

Crystal structure elucidation of Bis(4-chlorophenyl) sulfone (BCPS)

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1 Introduction

In this study, single crystal X-ray diffraction was employed to investigate the structure of Bis(4-chlorophenyl) sulfone (BCPS). Data analysis was conducted using the CrysAlisPro software suite, while structure solution and refinement were performed with the JANA software using the super-flip method. The space group for BCPS was determined to be $C2/c$, with a reliability factor (R) of 4.67%. All experimental procedures and data acquisition for the X-ray diffraction of the single crystal sample were carried out using a different research sample at the Institut de Physique de Rennes (IPR), Université de Rennes.

2 Experimental Method

To obtain X-ray diffraction patterns from the single crystal (SC), the process begins with mounting the SC onto a sample holder, which is then placed within the goniometer and installed in the diffractometer. Initially, the SCs are spread on a glass slide and inspected under a microscope to assess their dimensions and visible features, as shown in Figure 1.

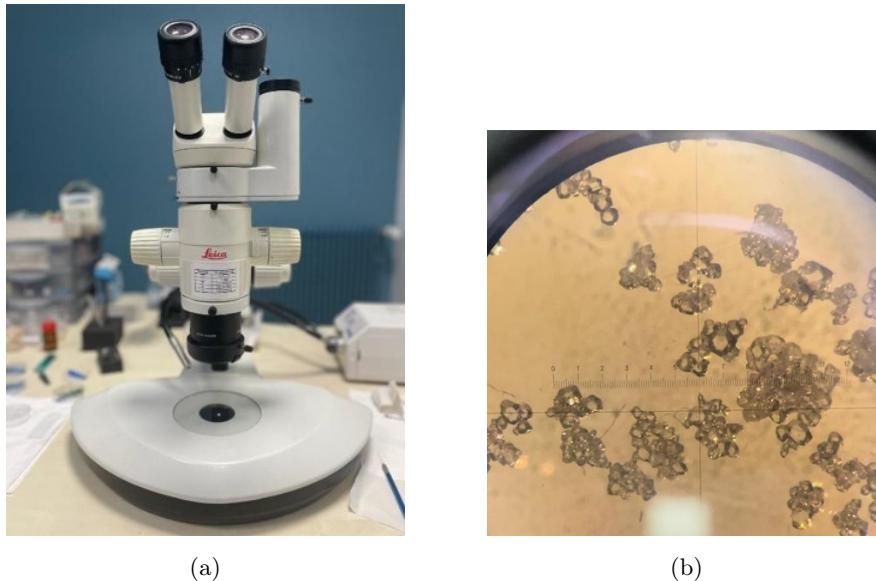


Figure 1: Microscopic inspection of single crystals.

After careful examination, a few crystals with the most uniform shapes and sizes not exceeding 300 nm (to prevent significant absorption corrections) are chosen. The following steps involve attaching these crystals to a support (in this case, a cactus needle), fixing the needle to a metal head as shown in Figure 2a, and then securing

this assembly onto the kappa goniometer before installing it in the diffractometer. The crystals are affixed to the tip of a sharp cactus needle using viscous oil. The needle is then secured in a metal holder with wax and positioned inside the single crystal diffractometer, as shown in Figure 2b. The goniometer is then aligned by adjusting the X, Y, and Z directions until the sample is centered under the cross-hairs for all crystal orientations. The measurement utilized Mo-K α_1 X-rays ($\lambda = 0.709 \text{ \AA}$).

