(s, CH_3), 1.34 (s, *t*-Bu), 1.30 (s, CH_3), 1.29 (s, CH_3), and 1.28 (s, *t*-Bu). Mass spectrum, *m/e* (relative abundance: 370 (M^+, 0.4), 220 (8), 205 (7), 152 (11), 151 (100), 123 (87), 109 (34), 95 (12), 93 (10), 91 (12), 81 (43), and 79 (12). Anal. Calcd for $C_{25}H_{38}O_2$: C, 81.03; H, 10.33. Found: C, 80.91; H, 10.31.

2,6-Di-*tert*-butyl-4-methylphenyl *trans*-2-(3-Cyclohexen-1-yl)cyclopropanecarboxylate (10). Cyclopropane derivatives were formed in 94% and 92% yield, respectively, from reactions catalyzed by $Rh_2(OAc)_4$ and $Rh_4(acam)_4$. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2 H), 5.68 (s, 2 H), 2.30 (s, CH_3), 2.24–1.80 (m, 5 H), 1.76 (quin, J = 4.1 Hz, 1 H), 1.56–1.41 (m, 2 H), 1.35 (s, 9 H), 1.33 (s, 9 H), 1.37–1.22 (m, 1 H), 1.16–1.00 (m, 1 H), and 0.94 (d of d of d, J = 10.8, 8.3, 4.1 Hz, 1 H). Mass spectrum, *m/e* (relative abundance): 368 (M^+, 2), 220 (2), 161 (5), 149 (86), 131 (65), 121 (49), 119 (14), 105 (15), 93 (50), 91 (28), 79 (79), 77 (15), 71 (12), 67 (38), 57 (36), and 55 (100).

Catalytic Decomposition of BDA in the Absence of Alkene. The reaction was performed in dichloromethane with rhodium(II) acetate catalysis as previously described, and three dimeric products were isolated by flash chromatography and characterized spectroscopically. Fumarate ester (74%), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.15 (s, 4 H), 7.10 (s, 2 H), 2.34 (s, 6 H), and 1.34 (s, 36 H). Mass spectrum, *m/e* (relative abundance): 520 (M^+, 2), 220 (42), 217 (23), 205 (19), 203 (29), 82 (12), 57 (100). Maleate ester (13%), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.28 (s, 4 H), 6.63 (s, 2 H), 2.29 (s, 6 H), and 1.33 (s, 36 H). Azine (13%), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.16 (s, 4 H), 4.62 (s, 2 H), 2.32 (s, 6 H), and 1.34 (s, 36 H).

Reduction of BHT Cyclopropane Esters. 2,6-Di-*tert*-4-methylphenyl cyclopropanecarboxylate (1.5 mmol) in 10 mL of anhydrous ether was added dropwise over a 15-min period to a suspension of $LiAlH_4$ (6.0 mmol) in 30 mL of refluxing ether. The mixture was refluxed for an additional 24–48 h and then quenched with ethyl acetate, and the products were isolated after acidification and extraction. With the 2-*n*-butylcyclopropanecarboxylate (trans/cis = 2.0), the product mixture contained 67% *trans*-2-(*n*-butyl)cyclopropanemethanol, 7% *cis*-2-(*n*-butyl)cyclopropanemethanol, and 26% 2,6-di-*tert*-butyl-4-methylphenyl *cis*-2-(*n*-butyl)cyclopropanecarboxylate after a reaction time of 34 h. Similar results were obtained with the 2-phenylcyclopropanecarboxylate esters. In contrast, both cis and trans isomers of 2,6-di-*tert*-butyl-4-methylphenyl 2-ethoxycyclopropanecarboxylate were reduced by $LiAlH_4$ after 24 h in refluxing ether, and no isomerization of reactants or products was evident. Reductions of BHT cyclopropane esters formed from 1-hexene and styrene were virtually complete after 72 h (1-hexene, <5% cis BHT ester) adn 15 h (styrene) in refluxing THF. However, neither the trans nor the cis isomer of the BHT chrysanthemate ester **4j** underwent reduction in refluxing THF.

Relative Reactivities of Alkenes in Cyclopropanation Reactions. The diazo compound, (0.50 mmol), either ODA or BDA, in 3.0 mL of anhydrous methylene chloride was added at a controlled rate over a 5-h period to a stirred mixture of two alkenes (minimum amount of each olefin: 5.0 mmol), which normally included 1-hexene, and either $Rh_2(OAc)_2$ or $Rh_2(acam)_4$ (0.005 mmol) in 3.0 mL of dichloromethane. Reactions catalyzed by $Rh_2(OAc)_4$ were performed at room temperature, and those catalyzed by $Rh_2(acam)_4$ were run in refluxing dichloromethane, both under nitrogen. Products were isolated as previously described, and relative reactivities were obtained from product ratios determined by GC and ^1H NMR analyses. Duplicate experiments were performed for each pair of alkenes, and cross-checks of relative reactivity values were obtained from experiments with different sets of alkenes. Typical values for $Rh_2(OAc)_4$-catalyzed reactions of BDA were ethyl vinyl ether/1-hexene, 13; styrene/1-hexene, 3.8; and ethyl vinyl ether/styrene, 3.4.

Acknowledgment. We are grateful to the National Science Foundation for their support of this research and to the Johnson Mathey Co. for their loan of rhodium(III) chloride. Cassandra Eagle was a Camille and Henry Dreyfus Foundation Teaching and Research Fellowship recipient.

Effects of Hydrogen Bonding on the Low-Lying Electronic States of a Model Polyene Aldehyde

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Received June 12, 1989

Abstract: Absorption spectra of crotonaldehyde in several alcohols demonstrate linear relationships between the energies of the lowest lying $^1\pi\pi^*$ and $^1n\pi^*$ transitions and the solvent pK_a, with the $^1\pi\pi^*$–$^1n\pi^*$ energy difference decreasing from 14 800 to 8500 cm^{-1} in changing from ethanol (pK_a = 16.0) to perfluoro-*tert*-butanol (pK_a = 5.2). These results indicate that the pK_{HB} for hydrogen-bond formation is proprotional to the pK_a of the alcohol solvent in both the ground and excited states. The ability of strong hydrogen bonders to differentially shift low lying $^1\pi\pi^*$ and $^1n\pi^*$ states in polyene aldehydes has been used to invert the $^1\pi\pi^*$/$^1n\pi^*$ ordering and induce fluorescence in 2,4,6,8-decatetraenal, a model compound which does not emit in hydrocarbon environments. Absorption, fluorescence, and fluorescence excitation spectra of decatetraenal have been obtained in several hydrogen-bonding solvents over a range of temperatures. The fluorescence intensities are strongly temperature dependent and can be fit to a simple model involving a low-temperature ($T \leq 77$ K) equilibrium between a nonemitting, hydrogen-bonded complex and a fluorescent species which is either protonated or strongly hydrogen bonded. The changes in the optical spectra with temperature and the pK_a of the hydrogen bonder lead to a model in which the allowed transition between the hydrogen-bonded ground ("1^1A_g") and excited ("1^1B_u") states is followed by relaxation into an excited $^1\pi\pi^*$ state that at low temperatures favors a strongly hydrogen bonded or protonated form. Protonated decatetraenal has $^1\pi\pi^*$ lower than $^1n\pi^*$, thus accounting for the observed fluorescence. Molecular orbital calculations support this model and also indicate an inversion of the "1^1B_u" and "2^1A_g" energy levels upon protonation.

1. Introduction

Linear polyenes are employed as chromophores in several important photobiological processes. Vision, photosynthesis, and photoperiodism all depend on the unique chemistries of polyene excited states, and the characterization of these states has been a subject of considerable interest.[1-3] In addition to their roles in natural processes, polyenes are of intrinsic interest as "one-dimensional" conjugated systems, and progress in understanding

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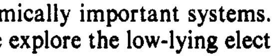
the electronic properties of such systems has required close interplay between theory and experiment.

Recent optical experiments have concentrated on simple, unsubstituted polyene hydrocarbons that exhibit well-resolved (and thus *informative*) vibronic spectra even in 77 K glasses.[4,5] These spectra as well as high-resolution spectra of low-temperature mixed crystals[2,6,7] and gases in supersonic jets[8,9] have furnished a greatly improved picture of excited-state symmetries and structures in model polyene hydrocarbons. Our knowledge of polyene aldehydes and Schiff bases, however, is considerably more limited than that of their hydrocarbon counterparts. These limitations are significant since it is just in these substituted forms that polyenes carry out their photobiological roles.

