THE PHOTOCHEMISTRY OF ANNULENYLION-ANNULENONE CYCLE AS A MODEL OF BACTERIORHODOPSIN

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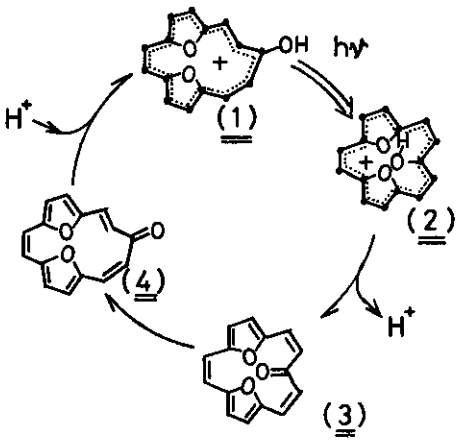
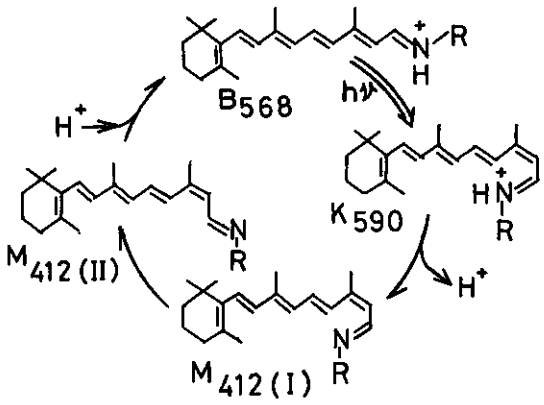
Photo-driven cycle of an oxygen bridged [15]annulenylion-[15]annulenone was discussed in connection with the model of the real biological cycle of bacteriorhodopsin. The annulenylion-annulenone cycle is made up of four sequential steps, in principle, viz., (i)photoisomerization of trans[15]annulenyl ion (1) into cis [15]annulenyl ion (2) by irradiation of visible light [light source: 750W projector lump through a Y-46 filter at -50°C, 5 min. in CH_2Cl_2 solution] with a high quantum yield: (ii) deprotonation of the cis[15]annulenyl ion (2) as a consequence of the lowered pk_a value of (2) on the isomerization: (iii) thermal equilibration of the cis[15]annulenone (3) with trans[15]-annulenone (4), whose stabilization was induced by dipolar solvents such as MeOH, H_2O and by H^+: (iv) predoninant protonation of the trans annulenone due to the higher H^+-affinity of (4).

The low temperature electronic spectroscopy indicated that the cis annulenyl ion (2) is capable of exsistence only below -50°. The observed Δpk_a between two isomeric [15]annulenyl ions was ca. 1.5 pk_a unit in CH_2Cl_2 (FSO_3H used as a proton source at -50°C).



The [15]annulenylion-[15]annulenone Cycle



The bacteriorhodopsin cyle