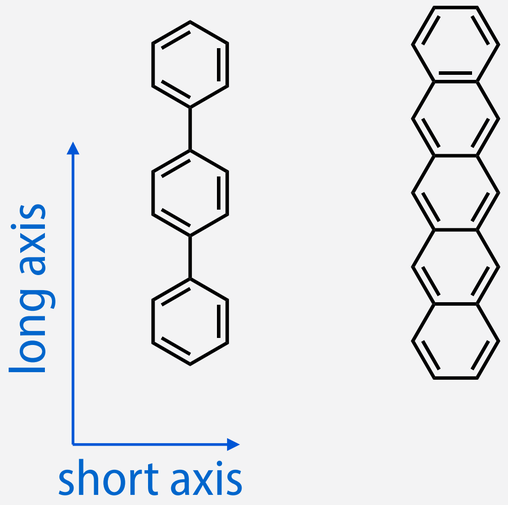
3.2 Supramolecular Organisation in Solid State

Shapes of π-Conjugated Molecules

- π-conjugated molecules can be calamitic (rod-like) or discotic (disk-like)

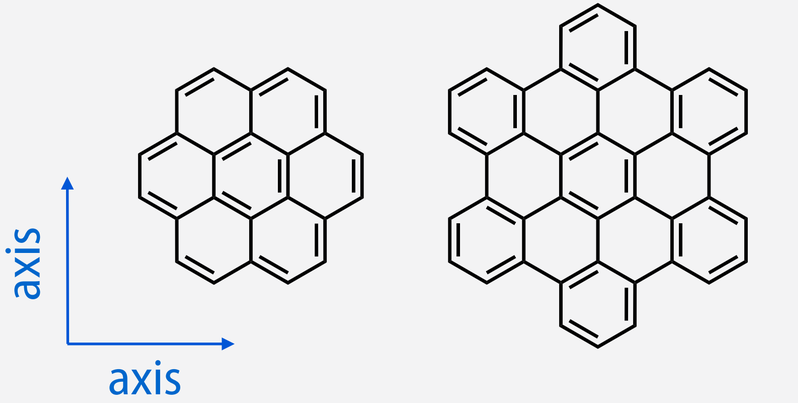
calamitic molecules

terphenyl pentacene



discotic molecules

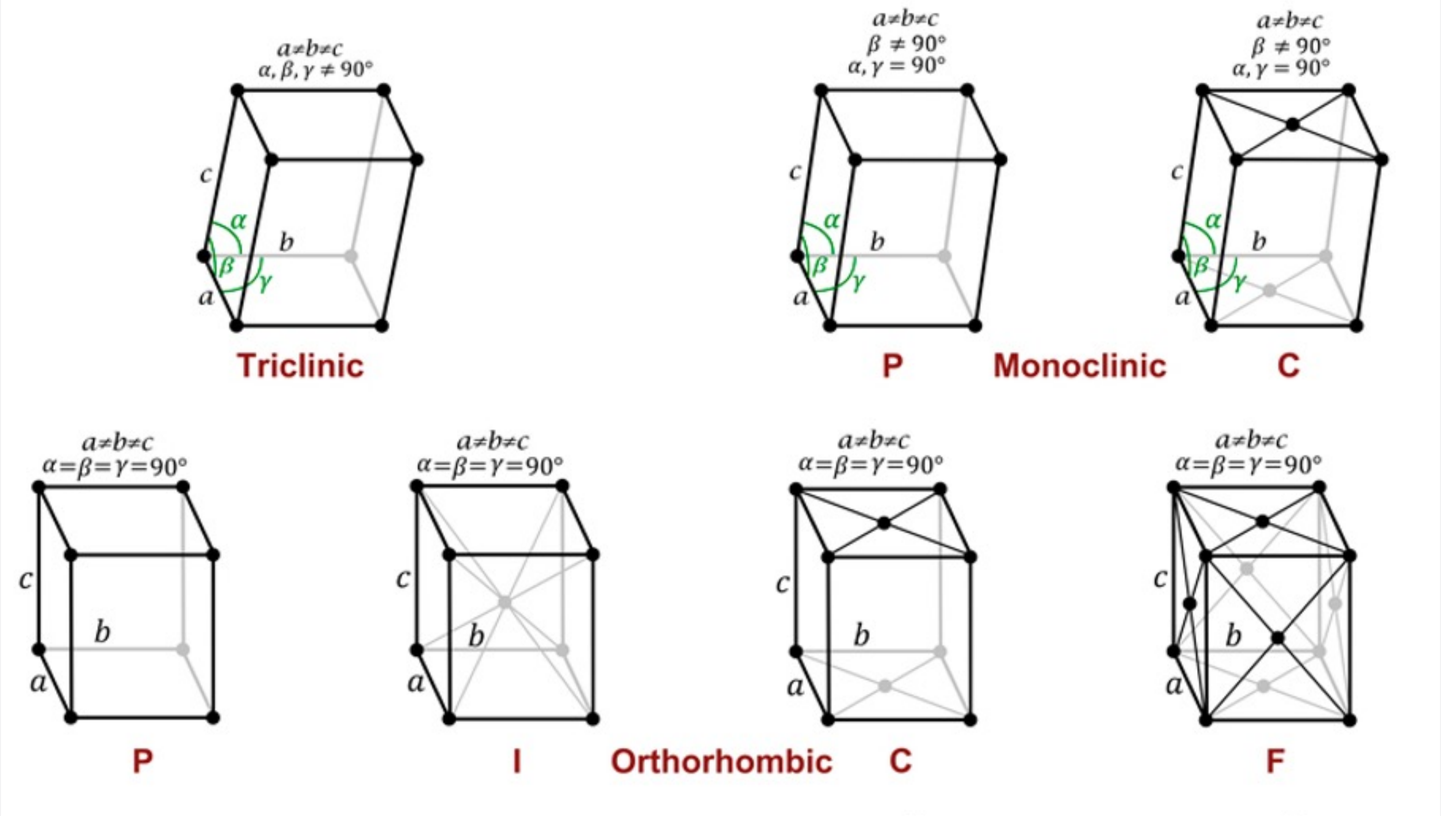
coronene hexabenzocoronene



- **calamitic molecules are elongated, molecular long axis and short axis, aspect ratio >1**
- **discotic molecules have roughly equal molecular axes, aspect ratio ≈1**
- **third molecular axis always corresponds to Van der Waals radius of sp^2 carbon (≈3.4 Å)**

Basic Crystal Structure Types of π-Conjugated Hydrocarbons

- π-conjugated molecules form close-packed arrangements limited by Van der Waals radius
- most common unit lattices in organic crystals are the following Bravais lattices:

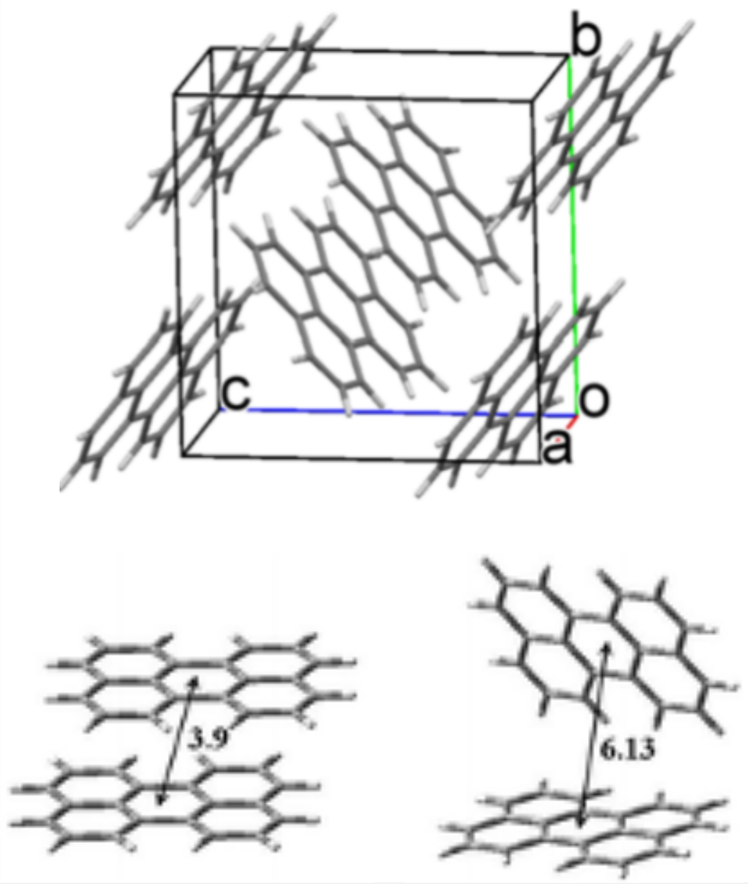


- **with a basis of one, two, or four atoms / molecules per unit cell**

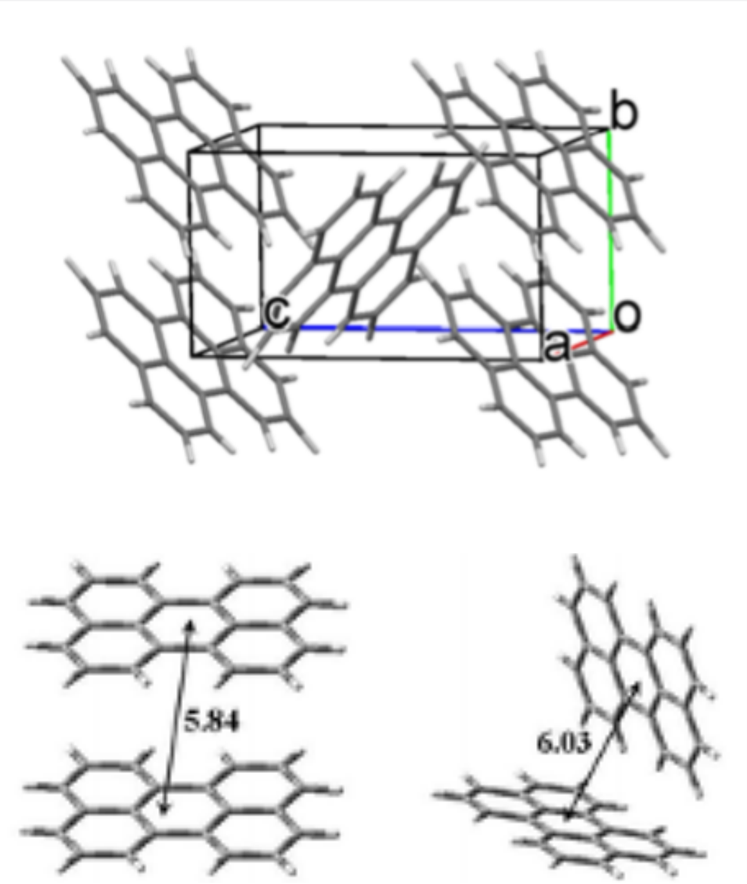
Polymorphism

- some molecules crystallize in different structures, depending on crystallization conditions

α-Perylene



β-Perylene

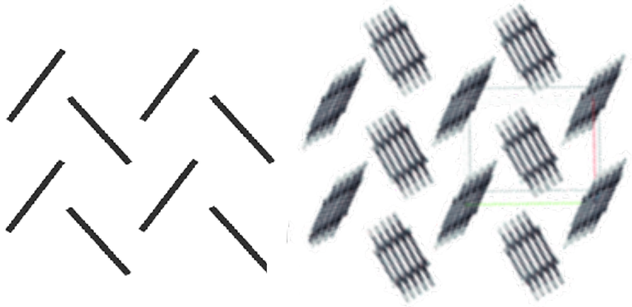


Salzillo, *Cryst. Growth and Des.* **2016**, *16*, 3028.

