

# ***In-situ* single-crystal X-ray diffraction analysis of photochromic dibenzobarrelene derivative.**

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11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene, (DBB-9,10-dimethyl), **1** shows the reversible color change from pale-yellow to pink in the solid state by UV/Vis irradiation.<sup>[1]</sup> However, the structure of the colored form is still unknown. On the other hand, the tri- $\pi$ -methane rearrangement of **1** was observed in oxygen-free solution to give a mixture of dibenzocyclooctatetraene and the dibenzopentalene derivative.<sup>[2]</sup> Our previous study have shown that the structure of a bis-benzylic biradical, assumed as an intermediate of the tri- $\pi$ -methane rearrangement, was directly observed in the crystalline state photoreaction of another dibenzobarrelene derivative (DBB-9-acetyl-10-methyl). In this study, we tried to observe the structure of the pink colored form of **1**, by using *in-situ* single-crystal X-ray diffraction analysis, and make clear the mechanism of its photochromism.

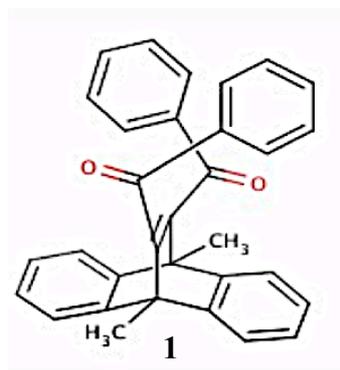


Fig1. 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene, **1** (DBB-9,10-dimethyl)

The single crystals of **1** were irradiated by UV light, and a reversible color change was observed in them after UV irradiation. Another single crystal was analyzed by X-rays before and after UV irradiation at 90K. In the crystal structure, we observed not intermediates or products by the tri- $\pi$ -methane rearrangement but disordered electron density around methyl group at 9,10-position. The disorder disappeared with the pink color when the crystal was maintained at room temperature for several hours. This means that some kind of motion or reaction of the methyl group will be involved in its photochromism. Diffuse reflectance spectroscopies of **1** after the UV irradiations, which were carried out in the powdered state and in the single crystalline state, shows different UV/vis spectra depending on the irradiation state. The former is brown, the latter is pink. This result means that the photoproducts have different structures and both of them turned back to **1** in solution immediately with disappearance of the colors.

## References

- [1] M. C. Sajimon, D. Ramaiah, C. H. Suresh, W. Adam, F. D. Lewis, and M. V. George *J. Am. Chem. Soc.* **2007**, *129*, 9439-9445.
- [2] D. Ramaiah, M. C. Sajimon, J. Joseph and M. V. George *Chem. Soc. Rev.*, **2005**, *34*, 48-57.