Polyene aldehydes and Schiff bases have several features of potential photochemical importance. Their reduced symmetries lead to *polar* electron distributions that vary both with electronic state and solvent environment. Nonbonded electrons can participate in reactions involving hydrogen bonding and proton transfer, and changes in polarity and basicity upon excitation offer additional mechanisms by which electronic excitation can be communicated to and modulated by the surroundings.

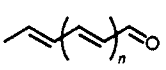
The spectroscopy of polyene aldehydes and Schiff bases has been hindered by many of the same features that make them so interesting. Low-lying $n\pi^*$ states contribute to spectral broadening[10] and in shorter systems (≤ 6 conjugated double bonds) severely reduce or completely eliminate fluorescence.[11-16] Hydrogen bonding can lead to complicated distributions of solute/solvent complexes and further hinder interpretation of spectra.[12,13,17-19] As a result, theoretical calculations on these systems have not been subjected to the same experimental scrutiny as those for corresponding hydrocarbons, though vibronically resolved optical spectra of model aldehydes and Schiff bases have begun to contribute toward a better picture of the excited states of these photochemically important systems.[6,11,12]

In this study we explore the low-lying electronic energy levels of *all-trans*-decatetraenal. Previous studies by Becker[11] and others



all-trans-2, 4, 6, 8-decatetraenal

on model polyene aldehydes suggest that in decatetraenal and



shorter polyene aldehydes ($n \leq 3$) the lowest energy singlet state is ${}^1n\pi^*$. In the shortest members of this series (e.g., crotonaldehyde, $n = 0$), the ${}^1n\pi^*$ state can be observed directly.[20] For longer compounds (n = 1, 2, and 3) the presence of a low-lying ${}^1n\pi^*$ state is inferred from the lack of fluorescence that contrasts with the substantial emission yields of analogous hydrocarbons.[2,6,7] The quenching of polyene fluorescence by low-lying ${}^1n\pi^*$ states has been attributed to enhanced intersystem crossing into nonradiative triplets.[21,22] Long polyene aldehydes ($n > 5$) fluoresce, even in nonhydrogen-bonding solvents, and this diagnostic leads to the assignment of $E({}^1n\pi^*) > E({}^1\pi\pi^*)$ in longer systems. For $n = 4$, the $n\pi^*$ and $\pi\pi^*$ energies apparently are very close. For example, the visual chromophore, retinal, does not fluoresce in dry, hydrocarbon solvents, indicating $E({}^1n\pi^*) < E({}^1\pi\pi^*)$ for the free species.[18,19] The fluorescence properties of dodecapentaenal, however, are less certain. Becker et al.[13] claim fluorescence in dry solvents, while Hudson and Loda[12] indicate that fluorescence is due to hydrogen-bonded species. The important point is that $E({}^1n\pi^*) \approx E({}^1\pi\pi^*)$ for $n = 4$ and $E({}^1n\pi^*) < E({}^1\pi\pi^*)$ for shorter polyene aldehydes.

We have carried out detailed spectral studies of decatetraenal in several hydrogen bonders (alcohols and fluorinated alcohols) with pK_a's ranging from 4.7 to 17.0. These solvents have provided control over the equilibria between free and hydrogen-bonded species and have yielded samples in which the state of complexation is well understood. Spectra of these samples have proven simpler to interpret than those obtained from previous comparisons of "dry" vs "wet" solvents.[12,13,18,19]

The initial aim of this work was to obtain spectra of homogeneously hydrogen-bonded polyene aldehydes under conditions where $E({}^1\pi\pi^*) < E({}^1n\pi^*)$. These systems should exhibit fluorescence spectra similar to those of analogous polyene hydrocarbons and provide comparable spectroscopic information, e.g., the energies of the lowest lying ${}^1\pi\pi^*$ states (1^1B_u and 2^1A_g).[2] (The state symbols strictly apply to the symmetric polyene hydrocarbons and are only approximate for the polyene aldehydes.) Observing and locating the 2^1A_g states in these systems invariably rests on the detection of emission, either by direct observation of fluorescence origins or by detecting these origins in fluorescence excitation spectra (both one- and two-photon).[23,24] Determination of $1\pi\pi^*$ energies and in particular the $1^1A_g \leftrightarrow 2^1A_g$ transition energy would provide a direct comparison with corresponding energies in polyene hydrocarbons. This would be useful in evaluating calculations of low-lying ${}^1\pi\pi^*$ states in a variety of polyene aldehydes, Schiff bases, and protonated Schiff bases.[25] Theoretical understanding of the energies and properties of the low-energy states in the latter compounds are of particular significance in understanding the photochemistry of the visual pigment rhodopsin.[25]

While our primary goal was simply to use hydrogen bonding as a tool to reveal low-lying ${}^1\pi\pi^*$ states in polyene aldehydes, we also have learned something about the nature of hydrogen bonds in a prototypical polyene system. Apparent changes in hydrogen-bond strength upon electronic excitation and the possible effects of proton movement either on or off the carbonyl group present issues of potential photochemical interest. Comparisons of hydrogen bonding in polyene aldehydes and Schiff bases also are discussed.

2. Experimental Section

2.1. Samples. Crotonaldehyde (Aldrich) was purified by distillation. Room-temperature, UV absorption spectra were obtained of 10^{-2} M solutions of crotonaldehyde in ethanol (U.S. Industrial Chemicals), methanol (Burdick and Jackson), 2,2,2-trifluoroethanol (Aldrich), 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich), and perfluoro-*tert*-butanol (PCR Incorporated), providing solvent pK_a's of 16.0,[26] 15.0,[26] 12.4,[27]

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9.3,[28] and 4.7,[29] respectively. Trifluoroethanol and hexafluoro-2-propanol were distilled prior to their use as solvents in low-temperature emission and excitation spectra. Other solvents were used without further purification.

all-trans-2,4,6,8-Decatetraenal was obtained from the acid-catalyzed condensation of crotonaldehyde and hexadienal.[30,31] The tetraenal was purified by HPLC with use of a silica column (Altex-Spherisorb) and a mobile phase of hexane/ether (95%/5%, vol/vol). Purified samples of decatetraenal were stable (gave reproducible UV spectra) for periods of several weeks, if stored in dilute hexane at −20 °C. Samples for spectral measurements were prepared by evaporating a few milliliters of the hexane stock solution with a stream of nitrogen gas and then reconstituting the aldehyde in the appropriate hydrogen bonding solvent.

Low-temperature (10–100 K) optical measurements were obtained by cooling samples with a closed-cycle helium refrigerator (Air Products, Displex Model DE202). The sample cell was based on the design of Carter and Gillespie[32] and employed a cylindrical quartz tube (~8 mm internal diameter) mounted around a cylindrical copper cold finger (~6 mm in diameter) that was in good thermal contact with the last stage of the helium refrigerator. Samples mounted this way thus were contained within a 1-mm thick layer between the quartz sample tube and cold finger. High-resolution fluorescence spectra obtained in a previous study exhibited constant line widths, independent of the location of excitation, indicating constant temperatures throughout the sample volume. Temperatures reported here are accurate to one degree.

Certain spectra at 77 K were more conveniently obtained by immersing a long cylindrical sample tube in a standard liquid nitrogen cryostat. Sample placement under these conditions was found to be very reproducible and allowed accurate (<5% error) comparison of relative fluorescence intensities in different hydrogen-bonding solvents.

2.2. Spectral Measurements. Absorption spectra of room-temperature solutions and 77 K glasses (ethanol/methanol, 4:1 vol/vol) were obtained on a Shimadzu UV240 spectrophotometer interfaced to a microcomputer. Low-temperature (10–77 K) absorption spectra in nonglassy, snowy solvent matrices were acquired on a homebuilt apparatus. Light from a 150-W Xenon lamp was filtered and then focused through masks into a small hole (3-mm diameter) drilled normal to the axis of the copper cold finger. Light scattered through to the other side of the hole was collected and focused onto the slit of a 1-m monochromator (Instruments SA) and the intensity digitally recorded as a function of wavelength. Similar spectra were recorded without the decatetraenal (but with the highly scattering solvent) and the absorption obtained from the logarithmic ratio of the two spectra. Spectra were then smoothed by using standard digital techniques. Room-temperature absorption spectra taken in this way compared well with spectra obtained on the Shimadzu spectrophotometer. Spectra (77 K) of ethanol/methanol glasses also were in good agreement, thus providing some confidence that absorption spectra of low-temperature, highly scattering samples also were accurate.