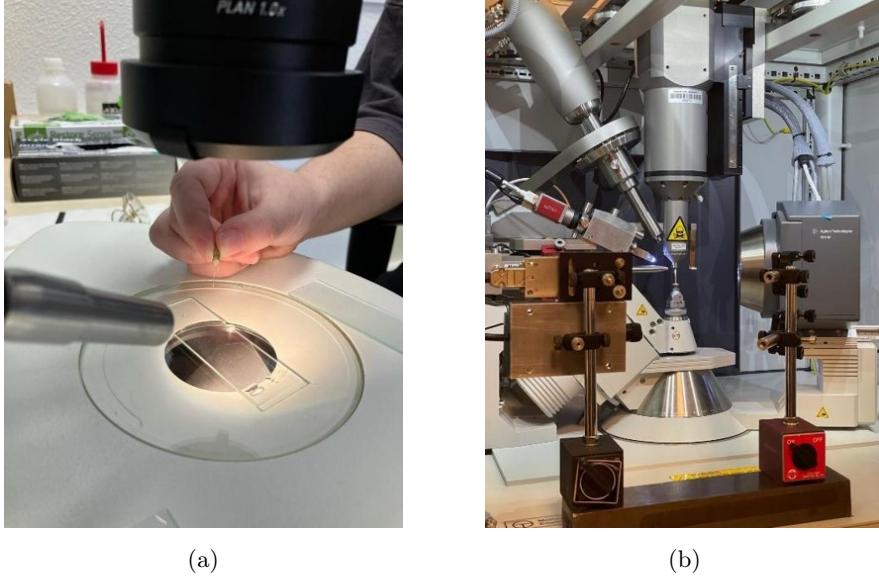


Figure 2: Mounting and installation of crystals on the goniometer.

3 Data Collection and Processing: Symmetry analysis of the crystal.

Using the Xcalibur, a series of images were collected to record Bragg scattered intensities at various orientations of a crystal exposed to a quasi-parallel and monochromatic X-ray beam during the scattering experiment. Each image was obtained through a small oscillation about one of the motors, specifically the ω scan, around the mean position.

The resulting files from the data collection include:

- **.par** file: Contains information on the experimental parameters such as wavelength, distance, and geometry.
- **.run** file: Represents the set of data collection runs.
- **.img** files: Comprise all the images taken during data collection.

The CrysAlisPro software package by Rigaku Oxford Diffraction was employed for data processing. This involved several critical steps:

1. Peak detection: Using the software's peak hunting procedure (`ph s` command) to identify Bragg spots resulting from diffraction.
2. Determination of the unit cell: Indexation and reduction of the unit cell parameters.
3. Refinement: Optimizing the crystal parameters based on the diffraction pattern.
4. Reconstruction of lattice planes: Integrating and refining data to reconstruct the lattice structure.
5. Data integration and reduction: Processing the raw data into meaningful diffraction information.

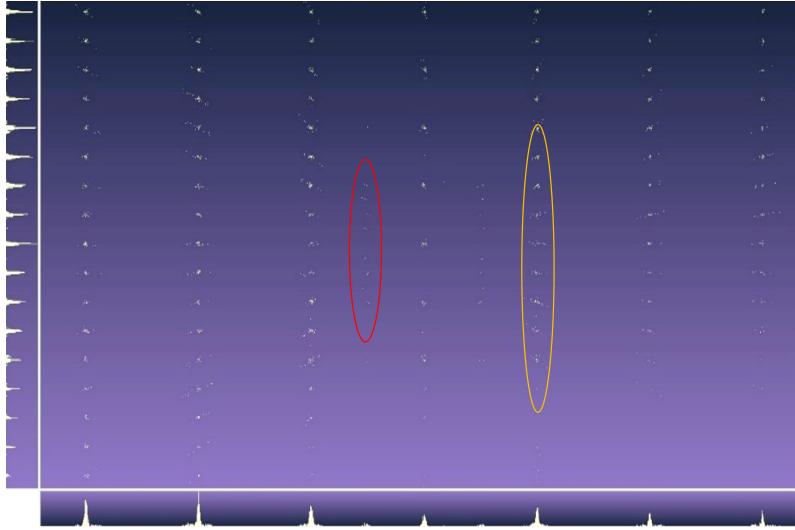


Figure 3: Visualization of reciprocal space showing diffraction peaks.

Upon opening the `.par` file in CrysAlisPro, we switched to the manual edit command window mode to execute specific commands. Visualization of the reciprocal space was facilitated using the command `pt ewald`, which allowed us to observe key features:

- Some peaks (indicated in yellow in Figure 3) exhibit significant dispersion.
- Other peaks (colored red in Figure 3) likely arise from contamination, specifically $\lambda/2$ in the incident radiation.

In the initial analysis, we can notice several features:

1. The reciprocal basis vectors are perpendicular or almost perpendicular to each other, and they all have different lengths, suggesting the lattice may correspond to an orthorhombic, monoclinic, or trigonal system.
2. There are several missing peaks, which can be related to screw axes or gliding mirrors, indicating that the space group is not symmorphic.

