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AROMATIC SCHIFF'S BASES AND FREQUENCY SHIFTS
ON THE C=N STRETCHING MODE UPON
PROTONATION AND DEUTERATION

presented by

JUAN LOPEZ GARRIGA

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Gerald T. Babcock
Major professor

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By

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ABSTRACT

AROMATIC SCHIFF'S BASES AND FREQUENCY SHIFTS ON THE C=N STRETCHING MODE UPON PROTONATION AND DEUTERATION

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Unprotonated, protonated and deuterated aromatic Schiff's bases seem to be important for modeling the C=N stretching frequency in porphyrins Schiff's bases and derivatives and for understanding the unexpected increase in the C=N stretching frequency which is observed upon protonation or deuteration of the Schiff's bases. The aromatic Schiff's base models are discussed and compared with analogous aldehydes and unsaturated Schiff's bases. The application of Raman and infrared spectroscopy are used to determine the C=N, C-$\overset{+}{N}$H and C=$\overset{+}{N}$D stretching frequencies. Other than the changes in the C=N stretching mode upon protonation, no significant shifts are observed in frequency bands related to the aromatic ring motions. The same kind of behavior is observed in the NMR data obtained for these compounds which suggests that the positive charge does not perturb the aromatic ring substituents uniformly. From these observations, it appears that protonation effects are localized at the Schiff's base environment.

To Carmen

ACKNOWLEDGMENTS

I would like to thank my fellow lab members, in particular, José, Brian, Assad, Tony and Bob for their assistance and I would especially like to thank Professor Jerry Babcock for his guidance and enthusiasm in this project.

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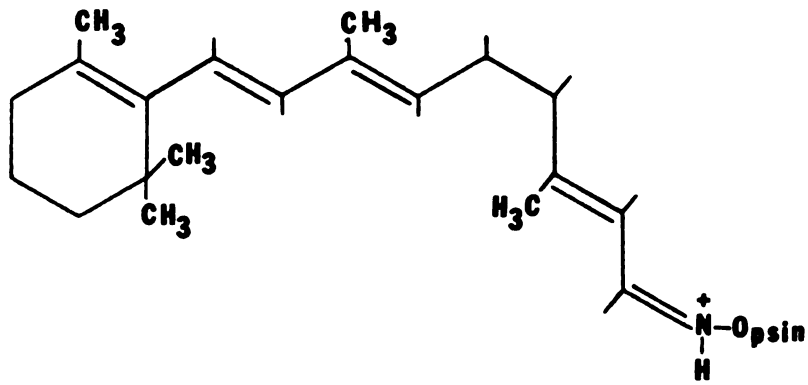
INTRODUCTION

The suggestion that the chromophore, retinal, is covalently associated with the protein opsin by a protonated Schiff's base linkage to form the photosensitive pigment rhodopsin (Figure 1a), has stimulated considerable spectroscopic work on the properties of free Schiff bases of retinal and of its protonated form. Because of the importance of the configuration of the Schiff's base in this conversion, Raman spectroscopy has been used extensively to monitor changes in the C=N stretching frequencies during the rhodopsin photocycle. A frequency change from 1620 cm^{-1} for the C=N stretch in the non-protonated species to a frequency of 1655 cm^{-1} for the protonated form and to 1630 cm^{-1} for the deuterated form has been observed (see, for example, Ottolenghi, 1980; Marcus et al., 1979; and Aton et al., 1980).

Recent work by Ward et al. (1983), modeling interactions between the carbonyl group of heme a and an amino donor group, show that the metalloporphyrin Schiff's bases (see Figure 1d) which results upon protonation have unusual spectra properties. The C=N stretching frequency

Figure 1. a. Rhodopsin.
b. Bacteriorhodopsin br_{570}, all trans-retinal + opsin.
c. Bacteriorhodopsin br_{603}, all trans-3-dehydro retinal + opsin.
d. Nickel (II) formylvinylporphyrin.

1a



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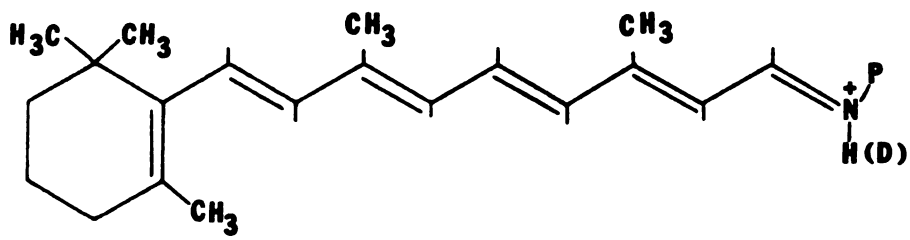

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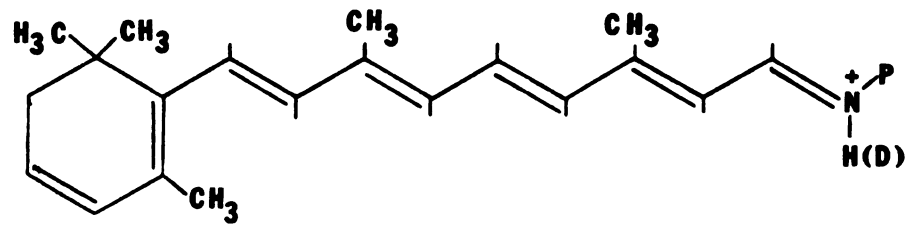

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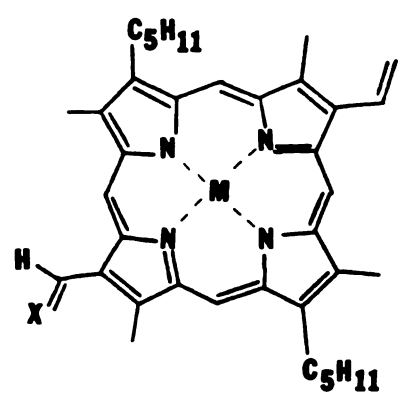

1. X = O M = Ni
2. X = N Bu
3. X = $\overset{+}{N}$HBu
4. X = $\overset{+}{N}$DBu

Figure 1

for the Schiff's base appears at 1639 cm^{-1}, upon protonation this frequency shifts to 1650 cm^{-1} and, if the proton is replaced by a deuteron, the stretching vibration is observed at 1640 cm^{-1}.

In both cases the observed Raman frequencies corresponding to the protonated and deuterated Schiff's base are difficult to understand on intuitive grounds, since, in general, it is expected on the basis of a simple mass effect that protonation will decrease the C=N stretching frequency. Moreover, these C=N frequency changes are not consistent with changes in the nature of the groups on the Schiff's bases. For example, the C=N stretching frequency is higher in the metalloporphyrin Schiff's base, 1639 cm^{-1}, than in the unprotonated retinal Schiff's base, 1620 cm^{-1}, even though the resonance system is more extended and the reduced mass is higher in the former system than in the latter.

In the case of visual pigments and their model compounds, the frequency changes which occur for the C-N bond upon protonation and deuteration have been discussed by Marcus et al., (1979). They suggested that the interaction of the Schiff's base C=N bond with the N-H bending mode, in the protonated case, contributes significantly to the increase in the frequency of the C=N stretching mode. Support for this model was claimed from the fact that these frequency changes cannot be attributed to a simple reduced mass effect because substitution of the

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proton by a deuteron decreases the stretching frequency by 25 cm^{-1} while N^{15} enrichment shifts this mode by only 13 cm^{-1}. Aton et al., (1980) tested this proposal by carrying out calculations on a hypothetical triatomic molecule, C=N-H. Their results showed that by allowing the C=N stretching frequency to interact with the N-H bending mode, they could produce an increase in the C=N vibrational frequency.

On the other hand, Massing et al., (1982) suggested another possibility for the increase in the C=N stretching frequency upon protonation which involves mixing between the C=N stretch and an adjacent C-C stretch. At the same time, there are other factors which affect the characteristic group frequency. Woffe (1975), pointed out that the characteristic carbonyl group frequency depends, in general, on steric effects, reduced mass, conjugative effects, electron delocalization, on the electron donating and electron withdrawing ability of the substituents. Perjessy (1973) indicates that transmission of polar effects due to the CH=CH group also effect the C=O stretching frequency. Seth-Paul (1981) discussed the dependence of this group frequency on the δCCOC angle.

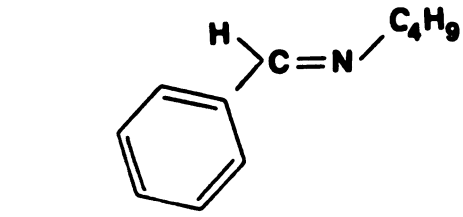
In general, it is known that there is a decrease in the C=O force constant with increasing polarity of the carbonyl group. Thus, when a halogen atom is introduced into the methyl group of acetaldehyde or acetone the carbonyl bond becomes less polar and the C=O stretching

frequency shifts to higher values. This behavior was attributed by Bralóz et al., (1961) to a variation of the effective electronegativity of the carbonyl carbon atom.

In addition, Besnainau et al., (1966) showed that halogen substitution on similar nitrile compounds produces the same behavior. Furthermore, a hyperconjugation effect was discussed by Howell (1976) and Christen et al., (1982), as the main factor in the variation in bond distance of methyleimine halogen derivative.

To examine the frequency changes in the imine bond which occur upon going from an unsaturated substituent to an aromatic substituent, as well as to study the possible analogy that exists between the effect of protonation and deuteration of the C=N bond in metalloporphyrin Schiff's bases with respect to the retinal Schiff's bases, nuclear magnetic resonance, infrared and Raman spectroscopic studies have been carried out. One, two and three ring aromatic Schiff's bases (Figure 2) and their protonated and deuterated derivatives were studied. With the identification of the C=N stretching frequency in the various compounds, it is possible to establish whether the increase in the C=N frequency mode of the aromatic Schiff's bases relative to the unsaturated Schiff's bases, follows the same trend as that observed for the carbonyl stretching frequency and the nitrile stretching frequency in an analogous series of compounds. These studies provide

Figure 2. a. n-benzylidene-n-butylamine.
b. n-benzylidene-n-butylammonium ion.
c. 2-naphthalidene-n-butylamine.
d. 2-naphthalidene-n-butylammonium ion.
e. 9-anthralidene-n-butylamine.
f. 9-anthralidene-n-butylammonium ion.
g. benzophenilidene-n-butylamine.
h. benzophenilidene-n-butylammonium ion.



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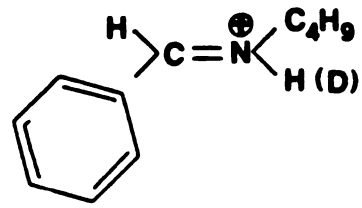

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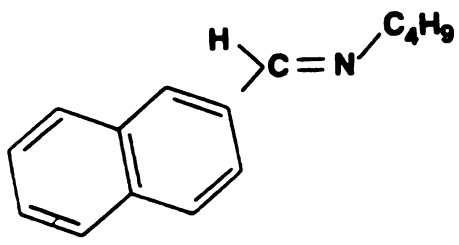

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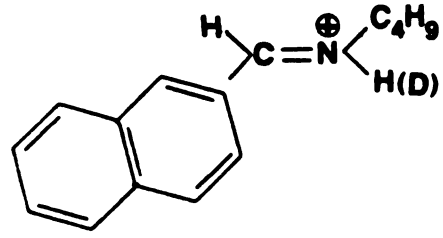

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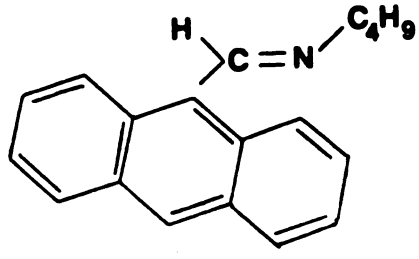

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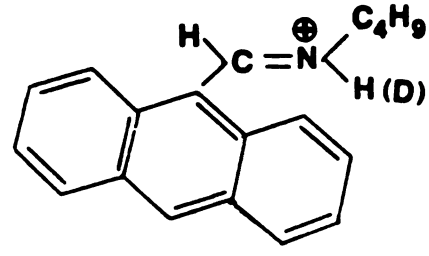

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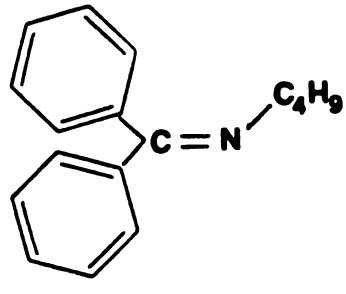

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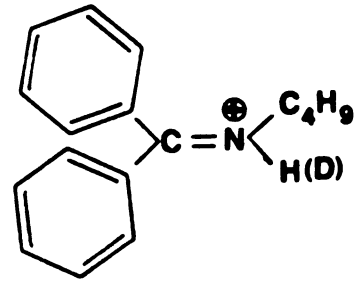


h

Figure 2

information on the question of whether the increase in the C=N stretching frequency in metalloporphyrin Schiff's bases, which occurs upon protonation and deuteration, is an isolated case or can be generalized as a common characteristic of aromatic Schiff's bases. Furthermore, the identification of the N-H and N-D bending modes will provide information that can be used in future work to test the hypothesis that the interaction between the C=N stretching vibration and the N-H or N-D bending modes is responsible for the observed increase in stretching frequency of the imine bond upon protonation or deuteration (Aton et al., 1980).

CHAPTER II

EXPERIMENTAL

A.1 Sample Preparation

Benzaldehyde was purified by distillation in vacuum, 2-naphthaldehyde and 9-anthraldehyde were recrystallized from a methanol-water mixture. Benzophenone and n-butylamine were used with no further purification. Methylene chloride and chloroform were distilled in the presence of calcium hydride. N-benzylidene-n-butylamine, 2-naphthalidene-n-butylamine and 9-anthralidene-n-butylamine were prepared by producing a reaction with 10 ml of the appropriate aldehyde in a 4 h. reflux with dry benzene containing an excess of n-butylamine (20 ml). Benzene acts as the azeotropic agent which allows for the removal of the water produced by the reaction (Cordes et al., (1963) and Layer, (1963)).

$$\underset{\diagdown\ \diagup}{C{=}O} + RNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HO\underset{\diagdown\ \diagup}{\overset{\diagdown}{C}}\text{-}\overset{H}{\underset{|}{N}}H \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\diagdown\ \diagup}{C} = N\text{-}R + H_2O \qquad (1)$$

Lyophilization yields pure Schiff's bases (Ward et al., 1983). After the reaction was completed, the excess n-butylamine and the benzene were removed in a rotavapor

system. N-benzylidene-n-butylamine was purified by distillation in a vacuum, while 2-naphthalidene-n-butylamine and 9-anthralidene-n-butylamine were recrystallized in a mixture of methylene chloride and petroleum ether. Since aromatic ketones react with amines more slowly than aromatic aldehydes, aluminum chloride was used as a Lewis acid, thus making the reaction possible. Benzophenone Schiff's base was used without further purification.

A.2 U.V. Measurements and Results

In order to verify the formation of the imines, ultraviolet absorption spectroscopic measurements of approximately 1×10^{-4} M solutions in methylene chloride or chloroform were carried out with a Perkin Elmer Lambda 5, UV/Vis spectrophotometer. Table I shows the blue shift relative to the free carbonyl species upon Schiff's base formation (El-Aasser et al., 1971).

Table I. λ_{max}(nm) of Aldehydes and Schiff's bases

	ArCHO	ArCH=NBu	$ArCH=\overset{+}{N}Bu$	$ArCH-\overset{+}{N}DBu$
C_6H_5	248	247	278	277
$C_{10}H_8$	252	251	275	275
$C_{14}H_{10}$	265	260	270	—

Protonated and deuterated Schiff's bases were prepared by adding equivalent amounts of dry $HCl_{(g)}$ or $DCl_{(g)}$ to 0.25 M of imine solutions in methylene chloride or chloroform as solvent. Solutions of approximately 1×10^{-4} M were used to verify the red shift of the $\pi \rightarrow \pi^*$ transition in the U.V. region (Santerre et al., 1958) due to the presence of protonated or deuterated Schiff's bases. (See Table I and Figure 3). However, in some cases, the $\pi \rightarrow \pi^*$ transition for aromatic aldehydes, benzaldehyde and 2-naphthaldehyde and the corresponding aromatic Schiff's bases cannot be differentiated. Therefore, another spectroscopic technique is required in order to establish the formation of the Schiff's bases.

A.3 NMR Measurements and Results

Nuclear magnetic resonance spectroscopy is a very good technique for identifying aldimines Schiff's bases, since the proton attached to the carbon in the imine bond has a characteristic environment (Parry et al., 1970). In addition, protonated Schiff's bases can be observed due to the NH proton interactions. The nitrogen proton (NH) may undergo a rapid, intermediate or slow rate exchange (Silverstein et al., 1981). In the case of rapid exchange, the proton is decoupled from the N atom and from adjacent protons. Therefore, the CH protons will not be split by the NH proton. The same observation applies when the NH

Figure 3. U.V. spectra of Benzaldehyde (———), N-Benzylidene-n-butylamine (—— —— ——), N-Benzylidene-n-butylammonium ion (——·——·——), and N-Benzylidene-n-butyldeuteroammonium ion (------) in chloroform.

