Acknowledgment. This work has been started at the CECAM Workshop "On Sudden Polarization Effect", 1979. We thank Professors J. Koutecký, J. Michl, and J. Paldus for very interesting discussions. The support of the Deutsche Forschungsgemeinschaft in the form of research grant Bo 627/4-2 is gratefully appreciated. The services and computer time of the Informatik-Rechenbetrieb (Technische Universität Berlin) are acknowledged.

Appendix

Expansion of the CI Wave Functions in the Basis of Localized Orbitals of Butadiene. The two highest occupied and two lowest unoccupied MO's of 90° terminally twisted butadiene are taken as localized reference orbitals $|R_J\rangle$ (cf. Scheme II, a − 1, ..., b + 1). Small AO coefficients at hydrogen atoms or the contribution of σ orbitals to four MO's are neglected so that entire localization at the CH_2 and at the allylic fragments is introduced.

For any twist angle $\theta \neq 90$ a rotation around the z axis is applied to HOMO yielding perpendicular conformation with respect to the CH_2 fragment. The localized orbitals $|R_J\rangle$ are then renormalized.

In order to obtain localized orthonormal orbitals $|L_1\rangle ... |L_4\rangle$, we apply a unitary transformation **U** to the set of MO's $|M_1\rangle ... |M_4\rangle$ for any twist angle θ:

$$\{...|L_J\rangle...\} = \{...|M_I\rangle...\}\mathbf{U} \qquad \text{(A1)}$$

with

$$u_{IJ} = \langle M_I|L_J\rangle \qquad \text{(A2)}$$

The **U** matrix is determined through an iterative procedure according to the maximum-overlap criterium between the resulting $|L_J\rangle$'s with the reference orbitals $|R_J\rangle$:

$$\sum_J \langle R_J|L_J\rangle^2 = \max \qquad \text{(A3)}$$

The transformation of Slater determinants ϕ_K built from the SCF MO's

$$\phi_K = \frac{1}{(4!)^{1/2}}\hat{\mathcal{A}}[|M_{K_1}\alpha\rangle|M_{K_2}\alpha\rangle|M_{K_3}\beta\rangle|M_{K_4}\beta\rangle] \qquad \text{(A4)}$$

into the Slater determinants ϕ_L' built from the localized orbitals

$$\phi_J' = \frac{1}{(4!)^{1/2}}\hat{\mathcal{A}}[|L_{J_1}\alpha\rangle|L_{J_2}\alpha\rangle|L_{J_3}\beta\rangle|L_{J_4}\beta\rangle] \qquad \text{(A5)}$$

is where the $u_{K_iL_j}$ are defined by eq A2. The expansion of the

$$\langle\phi_K|\phi_J'\rangle = \det\begin{pmatrix} u_{K_1L_1} & u_{K_1L_2} \\ u_{K_2L_1} & u_{K_2L_2} \end{pmatrix} \det\begin{pmatrix} u_{K_3L_3} & u_{K_3L_4} \\ u_{K_4L_3} & u_{K_4L_4} \end{pmatrix} \qquad \text{(A6)}$$

correlated wave function for each state considered is

$$\Psi = \sum_{J=1}^{20}\sum_{K=1}^{8} c_K\langle\phi_K|\phi_J'\rangle\phi_J' \qquad \text{(A7)}$$

Registry No. Butadiene, 106-99-0.

Optical Studies of a Simple Polyene Schiff Base: Low-Lying Electronic Levels in the Free, Hydrogen-Bonded, and Protonated Species

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Abstract: Fluorescence and fluorescence excitation spectra of a model polyene Schiff base, *N*-(2,4,6,8,10-dodecapentaenylidene)butylamine, have been obtained in 77 K hydrocarbon glasses. The low-energy electronic transitions of this polyene Schiff base have been studied in a variety of hydrogen-bonding and protonating environments. All spectra are well resolved and allow the accurate location of electronic origins. For all three species, i.e., free Schiff base, hydrogen-bonded Schiff base, and protonated Schiff base, the fluorescence origins are substantially red shifted (3108, 2774, and 2238 cm^{-1}) from the origins of the strongly allowed absorptions. These experiments show that the lowest excited singlet in each of these Schiff base species correlates with the forbidden A_g^- states observed in analogous polyene hydrocarbons. These findings are compared with current theoretical predictions and discussed with regard to their implications for the photochemistries of other polyene Schiff bases, including rhodopsin.

