Smilgies: Molecular Axes and Planes as an Eigenvalue Problem (J Appl Cryst)

Supplementary Information

MathCAD code is replicated as it appears on the MathCAD graphical user interface

A copy of the MathCAD program can be obtained from the author on request (dms79@cornell.edu)

Pentacene, based on Campbell et al., Acta Cryst. (1961). 14, 705-711.

table of irreducible atom positions

$$R1 := \begin{pmatrix} 0.1484 & 0.0183 & 0.4071 \\ 0.1707 & 0.1361 & 0.3491 \\ 0.103 & 0.0604 & 0.2508 \\ 0.1274 & 0.165 & 0.1894 \\ 0.0572 & 0.0951 & 0.095 \\ 0.0925 & 0.2095 & 0.0335 \\ -0.0227 & -0.1227 & 0.0567 \\ -0.054 & -0.2325 & 0.1225 \\ 0.015 & -0.1516 & 0.2149 \\ -0.0152 & -0.2634 & 0.2786 \\ 0.0519 & -0.18 & 0.3706 \end{pmatrix} \qquad R2 := \begin{pmatrix} 0.5627 & 0.5733 & 0.4014 \\ 0.5035 & 0.6805 & 0.3286 \\ 0.521 & 0.5876 & 0.2434 \\ 0.4582 & 0.701 & 0.1686 \\ 0.481 & 0.6062 & 0.0846 \\ 0.4231 & 0.7138 & 0.01 \\ 0.5622 & 0.3794 & 0.0754 \\ 0.6103 & 0.2743 & 0.1483 \\ 0.6061 & 0.3652 & 0.2342 \\ 0.6549 & 0.257 & 0.3094 \\ 0.6496 & 0.3487 & 0.3925 \end{pmatrix}$$

$\mathrm{rows}(R1) = 11$ $\qquad$ $\mathrm{rows}(R2) = 11$

Complete molecule by adding symmetry-related positions (space group P-1)

$N := \mathrm{rows}(R1)$ $\qquad$ $i := 0 .. N - 1$

1st molecule

$X1_i := \left(R1^{\langle 0 \rangle}\right)_i$ $\qquad$ $Y1_i := \left(R1^{\langle 1 \rangle}\right)_i$ $\qquad$ $Z1_i := \left(R1^{\langle 2 \rangle}\right)_i$

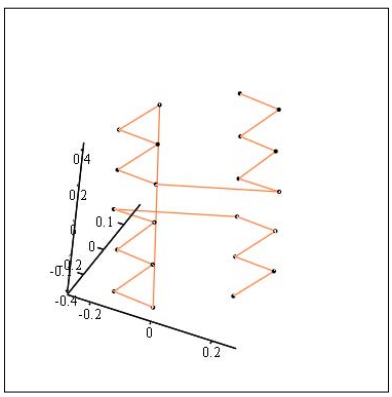
$X1_{N+i} := -X1_i$ $\qquad$ $Y1_{N+i} := -Y1_i$ $\qquad$ $Z1_{N+i} := -Z1_i$

2nd molecule at Wyckoff position (0.5,0.5) was moved to the origin first

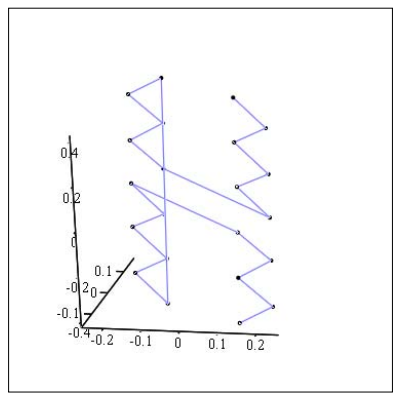
$X2_i := \left(R2^{\langle 0 \rangle}\right)_i - 0.5$ $\qquad$ $Y2_i := \left(R2^{\langle 1 \rangle}\right)_i - 0.5$ $\qquad$ $Z2_i := \left(R2^{\langle 2 \rangle}\right)_i$

$X2_{N+i} := (-X2)_i$ $\qquad$ $Y2_{N+i} := (-Y2)_i$ $\qquad$ $Z2_{N+i} := -Z2_i$

graphical check




$(X1, Y1, Z1)$




$(X2, Y2, Z2)$

table of coordinates for complete molecule 1 and 2

$R1 := \mathrm{augment}(X1, \mathrm{augment}(Y1, Z1))$ $\qquad$ $\mathrm{rows}(R1) = 22$

$R2 := \mathrm{augment}(X2, \mathrm{augment}(Y2, Z2))$ $\qquad$ $\mathrm{rows}(R2) = 22$

lattice parameters (from Campbell et al., erratum, Acta Cryst. (1962). 15, 289-290.)