The command `um ttt` was used to determine the orientation matrix (see Image 4a). To refine the orientation matrix and index the observed peaks, the `um i` command was employed, successfully indexing 87.97% of the peaks. Two possible crystallographic results were obtained: a triclinic system without constraints and a monoclinic system with constraints. Given that the standard error of the two angles was of the same order of magnitude to their deviation from 90° , we confirmed the monoclinic system as our working model. Based on this assumption, the `refine model` command was applied to refine the crystal parameters, thereby improving the accuracy of the diffraction pattern predictions

For the analysis described, the entire raw data was utilized (both strong and weakly indexed peaks), i.e. no peaks were removed using the `pt e` command. The peak table was saved using the `wd t` command. Next, we determined the spatial grouping of the sample. By employing the `dc unwarp` command, we extracted specific planes in reciprocal space: $(h k 0)$, $(h k 1)$, $(h 0 l)$, $(h 1 l)$, $(0 k l)$, $(1 k l)$ (see Fig. 5a).

The following selection rules were determined (the intensity is not zero). For:

- $(h k 0)$: $h + k = 2n$,
- $(h k 1)$: $h + k = 2n + 1$ and if $k = 0$ then $h = 2n$,
- $(h 0 l)$: $h = 2n$ and $h + l = 2n$,
- $(h 1 l)$: $h + l = 2n + 1$,

```

No constraint
UB - matrix:
-0.030017 -0.034963  0.028615 ( 0.000008  0.000015  0.000004 )
-0.049836  0.021712 -0.017531 ( 0.000009  0.000016  0.000005 )
-0.000308 -0.136472 -0.010164 ( 0.000011  0.000021  0.000006 )
M - matrix:
0.003385  0.000009  0.000018 ( 0.000001  0.000002  0.000000 )
0.000009  0.020318  0.000006 ( 0.000002  0.000006  0.000001 )
0.000018  0.000006  0.001229 ( 0.000000  0.000001  0.000000 )
Constraint
UB - matrix:
-0.030017 -0.034963  0.028615 ( 0.000008  0.000015  0.000004 )
-0.049836  0.021712 -0.017531 ( 0.000009  0.000016  0.000005 )
-0.000308 -0.136472 -0.010164 ( 0.000011  0.000021  0.000006 )
M - matrix:
0.003387  0.000000  0.000017 ( 0.000001  0.000000  0.000001 )
0.000000  0.020314  0.000000 ( 0.000000  0.000006  0.000000 )
0.000017  0.000000  0.001229 ( 0.000001  0.000000  0.000000 )
UB fit with 2174 obs out of 2469 (total:2469,skipped:0) (88.05%)
unit cell:
12.1922(17) 4.9761(7) 20.230(3)
90.068(12) 90.502(11) 90.065(12)
V = 1227.3(3)
unit cell:
12.188(2) 4.9763(8) 20.236(3)
90.0 90.479(18) 90.0
V = 1227.3(4)

No constraint
UB - matrix:
-0.030095 -0.034930  0.028648 ( 0.000008  0.000014  0.000004 )
-0.049890  0.021707 -0.017555 ( 0.000008  0.000016  0.000004 )
-0.000262 -0.136537 -0.010127 ( 0.000011  0.000021  0.000006 )
M - matrix:
0.003395  0.000004  0.000016 ( 0.000001  0.000002  0.000000 )
0.000004  0.020334  0.000001 ( 0.000002  0.000006  0.000001 )
0.000016  0.000001  0.001231 ( 0.000000  0.000001  0.000000 )
Constraint
UB - matrix:
-0.030095 -0.034930  0.028648 ( 0.000008  0.000014  0.000004 )
-0.049890  0.021707 -0.017555 ( 0.000008  0.000016  0.000004 )
-0.000262 -0.136537 -0.010127 ( 0.000011  0.000021  0.000006 )
M - matrix:
0.003393  0.000000  0.000016 ( 0.000001  0.000000  0.000001 )
0.000000  0.020335  0.000000 ( 0.000000  0.000006  0.000000 )
0.000016  0.000000  0.001231 ( 0.000001  0.000000  0.000000 )
UB fit with 2172 obs out of 2469 (total:2469,skipped:0) (87.97%)
unit cell:
12.1741(16) 4.9742(7) 20.213(3)
90.011(12) 90.457(11) 90.028(12)
V = 1224.0(3)
unit cell:
12.175(2) 4.9733(7) 20.216(3)
90.0 90.444(17) 90.0
V = 1224.0(4)

