to give 0.279 g (60%) of a pale yellow solid: mp 180 °C dec; $[\alpha]^{23}_D$ +745° (*c* 0.0042, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.0-3.1 (ddd, 1 H, *J* = 1.33, 11.56, 16.46 Hz), 3.7 (dd, 1 H, *J* = 3.90, 16.48 Hz), 4.6 (dd, 1 H, *J* = 4.62, 11.50 Hz), 5.1 (m, 2 H), 6.5 (m, 1 H), 6.9 (m, 2 H), 7.3-7.4 (m, 7 H), 7.5 (d, 1 H, *J* = 8.21 Hz); ^{13}C NMR ($CDCl_3$) 168.30, 162.40, 148.81, 136.60, 129.85, 129.62, 128.80, 127.65, 126.73, 125.73, 125.05, 124.05, 122.09, 117.88, 115.04, 94.42, 58.69, 30.58, 14.95 (1 carbon atom missing); HRMS calcd for $C_{22}H_{18}N_2O_3$ M + 1 358.1318, M - C_6H_6N 266.0817, found M + 1 358.1327, M - C_6H_6N 266.0819.

Enyne 23. A mixture of 0.375 g (0.780 mmol) of vinyl triflate **19**, 0.347 g (0.936 mmol, 1.2 equiv) of 3,3-dimethyl-1-(tributylstannyl)-1-butyne, 99.2 mg (2.34 mmol, 3.00 equiv) of lithium chloride, and 36.0 mg (4 mol%) of tetrakis(triphenylphosphine)palladium(0) in 30 mL of THF was heated to reflux overnight. The reaction was cooled and then poured into $CHCl_3$. The organic layer was washed with several portions of water and then with 10% aqueous ammonium hydroxide. The organic layer was dried over $MgSO_4$. Filtration and evaporation of solvent in vacuo left a black residue, which was further purified by column chromatography (25% EtOAc/hexanes) and recrystallized from EtOAc/hexanes to give 209 mg (65%) of thin, golden needles: mp 205-206 °C; $[\alpha]^{23}_D$ +682° (*c* 0.0038, EtOAc); ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 2.3 (s, 3 H), 3.0 (ddd, 1 H, *J* = 2.28, 11.56, 16.67 Hz), 3.7 (ddd, 1 H, *J* = 1.81, 4.51, 16.67 Hz), 4.5 (dd, 1 H, *J* = 4.52, 11.53 Hz), 7.00 (d, 1 H, *J* = 8.24 Hz), 7.04 (t, 1 H, *J* = 2.03 Hz), 7.3-7.4 (m, 6 H), 7.48 (d, 1 H, *J* = 8.19 Hz); ^{13}C NMR ($CDCl_3$) δ 168.04, 161.98, 148.76, 136.55, 131.22, 129.82, 128.77, 127.65, 125.80, 125.68, 124.10, 122.11, 117.81, 107.41, 103.64, 94.31, 72.48, 58.22, 35.02, 30.88, 28.18, 14.95; HRMS calcd for $C_{26}H_{24}N_2O_3$ M^+ 412.1788, M - CH_3 397.1553, M - $C_{11}H_{12}NO$ 238.0868, found: M^+ 412.1806, M - CH_3 397.1562, M - $C_{11}H_{12}NO$ 238.0864. Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.70; H, 5.86; N, 6.79. Found: C, 75.62; H, 5.89; N, 6.73.

Anthramycin Methyl Ether 1b.[18] A solution of 200 mg (0.500 mmol) of alcohol **22** and 50 mL of methanol and 30 mL of a 0.02 M aqueous hydrochloric acid was stirred for 2 days at ambient temperature. The solution was neutralized with $NaHCO_3$ and then all of the solvent was removed in vacuo at ambient temperature to leave a yellow residue. The residue was dissolved in 50 mL of methanol, filtered through a plug of glass wool and then stirred at 45 °C for 2 h. The solvent was removed in vacuo to obtain the crude anthramycin: ^1H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 2.69 (q H_c, *J* = 5.85, 15.89 Hz), 3.10 (q H_d, *J* = 11.23, 15.4 Hz), 3.24 (s, 3 H), 4.2 (q, H_b, *J* = 5.48, 11.30 Hz), 4.7 (d, H_a, *J* = 6.54 Hz), 5.7 (d, H_g, *J* = 15.37 Hz), 6.49 (d, H_i, *J* = 8.55 Hz), 7.2 (d, H_f, *J* = 15.6 Hz), 7.29 (s, H_e). See **1b** of Scheme II for proton designation. This spectrum contained the same peaks as that of an authentic sample.