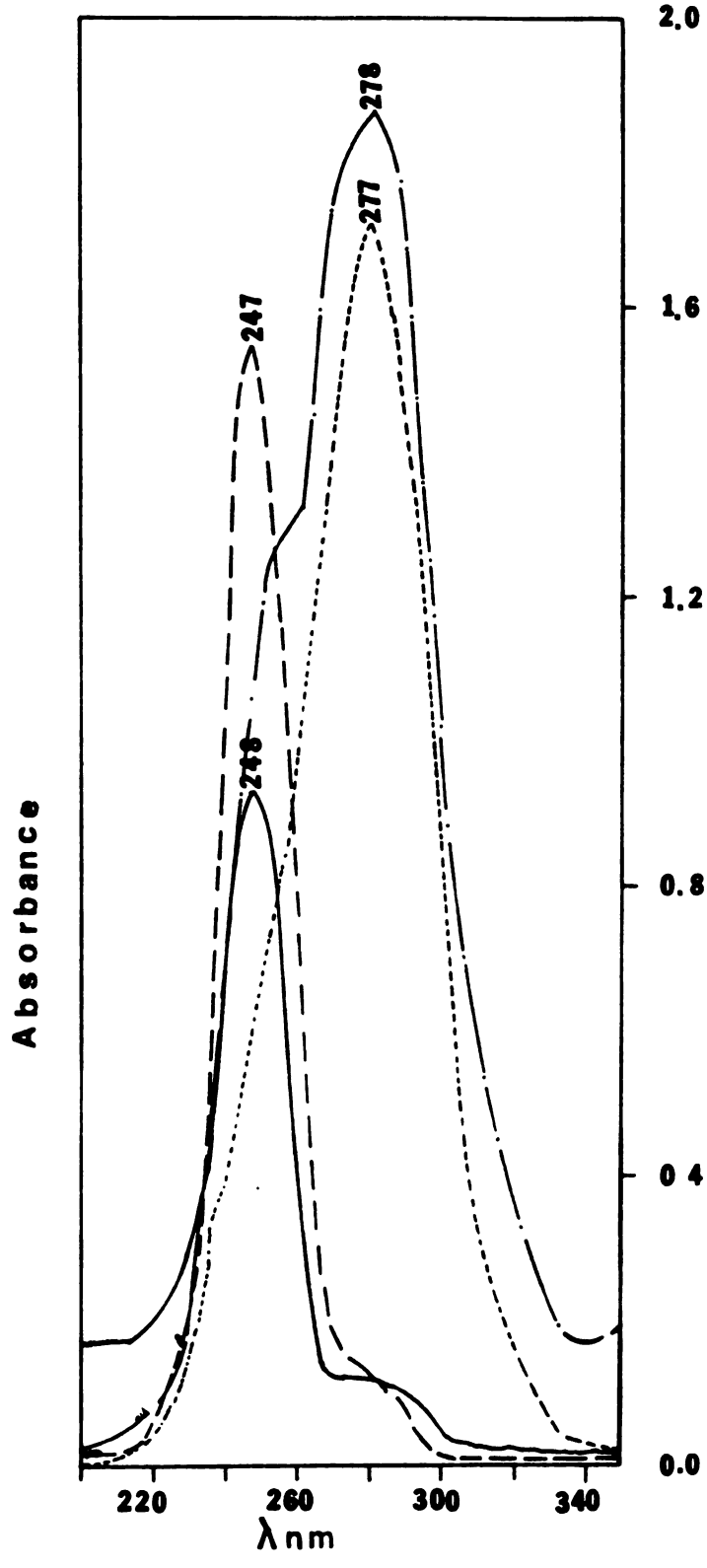


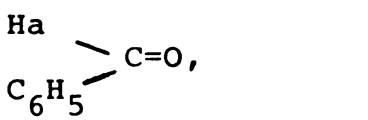
Figure 3

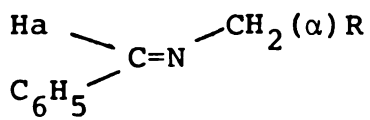
proton undergoes an intermediate rate exchange, since the NH proton is only partially decoupled. However, when the exchange rate is slow, the coupling of the NH proton with adjacent CH protons can be observed. Therefore, the chemical shift and the splitting pattern of the protons can be used to detect the presence of unprotonated and protonated Schiff's bases.

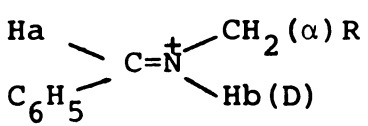
Aldehydes and imines were prepared at a concentration of 0.1 M in deuterated chloroform. Protonated and deuterated forms were obtained by adding equivalent amounts of dry $HCl_{(g)}$ and $DCl_{(g)}$, respectively. NMR spectra were recorded on a Varian T_{60} NMR spectrometer at a 0.1 RF power level, at a spectrum amplitude of 10 and at a spinning rate of 40 rps.

Figures 4 through 6 show the NMR spectra of n-benzylidene-n-butylamine, n-naphthalidene-n-butylamine, n-anthracylidene-n-butylamine, its protonated forms, and its carbonyl analogs. Table II contains data of the Ha and αCH_2 protons, with assignments based on those of Sharma et al., (1973) and Parry et al., (1970). The change in the chemical shift of the Ha proton indicates the formation of the aromatic Schiff's base from the corresponding aldehyde. The results also indicate that, when the Schiff's base is protonated, the splittings of the Ha proton into a doublet and of the αCH_2 protons into quartets are due to the Hb proton present on the imine nitrogen. On the other hand, in the deuterated solution

Figure 4. 60-MHz NMR spectra of Benzaldehyde (BCHO), N-Benzylidene-n-butyl amine (BnBI), N-Benzylidene-n-butylammonium ion ($BnBIH^+$) and N-Benzylidene-n-butyldeteroammonium ion ($BnBID^+$).







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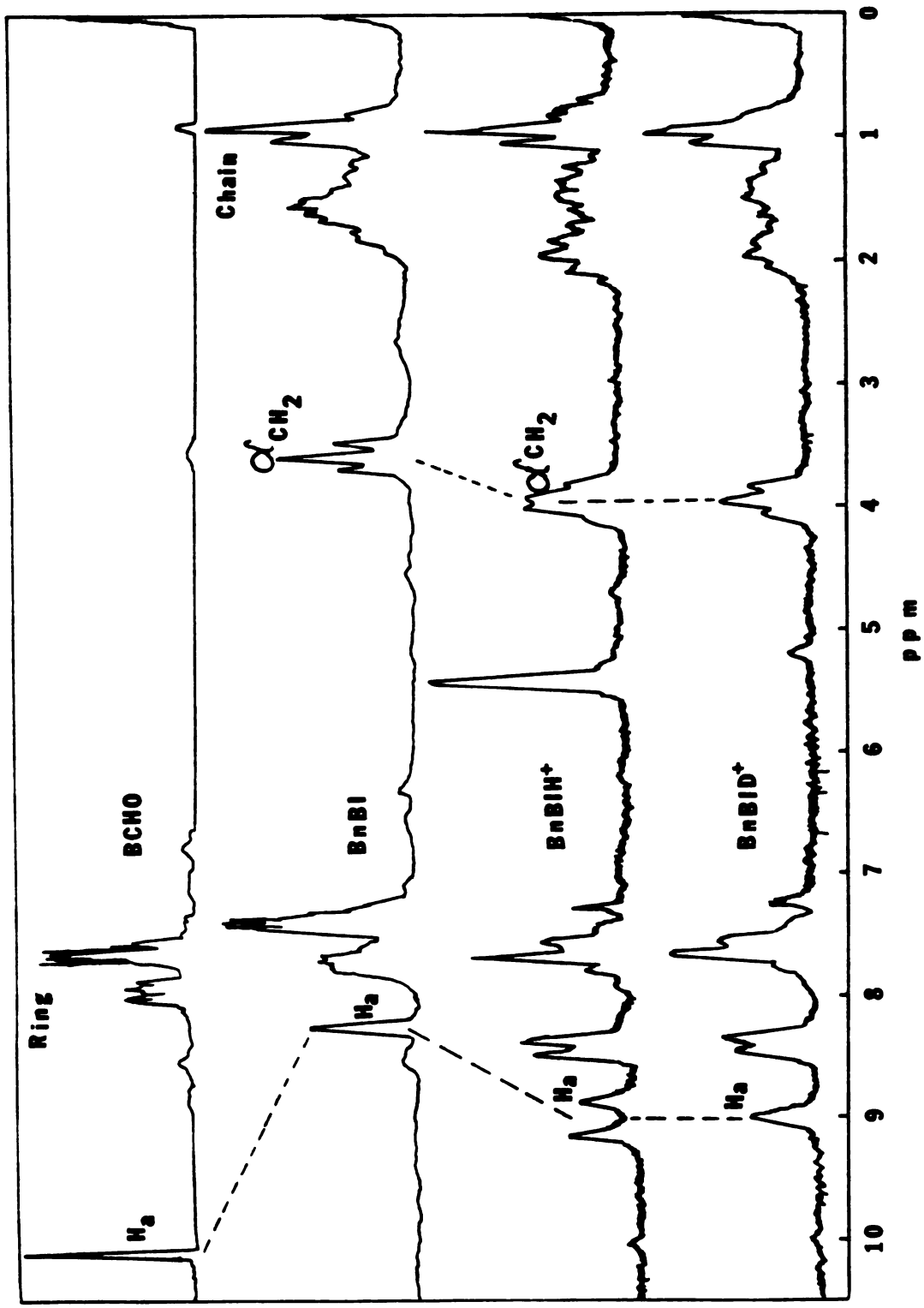
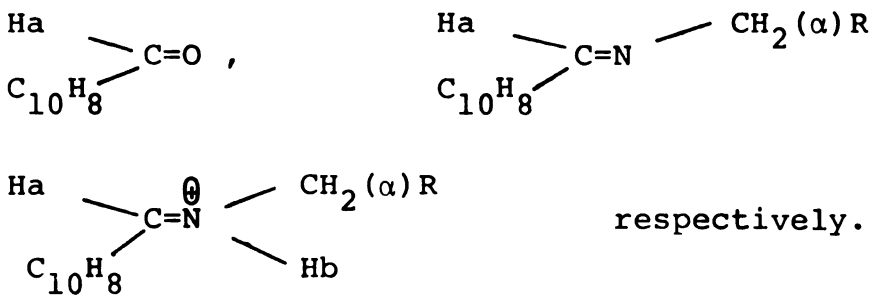

Ring
BCHO
Chain
H_a
$\alpha'CH_2$
BnBI
BnBIH+
BnBID+
ppm
0
1
2
3
4
5
6
7
8
9
10

Figure 4

Figure 5. 60-MHz NMR spectra of 2-Naphthaldehyde (NapCHO), 2-Naphthalidene-n-butyl amine (NapBI), 2-Naphthalidene-n-butylammonium ion ($NapBIH^+$) and 2-Naphthalidene-n-butyldeteroammonium ion ($NapBID^+$).



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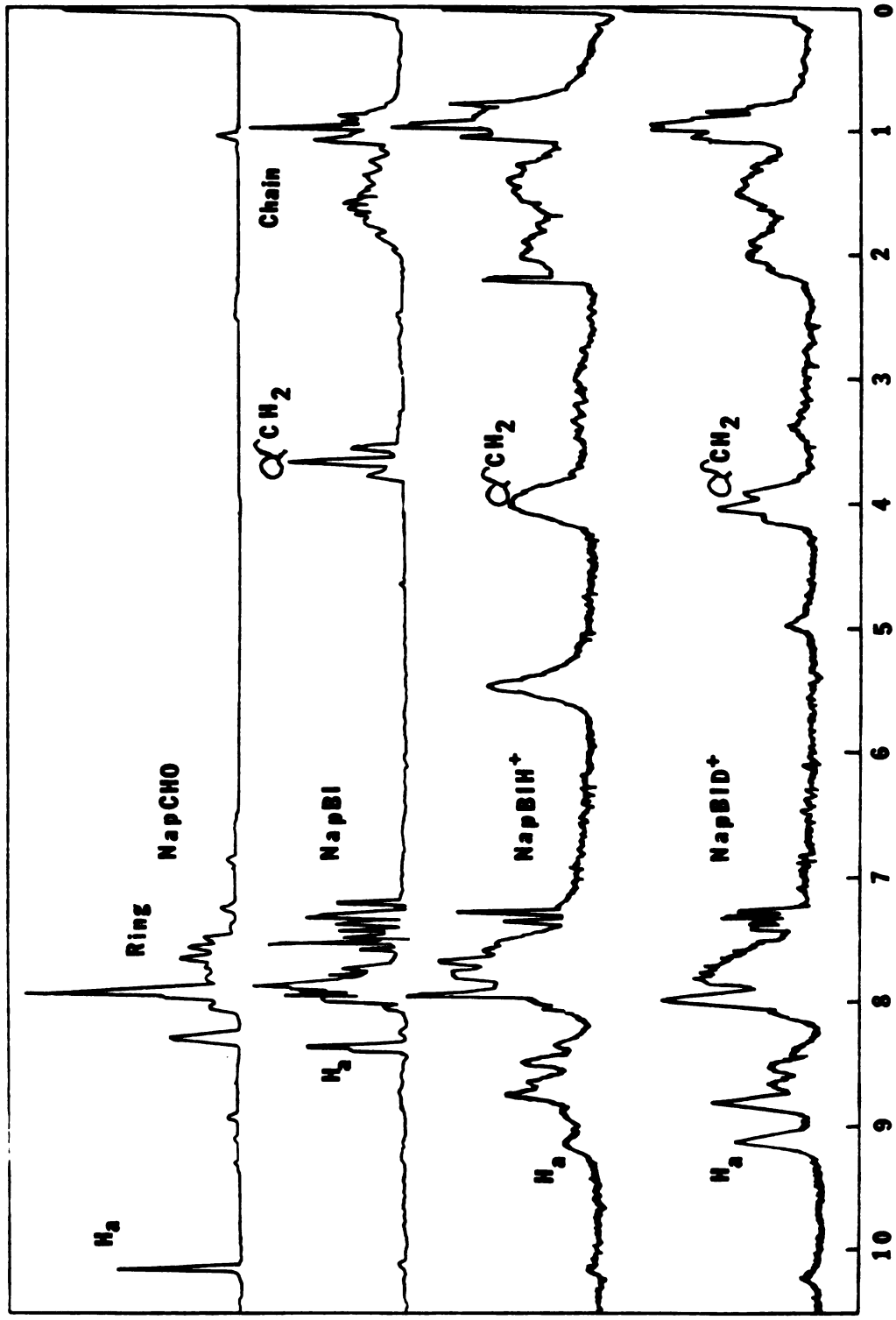
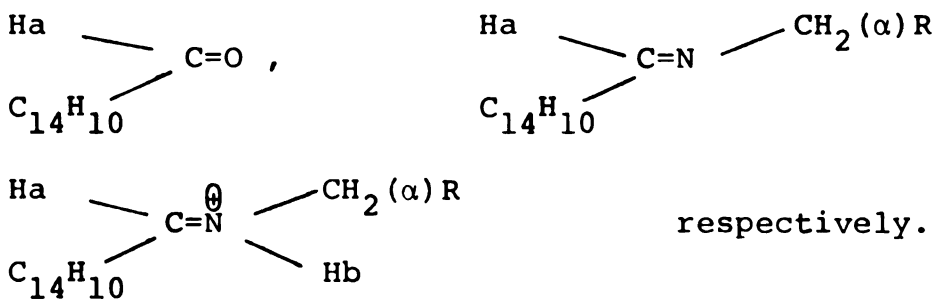

Ha
Ring
NapCHO
NapBI
Ha
αCH2
Chain
NapBIH+
Ha
αCH2
NapBID+
Ha
αCH2
10
9
8
7
6
5
4
3
2
1
0
ppm

Figure 5

Figure 6. 60-MHz NMR spectra of 9-Anthraldehyde (AnCHO), 9-Anthralidene n-butylamine (AnBI), 9-Anthralidene-n-butylammonium ion ($AnBIH^+$).



respectively.

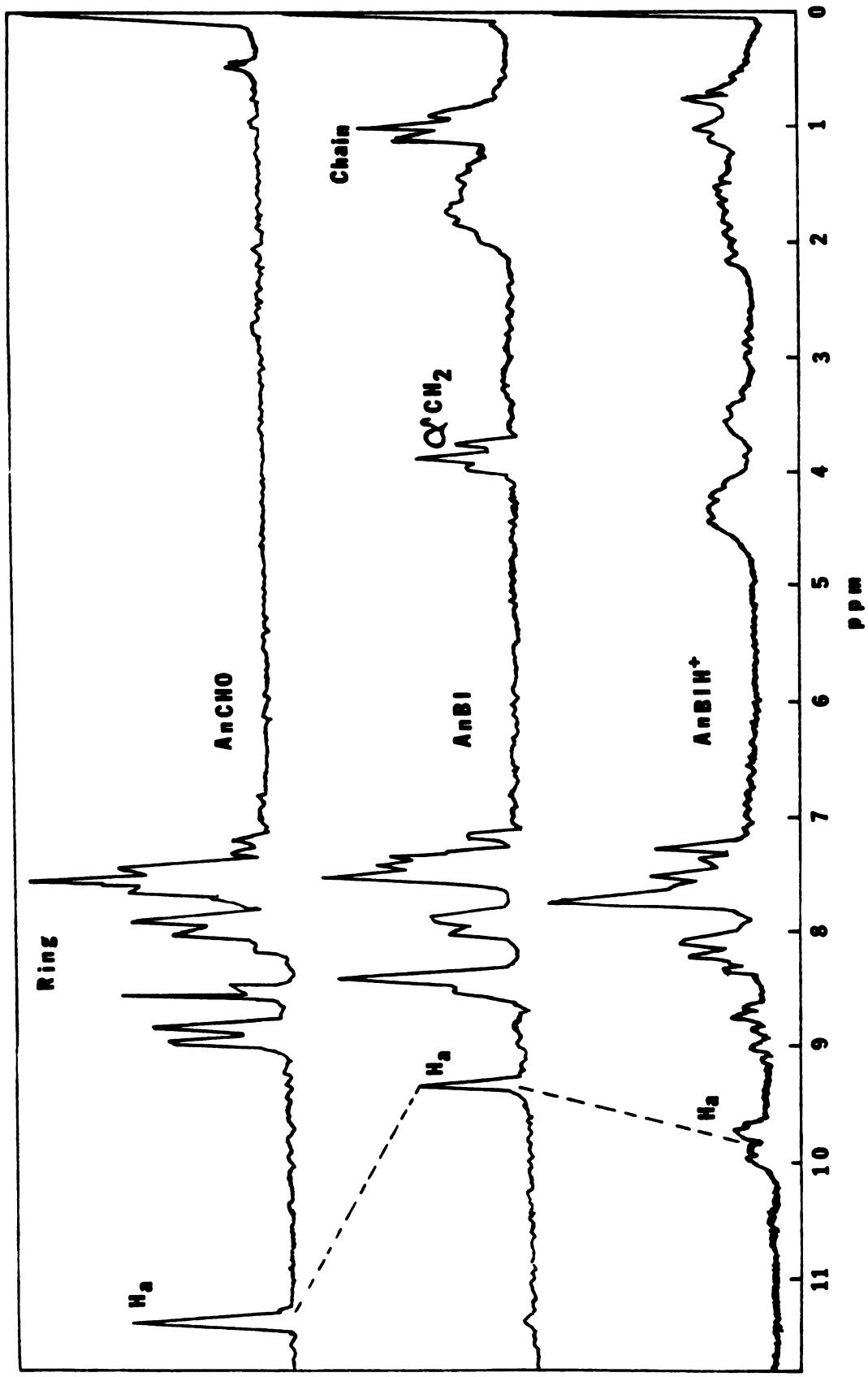
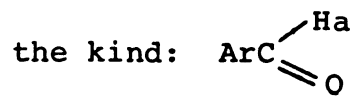
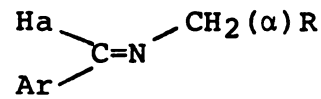
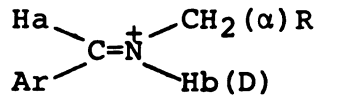

Ring
AnCHO
Chain
Q^1CH_2
AnBI
$AnBIH^+$
H_a
H_a
H_a
0
1
2
3
4
5
6
7
8
9
10
11
ppm

Figure 6

Table II. Chemical shift for carbonyl and imine protons of the kind:  ,  and 

Ar	Substituent	Ha	αCH$_2$
C_5H_5	Carbonyl	9.96(s)	
	Imine	8.17(s)	3.57(t)
	Prot. Imine	8.8 (d)	3.97(q)
	Deut. Imine	8.9 (s)	3.92(t)
$C_{10}H_8$	Carbonyl	10.04(s)	
	Imine	8.30(s)	3.60(t)
	Prot. Imine	8.8 (s)	3.95(b)
	Deut. Imine	8.9 (s)	3.95(t)
$C_{14}H_{10}$	Carbonyl	11.32(s)	
	Imine	9.28(s)	3.86(t)
	Prot. Imine	9.75(b)	4.29(b)

R = propyl group; s = singlet; d = doublet; t = triplet; q = quartet; b = broad.

and in the unprotonated Schiff's bases the azomethine proton gives a singlet and the α-methylene protons appear as triplets. The data from Table II suggest that, upon protonation of the Schiff's bases, there is an increase in the effective electronegativity of the carbons, the Ha and αH hydrogens, since resonances of the two shift downfield upon protonation. This observation is consistent with the results reported by Sharma et al., (1973) and Blatz et al., (1975) for similar Schiff's bases. In contrast, Figures 4-6 suggest that upon protonation, the positive charge in the Schiff's base is not uniformly distributed in the substituent system, since the observed chemical shift for other peripheral hydrogens on the ring is smaller. Therefore, it appears that protonation of the Schiff's bases increases the electron withdrawing nature of the C=N group but that the charge does not delocalize to a large extent into the ring system. Similar results were observed by Ward et al., (1983) in the study of heme a Schiff's base models.