```

(a)

(b)

Figure 4: Orientation matrix after the command (a) `um ttt` and (b) `refine model`

- $(0\ k\ l)$: $k + l = 2n$,
- $(1\ k\ l)$: $k + l = 0$ and $k \neq 0$,

From the extinction rules, we can determine that the chosen basis exhibits body-centering (extinction rule: $h+k+l=2n$) and a glide mirror perpendicular to the a -axis ($h = 2n$ if $\mathbf{H} = [h, 0, l]$). The corresponding space group is I2/a. To verify this assumption, we used the command `um c` to change the basis using the orthogonal transformation M (the new lattice parameters are listed at the end of this section):

$$M = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

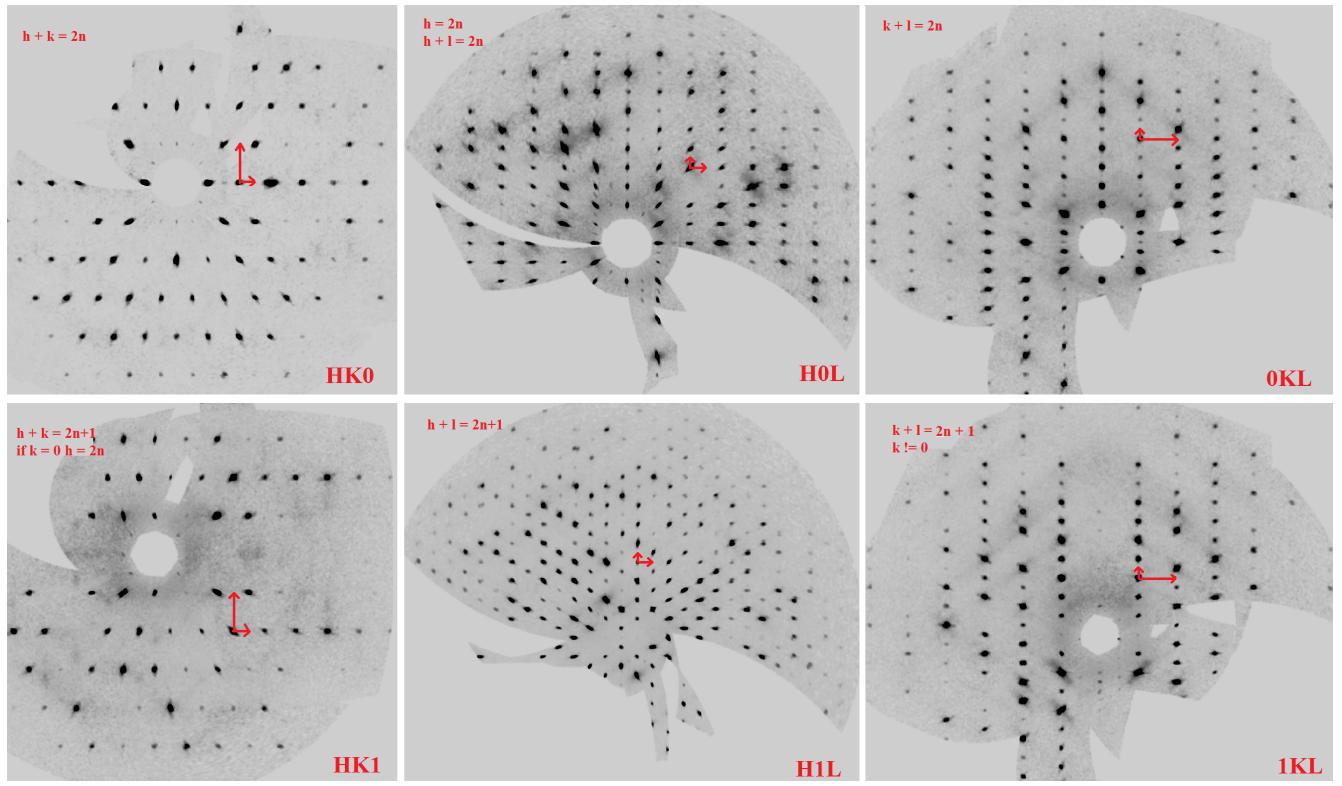
This transformation converts I-centering to C-centering and a-glide mirror to c-glide mirror. After the transformation, the extinction rules are: $h + k = 2n$, and $l = 2n$ when $\mathbf{H} = [h, 0, l]$, so they refer to different Miller indices and are easy to observe (see. Fig 5b). The disappeared Bragg reflection lines in the $(h\ 0\ l)$, $(h\ 1\ l)$ planes correspond to the c-centering, whereas the c-glide mirror leads to the disappearance of the reflection with even l on the $(h, 0, l)$ plane.