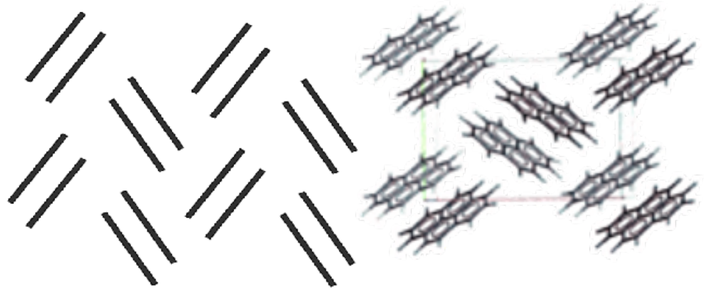
Basic Crystal Structure Types of π-Conjugated Hydrocarbons

- polycyclic hydrocarbons adopt one of four main structure types

herringbone (HB)
calamitic molecules

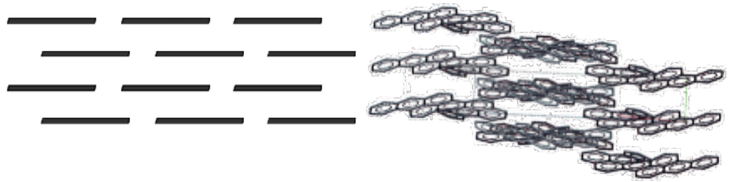


sandwich herringbone (SHB)
small discotic molecules



columnar (γ)
large discotic molecules

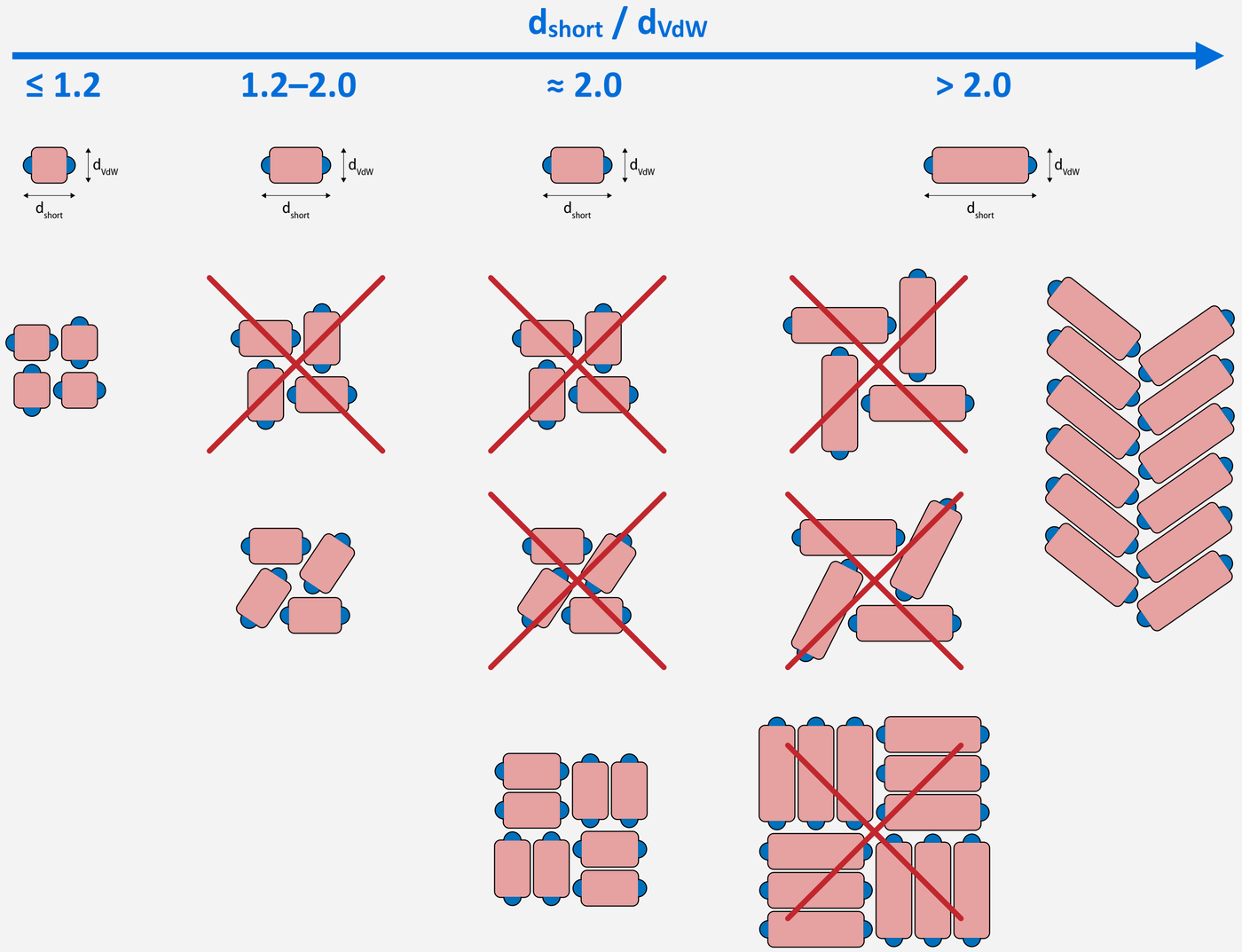
graphitic (β)
odd-shaped / very large molecules



- **a fourth crystal type (graphitic, β) is sometimes observed for odd-shaped molecules**
- **some molecules can crystallize in several structure, all being potential energy minima (isomorphism)**

KEY CONCEPT: see Desiraju, *J. Chem. Soc. Chem Commun.* **1989**, 621.

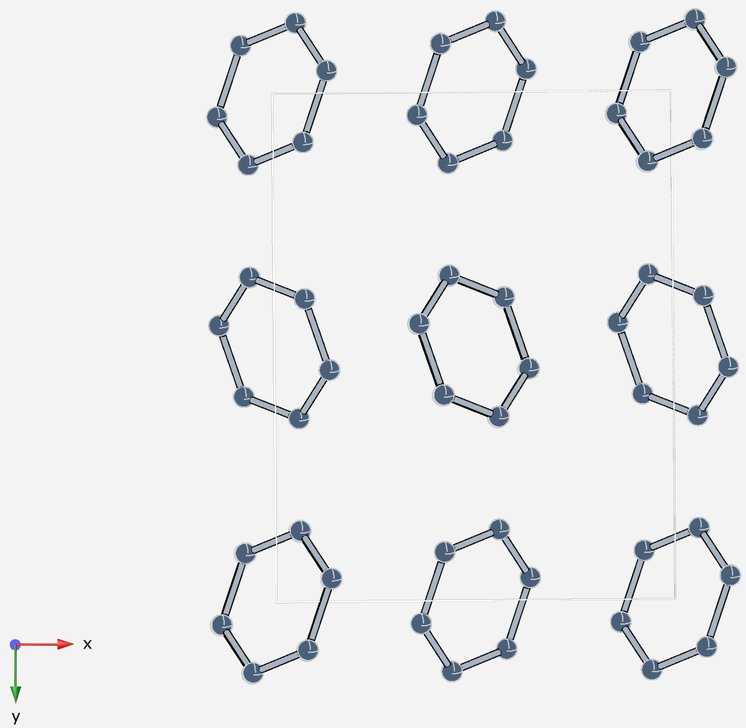
Packing Arguments for Observed Structures

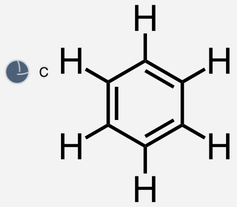


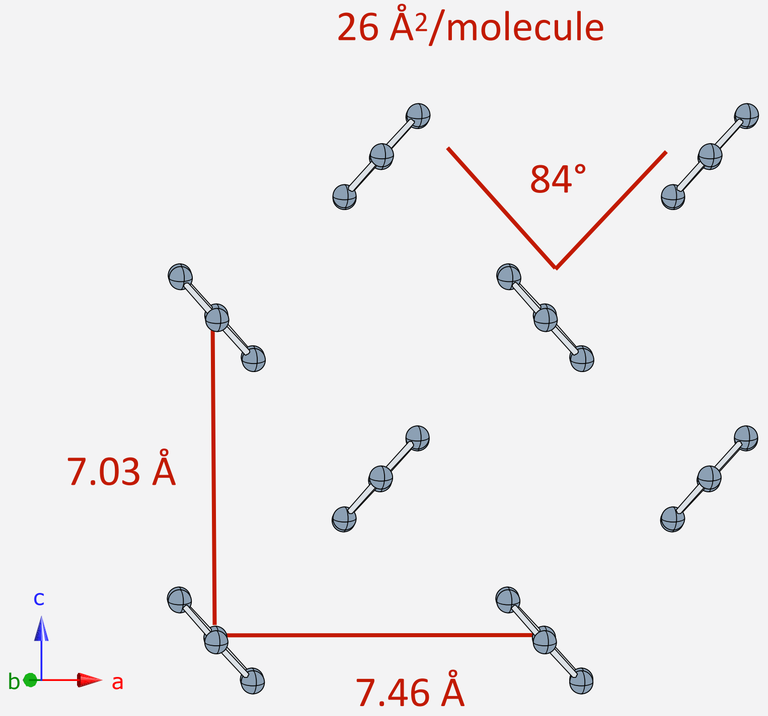
- space-efficient packing, and dispersive interactions become ever more important & efficient

Crystal Structure of Benzene

- benzene packs into complex herringbone packing in three dimensions







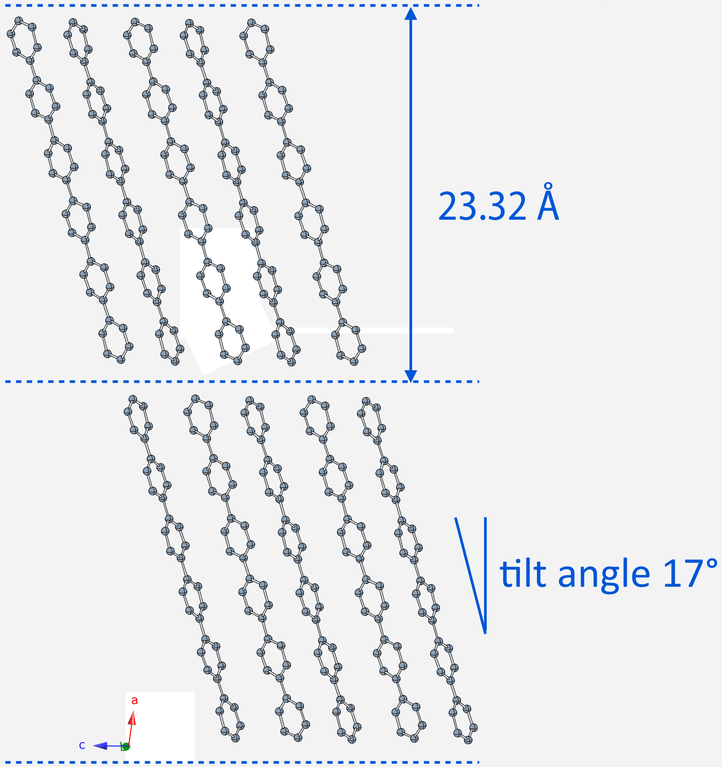
- **in side view, benzene molecule has two almost identical dimensions due to π-system**
- **space-filling packing with and edge-to-face and parallel-displaced π–π stacking interactions**
- **optimized for both dispersive and, predominantly, quadrupolar electrostatic interactions**

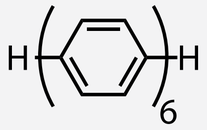
Cox, *Proc. Royal Soc. London, Ser. A* **1958**, *247*, 1.

Crystal Structure of Hexaphenylene

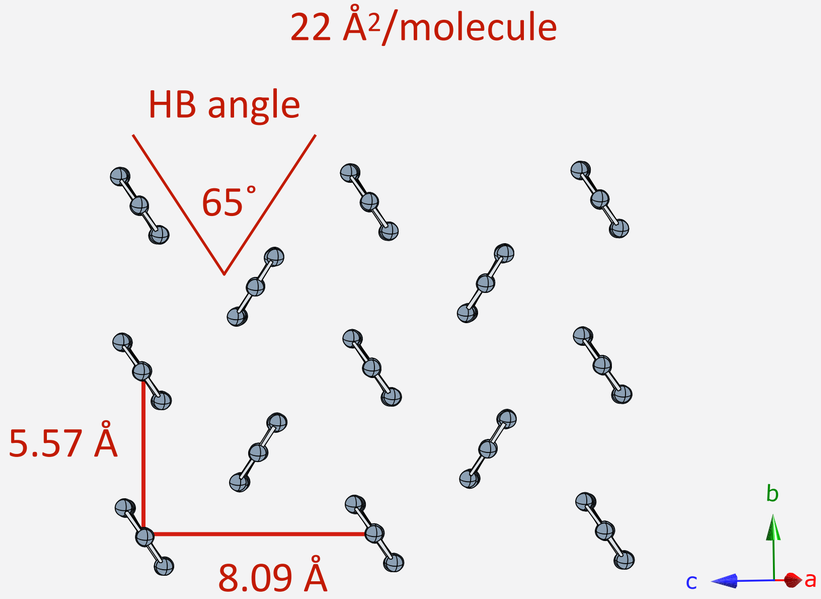
- hexaphenylene is a calamitic molecule, one extended molecular axis

side view of layers in *bc* plane





top view of layers along *a* axis
herringbone packing

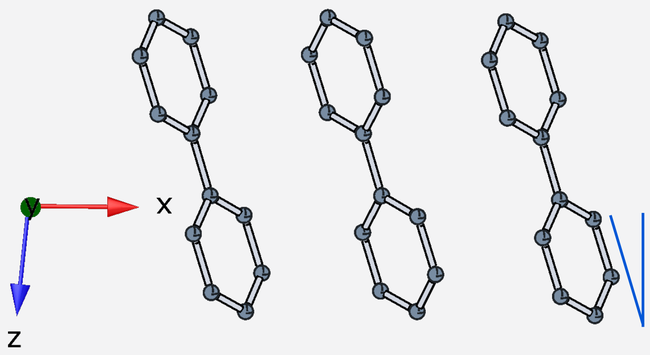


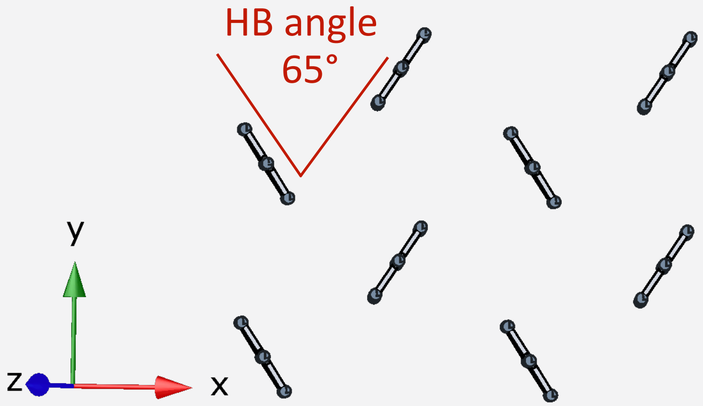
- **quasi-homeotropic alignment of calamitic molecules into 2D layers**
- **tilt angle, parallel-displaced packing along long axes, edge-face interactions along short axes**
- **layered 2D herringbone is a universal packing mode for calamitic molecules**

Resel, *Thin Solid Films* **2003**, *433*, 1.