CHAPTER III

RAMAN AND INFRARED STUDIES

A.1 Instrumentation

Raman spectra were obtained by utilizing two different laser light sources. For n-benzylidene-n-butylamine and derivatives, spectra were obtained with the 514.5 nm line of a Spectra Physics 165 argon-ion laser. For 2-naphthalidene-n-butylamine, 9-anthralidene-n-butylamine and derivatives, $\lambda ex = 647.1$ nm from a Spectra-Physics 165 Krypton-ion laser was used. For the latter species, fluorescence from the samples necessitated the use of the larger wavelength exciting line. The Raman spectrometer used in the experiments was a Spex 1401 double monochromator together with its related electronics. The solutions for Raman studies were .25 M of the species of interest in methylene chloride or chloroform and a static arrangement was used. A scan speed of 20 cm^{-1}/minute, and a time constant of 1 second were used to record all the spectra. The delta frequency position was calibrated by using benzene as the standard before each experiment.

For the infrared spectra, solutions of 0.05 M of the aromatic aldehydes, aromatic Schiff's bases and derivatives

were prepared in chloroform. The I.R. spectra were obtained with a Perkin-Elmer 283B infrared spectrophotometer at a resolution of 2 cm^{-1}.

In general, the purity of the samples, as judged by NMR, I.R. and Raman spectroscopy, was good although the samples deteriorated in storage, the protonated and deuterated Schiff's bases deteriorated at a faster rate than was the case with the unprotonated Schiff's bases.

A.2 N-benzylidene-n-butylamine and Derivatives

N-benzylidene-n-butylamine and derivatives were prepared as described in Chapter II. The Raman spectra of 0.25 M solutions of benzaldehyde, unprotonated, protonated and deuterated Schiff's bases in methylene chloride or chloroform were obtained with a $\lambda ex = 514.5$ nm line. The spectral slit width used was 2 cm^{-1} resolution, the laser output was between 75-80 mW. Other spectral conditions were set as follows: range 1×10^5 count/sec; PMT voltage 1800 v; scan speed, 20 cm^{-1}/min; time constant, 1 sec; and chart speed, 1 cm/min. Before recording the spectra, the imine samples were irradiated for half an hour. The spectra were recorded within a resolution of 2 cm^{-1}.

Figure 7 shows the Raman spectra of 0.25 M methylene chloride solutions of benzaldehyde, n-benzylidene-n-butylamine, protonated and deuterated Schiff's base derivatives. Figures 8 and 9 show the Raman and infrared spectra of the

Figure 7. Raman spectra of Benzaldehyde (BCHO), N-Benzylidene-n-butylamine (BnBI), N-Benzylidene-n-butylammonium ion ($BnBIH^+$) and N-Benzylidene-n-butyl-deuteroammonium ion ($BnBID^+$) in methylene chloride.

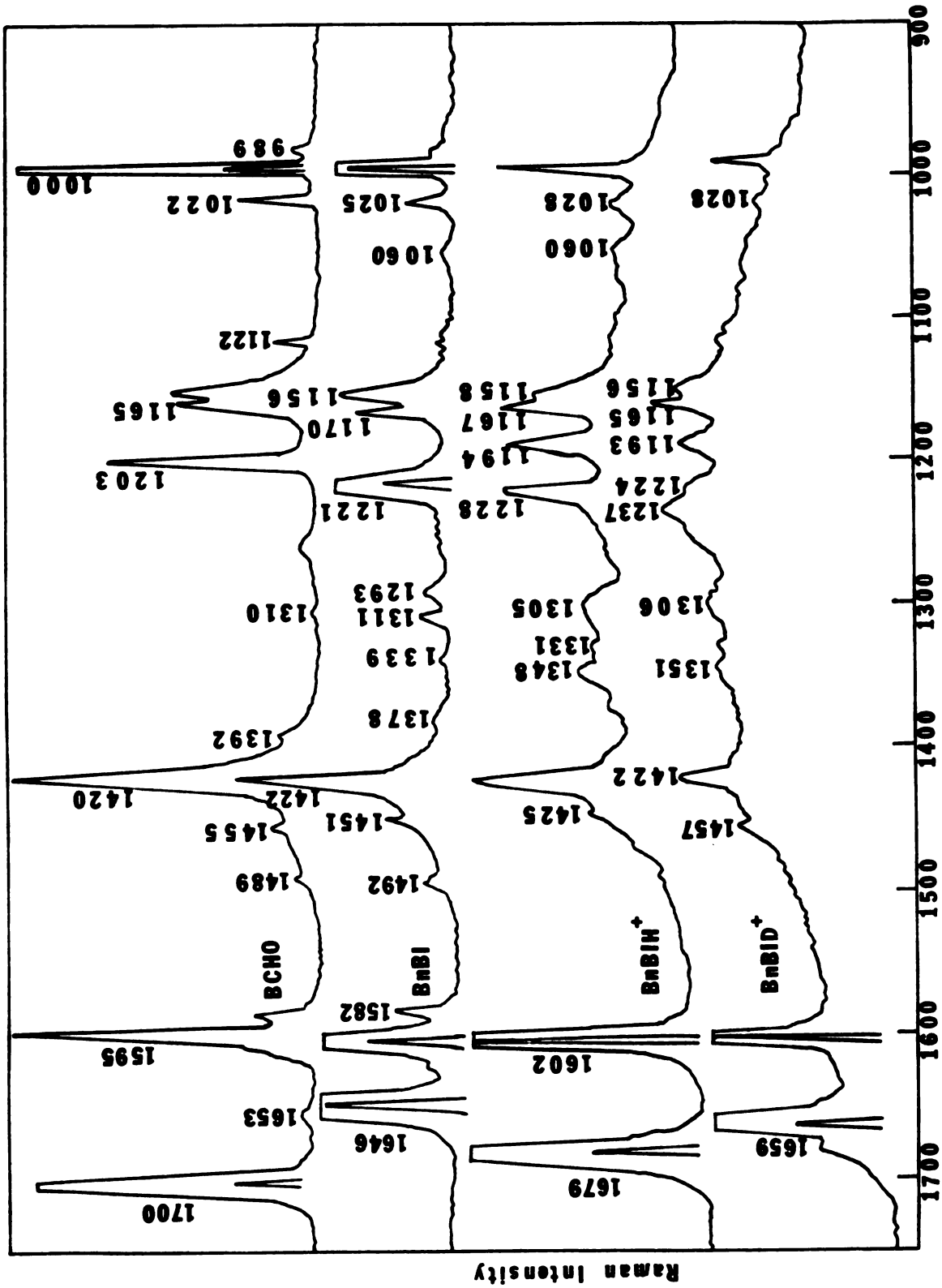

Raman Intensity
Δ (cm⁻¹)
900
1000
1100
1200
1300
1400
1500
1600
1700
BCHO
BnBI
BnBIH⁺
BnBID⁺
1700
1653
1595
1582
1646
1489
1492
1455
1451
1422
1420
1392
1378
1339
1311
1293
1310
1221
1203
1170
1165
1156
1122
1060
1025
1022
1000
989
1659
1602
1679
1457
1425
1422
1351
1348
1331
1306
1305
1237
1228
1224
1193
1194
1165
1167
1156
1158
1028
1060
1028

Figure7

Figure 8. Raman spectra of N-Benzylidene-n-butylamine (BnBI), N-Benzylidene-n-butylammonium ion ($BnBIH^+$) and N-Benzylidene n-butyldeuteroammonium ion ($BnBID^+$) in chloroform.

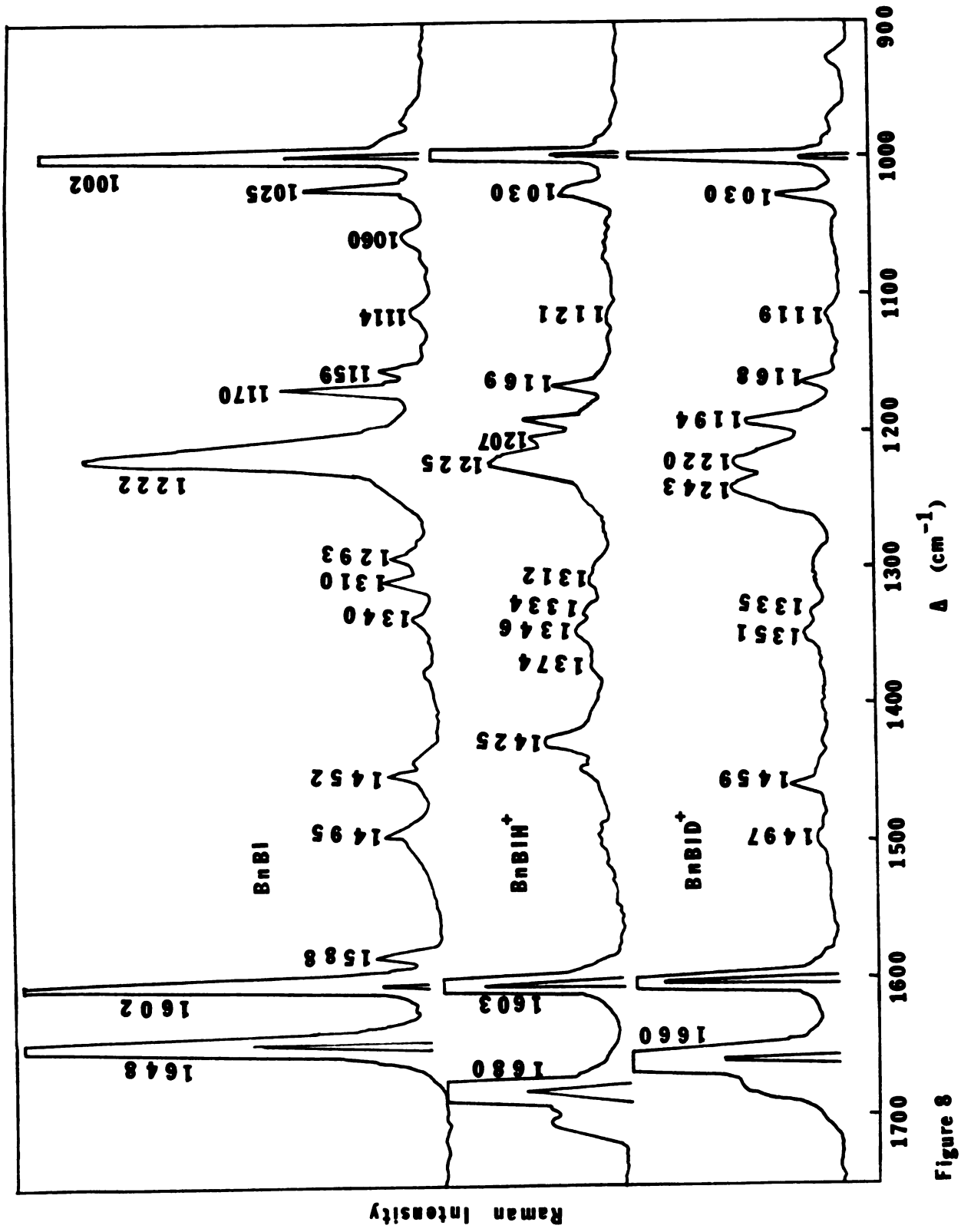

Raman Intensity
BnBI
BnBIH+
BnBID+
1648
1602
1588
1495
1452
1340
1310
1293
1222
1170
1159
1114
1060
1025
1002
1680
1603
1425
1374
1346
1334
1312
1225
1207
1169
1121
1030
1660
1597
1459
1351
1335
1243
1220
1194
1168
1119
1030
1700
1600
1500
1400
1300
1200
1100
1000
900
Δ (cm-1)

Figure 8

Figure 9. Infrared spectra of N-Benzylidene-n-butylamine (BnBI), N-Benzylidene-n-butylammonium ion ($BnBIH^+$) and N-Benzylidene-n-butyldeutero-ammonium ion ($BnBID^+$) in chloroform.

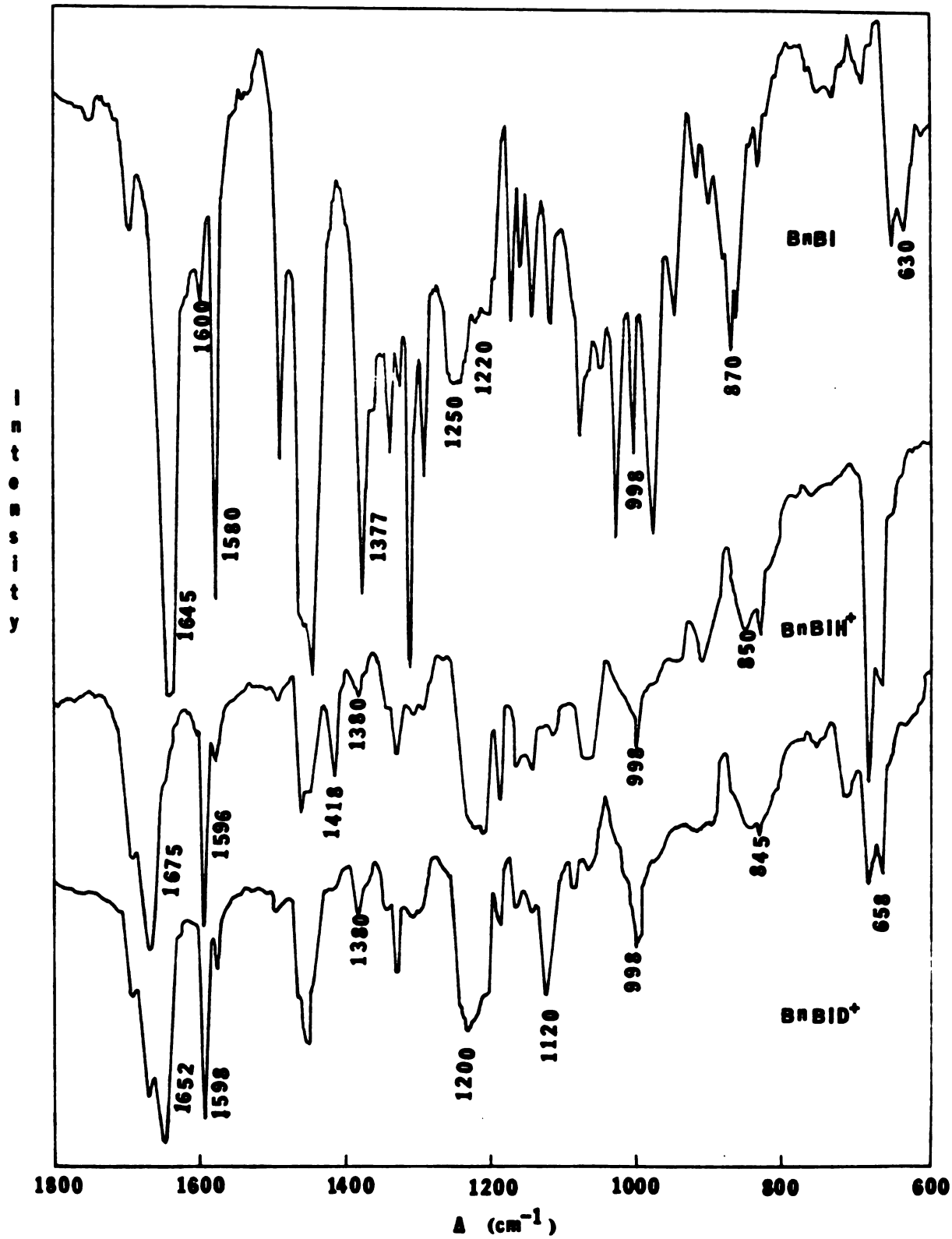

BnBI
BnBIH+
BnBID+
1645
1600
1580
1377
1250
1220
998
870
630
1675
1596
1418
1380
998
850
1652
1598
1380
1200
1120
998
845
658
1800
1600
1400
1200
1000
800
600
A (cm-1)

Figure 9

same Schiff's base in chloroform solutions. The frequency assignments for the Schiff's bases and derivatives are shown in Table III. The work of Zwarich et al., (1971) on benzaldehyde provided the main assignments for the ring and related vibrational motion of the imines. Thus, the band at 1203 cm^{-1} is assigned to the vibrational mode between the aldehyde group and the benzyl group in C_6H_5-CHO. This frequency is absent from the Raman spectra of the Schiff's base, in methylene chloride solutions a new band appears at 1221 cm^{-1}, being replaced by a band at 1228 cm^{-1} and at 1224 cm^{-1} upon protonation and deuteration, respectively. Therefore, this frequency motion may be assigned as ($C_6H_5CH=NR$), ($C_6H_5CH=\overset{\oplus}{N}HR$) and ($C_6H_5CH=\overset{\oplus}{N}DR$). The same observations can be made for the Raman and I.R. spectra of Schiff's base on chloroform solutions, but in this case there is some overlap between a solvent band and the $C_6H_5CH=NR$ band.