Thus, we determined the space group of the BCPS crystal: **C2/c** (equivalent to I2/a), and its lattice parameters: $a = 23.673(7)$, $b = 4.9761(17)$, $c = 20.210(6)$, $\beta = 30.94(6)^\circ$, with the unit cell volume $V = 1224.2(4)^3$

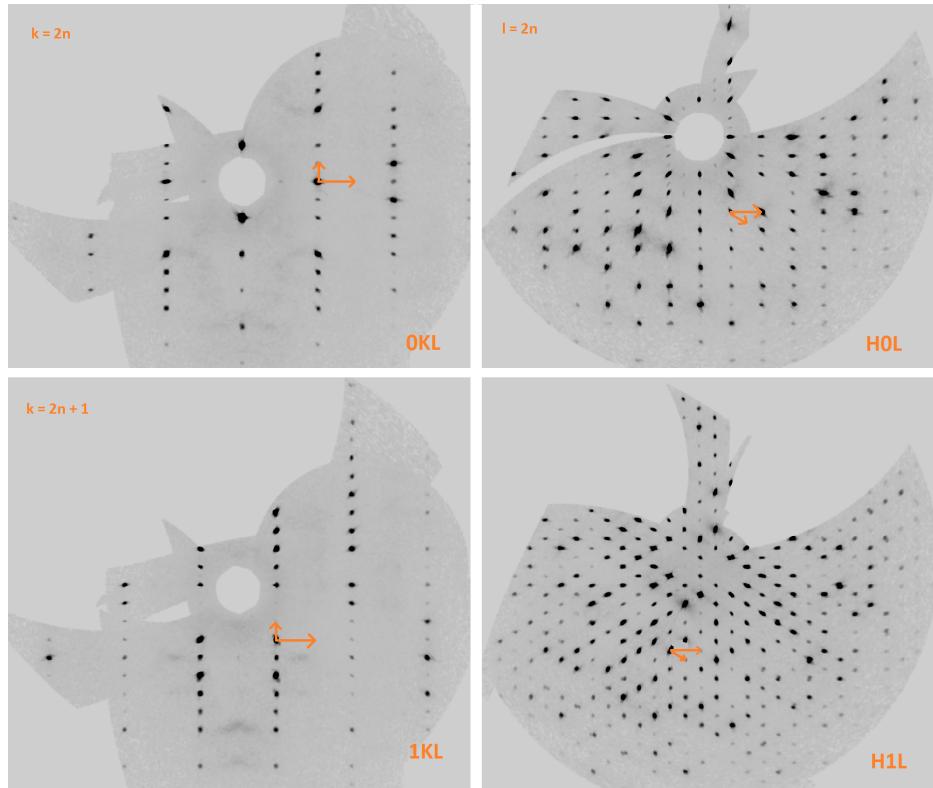
Finally, the command `dc proffit` was used to initiate the integration process, which, along with the space group determination, was conducted with the default settings. In the final step, the space group C2/c was selected instead of the initially proposed I2/a. The chemical formula of BCPS C₆H₄S_{0.5}OCl was entered with the multiplicity of the general position for the C2/c space group being $Z = 8$ [?]. A new lattice basis was adopted with the lattice parameters: $a = 23.6850(13)$, $b = 4.97741(16)$, $c = 12.1768(8)$, $\beta = 121.426(8)^\circ$, with the unit cell volume $V = 1224.95(11)^3$. New files were generated for the subsequent structure refinement using Jana2020 software [?]

4 Structure solution and refinement with Jana2020

The `.cif` file generated in the previous step using CrysAlis was imported into Jana2020. The `.hkl` file, which contains information about the Bragg reflections was used for space group refinement, with all procedures carried out using default settings. The refinement yielded new unit cell parameters: $a = 23.5607$, $b = 4.49771$, $c = 12.1762$, $\beta = 120.698^\circ$, and $V = 1224.9^3$. Following the space group refinement, the superflip method was employed for structure determination, resulting in an R-value of $R = 16.128\%$ and the formula C₆H₀S₀O Cl 1.5.



