Spectroscopy of Pyridoxal Analogues. 2. N-Ethylsalicylaldimines

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The intense electronic transitions found at $\lambda > 1900$ Å in four chemical variants of N-ethylsalicylaldimine (and by analogy all N-alkyl derived molecules) are presented and transition assignments are made. The ${}^{1}A'' \leftarrow 1{}^{1}A'$ $(\pi^* \leftarrow \sigma(n))$ transitions calculated to lie at $\lambda > 1900$ Å have not been located experimentally but tentative conclusions based on previous work are made. The major effect of the solvent medium on the neutral/dipolar ion-molecule equilibrium appears to be quite specific to proton-donating alcohol solvents. A reasonable model for solvent alcohol interaction suggests intermolecular hydrogen bonding with the oxygen atom of the aldimine.

Introduction

Salicylaldehydes (o-hydroxybenzaldehydes) and their N-alkyl Schiff's bases (o-hydroxybenzaldimines) are chemical prototypes of pyridoxal and, in general, the B_6 vitamins. In a previous paper¹ the electronic absorption spectroscopy of the parent molecule salicylaldehyde was presented. In this communication we report on the spectroscopy of N-ethylsalicylaldimines. In subsequent papers we shall present the luminescence spectroscopy of these molecules and their trivalent metal chelates.

The basic structure of N-alkylsalicylaldimines is (R = methyl, ethyl, etc.)



and embodies several key molecular features common to pyridoxal mediated biocatalytic reactions. First, exocyclic groups OH and (-CH=N-) are able to intramolecularly hydrogen bond and this is similar to salicylaldehyde itself.¹ Second, the strength of the intramolecular hydrogen bond in salicylaldimines is of sufficient magnitude to permit proton tautomerism to occur in the planar structure.² The end result of proton tautomerism is, thus, formation of an internal dipolar ion. Third, salicylaldimines are capable of forming bis chelates with a series of trivalent metals and the properties of such chelates relate directly to extensive studies³ on model vitamin B₆ reactions.

Proton tautomerism and chemical protonation of *N*-alkylsalicylaldimines constitute a set of isoelectronic processes and these are shown in Scheme I. As the now extensive literature^{2,3} on pyridoxal analogues indicates, these structural and chemical processes are fundamental to the observed spectral behavior of the B₆ vitamins. Apart from relatively subtle differences, the electronic spectra of *N*-derived salicylaldimines is represented by *N*-ethylsalicylaldimine whose chemical stability allows detailed examinations to be made. Thus, the spectroscopy of this molecule assumes a significant role in elucidation of the spectroscopy of vitamin B₆.

Neglecting quite small $\sigma\pi$ mixing effected by nonplanar exocyclic chemical groups (e.g., $\mathbf{R} = C_2 \mathbf{H}_5$), the electronic states of N-alkylsalicylaldimines (and, indeed, most pyridoxal analogues) may be described within the C_s point group. The ground and all monoexcited $\pi\pi^*$ states are of orbital symmetry A'; all $\sigma(n)\pi^*$ states of species A''. Beginning with the ground electronic singlet state (= 1¹A') excited states are designated as follows: $1^3A'$, $2^{1,3}A'$, ...; $1^{1,3}A''$, $2^{1,3}A''$, In the singlet manifold, all $\pi^* \leftarrow \sigma(n)$ Scheme I



transitions (i.e., ${}^{1}A'' \leftarrow 1{}^{1}A'$) are out-of-plane (z) polarized; all $\pi^* \leftarrow \pi$ transitions (i.e., ${}^{1}A' \leftarrow 1{}^{1}A'$) are in-plane (x,y) polarized.

Experimental Section

N-Ethylsalicylaldimine was prepared by allowing 100 mL of salicylaldehyde (Fisher) to react with 150 mL of anhydrous ethylamine (Eastman) in 150 mL of methanol. The formation of the aldimine was driven to completion by final refluxing of the reaction mixture for 2 h. After evaporation of residual ethylamine and methanol solvent, the yellow liquid product was dried over anhydrous sodium sulfate and vacuum distilled. N-Ethylsalicylaldimine was collected at 87-88 °C and 5 mm of pressure. Comparison of the spectra of the product with those of salicylaldehyde showed the aldimine to be more than 99% pure. Acids, bases, and solvents were used as commercially available spectroscopic or analytical grade without further purification. Electronic survey spectra were taken on a Cary 14 spectrophotometer using either a 10 cm gas cell or 1 cm liquid cell at 300 K.

