THE CRYSTAL STRUCTURE OF BROMOBENZOIC ACID ©

Student Instructions

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The crystal structure of the compound has been reported by G. Ferguson and G. A. Sim in Acta Crystallographica, Vol. 15, page 346, (1962). The unit cell data:

$$\lambda := 1.5418 \qquad a := 14.82 \qquad b := 4.10 \qquad c := 25.90$$

$$\beta := 118.25 \qquad \rho := 1.929 \quad \text{grams/cm}^3$$

with the wavelength λ and a, b, c, in A (1A=10^{-8} cm) and the angle β between the a and c axes in degrees. The unit cell is monoclinic with symmetry described by the space group C2/c. The reflection intensities from 1145 crystal planes (hkl) were measured from photographic films. The formula is $C_7H_8O_2Br$ with a molecular weight of 201.0 grams/mole.

The purpose of this computer exercise is to resolve a two-dimensional image of the structure in order to find out which isomer (ortho, meta, or para) is present and to speculate on the pattern of possible hydrogen bonding.

EXERCISE 1
Draw and name the three isomers of bromobenzoic acid.

EXERCISE 2
Calculate the number of molecules per cell. This is the ratio of the
weight of the unit cell to the weight of a single molecule. You may use
MATHCAD in the space provided in the computational document, or you
may use your calculator.

EXERCISE 3
Calculate the interplanar spacing for the 100, 010, and 001 reflections.
You may use MATHCAD in the computational document.

    In order to simplify this problem we will develop a projection image
looking down the b axis onto the xz plane. This image is calculated
using only the h0l X-ray reflections, so there will be only 216 reflections.
The projection of the structure onto the xz plane has repeat distances of
a/2 and c/2, so we can use a unit cell only 1/4 as large which can be
described by the plane group symmetry P2 with two molecules in the
smaller cell. Consistent with this choice the values of h and l have been
divided by 2 compared to those for the larger cell in the original
publication.

CRYSTAL STRUCTURE IMAGES AND THE PHASE PROBLEM

    One way to think about the image of a crystal unit cell is to picture ρ
an electron density function. It may be calculated at many points X,Y,Z
in the unit cell. At the centers of atoms it will have large values, while in
the empty spaces between molecules it will have values near zero. The
formula for the electron density is:

$$\rho(X,Y,Z) := \frac{8}{V} \cdot \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} Fo \cdot \exp(-2 \cdot \pi \cdot (h \cdot X + k \cdot Y + l \cdot Z))$$

where Fo is the amplitude of the reflection hkl and V the volume of
the unit cell. If we could calculate this function directly we would
be able to locate the peaks and determine the positions of the
atoms. It is not so easy. What we measure in the laboratory are
values of Fo^2 or the intensities of the diffracted X-rays. When we
take the square root of Fo^2 a sign ambiguity arises - the value of Fo
can be + or -. This sign problem (or in general phase angle
problem) is called the phase problem in X-ray crystallography. A
great deal of time and effort has been expended to find the signs
or relative phases of X-ray reflections.

   One route to solving the phase problem was developed by A. L.
Patterson which uses values of Fo^2 rather than Fo for the calculation.

$$P(U, V, W) := \frac{8}{V} \cdot \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} Fo^2 \cdot \exp(-2 \cdot \pi \cdot (h \cdot U + k \cdot V + l \cdot Z)) \quad \square$$

The Patterson function is not the same as the electron density, but
it is an interatomic vector map. This function describes the
simultaneous probability of finding an atom at coordinates X,Y,Z
and another atom at coordinates X+U,Y+V,Z+W. Thus for every
pair of atoms in the structure there is a vector U,V,W from the first to
the second and another vector -U,-V,-W from the second to the
first.   The heights of peaks in the Patterson function at these two
positions are proportional to the product of the number of electrons
of the two atoms. For a structure with n atoms in the unit cell there
can be $2n^2$ peaks in the resulting Patterson function.