Fluorescence and fluorescence excitation spectra were obtained on a SPEX Model 212 spectrofluorimeter, equipped with a SPEX DM1B data station for acquisition and storage of digitized spectra. All spectra were corrected for the wavelength dependencies of optical components and then transferred to a main frame computer for subsequent manipulation and hard copy display. Corrected excitation of standard samples such as naphthalene and anthracene were in excellent agreement with absorption spectra taken on the Shimadzu spectrophotometer, showing that the excitation correction procedures were valid over the wavelength range of interest (300–400 nm).

2.3. Molecular Orbital Computions. The AM1 model[33] was used to map the ground-state potential energy as a function of proton position in the hydrogen bond between crotonaldehyde and methanol. The O···O distance was fixed at 0.273 nm,[34] and the proton position was changed in 0.01-nm increments. The geometries of both molecules were optimized at each position.

The ZINDO model[35] was used to compare the $1^1A_g \rightarrow 2^1A_g$, 1^1B_u, and $^1n\pi^*$ electronic transition energies of protonated decatetraenal (hydrogen bonded to methoxide ion) with those of its hydrogen-bonded and free forms. The AM1 optimized ground-state geometries were used and held fixed to give vertical transitions. Mataga–Nishimoto repulsion integrals were chosen, and the configuration interaction included 49 singly excited and 96 doubly excited configurations.

Table I. $^1n\pi^*$ and $^1\pi\pi^*$ (1^1B_u) Transition Energies of Crotonaldehyde in Several Alcohol Solvents at Room Temperature[a]

solvent	pK_a	$^1n\pi^*$ (nm)	$^1\pi\pi^*$ (nm)	$^1\pi\pi^*-{}^1n\pi^*$ (cm^{-1})
ethanol	16.0	315.0	215.0	14 800
methanol	15.0	315.4	216.8	14 400
TFE	12.4	298.0	220.0	11 900
HFIP	9.3	286.4	223.6	9 900
PFTB	5.2	282.1	227.5	8 500

[a] Transition energies refer to band maxima rather than to electronic origins. Solvents: TFE (2,2,2-trifluoroethanol), HFIP (1,1,1,3,3,3-hexafluoro-2-isopropyl alcohol), and PFTB (perfluoro-*tert*-butanol).

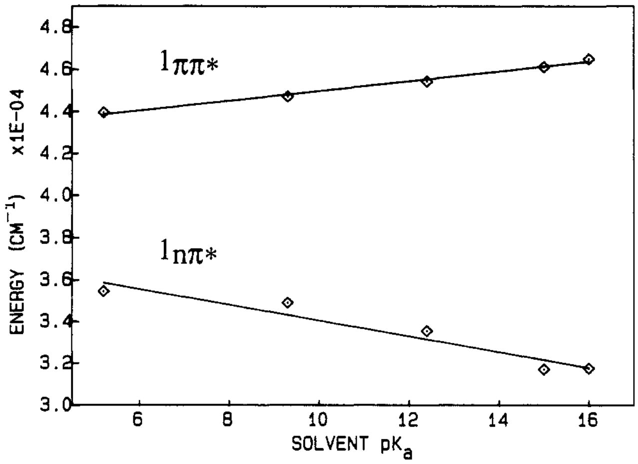

Figure 1. $^1n\pi^*$ and $^1\pi\pi^*$ energies of crotonaldehyde as a function of solvent pK_a. Energies refer to band maxima.

3. Results

In our previous study, fluorescence and fluorescence excitation spectra of a simple polyene Schiff base, *N*-(2,4,6,8,10)-dodecapentaenylidene, were obtained in a 77 K hydrocarbon glass.[36] Spectra were obtained for a one-to-one complex between the Schiff base and perfluoro-*tert*-butyl alcohol and for complexes containing several molecules of the alcohol that we assumed were linked together to form a polar solvent cage around the Schiff base nitrogen. These spectra were sufficiently resolved to permit the accurate location of electronic origins in the free, hydrogen-bonded, and protonated Schiff base species. A later study by Blatz et al.[37] on the same Schiff base investigated the temperature and solvent dependence of the equilibria between the three species. These experiments demonstrated that ground-state polyene Schiff bases can be both readily hydrogen bonded and protonated at low temperatures (T < 200 K).

Parallel hydrogen bonding studies on decatetraenal and other polyene aldehydes have not met with the same success. Decatetraenal exhibited well-resolved absorption, but no detectable emission in dry, hydrocarbon glasses. Addition of equimolar amounts of perfluoro-*tert*-butanol had no perceptible effect, either in shifting the absorption or in inducing fluorescence. Systematic addition of additional amounts of hydrogen bonder (up to a 200-fold excess) gave rise to both red-shifted absorption and emission. However, the lack of correspondence between absorption and fluorescence excitation spectra and the dependence of the fluorescence on the wavelength of excitation suggested a complicated equilibrium between several emitting and nonemitting species. In addition, the concentration dependence of the observed

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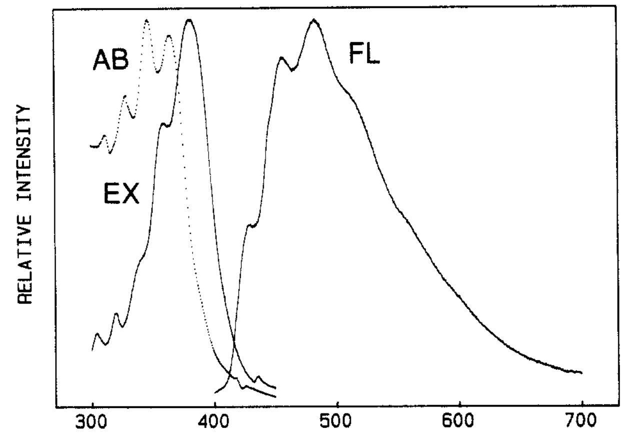

Figure 2. 77 K absorption (AB), 10 K fluorescence (FL), and 10 K fluorescence excitation (EX) spectra of decatetraenal in ethanol/methanol glass (pK_a = 15.0). Fluorescence was obtained with 380-nm excitation, and the excitation spectrum was monitored at 500 nm.

spectra and the overall loss of absorption with increasing hydrogen bonder concentration signaled aggregation and/or precipitation in our samples. This work suggested that hydrogen-bonded polyene aldehydes are considerably less soluble and/or considerably less stable in nonpolar environments than the closely related Schiff bases. This may be due to the higher electronegativity of the aldehyde oxygen compared with the Schiff base nitrogen.

In preparation for hydrogen-bonding studies of polyene aldehydes in polar solvents, we investigated the low-energy electronic transitions in crotonaldehyde

a prototypical polyene aldehyde for which the low-lying $^1n\pi^*$ and $^1\pi\pi^*$ states are readily discernible even in room-temperature absorption solution spectra.[20] Absorption spectra of crotonaldehyde were obtained in several alcohol solvents with a wide range of hydrogen bonding capabilities. Energies of the low-energy $^1n\pi^*$ and $^1\pi\pi^*$ (^1B_u) states are given in Table I and plotted as a function of solvent pK_a in Figure 1. (It should be noted that the energies given refer to band maxima, rather than (0–0) transition energies.) Both the $^1n\pi^*$ and ^1B_u energies appear to be linearly related to the pK_a of the solvent. The transition energies did not correlate as well with the solvent refractive index and correlated poorly with the solvent dipole moment and dielectric constant.

Regardless of the source of the spectral shifts, the data presented in Figure 1 suggests the use of the various alcohols to "tune" the $^1n\pi^*/^1\pi\pi^*$ energy differences in crotonaldehyde and longer polyene aldehydes. Relative shifts > 10^4 cm^{-1} can be realized, thus providing a potentially useful tool for inverting $n\pi^*/\pi\pi^*$ state orderings, particularly in polyene aldehydes (and Schiff bases) such as decatetraenal where the low-lying $^1n\pi^*$ and $^1\pi\pi^*$ states are within a few 1000 cm^{-1} in uncomplexed species. State inversions should have significant effects on the rates of radiative and nonradiative decay in these systems.