Crystal Structure of Oligophenylenes

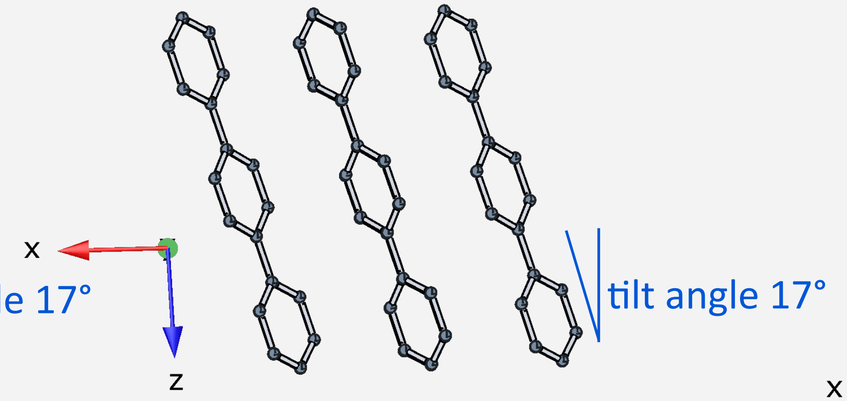
biphenylene

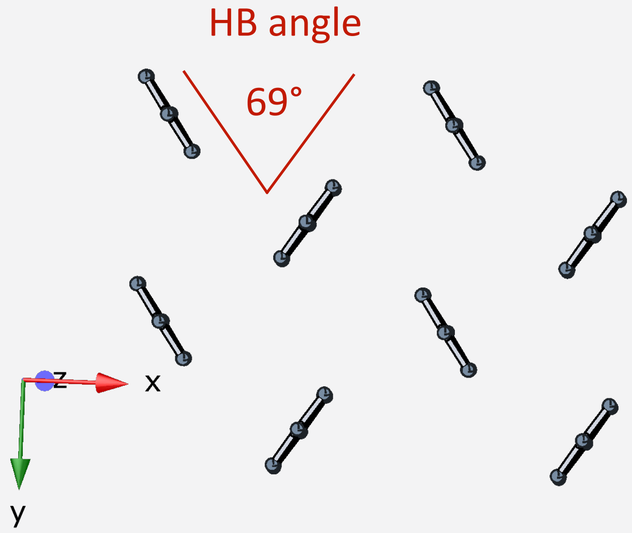




Trotter, *Acta Crystallogr.* **1961**, *14*, 1135.

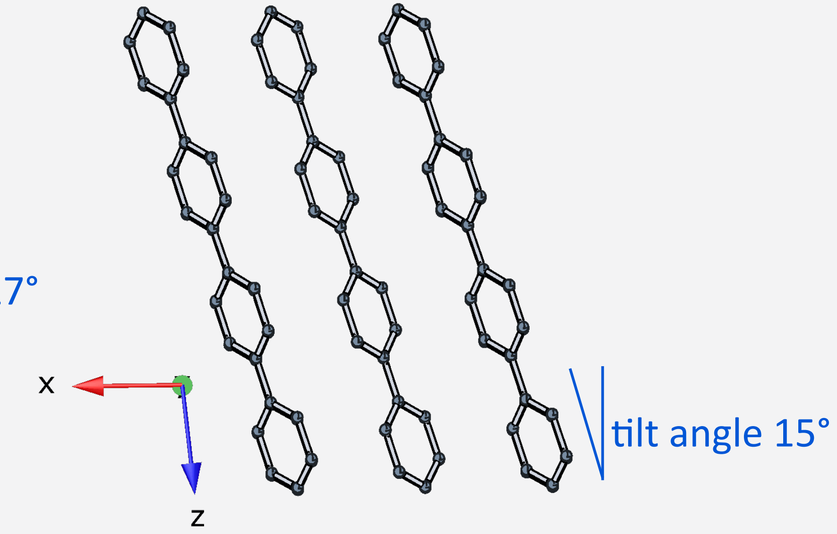
triphenylene

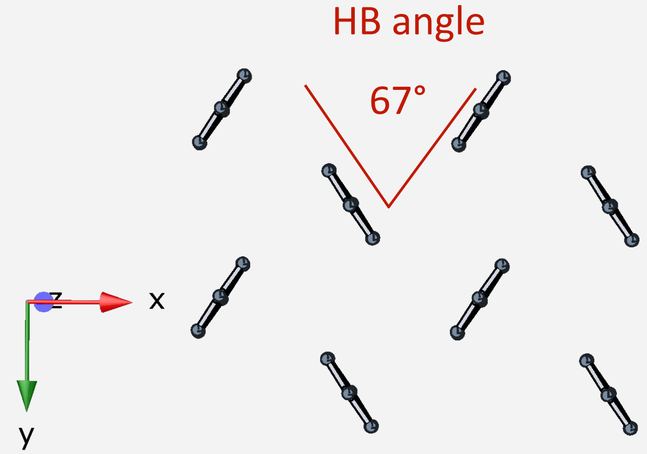




Rietveld *et al.*, *Acta Crystallogr. B: Struct. Sci. Cryst. Eng. Mater.* **1970**, *26*, 693.

tetraphenylene



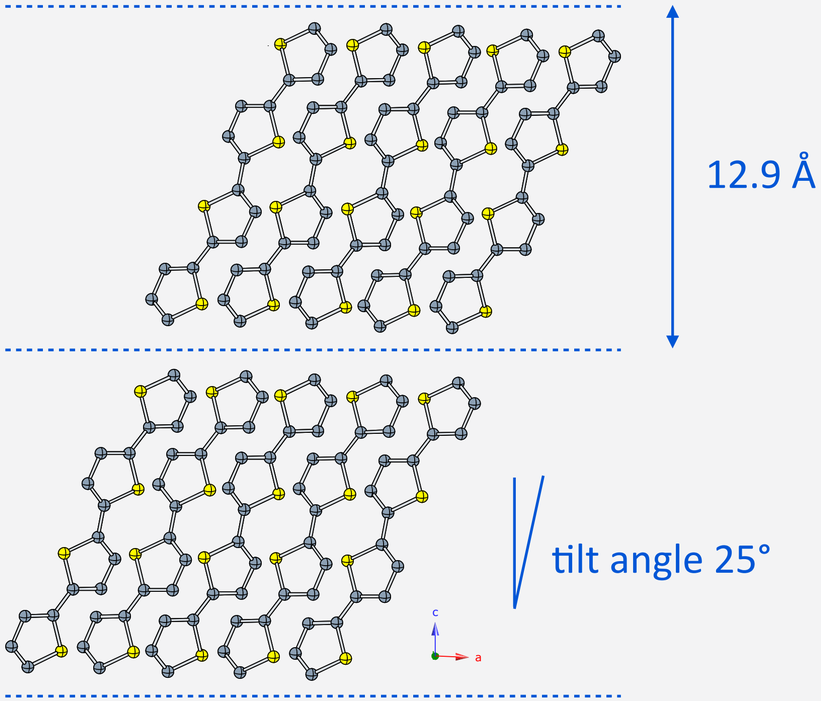


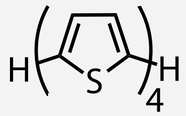
Delugeard *et al.*, *Acta Crystallogr. B: Struct. Sci. Cryst. Eng. Mater.* **1976**, *32*, 702.

Crystal Structure of α-Quaterthiophene

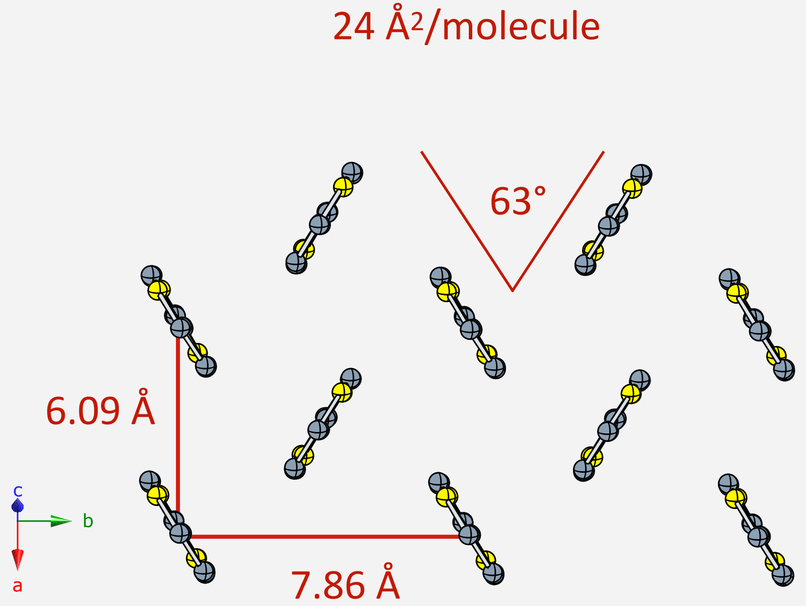
- quaterthiophene is a calamitic molecule, one extended molecular axis

side view of layers in *ab* plane





top view of layers along *c* axis
herringbone packing

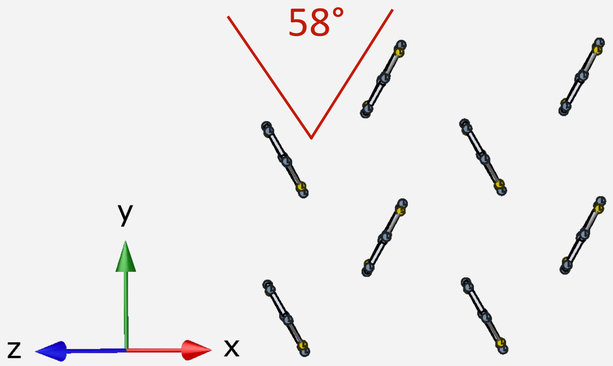


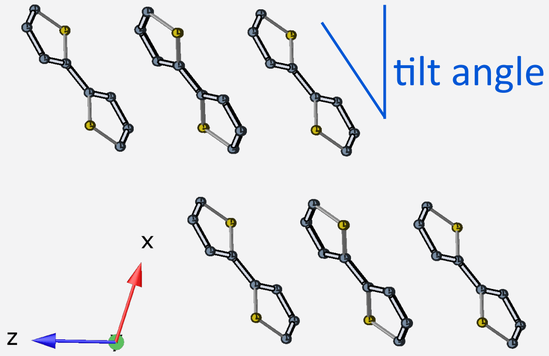
- **parallel-displaced packing along short axes, edge-face interactions, additional S···S contacts**
- **layered 2D herringbone is a universal packing mode for calamitic molecules**

Siegrist, *Adv . Mater.* **1998**, *10*, 379.

Crystal Structure of Oligothiophenes

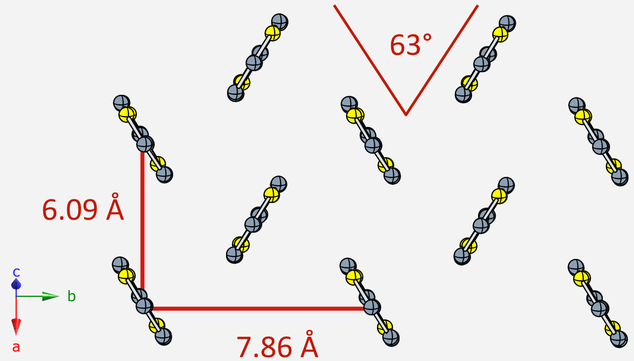
bithiophene

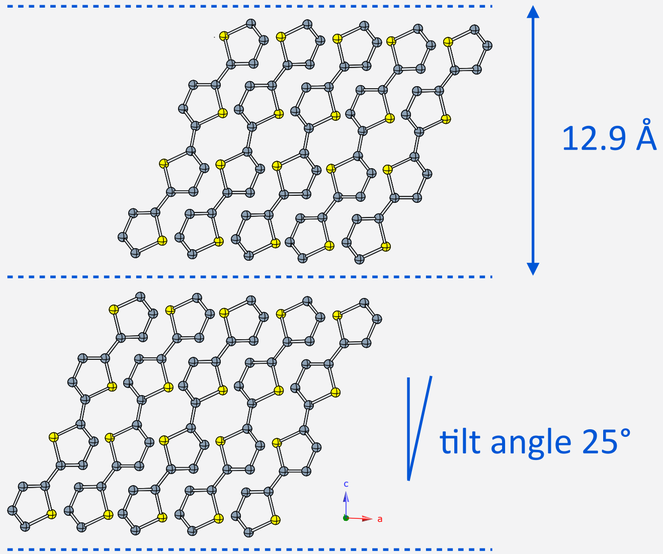




Visser *et al.*, *Acta Crystallogr. B: Struct. Sci. Cryst. Eng. Mater.* **1968**, *24*, 467.