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Comparison of the Structure and Charge Delocalization in an Unsaturated Imine and Its Corresponding Iminium Salt[1]

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Abstract: The crystal structures of *N*-phenyl-3-(*p*-chlorophenyl)-2-propenimine, **1**, and *N*-methyl-*N*-phenyl-3-(*p*-chlorophenyl)-2-propeniminium perchlorate, **2**, have been determined by single-crystal X-ray techniques. Both compounds exist as monoclinic crystals, space group $P2_1/c$, with four molecules per unit cell. The imine **1** has cell dimensions of *a* = 14.438 (4) Å, *b* = 14.348 (4) Å, *c* = 6.240 (2) Å, and β = 101.57 (3)°. The corresponding iminium salt **2** has cell dimensions of *a* = 7.811 (2) Å, *b* = 16.811 (5) Å, *c* = 13.876 (3) Å, and β = 113.26 (2)°. The three-dimensional structures of **1** and **2** are remarkably similar in terms of geometry and bond lengths. However, the C_1,N bond in **2** is significantly longer than in **1**. It was concluded that the C_1,N bond lengthening and close anion contact to C_1 in **2** are a result of positive charge delocalization to C_1. The conclusions reached from the crystallographic data have been compared with ^{13}C NMR spectroscopic data as well as theoretical studies.

The visual pigment rhodopsin and the light harvesting protein bacteriorhodopsin each contain a retinal chromophore linked to a lysine residue of a protein backbone via a protonated Schiff base.[2] Despite the existence a great number of studies on the properties and chemistry of the in vivo chromophore and in vitro studies on the corresponding iminium salts of retinal lacking the protein backbone, there remain many fundamental questions about these systems. These include detailed information on their structure, conformation and charge delocalization, the way such properties change between an imine and its corresponding iminium salt, and the importance of the nature and placement of the corresponding

Table I. ^{13}C NMR Data

	1^a	2^b	2(s)
C(1)	161.5	169.6	170.8
C(2)	126.5	116.4	118.5
C(3)	142.6	164.8	163.0
C(4)	134.8	131.9	131.5
C(5), C(9)	129.5	132.0	131.5
C(6), C(8)	129.5	130.1	131.5
C(7)	142.6	142.6	138.8
C(10)	152.2	144.5	143.7
C(11), C(15)	121.2	122.1	123.8
C(12), C(14)	129.1	130.6	131.5
C(13)	126.5	131.5	131.5
C(16)		41.8	41.4

[a] CD_2Cl_2. [b] Trifluoracetic acid.

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Table II. Bond Lengths (Å) and Angles (deg) for *N*-Phenyl-3-(*p*-chlorophenyl)-2-propenimine (**1**) and *N*-Phenyl-*N*-methyl-3-(*p*-chlorophenyl)-2-propeniminium Perchlorate (**2**)

	1	**2**		**1**	**2**
		Bond Lengths			
C(1)-N	1.274 (4)	1.325 (8)	C(1)-C(2)	1.444 (4)	1.410 (8)
C(2)-C(3)	1.327 (5)	1.330 (10)	C(3)-C(4)	1.461 (4)	1.448 (8)
C(4)-C(5)	1.401 (4)	1.398 (9)	C(4)-C(9)	1.388 (4)	1.377 (7)
C(5)-C(6)	1.376 (4)	1.371 (8)	C(6)-C(7)	1.380 (4)	1.369 (7)
C(7)-C(8)	1.380 (4)	1.364 (9)	C(7)-Cl(2)	1.733 (3)	1.739 (6)
C(8)-C(9)	1.378 (5)	1.366 (8)	C(10)-N	1.415 (3)	1.438 (6)
C(10)-C(11)	1.392 (4)	1.374 (8)	C(10)-C(15)	1.385 (4)	1.400 (9)
C(11)-C(12)	1.378 (5)	1.369 (9)	C(12)-C(13)	1.377 (5)	1.379 (13)
C(13)-C(14)	1.375 (5)	1.376 (12)	C(14)-C(15)	1.375 (5)	1.398 (10)
C(16)-N		1.483 (9)	Cl(1)-O(1)		1.351 (7)
Cl(1)-O(2)		1.341 (5)	Cl(1)-O(3)		1.411 (4)
Cl(1)-O(4)		1.350 (8)			
		Bond Angles			
C(2)-C(1)-N	122.1 (2)	126.2 (5)	C(1)-C(2)-C(3)	123.5 (3)	118.0 (5)
C(2)-C(3)-C(4)	127.3 (3)	126.8 (5)	C(3)-C(4)-C(5)	122.7 (3)	119.7 (5)
C(3)-C(4)-C(9)	119.9 (2)	122.4 (5)	C(4)-C(5)-C(6)	121.3 (3)	122.0 (5)
C(5)-C(6)-C(7)	119.2 (3)	118.4 (6)	C(6)-C(7)-C(8)	121.3 (3)	120.4 (5)
C(6)-C(7)-Cl,Cl(2)	119.8 (2)	119.2 (5)	C(8)-C(7)-Cl,Cl(2)	119.0 (2)	120.4 (4)
C(7)-C(8)-C(9)	118.6 (3)	121.4 (5)	C(4)-C(9)-C(8)	122.2 (3)	119.8 (8)
C(11)-C(10)-N	117.8 (2)	119.2 (5)	C(15)-C(10)-N	123.8 (3)	119.1 (5)
C(10)-C(11)-C(12)	121.0 (3)	120.0 (7)	C(11)-C(12)-C(13)	119.9 (3)	120.0 (7)
C(12)-C(13)-C(14)	119.7 (3)	120.4 (7)	C(13)-C(14)-C(15)	120.6 (3)	121.0 (7)
C(10)-C(15)-C(14)	120.6 (3)	116.9 (6)	C(1)-N-C(10)	119.1 (2)	119.6 (5)
C(1)-N-C(16)		121.3 (5)	C(10)-N-C(16)		119.1 (5)
O(1)-Cl(1)-O(2)		108.5 (4)	O(1)-Cl(1)-O(3)		107.8 (3)
O(1)-Cl(1)-O(4)		104.2 (5)	O(2)-Cl(1)-O(3)		114.4 (3)
O(2)-Cl(1)-O(4)		110.4 (4)	O(3)-Cl(1)-O(4)		111.0 (4)