Low-temperature (10 K) optical spectra of decatetraenal in an ethanol/methanol glass (4/1, vol/vol) are presented in Figure 2. These samples clearly fluoresce. However, the lack of agreement between absorption and fluorescence excitation spectra indicates that the emission is due to a minor, red-shifted species. A substantial fraction of the decatetraenal remains nonemitting. The stronger hydrogen bonders, trifluoroethanol (pK_a = 12.4) and hexafluoroisopropol alcohol (pK_a = 9.3) give decidedly different results (Figures 3 and 4). In both of these solvents, the absorption and excitation spectra are in good agreement, indicating a considerably larger fraction (>90%) of emitting species. It also is important to note that for all three solvent systems the fluorescence spectra are independent of the wavelength of excitation and the excitation spectra do not depend on the wavelength of emission. This strongly suggests that, for each case, emission is from a rather homogeneous distribution of solvent/solute complexes. A summary of the 10 K absorption, excitation, and emission band maxima in the three hydrogen-bonding solvents is provided in Table II.

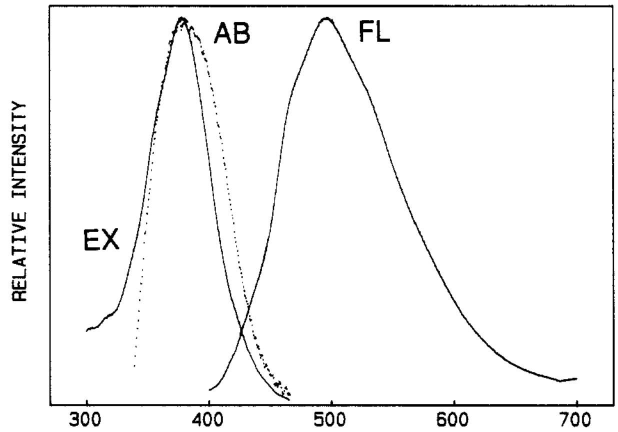

Figure 3. 10 K absorption (AB), fluorescence (FL), and fluorescence excitation (EX) spectra of decatetraenal in trifluoroethanol (pK_a = 12.4). Fluorescence was obtained with 380-nm excitation, and the excitation spectrum was monitored at 500 nm.

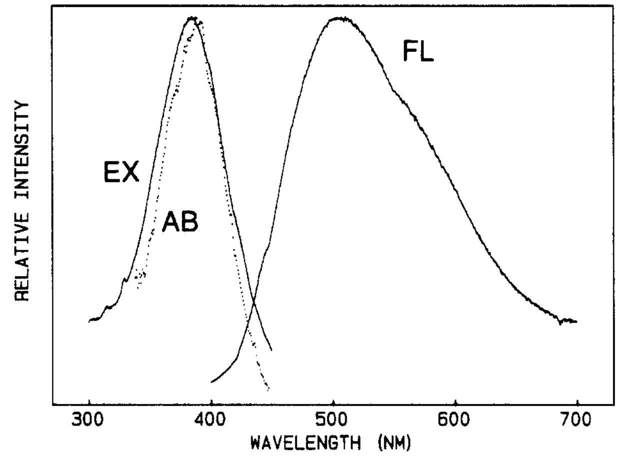

Figure 4. 10 K absorption (AB), fluorescence (FL), and fluorescence excitation (EX) spectra of decatetraenal in hexafluoroisopropyl alcohol (pK_a = 9.3). Fluorescence was obtained with 380-nm excitation, and the excitation spectrum was monitored at 500 nm.

Table II. Absorption, Fluorescence Excitation, and Fluorescence Band Maxima of Decatetraenal at 10 K in Different Hydrogen Bonding Solvents[a]

	band maxima (nm)		
solvent	absorption	excitation	emission
EtOH/MeOH	365	380	483
TFE	375–380	378	498
HFIP	385–390	385	511

[a] Solvents: ethanol/methanol (4:1, vol/vol), trifluoroethanol (TFE), and hexafluoroisopropyl alcohol (HFIP)

The other major difference between hydrogen bonders can be seen in the temperature dependences of their emission intensities (Figure 5). At 77 K the three solutions give comparable intensities. At 10 K, however, both the decatetraenal/hexafluoroisopropyl alcohol and decatetraenal/trifluoroethanol fluorescences are 4–5 times more intense than the emission observed in ethanol/methanol. The net fluorescence yield of decatetraenal is thus sensitive both to the hydrogen bonder and the temperature. It should be mentioned, however, that for a given hydrogen bonder, the relative shapes and positions of the absorption, emission, and excitation spectra are independent of temperature. This is illustrated by a comparison of excitation and emission spectra of decatetraenal/hexafluoroisopropyl alcohol at

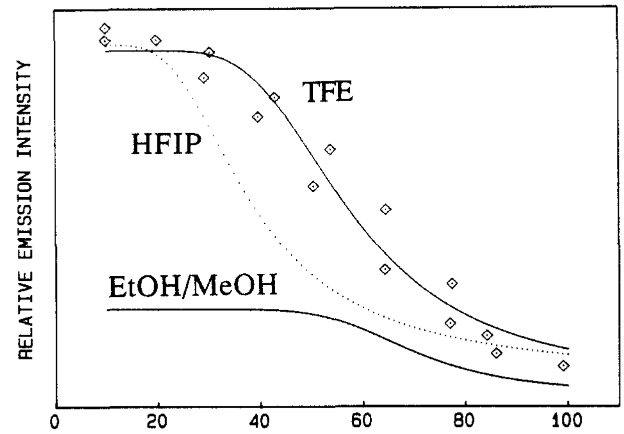

Figure 5. Temperature dependence of decatetraenal fluorescence intensity (band maximum) in ethanol/methanol (EtOH/MeOH), trifluoroethanol (TFE), and hexafluoroisopropyl alcohol (HFIP). Curves represent best fits of fluorescence intensities to simple, two-species equilibria (eq 1). Points represent data for TFE obtained with both increasing and decreasing temperatures.

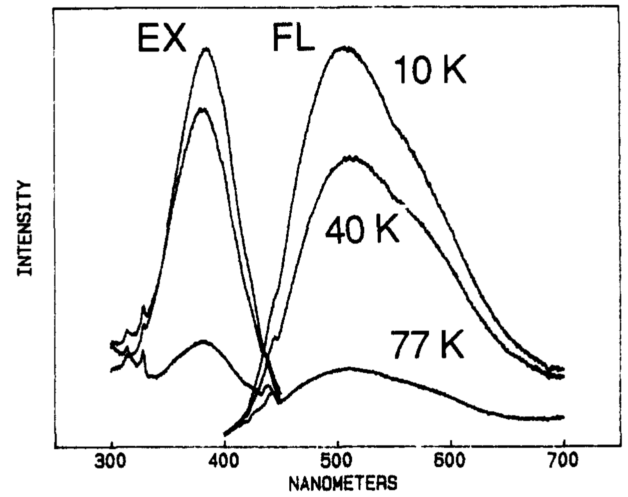

Figure 6. Decatetraenal/hexafluoroisopropyl alcohol fluorescence and fluorescence excitation spectra as a function of temperature.

several temperatures (Figure 6).

For each of the hydrogen-bonding solvents the increase in fluorescence intensity with decreasing temperature can be accounted for by a simple equilibrium between an emitting and a nonemitting species (see Figure 5). The equilibrium expression,

$$\text{A (nonfluorescent)} \leftrightarrow \text{A}' \text{ (fluorescent)} \qquad (1)$$

$K_{eq} = [A']/[A]$, and the relation describing the partition of the aldehyde between emitting and nonemitting species ($[A]_0 = [A] + [A']$) give the following:

$$K_{eq}/(K_{eq} + 1) = [A']/[A]_0 \qquad (2)$$

By using the linear relationship between the fluorescence intensity and the concentration of emitting species ($I_f = k[A']$) and the expression for the temperature dependence of the equilibrium constant

$$K_{eq} = \exp(\Delta S/R - \Delta H/RT) \qquad (3)$$

leads to the following relationship between the fluorescence intensity and relevant thermodynamic parameters

$$I_f = k' \exp((T\Delta S - \Delta H)/RT)/[1 + \exp((T\Delta S - \Delta H)/RT)] \qquad (4)$$

where k' is a constant proportional to the initial free aldehyde concentration, the fluorescence yield of the emitting species, the excitation light intensity, and other instrumental factors. The thermodynamic parameters ΔH and ΔS were assumed to be independent of temperature over the 10–100 K range of our experiments. Intensity versus temperature data were fit to eq 4 by using a SIMPLEX algorithm[38,39] with k', ΔH, and ΔS as adjustable parameters. A representative fit for the trifluoroethanol/decatetraenal system is given in Figure 5. Final data sets included intensities measured as the temperature was both decreased and increased. The thermodynamic parameters permit the equilibrium constants to be calculated at different temperatures, and a summary of extracted constants is presented in Table III.