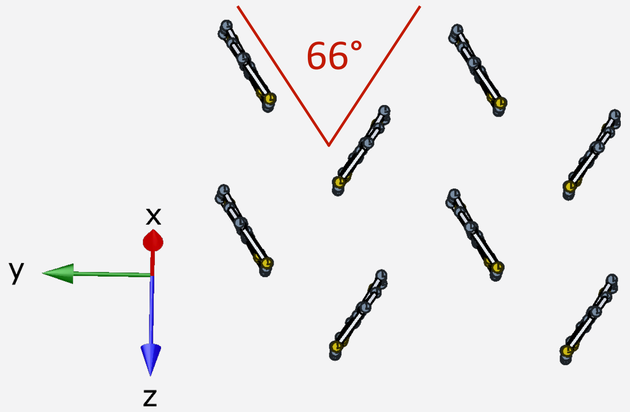
quaterthiophene

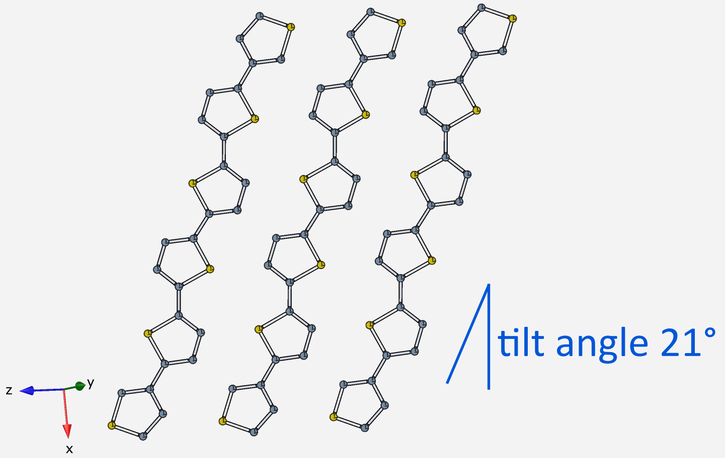




Siegrist, *Adv . Mater.* **1998**, *10*, 379.

sexithiophene

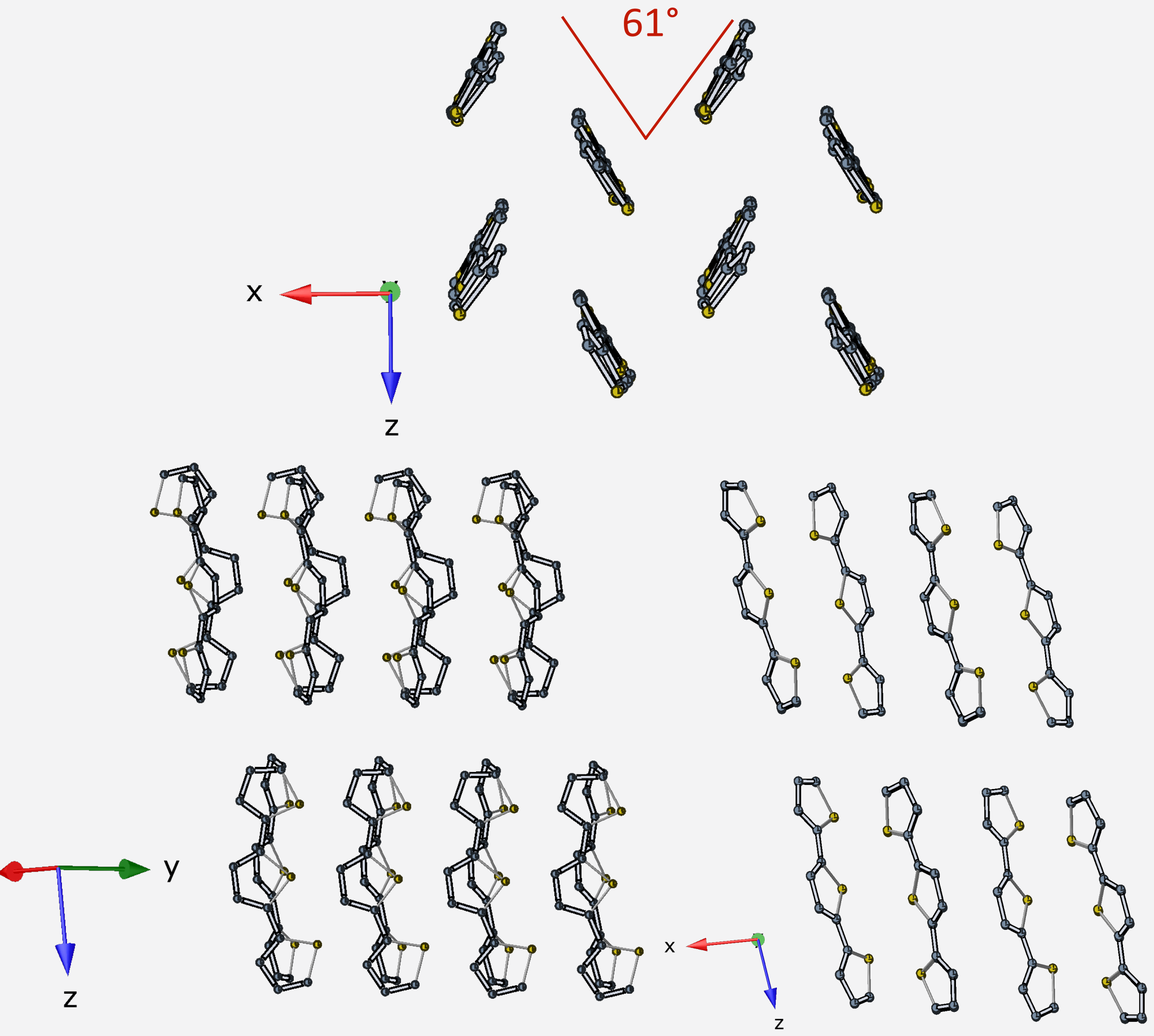




Chisaka *et al.*, *Chem. Mater.* **2007**, *19*, 2694.

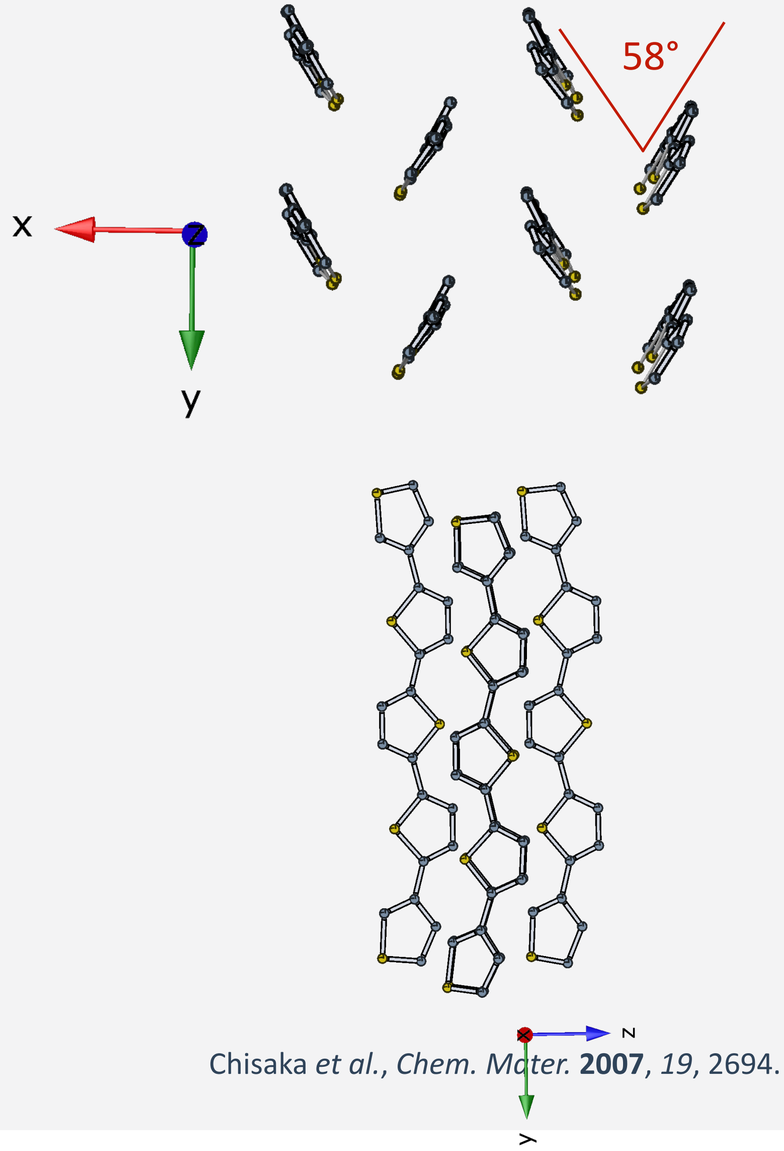
Crystal Structure of Trithiophene

terthiophene



Chunhua, *CSD Communication* **2020**

pentathiophene

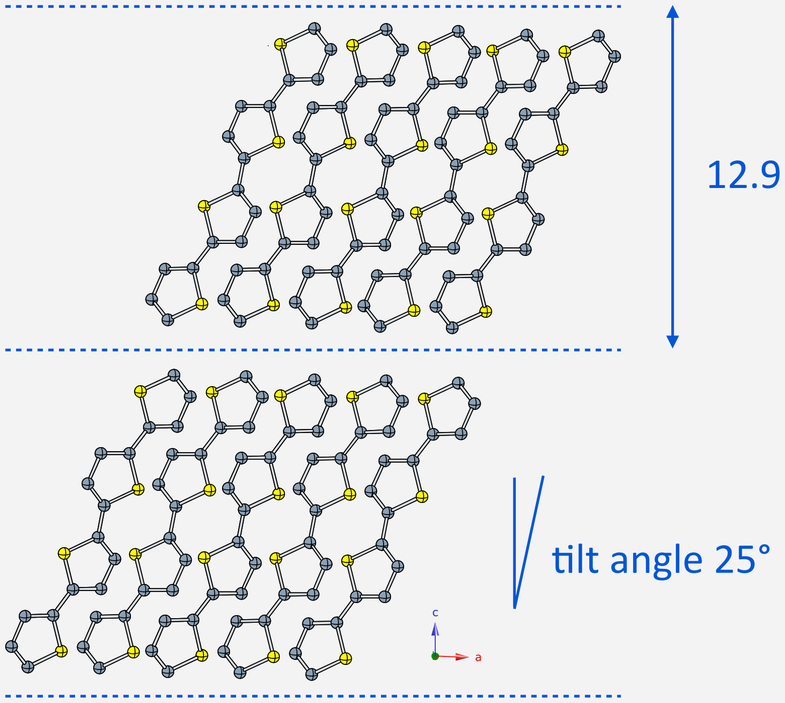


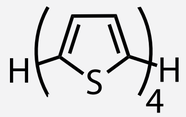
Chisaka *et al.*, *Chem. Mater.* **2007**, *19*, 2694.