The Patterson function is most useful when one of the atoms in a molecule has a much larger atomic number than the rest. Bromobenzoic acid is a good test case. The peaks representing the probability of finding a Br atom at X,Y,Z and another Br atom at X+U,Y+V,Z+W will be much larger than Br-C. C-O, C-C or other combinations. These very large peaks can be used to locate the Br atoms.

The crystal symmetry often dictates the relationship of the coordinates of one heavy atom with another. If two molecules such as bromobenzoic acid are related by a screw axis through the origin extending in the y direction, then one Br atom will have coordinates X,Y,Z and the other Br will have coordinates -X, 1/2+Y,-Z. The Patterson function will have large peaks corresponding to the vectors representing the differences in these coordinates. We shall construct a table displaying the differences between the coordinates across the top and those down the side.

	x, y, z	-x, y + 1/2, -z
x, y, z	0, 0, 0	-2x, 1/2, -2z
-x, y + 1/2, -z	2x, -1/2, 2z	0, 0, 0

For example, a Patterson map of a structure with this symmetry has peaks at U,V,W = 0.42 ,0.50, 0.72 and 0.58, 0.50, 0.28. First note that the U value of 0.58 for the second peak does correspond to -0.42 and the W value of 0.28 corresponds to -0.72. Also there is no difference between +0.50 and -0.50 since they are related by translational symmetry. Thus the X values of the two heavy atoms are +0.21 and -0.21 (or +0.79) and the z values are +0.36 and -0.36 (or +0.64). The value of Y cannot be determined in an absolute sense, but in this case one Y value could be arbitrarily set at 0 and the other is at y=0.50.

Exercise 4:

   A crystal structure has P-1 symmetry with a center of symmetry at the
origin. The equivalent positions are X, Y, Z, and -X, -Y, -Z. Develop
a table as above to find the differences in these coordinates. The
Patterson function has peaks at U, V, W, of 0.72, 0.68, 0.46 and
0.28, 0.32, 0.54. What are the locations X, Y, Z, for the heavy
atoms?

 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:

$$P(U,W) := \frac{8}{V} \cdot \sum_{l\,=\,minl}^{maxl}\; \sum_{h\,=\,0}^{maxh} Fo^2 \cdot \cos(2 \cdot \pi \cdot (h \cdot U + l \cdot W))$$

   Using this formula it is possible to calculate the function summing
over all of the Fo^2 values for each of several thousand 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

$$P(U,W) := \frac{8}{V} \cdot \sum_{l\,=\,minl}^{maxl}\; \sum_{h\,=\,0}^{maxh} Fo^2 \cdot (\cos(2 \cdot \pi \cdot l \cdot W) \cdot \cos(2 \cdot \pi \cdot h \cdot U) - \sin(2 \cdot \pi \cdot l \cdot W) \cdot \sin(2 \cdot \pi \cdot h \cdot U))$$

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.

   Don't worry about all the details of how the calculation, but the
information is there if you are curious.

INTERPRETATION OF THE PATTERSON FUNCTION

   Just to review.. There are two bromobenzoic acid molecules in the
unit cell of this X, Z projection. These molecules are related by the
symmetry group P2 which requires that there are two-fold axes
perpendicular to the X, Z plane at the origin 0, 0. Because of
translational symmetry there are two-fold axes at 0, 1/2; 1/2, 0; and
1/2.1/2. The equivalent positions are X, Z and -X, -Z.

Exercise 5
By looking at the Patterson map obtain the coordinates of the Br-Br
vectors. Please remember that W reads accross and U reads up.
What are the X and Z coordinates of the bromine atoms? Review the
reasoning in Exercise 4 if you are stuck. You have now located the
two heaviest atoms in the unit cell. This will prove very helpful in
locatingthe rest of the atoms.

