# 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

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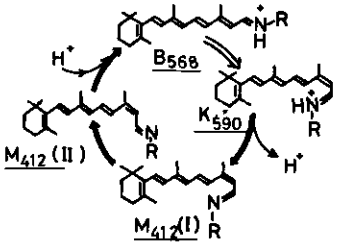
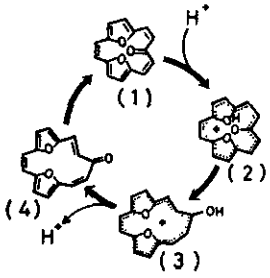
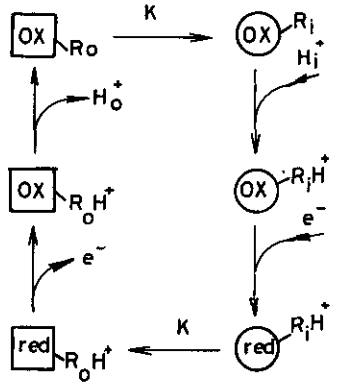
Firstly, novel synthesis of a thermally unstable isomer of an oxygen-bridged annulene (4) was described, whose preparation was difficult so far because of its rapid isomerization to the cis isomer (1). The $^1$H-NMR spectrum of (4) showed a wide spread of the positions of the inner proton signals ranging from the original chemical shift ($\delta$ = 4.60 ppm, in $CDCl_3$) to those associated with the protic solvent such as $CD_3OD/D_2O$ , 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 14π [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