Upon protonation of the Schiff's base, the N-H bending motion is assigned to 1423 cm^{-1} in Raman and to 1418 cm^{-1} in the I.R. because in the unprotonated or in the deuterated spectra this band is absent. In addition, it is near the N-H bending mode region observed for protonated all-trans retinal Schiff bases by Massing et al., (1982) and Aton et al., (1980). This band cannot be observed clearly in methylene chloride solutions due to overlap with the solvent band. In a similar manner, the I.R. band at 1121 cm^{-1} in deuterated Schiff's bases was assigned to the

Table III. Raman and Infrared Frequencies for n-benzylidene-n-butylamine (BnBI), n-benzylidene-n-butylammonium ion ($BnBIH^+$) and n-benzylidene-n-butyldeutero ammonium ion ($BnBID^+$) in chloroform and methylene chloride.

BCHO/$CHCl_3$		BnBi pure	BnBI/	$BnBIH^+$/ CH_2Cl_2	$BnBID^+$/ CH_2Cl_2	BnBI/$CHCl_3$		$BnBIH^+/CHCl_3$		$BnBID^+/CHCl_3$		Assignment
IR	Raman	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
						630m		658m		652m		ν_{23}
650ms						642m		678m		678m		ν_{22}
										705m		
834s								828m		828m		ν_1
						870w		850m		845m		
						865ms						
						948mw		948mw		948mw		chain
						978mw		978mw		978mw		
1006s	1000s	1002s	1002s	1002s	1002s	1000m	1002s	998m	1002s	998m	1002s	ν_{12}
	1022m	1025m	1025m	1028m	1028m	1025m	1026m	1025m	1030m	1025m	1030m	ν_{19a}
		1060w	1060w	1059w	1059w		1060w		1059vw		1059	ν_{C-C} chain
1074w	1075w					1076w		1055w		1065w		ν_{19b}
										1084w		
							1114w					
	1122w								1121vw	1120ms	1119w	ν_{ND} bending

Table III Continues.

Table III Continued.

BCHO/$CHCl_3$		BnBI pure	BnBI/	$BnBIH^+$/ CH_2Cl_2	$BnBID^+$/ CH_2Cl_2	BnBI/$CHCl_3$		$BnBIH^+/CHCl_3$		$BnBID^+/CHCl_3$		Assignment
IR	Raman	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
	1156m	1157s	1156m	1158	1156	1158w	1157m	1160w		1162w		
1170m	1165m	1168m	1170m	1167m	1165m		1170m		1169m		1168w	ν_{9b}
				1194m	1193m				1194ms		1194m	
1204s	1203s											$\nu_{(\phi\text{-CHO})}$
		1121vs	1221s	1228m	1224mw	1220ms	1225vs	1225m	1228m	1220m	1220m	$\nu_{(\phi\text{-C=N-R})}$
							1222s		1222m		1222m	solvent
1294w		1293w	1293w	1294w	1294w	1290w	1293w	1295w	1294w	1295w	1294w	ν_{14}
				1305w	1306w				1306w		1306w	
1313m	1310w	1310vw	1311vw	1311vw	1310vw	1310w	1310w	1309w	1312w	1309w	1311w	ν_3
				1331w	1334w				1334w		1335w	
		1339w	1339w				1340w					
				1348w	1351w				1346w		1351w	
		1378w	1378vw	1378vw	1379vw	1377ms	1378vw	1380mw	1374vw	1380mw	1374vw	ν_{CH} imine
1394w	1392w											$_{CH}$ aldehyde
	1420s		1422m	1422m	1422m							solvent
				1425m		1418m	1425m					ν_{N-H} bending
		1440vw	1440vw				1440w		1440w		1440w	
1458m	1455w	1451w	1451w	1450w		1448s	1452w	1450s	1459w	1451s		ν_{18b}

Table III Continues.

Table III Continued.

BCHO/$CHCl_3$		BnBI pure	BnBI/	$BnBIH^+$/ CH_2Cl_2	$BnBID^+$/ CH_2Cl_2	BnBI/$CHCl_3$		$BnBIH^+/CHCl_3$		$BnBID^+/CHCl_3$		Assignment
IR	Raman	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
	1156m	1157s	1156m	1158	1156	1158w	1157m	1160w		1162w		
1170m	1165m	1168m	1170m	1167m	1165m		1170m		1169m		1168w	ν_{9b}
				1194m	1193m				1194ms		1194m	
1204s	1203s											$\nu_{(\phi\text{-CHO})}$
		1121vs	1221s	1228m	1224mw	1220ms	1225vs	1225m	1228m	1220m	1220m	$\nu_{(\phi\text{-C=N-R})}$
							1222s		1222m		1222m	solvent
1294w		1293w	1293w	1294w	1294w	1290w	1293w	1295w	1294w	1295w	1294w	ν_{14}
				1305w	1306w				1306w		1306w	
1313m	1310w	1310vw	1311vw	1311vw	1310vw	1310w	1310w	1309w	1312w	1309w	1311w	ν_3
				1331w	1334w				1334w		1335w	
		1339w	1339w				1340w					
				1348w	1351w				1346w		1351w	
		1378w	1378vw	1378vw	1379vw	1377ms	1378vw	1380mw	1374vw	1380mw	1374vw	ν_{CH} imine
1394w	1392w											ν_{CH} aldehyde
	1420s		1422m	1422m	1422m							solvent
				1425m		1418m	1425m					ν_{N-H} bending
		1440vw	1440vw				1440w		1440w		1440w	
1458m	1455w	1451w	1451w	1450w		1448s	1452w	1450s	1459w	1451s		ν_{18b}

Table III Continues.

Table III Continued.

BCHO/$CHCl_3$		BnBI pure	BnBI/	$BnBIH^+$/ CH_2Cl_2	$BnBID^+$/ CH_2Cl_2	BnBI/$CHCl_3$		$BbBIH^+/CHCl_3$		$BnBID^+/CHCl_3$		Assignment
IR	Raman	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
					1457w	1470m		1461m		1460m	1459m	
1490m	1489w	1492w	1492w			1495m	1493w	1494w	1495w	1495w	1497w	ν_{18b}
1588m	1584w	1582w	1582w			1580s	1582w	1580w		1580w		ν_{8a}
1600s	1595s	1600s	1602vs	1602vs	1601vs	1600s	1602s	1596s	1603	1598s	1601	ν_{8a}
		1646vs	1646vs	1680vs	1660vs	1645s	1646s	1675s	1680s	1652s	1660s	$\nu_{C=N}$
1657w	1653w											combination
1700s	1700s											$\nu_{C=O}$

vs = very strong.
s = strong.
ms = medium strong.
m = medium.
w = weak.
vw = very weak.

N-D bending mode. However, a band at 1237 cm^{-1} in the I.R. spectra and at 1243 cm^{-1} in the Raman spectra behave in the same way. However, for br_{570} and br_{603}, the difference between the frequency of the CNH bending and the CND bending is 370 cm^{-1} (Massing et al., 1982). Therefore, it appears that the former frequency and not the latter can be assigned as the N-D bending mode.

Another important change occurs in the band at 1696 cm^{-1} assigned to the C=O stretching frequency in benzaldehyde. This band, upon formation of the imine, is shifted to 1648 cm^{-1} and is assigned to the C=N stretching frequency. Upon protonation and deuteration this frequency mode shifts to 1680 cm^{-1} and to 1660 cm^{-1}, respectively. This is in agreement with the previous observed increase in the C=N stretching frequency in protonated and deuterated Schiff's bases (Aton et al., 1980; Marcus et al., 1979 and Ward et al., 1981).

It is known that the Raman intensity of certain molecular vibrations depends on the conjugation. Schmid et al., (1977) investigated the Raman intensity changes of the ν_8 mode (in compounds of the type C_6H_5COX) with changes in the electron withdrawing character of the group X, and indicate that an increase in the ν_8 mode intensity is related to an increase in the electron withdrawing character of the group X. Also, Schmid et al., (1983), investigated the Raman intensity of the phenyl ν_8 mode changes with the angle of twist in biphenyls. Therefore,

it can be assumed that for phenylimine the intensity of the ν_8 mode is indicative of the extent of conjugation. Therefore, it is possible to deduce that protonation and deuteration of phenyl Schiff's base changes to some extent the state of conjugation between the imine group and the ring. Since there is a relative intensity variation of the ν_8 frequency mode with respect to the C=N frequency mode.

A.3 2-Naphthalidene-n-butylamine and Derivatives

2-Naphthalidene-n-butylamine and derivatives were prepared as described in Chapter II. The Raman spectra were obtained with a $\lambda ex = 647.1$ nm and after an irradiation period of 3 hours at a power of 500-600 mw. The spectral slit width used was 3 cm^{-1} resolution, the range 1×10^4 count/sec and the PMT voltage was 1860 v. The other conditions were the same as in N-benzylidene-n-butylamine.

Figures 10 through 13 show the Raman and infrared spectra of the corresponding Schiff bases in methylene chloride and chloroform respectively.

The frequency assignments were made based on the work of Sharma et al., (1974) for α and β naphthaldehydes. Other bands were assigned by comparing with N-benzylidene derivatives. Table IV contains the more probable assignments for the observed vibrational modes. As expected, the greatest frequency changes were observed

Figure 10. Raman spectra of 2-Naphthaldehyde (NapCHO) and 2-Naphthalidene-n-butylamine (NapBI) in methylene chloride.

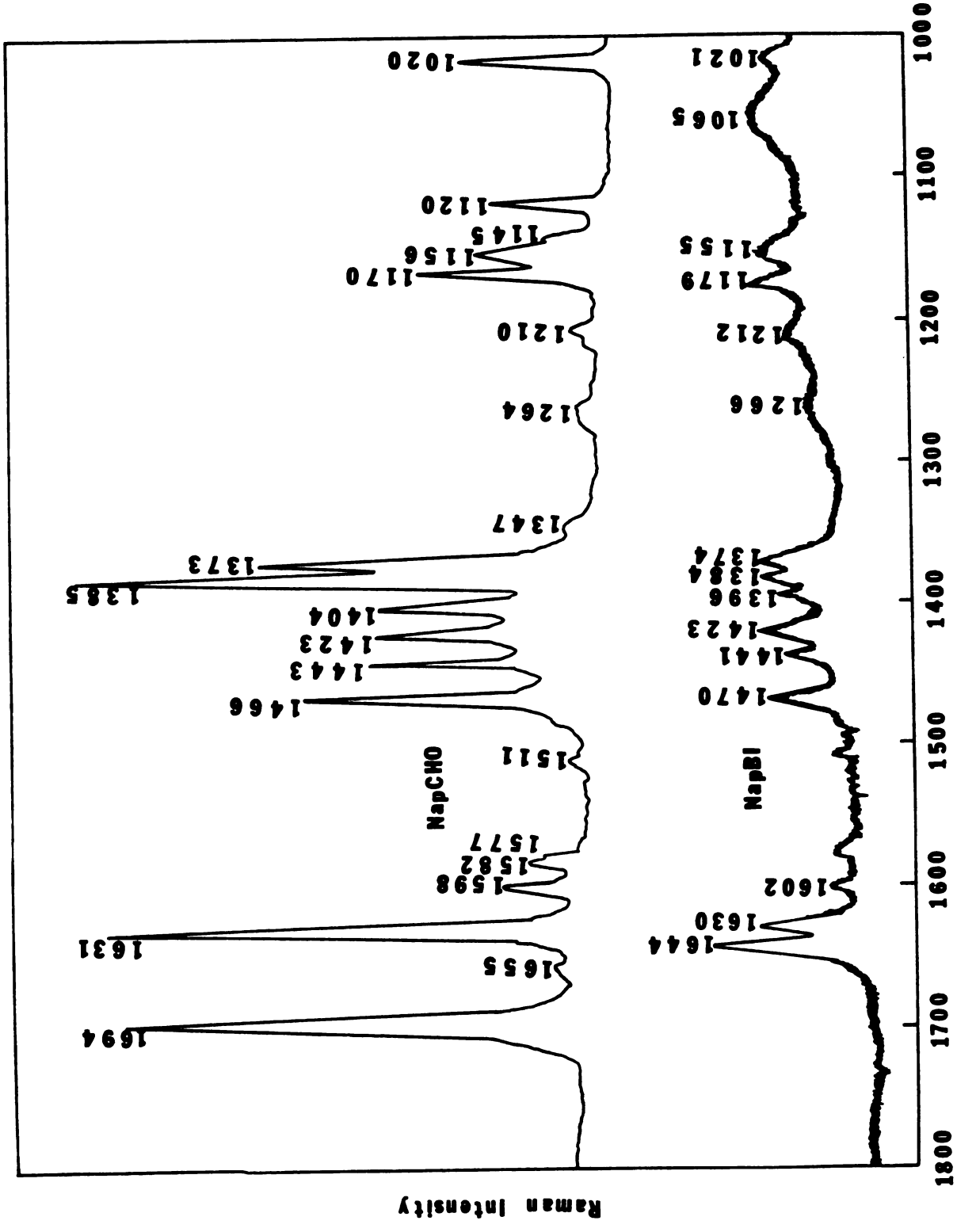

1694
1631
1655
1598
1582
1577
1511
1466
1443
1423
1404
1385
1373
1347
1264
1210
1170
1156
1145
1120
1020
1021
1065
1155
1179
1212
1266
1374
1384
1396
1423
1441
1470
1602
1630
1644
NapCHO
NapBI
1800
1700
1600
1500
1400
1300
1200
1100
1000
Raman Intensity
Δ (cm⁻¹)

Figure 10

Figure 11. Raman spectra of 2-Naphthalidene-n-butylamine (NapBI), 2-Naphthalidene-n-butylammonium ion ($NapBIH^+$) and 2-Naphthalidene-n-butyldeuteroammonium ion ($NapBID^+$) in methylene chloride.

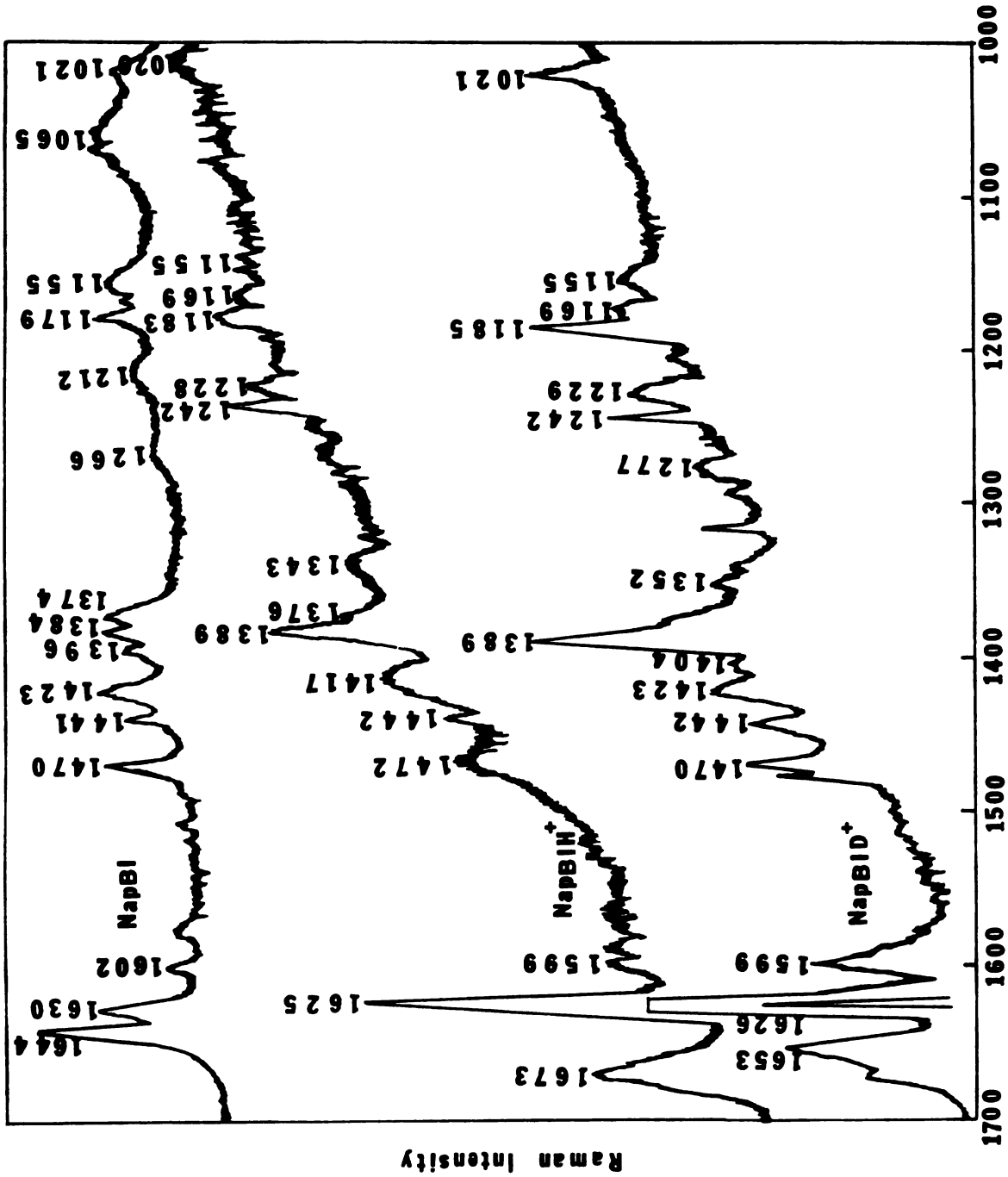

NapBI
NapBIH+
NapBID+
1644
1630
1602
1470
1441
1423
1396
1384
1374
1266
1242
1228
1212
1183
1179
1169
1155
1065
1028
1021
1673
1625
1599
1472
1442
1417
1389
1376
1343
1653
1626
1599
1470
1442
1423
1404
1389
1352
1277
1242
1229
1185
1169
1155
1021
1000
1100
1200
1300
1400
1500
1600
1700
Δ (cm-1)
Raman Intensity

Figure11

Figure 12. Raman spectra of 2-Naphthalidene-n-butylamine (NapBI), 2-Naphthalidene-n-butylammonium ion ($NapBIH^+$) and 2-Naphthalidene-n-butyl deuteroammonium ion ($NapBID^+$) chloroform solutions.

