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ON THE ABSORPTION MAXIMA OF PROTONATED AROMATIC RETINAL SCHIFF BASE. AN INTERACTION WITH NON-CONJUGATED POSITIVE CHARGE

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The absorption maxima of iminium salts of aromatic retinals are less affected by non-conjugated charge in the vicinity of the ring than iminium salts of retinals.

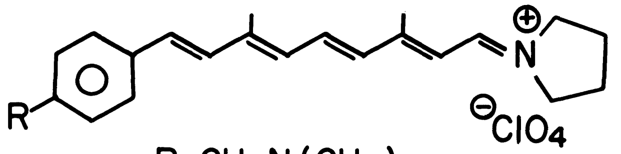
The purple membrane is a novel light energy transducing membrane which constitutes part of a plasma of halobacterium halobium. Its purple color is due to a pigment which has its absorption maxima at 570 nm (in its light-adapted form), and has all-trans retinal as its chromophoric group linked to a lysine through a protonated Schiff base.[1)]

The all-trans retinal protonated Schiff base formed from n-butylamine has its absorption maxima at 440 nm in methanol. The red shift of 5180 cm^{-1} observed in bacteriorhodopsin (compared with methanol solution), which is due to the effect of the protein environment, was called "opsin shift.[2)]

Recently, Nakanishi and Honig[2)] proposed an external point charge model which places, in addition to a counter-anion near the Schiff base iminium nitrogen, a second negative charge in the vicinity of the ionone ring, which causes the observed red shift.

It was predicted[3)] that pigments derived from tailored retinals with altered ring structure like aromatic retinals, would exhibit smaller red shifts and would provide a tool to check the validity of the external point charge model. Indeed, a smaller opsin shift was observed for artificial aromatic pigment as well as with naphthyl analog.[3,4)] The decreased opsin shifts are interpreted in terms of perturbations at the ring binding site which affect the interactions with the second charge. These decreased opsin shifts may originate from steric effects or electronic perturbations. Steric effects may induce an increased separation between the polyene system and the ring charge, resulting in a blue shift in the spectrum. Electronic perturbations may arise, due to the aromaticity of the ring which shields the polyene from the negative charge and decreases its influence on the spectrum.

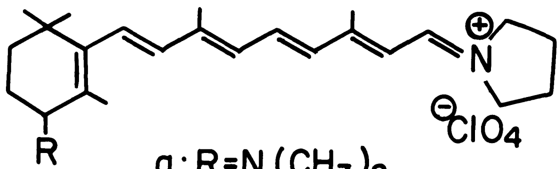
In order to compare the influence of non-conjugated charges on the absorption maxima of protonated Schiff base of all-trans aromatic retinal and all-trans retinal, we synthesized compound 1 and compared it to compound 2.5)



1

a; R=$CH_2N(CH_3)_2$

b; R=$CH_2\overset{\oplus}{N}H(CH_3)_2$



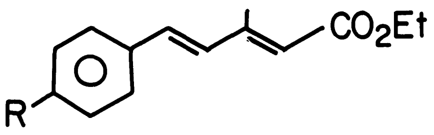
2

a; R=$N(CH_3)_2$

b; R=$H\overset{\oplus}{N}(CH_3)_2$

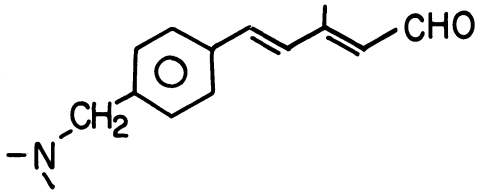
Terephthalaldehyde was condensed with one equivalent of sodium salt of triethyl 3-methyl-4-phosphonocrotonate at 25 °C to give, after separation, ester-aldehyde 3.

Reductive-amination of 3 using methylamine and sodium borohydride, followed by methylation with paraformaldehyde afforded amino ester 4. The ester group was converted into an aldehyde by reduction with diisobutylaluminium hydride, followed by oxidation with MnO_2, to give aminoaldehyde 5. An additional condensation of 5 with sodium salt of triethyl 3-methyl-4-phosphono-crotonate, followed by similar reduction and oxidation afforded aldehyde 6.6) Compound 6 was condensed with pyrrolidine perchlorate to give iminium salt 1.



