

Stereospecific Formation of Chiral Cytosine Crystal by Dehydration from Achiral Cytosine·monohydrate Crystal

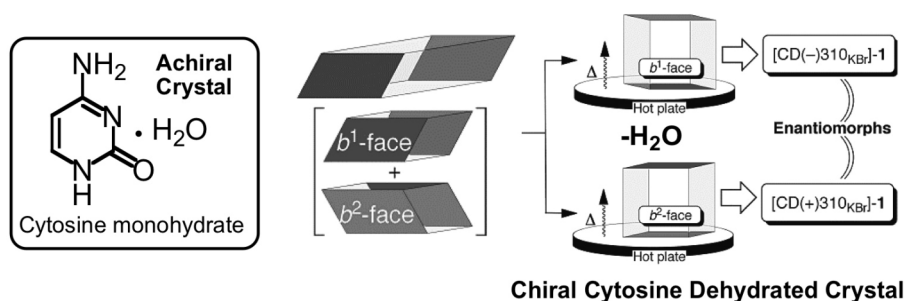
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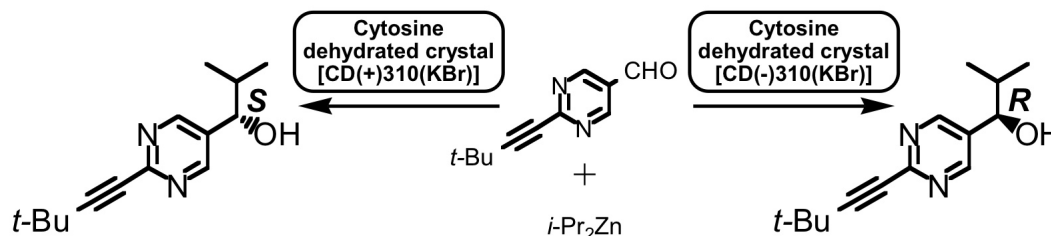
Cytosine is a nucleic acid base and is known as a prebiotic molecule. Crystal of cytosine obtained from MeOH belongs to chiral space group $P2_12_12_1$. Previously, we have reported the asymmetric autocatalysis using this chiral crystal [1].

However, cytosine recrystallized from water forms achiral crystal, which belongs to achiral space group $P2_1/c$.

We found the correlation between the shape of the crystal face and the chirality of resulting dehydrated crystal of cytosine. In the single crystal of cytosine monohydrate, there are two enantiomeric faces, which form parallelogram shapes (b^1 - and b^2 -faces). The each crystal was heated from b^1 - and b^2 -faces, respectively. The crystal heated from b^1 -face was found to induce the negative cotton effect in the solid-state CD. On the other hand, the crystal that heated from b^2 -face exhibited negative cotton effect.



Using these crystals, we examined asymmetric autocatalysis. Cytosine crystal possessing positive cotton effect induces the formation of (*S*)-pyrimidyl alkanol with high ee. On the contrary, cytosine crystal possessing negative cotton effect induces the formation of (*R*)-pyrimidyl alkanol with high ee [2].



[1] Kawasaki, T.; Suzuki, K.; Hakoda, Y.; Soai, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 496–499.

[2] Kawasaki, T.; Hakoda, Y.; Mineki, H.; Suzuki, K.; Soai, K. *J. Am. Chem. Soc.* **2010**, *132*, 2874–2875.