Crystal Structure of α-Quaterthiophene

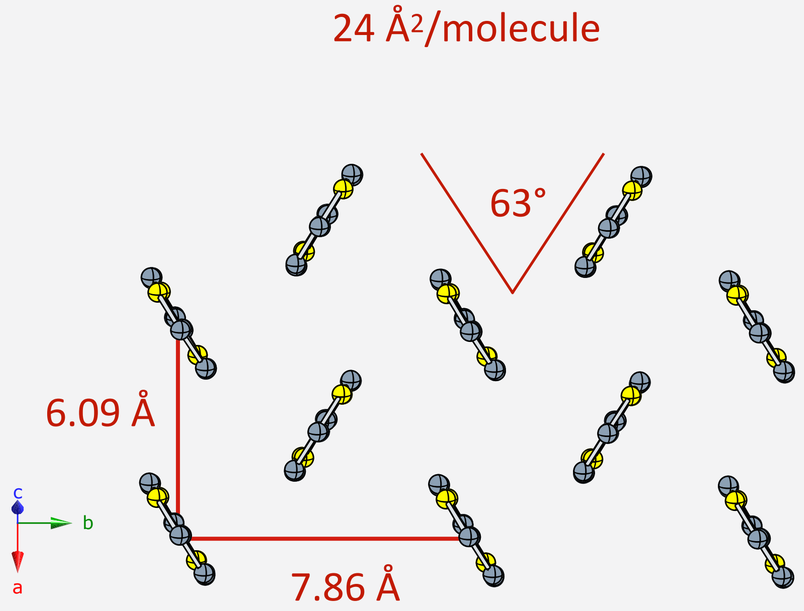
- quaterthiophene is a calamitic molecule, one extended molecular axis

side view of layers in *ab* plane





top view of layers along *c* axis
herringbone packing



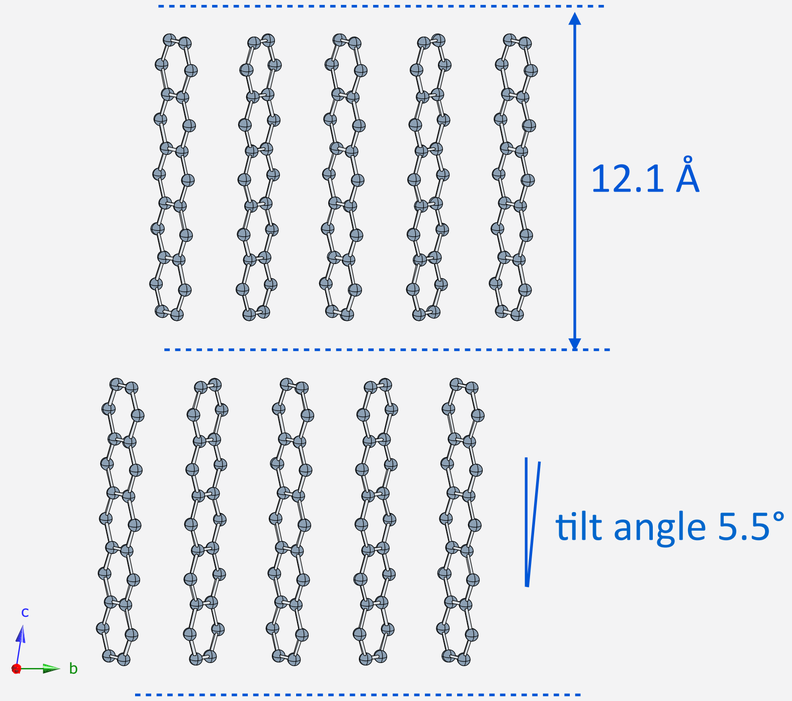
- **quasi-homeotropic alignment of calamitic molecules into 2D layers**
- **tilt angle, parallel-displaced packing along long axes, edge-face interactions along short axes**
- **layered 2D herringbone is a universal packing mode for calamitic molecules**

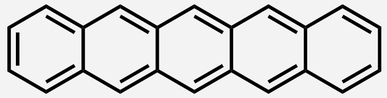
Siegrist, *Adv . Mater.* **1998**, *10*, 379.

Single-Crystal Structure of Pentacene

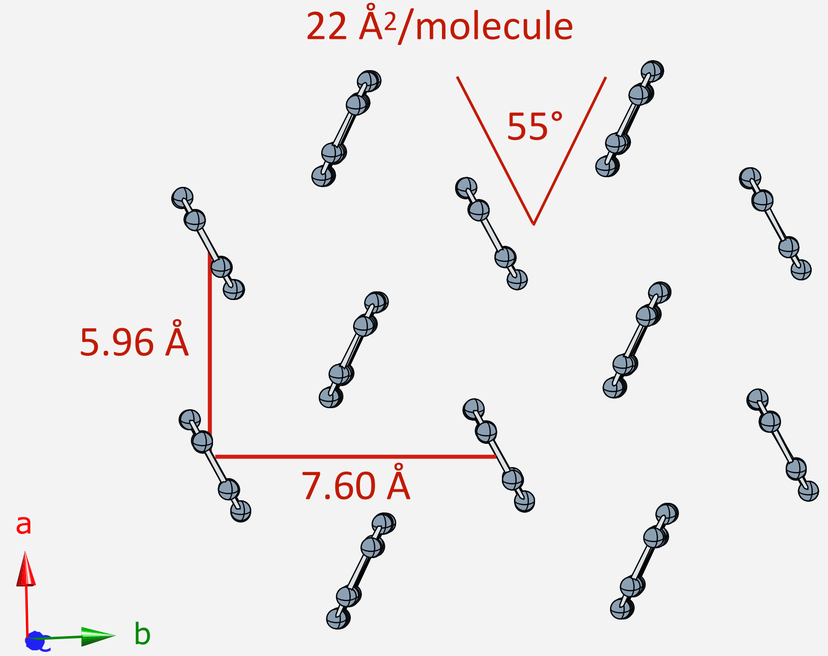
- pentacene is a calamitic molecule, one long axis and larger short axis compared to benzene

side view of layers in *ab* plane





top view of layers along *c* axis
herringbone packing



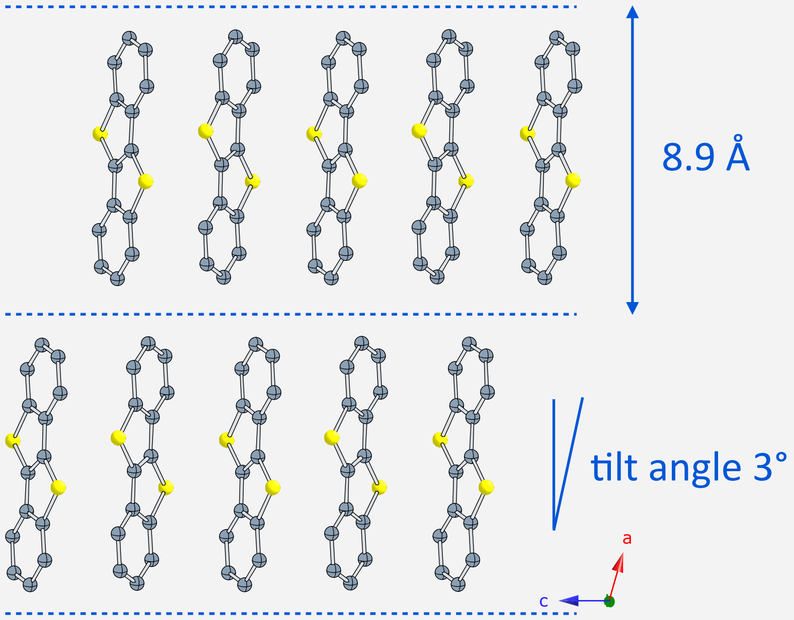
- **quasi-homeotropic alignment of calamitic molecules into 2D layers**
- **small tilt angle, minimal parallel-displaced packing (long axes(, edge-face interactions (short axes)**
- **layered 2D herringbone is a universal packing mode for calamitic molecules**

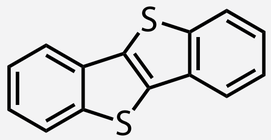
Schiefer, *J. Am. Chem. Soc.* **2007**, *129*, 10316.

Crystal Structure of Benzothienobenzothiophene (BTBT)

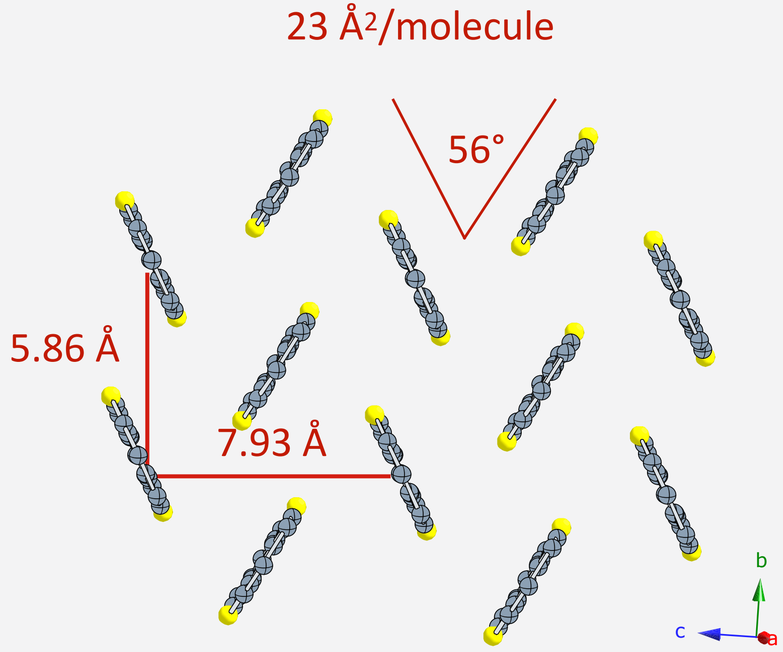
- benzothienobenzothiophene is calamitic, one extended molecular axis, larger short axis

side view of layers in *bc* plane





top view of layers along *a* axis
herringbone packing

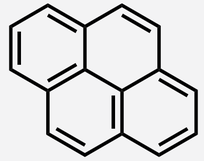


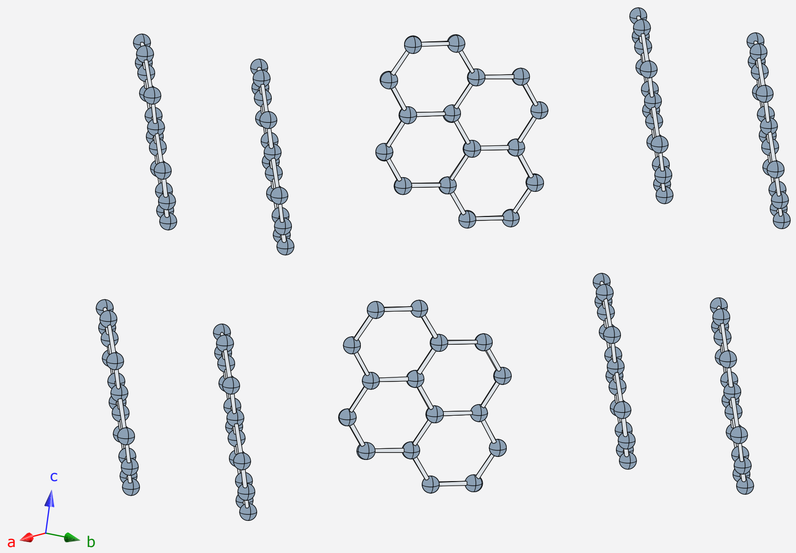
- **quasi-homeotropic alignment of calamitic molecules into 2D layers**
- **small tilt angle, minimal parallel-displaced packing (long axes(, edge-face interactions (short axes)**
- **layered 2D herringbone is a universal packing mode for calamitic molecules**

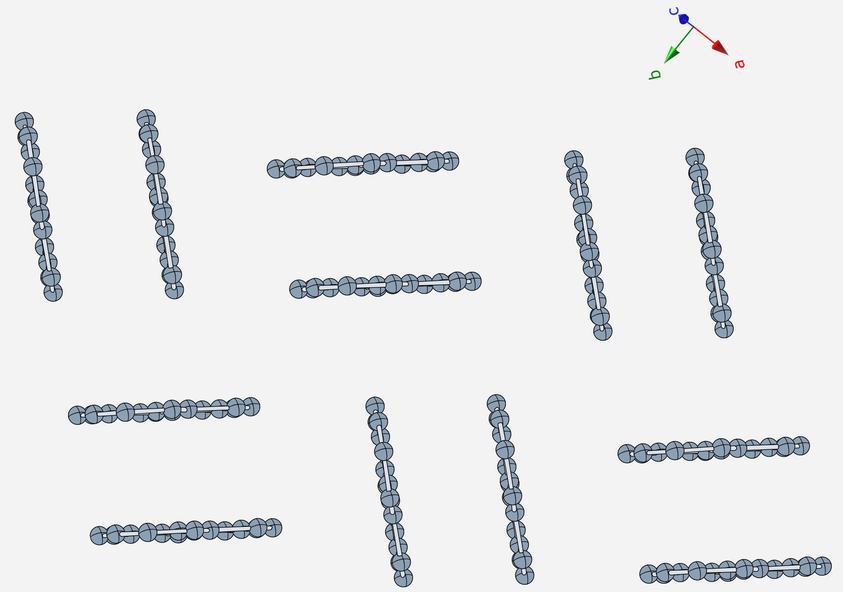
Vyas, *Cryst. Eng. Comm.* **2014**, *16*, 7389.