Linearly conjugated π-electron systems have received considerable experimental and theoretical attention in recent years. This in large part stems from the involvement of polyenes (retinylidene Schiff bases) as chromophores in vision and certain photosynthetic processes.[2-4] The investigation of the *initial* photochemical events in these important biological processes has been an area of active interest.[5] Many studies have tried to develop a better description of polyene electronic states in order to consider possible mechanisms by which these chromophores funnel electronic excitations into specific chemical events, e.g., isomerizations and proton transfers.

A large share of the recent spectroscopic and theoretical work on polyenes has centered on simple hydrocarbons.[6-9] These systems offer several critical advantages. Their symmetries (C_{2h} point group for all-trans isomers) relieve computational burdens

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while also providing unambiguous answers (e.g., "allowed" or "forbidden") to questions relating to the absolute assignment of vibronic states.[7,9,10] The simple hydrocarbons also are experimentally more tractable. Their optical spectra exhibit considerable vibronic structure even in room-temperature solutions. This facilitates the identification of electronic origins, a prerequisite for unambiguous state assignments. The advantages of vibronic structure can be further extended by incorporating these simple, symmetrical molecules into high-resolution mixed-crystal environments.[7,9,10]

One important conclusion drawn from both moderately resolved (77 K and room-temperature solutions) and highly resolved (4.2 K mixed crystals) optical spectra is that for polyene hydrocarbons comparable to the retinals, the lowest excited singlet ($2^1A_g^-$) lies well below the $1^1B_u^+$ states responsible for the strong absorptions. This conclusion is supported by a wealth of one-photon[8,10] and two-photon[7,9] spectroscopic evidence and can be understood by certain extensions (sufficient configuration interaction) of standard molecular orbital treatments.[11,12] Both experiment and theory point to the markedly different electronic properties of the low-lying $2^1A_g^-$ and $1^1B_u^+$ states. For example, recent calculations of Lasaga et al.[13] show that the magnitudes of carbon–carbon bond order rearrangements are considerably greater for $1^1A_g^- \rightarrow 2^1A_g^-$ than for $1^1A_g^- \rightarrow 1^1B_u^+$. Such effects certainly must bear on the reactivities of the various excited states, e.g., with respect to cis–trans isomerization. Inasmuch as the photochemistries are most likely determined by the nature of the lowest excited singlet, it is important to ascertain the $\pi\pi^*$ state orderings ($1^1B_u^+ >$ or $< 2^1A_g^-$) in these systems.

For the polyene hydrocarbons a great deal of evidence has accumulated which indicates $1^1B_u^+ > 2^1A_g^-$ for molecules with conjugated π-electron systems comparable to those of the retinyl polyenes.[6–9] On the other hand, very little information exists on the low-lying states of polyenes which better model the retinyl Schiff bases found in nature. The Schiff bases possess several features which may figure in their unique roles in photobiology. Their reduced symmetry should lead to *polar* ground- and excited-state electronic distributions which are significantly different from those of the hydrocarbons.[14,15] In addition, the nonbonded electrons on the Schiff base nitrogen can be involved both in hydrogen bonding and protonation. Changes in polarity and basicity as a function of electronic state offer many channels by which the electronic excitation of a Schiff base can be communicated to its surroundings.[16] Such photochemical pathways are not available in the polyene hydrocarbons.

Study of these more appropriate polyene models, however, has been hindered by many of the same features which make them so interesting. Their most significant shortcoming is that both room-temperature solution and low-temperature glass spectra tend to be diffuse and unresolved. This in part is due to the stronger, nonhomogeneous interactions between solvents and polar solutes.[17] In addition, the nonbonded electrons result in $n\pi^*$ states which can add further congestion to the spectra.[18,19] Hydrogen-bonding effects also can contribute to a complicated (and spectrally broad) distribution of solute/solvent complexes.

Prior optical studies of polyene Schiff bases have concentrated almost entirely on those made from the retinals and related aldehydes.[20–23] Spectra of these retinyl systems suffer from additional broadness due to nonhomogeneous interactions between the cyclohexenylidene ring and the polyene side chain.[18] As a result, the polyene Schiff base spectra previously published are completely unresolved. Assignment of the low-lying electronic states in these systems, therefore, has relied on indirect evidence, including a great deal of extrapolation from the better understood hydrocarbons.

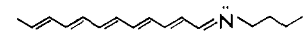

Figure 1. *N*-(2,4,6,8,10-Dodecapentaenylidene)butylamine ("12SB").

