

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

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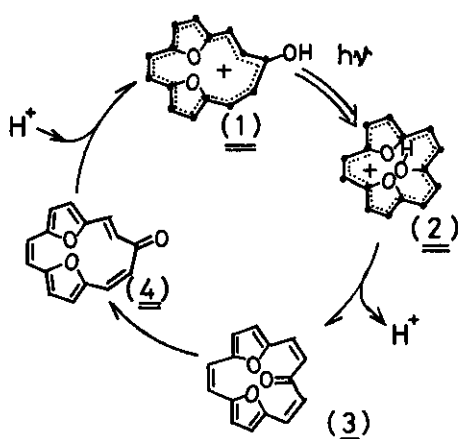
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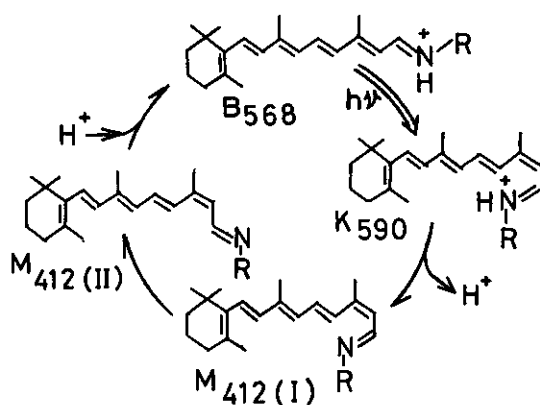
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Photo-driven cycle of an oxygen bridged [15]annulenylion-[15]annulenone was discussed in connection with the model of the real biological cycle of bacteriorhodopsin. The annulenylion-annulenone cycle is made up of four sequential steps, in principle, viz., (i) photoisomerization of trans[15]annulenyl ion (1) into cis [15]annulenyl ion (2) by irradiation of visible light [light source: 750W projector lamp 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 $\text{p}K_{\text{a}}$ 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) predominant 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 existence only below -50° . The observed $\Delta\text{p}K_{\text{a}}$ between two isomeric [15]annulenyl ions was ca. 1.5 $\text{p}K_{\text{a}}$ unit in CH_2Cl_2 (FSO_3H used as a proton source at -50°C).



The [15]annulenylion-[15]annulenone Cycle



The bacteriorhodopsin cycle