nm region. On the other hand, it is possible that the ganglioside has the oligosaccharide in quite a different conformation from that in which the free oligosaccharide is found. The ganglioside could form micelles in aqueous solution and this could lead to a dramatic conformational change which we see in the CD spectrum. The differences between our data and those of Stone and Kolodny (1971) on bovine G_{M3} indicate that the ceramide has a substantial influence on the conformation of the oligosaccharide (2→3)NAcN-Lac.

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Effect of Selected Anions and Solvents on the Electronic Absorption, Nuclear Magnetic Resonance, and Infrared Spectra of the *N*-Retinylidene-*n*-butylammonium Cation[†]

Paul E. Blatz[*] and Jonathan H. Mohler

ABSTRACT: The specific counteranion and the solvent have been shown to regulate the electronic excitation energy of the *N*-retinylidene-*n*-butylammonium cation. Halogenated hydrocarbon solvents which can hydrogen bond with the anion shift the λ_{max} to longer wavelengths, whereas the solvent dipole, acting as a bulk effect, shifts the λ_{max} to shorter wavelength. Here solvents which can donate two hydrogens for hydrogen bonding, such as *cis*- and *trans*-1,2-dichloroethylene and *cis*- and *trans*-1,2-dichlorocyclohexane, are used as solvents for the Cl^-, Br^-, and I^- salts. As expected the cis solvents allow longer wavelengths than do the trans solvents. Results of nuclear magnetic resonance spectroscopy are shown to be in agreement with electronic absorption spectroscopy. The C-11 proton and the C-13 and C-9 methyl protons show a considerable downfield shift in the salts with respect to the Schiff base. Furthermore the same protons show a continuing downfield shift as the anions are exchanged from Cl^-, Br^- to I^-. This is in agreement with the interpretation of greater positive charge delocalization as the anions are changed in the above manner. The infrared absorptions of the C=N group in the Schiff base and the protonated form are shown to be almost similar. This is rationalized by showing that the force constant can remain constant as the highly related factors bond order, bond distance, and the effective electronegativity are changed in a self-compensating manner.

A general introduction to the problems concerning the bathochromic shift in *N*-retinylidene-*n*-butylammonium salts, i.e., model chromophores of visual pigments, is given in Blatz et al. (1972). It was shown that in certain solvents the λ_{max} of the salt is a function of the counteranion. The excitation energy of the salt increased linearly with the reciprocal of the square of the distance between the centers of cationic and anionic charges. The limiting value of the excitation energy as $1/d^2$ approaches zero is approximately the excitation energy of the retinylic cation and is equivalent to a λ_{max} of 589 nm. Certain solvents such as methanol, etha-

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Table I: Comparison of the Deviation of Observed Absorption Maxima from those Predicted by Dipole Moment in Group 3 Solvents.

			λ_{max} in nm observed and (predicted)		
Solvent	ϵ20°	μ (D)	NRBA$^+$Cl$^-$	NRBA$^+$Br$^-$	NRBA$^+$I$^-$
CH_2ClCH_2Cl	10–65	1.4–2.9^a	449 (428)^c	458 (435)^c	473 (450)^c
$CHCl_2CHCl_2$		1.82^a	460 (448)	469 (456)	488 (467)
cis-CHCl:CHCl	9–20	1.80^a	458 (448)	467 (456)	478 (467)
trans-CHCl:CHCl	2–10	0.00^a	440 (483)	448 (491)	456 (496)
cis-$CHClCHCl(CH_2)_3CH$	8.67	3.12^b	464 (423)	470 (431)	474 (446)
trans-$CHClCHCl(CH_2)_3CH_2$	6.85	2.40^b	440 (437)	448 (445)	459 (458)

^{a} McClellan (1963). ^{b} Tulinskie et al. (1953). ^{c} Based on μ of pure solvent at 25°.