Concentration ratio measurements (cf. Figure 2) were made from deconvoluted spectra of dipolar ion/neutral molecule mixtures in various solvents. The estimated



Figure 1. The low resolution survey spectrum of *N*-ethylsalicylaldimine vapor at 300 K. The absorption due to the vapor cell alone is negligible in the wavelength region shown.

accuracy for this procedure is $\pm 10\%$.

Results and Discussion

N-Ethylsalicylaldimine Vapor. N-Ethylsalicylaldimine vapor exhibits three intense broad absorptions at $\lambda \geq 1900$ Å as shown in Figure 1. On the basis of intensity alone, these electronic absorption bands must be attributed to ${}^{1}A' \leftarrow 1{}^{1}A'$ ($\pi^{*} \leftarrow \pi$) transitions of the planar aromatic portion of the molecule. Comparison of solution- and gas-phase molecule spectra shows that the structure of the exocylic hydrogen-bonded atoms must be that of an internally neutral species (cf. Scheme I). The three absorption bands of the gas-phase molecule are discussed in more detail below.

3100-Å Absorption Band. The 3100-Å absorption band is featureless and corresponds to the 3200-Å band of salicylaldehyde.¹ Measurement of its oscillator strength gives a value of f = 0.093 in cyclohexane solvent (vide infra). On the bases of intensity and analogy with salicylaldehyde,¹ the 3100-Å absorption of N-ethylsalicylaldimine is assigned as $2^{1}A' \leftarrow 1^{1}A'$.

2500-Å Absorption Band. The 2500-Å absorption band of N-ethylsalicylaldimine carries high oscillator strength (f = 0.18 in cyclohexane solvent) and a suggestion of vibrational definition. The lack of extensive vibrational structure in the 2500-Å transition is to be contrasted with the structured 2525-Å salicylaldehyde band system which is its electronic counterpart. In every other way, however, the aldimine 2500-Å absorption is analogous to that in salicylaldehyde and may be straightforwardly designated $3^{1}A' \leftarrow 1^{1}A'$.

2100-Å Absorption Band. The 2100-Å absorption band has high oscillator strength (f = 0.73 in cyclohexane solvent), shows no vibrational definition, and corresponds to the 2100-Å absorption in salicylaldehyde.¹ As in the latter case, the aldimine 2100-Å band may contain intensity from more than one $\pi^* \leftarrow \pi$ transition (vide infra).

N-Ethylsalicylaldimines in Solution. The electronic absorption spectroscopy of solution-phase salicylaldimines differs significantly from that of salicylaldehydes.¹ These differences are marked and ultimately attributable to differences between isoelectronic exocyclic groups (-CH=N-) and -CHO.

Neutral and Dipolar Ion Molecules. It is well known²⁻⁴ that uncharged aldimines of pyridoxal analogues in polar solvents can exist as equilibria between internally neutral and dipolar-ion forms. However, little is known about the role of the solvent medium in the formation of these species, albeit speculation does exist in the literature.⁴ We have measured the effects of the solvent medium (16



Figure 2. The internally neutral to dipolar-ion-molecule concentration ratio as a function of the number of aliphatic carbon atoms in a series of straight chain alcohols, ROH (R = H, CH₃, etc.). The dashed line represents the approximate linear relationship.

solvents) on the neutral/dipolar ion-molecule equilibrium and find several interesting results:

(1) The role of solvent polarity, per se (e.g., bulk solvent dielectric constant), is slight in determining the ratio of the concentration of the two chemical forms. For example, the ratios of concentrations of the neutral to dipolar-ion form at 300 K are as follows: chloroform, 15; methylene chloride, 18; acetonitrile, 17. However, the polarity of the solvent medium does appear to limit the presence of the dipolar ion in cases of totally nonpolar media: carbon tetrachloride, >350; *n*-hexane, >60; 1,4-dioxane, >90.

