Crystallography

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Dynamic and Thermodynamic Properties of Crystalline Glycine Polymorphs from Multi-Temperature X-ray Diffraction Data

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Introduction

Glycine having three polymorphs (α, β and γ) at ambient conditions differs in the arrangement of zwitterions in the hydrogen-bonding network and the physical and chemical properties. For insight into the differences in the relative thermodynamic stability of the glycine polymorphs, we apply a novel method of concurrent analysis of multi-temperature atomic displacement parameters (ADPs) [1] to investigate the dynamics of molecules in the crystal and the thermodynamic properties. This report presents the preliminary results of γ-glycine in addition to the previous report of α-glycine.

Experimental

Synchrotron data to 0.5 Å resolution of the γ-polymorph of glycine were collected at 10, 70, 130, 190, 250 and 298 K at KEK Photo Factory, Japan. Prior to data processing with RAPID AUTO, all raw diffraction images were applied for imaging-plate linearity correction. The 250 K data have low completeness and hence they are excluded from further analysis.

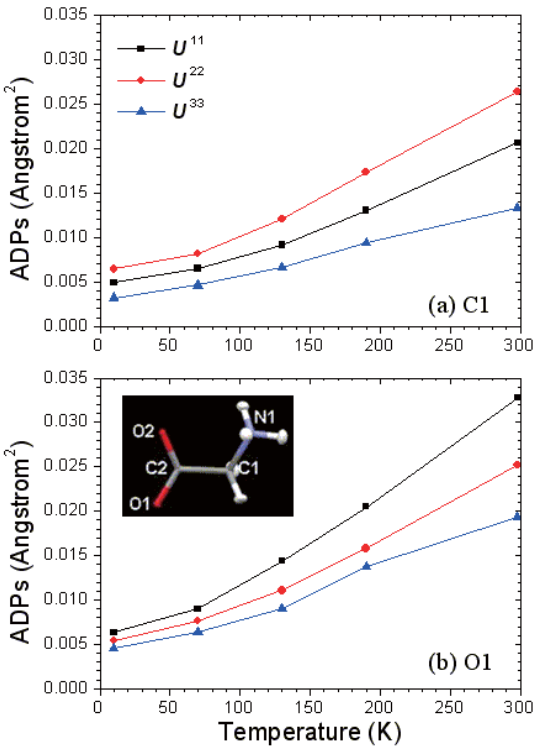

Figure 1. ADPs as a function of temperature of (a) C1 and (b) O1 of γ-glycine. Standard deviations are 2×10^{-4} Å^2.

Results and Discussion

Data are merohedrally twinned because all $F_o^2 >> F_c^2$ and the Δρ values are unusually high and hence the twin refinement is applied using SHELXL-97. The final *R*-factors = 3–5%. The variable-temperature ADPs of γ-glycine shows normal behaviour although the ADP curves are not completely smooth (Figs. 1 and 2). However, the H-atom ADPs are not accurately determined. The preliminary results of normal mode analysis show that the simple model of motion (rigid body + anharmonic effect accounted for by the Grüneisen constant + internal vibration effect by three epsilons) gives external vibration frequencies (64.7, 76.5, 80.5 and 118 cm^{-1}) in fair agreement with the experimental values (90, 105, 138, 152 and 173 cm^{-1}) [2].

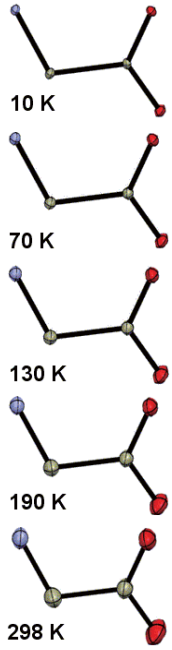

Figure 2. Temperature evolution of ADPs of γ-glycine shown with ORTEP plots (50% probability level). H-atoms are omitted for clarity.

References

[1] H.-B. Bürgi et al., Acta Cryst. A56, 425 (2000).
[2] K. Balasubramanian et al., Bull. Chem. Soc. Jpn. 35, 1303 (1962).

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