THE CRYSTAL STRUCTURE OF BROMOBENZOIC ACID©

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COMPUTATIONAL DOCUMENT

You should be using a paper copy of the instructions for this program which are in the file brbins.mcd.

For exercise 2 you may use the data below to calculate the number of mulecules per unit cell.

$\lambda := 1.5418$ $a := 14.82$ $b := 4.10$ $c := 25.90$ all in A

$\beta := 118.25$ $\rho := 1.929$ grams/cm^3

You may use the same data for exercise 3.

INPUT OF THE MEASURED AMPLITUDES Fo

The measured amplitudes are stored in a disk file called brbdata.prn

$A := READPRN(brbdata)$

The first 12 reflections are listed at the left.

$A =$

	h	k	l	Fo
0	0	0	1	34
1	0	0	2	98
2	0	0	3	144
3	0	0	4	205
4	0	0	5	75
5	0	0	6	99
6	0	0	7	116
7	0	0	8	109
8	0	0	9	8
9	0	0	10	23
10	0	0	11	54
11	0	0	12	60
12	0	0	13	7

Set up column vectors H, K, L, and Fo for the observed reflections.

$H := A^{<0>}$ $K := A^{<1>}$ $L := A^{<2>}$ $Fobs := A^{<3>}$ $nref := rows(A)$

Obtain the maximum and minimum Miller indeces h and l.

$minh := min(H)$ $maxh := max(H)$ $minl := min(L)$ $maxl := max(L)$

$minh = 0$ $maxh = 9$ $minl = -16$ $maxl = 14$

COMPUTATION OF THE PATTERSON FUNCTION

For the P2 symmetry of bromobenzoic acid the Patterson function for the U, W projection using the h0l reflections becomes:

$$P(U,W) := \sum_{l=minl}^{maxl} \sum_{h=0}^{maxh} Fo^2 \cdot \cos(2\cdot\pi\cdot(h\cdot U + l\cdot W))$$

Using this formula it is possible to calculate the function summing over all of the Fo^2 values for each of several hundred points. This takes a great amount of computer time. Using the formula cos(a+b)=cos(a)cos(b)-sin(a)sin(b) the expression becomes

$$P(U,W) := \sum_{l=minl}^{maxl} \sum_{h=0}^{maxh} Fo^2 \cdot (\cos(2\cdot\pi\cdot l\cdot W)\cdot\cos(2\cdot\pi\cdot h\cdot U) - \sin(2\cdot\pi\cdot l\cdot W)\cdot\sin(2\cdot\pi\cdot h\cdot U))$$

where the sum over h*U can be performed first and the sums over l*W performed later with a great saving of computer time.

We set up an array of Fo^2 values preparing for the Patterson map. Since the range of l is -16 to +14 we define a new index lp covering the range 0 to 30. Since h values are 0 or positive, the range of h is 0 to maxh.

$lp := 0 .. maxl - minl \qquad h := 0 .. maxh$

Fill in the table with the observed values.

$i := 0 .. nref - 1$

$$Fsqo_{\left[H_i,\left(L_i - minl\right)\right]} := \left(Fobs_i\right)^2$$

We now comput the first sums FSCOS and FSSIN which are the cos and sin coefficients. The calculations in U are made at point intervals of 1/60 of a unit cell. These are accumulated in tables with l values on one axis and U values in the other dimension.

$i := 0 .. 60$

$lp := 0 .. maxl - minl$

$U_i := \frac{i}{60}$

$$FSCOS_{lp,i} := \sum_{h=0}^{maxh} Fsqo_{h,lp} \cdot \cos\left(2 \cdot \pi \cdot U_i \cdot h\right)$$

$$FSSIN_{lp,i} := \sum_{h=0}^{maxh} Fsqo_{h,lp} \cdot \sin\left(2 \cdot \pi \cdot U_i \cdot h\right)$$

The second summation is now computed over l and W. The points in W are calculated every 1/60 of a unit cell. The values of P(U,V,W) are contained in array Pji. We calculate half of this array and then generate the rest by symmetry.