counterion on the chemistry of the systems.[3] There is a paucity of direct information on the basic properties not only for these imines and iminium salts of retinal but also for simpler analogues of these systems.

The most direct technique to produce accurate structural information about a particular molecule is single-crystal X-ray crystallography. This has been used successfully to obtain bond lengths and angles for *all-trans*[4] and 11-*cis*-retinal,[5] the parent aldehyde chromophore found in bacteriorhodopsin and rhodopsin, respectively. Unfortunately, the structures of few conjugated imines or iminium salts,[6] which more closely mimic the chromophores found in the natural pigments, have been determined. Indeed there are few reports of the structure determinations of imines or iminium salts of any type.[7] There has been no report of the determination of the structure of a retinylidene iminium salt in the open literature.[8]

A variety of less direct methods have been used to probe the structures of conjugated imines and iminium ions. These include ^{1}H and ^{13}C NMR spectroscopy, infrared, resonance Raman, and absorption spectroscopy, and theoretical techniques.[3,9] In many

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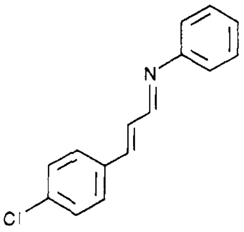
of these studies, attempts have been to assess the charge delocalization in the molecules.

In the current work, the structures of a simple α,β-unsaturated imine and its related iminium salt have been determined by single-crystal X-ray crystallographic techniques. The structural information obtained is used in order to determine the charge delocalization in iminium salts. The conclusions reached from the crystallographic data have been compared with ^{13}C NMR spectroscopic data as well as theoretical studies.

Results and Discussion

The compounds chosen for this study were *N*-phenyl-3-(*p*-chlorophenyl)-2-propenimine **1**, and *N*-methyl-*N*-phenyl-3-(*p*-chlorophenyl)-2-propeniminium perchlorate, **2**. These molecules were selected because they both exist as solids at room temperature and, in the case of **2**, a considerable amount of photochemical and thermal isomerization data has been accumulated.[10] These α,β-unsaturated systems differ by the presence of an *N*-methyl group on **2**.



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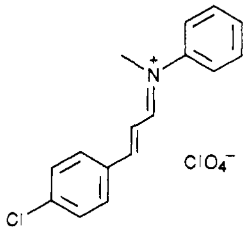


2

The imine **1** and salt **2** were synthesized as previously described.[10a] The ^{1}H NMR spectra of **1** and **2** were similar to those previously reported, and in each case it was clear that after crystallization only one stereoisomer about the C=N bond was present. However, the configurations of **1** and **2** could not be readily determined by ^{1}H NMR spectroscopic techniques.

The ^{13}C NMR spectra of solutions of **1** and **2** were obtained (Table I). As can be noted from Table I, the most significant differences in the ^{13}C NMR spectra of **2** as compared to those of **1** are the small shifts to lower field of C_1 and higher field of C_2, coupled with a relatively large 20 ppm shift to lower field of C_3. These changes are fully consistent with the cationic nature of **2**.

The ^{13}C NMR spectrum of **2** was also obtained in the solid state with use of cross-polarization magic angle spinning (CPMAS) techniques. Quaternary and methyl resonances in the spectrum were assigned with use of a delay without decoupling sequence.[11] As can be seen from the data in Table I, the ^{13}C resonances for **2** are similar in the solution and solid-state spectra. This suggests that no major difference in the structure or charge delocalization of **2** exists in these two phases. Examination of the electronic absorption spectra of **2** in both the solid and solution phases verified this finding. The absorption spectrum of **2** in the solid state (370 nm) was approximately the same as that in benzene (362 nm), suggesting that the cation/anion interactions in **2** are similar in both phases.