Crystal Stucture of Pyrene

- pyrene is a small discotic molecule (or a small calamitic molecule with low aspect ratio)

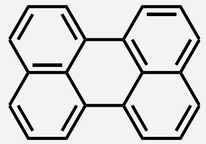


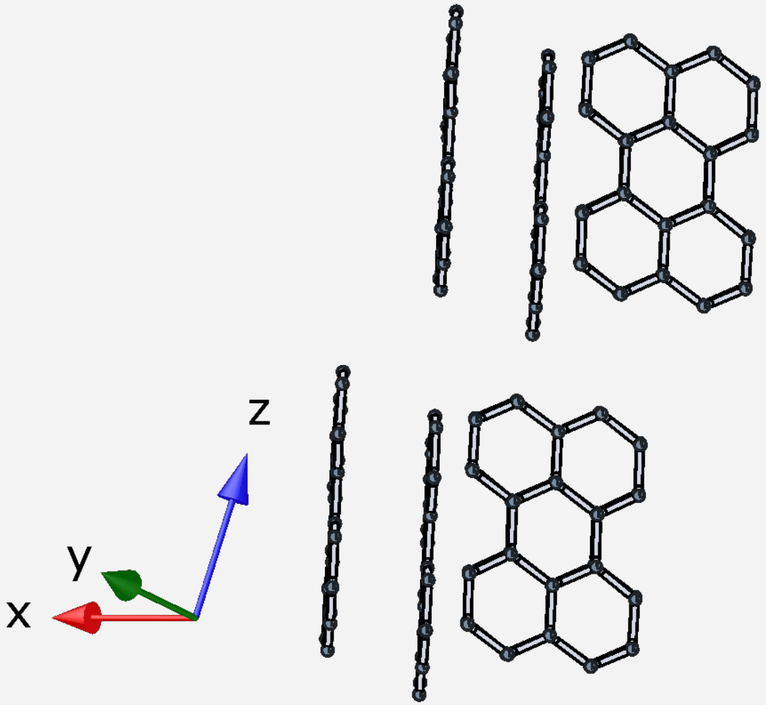


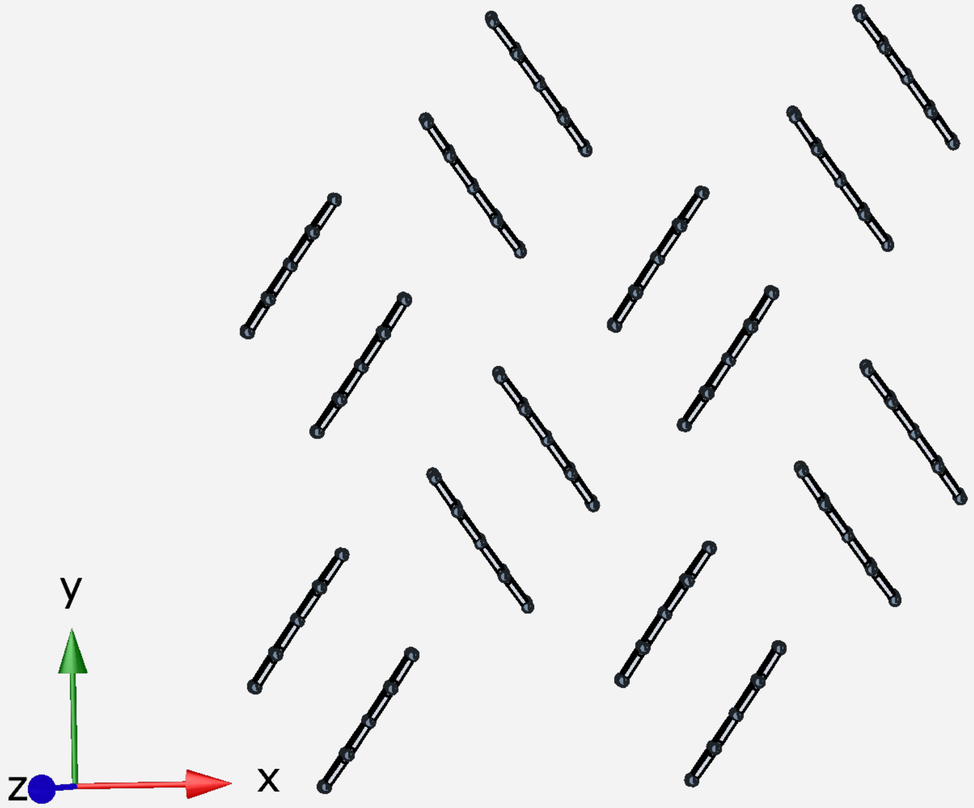


- **short axis incommensurate with herringbone packing, would create voids**
- **instead layered sandwich herringbone packing of dimers**

Crystal Structure of Perylene





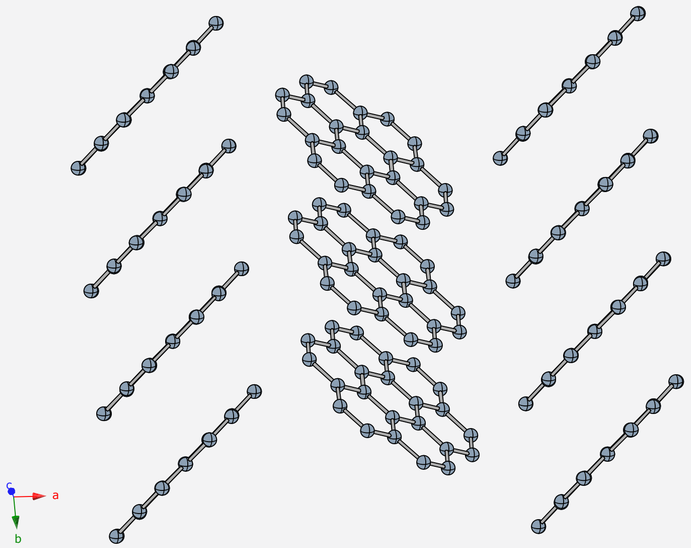


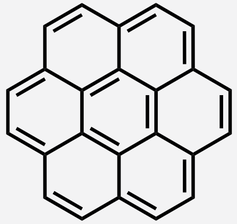
Camerman *et al.*, *R. Soc. Lond.* **1964**, *279*, 129.

Crystal Structure of Coronene

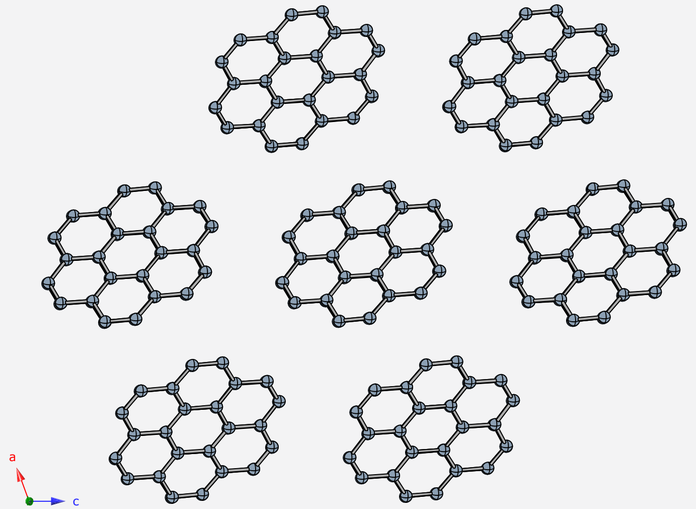
- coronene is a mdeium-size discotic molecule, two extended dimensions, one short axis

side view of the columns





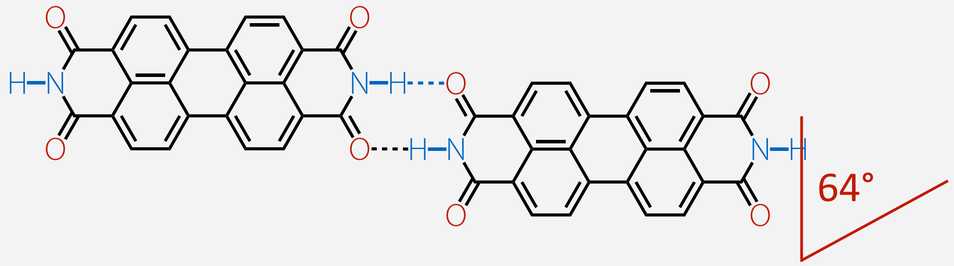
view along the columns

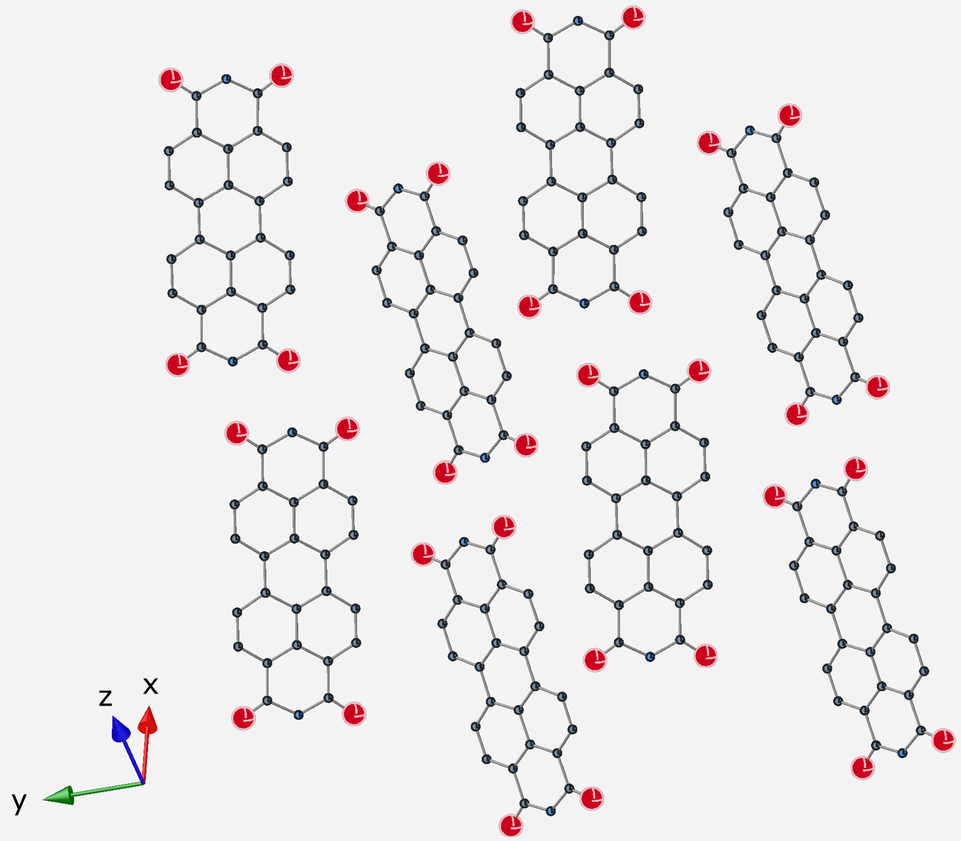


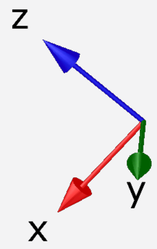
- **large discotic molecules cannot assume herringbone packing, would create voids**
- **instead, parallel-displaced π–π stacking into densely packed columns**

Echigo, *American Mineralogist* **2007**, *92*, 1262.