$j := 0 .. 30$

To shorten the notation we make some substitutions:

$W_j := \frac{1}{60} \cdot j$

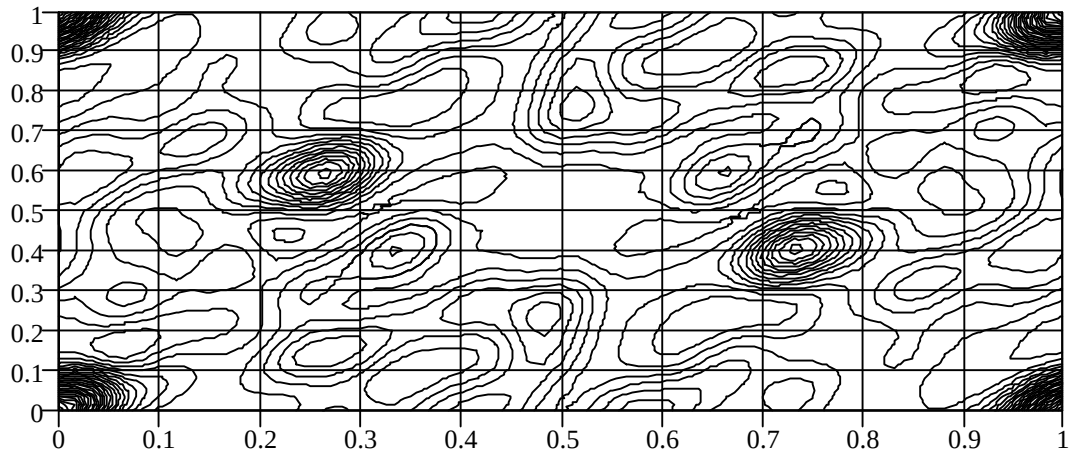
$C := FSCOS \quad S := FSSIN$

$$P_{j,i} := \sum_{lp=0}^{maxl-minl} C_{lp,i} \cdot \cos\left[2 \cdot \pi \cdot W_j \cdot (lp + minl)\right] - \sum_{lp=0}^{maxl-minl} S_{lp,i} \cdot \sin\left[2 \cdot \pi \cdot W_j \cdot (lp + minl)\right]$$

$j := 31 .. 60 \quad i := 0 .. 60 \quad P_{j,i} := P_{60-j,60-i}$

THE PATTERSON MAP

We have evaluated the Patterson function at 3721 points in a two-dimensional array. The origin of the contour map below is at the lower left corner with U extending upward and W to the right. The map is displayed roughly in relation to the cell dimensions, but the oblique coordinates have not been shown.



P

Patterson Map for bromobenzioic acid.

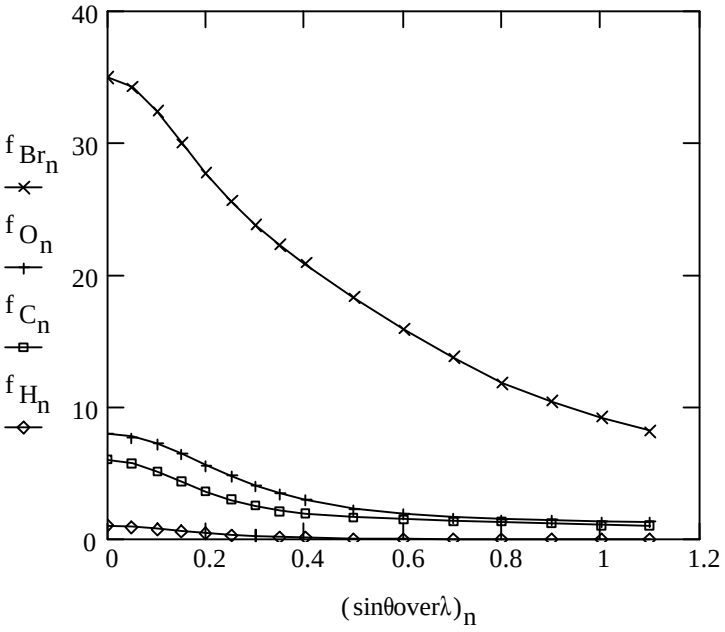
SCATTERING FACTOR TABLES

The scattering factors for H, C, O, and Br are read in as functions of sinθ/λ.