X-ray Crystallographic Analysis. Single crystals of **1** and **2**, suitable for X-ray crystallographic determination, were grown by distillation of diethyl ether into acetonitrile solutions of the respective compound. The crystals were stable at room temperature in the absence of moisture. Details of the collection of data and the solution of the structures can be found in the Experimental Section. Interatomic distances and angles for each structure are given in Table II. The structures of **1** and **2** are shown in Figure 1.

The notable feature of the structures of **1** and **2** is their similarity. This is shown, for example, by comparing the corresponding bond distances of **1** and **2** presented in Table II. The only significant differences ($>3\sigma$ where $\sigma = \surd/(\sigma_1^2 + \sigma_2^2)$) in bond distances are found for C_1,N (5.7σ), C_1C_2 (3.8σ), and C_{10},N (3.4σ). Angular changes are also noticed: C_2C_1N is larger (7.6σ), whereas $C_1C_2C_3$ is smaller (-9.4σ).

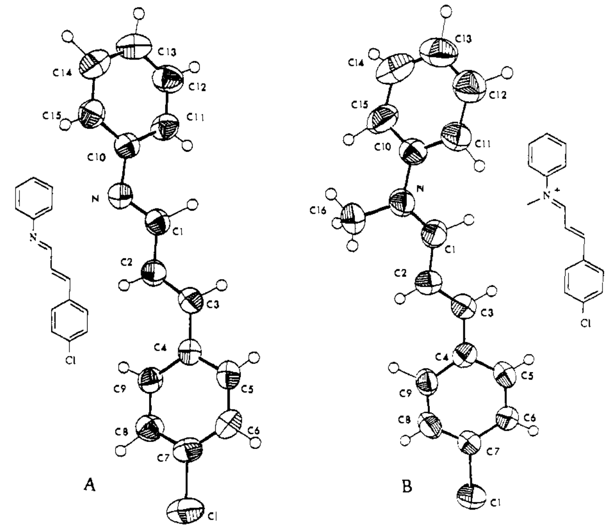
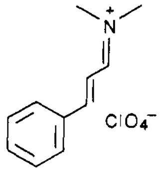


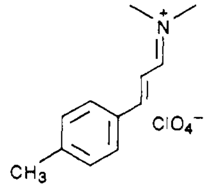
Figure 1. Structures of **1**, A, and **2**, B.

The overall conformations of **1** and **2** are similar despite these molecules having quite different crystal-packing arrangements (Figure 2). In each case, three well-defined planes can be assigned: (A) N,C_{1-3}, (B) C_{4-9}, and (C) C_{10-15}. The maximum deviations from planarity were found to be 0.050 Å at C_2 in plane A of **1**, and 0.012 Å at C_8 in plane B and 0.012 Å at C_{14} in plane C in **2**.

The angles between planes A, B, and C for **1** and **2** are shown in Figure 3. The angle between the A and B planes in **1** is approximately 21.5° and is consistent with the angle of 24.8° found in a similar imine.[12] In the iminium salt **2**, the corresponding angle between the A and B planes is only 9.8°, which is significantly smaller than that found in the imine **1**. This smaller dihedral angle in **2** compared to **1** could indicate increased conjugation of the *C*-phenyl ring with the iminium function and positive charge delocalization in **2** from nitrogen through C_1, C_2, and C_3 and into the *p*-chlorophenyl ring. In the related iminium salts **3** and **4**, the phenyl substituents were found to lie either in or very close to the plane defined by the iminium portions of the cations.[6a] No structures of the imines corresponding to **3** and **4** have been reported.



3



4

In the imine **1**, the C_1,N bond length is 1.274 (4) Å. This is well within the range of 1.23–1.29 Å found in previous X-ray crystallographic determinations for the C=N bond in simple conjugated imines[12] or 1.279 (8) Å in C_1-aryl-substituted imines.[13] The corresponding C_1,N bond in the iminium salt **2** is substantially lengthened (1.325 (8) Å) as compared to that of **1**. Accompanying this change in the C=N bond length in **2** is a decrease in the C=N stretching frequency in its infrared spectrum; 1622 cm^{-1} was observed as compared to 1628 cm^{-1} in **1**. The increased length of the C_1,N bond and the decreased C=N stretching frequency in **2** compared to **1** are indicative of positive-charge delocalization