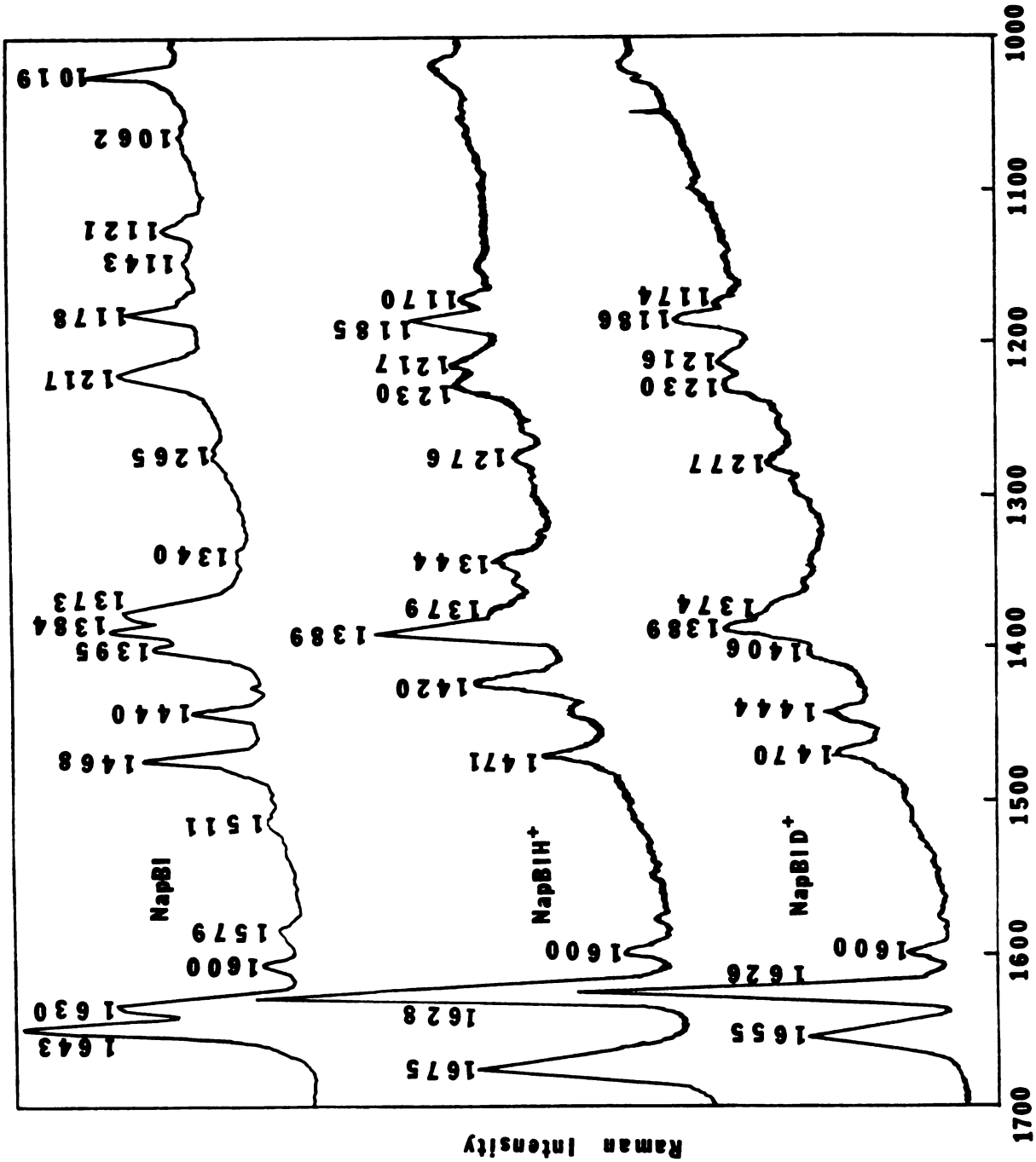

NapBI
1643
1630
1600
1579
1511
1468
1440
1395
1384
1373
1340
1265
1217
1178
1143
1121
1062
1019
NapBIH+
1675
1628
1600
1471
1420
1389
1379
1344
1276
1230
1217
1185
1170
NapBID+
1655
1626
1600
1470
1444
1406
1389
1374
1277
1230
1216
1186
1174
1700
1600
1500
1400
1300
1200
1100
1000
Δ (cm-1)
Raman Intensity

Figure 12

Figure 13. Infrared spectra of 2-Naphthalidene-n-butyl amine (NapBI), 2-Naphthalide-n-butylammonium ion ($NapBIH^+$) and 2-Naphthalidene-n-butyl deuteroammonium ion ($NapBID^+$) chloroform solutions.

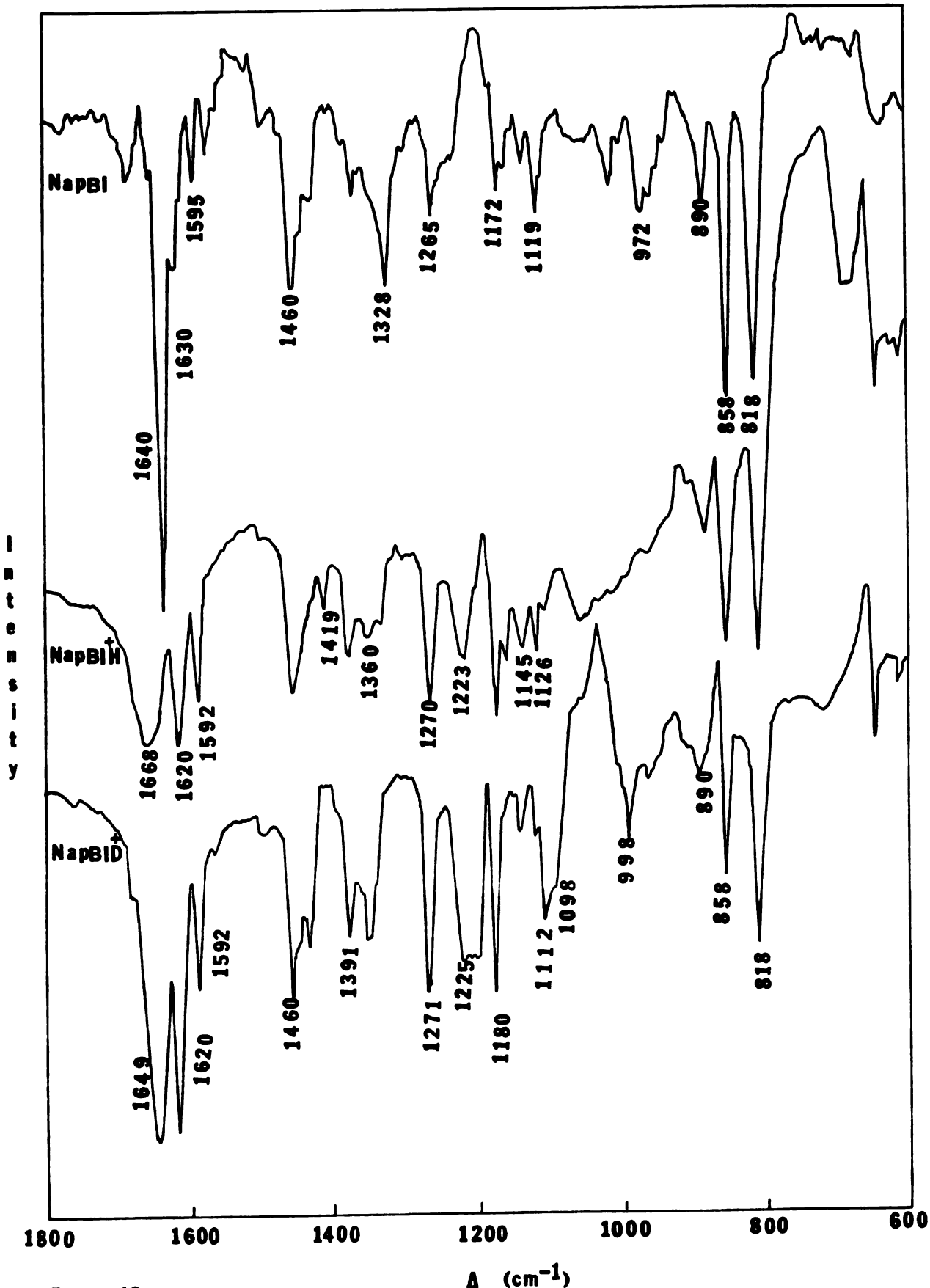

NapBI
1640
1630
1595
1460
1328
1265
1172
1119
972
890
858
818
NapBIH+
1668
1620
1592
1419
1360
1270
1223
1145
1126
NapBID+
1649
1620
1592
1460
1391
1271
1225
1180
1112
1098
998
890
858
818
1800
1600
1400
1200
1000
800
600
Δ (cm-1)

Figure13

Table IV. Raman and infrared frequencies of 2-naphthalidene-n-butylamine and derivatives.

NapCHO/CH_2Cl_2		NapBI/ CH_2Cl_2	NapBIH$^+$/ CH_2Cl_2	NapBID$^+$/ CH_2Cl_2	NapBI/CH_2Cl_2		NapBIH$^+$/CH_2Cl_2		NapBID$^+$/CH_2Cl_2		Probable Modes of Vibration
IR	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
620w											skeletal distortion
					640w		652m		652m		
							685m				
									728w		
816ms					818ms		815ms		815ms		νCH bending
858ms					858ms		860ms		860m		νCH bending
880w											skeletal distortion
896w					890w		890w		890w		νCH bending
950w					960w						νCH bending
					972w		970w		968w		
									998m		
1020w	1020m	1019m	1019w	1019w	1020w	1021w	1020w	1020w	1020w	1021w	νCH bending
		1058b					1062b				
									1112m		νN-D bending
1118m	1120m	1123w			1119w	1121w	1126w		1126w		νCH bending

Table IV Continues.

Table IV Continued.

NapCHO/CH_2Cl_2		NapBI/ CH_2Cl_2	$NapBIH^+$/ CH_2Cl_2	$NapBID^+$ CH_2Cl_2	NapBI/CH_2Cl_2		$NapBIH^+/CH_2Cl_2$		$NapBID^+/CH_2Cl_2$		Probable Modes of Vibration
IR	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
1150w	1157m	1155w	1156w	1155w	1160w		1165w		1160w		νCH bending
1170m	1170s							1169w		1169w	
		1179m	1185m	1185ms	1175m		1180ms	1185m	1180ms	1186m	
1220w	1218w								1211m		νCH bending
						1221w		1221v		1221w	solvent ($CHCl_3$)
			1228m	1229m			1223ms	1230	1225m	1230	
1258m	1264w	1266w	1278vw	1277w	1265m	1265w	1270ms	1276	1271ms	1277	skeletal distortion
1348m	1347w				1330m	1340vw	1340w	1344w			νC-C stretch
							1350w		1352m		
	1373s	1374m	1376m	1375m	1378w	1373m	1360w	1379w		1374w	νC-C stretch
	1385vs	1384m	1389s	1389s		1395m	1385m	1389m	1391m	1389m	νC-C stretch
	1404s			1404w						1406v	νC-C stretch
			1417				1419	1420			νN-H
	1423s	1423m	1423	1423m							solvent (CH_2Cl_2)
1440w	1443s	1441m	1442w	1442w	1438w	1440m	1440vw	1441w	1438	1444w	νC-C stretch

Table IV Continues.

Table IV Continued.

NapCHO/CH_2Cl_2		NapBI/ CH_2Cl_2	$NapBIH^+$/ CH_2Cl_2	$NapBID^+$ CH_2Cl_2	NapBI/CH_2Cl_2		$NapBIH^+/CH_2Cl_2$		$NaBID^+/CH_2Cl_2$		Probable Modes of Vibration
IR	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
1460m	1466s	1470m	1472m	1470m	1460m	1468ms	1461m	1471ms	1463m	1470m	νC-C stretch
1152w	1510w	1511vw			1500w	1511w	1505	1511w	1508w	1510vw	νC-c stretch
1578w	1577w	1579w	1588vw	1590vw							νC-C stretch
1595m	1598m	1602m	1599w	1599w	1595m	1600w	1592m	1600w	1592m	1600w	νC-C stretch
1625s	1631vs	1630vs	1629s	1626s	1630m	1630s	1620s	1628s	1620s	1626s	νC-C stretch
		1644vs	1673s	1653vs	1640vs	1643vs	1668s	1675s	1649s	1655s	νC=N
1690s	1694vs										νC=O

for the C=N stretching frequency upon protonation and deuteration. Thus, for example, there was a change from 1644 cm^{-1} (Schiff's base) to 1673 cm^{-1} (protonated Schiff's base) and to 1653 cm^{-1} (deuterated Schiff's base) respectively. In addition, some small changes on the C-C stretching frequency of the ring were observed. These, together with variations in the relative intensities of the bands at 1630 cm^{-1} with respect to the C=N stretching frequency, may indicate, as in N-benzylidene-n-butylamine derivatives, a change in the state of conjugation between the aromatic system and the C=N group upon protonation of the Schiff's base.

A.4 9-Anthralidene-n-butylamine and Derivatives

9-Anthralidene-n-butylamine and derivatives were prepared as described in Chapter II. The Raman spectra were obtained with $\lambda ex = 647.1$ nm with a period of irradiation of 5 hours at a power of 500-600 mw. The other conditions were the same as in 2-naphthalidene-n-butylamine.

Figures 14 through 17 show the Raman and infrared spectra of the imine and its derivative in methylene chloride and chloroform respectively. The frequency assignments were based on the work of Ohta et al., (1977) related to vibronic coupling studies on anthracene. Table V presents the more probable assignments for some

Figure 14. Raman spectra of 9-Anthraldehyde (AnCHO) and 9-Anthralidene-n-butylamine (AnBI) in methylene chloride solutions.

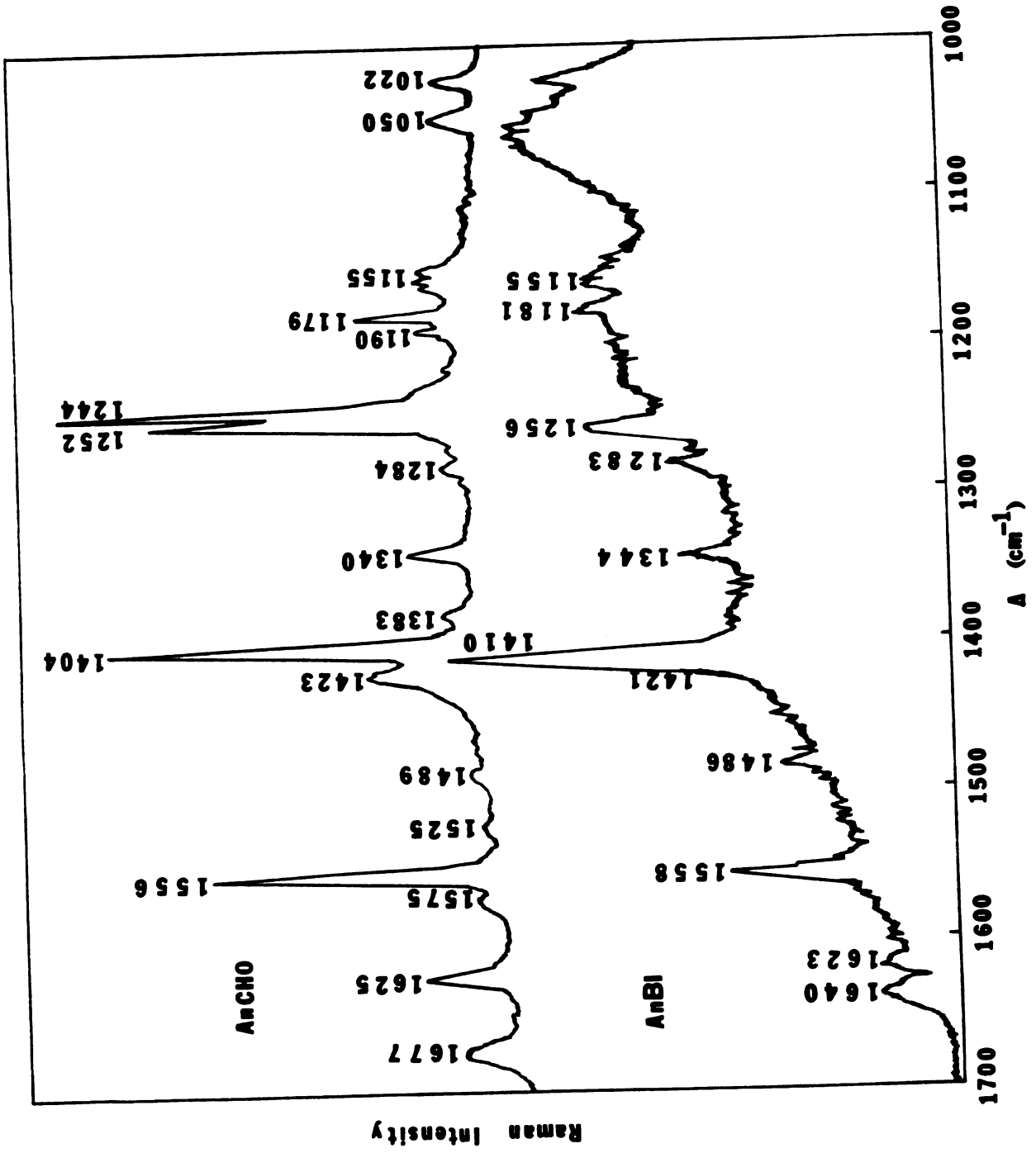

AnCHO
AnBI
1677
1625
1575
1556
1525
1489
1423
1404
1383
1340
1284
1252
1244
1190
1179
1155
1050
1022
1640
1623
1558
1486
1421
1410
1344
1283
1256
1181
1155
1000
1100
1200
1300
1400
1500
1600
1700
Δ (cm⁻¹)
Raman Intensity

Figure 14

Figure 15. Raman spectra of 9-Anthralidene-n-butylammonium ion ($AnBIH^+$) and 9-Anthralidenebutyldeuteroammonium ion ($AnBID^+$) in methylene chloride solutions.