(a)



(b)

Figure 5: Reconstructed reciprocal lattice planes before (a) and after (b) the basis transformation.

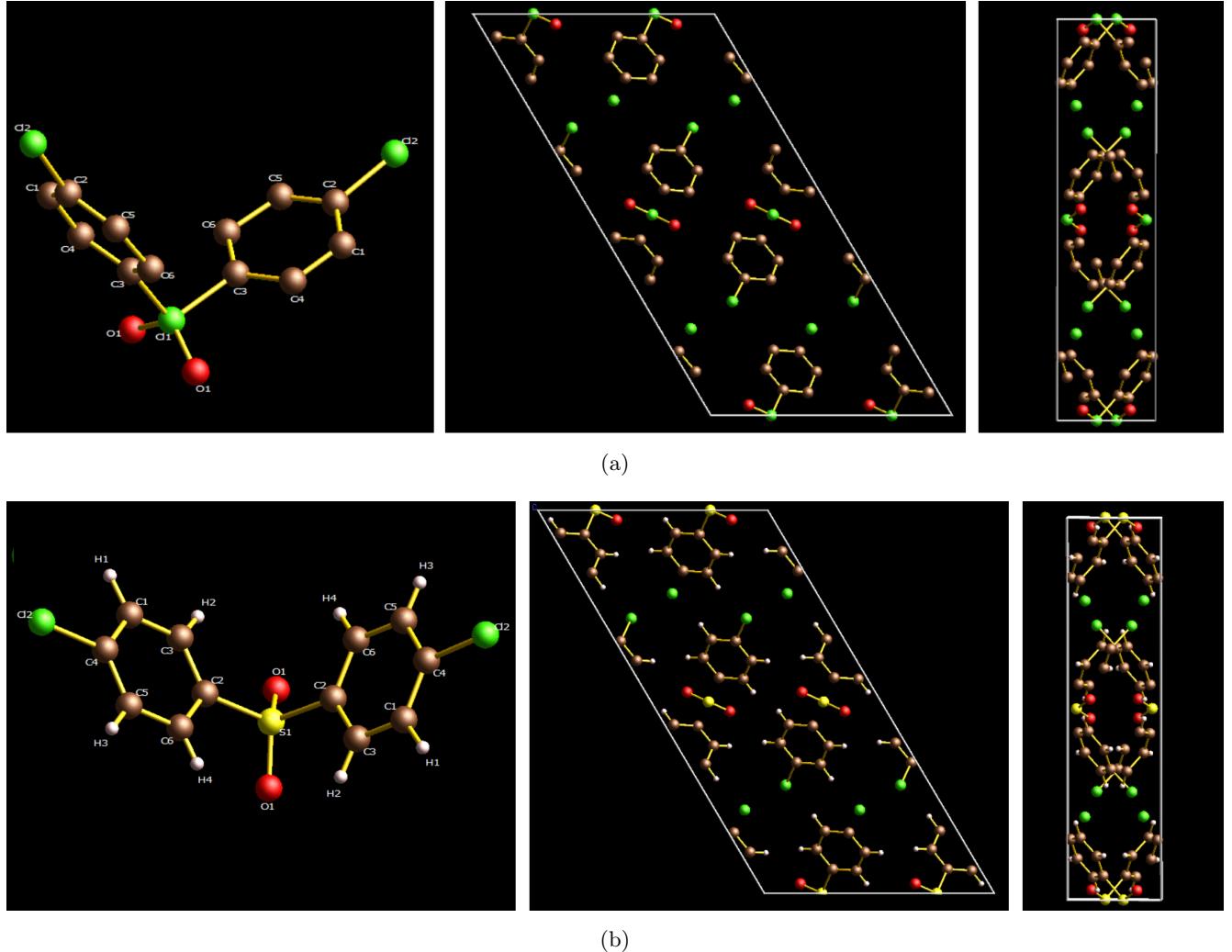


Figure 6: (a): the initial BCPS structure solution by the superflip algorithm, and (b): the final structure of the BCPS

The initial structure is illustrated in Fig. 6a. No atom translations using symmetry operations were necessary as all independent atoms in the solved structure were correctly positioned.