Table III. Thermodynamic Constants for Decatetraenal/Alcohol Equilibria (Eq 1)[a]

solvent	pK_a	ΔH (kJ/mol)	ΔS (J/mol K)	K_{eq} (77 K)	K_{eq} (10 K)
HFIP	9.3	−1.15 ± 0.09	−28.3 ± 2.9	0.19 [illegible] 0.07	$\approx 10^4$
TFE	12.4	−2.26 ± 0.32	−38.2 ± 5.1	0.34 ± 0.27	$\approx 10^9$
EtOH/MeOH	16.0	−4.01 ± 0.56	−57.2 ± 7.8	0.53 ± 0.69	$\approx 10^{17}$

[a] Solvents: hexafluoroisopropyl alcohol (HFIP), trifluoroethanol (TFE), and ethanol/methanol (4:1, vol/vol).

4. Discussion

The data presented in Figure 1 show the expected red shifts of the $\pi \rightarrow \pi^*$ transition and the blue shifts of the $n \rightarrow \pi^*$ transition in hydrogen-bonding solvents.[40] The $\pi \rightarrow \pi^*$ transition presumably increases the electron density on the polyene oxygen, resulting in hydrogen bonds that are stronger in the 1^1B_u excited state than in the 1^1A_g ground state. The $n \rightarrow \pi^*$ transitions, on the other hand, remove electron density from the hydrogen-bonded oxygen, and it often is considered that the hydrogen bond is severely weakened or broken in the $n\pi^*$ state, thus leaving its energy unaffected by hydrogen bonding. This leads to the blue shifts observed in crotonaldehyde and a wide range of other organic compounds. Indeed, the blue shift phenomenon has been a widely used criterion for identifying $n\pi^*$ bands.[41]

Spectral shifts for a solute capable of hydrogen bonding with the solvent result from dispersion forces, dipole-induced–dipole forces, and dipole–dipole forces as well as hydrogen-bonding interactions. These non-hydrogen-bonding forces are significant as indicated by the fact that crotonaldehyde in dry acetonitrile exhibits large spectral shifts (1065 cm^{-1} for the $n\pi^*$ state and 1215 cm^{-1} for the $\pi\pi^*$ state) relative to hexane as a solvent. The poor correlation with solvent polarity and polarizability, however, indicates that for the alcohol series pK_a appears to be the most important variable.

Previous studies of hydrogen-bond formation in the electronic ground states of aromatic compounds have shown that the pK_{HB} for hydrogen-bond formation is proportional to the pK_a of the alcohol solvent.[42] Although these studies were done on ground states, it is reasonable to assume that the excited-state equilibrium constants exhibit a similar proportionality, i.e.,

$$\text{p}K_{HB}(\text{GS}) = \alpha \cdot \text{p}K_a \quad \text{and} \quad \text{p}K_{HB}(\text{ES}) = \beta \cdot \text{p}K_a \qquad (5)$$

where pK_{HB}(GS) and pK_{HB}(ES) refer to the hydrogen-bonding equilibria in the ground and excited states and where α and β are constants.

Following standard solvent shift and thermodynamic analysis,[40] the spectral shifts associated with hydrogen bonding can be related to the ground- and excited-state bond energies as follows:

$$\Delta\bar{\nu} = (\Delta H_{GS} - \Delta H_{ES}) = 2.303RT(\text{p}K_{HB}(\text{GS}) - \text{p}K_{HB}(\text{ES})) + T(\Delta S_{GS} - \Delta S_{ES}) \qquad (6)$$

whrere ΔH_{GS}, ΔS_{GS}, ΔH_{ES}, and ΔS_{ES} refer to enthalpy and entropy changes for hydrogen-bond formation in the two electronic

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(38) Nedler, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.

(39) Routh, M. W.; Swartz, P. A.; Denton, M. B. *Anal. Chem.* **1977**, *49*, 1422–1428.

(40) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker; New York, 1970; pp 333–346.

(41) Brealey, G. J.; Kasha, M. *J. Am. Chem. Soc.* **1955**, *77*, 4462–4468.

(42) Gordon, J. E. *J. Org. Chem.* **1961**, *26*, 738.

states. ΔS (and thus $T\Delta S$) should be constant for this series of similar alcohols. This approximation, along with the relationships given in eq 5, allows us to simplify eq 6, giving

$$\Delta\bar{\nu} = 2.303RT(\alpha - \beta)\text{p}K_a + \delta \qquad (7)$$

where δ is a constant for a series of similar hydrogen-bonding alcohols. The linear relationships between the shifts in electronic transition energies and the solvent pK_a that we have observed for crotonaldehyde (Figure 1) thus can be rationalized. It also is interesting to note that $(\alpha - \beta) > 0$ for the $\pi\pi^*$ transitions and < 0 for the $n\pi^*$ transitions, giving rise to the well-known "red" and "blue" shifts used to characterize these transitions.[41] We assume that similar hydrogen-bonding interactions operate in longer polyene aldehydes where the $n \rightarrow \pi^*$ transitions are not as clearly discernible as in crotonaldehyde.

The induction of fluorescence in decatetraenal supports previous studies of Becker and others on several shorter and longer members of the polyene aldehyde series.[11-19] Indeed, the absorption, fluorecence, and fluorescence excitation spectra of decatetraenal in an ethanol/methanol glass (Figure 2) are very similar to spectra obtained by Das and Becker[11] in an EPA glass. The mismatch between the absorption and fluorescence excitation spectra of these samples also is comparable to spectra obtained of retinal in "wet" hydrocarbon solvents.[18,19] Fluorescence in these samples can be assigned to aldehyde species that are complexed with hydrogen bonders. The difference between excitation and absorption spectra seen in Figure 2 indicates that only a small fraction of the decatetraenal species are hydrogen-bonded, even in a system such as ethanol/methanol where the polyene aldehyde (10^{-5} M) should be overwhelmed by the hydrogen-bonding solvent. In the hydrogen-bonded complexes the low-lying $^1n\pi^*$ states are shifted above the low-energy $^1\pi\pi^*$ states, resulting in fluorescence spectra similar to those obtained for analogous polyene hydrocarbons. The inability of the ethanol/methanol glass to completely complex the polyene aldehyde can be traced to the propensity of alcohols to self-associate. For example, room-temperature studies of pure ethanol indicate that cyclic and linear tetramers are much more abundant than the alcohol monomer.[43] Self-association drastically reduces the ability of ethanol (and methanol) to hydrogen bond to the aldehyde, and the difference between the absorption and excitation spectra seen in Figure 2 suggests that the dominant aldehyde species in these low-temperature glasses is not hydrogen bonded. The free aldehydes thus retain $^1n\pi^*$ as the lowest energy excited state and remain nonfluorescent.

In contrast to the ethanol/methanol glass, pure trifluoroethanol and hexafluoroisopropyl alcohol completely complex the polyene at 77 K. The absorption and excitation spectra are in good agreement, indicating that little if any free aldehyde exists at low temperature. That the fluorescence spectra are independent of the wavelength of excitation and the excitation spectra do not depend on the wavelength of analysis also supports the idea that the emission comes from a homogeneous distribution of solvent/solute complexes. The stronger hydrogen bonders thus realize the goal of complete inversion of the $^1n\pi^*/^1\pi\pi^*$ state ordering, giving excitation and emission spectra similar to those obtained for comparable polyene hydrocarbons. The polyene aldehyde spectra, however, remain broad with little vibronic structure. This may be due to the stronger interactions between the polar, hydrogen-bonded complexes and the polar solvent environment as well as mixing between the $^1n\pi^*$ and $^1\pi\pi^*$ states.[44]

The unusual temperature dependences of the fluorescence give further insights into the nature of the emitting species in these samples. The fluorescence intensities (Figure 5) are well accounted for by a simple equilibrium (eq 1) between two types of polyene aldehydes: a high-temperature, nonemitting form and a low-temperature, emitting form. The presence of a single emitting species also is required by the temperature independence of both the excitation and fluorescence spectra. Because the equilibrium occurs in high viscosity glasses and rigid matrices the two species must have very similar geometries. This rules out, for example, the possibility that the nonemitting species is free aldehyde and the emitting species is hydrogen bonded. We thus suggest that at 77 K both the hexafluoroisopropyl alcohol and the trifluoroethanol form hydrogen-bonded complexes with the aldehyde in essentially 100% yield. The ethanol/methanol glass, on the other hand, only partially complexes the aldehyde due to the dominance of self-associated alcohols.