nol, and tetrahydrofuran do not allow the expression of the anion effect; these are called leveling solvents (Erickson and Blatz, 1968). Three classes of nonleveling halogenated hydrocarbon solvents were recognized: (1) those with no hydrogen bound to a halogen-bearing carbon, (2) those with hydrogen bound to a single halogen-bearing carbon atom, and (3) those with hydrogen bound to two adjacent halogen-bearing carbon atoms (vicinal solvents) (Blatz and Mohler, 1972). Solvents in class 2 cause *N*-retinylidene-*n*-butylammonium salts (NRBA$^+$ salts)[1] to absorb at a longer wavelength than do solvents of class 1. This is attributed to a hydrogen bonding effect on the anion. Solvents of class 2 cause the λ_{max} of the salt to show a linear decreasing relationship with the solvent dipole moment. The hydrogen bonding effect is a specific or molecular effect, whereas the dipole effect is a bulk property. In this paper the solvent studies are extended to include those of class 3. Additional studies in leveling solvents are also reported.

Blatz et al. (1972) visualized that as the anion size increases and the center of negative charge is withdrawn from the nitrogen, the positive charge is less localized on nitrogen and is free to delocalize over the entire polyene chain. In theory this should give rise to a change in proton environment that is detectable by nuclear magnetic resonance (NMR) spectroscopy. Relevant studies are reported herein.

In addition to the electronic absorption and NMR spectra, the infrared (IR) spectra of the salts are examined and reported on.

Experimental Procedures

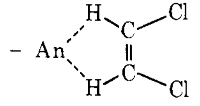
all-trans-N-Retinylidene-n-butylamine's preparation and the preparation of pure salts have been reported elsewhere (Blatz et al., 1972).

Solvent Purification. Great care must be taken to have fresh, pure, dry solvents for the spectroscopic examination. Solvents were usually distilled through a 40-cm jacketed column packed with 2–3-mm glass beads and protected from atmospheric contamination during distillation by bubbling nitrogen continuously. The purified solvents, especially the halogenated hydrocarbons, were stored in brown bottles under nitrogen and over molecular sieve and kept in the refrigerator. (1) 1,2-Dichloroethane. Purification reported previously (Blatz et al., 1971). (2) 1,1,2,2-Tetrachloroethane. Purified by washing twice with concentrated H_2SO_4, then water, and then twice with K_2CO_3 solution. The washed material was dried over anhydrous K_2CO_3 and distilled over molecular sieve 4A. (3) *cis*- and *trans*-Dichloroethylene. Both solvents distilled over molecular sieve. (4) *trans*-1,2-Dichlorocyclohexane. This solvent was vacuum distilled through a 16-cm glass, bead packed column; its boiling point was 70–70.7° at 15 mm. (5) *cis*-1,2-Dichlorocyclohexane. This compound was prepared by the method of Campbell et al. (1966). Gas chromatography showed a small amount of cyclohexene oxide and *trans*-1,2-dichlorocyclohexane to be present. These were removed by passing solvent over a column of neutral alumina (activity III). No impurities could be detected by gas chromatography. Elemental analysis gave: C, 47.5 (47.0); H, 6.63 (6.50); Cl, 46.0 (46.4); theoretical values are in parentheses. (6) Acetone. Purified by distilling over molecular sieve. (7) *tert*-Butyl alcohol. Purified by distilling from CaO. (8) Acetonitrile and Tetrahydrofuran. Reported elsewhere (Blatz et al., 1972).

Instruments. Ultraviolet and visible spectra were recorded on a Beckman DK-2A uv–visible spectrophotometer; infrared spectra were recorded on a Perkin Elmer 621 infrared spectrophotometer and NMR spectra on a Varian HA-100 nuclear magnetic resonance spectrometer.

Results

A. Vicinal Solvents. Vicinal solvents or class 3 solvents, i.e., solvents with hydrogen bound to two adjacent halogen-bearing carbon atoms, present an interesting case. Consider 1,2-dichloroethylene when the halogens are cis (as shown in **1**); there are two hydrogen atoms available for hydrogen



1

bonding to the anion and the dipole moment is high, 1.80 D. In the trans isomer the anion can only be single hydrogen bonded while the dipole moment is 0 OD. It has been shown that solvents which hydrogen bond to the anion cause a bathochromic effect in the cation, whereas solvents with a larger dipole moment give a hypsochromic effect to the λ_{max} of the cation (Blatz and Mohler, 1972). In principle, then, the use of solvents such as 1,2-dichloroethylene should allow for qualitative evaluation of the two effects.