$a := 7.90 \quad b := 6.06 \quad c := 16.01 \quad \alpha := 101.9 \cdot deg \quad \beta := 112.6 \cdot deg \quad \gamma := 85.8 \cdot deg$

reciprocal lattice (including factor of 2 PI)

$$V := a \cdot b \cdot c \cdot \sqrt{1 + 2 \cdot \cos(\alpha) \cdot \cos(\beta) \cdot \cos(\gamma) - \cos(\alpha)^2 - \cos(\beta)^2 - \cos(\gamma)^2}$$

$$as := \frac{2 \cdot \pi \cdot b \cdot c \cdot \sin(\alpha)}{V} \qquad bs := \frac{2 \cdot \pi \cdot c \cdot a \cdot \sin(\beta)}{V} \qquad cs := \frac{2 \cdot \pi \cdot a \cdot b \cdot \sin(\gamma)}{V}$$

$$\gamma s := acos\left(\frac{\cos(\alpha) \cdot \cos(\beta) - \cos(\gamma)}{|\sin(\alpha) \cdot \sin(\beta)|}\right)$$

$$\alpha s := acos\left(\frac{\cos(\gamma) \cdot \cos(\beta) - \cos(\alpha)}{|\sin(\gamma) \cdot \sin(\beta)|}\right)$$

$$\beta s := acos\left(\frac{\cos(\alpha) \cdot \cos(\gamma) - \cos(\beta)}{|\sin(\alpha) \cdot \sin(\gamma)|}\right)$$

numerical values

$as = 0.862 \qquad bs = 1.06 \qquad cs = 0.433 \qquad d001 := \frac{2 \cdot \pi}{cs} \qquad d001 = 14.502$

$\alpha s = 78.849\,deg \qquad \beta s = 67.77\,deg \qquad \gamma s = 89.619\,deg$

crystallographic B matrix (including 2 PI)

$$BMat := \begin{pmatrix} a & b \cdot \cos(\gamma) & c \cdot \cos(\beta) \\ 0 & b \cdot \sin(\gamma) & -c \cdot \sin(\beta) \cdot \cos(\alpha s) \\ 0 & 0 & \frac{2 \cdot \pi}{cs} \end{pmatrix} \qquad BMat = \begin{pmatrix} 7.9 & 0.444 & -6.153 \\ 0 & 6.044 & -2.858 \\ 0 & 0 & 14.502 \end{pmatrix}$$

3D lattice vectors of pentacene unit cell

$A := BMat^{\langle 0 \rangle} \qquad B := BMat^{\langle 1 \rangle} \qquad C := BMat^{\langle 2 \rangle}$

checks

$|A| = 7.9 \qquad a = 7.9 \qquad |B| = 6.06 \qquad b = 6.06 \qquad |C| = 16.01 \qquad c = 16.01$

$$acos\left(\frac{B \cdot C}{b \cdot c}\right) = 101.9\,deg \qquad acos\left(\frac{A \cdot C}{a \cdot c}\right) = 112.6\,deg \qquad acos\left(\frac{A \cdot B}{a \cdot b}\right) = 85.8\,deg$$

$\alpha = 101.9\,deg \qquad \beta = 112.6\,deg \qquad \gamma = 85.8\,deg$

## cartesian coordinates for molecule 1 and 2

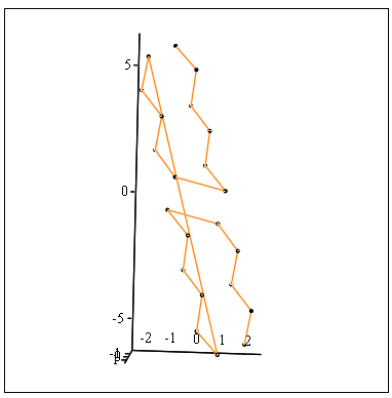
$r1 := R1 \cdot BMat^T$ $\quad N := rows(R1)$ $\quad N = 22$

$x1 := r1^{\langle 0 \rangle}$ $\quad y1 := r1^{\langle 1 \rangle}$ $\quad z1 := r1^{\langle 2 \rangle}$