Data presented in table III show that at 77 K only a fraction of the complexes are in the fluorescent form ($K_{eq} < 1$). Cooling the samples to 10 K results in the complete conversion to emissive species ($K_{eq} \gg 1$). The lower 10 K fluorescence intensity in ethanol/methanol partly reflects the dominance of uncomplexed aldehyde species in the rigid glass. Indeed, the ratio between 10 K emission intensities indicates that no more than 20–25% of the aldehydes are complexed to ethanol or methanol during formation of the glass. This also accounts for the differences between the absorption and excitation spectra seen in Figure 2. For the other two alcohol solvents the aldehydes are completely complexed at all temperatures ($T < 100$ K). We thus distinguish between three types of aldehydes: *Free aldehyde* species remain nonfluorescent at all temperatures. *Complexed aldehydes* are assumed to exist in two forms in thermal equilibrium, a hydrogen-bonded form for which the nonemissive $^1n\pi^*$ state remains below the 2^1A_g and 1^1B_u levels and an emissive, protonated form for which the $^1n\pi^*$ and $^1\pi\pi^*$ levels are inverted.

An additional issue is the assignment of the lowest energy excited $\pi\pi^*$ state (2^1A_g or 1^1B_u) in complexed decatetraenal. Das and Becker estimate that the 2^1A_g state lies 2100 ± 700 cm^{-1} below the 1^1B_u state for non-hydrogen-bonded decatetraenal in EPA at 77 K.[11] Our ZINDO calculations also predict 2^1A_g below 1^1B_u for free decatetraenal but with a high degree of mixing between the two states in agreement with the experimental observations of Das and Becker.[11] The 2^1A_g–1^1B_u separation is comparable to that found in dodecapentaenal (3400 ± 500 cm^{-1})[11] and its Schiff base (3100 cm^{-1})[36] and in *all-trans*-retinal (2400 cm^{-1})[45] and its Schiff base (2800 cm^{-1}).[45] This gap is expected to decrease as the number of double bonds decreases as for model polyene hydrocarbons.[4,5]

The 2^1A_g state is presumed to remain below the 1^1B_u in hydrogen-bonded decatetraenal based on the ZINDO calculations that predict a similar red shift for the corresponding transitions upon hydrogen bonding. The energy gap should narrow, however, since hydrogen bonding stabilizes the "ionic" 1^1B_u state preferentially.[25,45] If the 2^1A_g state does lie below the 1^1B_u, it must still be above the $^1n\pi^*$ state since emission is not observed for the hydrogen-bonded aldehyde. From our excitation spectra and the data of Das and Becker,[11] the 1^1B_u–$^1n\pi^*$ gap is about 1900 cm^{-1} in ethanol/methanol and only 600 cm^{-1} in HFIP. Two-photon absorption studies[45] would be useful in more precisely locating the position of the 2^1A_g state of decatetraenal in these solvents.

The ZINDO theory predicts a very large (~10 000 cm^{-1}) red shift for the $1^1A_g \rightarrow 1^1B_u$ transition upon protonation and a slight (~1000 cm^{-1}) blue shift of the $1^1A_g \rightarrow 2^1A_g$ transition, indicating that the two excited states invert in going from the hydrogen-bonded to protonated decatetraenal. These results agree both with the molecular orbital predictions and experimental data for retinyl Schiff bases.[25,45] However, it is important to note that the hydrogen-bonding network in the alcohol solvents very likely results in a delocalized counterion for the protonated aldehyde.[36] Our calculated shifts thus may be too large as a result of a geometry that represents a localized counterion and perhaps "overprotonation" of the aldehyde.[36,45] The calculations also neglect solvent interactions. The two $\pi\pi^*$ states are so close to one another in the hydrogen-bonded species, however, that only slight shifts could result in state inversion. The separation (nearest peaks) between the 1^1B_u absorption of the free decatetraenal and the emission of the protonated species is 3900 cm^{-1} in ethanol/methanol. This energy is similar to the 3700-cm^{-1} separation between the 1^1B_u absorption in the free and protonated forms of

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(44) Hochstrasser, R. M. *Acc. Chem. Res.* **1968**, *1*, 266–274.

(45) Birge, R. R.; Murray, L. P.; Zidovetski, R.; Knapp, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 2090–2101.

the *all-trans*-retinal Schiff base.[45] This also suggests that the emitting state in protonated decatetraenal is 1^1B_u.

The equilibrium between a hydrogen-bonded adduct and a protonated adduct does not require significant geometry changes and, therefore, could occur in a low-temperature matrix. Whether the emitting species is completely protonated might be ascertained from the emission spectra in the three alcohol solvents. If all of the fluorescent species were protonated, then we might expect similar spectra with small differences arising from general solvent effects, e.g., differences in dielectric constants. Fluorescence maxima do vary (483 nm in ethanol/methanol, 498 nm in trifluoroethanol, and 511 nm in hexafluoroisopropyl alcohol) which indicates that the proton probably retains some association with the alcohol anion. This suggests the following equilibrium:

$$\mathrm{HRC{=}O{\cdots}HOR'} \leftrightarrow \mathrm{HRC{=}OH^{+}{\cdots}{}^{-}OR'} \qquad (8)$$

Theoretical work by Kollman and Allen[46,47] shows that the potential curves associated with these types of equilibria may include double minima along the hydrogen-bonding coordinate. The barrier arises from geometries in which the proton is loosely associated with both the aldehyde and the alcohol, and its height and the difference in energy between the two minima will depend on the distance between the proton-donating and proton-accepting oxygens as well as general solvent coordinates. The two minima thus may be identified with the hydrogen-bonded and protonated adducts discussed above. It also should be noted that fluctuations in the separation between the heavy atoms and changes in the solvent orientation may strongly modulate proton-transfer rates, especially in situations with low and narrow barriers where tunneling effects often dominate.[48,49]

A double minimum potential curve and the equilibrium between the two species might occur in the ground state or the excited $^1\pi\pi^*$ states monitored by our spectra. If the equilibrium occurred in the ground state, we would expect a significant shift in absorption and excitation spectra as a function of temperature such as has been observed in analogous polyene Schiff bases. For example, Blatz et al.[37] observed a shift of the $1^1A_g \rightarrow 1^1B_u$ (0–0) from 374 to 396 nm when an EPA (ether/isopentane/ethanol) solution of *N*-2,4,6,8,10-dodecapentanenylidene-*n*-butylamine was cooled from 303 to 96 K. Stronger hydrogen bonders such as phenol induced even larger temperature-dependent red shifts (371 nm at 303 K to 450 nm at 179 K). For decatetraenal, however, the absorption ($1^1A_g \rightarrow 1^1B_u$) spectra are independent of temperature (Figure 6), indicating ground states of a single stable species.

We thus propose a model (Figure 7) in which the equilibrium occurs in the excited state with only a single minimum in the ground-state potential energy surface as a function of the proton coordinate. The 1^1A_g state in HFIP solvent is taken as the reference point and is placed about 1000 cm^{-1} below the ground state in EtOH/MeOH. This energy difference represents the solvent shift of the n → π^* transition assuming this results entirely from ground-state stabilization. This shift cannot be measured directly since decatetraenal's $^1n\pi^*$ state is hidden but is comparable to the shift observed for crotonaldehyde. The $^1n\pi^*$ and 2^1A_g states for the hydrogen-bonded species in EtOH/MeOH are placed 24 400 (410 nm) and 25 300 cm^{-1} (395 nm), respectively, above the ground state, consistent with the results of Das and Becker.[11] The 1^1B_u state is located at 26 300 cm^{-1} (380 nm) in EtOH/MeOH and 26 000 cm^{-1} (385 nm) in HFIP according to our excitation spectra (Table II). The 2^1A_g state for hydrogen-bonded decatetraenal in HFIP must lie above the $^1n\pi^*$ state since there is no fluorescence from this species. This places the three low-lying excited states within 500–1000 cm^{-1} of each other as indicated in the figure.