Pure Cl$^-$, Br$^-$, and I$^-$ salts of NRBA$^+$ were dissolved in the solvents listed in Table I in concentrations approximate-

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[1] Abbreviation used is: NRBA$^+$ salts, *N*-retinylidene-*n*-butylammonium salts.

Table II: Absorption Maxima of *all-trans-N*-Retinylidene-*n*-butylammonium Salts in Nonleveling Solvents.

	Absorption Maximum (nm) in		
Salt	Acetone	Acetonitrile	*tert*-Butyl Alcohol
NRBA-HCl	428	443	440
NRBA-HBr	439	447	448
NRBA-HI	445	446	
NRBA-pTSA[a]	442	449	452
NRBA-Pi[b]	439	440	448

[a] *p*-Toluenesulfonic acid. [b] Picric acid.

Table III: Chemical Shift of Protons on or Near the Conjugated Chain of *all-trans-N*-Retinylidene-*n*-butylammonium Salts in $CDCl_3$.

	δ(ppm)				
Compound	C-11-H	C-13-CH_3	G-9-CH_3	C-5-CH_3	λ_{max} (nm) in $CHCl_3$
NRBA	6.85	2.08	1.97	1.70	366[a]
$NRBA^+Cl^-$	7.10	2.31	1.98	1.66	460
$NRBA^+Br^-$	7.32	2.33	2.02	1.70	468
$NRBA^+Br^-$	7.38	2.37	2.03	1.69	478

[a] From Blatz et al. (1972).

ly 1.5×10^{-5} *M* and their spectra were recorded. The λ_{max} values are reported as well as the literature values for the dipole moments and dielectric constants. The λ_{max} given in parentheses is the value for the given salt obtained from the plots of λ_{max} vs. dipole moment as reported previously for class 2 solvents (Blatz and Mohler, 1972). For example, in the case of *cis*-1,2-dichloroethylene as solvent, the λ_{max} value obtained from the $NRBA^+$ chloride salt plot which corresponds to a dipole moment of 1.82 D is a value of 448 nm; the observed value is 458 nm.

It is interesting to compare the λ_{max} values of the salts for the two isomers of 1,2-dichloroethylene since these two isomers have a fixed geometry. The salts absorb at a wavelength that is approximately 20 nm longer in the cis solvent. This is true even though the dipole moment of 1.82 D would be expected to shift λ_{max} to shorter wavelengths. Using dipole moments as the sole criterion, it can be predicted from the λ_{max} vs. D plots that the trans solvent should cause the salt to absorb at a wavelength longer by 35 nm, at 483 nm. However, experimental results clearly show that the cis solvent causes the salts to absorb at wavelengths longer than predicted by dipole moments, and the trans solvent causes the salts to absorb at a wavelength less than the predicted value. It can be concluded that the hydrogen arrangement exerts a more dominant influence than does dipole moment.

When the λ_{max} values of the salts were examined in *cis*- and in *trans*-1,2-dichlorocyclohexane, the results were quite similar to those obtained in 1,2-dichloroethylene. Although the geometry in 1,2-dichloroethane and 1,1,2,2-tetrachloroethane is not fixed, the same relationship between predicted and experimental values is observed. These data support the role of anion-hydrogen bonding for selected solvents. The representation given in **1** is supported. The data also support the role of solvent dipole as a bulk effect.