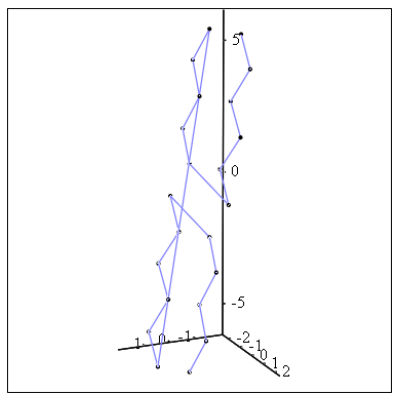
$r2 := R2 \cdot BMat^T$ $\quad N := rows(R2)$ $\quad N = 22$

$x2 := r2^{\langle 0 \rangle}$ $\quad y2 := r2^{\langle 1 \rangle}$ $\quad z2 := r2^{\langle 2 \rangle}$

## graphical check




$(x1, y1, z1)$




$(x2, y2, z2)$

## covariance matrices for molecule 1 and 2

$$CoV1 := \frac{r1^T \cdot r1}{N} \qquad CoV2 := \frac{r2^T \cdot r2}{N}$$

$$CoV1 = \begin{pmatrix} 1.309 & 1.454 & -3.569 \\ 1.454 & 1.772 & -3.27 \\ -3.569 & -3.27 & 12.921 \end{pmatrix} \qquad CoV2 = \begin{pmatrix} 1.293 & 0.467 & -3.862 \\ 0.467 & 1.71 & -3.051 \\ -3.862 & -3.051 & 13.312 \end{pmatrix}$$

Molecular main axes by diagonalization of covariance matrix

-> maximum variance: long molecular axis
-> minimum variance: normal vector of molecular plane

$$\text{var1} := \text{eigenvals}(\text{CoV1}) \qquad \text{var1} = \begin{pmatrix} 1.148 \times 10^{-3} \\ 1.113 \\ 14.888 \end{pmatrix} \qquad \begin{aligned} \min(\text{var1}) &= 1.148 \times 10^{-3} \\ \max(\text{var1}) &= 14.888 \end{aligned}$$

$$\text{var2} := \text{eigenvals}(\text{CoV2}) \qquad \text{var2} = \begin{pmatrix} 1.172 \\ 6.21 \times 10^{-4} \\ 15.144 \end{pmatrix} \qquad \begin{aligned} \min(\text{var2}) &= 6.21 \times 10^{-4} \\ \max(\text{var2}) &= 15.144 \end{aligned}$$

3D vectors of molecular axes as eigenvectors associated with the maximum variance

$$\text{MA1} := \text{eigenvec}(\text{CoV1}, \max(\text{var1})) \qquad \text{MA1} = \begin{pmatrix} -0.271 \\ -0.261 \\ 0.926 \end{pmatrix} \qquad |\text{MA1}| = 1$$

$$\text{MA2} := \text{eigenvec}(\text{CoV2}, \max(\text{var2})) \qquad \text{MA2} = \begin{pmatrix} -0.269 \\ -0.222 \\ 0.937 \end{pmatrix} \qquad |\text{MA2}| = 1$$

3D vectors of molecular planes as eigenvector associated with the minimum variance

$$\text{MP1} := -\text{eigenvec}(\text{CoV1}, \min(\text{var1})) \qquad \text{MP1} = \begin{pmatrix} 0.858 \\ -0.502 \\ 0.11 \end{pmatrix} \qquad |\text{MP1}| = 1$$

$$\text{MP2} := \text{eigenvec}(\text{CoV2}, \min(\text{var2})) \qquad \text{MP2} = \begin{pmatrix} 0.871 \\ 0.36 \\ 0.335 \end{pmatrix} \qquad |\text{MP1}| = 1$$

check of orthogonality

$$\text{MA1} \cdot \text{MP1} = 0 \qquad \text{MA2} \cdot \text{MP2} = 0$$

## Numerical results, part 1

### Intermolecular angles

- angle between molecular axes

$\delta 12 := \left|\mathrm{acos}(MA1 \cdot MA2)\right|$ $\qquad$ $\delta 12 = 2.311\,\mathrm{deg}$

- angle between molecular planes (herring bone angle)

$\varepsilon 12 := \left|\mathrm{acos}(MP1 \cdot MP2)\right|$ $\qquad$ $\varepsilon 12 = 52.884\,\mathrm{deg}$