STRUCTURE FACTORS FOR BROMOBENZOIC ACID

   Our long-range objective is to visualize the structure using the
electron density function.

$$\rho(X,Y,Z) := \frac{8}{V} \cdot \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} Fo \cdot \exp(-2 \cdot \pi \cdot (h \cdot X + k \cdot Y + l \cdot Z))$$

To calculate this function we need the values of Fo with their algebraic signs. From the X-ray measurements we can only obtain the absolute magnitudes of the Fo values When we know the positions of the atoms (or at least some of them) we can calculate values of Fcalc with their signs. Then we attach the signs of Fcalc to Fo, and calculate the electron density function. The formula for Fcalc for the mth reflection is as follows:

$$\text{Fcalc}(h,k,l)_m := \sum_{n=1}^{\text{noatoms}} f_n \cdot \exp\left[2 \cdot \pi \cdot \left(h_m \cdot x_n + k_m \cdot y_n + l_m \cdot z_n\right)\right]$$

where f_n is the scattering factor for the nth atom and x_n, y_n, z_n are the fractional coordinates of the nth atom in the unit cell. The summation is carried out over the atoms in the unit cell. The f values are the scattering powers of the atoms for X-rays. We shall use the tables of the f's published in the International Tables for Crystallography. They are read in and plotted in the computational document. This graph shows dramatically how Br dominates the scattering relative to the other atoms. If you wish to see the tabulated values for the first few reflections type 'scat='. θ is the Bragg angle for the X-rays and λ the wavelength of the radiation. The thermal motion of the atoms will be accounted for by use of an overall temperature factor B.

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

For this crystal structure with P2 symmetry and including only h0l reflections

$$F(h,k,l)_m := 2 \cdot \exp\left[-B \cdot \left(\frac{\sin\theta_m}{\lambda}\right)^2\right] \cdot \sum_{n=1}^{natoms} f_n \cdot \exp\left(h_m \cdot x_n + l_m \cdot z_n\right) $$

Using this formula we need only include atoms from one molecule. The scattering from symmetrically located atoms is included automatically.

EXERCISE 6
The crystal structure of CsCl consists of a Cs+ ion at the origin and Cl- ion in the middle of the cell at 1/2, 1/2, 1/2. Assume that the B values are zero. Calculate F(2,3,3) using the approximation that the scattering factor f_j = atomic number.

EXERCISE 7
Use the matrix display feature (Fobs=, then F9) to display arrays Fobs, Fcalc, and Fcoef. Record the values listed for the fourth reflection in the lists. This is the hkl = 004 reflection. How are the values of Fcoef obtained?

This map should make chemical sense if all has gone well up to now. The calculation of the Fcalc's was based on only one atom. Hopefully the Br atom has dominated the signs of the structure factors enough so that other atoms will show up.

EXERCISE 8
 Do the Br atoms come up in the expected positions?

EXERCISE 9
Can you spot the benzene ring and the carboxyl group? If you can get a paper copy mark the atoms in the bromobenzoic acid molecule. Read off the coordinates of each atom and make a table of Ele, X, and Z for each atom. Remember that X reads up, Z to the right.

EXERCISE 10

Can you determine which isomer of benzoic acid this is (o, m, or p)?
Can you speculate on the form of hydrogen bonding is present? Is it
chains, dimers, or some other arrangement?

The electron density map you have obtained is not the best possible.
Make the following changes in the document: On page 7 change the
number of atoms to 10. Set up a 10 atom matrix on page 8. This matrix
called ATOMS should have ten rows and four columns: the first one is
Ele an index indicating the element, the next columns are x, y, z
coordinates. On page 9 change the file from FC1 to FC2 where the
results are stored.

EXERCISE 11

How has the R factor improved. How has the map improved?

Open a new document called Brbfiles and use the Math menu
'Calculate Worksheet' to get it to compute. Now get out of MATHCAD
and print out the file brbfile.prn. The columns in this output are h, k, l,
Fcalc for the one-atom calculation, Fcalc for the 10-atom calculation,
and finally the product of the Fcalc values for the two calculations. A
negative product indicates that a sign of a structure factor has changed.

EXERCISE 12

Which reflections had incorrect signs in the first calculation?