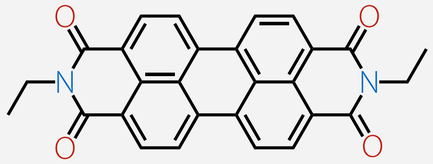
Crystal Structure of Perylenebisimide

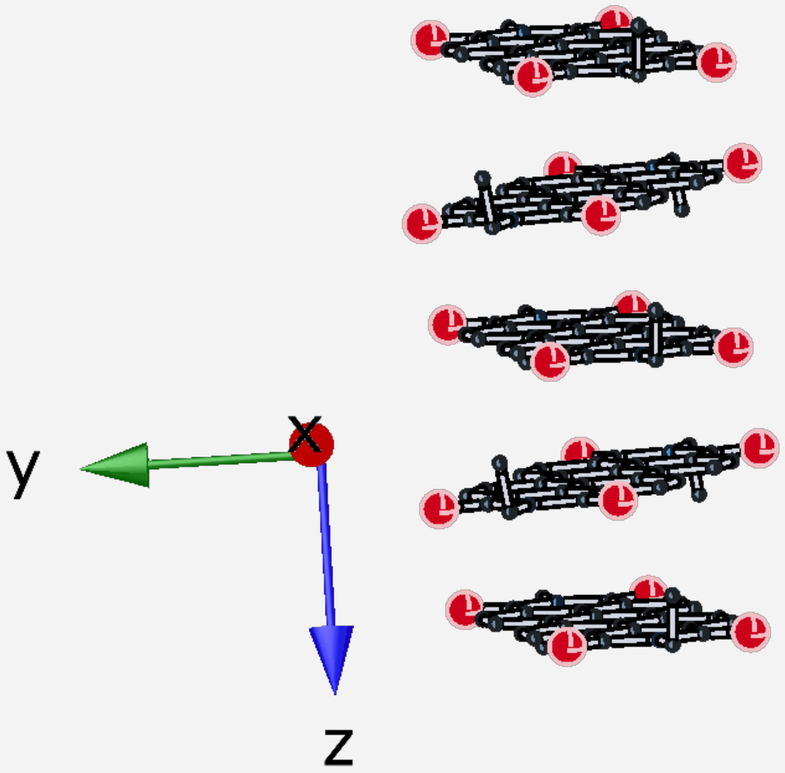


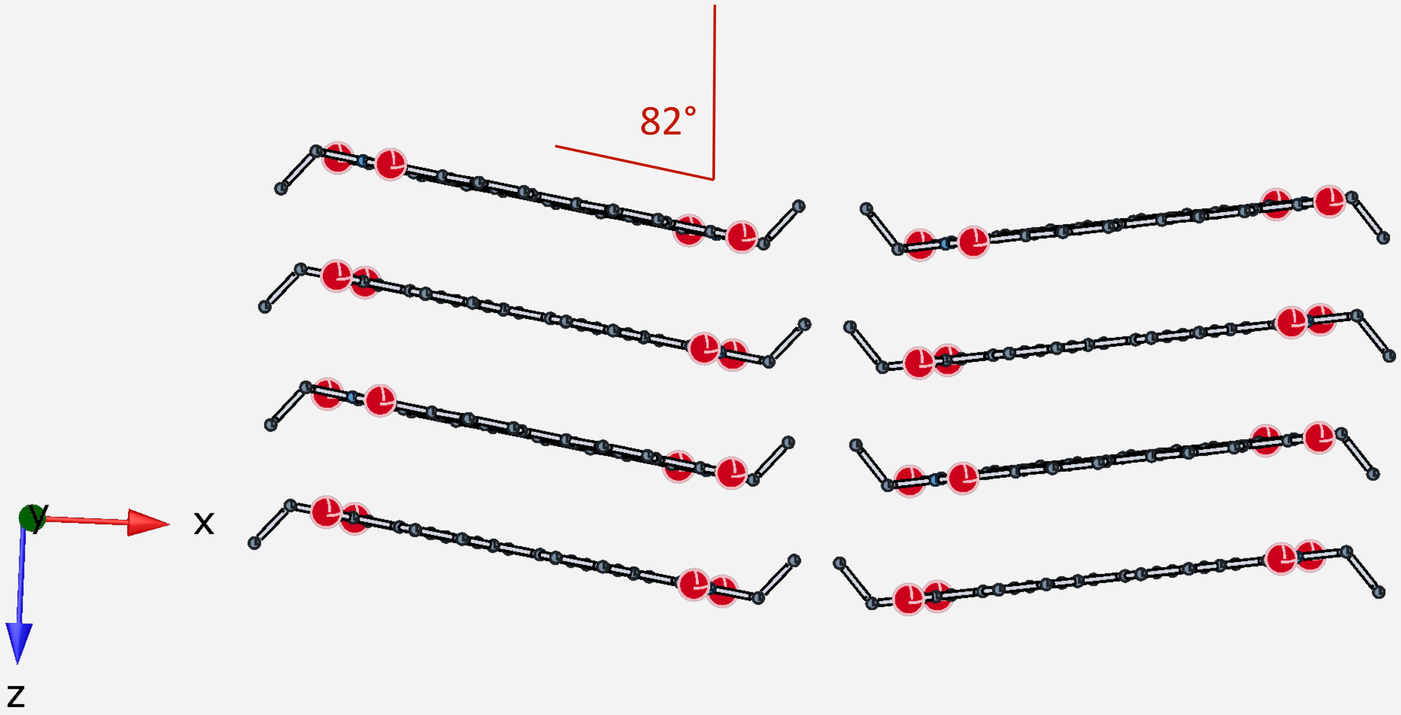




Crystal Structure of Diethylperylenebisimide



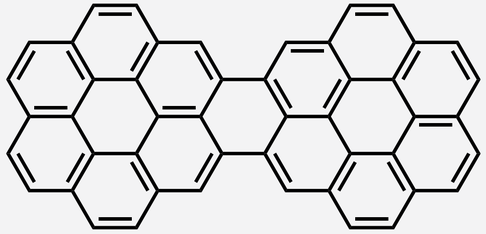




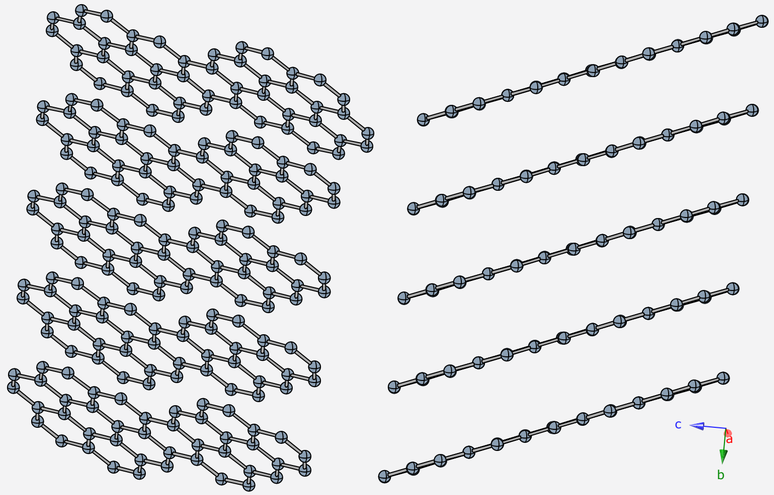
Hadicke and Graser, *Acta Cryst. C* **1986**, *42*, 195.

Crystal Structure of Bisbenzocoronene

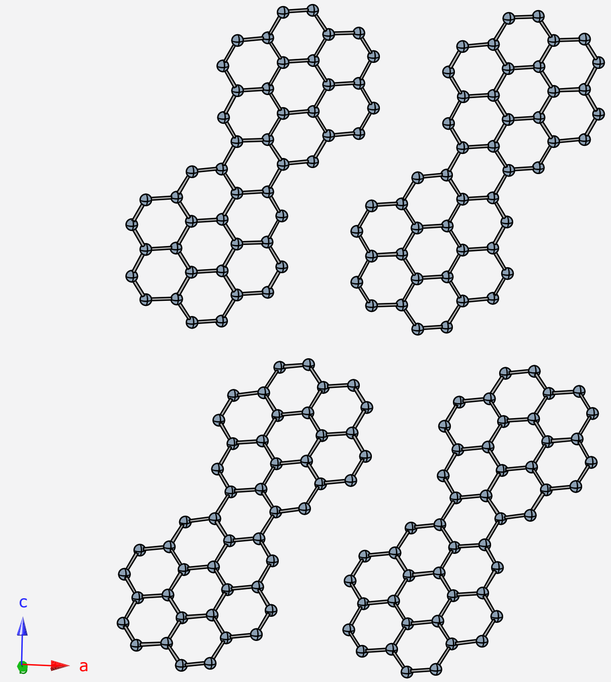
- bisbenzocoronene is a large discotic molecule, two extended dimensions, one short axis



side view of the columns



view along the columns



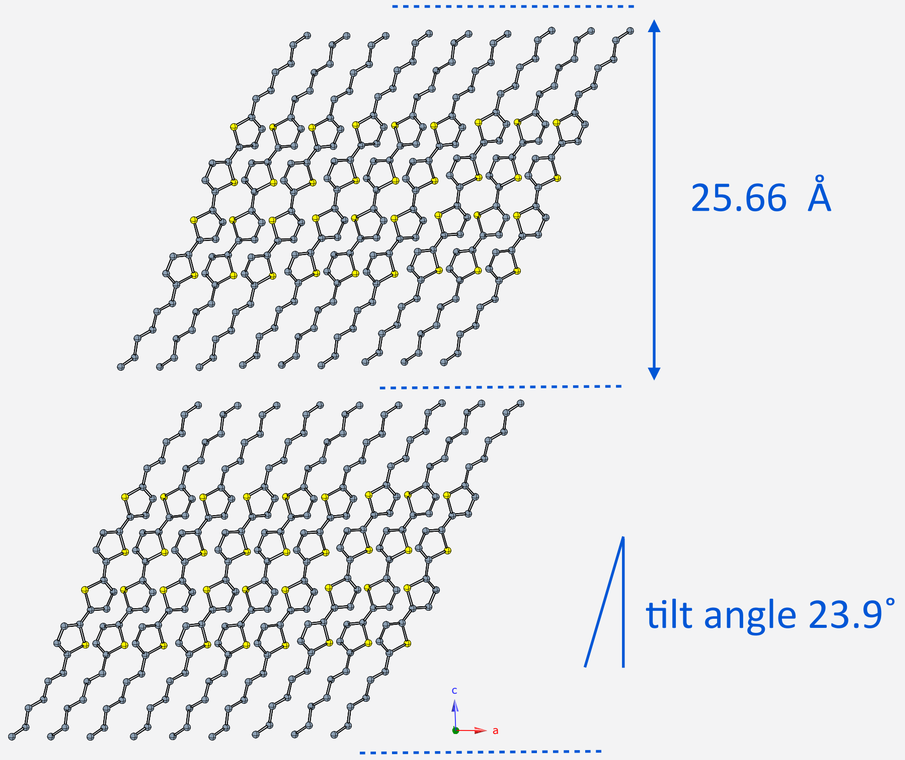
- **large discotic molecules cannot assume herringbone packing**
- **stacking into densely packed columns along short axes, parallel-displaced π–π stacking**

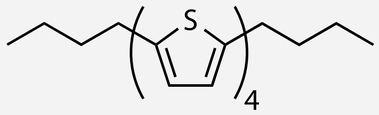
Williams, *Angew. Chem. Int. Ed.* **1992**, *31*, 1655.

Crystal Structure of Dihexylquaterthiophene

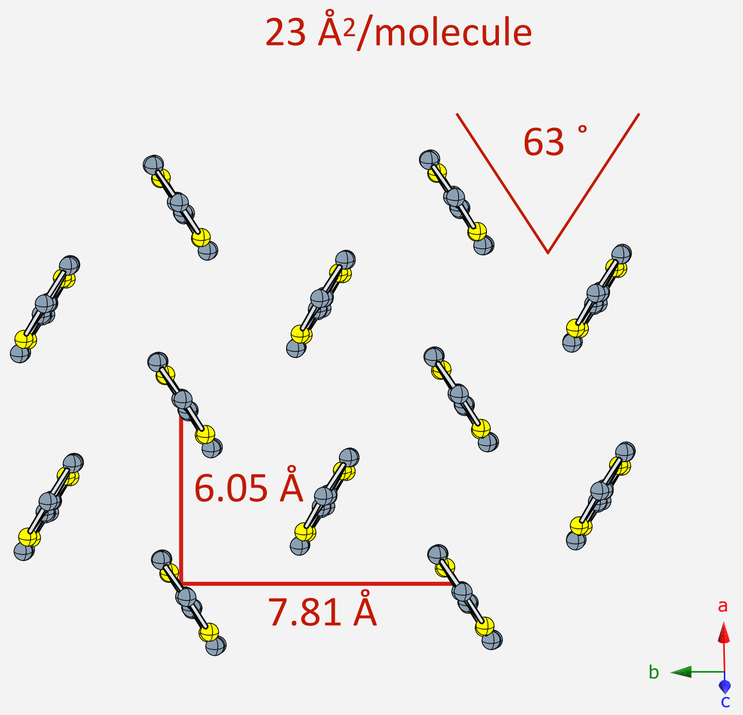
- dihexylquaterthiophene is a calamitic (rod-like) molecule, with one extended dimension

side view of layers in *ab* plane





top view of layers along *c* axis
herringbone packing



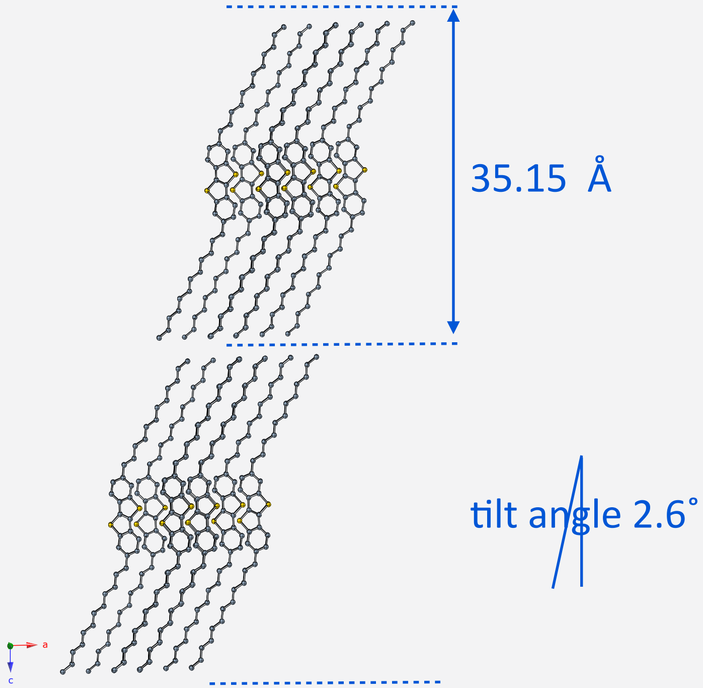
- **phase segregation of π-conjugated core and alkyl substituents reinforces layered packing**
- **layered 2D herringbone almost identical to the unsusbtituted quaterthiophene**

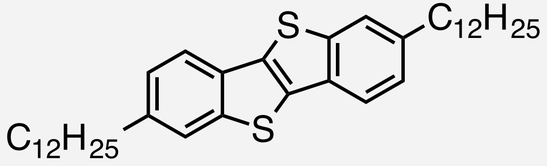
Siegrist, *Adv . Mater.* **1998**, *10*, 379.