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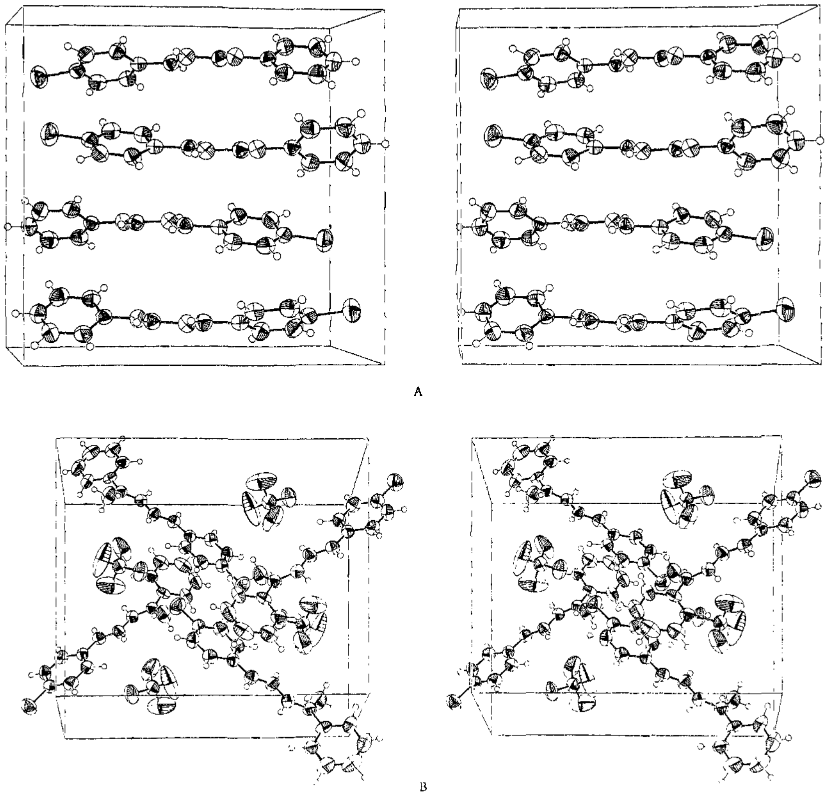

Figure 2. The packing of **1**, A, and **2**, B.

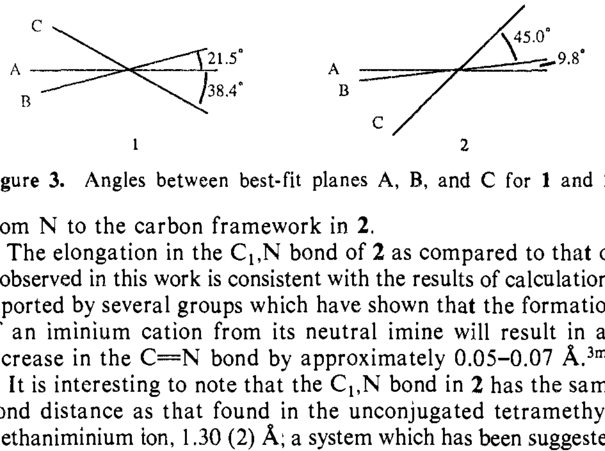

Figure 3. Angles between best-fit planes A, B, and C for **1** and **2**.

from N to the carbon framework in **2**.

The elongation in the C_1,N bond of **2** as compared to that of **1** observed in this work is consistent with the results of calculations reported by several groups which have shown that the formation of an iminium cation from its neutral imine will result in an increase in the C=N bond by approximately 0.05–0.07 Å.[3m,8]

It is interesting to note that the C_1,N bond in **2** has the same bond distance as that found in the unconjugated tetramethylmethaniminium ion, 1.30 (2) Å; a system which has been suggested to represent a "pure" $C{=}N^+$ bond.[7a] the C_1,N bond of **2** is longer than those reported for the same internuclear distances in the conjugated iminium salts **3** (1.284 (9)) (3.4σ) and **4** (1.290 (6)) (3.5σ) with methyl substituents on the N atom. This variation in C=N bond length in iminium salts, such as **2**–**4**, suggests that care should be exercised in making structural comparisons on iminium salts which have different substituents on nitrogen. It should be noted that there is no significant difference in any of the C–C internuclear distances in **3** and **4** as compared to the corresponding bonds in **2**.

As was noted, the C_1,C_2 bond is shorter and N,C_{10} bond is longer in **2** as compared to those of **1**. These differences in bond lengths, which are just beyond the bounds of experimental error, could be caused by the effect of the positive charge present in **2**. In the case of the C_1,C_2 bond, this shortening could be the result of enhanced conjugation of the system and delocalization of the charge onto the carbon framework. It is interesting that calculations of the geometries of retinal imines and iminium salts have given directly comparable bond distances to those found here for C_1,N, C_1,C_2, and N,C_{16}.[3m]

The C_2,C_3 bonds, in **1** and **2** (1.330 (10) Å and 1.327 (5) Å, respectively), are the same within experimental error, suggesting that no significant change in the C=C bond length occurs upon conversion of **1** to **2**. The C_2,C_3 bond lengths in **1** and **2** are typical of those found in ethylene or the double bonds in polyenes.[13] This lack of lengthening of the C_2,C_3 bond suggests that a formal double bond is present and that positive charge in **2** is not extensively delocalized to C_3 or the *C*-phenyl substituent. The C=C bond distance of **1** and **2** found here are different from the results of calculations on retinal systems where considerable lengthening of the C_{13},C_{14} bond is found in the iminium salts.[3m]

Overall, comparison of the structures of **1** and **2** suggests that in the iminium salt **2** most of the positive charge is located on nitrogen with a lesser amount being delocalized to C_1. This conclusion is open to test in terms of the changes observed in ^{13}C NMR chemical shifts between these two systems.

