APPLICATION NOTE

Rigaku oxford diffraction

Analysis of Very Small Organic Crystals with the XtaLAB Synergy-S

Introduction

As research projects multiply and diversify, and chemists attempt the synthesis of ever more exotic molecules, the isolation and crystallization of these molecules for subsequent characterization often represents the bottleneck for advancement of the project. So when crystallographers are presented with a batch of tiny crystals, they must be able to rely on a powerful X-ray diffractometer to collect the data required to elucidate the structure of these new compounds and characterize them without any ambiguity. To address such difficult applications, the Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer features a powerful 50 watt microfocus sealed tube with a small FWHM beam size of 110 µm, ensuring that most of the X-ray photons are concentrated on the important area, the crystal. In addition, the Rigaku Oxford Diffraction XtaLAB Synergy-S is configured with a HyPix-6000HE hybrid photon counting (HPC) detector. HPC detectors have been used at most synchrotron beamlines around the World because of their high sensitivity and very low electronic noise. These features are also critical to collect precise and accurate data on weakly diffracting crystals on home diffractometers. Here, we demonstrate the performance of the XtaLAB Synergy-S on a tiny organic crystal of benzophenone.

Experimental Overview

A very small crystal of benzophenone, with dimensions 0.015 x 0.018 x 0.027 mm^3, was captured on a MiTeGen Kapton loop mounted on a magnetic base, using paratone oil. The crystal was mounted on the goniometer, centered in the beam using a video camera and data were collected at 100 K. With the Rigaku Oxford Diffraction program CrysAlis^{Pro} [1].

Table 1: XtaLAB Synergy-S specifications.

X-ray source	PhotonJet-S Cu source with continuously variable divergence slit Beam FWHM = 110 µm
Operating power	50 kV x 1 mA = 50 W
Goniometer **Detector distance range**	4-circle Kappa with telescoping 2Theta arm 30 –250 mm
Detector **Active area** **Frame rate** **Readout speed** **Pixel size** **Cooling**	Hybrid photon counting HyPix-6000HE 77.5 x 80.3 mm^2 Up to 100 Hz 0 ms in ZeroDeadTime mode 100 µm air-cooled

Figure 1: Side view of the benzophenone crystal mounted on the goniometer.

Data collection

Benzophenone crystallizes in a non-centrosymmetric space group. Therefore, a target redundancy of 7 at 0.837 Å on the unmerged Friedel mates was used to calculate the strategy in CrysAlis^{Pro}. The exposure time was estimated by CrysAlis^{Pro} for a target <I/σ(I)> of 30 at 0.837 Å for the unmerged data, based on the <I/σ(I)> calculated upon screening. The full data collection time was 8 hours and 22 minutes. Table 1 shows the data collection parameters.

Table 1: Data collection parameters.

Generator settings	50 W (50 kV, 1 mA)
Wavelength	1.54184 Å
Temperature	100 K
Detector distance	34 mm
Low resolution exposure time	3 seconds
High resolution exposure time	12 seconds
Scan width	0.5 °
Total frames	4040
Total time	8 hours 22 minutes

With exposure times of 3 seconds and 12 seconds per 0.5 ° for the low resolution and high resolution scans, respectively, diffraction from the crystal yielded small, very sharp reflections across the resolution range (Figure 2).