(2) Wide variation in the concentrations of the neutral and dipolar-ion forms is found specifically for protondonating alcohol solvents. This behavior is shown in Figure 2 for a series of straight chain alcohol solvents. That the variation of the neutral to dipolar-ion concentration ratio is roughly linear with number of solvent carbon atoms is puzzling but suggests formation of intermolecular hydrogen-bonded complexes between solvent molecules and the oxygen atom of the aldimine. This sort of intermolecular interaction would tend to reduce internal aldimine -OH bond strength and, thus, favor proton transfer to the nitrogen center. The variation in concentration ratios with size of aliphatic carbon chain in ROH may then be attributed to proton-donating ability of the hydroxyl group of the alcohol.⁵

(3) The absorption maxima of the $2^{1}A' \leftarrow 1^{1}A'$ ($\pi^{*} \leftarrow \pi$) transitions in the neutral and dipolar-ion forms shift little over a wide range of solvent polarity. For example, wavelength shifts of ~50 Å for the neutral and ~100 Å for the dipolar ion are found in comparing the absorption maxima in carbon tetrachloride and acetonitrile solvents, respectively. The smallness of these wavelength shifts for both chemical forms argues strongly for little intramolecular charge-transfer character in their $2^{1}A' \leftarrow 1^{1}A'$ transitions.

Anionic and Cationic Molecules. Cation. The electronic absorption spectrum of the monoprotonated cation (i.e., protonation at the nitrogen atom) of N-ethylsalicylaldimine is shown in Figure 3. The integrated intensities of the 3550-Å (f = 0.12) and the 2750-Å (f = 0.26) bands require that these transitions be assigned as $2,3^{1}A' \leftarrow 1^{1}A'$ analogous with those found in the neutral molecule. In the case of the cation the $2,3^{1}A' \leftarrow 1^{1}A'$ transitions are red-shifted relative to the dipolar-ion molecule. This behavior appears to be typical of most, if not all, vitamin B₆ related molecules in solution.¹⁻⁴

TABLE I

 CNDO/S-CI(60)				Experiment		
Transition	Energy, eV	Oscillator strength	Polarization ^a	Energy (fwhm), eV	Oscillator strength	
 Neutral molecule	e				· · · · · · · · · · · · · · · · · · ·	
$1'A'' \leftarrow 1^1A'$	3.66	0.005	z			
$2^{i}A' \leftarrow 1^{i}A'$	4.32	0.105	xy	3.69 - 4.48	0.09	
3'A' ← 1'A'	5.06	0.349	y	4.71 - 5.12	0.18	
$4^{1}\mathbf{A}' \leftarrow 1^{1}\mathbf{A}'$	5.95	0.602	xy	5.39-6.14	0.73	
Dipolar ion mole	ecule					
$1^{1}\mathbf{A}^{\prime\prime} \leftarrow 1^{1}\mathbf{A}^{\prime}$	2.70	0.000	z			
$2^{1}A' \leftarrow 1^{1}A'$	3.21	0.235	xy	2.89 - 3.42	$\epsilon_{max}^{b} 7.2 \times 10^{3}$	
$3^{1}A' \leftarrow 1^{1}A'$	4.80	0,164	y	4.36-4.68	III	
$2^{1}A'' \leftarrow 1^{1}A'$	4.96	0.000	z			
$4^{1}A' \leftarrow 1^{1}A'$	5.04	0.041	xy	5.16(max)		
$5^{1}A' \leftarrow 1^{1}A'$	5.48	0.766	y			
Anionic molecul	.e					
$1^{1}A^{\prime\prime} \leftarrow 1^{1}A^{\prime}$	3.22	0.001	z			
$2^{1}A' \leftarrow 1^{1}A'$	3.44	0.246	xy	$3.34 - 3.84^{b}$	$\epsilon_{max}^{b} 6.7 \times 10^{3}$	
$2^{1}A'' \leftarrow 1^{1}A'$	4.15	0.002	z		113003	
$3^{1}A^{\prime\prime} \leftarrow 1^{1}A^{\prime}$	4.76	0.008	z			
$3^{1}A' \leftarrow 1^{1}A'$	4.81	0.062	xy	$4.82(\max)^b$		
$4^{1}A' \leftarrow 1^{1}A'$	5.11	0.083	xy	, <i>,</i>		
$5^{1}A' \leftarrow 1^{1}A'$	5.77	1.24	xy			
Cationic molecu	le					
$2^{1}A' \leftarrow 1^{1}A'$	3.80	0.106	x	3.29-3.85	0.12	
$3^{1}A' \leftarrow 1^{1}A'$	4.68	0.575	У	4.3079	0.26	
$1^{1}A^{\prime\prime} \leftarrow 1^{1}A^{\prime}$	4.93	0.001	z			
$4^{i}A' \leftarrow 1^{i}A'$	5.57	0.010	xy	$5.51(\max)$		