State assignments for the retinyl Schiff bases rest mainly on the discrepancies between observed fluorescence lifetimes and excited-state lifetimes calculated from the fluorescence quantum yield and the integrated intensity of the first strong absorption band ("$1^1A_g^-$" → "$1^1B_u^+$").[23,24] Observed lifetimes have been shown by Becker et al.[21,23] to be 20–50 times longer than those calculated for emission from "$1^1B_u^+$". These differences are similar to those seen in comparable polyene hydrocarbons and are consistent with "$2^1A_g^-$" as the lowest excited singlet.[23,24] For the hydrocarbons this assignment can be rigorously proven by detailed analysis of vibronic spectra.[7,9,10,24] For the retinyl Schiff bases, however, the complete lack of vibronic structure precludes a direct assignment of electronic states. The lifetime data[21,23] do indicate "$1^1B_u^+$" > "$2^1A_g^-$". This conclusion is further supported by recent[25] fluorescent lifetime and quantum yield measurements on the model Schiff base discussed below (see Figure 1).

For *protonated* Schiff bases, even less experimental data is available. The electronic spectra of protonated all-trans retinyl Schiff base are predictably broad, and the discrepancy between the observed (~1 ns) and calculated (~0.2 ns) fluorescence lifetimes is considerably smaller than the differences observed for unprotonated Schiff bases and comparable hydrocarbons.[23,24] This has been explained by Becker et al. as due to either increased mixing of "$1^1B_u^+$" with "$2^1A_g^-$" or a reversal of state ordering ("$1^1B_u^+$" < "$2^1A_g^-$") in the protonated species.[23] The latter possibility is heavily favored by theory. Calculations by Birge et al.[4,26,27] and by Schulten et al.[28] have extended the PPP-SCF-CI treatments used on polyene hydrocarbons to polyene Schiff bases. INDO-CI and CNDO/S-CI methods have been employed in order to account for the effects of σ–π mixing. As with the PPP calculations on polyene hydrocarbons,[12] the extent of CI is critical, especially in determining the relative energies of the states correlating with $2^1A_g^-$ and $1^1B_g^+$. Extending the configuration interaction beyond that due to single and double excitations lowers excited-state energies relative to the ground state but leads to no further reordering of the excited states.[28] For the present paper, the most significant conclusion of these recent calculations is that for simple protonated Schiff bases comparable to the protonated Schiff bases of retinal the first excited singlet should correlate with $1^1B_u^+$ and not $2^1A_g^-$.

Birge and Hubbard[27] have pointed out that there is little experimental data to either support or oppose the theoretical predictions of state orderings in protonated Schiff bases. These results are rooted in the same PPP-SCF formalism which provides a good account of the electronic energy levels of polyene hydrocarbons as well as free Schiff bases. Evaluation of the calculations on *protonated* Schiff bases, however, has awaited more detailed spectroscopic data. Fluorescence lifetimes and quantum yields for both protonated and unprotonated Schiff bases are available,[23,25] but vibronically resolved spectra even of simple model compounds have not heretofore been reported.

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The present study addresses this problem. We have synthesized and obtained low-temperature fluorescence and fluorescence excitation spectra of *N*-(2,4,6,8,10-dodecapentaenylidene)butylamine ("12SB") (Figure 1). This molecule is closely related to systems treated in recent calculations.

We have obtained optical spectra of 12SB in a range of hydrogen-bonding and protonating solvent environments. We present in this paper our studies of complexes formed between 12SB and perfluoro-*tert*-butyl alcohol. This alcohol is both quite acidic (pK_a = 5.2) and soluble in nonpolar solutions. We thus have been able to obtain spectra of 12SB/H-bonder complexes under conditions which retain vibronic resolution. We have identified two complexes as hydrogen-bonded 12SB (12HSB) and protonated 12SB (12PSB). The vibronically resolved fluorescence and fluorescence excitation spectra show that each of the three species, 12SB, 12HSB, and 12PSB, exhibits a substantial energy difference between the origin of the strongly allowed absorption ("$1^1A_g^-$" → "$1^1B_u^+$") and the origin of fluorescence. The optical spectra of these compounds thus repeat the patterns observed for analogous polyene hydrocarbons and lead us to assign the lowest excited singlets as "$1^1B_u^+$" > "$2^1A_g^-$".