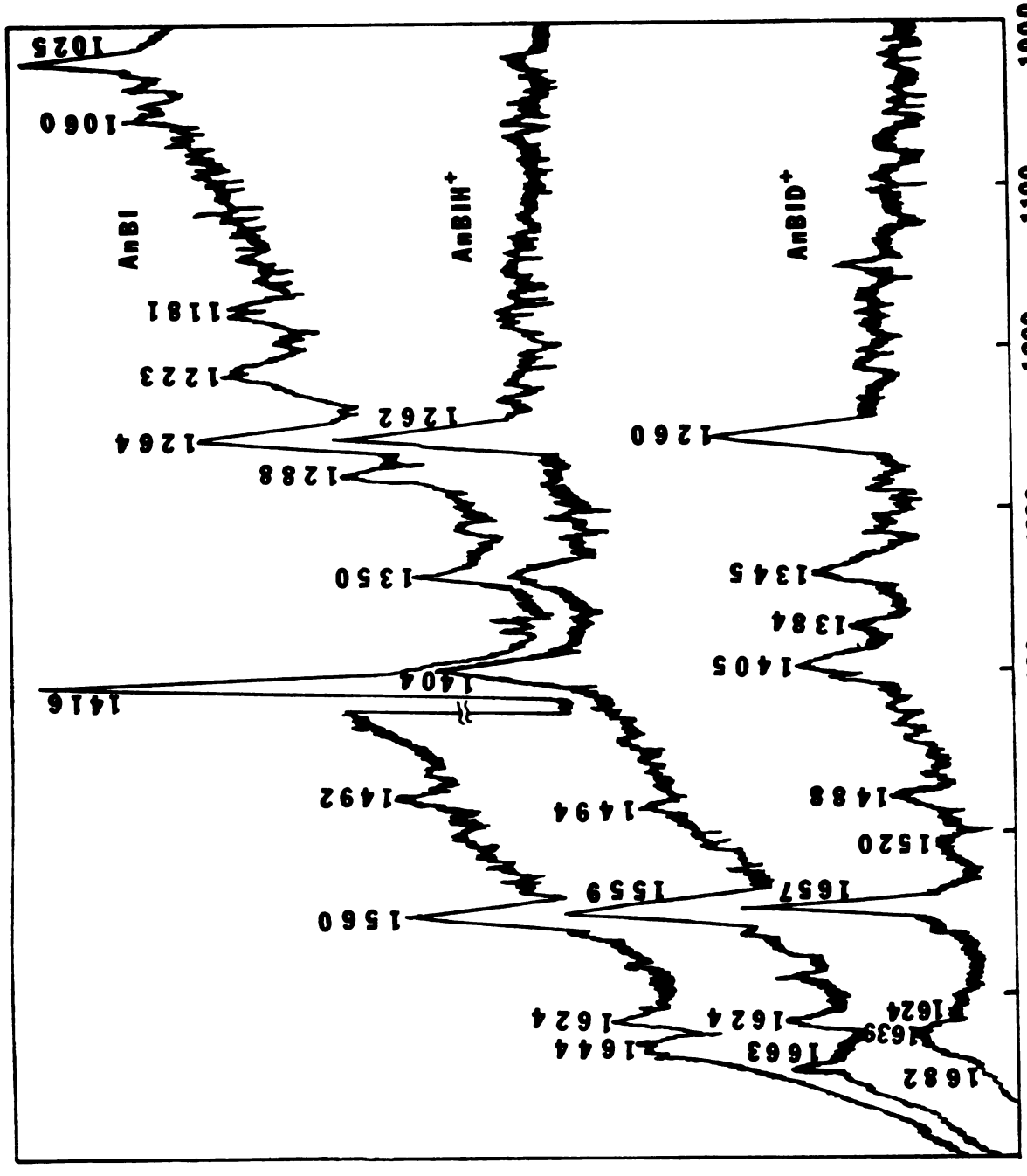

AnBI
AnBIH+
AnBID+
1025
1060
1181
1223
1262
1264
1288
1350
1404
1416
1492
1494
1560
1559
1624
1624
1644
1663
1639
1682
1260
1345
1384
1405
1488
1520
1657
1000
1100
1200
1300
1400
1500
1600
1700
Δ (cm-1)
Raman Intensity

Figure 15

Figure 16. Raman spectra of 9-Anthralidene-n-butylamine (AnBI), 9-Anthralidene-n-butylammonium ion ($AnBIH^+$) and 9-Anthralidene-n-butyldeuteroammonium ion ($AnBID^+$) in chloroform.

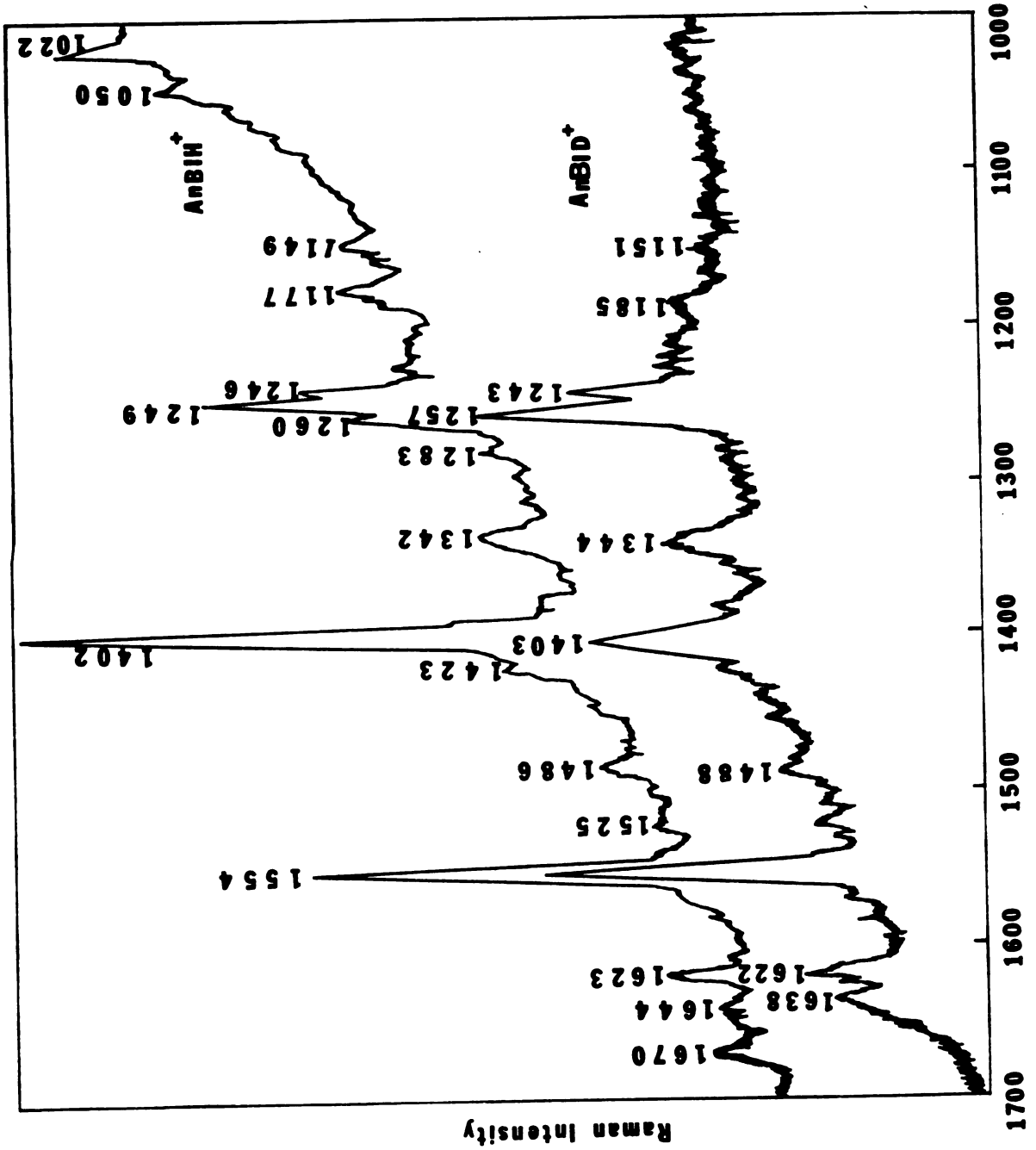

Raman Intensity
1700
1600
1500
1400
1300
1200
1100
1000
Δ (cm⁻¹)
AnBIH⁺
AnBID⁺
1670
1638
1644
1622
1623
1554
1525
1486
1488
1423
1403
1402
1344
1342
1283
1257
1260
1249
1243
1246
1185
1177
1151
1149
1050
1022

Figure16

Figure 17. Infrared spectra of 9-Anthralidene-n-butylamine (AnBI), 9-Anthralidene-n-butylammonium ion ($AnBIH^+$) and 9-Anthralidene-n-butyldeutero-ammonium ion ($AnBID^+$) in chloroform.

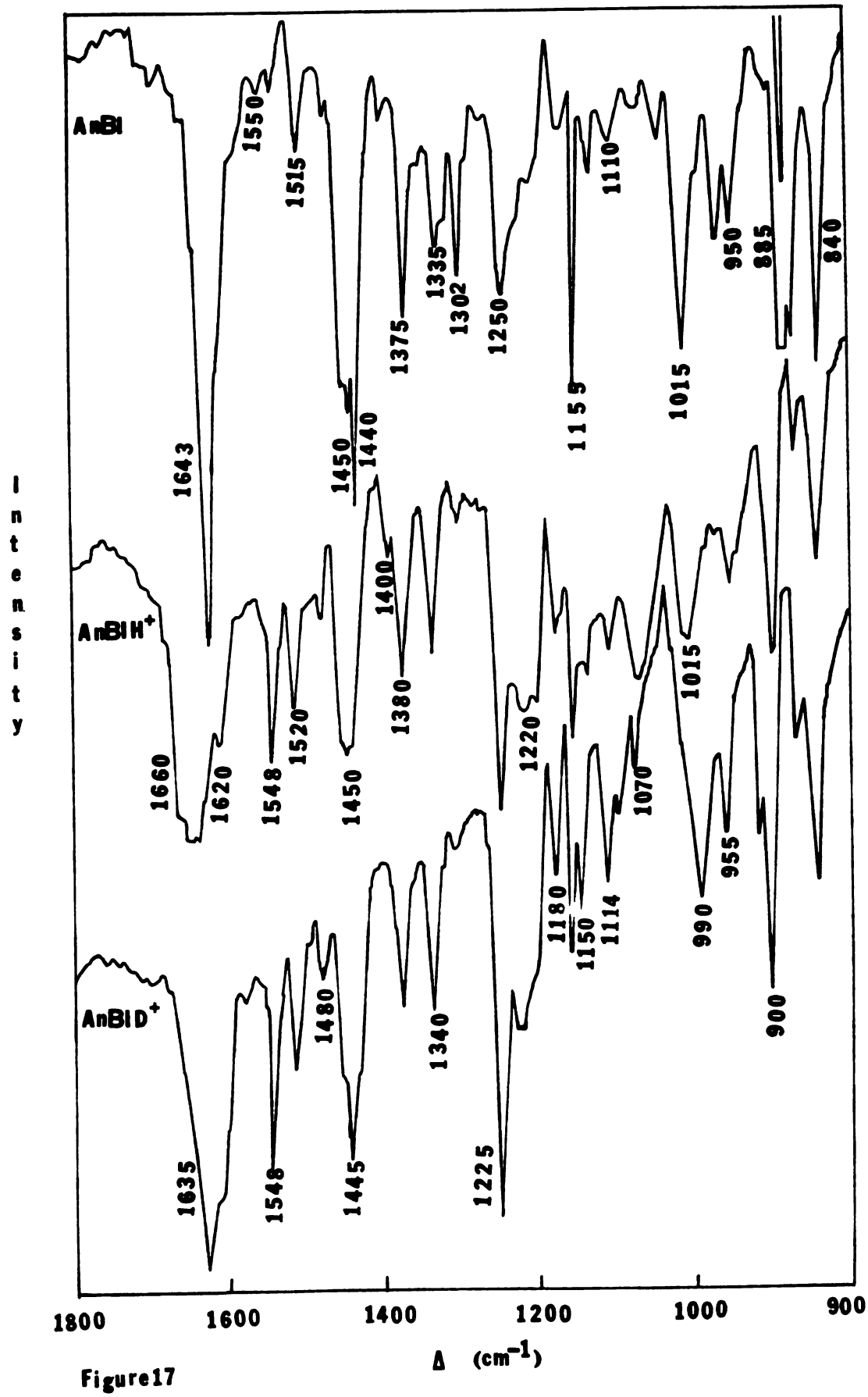

AnBI
1643
1550
1515
1450
1440
1375
1335
1302
1250
1155
1110
1015
950
885
840
AnBIH+
1660
1620
1548
1520
1450
1400
1380
1220
1180
1150
1114
1070
1015
990
955
900
AnBID+
1635
1548
1480
1445
1340
1225
1800
1600
1400
1200
1000
900
Δ (cm-1)
Intensity

Figure17

Table V. Raman and infrared frequencies of 9-anthralidene-n-butylamine and derivatives.

AnCHO		AnBI/ CH_2Cl_2	$AnBIH^+$/ CH_2Cl_2	$AnBID^+$/ CH_2Cl_2	AnBI/$CHCl_3$		$AnBIH^+$/$CHCl_3$		$AnBID^+$/$CHCl_3$		
IR	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
840w					840m		840		840m		νCH bending
870m					864m		862w		860w		νCH bending
900m					885vs		900vs		900vs		νCH bending
					910w				910w		
					950m		955s		955m		
					970m		974w				
1020w	1022w	1022w	1022w		1015s	1025w	1015s		990s		νCH bending
1048s	1050w				1050w	1050		1050w			
							1070m		1079m		
					1110w		1112w		1114ms		νND
					1145w		1140w				
									1150m		
1160m	1155w	1156w	1149w	1152w	1155s		1160m		1160m		
1175w	1179vw	1177m	1183w	1185w	1175w	1177w	1180m	1185w	1180m		
1205w					1205w		1205m		1205m		
1220w					1220w	1223m	1220w		1222m		
	1242m		1242	1242m							νCH_3I

Table V Continues.

Table V Continued.

AnCHO		AnBI/ CH_2Cl_2	$AnBIH^+$/ CH_2Cl_2	$AnBID^+$/ CH_2Cl_2	$AnBI/CHCl_3$		$AnBIH^+/CHCl_3$		$AnBID^+/CHCl_3$		
IR	Raman	Raman	Raman	Raman	IR	Raman	IR	Raman	IR	Raman	
1248s	1254	1256	1260s	1257s	1250s	1264s	1255s	1262s	1255s	1260s	
1280w	1284w	1283m	1283w	1279vw	1280w	1288m	1280w				
1305w					1305m		1310w		1310w		
1334m	1340w	1344m	1342m	1344m	1335 pph	1350w	1340m	1356m	1340m	1345m	νC-C stretch
1400w	1404s	1410s	1402s	1403s	1410w	1416s	1400w	1404s	1400w	1405m	
	1423m	1423m	1423m	1423m							solvent (CH_2Cl_2)
1440m					1440s		1450s		1445s		νC-C stretch
1485w	1489vw	1486w	1488w	1488w	1480w	1492w	1480w	1494w	1480w	1488w	νC-C stretch
1520w	1525vw	1521w	1525w	1525w	1515m		1520m		1520m	1520w	
1550s	1556s	1558m	1554s	1554m	1550w	1560m	1548s	1559s	1548s	1657m	νC-C stretch
1620w	1625m	1623m	1623m	1622m	1620m	1624m	1620m	1624m	1620m	1624w	νC-C stretch
		1640m	1670m		1643s	1744m	1660s	1663	1635s	1639m	νC=N
1670s	1674m										νC=O

of the observed frequencies. The C=N stretching frequency behaves as before, increasing in frequency upon protonation of the Schiff's base. However, the frequency corresponding to the N-H bending mode cannot be assigned since there is a very strong band in the 1400-1404 cm^{-1} region which may overlap the expected N-H bending frequency.

A.5 Benzophenone Schiff's Base and Derivatives

Benzophenone Schiff's base and derivatives were prepared as described in Chapter II. The Raman spectra were obtained with the excitation at 647.1 nm and the instrument conditions were the same as 9-anthralidene-n-butylamine. These are shown in Figures 18 and 19. The band observed at approximately 1600 cm^{-1} can be assigned as the analog to ν_8 in benzene. The frequency at 1656 cm^{-1} on benzophenone is characteristic of the C=O stretching frequency, while the frequencies at 1618 cm^{-1}, 1636 cm^{-1} and 1616 cm^{-1} are assigned to be the C=N stretching frequency of the unprotonated, protonated and deuterated Schiff's bases respectively.

Figure 18. Raman spectra of Benzophenone (bO) in chloroform.

Figure 19. Raman spectrum of Benzophenone Schiff's base (bSb), its protonated form ($bSbH^+$) and its deuterated form ($bSbD^+$) in chloroform.