3 R=CHO

4 R=$H_2C-N(CH_3)_2$



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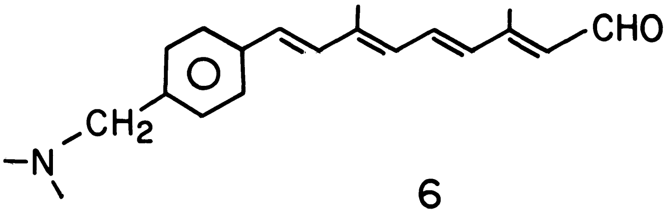
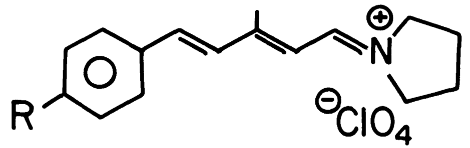


6

Compound 1a absorbs at 462 nm in EtOH. Introducing a non-conjugated positive charge by protonation of the amino group (compound 1b) caused a blue shift to 451 nm. This blue shift (530 cm^{-1}) was somewhat increased (620 cm^{-1}) by taking the absorption maxima in $CHCl_3$ (Table 1).

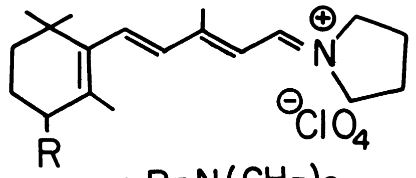
Compound 2 exhibited a blue shift of 1110 cm^{-1} ($CHCl_3$) by protonation of the amino group, which is larger than the shift observed in the aromatic retinal case. For further insight into the interaction of non-conjugated charge with aromatic retinal iminium salts, we investigated compounds 7 and 8.



7

a; $R=CH_2N(CH_3)_2$

b; $R=CH_2\overset{\oplus}{N}H(CH_3)_2$



8

a; $R=N(CH_3)_2$

b; $R=H\overset{\oplus}{N}(CH_3)_2$

Compound 7 was prepared by condensation of aldehyde 5 with pyrrolidine perchlorate. Protonation of the amino group caused a blue shift of 1200 cm^{-1} in $CHCl_3$ (Table 1), while in compound 8 we observed a blue shift of 3540 cm^{-1} in $CHCl_3$.

Table 1. λ_{max}/nm of Perchlorate Iminium Salts

Chromophore	λ_{max}/nm[a]	Solvent	$\Delta\nu/cm^{-1}$[b]
1	462(451)	EtOH	530
1	481(467)	$CHCl_3$	620
2	443(430)	EtOH	680
2	467(444)	$CHCl_3$	1110
7	382(367)	EtOH	1070
7	397(379)	$CHCl_3$	1200
8	378(337)	EtOH	3220
8	393(345)	$CHCl_3$	3540

[a] Absorption maxima at pH 8 and pH 2 (in parenthesis).

[b] Between pH 8 and pH 2.

The results demonstrate that a non-conjugated positive charge in the vicinity of the aromatic ring can induce a blue shift in the absorption spectra of aromatic retinal iminium salts. However, the effect is considerably smaller than the one found in an all-trans retinal analog, in spite of the fact that the positive charge is located at a similar distance from the chromophore system, in both molecules.

The blue shift is probably caused by destabilization of the excited state (relative to the ground state) which is due to decreased charge distribution along the polyene as a result of an electrostatic interaction with a non-conjugated positive charge.$^{7)}$ The considerably smaller effect observed in aromatic retinal is attributed to the aromatic ring which shields the polyene from the external charge and decreases its influence. The effect is more pronounced in a short polyene in which the charge is distributed between a smaller number of carbons, and the effect of the external charge is stronger.

The present work demonstrates that the absorption maxima of protonated retinal Schiff bases are less affected by non-conjugated charge in the vicinity of the ring, than in the case of protonated retinal Schiff base. This phenomenon probably contributes to the decreased opsin shift observed in artificial pigments derived from aromatic retinal analogs and bacterioopsin

References

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6) ^{1}H n.m.r. ($CDCl_3$) 2.10 (3H, s), 2.25 (6H, s), 2.34 (3H, s), 3.44 (2H, s), 6.00 (1H, d, J=8.1 Hz), 6.37-6.45 (2H, m), 6.74 (1H, d, J=16.2 Hz), 6.86 (1H, d, J=16.2 Hz), 7.22 (1H, dd, J=16.2, 11.3 Hz), 7.29 (2H, d, J=8 Hz), 7.39 (2H, d, J=8 Hz), 10.11 (1H, d, J=8 Hz).

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