scatable := READPRN(SCATFAC2)

rows(scatable) = 16 sinθoverλ := scatable<0> n := 0..15

f_H := scatable<1> f_C := scatable<2> f_O := scatable<3> f_{Br} := scatable<4>



PREPARATION OF TABLES OF sin2θ and f

Next we set up expressions to get $\sin^2\theta$, $\sin\theta$, and the scattering factors for each ion for each reflection. These will be stored in a table $scat_{i,j}$ where j cycles through the elements and i cycles through the reflections.

$\lambda := 1.5418 \qquad i := 0 .. nref - 1$

$$sinsq\theta_i := \frac{\lambda^2}{4} \cdot \left[\frac{\left(\frac{H_i}{a^2}\right)^2 + \left(\frac{L_i}{c^2}\right)^2 - \frac{2 \cdot H_i \cdot L_i}{a \cdot c} \cdot \cos\left(\beta \cdot \frac{\pi}{180}\right)}{\left(\sin\left(\beta \cdot \frac{\pi}{180}\right)\right)^2} + \left(\frac{K_i}{b^2}\right)^2 \right]$$

$$sin\theta_i := \sqrt{sinsq\theta_i}$$

The table of scattering factors for each element j for each reflection i is made by an interpolation procedure described in the MATHCAD book on page 247.

$j := 1..4 \qquad k := 0..16$

$vs^{<j>} := cspline\left(scatable^{<0>}, scatable^{<j>}\right)$

$scat_{i,j} := interp\left(vs^{<j>}, scatable^{<0>}, scatable^{<j>}, \frac{\sin\theta_i}{\lambda}\right)$

STUDENT INPUT

The thermal parameter B on page 9 has been set to a reasonable value. It is a measure of the amplitude of vibration of the atoms, Such vibrations cause the X-ray scattering to be reduced, especially at high angles. This parameter may be changed later to get better agreement between the Fo and Fcalc values.

Next give the number of atoms to be included in the calculation.

$natoms := 1$

Next we create a matrix named ATOMS with four columns and one row for each atom. The first column contains the index Ele for the element. Note the table below:

Ele	Element
1	H
2	C
3	O
4	Br

The next 3 columns contain x, y, z, for each of the atoms. You should click on the matrix button under 'Text' and again on the matrix button which appears on the palette.

$$ATOMS := \begin{bmatrix} 4 & .30 & 0 & .134 \\ 3 & .47 & 0 & .37 \\ 3 & .70 & 0 & .47 \\ 2 & .59 & 0 & .38 \\ 2 & .68 & 0 & .32 \\ 2 & .87 & 0 & .34 \\ 2 & .98 & 0 & .28 \\ 2 & .88 & 0 & .17 \\ 2 & .67 & 0 & .13 \\ 2 & .57 & 0 & .20 \end{bmatrix}$$

$Ele := ATOMS^{<0>}$ $x := ATOMS^{<1>}$ $y := ATOMS^{<2>}$ $z := ATOMS^{<3>}$

$m := 0 .. nref - 1$

$$TF_m := \exp\left[-B \cdot \left(\frac{\sin\theta_m}{\lambda} \right)^2 \right]$$

$$Fcalc_m := \sum_{n=0}^{(natoms-1)} \left[scat^{\left\langle \left[(Ele)_n \right] \right\rangle} \right]_m \cdot TF_m \cdot \cos\left[2\cdot\pi\cdot\left(H_m\cdot x_n + K_m\cdot y_n + L_m\cdot z_n \right) \right]$$

The signs of Fcalc are now attached to the Fo values and placed in a column matrix Fcoef.

$$Fcoef_m := if\left(Fcalc_m < 0, -Fobs_m, Fobs_m \right)$$

The R factor is a measure of the agreement of |Fcalc| with Fo

$$R := \frac{\sum_{m=0}^{nref-1} \left| \left| (Scale\cdot Fobs)_m \right| - \left| Fcalc_m \right| \right|}{\sum_{m=0}^{nref-1} \left| (Scale\cdot Fobs)_m \right|}$$