B. Miscellaneous Solvents. Since methanol, ethanol, and tetrahydrofuran were found to act as leveling solvents and halohydrocarbons were found to be nonleveling, it became clear that other kinds of solvents should be investigated. In Table II we report the λ_{max} values of five salts in three additional solvents: acetone, acetonitrile, and *tert*-butyl alcohol. None of these solvents are leveling, and this is particularly interesting since *tert*-butyl alcohol might have been expected to be leveling. The λ_{max} values found in acetone are of interest in that the chloride salt absorbs at 428 nm. It will be recalled that all salts absorb at 430 nm in tetrahydrofuran. These two solvents have the ability to suppress the λ_{max} below 441 nm, the value in methanol usually taken as "the" λ_{max} value for protonated Schiff bases of retinal. Consideration of these results will be expanded in the discussion.

In addition to the λ_{max} values, the molar extinction coefficient was determined for $NRBA^+Cl^-$ in ethanol, tetrahydrofuran, acetone, acetonitrile, and *tert*-butyl alcohol. The respective values of ϵ are: 30,600; 28,400; 28,700; 30,200; and 29,200. It was necessary to add small amounts of additional HCl in order to stop deprotonation of the salt in these solvents.

C. NMR Examination. It has been suggested in earlier work that in protonated *N*-retinylidene-*n*-butylamine (NRBA), the positive charge is delocalized on the polyene chain (Blatz et al., 1972). Furthermore, it has been suggested that the size of the anion controls the extent of delocalization on the polyene chain. Recently it has been shown that charge delocalization can be detected by NMR when retinal is treated with CF_3CO_2H (Patel, 1969). Charge delocalization was revealed by deshielding of hydrogens on or near the conjugated chain upon acidification of a $CDCl_3$ solution of retinal. Hydrogens attached directly to a polyene carbon were shifted as much as 0.22 ppm, while the hydrogens on methyls on the conjugated chain were shifted only 0.07 ppm or less. Additional studies similar to those described here have been reported previously (Sharma and Roels, 1973). Consequently in this series of experiments, we obtained the NMR spectra of the hydrochloride, hydrobromide, and hydroiodide in $CDCl_3$. The absorptions are reported in Table III.

The spectrum of *n*-retinylidene-*n*-butylamine is similar to those previously reported and except for resonances arising from the *n*-butyl group are the same. Due to the splitting and in some cases, coincidence of the olefinic hydrogen resonances, we found it difficult to accurately measure the chemical shift of these protons. In fact only the C-11 proton resonance could be estimated, however, the methyl proton resonances can be measured precisely.

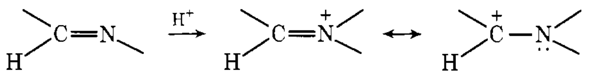
Two conclusions may be drawn. First the charge produced by protonation is delocalized into the polyene chain. This is indicated by the much larger downfield chemical shift in the protonated species as compared to the Schiff base. Second the amount of charge delocalization is related to the counteranion. The anion effect is unmistakable in the C-11 proton resonance shift while the C-13 and C-9 methyl proton resonance shifts change to a lesser but still measurable amount. Even more interesting is the fact that the C-11 proton and the C-9 methyl proton shifts follow the same order as the visible absorption maxima of the salts: $I^- > Br^- > Cl^-$.

D. Infrared Examination. Theoretical calculations, visible absorption spectroscopy, the anion effect, the effect of solvent, and nuclear magnetic absorption spectroscopy have all indicated and substantiated a considerable charge delocalization upon protonation of NRBA. In theory infrared spectroscopy could show large changes in absorption of the C=N bond upon protonation. The protonated azomethine

Table IV: Infrared —C=N— and —C=C— Absorption Frequencies of Various Schiff Bases and of *all-trans-N*-Retinylidene-*n*-butylammonium Salts.