^{13}C NMR Spectroscopic Analysis. Karplus and Pople developed a relationship between the change in ^{13}C chemical shift for a specific carbon of a charged and a neutral organic molecule and the accompanying change in carbon π-electron density.[14] From a series of organic molecules and ions, it has been found that a change of one electron is usually accompanied by a change in ^{13}C chemical shift ($\Delta\delta$) of between 160 and 180 ppm. For carbenium ions a value of 160 ppm/electron is generally accepted.[15]

An analysis of the $\Delta\delta$ values derived from the ^{13}C NMR chemical shifts of **1** as compared to those of **2** shows that the largest change is about 21 ppm at C_3 (Table I). The $\Delta\delta$ for C_1 is much smaller (8.3 ppm) than this. However, previous NMR studies have generally found that the chemical shift of a carbon α to a heteroatom is a poor indicator of the charge distribution.[15b,16]

The differences in chemical shifts of the various carbon resonances of **1** and **2** can be expressed in terms of the changes in charge density (Table III). It can be seen that the total charge induced on the carbon framework is +0.18. This estimate is undoubtedly approximate with no account being taken of the errors associated with assessing the charge on C_1 or the neglect of the charge on the *N*-methyl and *N*-phenyl groups.[17] However, the

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Table III. Calculated Charge Density Based on ^{13}C NMR Chemical Shift Data[a,b] for Compound **2**

position	charge density
C(1)	0.06
C(2)	-0.05
C(3)	0.13
C(4)	-0.02
C(5), C(9)	0.02 (each)
C(6), C(8)	0.01 (each)
C(7)	
	0.18 (total)

[a] Charge density for each carbon [δ(Ci(iminium salt)) − δ(Ci(imine))]/160. [b] Charge density changes for the *N*-aryl and *N*-methyl carbons are neglected.

Table IV. Crystal Data

compound	$(C_{16}H_{15}NCl^+)(ClO_4^-)$	$C_{15}H_{12}NCl$
FW	356.17	241.72
crystal size, mm	0.30 × 0.30 × 0.25 rough cube	0.30 × 0.30 × 0.10 plate
systematic absences	$0k0$ $k = 2n + 1$ $h0l$ $l = 2n + 1$	$0k0$ $k = 2n + 1$ $h0l$ $l = 2n + 1$
space group	$P2_1/c$	$P2_1/c$
unit cell		
a, Å	7.811	14.438
b, Å	16.811	14.348
c, Å	13.876	6.240
β, deg	113.26	101.57
volume, Å^3	1673.97	1266.39
Z	4	4
ρ_{calc}, g cm^{-3}	1.413	1.268
(Mo Kα), cm^{-1}	3.53	2.34
max 2θ, reflectn meas	45°, $h,k > l$	55°, $h,k > l$
standard reflectn (esd)	1 0 4 (0.041)	4 −3 2 (0.012)
	2 5 1 (0.015)	1 6 −2 (0.009)
temp, °C	22	22
no. unique reflectn	1927	2922
no. with $I > 0$	1317	1393
final R_1, R_2[a]	0.0980, 0.0542	0.0920, 0.0764
final shift/error, max (av)	0.044	0.020
x (secondary extinction)	0.00438	0.01092
final difference map		
max (e Å^{-3}); location	0.64; 0.20 0.74 0.84	0.26; 0.08 0.88 0.76
min (e Å^{-3}); location	−0.60; 0.38 0.80 0.32	−0.57; 0.10 0.66 0.52
weighting, w	σF^{-2}	$(\sigma F^2 + 0.000659F^2)^{-1}$
error in an obs of unit wt	2.5385	1.3278

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|\%$; $R_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{-1}$.

important point to note is that the total charge induced on the vinylic carbon framework is relatively small, supporting the conclusion reached on the basis of the structural changes that the bulk of the positive charge resides on the nitrogen atom of **2**.

Cation/Anion Interactions. To this point the structure of the cationic portion of the iminium salt **2** has been discussed with no reference to the counteranion. It has been previously shown that the anion can in certain instances have large effects on the absorption spectra of iminium salts.[3a-e,l] This has been shown to be a ground-state effect that results from a specific cation/anion interaction. It is interesting to examine this question in more detail with the results available from this work.