However, the chlorine atom was replaced by a sulphur atom in the solved structure. This adjustment is necessary because the approximation of the spherical symmetric distribution of the electron density for S is not adequately applicable in our case. The correction was done manually, followed by another refinement process. Since the experiment was conducted at room temperature, the Atomic Displacement Parameters (ADPs) were changed from isotropic to anisotropic (harmonic) and the refinement was reapplied. The ADPs were now represented by ellipsoids, reflecting the two main vibrational modes of the BCPS molecule: scissoring and twisting. After these adjustments, the R-value was 6.48%.

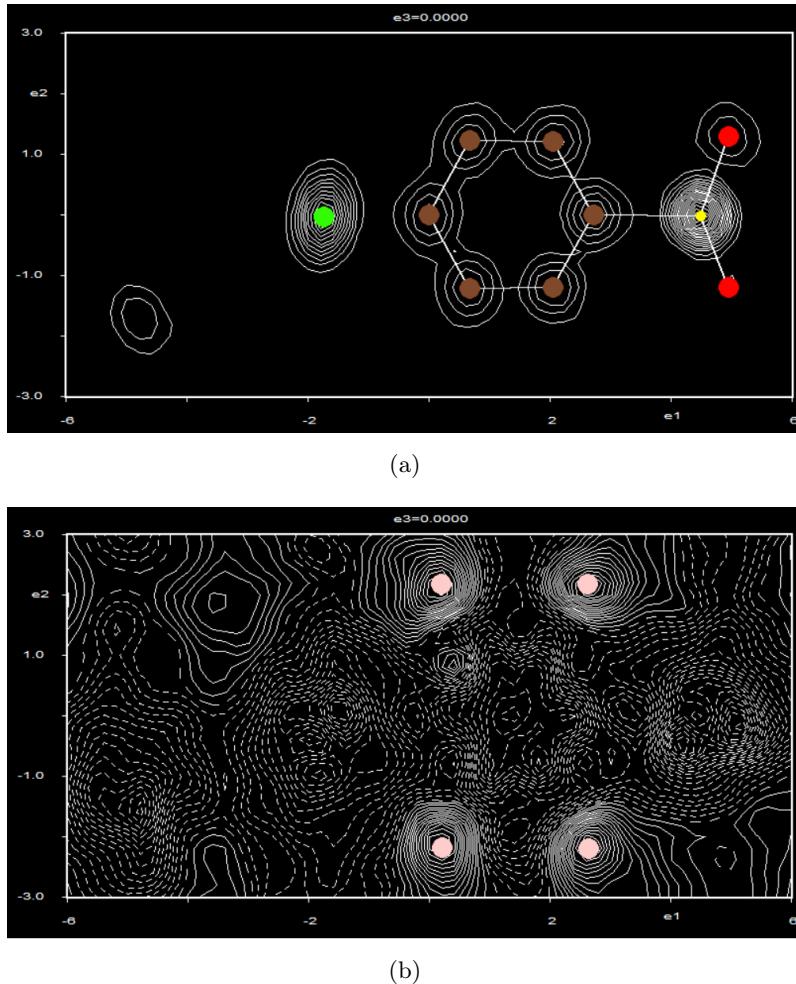


Figure 7: The Fourier map with atoms represented (a) and the difference Fourier map (b) with the found H-atoms

In the solved structure, all hydrogen atoms on the carbon ring were initially absent due to their negligible contribution to the scattering factor. To locate the four missing hydrogen atoms, the Fourier difference method was employed, and Fourier maps were generated (see Fig. 7). In the Fourier difference plot (see Fig. 7b), four distinct peaks corresponding to the hydrogen atoms were clearly identified. These hydrogen atoms were then added manually, and a final refinement was performed, accounting for thermal motion, resulting in an R-value of $R = 4.67\%$. The refined structure is shown in Fig. 6b.

5 Conclusion

The structure of Bis(4-chlorophenyl) sulfone (BCPS) with the chemical formula $C_6H_4S_{0.5}OCl$ (corresponding to one asymmetric unit) was examined using single crystal X-ray diffraction experiment. Under normal conditions, BCPS belongs to the monoclinic crystallographic group with space group $C2/c$. The lattice parameters are $a = 23.5607$, $b = 4.49771$, $c = 12.1762$, $\beta = 120.698^\circ$, with the unit cell volume $V = 1224.9^3$. The solved and refined (with the reliability factor (R) of 4.67%) crystal structure is depicted in Fig. 6b.

6 Acknowledgement

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