

CHEMICAL MODIFICATION OF BACTERIORHODOPSIN: REMARKABLE RED SHIFTS
OF PYRROLE POLYENAL PROTONATED SCHIFF BASES AND RECONSTRUCTION OF
A BACTERIORHODOPSIN ANALOG BY THE USE OF A PYRROLE POLYENAL

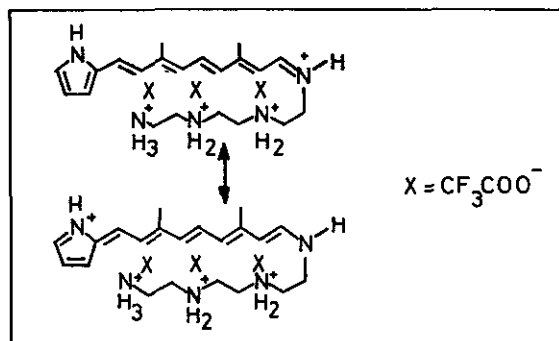
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3,7-Dimethyl-9-(pyrrol-2-yl)nona-2,4,6,8-tetraenal 1 was prepared as a retinal analog. 1 was reacted with $\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_n-\text{CH}_2-\text{CH}_2-\text{NH}_2 2 ($n = 0, 1, 2$ and 3) to form the corresponding Schiff bases. When protonated with CF_3COOH , large red shifts of the absorption maxima were observed on going $n = 0$ to $n = 2$. As the possible explanation of these shifts, effect of the presence of counter-anion CF_3COO^- , which are envisioned to be fixed by the polyamine chain as to be existed along the conjugated chain of the polyenal, was discussed.$

Absorption Maxima of Protonated Salts of Aldehyde Schiff Base in EtOH/ CF_3COOH		
Amine	Aldehyde	λ_{max} (nm)
$n=0$	<u>1</u>	542
$n=1$	<u>2</u>	561
$n=2$	<u>3</u>	567
$n=3$	<u>4</u>	562
$t\text{-BuNH}_2$	<u>5</u>	530
$n\text{-BuNH}_2$	all trans-retinal	445



When 1 was incorporated into bacteriorhodopsin, it exhibited a purple color showing two absorption maxima at 537 and 550 nm ($\text{pH} = 7.0$). On acidification it turned blue showing an absorption maximum at 610 nm ($\text{pH} = 1.5$). The reconstructed bR analog behaved similarly to the native bacteriorhodopsin with respects to the photo-bleaching (M_{412} formation) and its thermal back-isomerization to the initial state ($M_{412} \rightarrow B_{550}$). The reconstruction process was studied by Lineweaver-Burk plots. The thermal back-isomerization process was studied by using low-temperature UV-Vis spectroscopy. The rates and thermodynamic parameters collected from the binding process and from the back-isomerizations were compared with those obtained from the native and bR analog formed from 3,7-dimethyl-9-(2-furyl)-nona-2,4,6,8-tetraenal. Finally, effects of puttig nitrogen atoms on termini of the conjugated polyene chain were discussed in the light of the pyrrole polyenal incorporated bacteriorhodopsin.