFBC) 	Columnar (γ structure)	14.3 Å, 15.3 Å 
1129883 CORONE	Coronene 	Columnar (γ structure)	4.7 Å, 8.3 Å 
114447 PENCEN01	Pentacene 	Herringbone	4.2 Å, 6.3 Å 
172476 VOQBIM	6,13-bis(2-(Tri-isopropylsilyl)ethynyl)pentacene 	Brickwork layers (see slide 148, chapter 3.2)	7.6 Å 

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.

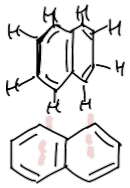
Face-to-face



Parallel-displaced



Edge-to-face



Face-to-face is never observed as the electrostatic interaction is very repulsive in this arrangement.

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.

   Herringbone – calamitic/rod-like molecules – e.g. oligothiophenes, pentacene. Parallel-displaced, edge to face, and most space filling configuration for calamitic molecules.

   Sandwich herringbone – small discotic molecules – e.g. pyrene. HB for these small discotic molecules is not favored due to generation of voids. SHB results in the formation of parallel-displaced dimers that are packed in a HB fashion to maximize packing.

   Columnar – large discotic molecules – e.g. coronene. Parallel-displaced and configuration maximizes packing for large discotic molecules.

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.

   In Figure 2 (Desiraju 1989), glide-stack area ratios S_g / S_{st} *are plotted as a function of total molecular surface areas* S_M *(*$S_M = S_g + S_{st}$*). From the value of* S_g / S_{st} *and* S_M*, we can predict the packing motif.*

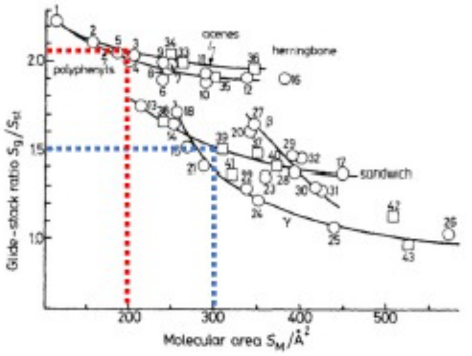
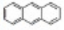
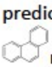
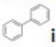
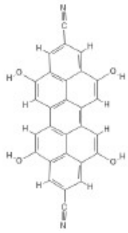


Figure 2. A mapping from molecular to crystal structure for polynuclear aromatic hydrocarbons. Glide–stack area ratios are plotted against available molecular surface areas. Compounds (**1**)—(**32**) are represented as open circles and compounds (**33**)—(**43**) as open squares.

Molecule	A	B	C
S_g/S_{st}	135/65 = 2.08	180/120 = 1.5	180/120 = 1.5
S_m	200	300	300
Packing	herringbone	Sandwich herringbone	Sandwich herringbone
Predicted motif	The point where two red lines intersect indicates "acenes" graph with herringbone packing. (3) Anthracene  Anthracene is a planar polycyclic aromatic hydrocarbon consisting of three fused benzene rings. If anthracene is a wrong prediction, (4) Phenanthrene  might be the alternative one. (5) Biphenyl  is not, because it is not planar	The point where two blue lines intersect indicates "sandwich" graph with sandwich herringbone packing. (39) Dibenzoperylene 	A derivative of (39) dibenzoperylene with <u>4 alcohol and 2 cyano groups</u> looks like below. 

Note: B and C have the same Sg/Sst despite having different structures. This shows you the limits of the "predictive mapping" that Desiraju proposes in the Homework paper (in reality, the packing of B and C won't be the same).

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.

   Inductive effect means the change in the polarization of a covalent bond due to the presence of an electronegative atom, electron-withdrawing, or electron-donating groups. The mesomeric effect is the movement of pi electrons toward or away from substituents or functional groups in a molecule.

   In perfluoropentacene, all the hydrogens of the hydrocarbon backbones are substituted with fluorine atoms, which is a strong electronegative element. Compared to pentacene, we can observe inverse quadrupole moment in perfluoropentacene, caused by mainly negative inductive effect from fluorine atoms. Lone-pair electrons of fluorine atoms can also contribute to a weak positive mesomeric effect.

Example of a molecule that shows the other effect: Aniline ($C_6H_5NH_2$) shows a mesomeric effect (+M), where the –NH_2 group donates electron density into the ring.

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. *Both molecules are calamitic, rod-like structures, thus herringbone packing is observed for both cases with parallel-displaced and edge-to-face interactions. Herringbone angle of pentacene is smaller than its perfluoro derivative, perfluoropentacene*

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

Edge-to face interactions are not present, due to the lateral Cl substituents.
Parallel-displaced π-stacking into densely packed columns.

iv) What kind of molecular packing would be expected in tetracene without chlorine substitution and why?
In the absence of chlorine substituents, tetracene is calamitic, rod-like molecule, thus herringbone packing should be observed.

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.