The relative energies of the potential wells in the lowest $^1\pi\pi^*$ state, 335 cm^{-1} (4.01 kJ/mol) in EtOH/MeOH and 100 cm^{-1} (1.15 kJ/mol) in HFIP, are based on thermodynamic measurements (Table III). The barrier heights and widths are unknown at this time since our data reflect the thermodynamics but not the kinetics of the equilibrium process. Based on the discussion above, we assign the emission as originating from the 1^1B_u state of the protonated species. The energies of the 1^1A_g state for the protonated species are estimated from the fluorescence origins, 23 500 cm^{-1} (426 nm) in EtOH/MeOH and 22 800 cm^{-1} (438 nm) in HFIP (Figures 2 and 4, respectively). The shape of the ground-state potential surface and the energies of the 2^1A_g and $^1n\pi^*$ states for the protonated aldehyde are based on the molecular orbital calculations described previously (section 2.3). The 2^1A_g surface (assumed to be similar in shape to the ground state) and the 1^1B_u surface are both hypothetical.

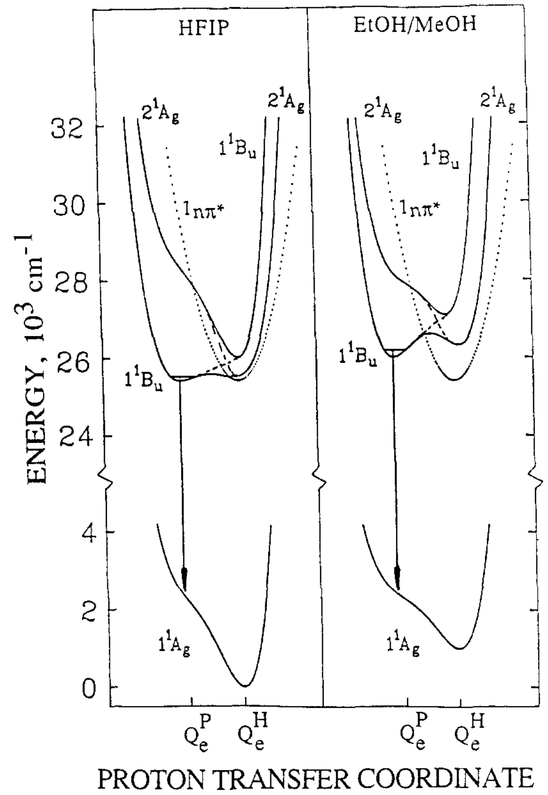

Figure 7. Potential energy as a function of proton position for the ground and lowest energy excited states of decatetraenal hydrogen bonded to hexafluoroisopropyl alcohol (HFIP) or ethanol/methanol (EtOH/MeOH). The oxygens are considered to be fixed by the rigid, low-temperature matrix. Q_e^P and Q_e^H represent the positions of the proton in the protonated and hydrogen-bonded forms. The $^1n\pi^*$ surfaces are indicated by dotted curves. The dashed curves indicate the 2^1A_g and 1^1B_u surfaces before interaction in the crossing region.

In our model the ground-state species is hydrogen-bonded. Excitation into 1^1B_u is followed by relaxation into a thermally equilibrated, lower $^1\pi\pi^*$ state which at low temperatures favors the protonated, fluorescent form. This $^1\pi\pi^*$ state results from the interaction and subsequent avoided crossing of the 2^1A_g and 1^1B_u surfaces. Movement of the proton from the alcohol to the aldehyde presumably is induced by an increased electron density in the π^* orbitals in the region between the aldehyde oxygen and the alcohol proton. The unusual temperature dependence of the fluorescence is due to the inversion of the $^1n\pi^*$ and $^1\pi\pi^*$ levels that accompanies the change from the hydrogen-bonded to protonated species.

The emission intensity at 10 K in HFIP and TFE is only about four times higher than in ethanol/methanol (Figure 5) even though the absorption and excitation spectra indicate much greater hydrogen bonding in the first two solvents. This implies that the quantum yield of fluorescence is lower in HFIP and TFE which could be related to the greater mixing of the close lying $^1n\pi^*$ and $^1\pi\pi^*$ states as indicated in Figure 7. This increased mixing also could be responsible for the increased spectral broadening of the

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(46) Kollman, P. A.; Allen, L. C. *J. Am. Chem. Soc.* **1971**, *93*, 4991–4500.
(47) Kollman, P. A.; Allen, L. C. *Chem. Rev.* **1972**, *72*, 283–303.
(48) Kosower, E. M.; Huppert, D. *Ann. Rev. Phys. Chem.* **1986**, *37*, 127–156.
(49) Borgis, D.; Hynes, J. T. *The Enzyme Catalysis Process*; Cooper, A., Ed.; NATO ASI Series, to be published, 1989.

aldehyde in the stronger hydrogen-bonding solvents. Figure 7 thus provides the best explanation for the absorption, fluorescence, and fluorescence excitation spectra over a range of temperatures in a range of hydrogen-bonding solvents.

The thermodynamic parameters (Table III) for the excited-state equilibrium (eq 8) are comparable to those reported for the ground-state proton-transfer equilibrium involving *n*-butylamine retinal Schiff base with chlorophenols:[50]

$$\mathrm{HRC{=}N\cdots HOR'} \leftrightarrow \mathrm{HRC{=}NH^{+}\cdots{}^{-}OR'} \qquad (9)$$

For example, the ΔH and ΔS values for 3,4-dichlorophenol (pK_a = 8.6) are −3.0 kJ/mol and −46.0 J/mol K, respectively. In agreement with our results, ΔS becomes more negative as ΔH becomes more negative. It is interesting to note, however, that as the pK_a of the alcohol decreases, ΔS and ΔH for the excited-state equilibrium involving the aldehyde become *less* negative while these thermodynamic parameters become more negative for the ground-state equilibrium involving the Schiff base. The latter behavior is expected since the more acidic alcohol should more readily protonate the acceptor.

The trends noted in the excited-state equilibria between the aldehyde and the alcohols can be understood by referring to Figure 7. The ground-state hydrogen-bonded complex has lower energy in HFIP (lower pK_a) than in ethanol/methanol. The excited-state hydrogen-bonded and protonated species also are more stable in HFIP than in ethanol/methanol. Thus the ΔH for the excited-state equilibrium is less negative in HFIP not because the protonated form is less stable but because the hydrogen-bonded species is relatively *more* stable than in ethanol/methanol. Likewise, the more tightly hydrogen-bonded complex in HFIP results in a smaller decrease in entropy upon protonation.

The fact that only the protonated form of decatetraenal fluoresces suggests that it may be difficult to induce fluorescence in shorter polyene aldehydes, e.g., octatrienal, where the $^1n\pi^*/^1\pi\pi^*$ energy gap in the free species is considerably larger. By the same token, the assumption that hydrogen-bonded species may be responsible for the fluorescence of retinal[18,19] and dodecapentaenal[12,13] in low-temperature glasses and mixed crystals may well be correct. In these systems the $^1n\pi^*$ state is only slightly lower than 2^1A_g in the free species and a normal hydrogen bond may be sufficient for inverting the state order and inducing emission. If the hydrogen-bonded species does emit, then decreasing the temperature should not significantly change the fluorescence intensity but should result in a red-shifted emission, if an equilibrium similar to that proposed in Figure 7 favors the protonated species.

5. Summary and Conclusions

In contrast to polyene Schiff bases,[36,37,50] ground-state polyene aldehydes cannot be complexed by using equimolar amounts of alcohol proton donors and aldehyde acceptors in hydrocarbon glasses. Large excesses of hydrogen bonders are required to complex the aldehydes, and this leads to a competition between self-association of the hydrogen bonders and the formation of alcohol/polyene complexes. Nevertheless, we have succeeded in fully complexing decatetraenal in the strongly hydrogen-bonding solvents, trifluoroethanol and hexafluoroisopropyl alcohol. We also have achieved our initial goal of inducing fluorescence in polyene aldehydes by using the differential effects of hydrogen bonding on the $n\pi^*$, $\pi\pi^*$, and ground electronic states to invert the $^1n\pi^*/^1\pi\pi^*$ ordering.