Experimental Section

N-(2,4,6,8,10-Dodecapentaenylidene)butylamine ("12SB") was prepared from *n*-butylamine and 2,4,6,8,10-dodecapentaenal. The dodecapentaenal was formed via the self-condensation of crotonaldehyde as described previously.[8] The dodecapentaenal was recrystallized from ethanol to yield an orange powder which melted at 166–167 °C (cf. published melting point of 166 °C).[29] The *n*-butylamine (Baker) was distilled and stored over molecular sieves (Linde, 3 Å) to remove water.

The Schiff base was prepared by dissolving dodecapentaenal in a large excess (~100-fold) of *n*-butylamine.[30] This solution was allowed to stand for 12 h at ~5 °C in the presence of molecular sieves. Upon completion of the reaction, the excess of *n*-butylamine was removed by rotary evaporation and the resultant residue then reconstituted in a small amount of hexane. The 12SB went into solution slowly (~12 h at room temperature) and left behind a fair amount of insoluble material. The soluble fraction was placed in a refrigerator overnight to yield orange crystals which were recovered and redissolved in hexane. After one final recrystallization, the 12SB was stored in dilute ($<10^{-3}$ M) hexane solutions in the dark and at −10 °C. Solutions stored in this way gave absorption and emission spectra which were reproducible for a period of several weeks.

Room-temperature absorption spectra of 12SB in hexane showed several well-defined vibronic bands, comparable to those seen in room-temperature spectra of the unsubstituted polyene hydrocarbons.[8,31] Bands at 373, 353, 335, and 322 nm gave molar extinction coefficients of 10.4×10^4, 9.8×10^4, 5.7×10^4, and 2.5×10^4 L mol^{-1} cm^{-1}.[31b] The high extinction coefficients and the well-resolved absorption (and emission, see below) spectra are indicative of reasonably pure preparations. The isomeric purity of our 12SB is not as easy to evaluate. It is assumed here that our samples are dominated by the thermodynamically favored, all-trans 12SB. Other isomers may be present, but these will not affect the conclusions of this paper.

Low-temperature optical spectra were obtained in PMH (isopentane/methylcyclohexane, 3/1 (v/v)) which had been stored over molecular sieves to remove traces of water. The hydrogen-bonding and protonation studies took advantage of the unique characteristics of perfluoro-*tert*-butyl alcohol (PCR Research Chemicals). This alcohol is soluble in hydrocarbon solvent systems while also possessing a rather acidic proton (pK_a = 5.2[32]). Stock solutions of perfluoro-*tert*-butyl alcohol in dry PMH were added to PMH solutions of 12SB to obtain known ratios of 12SB to hydrogen bonder. Most low-temperature spectra were obtained on solutions with 12SB and perfluoro-*tert*-butyl alcohol at 10^{-5}–10^{-6} M. At higher concentrations both the 12SB and the hydrogen bonder tend to aggregate and precipitate on cooling to 77 K.

Spectral Measurements. The 77 K fluorescence and fluorescence excitation spectra were obtained on a fluorimeter fabricated in our laboratory. Our apparatus employed a 75-W xenon lamp (Oriel), 0.25-m excitation monochromator (Jarrell-Ash), a Pyrex Dewar, a 1-m emission monochromator (Instruments SA), and a cooled photomultiplier (EMI 6256S (S-13 response)). In addition, various Corning and Schott (nonfluorescent) filters were employed to assist the monochromators in sorting out the exciting and emitting wavelengths. Due to relatively weak signals, the band-passes of the two monochromators were maintained near the widths of the vibronic lines (~2.5 nm).

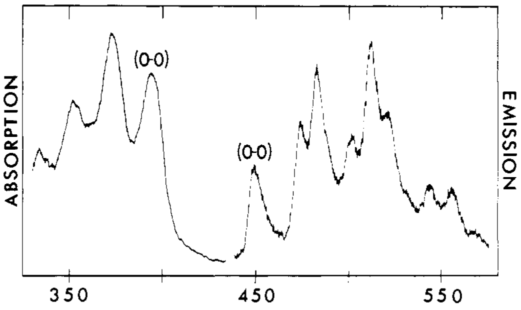

Figure 2. Fluorescence and fluorescence excitation spectra of 12SB in 77 K PMH. Fluorescence (uncorrected): excited at 375 nm (7-nm bandwidth), detected with 2.5-nm bandwidth. Fluorescence excitation (corrected): monitored at 512 nm (2.5-nm bandwidth), excitation scanned with 3-nm bandwidth.