The dominant feature of the packing of **2** in the unit cell is the π–π interactions between the phenyl rings which form stacks along the a direction at $b = {}^1/_2$, $c = {}^1/_2$ and $b = 0$, $c = 0$. The result is a nearly square cation grid and the anions sit in the resultant holes. Only one of the oxygen atoms of the anion is significantly restricted in its motion, O_3. The Cl_1–O_3 bond length (1.411 (4) Å) is significantly longer than the other C–O distances but it is not abnormally long. In fact, the other distances are probably artificially shortened because of the large thermal motions of the oxygen atoms. The packing precludes any close approach of an oxygen atom to the nitrogen atom, so the shortest N···O contacts (N···O_3' 3.68 Å, N···O_4'' 3.62 Å) are much longer than the van der Waals distance (2.90 Å). The oxygen atoms can approach the carbon atoms of the allicyclic chain, however, and there are three oxygen atoms adjacent to C_1, O_1 and O_3 from one perchlorate ion (C_1···O_1 3.38 Å, C_1···O_3 3.23 Å) and O_4 from another perchlorate ion (C_1···O_4^1 3.34 Å). This last atom also approaches C_2 (C_2···O_4^1 3.34 Å); O_2 from a third perchlorate ion approaches C_2 (C_2···O_2^1 3.26 Å). All distances are greater than the van der Waals distance (3.15–3.20 Å), implying that interactions are only van der Waals and therefore weak. This is consistent with the absence of significant differences in the ^{13}C NMR spectra of **2** in solution or solid state.

The placement of an anion with respect to a charged chromophore such as **2** has been suggested to be one of the factors responsible for the "red" shift in the natural visual chromophores. In the present case the UV spectrum of **2** in solution (λ_{max} 362 nm) and the solid state (λ_{max} 370 nm) are very similar, indicating once more that there are no major changes in structure of the cation in the two phases. One notes that, according to the work of Nakanishi and colleagues, an anion located adjacent to C_1 as is found here in the crystal lattice of **2** should have relatively little effect on the UV absorption.[3a,b]

It is interesting that the calculations on *all-trans*-retinylpyrrolidiniminium perchlorate reported by Birge and co-workers[3w] indicated two equilibrium positions for the ClO_4^- anions. These were above and below the polyene chain at either C_{15} or C_{15} and C_{13} jointly. These positions correspond to C_1 or C_1 and C_3 jointly in **2**. As was shown above in **2**, while no specific interactions of the ClO_4^- anions with the iminium ion occur that are less than the sum of the van der Waals distances, the oxygen atoms are found in the vicinity of C_1 (and C_2) but not C_3. There is no interaction of an oxygen of the perchlorate anion with C_3 of **2** that is closer than 3.584 (8) Å. If there were substantial positive charge at C_3 in this molecule, then it would be expected that an anion would be placed in close contact with this atom in the crystal lattice.[18]

Conclusion

The results presented here represent the first time that it has been possible to directly compare the structure of an imine and its related iminium salt. While the system discussed is a long way from the polyunsaturated iminium salts involved in the visual pigments chromophores, it is in principle possible to get substantial delocalization in **1** and **2** due to the phenyl ring on C_3. Despite the possibility of extensive delocalization, it clear, however, that in **2** most of the positive charge on the molecule resides on N and C_1.

Experimental Section

The reagents used in this work were commercially available. Diethyl ether was distilled from $LiAlH_4$ and stored over 3A molecular sieves. Cinnamaldehyde was distilled before use. The imine **1** was prepared from a condensation of aniline with *p*-chlorocinnamaldehyde in ether. The iminium salt **2** was prepared by stirring *p*-chlorocinnamaldehyde (2.0 g, 15 mmol) in ether while equimolar amounts of *N*-methylaniline (800 mg, 7 mmol) and $HClO_4$ were added dropwise until precipitation was complete. The yellow salt was recrystallized twice from CH_3CN/ether and dried under vacuum. The yield was 1.06 g, 72%.

^1H NMR spectra were obtained at 90 MHz on a Varian EM390 spectrometer, or at 250 MHz on a Bruker WM250 spectrometer. Unless otherwise noted, the probe temperature was 21 °C. ^{13}C NMR spectra

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(17) Comparison of the ^{13}C NMR spectra of *N*-methyl imines and their related iminium salts shows that *N*-methyl group is generally found at higher field in iminium salts (ca. 6 ppm). Compare, for example, the ^{13}C chemical shift of C_{16} in **2** with the *N*-methyl resonances reported (Table III) by Naulet et al. Naulet, N.; Filleux, M. L.; Martin, G. J.; Pornet, J. *Org. Magn. Reson.* **1975**, *7*, 326–330.

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were obtained at 62.9 MHz on a Bruker WM250 spectrometer. The solid-state ^{13}C NMR spectra of **2** was obtained using cross-polarization magic angle spinning (CPMAS) on a crystalline sample. The sample was packed into an alumina rotor under a nitrogen atmosphere and acquired at 50.3 MHz on a Bruker MSL200 spectrometer. Spinning rates were approximately 4000–4500 Hz. Methyl and quaternary carbon resonances were assigned with the delay without decoupling pulse sequence of Opella and Frey.[11] Adamantane was used as an external reference, having chemical shifts of 29.50 ppm (CH) and 38.56 ppm (CH$_2$) with respect to tetramethylsilane.[19]

The solution absorption spectra of **2** was obtained at 21 °C with the use of a Hewlett-Packard 8451A diode-array spectrophotometer. A concentration of approximately 10^{-5} M in benzene was employed. The solid-state absorption spectra of **2** was obtained on microcrystalline samples by the method of Kobayashi et al.[20] A thin layer of freshly crystallized iminium salt was placed on a quartz slide. A similar slide or one coated with KBr was used as a reference.

