**Photooxygenation of Rubrene (5,6,11,12-tetraphenylnaphthacene)** <u>Kiyoaki Shinashi</u><sup>a</sup>, Isao Oonishi<sup>b</sup>, <sup>a</sup>Department of Law, Faculty of Law, Chuogakuin University, Kujike 451, Abiko, Chiba, 270-1196, Japan. <sup>b</sup>Department of Biomolecular Science, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba, 274-8510, Japan. E-mail: kshinajp@yahoo.co.jp

It is well-known that when polycyclic aromatic hydrocarbons (PAHs) in solution are irradiated by light with their absorption wavelength, they react with molecular oxygen dissolved in solvent to form *endo*-peroxides. This photooxygenation occurs due to 1,4-cycloaddition of singlet oxygen to a PAH molecule in the ground state. When rubrene in benzene solution was irradiated by light, the color of solution gradually changed from reddish orange to colorless. The rubrene peroxide was crystallized from 1,4-dioxane solution and X-ray structure analysis was carrid out. A molecular oxygen bonds to 5 and 12 carbon pair of the naphthacene skeleton. Although the naphthacene moiety of rubrene has completely planar structure due to the crystallographic symmetry, that of the peroxide is largely bent at the positions where molecular oxygen binds.

The structure optimization of PAHs including rubrene and their peroxide was performed by applying semi-empirical molecular orbital calculation methods. The optimized structure was coincident with the experimentally determined structure. The photooxygenation reactivity of PAHs including rubrene was well explained by the differences in heats of formation between PAHs and their peroxide. **Keywords: rubrene, photooxygenation, PAH**