The signals from our photomultiplier were preamplified by a Keithley 610C electrometer and then stored on a Digital Equipment Corp. MINC-11 minicomputer for subsequent manipulation and display. The raw spectra were corrected for the spectral characteristics of our fluorimeter as follows. The wavelength dependence of the excitation optics (lamp, 0.25-m monochromator, lenses and filters) was obtained from the excitation spectrum of a concentrated (5 g/L in ethylene glycol) solution of Rhodamine B.[33] By monitoring the Rhodamine emission at 600 nm as a function of exciting wavelength, we could obtain an *excitation correction curve* from 300 to 580 nm. This curve was used to obtain corrected excitation spectra of several standard solutions (anthracene, quinine sulfate, perylene, fluorescein, and Rhodamine B). The concentrations of these solutions were in a range (10^{-5}–10^{-6} M) where the excitation spectra were unaffected by further dilutions. Such spectra should thus be directly comparable to standard absorption measurements on the same solutions. Our corrected excitation spectra were in good agreement with those obtained on a Beckman Model 24 UV–visible spectrophotometer and thus substantiate the validity of our correction factors over the 300–580 nm wavelength interval.

The *emission correction curve* was obtained by a more indirect procedure. Uncorrected fluorescence spectra of the dilute standard solutions described above were recorded on our experimental apparatus. Corrected fluorescence spectra of the same solutions then were obtained on a Perkin-Elmer Model 650-40 fluorimeter with a microprocessor-based Ordinate Data Processor. Division of the corrected spectra by the uncorrected spectra gave us a correction factor every 0.25 nm from 350 to 580 nm. This scheme ensures that the corrected emission spectra of polyene Schiff bases obtained on our fluorimeter are consistent with the low-temperature emission spectra that would be obtained on the Perkin-Elmer instrument. The accuracy of the Perkin-Elmer correction techniques has been confirmed by measuring the output from a tungsten lamp with a calibration traceable to the National Bureau of Standards.[34]

Results and Discussion

The 77 K fluorescence and fluorescence excitation spectra of 12SB in dry PMH are presented in Figure 2. The *uncorrected* fluorescence spectrum is given in order to emphasize the intensity in the regions near the electronic origin (0–0). The identification and location of both the absorption and emission origins are crucial to the assignment and ordering of the low-energy excited states in 12SB and related species.

12SB exhibits well-resolved patterns of vibronic intensity both in emission and in absorption. The analysis of these spectra can be guided by previous work on the relatively well-understood polyene hydrocarbons.[8,10,18,24] The vibronic intensities seen in Figure 2 are rather similar to those of the simple hydrocarbons and for the most part are due to the large Franck–Condon factors associated with carbon–carbon single (C–C) and carbon–carbon double (C=C) symmetric stretches. Recent analyses of polyene

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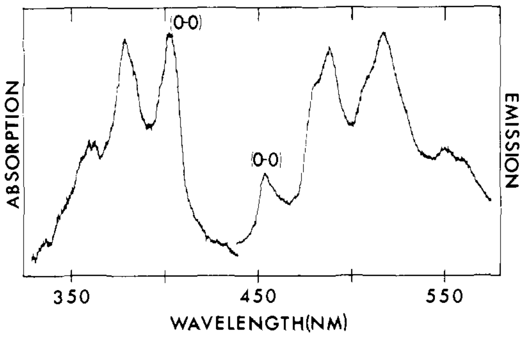

Figure 3. Fluorescence and fluorescence excitation spectra of 1:1 perfluoro-*tert*-butyl alcohol:12SB in 77 K PMH. Fluorescence (uncorrected): excited at 383 nm (7-nm bandwidth), detected with 2.5-nm bandwidth. Fluorescence excitation (corrected): monitored at 518 nm (2.5-nm bandwidth), excitation scanned with 3-nm bandwidth.

normal modes suggest that the observed modes also contain components of other stretches and bends.[13] Nevertheless, the observed vibronic patterns are remarkably simple and generally can be accounted for by combinations of two or three dominant vibrations built on well-defined electronic origins.

12SB also shares with its hydrocarbon analogues a clear separation ("energy gap") between the origin of emission (449 nm) and the origin of the strongly allowed absorption (394 nm). This separation locates the fluorescent state ("$2^1A_g^-$") 3100 cm^{-1} below the state ("$1^1B_u^+$") responsible for the strong absorption. This compares with the 5000-cm^{-1} separation between the absorption and emission origins of dodecahexaene,[8] a simple polyene hydrocarbon with the same extent of π delocalization as 12SB. For shorter polyene hydrocarbons, the necessary relationship between the existence of the energy gap and the state assignments ("$1^1B_u^+$" > "$2^1A_g^-$") has been rigorously demonstrated by high-resolution, one- and two-photon spectroscopy.[7,9,10] This state ordering also has been predicted for 12SB by extensions of the SCF-CI treatments used to account for the spectra of simple polyene hydrocarbons.[26] Our spectra thus provide the most direct verification of these calculations while also offering a quantitative check on their accuracy (see below).