Compound	Number of Carbon–Carbon Double Bonds	State and Medium	Band Frequencies (cm^{-1}) —C=N—	—C=C—
Butyrylidene-*n*-butylamine	None	Solid-mull halocarbon oil	1661	None
	None	Solid-mull halocarbon oil	1710 1710	None
Crotonylidene-*n*-butylamine	1	Solid-mull halocarbon oil	1650	1620
Trienylidene-*n*-butylamine	3	Solid-mull halocarbon oil	1625	1612
NRBA	5	Solid-mull halocarbon oil	1620 1620	1570 1577
NRBA-HF	5	Solid-mull halocarbon oil	1645	1560
NRBA-HCl	5	Solid-mull halocarbon oil	1650 1655	1564 1567
NRBA-HBr	5	Solid-mull halocarbon oil	1654	1566
NRBA-HI	5	Solid-mull halocarbon oil	1650	1559
NRBA-Cl_3CCOOH	5	Solid-mull halocarbon oil	1651	1562
NRBA-Pi	5	Solid-mull halocarbon oil	1645	1560
NRBA-HCl	5	Chloroform solution	1645	1540
NRBA-HBr	5	Chloroform solution	1645	1545
NRBA-HI	5	Chloroform solution	1640	1540

bond represented by resonance structures **3** and **4** would indicate that the length of the carbon to nitrogen bond would be somewhere between that of a single and double bond. Thus protonation could lead to frequencies that are considerably lower than the values of 1620–1650 cm^{-1} which are usually found for Schiff bases.



2 **3** **4**

In Table IV the frequencies of the C=N and C=C bonds are shown for a number of Schiff bases and also selected protonated forms. It was anticipated that the protonated form might show absorption that is quite different from the base. It was further hoped that the various salts would show unique absorption frequencies since the electronic spectra and the NMR spectra do so. Indeed the protonated species do show a very small change over the unprotonated, approximately 35 cm^{-1}, and the shift is in a direction opposite to that for single bond formation. However, a change in frequency is not detected as the anions are changed. These results are in agreement with infrared data (Poincelot et al., 1969) and with resonance enhanced Raman data (Heyde et al., 1971; Oseroff and Callender, 1974) reported earlier.

The experimental observation that ν of $C{=}N^+ > C{=}N$ implies that bond order is greater and consequently the bond length is shorter in the protonated species. On the other hand, valence bond considerations based on acceptance of **3** and **4** as the main resonance structures in the ground state suggest that $\nu_{C=N}$ should be much higher than $\nu_{C=N^+}$. This difficulty has been recognized by others (Elguero et al., 1967; Goulden, 1953).

Table V: Calculation of Infrared Absorption Frequencies for Various Bond Orders, Bond Lengths, and Charge State for the Carbon–Nitrogen Bond.

	Structure	Bond Length (d) (Å)	Bond Order	X_N	X_C	$\bar{\nu}$
1	C=N	1.30	2	3.00	2.5	1700
2	C—N	1.47	1	3.00	2.5	1100
3	$C{-}N^+$	1.47	1	8.00	2.5	1600
4	$C{=}N^+$	1.30	2	8.00	2.5	2400
5	$C\overset{\cdots}{-}N^{+1/2}$	1.39	1.5	5.50	2.5	1700

E. Calculation of C=N Absorption. Gordy's rule allows the value of the force constant to be evaluated (Gordy, 1946)

$$k = ap(X_aX_b/d^2)^{3/4} + b \qquad (1)$$

In this empirical equation, k is the force constant, a and b are constants having values of 1.67 and 0.30, respectively, p is the bond order, X_a and X_b are the Pauling electronegativities of the two atoms, and d is the bond length. Clearly bond order and bond distance but also electronegativity play a major role in the size of k. The Pauling electronegativities for C and N are 2.5 and 3.0, respectively. The bond distance is 1.47 for the single bond and 1.30 for the double bond. The frequency expressed in wave numbers is

$$\bar{\nu} = 1/2\pi\sqrt{k(m_C + m_N)/m_C m_N} \qquad (2)$$

or for a carbon-nitrogen bond

$$\bar{\nu} = 1307\sqrt{k0.1548}$$

Calculation of the $\bar{\nu}_{C=N}$ and $\bar{\nu}_{C-N}$ are straightforward, and the calculated frequencies are shown in Table V. The frequencies fall in the range of those observed experimentally.