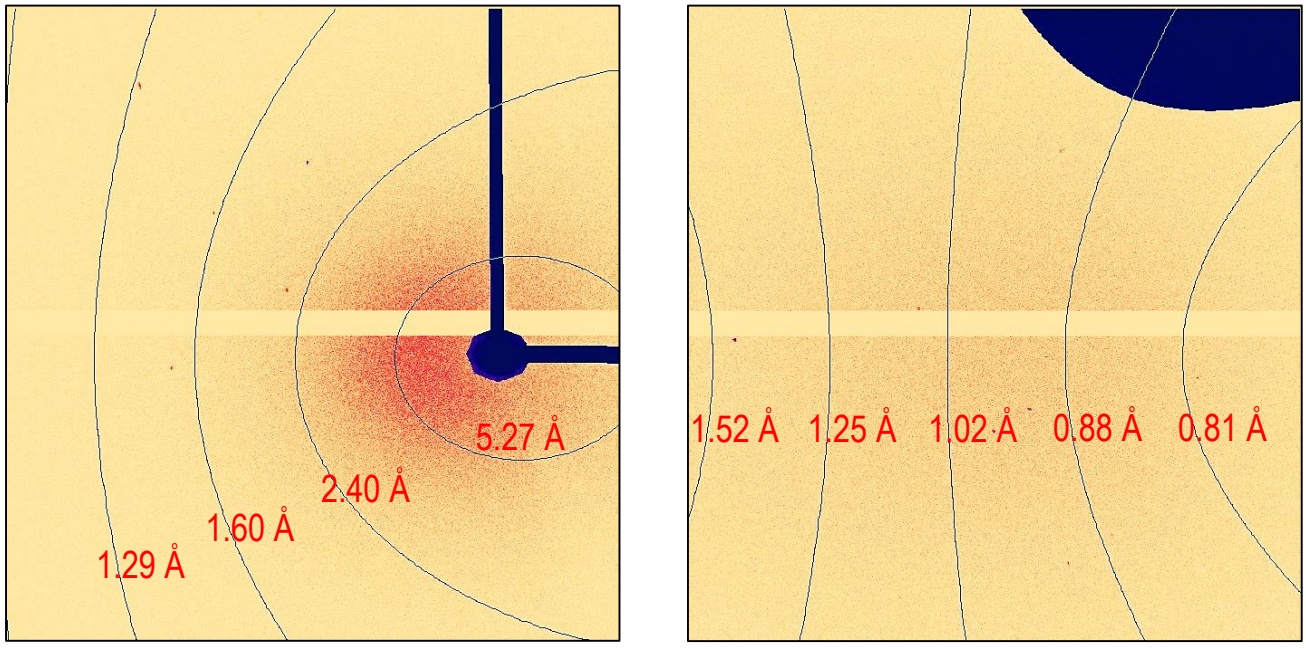

Figure 2: Example of diffraction images obtained at low resolution with 3 sec / 0.50° (left) and at high resolution with 12 sec / 0.50° (right).

Results

The data were processed with CrysAlis^{Pro} and yielded an overall R_{int} of 5.6% and <I/σ(I)> of 23.89 to 0.837 Å. At this resolution, the overall redundancy was 7.1 (Table 2). The crystal structure (Figure 3) was automatically solved by ShelxT[2] in space group $P2_12_12_1$ and refined with ShelxL[3] within the AutoChem[4] interface. Hydrogen atoms were placed according to their electron density Q peaks and refined as free atoms. Excellent structural statistics were obtained, with R_1 at 3.2%, GooF at 1.097 and the Flack parameter at 0.19(19).

Table 2: Experiment and refinement details for the Friedel pairs merged.

Space group	$P2_12_12_1$
Unit cell	7.74700(10), 10.24080(10), 12.0415(2) 90, 90, 90
Resolution	0.837 Å
Completeness (last shell)	100% (100%)
Redundancy (last shell)	7.1 (3.2)
<I/σ(I)> (last shell)	23.89 (11.62)
R_{int} (last shell)	5.6% (10.3%)
Final R factors [I>2σ (I)]	R_1 = 3.20% wR_2 = 7.04%
Goodness of fit	1.097
Largest residual peak/hole (eÅ^{-3})	0.188 / -0.144

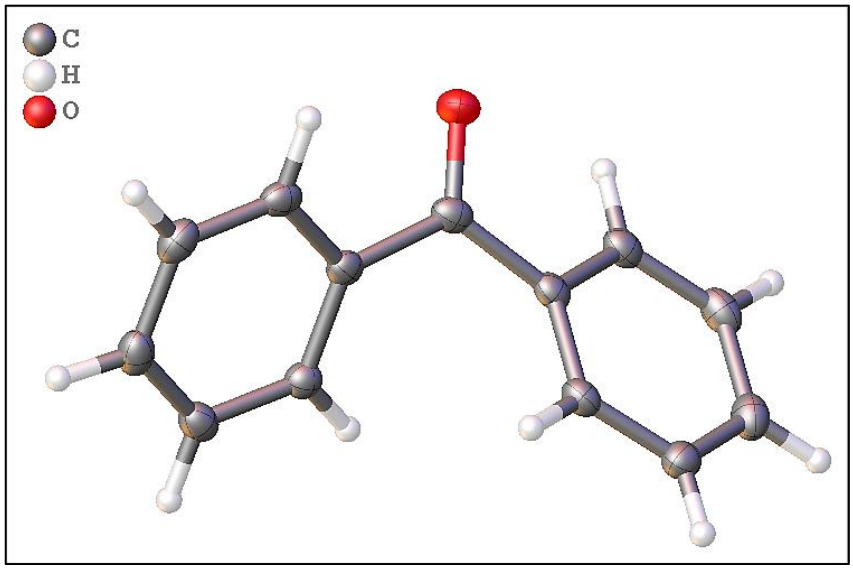

Figure 3: Representation of the model obtained for the benzophenone molecule after refinements to 0.837 Å.

Conclusion

A 7-fold redundant data set was collected on a crystal of benzophenone (0.015 x 0.018 x 0.027 mm^3) in about 8 hours, using the microfocus sealed tube X-ray generator equipped XtaLAB Synergy-S. Despite the small size of the crystal and the fact that it incorporated only light atoms, strong diffraction was obtained to IUCr limits. The crystal structure of benzophenone was solved readily and yielded excellent statistics, including the Flack parameter, demonstrating the high level of performance of the XtaLAB Synergy-S on small, organic crystals.

References

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2. Rigaku Oxford Diffraction, (2019), AutoChem 4.0 software system in conjunction with Olex2 1.3, Rigaku Corporation, Wroclaw, Poland
3. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H., *J. Appl. Cryst.* (2009), **42**, 339-341.
4. Sheldrick, G. M. (2015), *Acta Cryst.* **A71**, 3-8.

Rigaku Oxford Diffraction

9009 New Trails Drive, The Woodlands, TX 77381-5209
Tel.: (281) 362-2300 | FAX: (281) 364-3628 | www.Rigaku.com | info@Rigaku.com