^a For definition of axes see Scheme I. Axial specification of in-plane polarization is given according to dominant orientation (x or y) or heavily mixed orientation (xy). ^b Reference 4.



Figure 3. The electronic absorption spectrum of monoprotonated *N*-ethylsalicylaldimine in diethyl ether saturated with HCl(g) at 300 K. The dashed line represents an extrapolated baseline absorbance for the solvent/HCl(g) mixture. It is to be noted that the sample mixture is very slightly turbid at HCl(g) saturation.

Anion. The monoanion (i.e., proton released by the phenolic hydroxyl group) is not chemically stable in aqueous or alcoholic solvents except in the presence of a huge excess of ethylamine.⁴ However, the anion has a half-life of the order of 5 min in ethanol/base after initial deprotonation and measurement of the spectrum of the monoanion can be made. Our results are in agreement with those of Alexander and Sleet⁴ who measured the spectrum in aqueous ethylamine. (We refer the reader to Table I for a catalogue of transition assignments.) It is important to note that the absorption spectrum of the anion is very similar to those of trivalent metal chelates of N-alkylsalicylaldimines. The latter point is amplified

in detail in a forthcoming paper.

Quantum Chemical Results

All valence-electron molecular orbital calculations, i.e., CNDO/S-CI,^{6,7} were done on four chemical variants of salicylaldimine (cf. Scheme I; R = H). Configuration interaction was limited to the first 60 singly excited configurations and two-center electron repulsion integrals were taken according to the Mataga approximation.^{6,7} In all cases phenyl C-C and C-H bond distances were taken as 1.390 and 1.085 Å, respectively. Associated phenyl angles ∠CCC and ∠CCH were assumed to be 120°. Exocyclic hydroxyl group atom coordinates were taken as those in salicylaldehydes.¹ Imine group (-CH=-NH) geometry was assumed as follows: r(CH) = 1.071 Å; r(CN) = 1.300Å; r(NH) = 1.014 Å; all angles, 120°.

Comparison of calculations for salicylaldimines (R = H) with our experimental results for N-ethylsalicylaldimine ($R = C_2H_5$) is given in Table I. As our previous work⁸ and the literature specifically on pyridoxaldimines^{2,3} shows, alkylation results in small systematic spectral shifts which do not confuse assignments by such a comparison of calculation and experiment. Examination of Table I and allied computational results (which may be obtained from the author on request) result in several principal conclusions:

(1) Excepting the case of the cationic molecule, the lowest energy transition is calculated as $1^{1}A'' \leftarrow 1^{1}A'$. We are not yet able to give positive location of these $\pi^{*} \leftarrow n(\sigma)$ transitions. However, we have found that the lowest energy emitting level in the anion (which we presume is the lowest singlet) is the $2^{1}A'(\pi\pi^{*})$ state. This result is consistent with our experience^{1.8} that CNDO/S-CI computations place the $1^{1}A''(\sigma(n)\pi^{*})$ state too low in energy by 0.5-1.0 eV. Using this energy discrepancy as a diagnostic, we tentatively conclude that the neutral and dipolar ion may have $1^{1}A''$ lowest energy singlets. Our

1334

continuing luminescence measurements on these compounds should test this hypothesis.