Determination of Crystal Structures. Collection of Data. Crystals of the imine **1** and iminium salt **2** suitable for X-ray diffraction techniques were obtained from distillation of diethyl ether into an acetonitrile solution of each salt at about −20 °C. Each crystal was sealed in a Lindemann tube for data collection.

The space group of each compound was determined through precession photography. These showed that crystals were monoclinic and that the space group for each was $P2_1/c$. Accurate unit-cell parameters were determined from a least-squares fit of χ, ϕ, and 2θ. For **1**, 15 reflections where $18.6° < 2\theta < 25.9°$ were used. In **2**, a range of $19.6° < 2\theta < 31.3E$ was used for 15 reflections. Radiation was graphite monochromated Mo Kα, $\lambda = 0.71069$, and reflection intensities were measured with a Syntex P2$_1$ diffractometer having a coupled θ(crystal)–2θ(counter) scan. Selection of scan rates and initial data treatment have been previously described.[21] Corrections for Lorentz-polarization factors were made, but not for absorption. This will make the maximum error in F_o of 1.0% in **1** and 1.3% in **2**. All crystal data are summarized in Table IV.

Solution of Structures. In the iminium salt **2**, the coordinates of the chlorine atoms were found from a three-dimensional Patterson synthesis. All other atoms were located from three-dimensional electron-difference syntheses by use of a series of full-matrix least-squares refinements. The chlorine atom in the imine **1** was found by direct methods on 164 reflections with $|E| > 1.1$, and 20 sets of starting phases. All remaining atoms were found from the subsequent difference map. Refinement of the coordinates of all non-hydrogen atoms by full-matrix least-squares, which minimized $\Sigma\omega(|F_o| - |F_c|)^2$, was terminated when the maximum shift/error was 0.1. Throughout each refinement, scattering curves were taken from those in the International Tables.[22] Secondary extinction corrections were applied from SHELX. Positional parameters for non-hydrogen atoms of both structures are found in Tables II and III.

Acknowledgment. Technical assistance of R. Faggiani is gratefully acknowledged.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic temperature factors, hydrogen positional parameters, and bond lengths and angles involving hydrogen atoms (8 pages); listings of observed (F_o) and calculated (F_c) reflection intensities (26 pages). Ordering information is given on any current masthead page.

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NMR Study of Kinetic HH/HD/DD Isotope, Solvent, and Solid-State Effects on the Double Proton Transfer in Azophenine

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Abstract: Azophenine (AP, *N,N'*-diphenyl-3,6-bis(phenylimino)-1,4-cyclohexadiene-1,4-diamine) is subject in liquid solution to a fast intramolecular double proton transfer involving two degenerate tautomers. Rate constants of this reaction have been measured as a function of temperature by applying different methods of dynamic NMR spectroscopy to various isotopically labeled AP species dissolved in different organic solvents. The rate constants do not depend on the dielectric constant of the solvent, which was varied between 2 (toluene) and 25 (benzonitrile). For C$_2$D$_2$Cl$_4$ as solvent, the full kinetic HH/HD/DD isotope effects were obtained at different temperatures. The observed kinetic isotope effects of $k^{HH}/k^{HD} = 4.1$ and $k^{HD}/k^{DD} = 1.4$ at 298 K indicate a breakdown of the rule of the geometric mean. ^{15}N CPMAS NMR experiments on crystalline azophenine showed that the reaction also takes place in the solid state. However, the degeneracy of the tautomerism is lifted in this phase because of intermolecular interactions. The mechanism of this reaction is discussed in detail, especially with respect to the questions of whether tunneling is involved and whether one or two protons are transferred in the rate-limiting step. The kinetic isotope effects can best be explained in terms of a stepwise consecutive single proton transfer mechanism involving either a highly polar zwitterion or an apolar singlet–biradical as intermediate. The observation that solvent effects on the reaction rates are absent and that the activation entropy of the reaction almost vanishes excludes the formation of a strongly solvated zwitterionic intermediate. Static medium effects on the double minimum potential of the proton transfer are discussed, taking into account previous results of IR experiments on AP and of solid-state NMR experiments on double proton transfers in organic glasses.

In the past years there has been a particular interest in neutral multiple hydrogen transfer reactions[1] where at least two protons, hydrogen atoms, or hydride ions are transferred between heavy atoms. Intramolecular[2–9] as well as intermolecular[10–14] multiple proton transfers have been studied. The fact that ions are not

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(1) Since neither protons nor other ions are educts or products in these reactions, only the term hydrogen transfer would be correct, which includes the possibility of the transfer of protons, hydrogen atoms, or hydride ions; however, since protons are, generally, transferred in hydrogen-bonded systems we will use the term proton transfer.

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