## CHEMICAL SIMILARITIES OF DI-OXA[15]ANNULENONE CYCLE WITH BACTERIORHODOPSIN CYCLE

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Chemical similarities between the titled cycles were investigated in the following three points.

- 1. Equilibria of four chemical species in the [15]annulenone cycle (Fig. 1a) were studied as function of variable proton concentrations. It was shown that (i) the entire equilibria of  $TH^+$ ,  $CH^+$ , T and C can be described by  $K_{a_{1}}$ ,  $K_{a_{C}}$ , and  $\alpha$ ; and that (ii) unequal proton binding occurs as a consequence of photoisomerization  $TH^+ \Rightarrow CH^+$ , only when following inequalities are satisfied;  $pK_{a_{C}} > pK_{a_{1}}$  and  $\alpha < 1$ . <sup>1</sup>H-NMR experiments conducted in  $CD_{2}Cl_{2}$  FSO<sub>3</sub>H suggested that these requirements hold for  $TH^+$  and  $CH^+$  species.
- 2. <u>Mechanism of photoisomerization  $TH^+ \rightarrow CH^+$ </u> We obtained a strong experimental support which shows that the photoisomerization involves "Förster Mechanism". The  $pK_a^*$  of  $TH^+$  in excited state was obtained as <u>ca</u>. -5.5, whereas the  $pK_a$  of the same species at -60°C was + 5.2 in  $CD_2C1_2$ .
- 3. Thermal relaxation rates of the photoproducts The rates and temperature effects of thermal back-isomerization of photoproducts  $[CH^+ TH^+$  in the annulenone cycle, and  $M_{412} B_{568}$  in bacteriorhodopsin cycle (Fig. 1b)) were compared. These comparisons indicated that (i) rates are almost comparable in both cycles, and that (ii)methyl group introduction causes similar rate accelerations when compared with those of the corresponding desmethyl derivatives [ R = H in stead of Me in Fig. 1b and 1a].

Above results obtained led us to convince that the [15]annulenone cycle is mimic to bacteriorhodopsin cycle in its chemical transformations, in equilibria, and also in photoisomerizaton mechanism.

