# Environmental Effects on Salts of *N*-Retinylidene-n-butylamine

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*Summary* The absorption maximum of the chromophoric cation of *N*-retinylideneamine salts is, in certain solvents, affected by the nature of the anion, and the degree of this effect is proportional to the electrostatic interaction energy.

WE report that the anion of *N*-retinylidene-n-butylammonium salts has a large effect on the absorption maximum of the organic cation. We believe that these findings hold important implications for visual pigments.

The 11-*cis*-isomer of retinal is known to be the chromophoric molecule in visual pigments. All evidence is in agreement with formation of a Schiff-base linkage between the aldehyde of retinal and a primary amino-group.[1] This was first suggested from consideration of spectral properties of Schiff bases of retinal prepared from simple alkyl amines.[2] The spectroscopic behaviour of Schiff bases and their protonated forms is similar to that of visual pigments under certain experimental conditions. The $\lambda_{max}$ values of Schiff bases exhibit little variation in different solvents; however, their protonated forms show variation over a wide range.[3]

We have found that reproducible $\lambda_{max}$ values are difficult to obtain unless monoprotonated Schiff base salts are prepared. Retinal (30—50 mg) was added to a solution of 0·5 ml of n-butylamine in 5 ml of MeCN and allowed to stand over $K_2CO_3$ in the dark for two or three hr. The filtrate was roto-evaporated at room temperature, and the residue was extracted with EtOH and similarly evaporated. Another EtOH extraction and evaporation gave a residue that was dissolved in $Et_2O$, and at this point, either gaseous acid or an anhydrous acid solution was added. The precipitated salt was filtered, washed with petroleum ether, dried, and stored under $N_2$ in a deep-freeze in the dark.

The $\lambda_{max}$ values for eight salts measured in three solvents are reported in the Table.

*Absorption maxima of monoprotonated salts of* N-*retinylidene-n-butylamine in* $CCl_4$, $C_6H_6$, *and* $CHCl_3$

| Anion | In $CCl_4$ | $\lambda_{max}$ nm In $C_6H_6$ | In $CHCl_3$ |
|---|---|---|---|
| $Cl^-$ | 441* | 437* | 459* |
| $CCl_3{\cdot}CO_2^-$ | 442 | 439 | 457 |
| $NO_3^-$ | 445 | — | 464 |
| $F^-$ | 447 | — | 469 |
| $Br^-$ | 451* | 447* | 468* |
| $ClO_4^-$ | 457 | — | 480 |
| $I^-$ | 460* | 457* | 478* |
| Picrate | 464* | 458* | 467* |

* Average of several measurements.

In the solvents cited above, *N*-retinylidene-n-butylammonium salts would be expected to remain in more or less tight ion pairs. Since little or no covalent interaction is anticipated between an ammonium cation and its anion,[4] we believe that the interaction can be measured largely in terms of electrostatic attraction between the ions. The data for the absorption maxima of these salts in $CHCl_3$ are included to show the effect of greater anion solvation by this solvent. The $Cl^-$, $Br^-$, and $I^-$ salts show the same order in all three solvents, and furthermore the $\lambda_{max}$ changes by a constant amount in each series.

The Figure indicates a simple, direct relationship between the electrostatic interaction energy of the ions, commonly expressed by the equation $E = Z_1Z_2e^2/(r^- + r^+)$, and the energy of the light absorbed by the chromophoric species at its maximum absorption wavelength. Although several sets of values of ionic radii of $Cl^-$, $Br^-$, and $I^-$ are available, those reported by Wasastjerna[5] give the best linear plot. Two other sets were tried and found to give a satisfactory but a less precise correlation.[6,7] An estimate of the effective ionic radius of the picrate anion was arrived at by multiplying the ratio of the ionic radii of picrate to iodide, as determined from conductance measurements,[7] by the Wasastjerna radius for iodide. The $N^{3-}$ radius of Pauling (1·71 Å) was used for the cationic radius, although it is recognized that this would only be a lower limit for the effective radius of the cation involved in the measurements reported here. The data are plotted for solvents $CCl_4$ and benzene; although the same relationship holds in $CHCl_3$, the data are not plotted because of the pronounced anion solvation effect of this solvent. This direct energy relationship illustrated by the Figure means the weaker the electrostatic interaction between the cation and anion the longer will be the maximum absorption wavelength of the chromophoric cation.

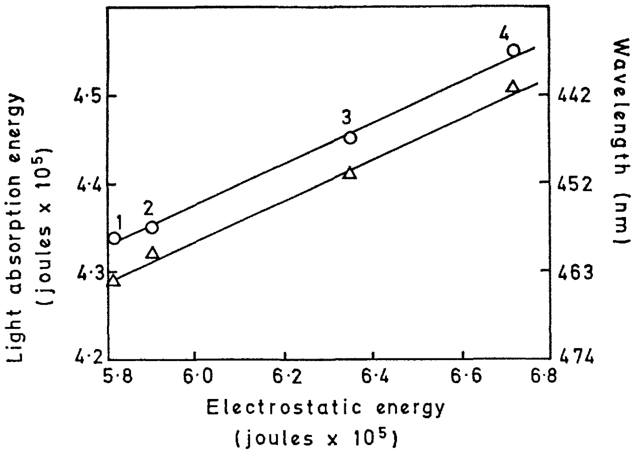

FIGURE. *Effect of ionic electrostatic interaction energy on the electronic absorption energy of the cation.* ○ *in* $C_6H_6$, △ *in* $CCl_4$: 1. *Picrate.* 2. *Iodide.* 3. *Bromide.* 4. *Chloride.*

One of us has shown that, according to the free-electron model, the protonated Schiff base of retinal should absorb at 565 nm.[8] This value of course accommodates the longest known wavelength of an $A_1$ pigment. It is interesting that a $\lambda_{max}$ value of 630 nm is predicted by extrapolation of the line shown in the Figure for measurements in benzene to zero electrostatic energy.

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