Poster Presentation

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Temperature-dependence of the structure of 2-(2'-hydroxyphenyl)benzimidazole studied by neutrons

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2-(2'-hydroxyphenyl)benzimidazole (1) has an intramolecular O-H…N hydrogen bond and shows excited-state intramolecular proton transfer, from the enol form to the keto form, by UV and visible light irradiation. So, 1 and its derivatives have been studied as a candidate of new photo-functional material such as a fluorescent probe and a laser-device. In 2012, Konoshima and co-workers showed that fluorescence excitation spectra of the α-form crystal of 1 showed a strong temperature dependence and suggested that the enol and keto form are in near thermal equilibrium and potential barrier between the enol and keto form should be very low [1].

In this research, we carried out single crystal neutron diffraction measurements of an α-form 1 crystal at room temperature and 4 K to observe the temperature dependent enol-keto equilibrium by diffraction technique. A 4.0 x 2.0 x 0.2 mm triangle shape crystal, prepared by slow evaporation from ethanol-water mixed solvent, was fixed on a aluminum rod, mounted on a closed-cycle pulse-tube cryostat with a 2-axes goniometer and set on SENJU, a time-of-flight Laue type single crystal neutron diffractometer at J-PARC [2]. Diffraction images were measured with 14 orientations at 4K and 15 orientations at room temperature, respectively. Neutron exposure time for one orientation was 3 hours. Finally, intensities of 17486 reflections with 0.4 Å d-minimum at 4 K and 7803 reflections with 0.6 Å d-minimum at room temperature were collected.

Structure refinements were carried out by using JANA2006 and SHELXL-2014. In both temperatures, positional and anisotropic displacement parameters of all hydrogen and non-hydrogen atoms were refined without structural restraint. Results of the refinements showed that the keto form of 1 was not observed even at room temperature. On the other hand, O-H distance of the intramolecular O-H…N hydrogen bond were slightly elongated. This temperature dependent elongation of the O-H bond can be an origin of the temperature dependence of fluorescence excitation spectra of 1.

[1] Konoshima, H. et al. (2012) Phys. Chem. Chem. Phys., 14, 16448-16457.
[2] Ohhara, T. et al. (2016) J. Appl. Cryst., 49, 120-127.

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