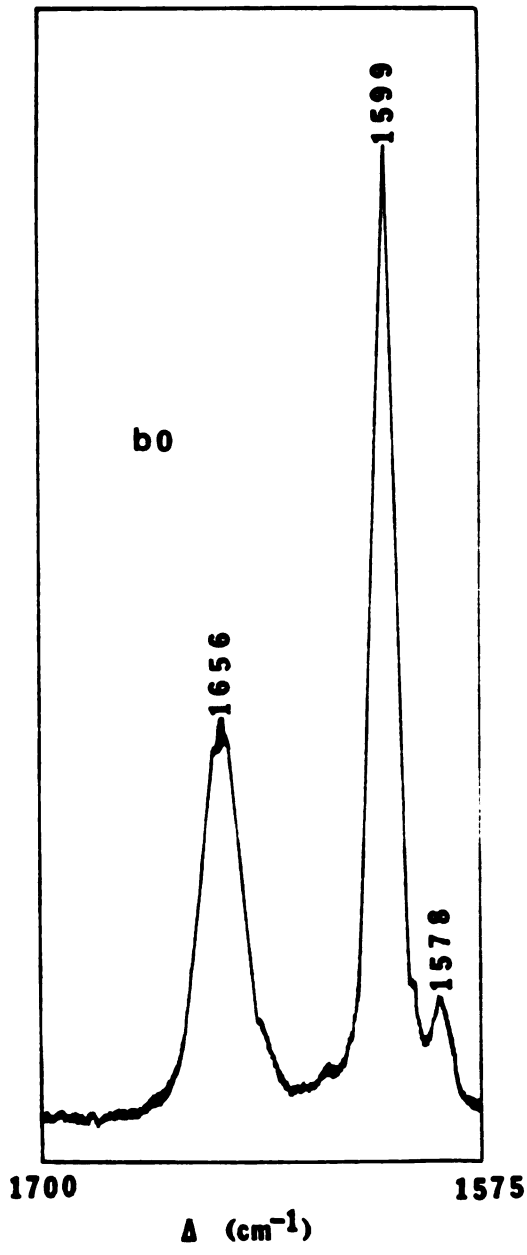


Figure 18

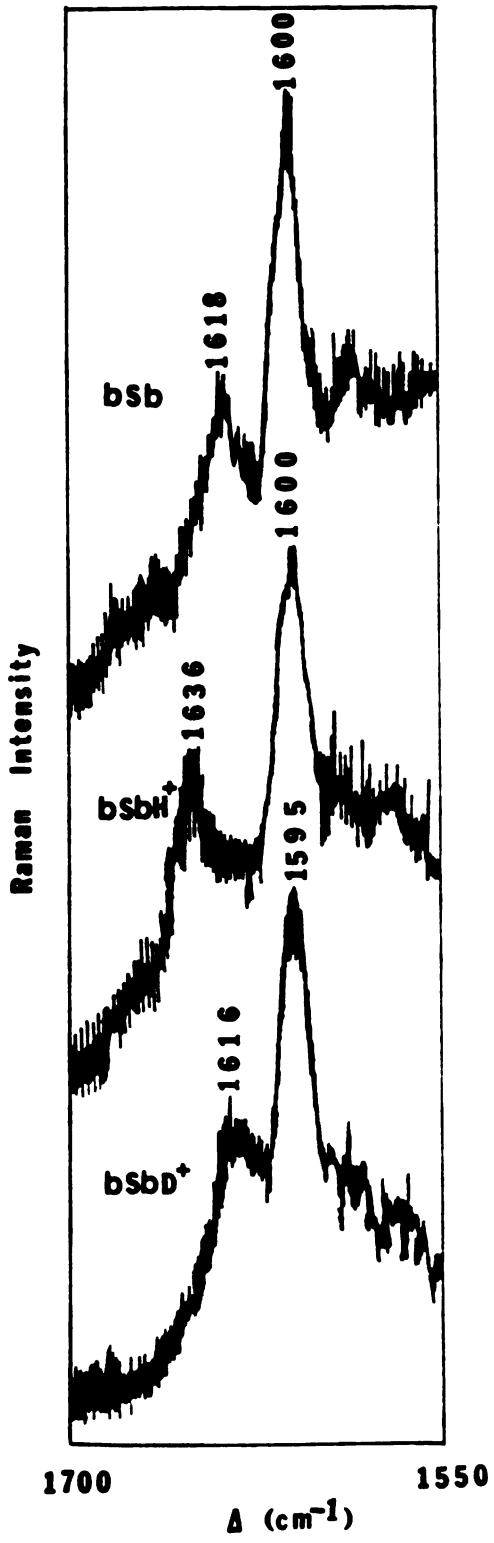


Figure 19

CHAPTER IV

SCHIFF'S BASES

A.1 Introduction

Schiff's base and protonated Schiff's base vibrational modes have been studied for at least the past three decades. Part of the interest in these species derives from the occurrence in biological systems of Schiff's base linkages, for example, in pyridoxal enzymes (e.g. Witkay and Beiler, 1954) and, more recently, in rhodopsin (e.g. Aton et al., 1980). Perhaps as a result, a systematic investigation of saturated, unsaturated and aromatic Schiff's bases and protonated Schiff's bases has not appeared. Rather most reports deal with compounds specific to the problem at hand. Thus, the C=N stretching frequency for saturated aldimines was assigned by Fabian et al., (1956), to the 1665-1674 cm^{-1} range which was extended by Steele (1964) to the 1665-1680 cm^{-1}. N-(n-propylidene)-n-propylamine, has an I.R. absorption at 1673 cm^{-1} (Fabian et al., 1956) while the simplest aldimine, methyleneimine, (Botschwina, 1974) has a C=N stretching frequency around 1642 cm^{-1}. The 31 cm^{-1} difference in the C=N stretching frequency between these

two imines could be due to the fact that for the CH_2NH species the C-C=N group structure is not present, whereas in propyleneimine it is. In methyleneimine, upon substitution of the hydrogen at the nitrogen by deuterium, the C=N stretching frequency decreases to 1629 cm^{-1} and upon N^{15} substitution this mode shifts to 1627 cm^{-1}. Christen et al., (1982), observed that when the hydrogens in methyleneimine are substituted by fluorine, the C=N stretching frequency increases to 1740 cm^{-1}, while substitution by chlorine decreases the frequency to 1728 cm^{-1}.

Aromatic aldimines of the type C_6H_5-CH=N-R exhibit a C=N stretch in the 1658-1629 cm^{-1} region, and in the 1637-1626 cm^{-1} range when the R group is substituted by a phenyl group (Fabian, 1956). Witkop et al., (1954) in a study of possible pyridoxal modes indicates a 1639-1626 cm^{-1} (Patai, 1970) range for aromatic Schiff's base models and a 1672-1646 cm^{-1} range for their salts. A further reduction of this mode to 1640-1610 cm^{-1} is obtained when the number of substituent phenyl rings increases.

In general, these reports show that the region over which the C=N stretching frequency occurs is relatively extensive, from 1600-1680 cm^{-1}. This, to some extent, suggests that the C=N stretch can be influenced by motions involving neighboring atoms. Therefore, the physical and chemical environment of the C=N group,

including such factors as the presence of electron donating or electron withdrawing substituents, conjugation effects, resonance effects and hydrogen bonding are the main determinants of the C=N stretching frequency variations. References such as Fabian (1956), Colthup et al., (1964) and Patai (1970) can be consulted for more details.

A.2 C=N Stretching Frequency in Unsaturated and Aromatic Schiff's Bases

The results indicate, as can be seen in Table VI, that the changes in C=N stretching frequency in unsaturated Schiff's bases follow the same trends as the carbonyl stretching frequency in aldehyde analogs. That is, as the number of unsaturated bonds increases, both the carbonyl group and the imine group decrease in their respective stretching frequencies. This behavior has been attributed to the mesomeric effect observed in these kinds of unsaturated bonds (Bratöz et al., (1961) and Yanovskaya et al., (1973)).

Similar changes in frequency can be observed in Table VI when aromatic aldehydes and aromatic Schiff's bases are compared; an increase in the resonance system leads to a decrease in frequency. However, the variation in the C=O stretching frequency is greater than the frequency change of the C=N stretching mode, for example, increasing the resonance system from benzaldehyde to cyt $\underline{a}^{3+}$ or cyt $\underline{a}^{2+}$ (both porphyrin systems) there is a

Table VI. Carbonyl and imine stretching frequency of unsaturated and aromatic compounds.

Comp	νC=O (cm^{-1})	Comp	νC=N (cm^{-1})
		$H_2C=NH$[h]	1642 (IR)
CH_3CHO[a]	1712 (IR)	$(CH_3)CHCH=NCH(CH_3)_2$[e]	1667 (IR)
$CH_3CH=CHCHO$	1690 (IR)	$CH_3(CH=CH)CH=NH(CH_3)_2$	1658 (R)
$CH_3(CH=CH)_2CHO$	1680 (IR)	$CH_3(CH=CH)CH=NH(CH_3)_2$	1658 (IR)
$CH_3(CH=CH)_3CHO$	1678 (IR)	$CH_3CH_2(CH=CH)_2CH=NCH(CH_3)_2$	1643 (R)
Trans-retinal[b]	1673 (R)	Trans-retinal + hexylamine[b]	1627 (R)
		M_{14} chromophore[g]	1620 (RR)
Benzaldehyde[c]	1694 (IR)	Benzylenebutylimine[l]	1646 (R)
			1645 (R)
Naphtaldehyde[d]	1684 (R)	Naphtalenebutylimine[l]	1644 (R)
			1642 (IR)
Anthraldehyde[l]	1677 (R)	Anthralenebutylimine[l]	1643 (R)
			1642 (IR)

Table VI Continues.

Table VI Continued.

Comp	νCO (cm^{-1})	Comp	νC=N (cm^{-1})
Cytochrome $\underline{a}_3^{3+}$[j]	1676 (RR)	Cytochrome $\underline{a}$ analog[g]	1639
Cytochrome $\underline{a}_3^{2+}$[k]	1665 (RR)		
		$(C_6H_5)C=N-H$[i]	1600 (R)
$(C_6H_5)_2-C=O$[i]	1664 (IR)		1598 (IR)
	1665 (R)		
		$(C_6H_5)_2C=N-(CH_2)_2CH_3$[e]	1618 (R)

[a]Yanovskaya et al., (1973); [b]Heyde et al., (1971); [c]Zwarich et al., (1971); [d]Sharma et al., (1974); [e]Favrot et al., (1979); [f]Massig et al., (1982); [g]Ward et al., (1983); [h]Botschwina (1974); [i]Datin et al., (1969); [j]Ondrias et al., (1980); [k]Salmeen et al., (1978); [l]this work.

change in the C=O stretching frequency of 18 and 29 cm^{-1}, respectively, while from benzyleneimine to the cyt a analog the difference in the C=N stretching frequency is only 7 cm^{-1}. These observations show that the C=N stretching frequency is relatively invariant to increases in the magnitude of the resonance system. On the other hand, the lower values observed for the C=N stretching frequency in ketimines shows that the axes of the π orbital of the additional phenyl rings are planar with respect to the π orbital of the C=N bond. In this way the presence of an aromatic ring on the carbon increases the extent of conjugation in the system which results in a corresponding decrease in the C=N frequency mode (Patai, 1970). Consistent with the general trends in Table VI, the difference in C=N stretching frequency between the M_{412} chromophore (1620 cm^{-1}) and the cyt a Schiff's base (1639 cm^{-1}) follow the same direction as the trends observed for unsaturated and aromatic Schiff's bases, respectively.

Bennainou et al., (1966) in a very well detailed study on the mechanical coupling and electronic perturbation that can affect the C≡N stretching frequency in nitriles, suggested that variations in the C≡N stretching frequency between unsaturated and aromatic nitriles are due to different degrees of conjugation. Mechanical coupling of different modes was shown to play a minor role in producing νC≡N frequency variations.

Since what is called the characteristic C=N frequency is a frequency characteristic of the CCN group rather than of the C=N bond, it is possible to suggest that the variation on the C=N between aromatic and unsaturated Schiff's bases is mainly due to electronic effects. Similar behavior was suggested by Besnainou et al., (1966) for the nitrile bond. The study indicates that in methylated and halogenated acetonitrile the inductive effect determines the behavior of the C≡N stretching frequency. For example, in halogen substituted acetonitriles the effective electronegativity of the α-carbon increases and then decreases as the number of chloro substituents increases. This behavior allows an increase and a decrease of the C≡N stretching frequency, respectively, depending on the number of chloro substituents on acetonitrile. The conjugation effect is operative in conjugated and aromatic nitriles. In order to calculate the C≡N force constant, it was assumed that its magnitude was dependent on the π electron structure of the molecules, as well as on the σ substitution, since the latter can affect the behavior of the π system. It was found that the two vibrations, $\nu_{C\equiv N}$ and ν_{CC}, provide the major contribution to the frequency observed and that the contribution to the C≡N stretching frequency of each of the other vibrations was on the order of only a fraction of a wave number. A similar approach was used by Bratǒz (1961) to determine the influence of

electronic effects on the C=O stretching frequency. He concluded that the variations in the C=O stretching frequency are mainly vibrational coupling interactions for cyclanones and that they do contribute to some extent to the C=O streching frequency in aldehydes. He also showed that when this vibrational coupling is small, the $\Delta\nu_{C=O}$ frequency shifts are mainly determined by the effective electronegativity of the carbon and in some cases by conjugation effects.

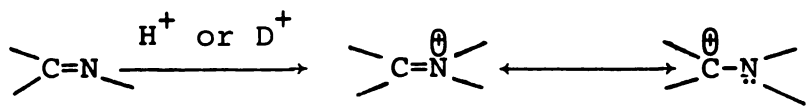
On the other hand, Kamarow et al., (1975) proposed that the change in energy for the singlet $\pi \rightarrow \pi^*$ state is greater for compounds of the type ArCHO (where Ar = phenyl, naphthyl, antracene) than for conjugated bond systems of the type H-(CH=CH)nCHO, and suggested that, with the same number of double bonds, the extent of conjugation is greater for unsaturated aldehydes than for aromatic aldehydes. For imines the extent of conjugation between the π orbital leads to an increase or decrease in the characteristic C=N frequency. Therefore, the availability of orbitals with appropriate symmetry on a series of adjacent atoms leads to delocalization through the resulting molecular orbital. As a result the bond lengths increase and the stretching frequency decreases.

In other words, the lower C=N stretching frequency observed for unsaturated imines with respect to the C=N stretching frequency observed for the aromatic imines (with the same number of double bonds) indicates that the

compatibility between the π orbital of the C=N bond (1 a" for methylene imine) with the π orbitals of the aromatic ring is to some extent smaller than the compatibility between this orbital and the π orbitals of the unsaturated analogs. Therefore, the extent of conjugation can be expected to be higher for unsaturated imines than for aromatic Schiff's bases with the consequent decrease in the C=N stretching frequency.

A.3 C=N Stretching Frequency on Protonated and Deuterated Aromatic Schiff's Bases

The experimental results are summarized in Table VII and indicate that upon protonation or deuteration of the aromatic Schiff's bases, an increase in the C-N stretching frequency occurs, which is similar to that observed upon protonation of the unsaturated Schiff's bases under the same conditions. This fact in terms of the simple relation between frequency and force constant suggests that the force constant of the C=N stretching mode increases upon protonation or deuteration of the Schiff's bases. On the other hand, the resonance structure of the charged Schiff's bases, i.e.,



indicate that the frequency of the C=N and therefore, the force constant to decrease. A similar argument was

Table VII. Raman and IR spectroscopic frequencies for unprotonated, protonated and deuterated unsaturated and aromatic Schiff's bases.

Compound	$\nu_{st}C=N(cm^{-1})$	$\nu_{st}C=\overset{+}{N}H(cm^{-1})$	$\nu_{st}C-\overset{+}{N}D(cm^{-1})$	$\nu_{B}N-H(cm^{-1})$	$\nu_{B}N-D(cm^{-1})$
$(CH_3)_2CHCH=NCH(CH_3)_2$ [a], (H^+)	1667(IR)	1704(IR)			
$CH_3CH=CHCH=NCH(CH_3)_2$, (H^+)	1658(IR)	1665(IR)			
$CH_3CH_2(CH=CH)_2CH=NCH(CH_3)_2$, (H^+)	1643(R)	1652(IR)			
Trans-retinal + hexylamine [b], (H^+)	1627(R)	1654(R)			
M_{412} chromophore [c]	1620(RR)				
All-transretinal + opsin (br_{570})		1642(RR)	1625(RR)	1350(RR)	976(RR)
All-trans-3-dehydroretinal + opsin (br_{603})		1641(RR)	1623(RR)	1346(RR)	976(RR)
Rhodopsin		1655(RR)	1630(RR)		

Table VII Continues.

Table VII Continued.

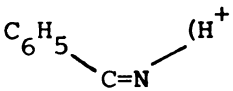
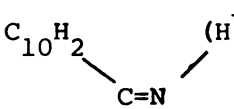
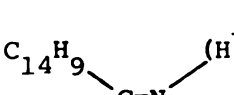
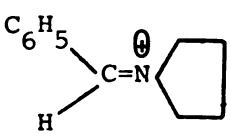
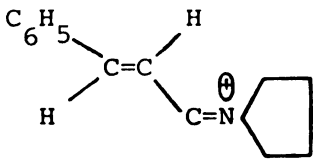
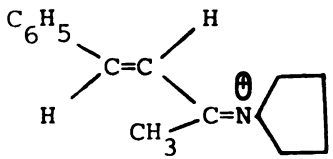
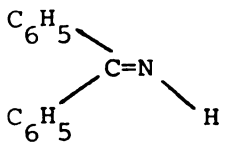
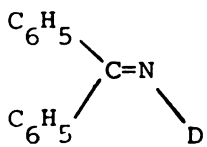
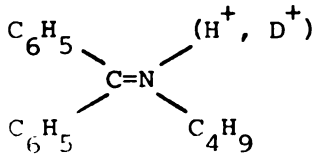
Compound	$\nu_{st}C=N(cm^{-1})$	$\nu_{st}C=\overset{+}{N}H(cm^{-1})$	$\nu_{st}C=\overset{+}{N}D(cm^{-1})$	$\nu_{B}N-H(cm^{-1})$	$\nu_{B}N-D)(cm^{-1})$
Ideal triatomic C=N-H [d]	1458(T)	1522(T)	1479(T)	1250(T)	947(T)
Ideal polyene	1624(T)	1659(T)	1633(T)		
 (I) [e]	1646(R)	1680(R)	1660(R)	1425(R)	1120(R)
	1645(IR)	1671(IR)	1653(IR)	1419(IR)	1121(IR)
 (II) [e]	1644(R)	1673(R)	1653(R)	1423(R)	
	1642(IR)	1665(IR)	1650(IR)	1418(IR)	1115(IR)
 (III) [e]	1643(R)	1660(R)	1638(R)		
	1635(IR)	1655(IR)	1632(IR)		1114(IR)
Cyt a analog [f] (IV)	1639(RR)	1650(RR)	1640(RR)		
 [g] (V)		1658(IR)			

Table VII Continues.

Table VII Continued.

Compound		$\nu_{st}C=N(cm^{-1})$	$\nu_{st}C=\overset{+}{N}H(cm^{-1})$	$\nu_{st}C-\overset{+}{N}D(cm^{-1})$	$\nu_{b}N-H(cm^{-1})$	$\nu_{b}N-D(cm^{-1})$
			1658(IR)			
	(VI)					
	(VII)		1660(IR)			
	(VIII)		1622(IR)			
	*h*	1600(R)			1364(R)	
	(IX)	1598(IR)			1363(IR)	
		1605(R)				1013(IR)
	(X)	1603(IR)				
	*e*	1618(R)	1636(R)	1616(R)		
	(XI)	1615(IR)	1630(IR)			

Notes to Table VII on p. 75.

Notes to Table VII.