### Angles between molecular axes and planes and the 3D lattice vectors

- angle of molecular axes with C lattice vector

$\rho 1 := \mathrm{acos}\left(\frac{C}{|C|} \cdot MA1\right)$ $\qquad$ $\rho 2 := \mathrm{acos}\left(\frac{C}{|C|} \cdot MA2\right)$

$\rho 1 = 8.103\,\mathrm{deg}$ $\qquad$ $\rho 2 = 7.305\,\mathrm{deg}$

- angle of molecular plane with A lattice vector

$\sigma 1 := \mathrm{asin}\left(\frac{A}{|A|} \cdot MP1\right)$ $\qquad$ $\sigma 2 := \mathrm{asin}\left(\frac{A}{|A|} \cdot MP2\right)$

$\sigma 1 = 59.096\,\mathrm{deg}$ $\qquad$ $\sigma 2 = 60.543\,\mathrm{deg}$

Transformation to Eulerian angles

- rotation of molecular axes from cartesian x-axis

$\theta 1 := \mathrm{atan2}(MA1_0, MA1_1)$ $\qquad \theta 1 = -136.12\,\mathrm{deg}$

$\theta 2 := \mathrm{atan2}(MA2_0, MA2_1)$ $\qquad \theta 2 = -140.417\,\mathrm{deg}$

- rotation of molecular axis into cartesian xz plane

$$Rz(\phi) := \begin{pmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$RMA1 := Rz(-\theta 1) \cdot MA1 \qquad RMA1 = \begin{pmatrix} 0.377 \\ 0 \\ 0.926 \end{pmatrix}$$

$$RMA2 := Rz(-\theta 2) \cdot MA2 \qquad RMA2 = \begin{pmatrix} 0.349 \\ 0 \\ 0.937 \end{pmatrix}$$

- tilt of molecular axis

$$\chi 1 := \mathrm{atan}\left(\frac{RMA1_0}{RMA1_2}\right) \qquad \chi 1 = 22.121\,\mathrm{deg}$$

$$\chi 2 := \mathrm{atan}\left(\frac{RMA2_0}{RMA2_2}\right) \qquad \chi 2 = 20.413\,\mathrm{deg}$$

- check: undo tilt of molecular axis

$$Ry(\chi) := \begin{pmatrix} \cos(\chi) & 0 & \sin(\chi) \\ 0 & 1 & 0 \\ -\sin(\chi) & 0 & \cos(\chi) \end{pmatrix}$$

$$RRMA1 := Ry(-\chi 1) \cdot RMA1 \qquad RRMA1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$RRMA2 := Ry(-\chi 2) \cdot RMA2 \qquad RRMA2 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

-> all information from molecular axis is extracted

- rotate molecular planes with rotations determined from molecular axes

$$RRMP1 := Ry(-\chi 1)\cdot Rz(-\theta 1)\cdot MP1 \qquad RRMP1 = \begin{pmatrix} -0.292 \\ 0.956 \\ 0 \end{pmatrix} \qquad RRMP1\cdot RRMA1 = 0$$

$$RRMP2 := Ry(-\chi 2)\cdot Rz(-\theta 2)\cdot MP2 \qquad RRMP2 = \begin{pmatrix} -0.961 \\ 0.277 \\ 0 \end{pmatrix} \qquad RRMP2\cdot RRMA2 = 0$$

- azimuth angle of molecular planes with regard to x-axis

-> for the molecular plane to lie within the xz-plane,
the normal vector MP points along the y-direction

check

$$\phi 1 := atan2(RRMP1_0, RRMP1_1) - \frac{\pi}{2} \qquad \phi 1 = 16.992\,deg \qquad Rz(-\phi 1)\cdot RRMP1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$\phi 2 := atan2(RRMP2_0, RRMP2_1) - \frac{\pi}{2} \qquad \phi 2 = 73.893\,deg \qquad Rz(-\phi 2)\cdot RRMP2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

Numerical results, part 2

- molecule 1: values of the Eulerian angles

$\phi 1 = 16.992\,deg \qquad \chi 1 = 22.121\,deg \qquad \theta 1 = -136.12\,deg$

- check

$$Rz(-\phi 1)\cdot Ry(-\chi 1)\cdot Rz(-\theta 1)\cdot MA1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad Rz(-\phi 1)\cdot Ry(-\chi 1)\cdot Rz(-\theta 1)\cdot MP1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

- molecule 2: values of the Eulerian angles

$\phi 2 = 73.893\,deg \qquad \chi 2 = 20.413\,deg \qquad \theta 2 = -140.417\,deg$