$B \equiv 20$

$Scale \equiv .155$

$R = 0.35$

Label the proper output file either FC1 or FC2. For the one atom calculation use FC1.

$$WRITEPRN(FC1) := Fcalc$$

$minh := \min(H)$ $maxh := \max(H)$ $minl := \min(L)$ $maxl := \max(L)$

$minh = 0$ $maxh = 9$ $minl = -16$ $maxl = 14$

Set up an array of Fcoef values preparing for the Electron Density

$l := 0 .. maxl - minl$ $h := 0 .. maxh$

Fill in the table with the Fobs with sign of Fcalc

$i := 0 .. nref - 1$

$Fo_{\left[H_i, \left(L_i - minl\right)\right]} := Fcoef_i$

Compute the first sum FS over h and x

$i := 0 .. 60$

$l := 0 .. maxl - minl$

$x_i := \frac{i}{60}$

$$FSCOS_{l,i} := \sum_{h=0}^{maxh} Fo_{h,l} \cdot \cos\left(2 \cdot \pi \cdot x_i \cdot h\right)$$

$$FSSIN_{l,i} := \sum_{h=0}^{maxh} Fo_{h,l} \cdot \sin\left(2 \cdot \pi \cdot x_i \cdot h\right)$$

$j := 0 .. 30$

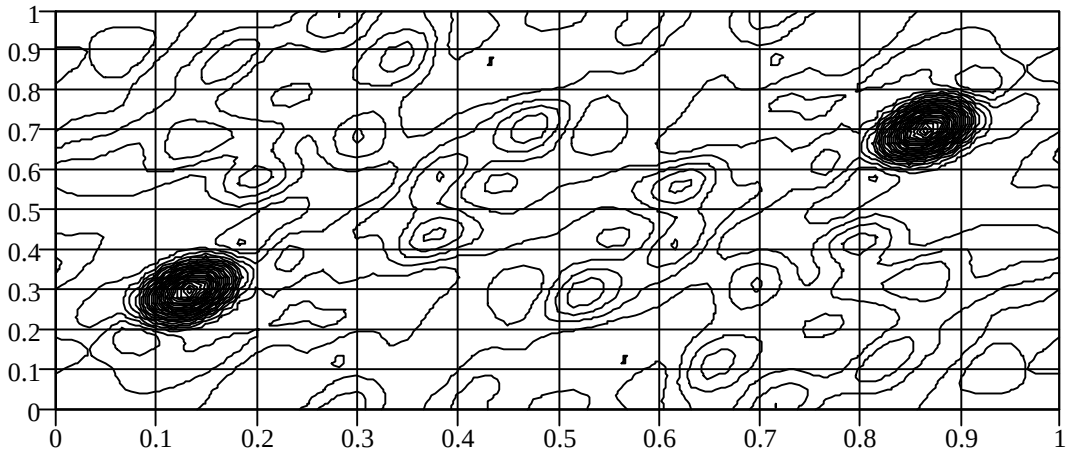
Once again we shorten the notation:
C=FSCOS and S=FSSIN

$z_j := \frac{1}{60} \cdot j$

$C := FSCOS \quad S := FSSIN$

$$P_{j,i} := \sum_{l=0}^{maxl - minl} C_{l,i} \cdot \cos\left[2 \cdot \pi \cdot z_j \cdot (l + minl)\right] - \sum_{l=0}^{maxl - minl} S_{l,i} \cdot \sin\left[2 \cdot \pi \cdot z_j \cdot (l + minl)\right]$$

$j := 31 .. 60 \qquad i := 0 .. 60 \qquad P_{j,i} := P_{60 - j, 60 - i}$



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Electron Density for Brb

$BRBMAP^{\langle 0 \rangle} := H \qquad BRBMAP^{\langle 1 \rangle} := K \qquad BRBMAP^{\langle 2 \rangle} := L$

$BRBMAP^{\langle 3 \rangle} := Fobs$

$WRITEPRN(BRBMAP) := BRBMAP$