[a]Favrot et al., (1979).
[b]Heyde et al., (1971).
[c]Massig et al., (1982).
[d]Aton et al., (1981).
[e]This work.
[f]Ward et al., (1983).
[g]Leonard et al., (1963).
[h]Datin et al., (1969).

presented before by Blatz et al., (1975); Elguero et al., (1967) and Goulden (1953). For rhodopsin and analogous Schiff's bases it was assumed by Aton et al., (1980) that protonation increases the extent of π-electron delocalization and therefore, the C=N stretching frequency should decrease. But since the observed frequency is greater for the protonated than for the unpronated Schiff's bases, it was suggested by Marcus (1979) and developed in detail by Aton et al., (1980), that in the case of unsaturated Schiff's bases, the increase in the C=N stretching frequency is due to the interaction between the C=N stretching frequency at 1624 cm^{-1} and the N-H bending mode at 1250 cm^{-1}. The interaction between these modes was suggested to increase the frequency of the higher mode to the value observed for the C=N stretch in the protonated form. If this is the case, it may also be supposed that aromatic Schiff's base will show a similar behavior. Thus, for example, in N-benzylidene-n-butylamine (compound I), the interaction between the N-H bending mode at 1425 cm^{-1} and the C=N stretching frequency at 1646 cm^{-1} would interact to increase the stretching frequency of the later mode to 1680 cm^{-1}. However, at this point, it is necessary to notice that although the C=N and N-H stretching frequencies are substantially different between the retinal Schiff's base analog and the n-benzyl Schiff's base, the difference in stretching frequency between their unprotonated and protonated

Schiff's base is practically the same, i.e., 35 cm^{-1}. Therefore, in order to determine whether the stretching-bending interaction model accounts for the frequency changes upon protonation of aromatic Schiff's base, a normal coordination analysis needs to be performed in the future. On the other hand, it is difficult to explain some of the C=N stretching frequencies, presented in Table VII, in terms of the bending mode interaction model. For example, the series of compounds from V to VII (which do not have N-H bending mode) present C=N stretching frequencies of 1658 cm^{-1}, 1658 cm^{-1}, and 1660 cm^{-1}, respectively. These frequencies are, in fact, higher than the C=N stretching frequency (1646 cm^{-1}) for the benzaldehyde Schiff's base analog (compound I). From simple arguments, one would expect that the presence of a ring on the nitrogen would decrease the C=N stretching frequency since an increase in conjugation can be expected (Parry et al., 1970). In addition to the above criticism the ketimine derivative prepared from benzophenone and NH_3, which contains N-H as a terminal group (compound X, Table VII) has a C=N stretching frequency at 1600 cm^{-1} (Datin et al., 1969), while the ketimine containing a butyl terminal group attached to the nitrogen (compound XI) has a C=N stretching at 1618 cm^{-1}. Similar ketimines, where the terminal group is $-CH_2CH_2CH$ or C_6H_5, present C=N stretching frequencies of 1616 cm^{-1} and 1614 cm^{-1}, respectively (Fabian et al., 1956). When the n-butyl

derivative Schiff's base is protonated, there is a 16 cm^{-1} increase in the C=N stretching frequency. So, if it is assumed that the N-H bending mode interacts with the C=N stretching frequency and increases the frequency of the latter, one would expect, by a simple mass effect, that the ketimine which contains only the N-H bond as a terminal group will have a higher C=N stretching frequency than the ketimines with alkyl substituents. However, this is not the case, since, as discussed above, the aromatic ketimine derivative from NH_3 has a C=N stretching frequency at 1600 cm^{-1}, while the protonated aromatic ketimine from n-butylamine Schiff's base has a C=N stretching frequency at 1636 cm^{-1}.

Therefore, at this point, it appears that the interaction between the N-H bending and the C=N stretching frequency cannot account for various of the observed increases in the C=N stretching vibration upon protonation of aromatic Schiff's base. Rather, the protonated Schiff's base case seems to be analogous to the situation which occurs when a proton is brought up to NH to give NH_2^+. The lone pair electrons forming the new N-H bond will not stay unaltered in their sp^2 hybrid orbital, neither will they be equally shared between N and H; they will assume some intermediate distribution (Brown, 1957). Thus, it appears that the possible change in the state of the electron lone pair, as well as the increase in the electronegativity of the nitrogen atom upon protonation of the Schiff's bases

play an important role in the CN^+ stretching frequency increase relative to the C=N frequency mode.

Bond order and bond distance also contribute to the magnitude of the $k_{C=N}$ value. The interplay between these and the increase in the electronegativity of the nitrogen determines the value of the C=N frequency in the Schiff's bases upon protonation or deuteration. For example, in $(CH_3)_2CHCH=NCH(CH_3)_2$ there is a shift of 37 cm^{-1} (from 1667 to 1704 cm^{-1}) upon protonation. At this point with only one double bond, there is no strong delocalization effect (no conjugation) which means to some extent that the increase in the electronegativity of the nitrogen controls the change in the C=N stretching frequency and, therefore, the change in frequency is relatively large. In $CH_3CH=CHCH=NCH(CH_3)_2$ there is only a 7 cm^{-1} change upon protonation which means that conjugation and electronegativity effect cancel to a large extent. For retinal a larger shift (approximately 27 cm^{-1}) is observed and Massing et al., (1982) indicate that there is no change in the C=N stretching frequency or in the C=N stretching frequency for the addition of a double bond on br_{570}. It can be suggested that the increase in the electronegativity in the nitrogen atom plays an important role in the increase of the C=N stretching frequency.

The compounds used for this study (I, II and III in Table VII) behave as if electronegativity effects dominate (i.e. delocalization is small). This is consistent with

the NMR data for heme a Schiff's base analog in the Ward et al., (1983) paper where strong electronegativity effects are observed but small delocalization effects (there is a possibility that the charge delocalizes over the C_β=C_β double bond on the pyrrole ring but it does not delocalize into the major porphyrin π electron system). The NMR data for the model compounds (see Tables II and Figures 4-6) suggest also that upon protonation or deuteration of the Schiff's bases, there is a strong electronegativity effect as can be deduced from the downfield shift of the Ha and αCH_2 protons, and that the extent of charge delocalization is not apparently uniform in the ring system.

Figure 21 shows that as the number of double bonds increases in the series of protonated aromatic Schiff's bases, the electronegativity contribution effect on the C=N stretching frequency appears to be smaller or the conjugation effect larger. Figure 20 also indicates that the variation on the C=N stretching frequency as a function of the number of double bonds is smaller for unprotonated Schiff's bases than for protonated Schiff's bases; the latter seems to follow a similar trend as the carboxylic group in analog aldehydes. With respect to the decrease on the C=N vibrational mode upon deuteration relative to the C=N mode upon protonation it can be observed in Table VII that it is not constant and appears to

Figure 20. Plot of $\nu_{C=O}$(○○○), $\nu_{C=N}$(□□□) and $\nu_{C\equiv N}$(●●●) stretching mode for unsaturated aldehydes versus the number of double bonds in the particular compound.

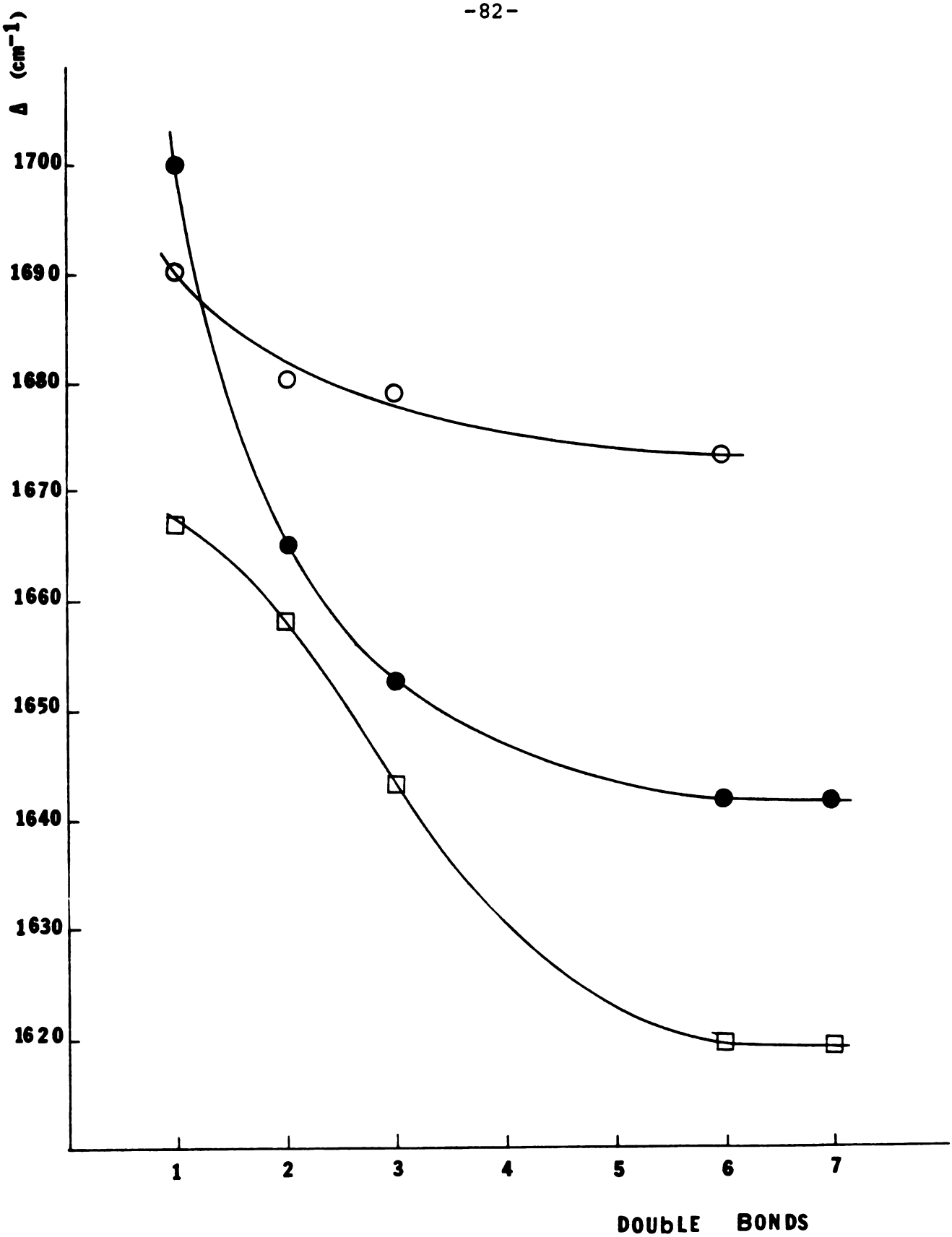

ν (cm⁻¹)
1700
1690
1680
1670
1660
1650
1640
1630
1620
1
2
3
4
5
6
7
DOUbLE BONDS

Figure 20

Figure 21. Plot of $\nu_{C=O}$(○○○), $\nu_{C=N}$(□□□), $\nu_{C=\overset{+}{N}H}$(●●●) and $\nu_{C=N\overset{+}{D}}$(Δ Δ Δ) stretching mode for aromatic aldehydes and imines versus the number of double bonds in the particular compound.

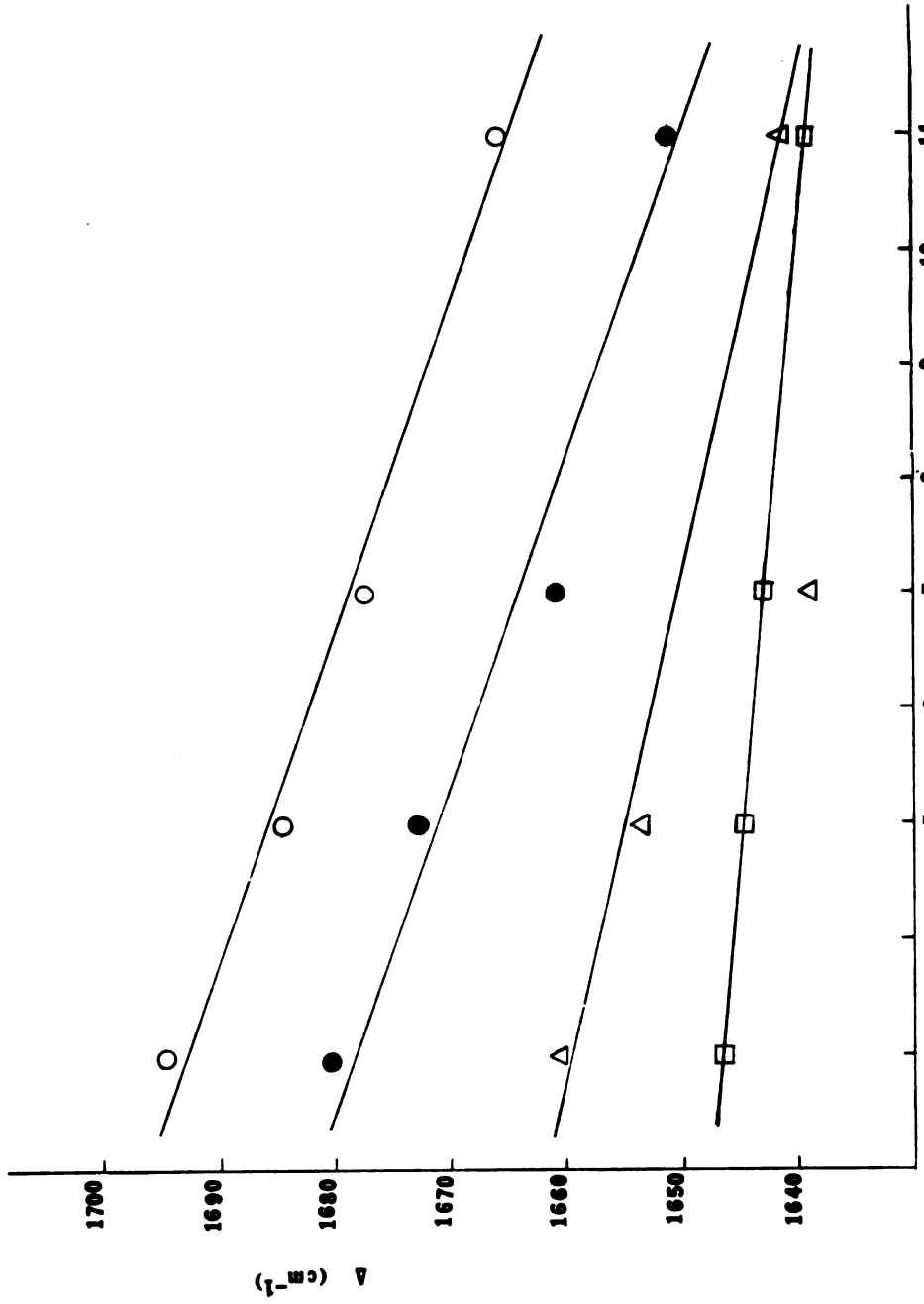

1700
1690
1680
1670
1660
1650
1640
Δ (cm⁻¹)
3
4
5
6
7
8
9
10
11
DOUBLE BONDS

Figure 21

depend to some extent on the magnitude of the aromatic substituent group.

On the other hand, a normal coordination analysis to modeling the N-H or N-D model interactions with the C=N stretch has not been performed yet. Until the nature of the C=N stretching increase upon protonation in aromatic Schiff's base with respect to the unprotonated Schiff's base is established, any attempt, at this point, to explain the frequency shifts between the C=N stretching frequency upon deuteration with respect to protonation in terms of bending mode interactions, conjugation effects or inductive effects will not have any firm basis and will only be speculative. However, it should be indicated that the difference in mass between hydrogen and deuterium can contribute to the difference in frequency between the $C=\overset{\oplus}{N}H$ and $C=\overset{\oplus}{N}D$ stretching modes (Marcus et al., 1979). It is not clear how much this mass effect can contribute to the difference in frequency of the stretching modes.

CHAPTER V

SUMMARY AND FUTURE WORK

A.1 Summary

The C=N, $C=\overset{+}{N}H$ and $C=\overset{+}{N}D$ stretching frequency for some aromatic and unsaturated Schiff's bases have been discussed and the corresponding C=N stretching modes assigned by I.R. and Raman spectroscopy and the chemical shift of the Ha and αCH_2 protons or protonated Schiff's bases have been determined by NMR. It was shown that the increase in the C=N stretching frequency in aromatic Schiff's bases relative to the C=N stretching mode in unsaturated Schiff's bases follow the same trend that the variation in the carbonyl stretching frequency in the aldehydes or in the nitriles of analogous compounds. Therefore, it appears that the difference in the C=N stretching frequency between the M_{412} chromophore and the metalloporphyrin Schiff's base (cytochrome a analog) is mainly due to electronic effects rather than mechanical coupling. At the same time, the C=N stretching frequency in aromatic Schiff's bases of the kind ArCH=N-R (where Ar = phenyl, naphthyl, antracene) shows a lesser degree of delocalization effects (with an increase in the number

of double bond systems) than the carbonyl group stretching mode in the analogous aromatic aldehydes. This fact also applies to the protonated and unprotonated Schiff's base. There is more similarity in the behavior of the conjugation effect between protonated aromatic Schiff's bases and analogous aldehydes than between protonated and unprotonated Schiff's bases.

The NMR, I.R. and Raman spectroscopic results have indicated that upon protonation of the aromatic Schiff's bases, the positive charge on the system is not uniformly distributed in the aromatic system. Rather than this, the large increase in the electronegativity in the nitrogen apparently increases the electron withdrawing character of the imine group and localizes, to some extent, the positive charge. This fact, together with the arguments presented in Chapter IV, indicates that the increase observed in the C=N stretching frequency upon protonation or deuteration of aromatic Schiff's bases cannot be attributed primarily to the coupling between the C=N stretching frequency and the N-H or N-D bending mode. It appears that the interaction between the lone pair electrons on the nitrogen with the hydrogen or deuterium upon N-H or N-D bond formation, with the corresponding increase on the nitrogen's electronegativity, play an important role in increasing the C=N stretching frequency. It was not possible to account for the nature of the deuterium shift that happens when the hydrogen atom on

the nitrogen is substituted by a deuteron. However, it is possible to indicate that differences in electronic effects such as electronegativity, inductive effect may play a decisive role in determining the small shift observed.

A.2 Future Work

The efforts for future experiments and calculations need to be focused on determining a good value for the C=N stretching force constant for unprotonated, protonated and deuterated aromatic Schiff's bases by using the compound presented here as models. However, since the geometry of the model Schiff's base is not known, it may be postulated that upon protonation of the Schiff's base there is an increase in the electronegativity of the nitrogen (Brown, 1957), and an increase in the electron withdrawing character of the C=N group (Ward et al., 1983). There is also the possibility that the lone pair electrons, upon formation of the new N-H bond, will not stay unaltered in their sp^2 hybrid orbital. *Ab initio* and semiempirical studies will be necessary in order to determine the charge distribution, the geometry and the force constants involving the unprotonated and protonated model Schiff's base.

Hanson et al., (1983, submitted publication) indicated that upon protonation of mono- and di-substituted porphyrin, chlorin and bacteriochlorin Schiff's base

complexes the observed red shift in the visible spectrum can be attributed to a drop in energy of the Schiff's base C=N π orbitals which then mix with the π orbitals of the porphyrin models. Therefore, similar calculations can be carried out in the unprotonated and protonated aromatic Schiff's bases, together with a Raman excitation profile to study the red shift observed in the U.V. spectra of the model Schiff's bases.

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