Single-Crystal Structure of Didodecyl Benzothienobenzothiophene

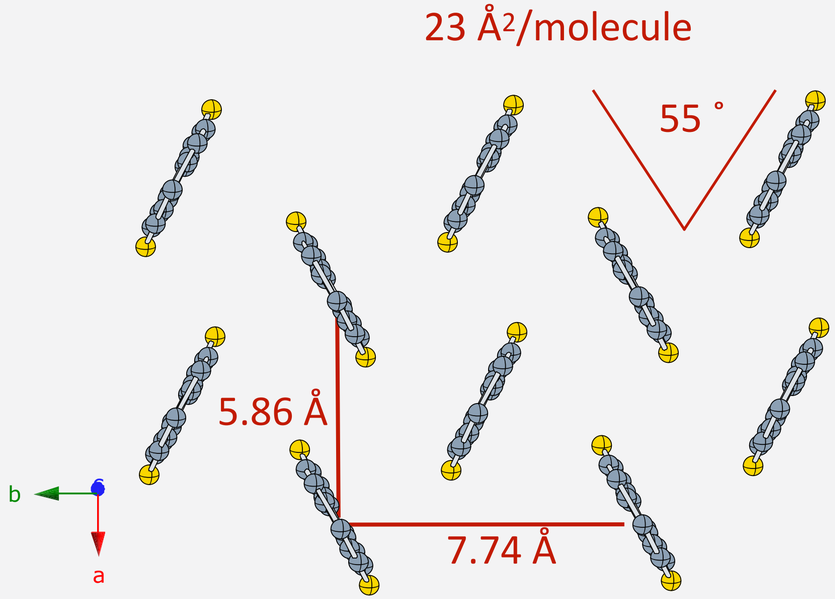
- didodecyl benzothienobenzothiophene is a calamitic molecule with terminal substituents

side view of layers in *ab* plane





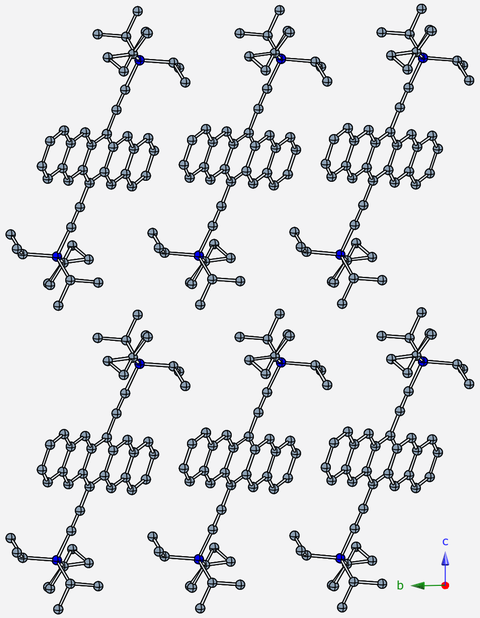
top view of layers along *c* axis

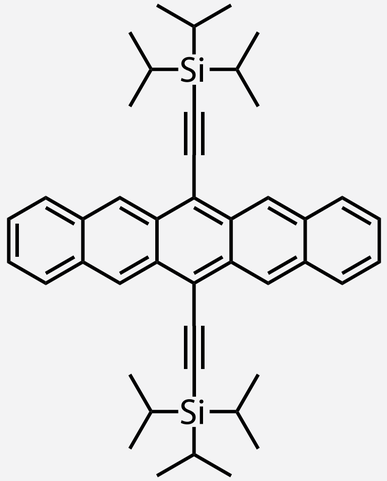


- **phase segregation of π-conjugated core and alkyl substituents reinforces layered packing**
- **layered 2D herringbone almost identical to the unsusbtituted quaterthiophene**

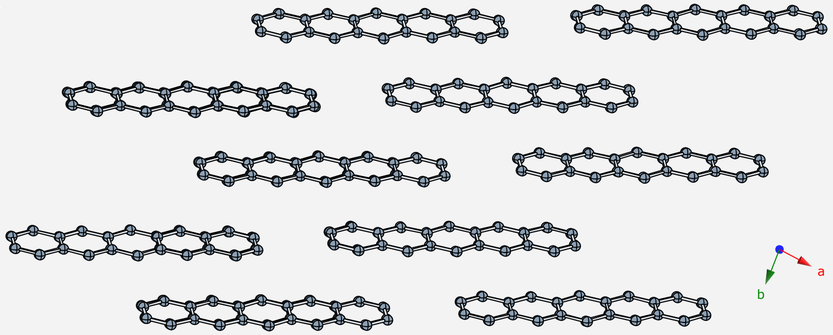
Single-Crystal Structure of TIPS-Pentacene

- TIPS-pentacene is a calamitic (rod-like) molecule with lateral substituents





top view of one layer (just the cores)

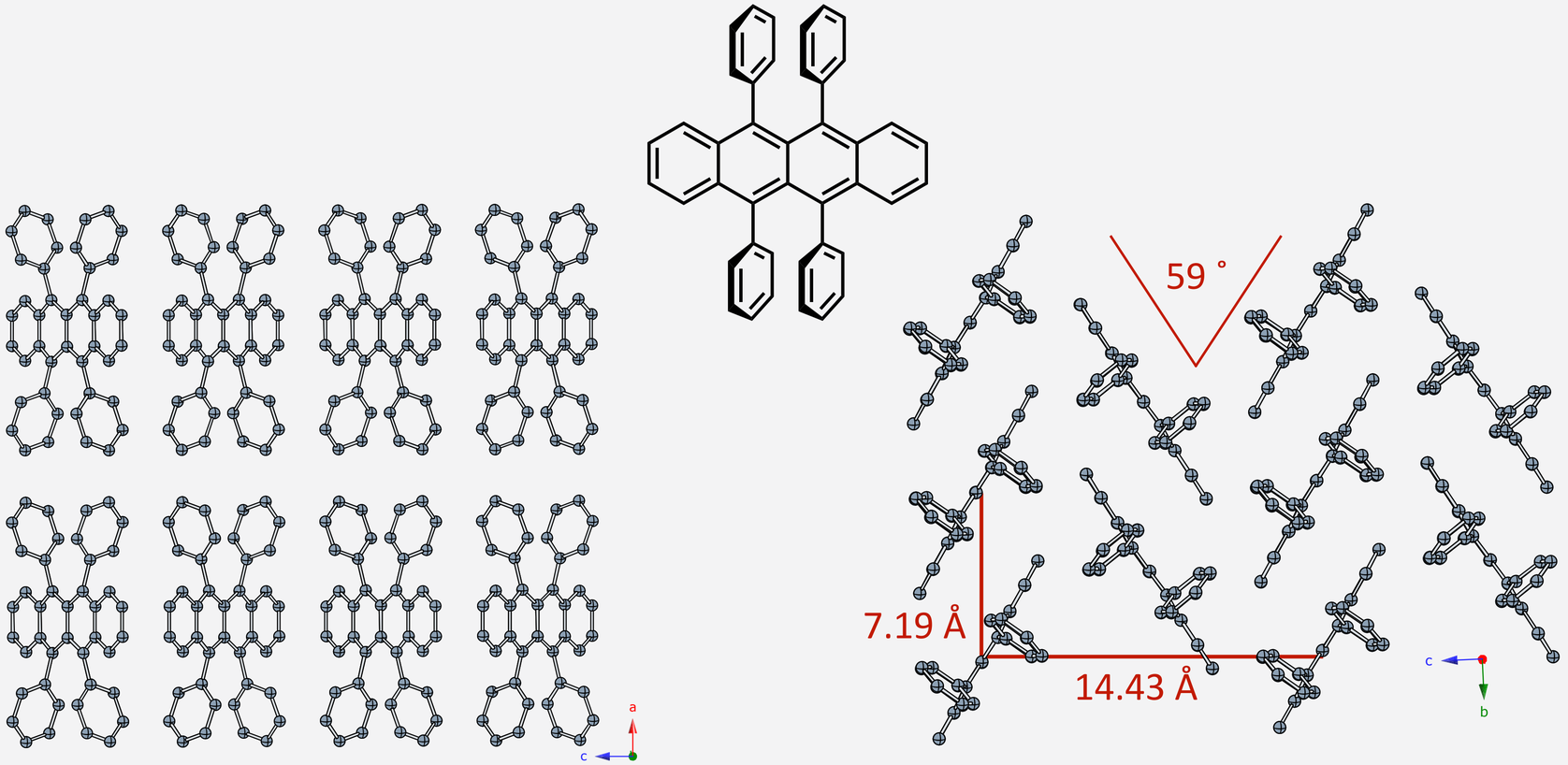


- **herringbone arrangement, edge-to face interactions impossible due to lateral substituents**
- **brickwork layers enforced by phase segregation between pentacene cores and substituents**
- **space-filling packing of substituents determines tilt angle, parallel-displaced π–π stacking**

Anthony et al., J. Am. Chem. Soc. 2001, 123, 9482.

Crystal Structure of Rubrene

- rubrene is a calamitic (rod-like) molecule with lateral substituents

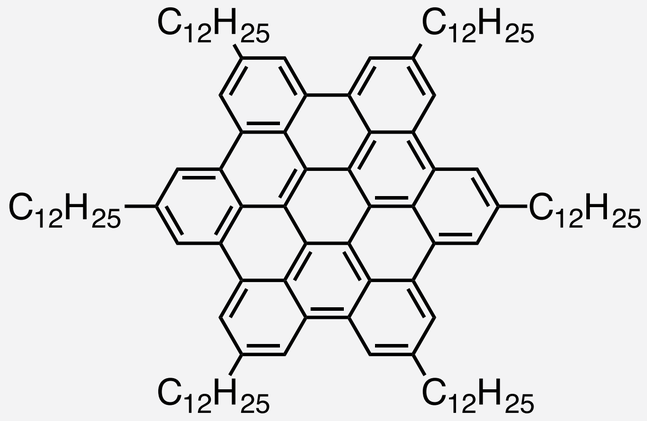


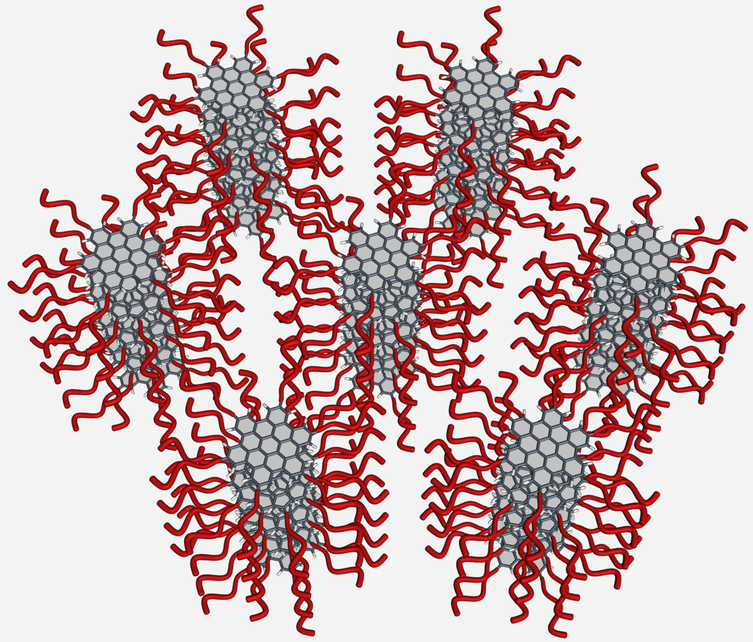
- **herringbone arrangement, edge-to face interactions impossible due to lateral substituents**
- **layers enforced by “phase segregation” between tetracene cores and substituents**
- **space-filling packing of substituents determines tilt angle, parallel-displaced π–π stacking**

Jurchesco, *Acta Crystallogr. Sect. B* **2006**, *62*, 330.

Discotic Molecules with Peripheral Substituents

- hexakis(dodecyl) hexabenzocoronene is a discotic molecule with peripheral substituents





- **phase segregation of alkyl substituents and π-conjugated core reinforces columnar packing**
- **π-π stacked along short axis, but peripheral substituents disordered, cannot pack efficiently**
- **crystallization strongly disfavored, instead liquid-crystalline “hexagonal columnar phases”**

Müllen, *Adv. Mater.* **1996**, *8*, 510.

Learning Outcome

- **packing in crystals balances quadrupolar moment and dispersive forces**
- **layered 2D herringbone structure is a universal motif of calamitic molecules**
  - 1D rows with parallel-displaced packing along long and short axes
  - edge-to face interactions between neighbors in different rows
  - fast growth directions promote 2D layers with smooth surface
  - terminal alkyl substituents do not disturb arrangement
- **small discotic molecules prefer 3D sandwich herringbone structure**
  - dense packing possible as long as axes ≤ dimer sandwich (≤ 7 Å)
- **large discotic molecules prefer columnar structure**
  - in hypothetical “trimer sandwich”, central molecule only π-stacked
  - if that were favorable, then it would be favorable for all molecules
- **2D packing into layers favorable for simple device geometries**