A problem arises in the calculation of cases with charged atoms. In such a calculation of judicious estimate of the bond order, bond length, and effective electronegativity must be made. First the bond order and bond length will be considered. Three cases have been calculated $C{=}N^+$,

$\mathrm{C}\overset{\cdots}{-}\mathrm{N}^+$, and $\mathrm{C{-}N}^+$ in which the bond order is taken as 2, 1.5 and 1, respectively. The corresponding bond lengths were then assumed to be 1.30, 1.39, and 1.47 Å, values found in the literature. In principal the effective electronegativity can be calculated from the electronegativity parameter h, i.e., $X_{\mathrm{N}^+} - X_{\mathrm{C}} = h$. The electronegativity parameter can be estimated from the values of the Coulomb integrals, α, and the resonance integral β_0, i.e., $\alpha_{\mathrm{N}^+} = \alpha_{\mathrm{c}} + h\beta_0$. In fact Wheland and Mann (1949) proposed that the value of α is linearly related to the charge; however, numerical evaluation of X_{N^+} remains controversial. α_{N^+} and α_{C} were evaluated by the method of Brown and Penfold (1956) and were found to be −36.343 and −22.248 eV. When $\beta_0 = -2.57$ eV, h assumes a value of 5.49 so that $X_{\mathrm{N}^+} = 8.0$. This is the value of X_{N^+} when X_{C} does not change, and the charge is assumed to be a value of 1. When the charge is one-half, the value of X_{N^+} is 5.5 and is found by interpolation. Substituting these values into eq 1 and 2, the values of $\tilde{\nu}_{\mathrm{C=N}^+}$, $\tilde{\nu}_{\mathrm{C}\cdots\mathrm{N}^+}$, and $\tilde{\nu}_{\mathrm{C-N}^+}$ were calculated and found to be 2400, 1700, and 1600 cm^{-1}, respectively. The value for the charged formal double bond is not in agreement with experiment, whereas the values for a bond order of 1.5 and 1 are in good agreement with observed values.

The calculations show that Gordy's rule allows a reasonable estimation of the IR absorption frequencies of the compounds represented by structures 1, 2, 3, and 5. Structures 1, 3, and 5 give results that do not allow their differentiation on first principles. Bond order, bond length, and the charge term ($X_{\mathrm{N}^+}X_{\mathrm{C}}$) appear to be intimately coupled in such a way as to render the force constant k to be constant or approximately so. This indicates that neither infrared nor Raman spectroscopy can be used to differentiate between Schiff bases and the protonated forms unless the differentiation is based on small changes determined in empirical correlation studies. Indeed this is in agreement with abundant experimental evidence.

Discussion

Except for *cis*- and *trans*-1,2-dichlorocyclohexane, the results of solvent experimentation are straightforward. The longer wavelengths in solvents such as 1,2-dichloroethane and in *cis*-1,2-dichloroethylene are attributable to the ability to engage in three center hydrogen bonding as shown in **1**. This effect is bathochromic, whereas increasing dipole moment is hypsochromic. This solvent effect is reflected in other physical properties. *O*-Chlorophenyltrimethylammonium perchlorate has a dissociation constant ten times larger in 1,2-dichloroethane than in 1,1-dichloroethane (Ramsey and Colichman, 1947). Denison and Ramsey (1950) attributed this result to the ability of an ion to preferentially attract the gauche form of 1,2-dichloroethane.

Special care should be used in the interpretation of the results obtained with dichlorocyclohexane as solvent. Note must be taken of the fact that there are axial and equatorial positions with respect to the chair form of the cyclohexane ring. The cis isomer is the same in either chair form of the ring with the carbon–hydrogen bonds involved in hydrogen bonding at an angle of 60° to each other. The trans isomer, on the other hand, has two different chair conformations: the diaxial conformer (with respect to chlorine atoms) and the diequatorial. The diaxial conformer holds the two hydrogens at 180°. This conformer is incapable of forming three center hydrogen bonds. Dipole moment studies have shown that the diequatorial conformer of *trans*-dichlorocyclohexane is the lowest energy form and represents 72% of the equilibrium mixture in benzene at 40° (Tulinskie et al., 1953). Furthermore straightening the chair to make the hydrogen atoms coplaner is a much higher energy process than flattening the chair (Eliel et al., 1965). Therefore, the cis isomer should more readily give the three-centered reaction and produce the longest wavelength.