The induced fluorescence intensities increased significantly when samples were cooled from 77 to 10 K. These changes are well accounted for by a simple equilibrium between nonemitting and emitting species, with the latter being strongly favored at low temperature. The restrictions on molecular motions and the preponderance of fluorescent species at 10 K indicate that the two species must be related by rather small geometry differences. Conversion between the free aldehyde species and a hydrogen-bonded complex thus appears to be unlikely, due to the substantial conformational changes required for a given alcohol to become disengaged from its hydrogen-bonded associations with other alcohols in order to bond to a free polyene. The data thus lead to the excited-state equilibrium given in eq 8 in which the proton moves between the two oxygens. Our calculations suggest that only the "ionic" 1^1B_u excited state has sufficient electron density on the carbonyl oxygen to compete for the alcohol protons. As a result, protonation takes place on the lowest $^1\pi\pi^*$ surface with a complete inversion of the $^1n\pi^* < 2^1A_g < 1^1B_u$ energy order found in the free aldehyde. The thermodynamic parameters describing the excited-state proton transfer closely parallel those observed for the ground-state equilibria between polyene Schiff bases and several hydrogen bonders (eq 9).[50]

Regardless of the details of interpretation, we have shown that the induction of fluorescence in polyene aldehydes requires both a large excess of a strongly hydrogen-bonding solvent and low temperatures (T < 77 K). Under these conditions we obtain spectra that indicate the dominance of a single, fluorescent species. Samples at higher temperatures (77 K) and in weaker hydrogen-bonding solvents may contain a complicated mixture of hydrogen-bonded and free polyene species. These observations clearly bear on the optical spectroscopy of polyene aldehydes in typical (77 K) glasses and suggest the use of lower temperatures to simplify the interpretation of these complex systems.

These results also have implications for the photochemistries of polyene aldehydes and Schiff bases in hydrogen-bonding environments. The propensity to form hydrogen-bonded and/or protonated complexes at low temperatures should be considered in extrapolating studies of chromophores in nonphysiological environments to those in functioning biological systems. For example, in investigating the low-temperature (<20 K) photochemistry of rhodopsin by using picosecond spectroscopy, Peters et al.[51,52] discovered a short-lived intermediate with unusual (non-Arrhenius) kinetics and a large deuterium isotope effect. These observations were ascribed to the photochemical translocation of a proton toward the Schiff base nitrogen of the retinal chromophore.[53] These experiments thus show parallels with our discovery of a strongly hydrogen-bonded or protonated form of decatetraenal that only appears in low-temperature equilibria. These similarities suggest that proton translocation would not play the same role at the temperatures of viable visual systems as in 20 K samples where the protonated form is favored thermodynamically.

The temperature-dependent effects described in this paper also are of intrinsic interest in understanding the movement of protons between alcohol donors and aldehyde acceptors. The low-temperature system described here furnishes a rigid framework that maintains the aldehyde and alcohol oxygens at a "fixed" distance and thus shares many of the features of aromatic systems that undergo *intra*molecular hydrogen bonding and proton transfer.[54,55] The movement of the proton between the oxygens has been described by asymmetric potential functions such as those proposed for decatetraenal. It also is interesting to note a similar distinction between "loose" and "tight" hydrogen-bonded complexes and the manifestations of these complexes in time-resolved measurements on aromatics.[56]

These studies and our previous work show that polyene aldehydes and their Schiff bases can be both hydrogen-bonded and protonated. Equilibria between the free, hydrogen-bonded and

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protonated species can be controlled by the pK_a of the proton donor, changing the solvent polarity, or by varying the temperature. Unlike Schiff bases, ground-state polyene aldehydes do not readily accept protons from alcohol donors. Excited aldehydes, on the other hand, can compete for protons, at least at low temperature.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, a Penta Corporation grant of the Research Corporation and a DuPont Fund grant to Bowdoin College for support of this research. We thank Sandra Antonovic for preliminary studies, Professor Paul Barbara for helpful discussions, Drs. G. Purvis and M. Zerner for providing the ZINDO program, Florida Institute of Technology and Bowdoin College for the use of their computing facilities. R.L.C. thanks Dr. Ken Ghiggino and the Chemistry Department of the University of Melbourne for their hospitality during the completion of this paper. Finally, we acknowledge the helpful comments of one of the referees who suggested that the low-lying $\pi\pi^*$ states may invert upon protonation.

Registry No. (*E*)-Crotonaldehyde, 123-73-9; *all-trans*-2,4,6,8-decatetraenal, 39806-05-8.

Reactions of Dimethoxycarbene and Fluoromethoxycarbene with Hydroxyl Compounds. Absolute Rate Constants and the Heat of Formation of Dimethoxycarbene

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Abstract: Dimethoxycarbene [$(MeO)_2C$] and fluoromethoxycarbene (FCOMe) were photochemically generated from the appropriate diazirines (**2a** and **2b**) and characterized by UV and IR spectroscopy in cold matrices and by UV in solution at 20–25 °C. Laser flash photolytic studies determined rate constants for the reactions of the carbenes with ethanol, methanol, chloroethanol, fluoroethanol, trifluoroethanol, hexafluoroisopropyl alcohol, and acetic acid. The reactivity of $(MeO)_2C$ with the alcohols spanned 4 orders of magnitude, with k_ψ for carbene decay in 1 M ROH/CH_3CN ranging from 3.2×10^4 s^{-1} (ethanol) to 6.7×10^8 s^{-1} (hexafluoroisopropyl alcohol). A Brønsted correlation ($\alpha = -0.66$) was obtained between log k_ψ for the decay of $(MeO)_2C$ in 1 M ROH/CH_3CN and the pK_a of ROH (in water). FCOMe was much less reactive toward ROH than $(MeO)_2C$; only with hexafluoroisopropyl alcohol ($k_\psi \sim 9 \times 10^3$ s^{-1} for carbene decay in 1 M ROH/CH_3CN) could quenching be observed. Products of some of the carbene/alcohol reactions were characterized. A photoacoustic calorimetry study of the $(MeO)_2$/MeOH reaction afforded $\Delta H_f \sim -61$ kcal/mol for $(MeO)_2C$; ΔH_f for FCOMe was estimated at ~ -53 to -56 kcal/mol. The mechanism(s) of the carbene/O–H insertion reactions are discussed. The results of ab initio and semiempirical molecular orbital calculations on FCOMe are presented.

The reaction of carbenes with hydroxylic substrates have long been studied by classical, product-based methods.[2] In the case of *singlet* carbenes, several mechanisms have been considered for the archetypal O–H "insertion" reaction: (a) electrophilic attack on an oxygen lone pair with the (possibly reversible) formation of an ylide that subsequently suffers O to C proton transfer; (b) *direct*, three-center O–H insertion; or (c) carbene protonation, followed by rapid collapse of the resulting carbocation/oxide ion pair.[2] Conventional wisdom dictates that a nucleophilic carbene, where the reactivity is dominated by the lone electron pair, ought to adhere to mechanisms (c) or possibly (b), whereas an electrophilic carbene, with reactivity centered in its vacant p orbital, should prefer mechanisms (a) or (b).

The advent of laser flash photolytic (LFP) methods,[3] and appropriate carbene precursors,[4] has now made it possible to obtain absolute kinetic data for many carbene reactions,[5-7] including those with hydroxyl compounds. The reactions of singlet carbenes with O–H bonds can now be directly monitored,[8] so that the mechanistic trichotomy can be subjected to renewed scrutiny. Indeed, we recently reported that the O–H insertion of nucleophilic[6] dimethoxycarbene into MeOH(D) was attended by a primary kinetic isotope effect of 3.3 ± 0.5, suggestive of substantial O–H to carbene proton transfer during the reaction.[9] Moreover, application of time-resolved photoacoustic calorimetry (PAC) to the carbene/O–H reaction provides experimental data from which one can estimate the heat of formation of the carbene.[10]

In this report, we apply both LFP and PAC to the reaction dynamics of dimethoxycarbene, $(MeO)_2C$, and fluoromethoxycarbene, FCOMe, with alcohols. The results that we obtain lead to a Brønsted correlation between the absolute rate constants of the $(MeO)_2C$/O–H reactions and the (aqueous) pK_a values of the OH moieties as well as a value of ~ -61 kcal/mol for the heat of formation of $(MeO)_2C$.

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