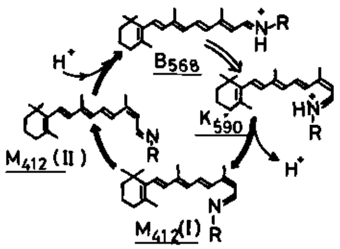
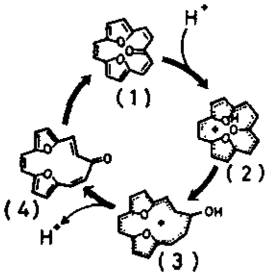
# CONSTRUCTION OF AN ANNULENE CYCLE DRIVEN BY PROTONATION-DEPROTONATION SEQUENCE: A PROPERTY OF AN ANNULENE-CYCLE AS A MODEL OF PROTON PUMP CYCLE OF BACTERIORHODOPSIN

Haru Ogawa*, Tadashi Inoue, Minoru Kuribayashi, Taiji Imoto
Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan
Izumi Miyamoto, Yōichi Taniguchi
Kurume National Technical College, Komorino, Kurume, 830, Japan

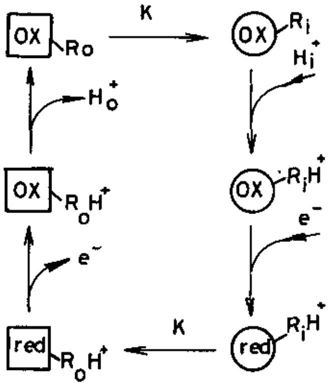
Firstly, novel synthesis of a thermally unstable isomer of an oxygen-bridged annulene (4) was described, whose preparation was difficult so far because of its rapid isomerization to the cis isomer (1). The $^1$H-NMR spectrum of (4) showed a wide spread of the positions of the inner proton signals ranging from the original chemical shift ($\delta$ = 4.60 ppm, in CDCl$_3$) to those associated with the protic solvent such as CD$_3$OD/D$_2$O , up to $\delta$ = 0.57 ppm), indicating that the ground state of (4) can be stabilized with water by increasing the charge separation structure of the $14\pi$ [15]annulenylium oxide structure, a Hückel type resonance-stabilized cation. Secondly, a convincing experimental evidence of the water-induced stabilization of the trans [15]annulenenone (4) could be also provided by kinetic rate measurements of the back-isomerization of (4)→(1). Thirdly, it was found that our oxygen-bridged [15]annulenone (1) can form a cycle, which is reminiscent of a real biological cycle of bacteriorhodopsin of Halobacterium halobium [reviewed by D. Oestelhelt, Angew. Chem., 88, 16 (1976)] and reaction cycle of cytochrome b [see, G.V. Jagow and W.D. Engel, FEBS Letters, 111, 1 (1980)], both of which were contrasted with the reaction scheme of our [15]annulenone cycle.



PROTON PUMP CYCLE
OF
Halobacterium halobium



[15] ANNULENONE CYCLE



Cytochrome b Proton translocator cycle