From chemical principles and from MO calculations, it is hypothesized that the anionic charge acts as a perturbation on the ground state of the protonated Schiff base (Blatz et al., 1972). Results with halogenated solvents given in this work and elsewhere are consistent with the interpretation that these solvents interact with the anion in such a way as to reduce their effective negative charge. The change in excitation energy ΔE is given as $\Delta E = \Delta E_0 + Z_1Z_{\mathrm{A}}e^2/\epsilon d$. The ionic bond energy is also given as $E_{\mathrm{i}} = Z_1Z_{\mathrm{A}}e^2/\epsilon d$. Consequently in changing from solvent to solvent the $\Delta(\Delta E) = \Delta(E_{\mathrm{i}})$. In other words in going from CCl_4 to $CHCl_3$ the difference between the excitation energies in both solvents will be an estimate of the hydrogen bond energy of chloroform with the halide anions. The hydrogen bonding energies calculated between chloroform and the Cl^-, Br^-, and I^- anions are 2.53, 2.30, and 2.34 kcal/mol, respectively.

The evidence presented previously and herein indicates that the halogenated hydrocarbon interacts principally with the counteranion of the salts. It is also reasonable to believe that in alcohol, the salts are completely dissociated. The anions are solvated through binding with the hydrogen of the alcohol, and the positive center of the cation is solvated by binding electrostatically with oxygen of the alcohol. Since the $\lambda_{\max}$ is 441 nm in methanol and 448 nm in ethanol, the alcohol oxygens in the solvent cage have approximately the same effect as one chloride ion in CCl_4. If $CHCl_3$ and like solvents interact principally with the anion, and if alcohol interacts with both the anion and cation, then one can speculate that solvents like acetone must interact principally with the cation. The partially negative oxygen attempts to bind electrostatically the positive center that is already interacting with the anion in a tight pair. Both interactions, i.e., the anion and the solvent, would tend to stabilize a ground state with the positive charge largely localized on the nitrogen. This additional electrostatic stabilization of the ground state increases the excitation energy as evidenced by the $\lambda_{\max}$ of 428 nm.

It is fascinating to compare the experimental results from visible, infrared, and NMR spectroscopy. Visible, or electronic absorption spectroscopy, clearly shows large changes in the $\lambda_{\max}$ of the main $\pi\pi^*$ transition upon protonation. This is readily interpreted in terms of a gross alteration of the ground state brought about by charge introduction, and any of the several methods of MO descriptions is consistent with delocalization of charge into the polyene chain. However, examination of the C=C and C=N absorptions in the infrared shows no gross change in frequency, and this, at first, might be interpreted to indicate no structural change. This is explained when it is realized that the dual effects of charge (electronegativity) and bond length appear to be compensating. The fascinating thing with respect to NMR is that it confirms both of these effects. Thus the work presented here and the work of Sharma and Roels (1973) clearly indicates deshielding and thus delocalization onto the polyene chain. We detect a substantial downfield shift of the C-11 proton. Additionally, deshielding is detected by the substantial downfield shift of the C-13 methyl protons. The work of Sharma and Roels is in agreement, and they show a large deshielding of resonance of 7-H, 11-H, and 14-H. Deshielding over such an extensive length of the polyene chain can only be caused by delocalization. At the same time, they, and seemingly contrary to the notion of delocalization, note that the protonation does not change the chemical shift of 15-H. Apparently, this proton, represented in structures **2, 3,** and **4,** does not detect a difference in state associated with protonation or deprotonation of the azomethine bond. This is explained by Sharma and Roels (1973): "The resonance of 15-H is not affected by protonation because the deshielding induced by the residual positive charge on the imine nitrogen is balanced by the decrease in double bond character and hence by the decrease in anistropy of the C–N bond." Thus they arrive at the same conclusion from NMR that we do from infrared studies.

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