(2) Agreement between calculated and experimental energies for $2,3,4^{1}A' \leftarrow 1^{1}A' (\pi^{*} \leftarrow \pi)$ transitions is excellent and corresponding assignments are straightforward. Comparison of measured and calculated oscillator strengths where spectral deconvolution is reliable (i.e., $\pm 10\%$) shows that computation is within a factor of 2 of experiment. It is important to note that trends in calculated oscillator strengths between and within molecular species are borne out by experiment. In this regard, these results are consistent with our previous experience.^{1,8}

(3) Several ${}^{1}A'' \leftarrow 1{}^{1}A' (\pi^* \leftarrow \sigma)$ transitions are predicted to lie at energies where their low intensity (f < 0.01) would be overwhelmed by surrounding ${}^{1}A' \leftarrow 1{}^{1}A'$ intensity $(f \geq 1)$ 0.1). We have no experimental information regarding location of these $\pi^{*} \leftarrow \sigma$ transitions and it is unlikely that they will be locatable by conventional absorption spectroscopy.

(4) Of the transitions which lie at $\Delta E \leq 6$ eV, only the $1^{1}A'' \leftarrow 1^{1}A'$ transitions are calculated to have significant intramolecular charge transfer character. Even in the case of the $2,3^{1}A' \leftarrow 1^{1}A'$ transitions of the anion, where charge transfer character might be anticipated, only slight amounts are calculated. Our computational results are, thus, in complete accord with measured solvent polarity insensitivity of the transitions of these molecules (vide supra).

Conclusions

The intense electronic transitions found at $\lambda > 1900$ Å in four chemical variants of N-ethylsalicylaldimine (and by analogy all N-alkyl derived molecules) are presented and transition assignments are made. The ${}^{1}A'' \leftarrow 1{}^{1}A'$ (π^* $-\sigma(n)$ transitions calculated to lie at $\lambda > 1900$ Å have not been located experimentally but tentative conclusions based on previous work^{1,8} are made. The major effect of the solvent medium on the neutral/dipolar ion-molecule equilibrium appears to be quite specific to proton-donating alcohol solvents. A reasonable model for solvent alcohol interaction suggests intermolecular hydrogen bonding with the oxygen atom of the aldimine.

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Temperature-Dependent Cation Distribution in Dehydrated Calcium-Exchanged Mordenite

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An equilibrium distribution of exchangeable cations in zeolites might reflect the Boltzmann distribution law, the occupancy ratios of the cation sites being related to the energy level differences and the absolute temperature. Dehydrated calcium mordenite ($Ca_{3,33}Al_{7,82}Si_{40,2}O_{96}$) was chosen to follow the variation of the Ca ion localization with temperature. Two crystals were studied: A at 25 and 350 °C (accidentally rehydrated) and B at 345 and 635 °C with single crystal x-ray diffraction methods. The Ca ions are distributed among four nonequivalent sites. A shift of the population parameters with temperature is observed, the sites yielding a better coordination to the cations becoming more and more stable. This indicates a change in the energy level of the sites. At all temperatures, site I is the most stable site, located in the center of a highly twisted eight-ring and coordinated to six framework oxygens. Sites III and VI have a one-sided coordination to four framework oxygens and site IV is located off-center on the eight-ring, coordinated to only two oxygens. The stability sequence of these sites, as calculated from the energy level differences is I > VI > IV > III at temperatures below 345 °C, site IV showing considerable destabilization at 635 °C. The presence of water molecules at 350 °C resulted in stabilization of sites I and IV by increasing the coordination of the cations.

Introduction

In the past two decades, zeolites became the subject of intensive research and have found numerous industrial applications as, e.g., heterogeneous catalysts or drying agents. Possible differing cation loadings by ion exchange, reversible dehydration, and their uniform but limited pore size allows the variation of specific physicochemical properties. Catalytic properties result from cationframework interactions allowing the formation of surface complexes as reactive intermediates. In most zeolites, cation sites can be distinguished, depending on framework coordination and adsorption capability. The cations are mobile to a large extent as shown by ion exchange and

electric conductivity. Interactions of the cations with the framework, with other cations, and with sorbed molecules determine the difference in energy level of the cation sites. Assuming a Boltzmann distribution of the cations over these sites, it is possible to calculate the differences in energy level as described earlier.¹ According to this formalism (logarithm of the site occupancy ratio being proportional to the energy level difference and the reciprocal absolute temperature), the temperature may influence the cation distribution either directly or indirectly by change of the energy level differences. Interpretations of catalytic phenomena (mostly at elevated temperatures) based on structural data obtained at room