- check

$$Rz(-\phi 2)\cdot Ry(-\chi 2)\cdot Rz(-\theta 2)\cdot MA2 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad Rz(-\phi 2)\cdot Ry(-\chi 2)\cdot Rz(-\theta 2)\cdot MP2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

molecules rotated to the main plane (cartesian xz plane)

$$Rr1 := \left(Rz(-\phi 1)\cdot Ry(-\chi 1)\cdot Rz(-\theta 1)\cdot r1^{T}\right)^{T} \qquad Rr2 := \left(Rz(-\phi 2)\cdot Ry(-\chi 2)\cdot Rz(-\theta 2)\cdot r2^{T}\right)^{T}$$

Rr1 =

| | 0 | 1 | 2 |
|---|---|---|---|
| 0 | -0.68 | 0.042 | 6.103 |
| 1 | -1.356 | 0.011 | 4.936 |
| 2 | -0.713 | -0.026 | 3.652 |
| 3 | -1.328 | 0 | 2.449 |
| 4 | -0.707 | -0.078 | 1.222 |
| 5 | -1.41 | -0.004 | -0.023 |
| 6 | 0.703 | 0.044 | 1.156 |
| 7 | 1.368 | -0.025 | 2.452 |
| 8 | 0.694 | 0.02 | 3.631 |
| 9 | 1.365 | -0.031 | 4.896 |
| 10 | 0.686 | -0.005 | 6.068 |
| 11 | 0.68 | -0.042 | -6.103 |
| 12 | 1.356 | -0.011 | -4.936 |
| 13 | 0.713 | 0.026 | -3.652 |
| 14 | 1.328 | -0 | -2.449 |
| 15 | 0.707 | 0.078 | -1.222 |

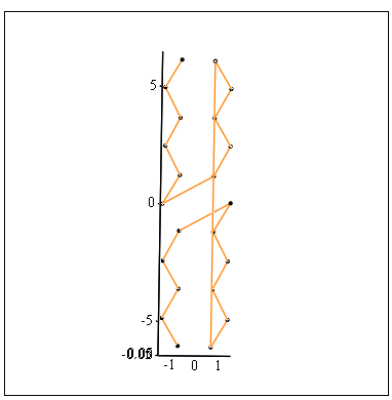
Rr2 =

| | 0 | 1 | 2 |
|---|---|---|---|
| 0 | -0.725 | 0.006 | 6.134 |
| 1 | -1.387 | -0.015 | 4.947 |
| 2 | -0.723 | -0.003 | 3.692 |
| 3 | -1.427 | -0.03 | 2.472 |
| 4 | -0.738 | 0.012 | 1.228 |
| 5 | -1.395 | 0.003 | 0.009 |
| 6 | 0.739 | 0.004 | 1.242 |
| 7 | 1.354 | -0.046 | 2.451 |
| 8 | 0.743 | 0.027 | 3.691 |
| 9 | 1.374 | -0.029 | 4.94 |
| 10 | 0.759 | 0.042 | 6.137 |
| 11 | 0.725 | -0.006 | -6.134 |
| 12 | 1.387 | 0.015 | -4.947 |
| 13 | 0.723 | 0.003 | -3.692 |
| 14 | 1.427 | 0.03 | -2.472 |
| 15 | 0.738 | -0.012 | -1.228 |

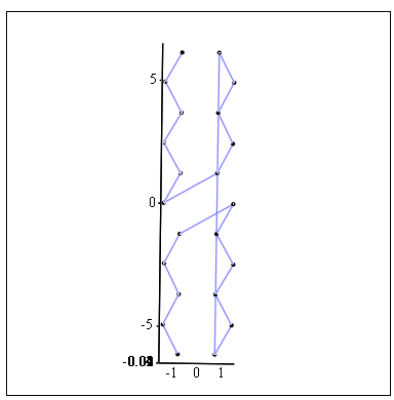
graphical check

$Rx1 := Rr1^{\langle 0\rangle}$ $\quad Ry1 := Rr1^{\langle 1\rangle}$ $\quad Rz1 := Rr1^{\langle 2\rangle}$

$Rx2 := Rr2^{\langle 0\rangle}$ $\quad Ry2 := Rr2^{\langle 1\rangle}$ $\quad Rz2 := Rr2^{\langle 2\rangle}$




(Rx1, Ry1, Rz1)




(Rx2, Ry2, Rz2)