Addition of a strong hydrogen bonder (perfluoro-*tert*-butyl alcohol, $pK_a = 5.2$) to 12SB in PMH shifts both the absorption and the emission to longer wavelengths. A quantitative titration shows that a 1:1 molar ratio of perfluoro-*tert*-butyl alcohol to 12SB completely converts the 12SB to its hydrogen-bonded form, "12HSB". Emission and excitation spectra taken during the course of this titration show only two species, 12SB and 12HSB. This fact along with the 1:1 stoichiometry prove that we are dealing with a simple equilibrium between 12SB and 12HSB and not a generalized, continuous solvent shift of the 12SB spectrum.[35] Weaker hydrogen bonders (e.g., trifluoroethanol, $pK_a = 12.4$,[36] and hexafluoroisopropyl alcohol, $pK_a = 9.3$[37]) give similar equilibria with the size of the spectral shifts correlating with the acidities of the hydrogen bonders.

The 77 K excitation and uncorrected fluorescence spectra of 12HSB (1:1 ratio of H bonder to Schiff base) are given in Figure 3. Some broadening of bands is evident, but the 12HSB spectra retain the same relative vibronic spacings and intensities seen in 12SB (cf. Figure 2). The absorption and fluorescence origins again are readily identified at 404 and 455 nm. These origins represent red shifts from 12SB of ~600 cm^{-1} in absorption and ~300 cm^{-1} in emission. These small shifts as well as the close similarities in vibronic intensities indicate that 12SB's electronic states are not greatly perturbed by this relatively strong hydrogen bonder. It thus seems quite reasonable to retain "$2^1A_g^-$", "$1^1B_u^+$" state descriptions used for 12SB.

Further addition of perfluoro-*tert*-butyl alcohol beyond the amount required for the 1:1 hydrogen-bonded complex gives rise to yet another set of red-shifted spectra. The 12HSB is completely converted to another species with a perfluoro-*tert*-butyl alcohol/12SB ratio of 5:1. Spectra taken at intermediate ratios (e.g., 3:1) indicate a clear equilibrium between 12HSB and the new species. As in the titration leading to 12HSB, we must again interpret the noncontinuous shift of absorption bands in terms of a "specific" rather than a "general" solvent shift.[35] The 77 K fluorescence and fluorescence excitation spectra of the new species are given in Figure 4. It is important to note that, within the spectral regions spanned by the three strongest vibronic bands, the fluorescence spectrum is independent of the wavelength of excitation and the excitation spectrum is independent of the wavelength of emission. We thus can be assured that the spectra given in Figure 4, as well as those given in Figures 2 and 3, are representative of single, well-defined species.

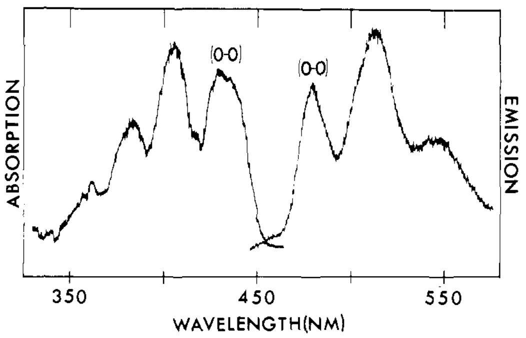

Figure 4. Fluorescence and fluorescence excitation spectra of 5:1 perfluoro-*tert*-butyl alcohol:12SB in 77 K PMH. Fluorescence (uncorrected): excited at 405 nm (7-nm bandwidth), detected with 2.5-nm bandwidth. Fluorescence excitation (corrected): monitored at 515 nm (2.5-nm bandwidth), excitation scanned with 3-nm bandwidth.

The vibronic structure seen in Figure 4 is significantly broadened from that in the spectra of 12SB and 12HSB. Nevertheless, there remains sufficient resolution to locate the band origins for the two transitions at 431 and 477 nm. These spectra are thus red shifted from those of 12SB by ~2200 cm^{-1} in absorption and ~1300 cm^{-1} in emission. The corrected excitation spectrum shows a pattern of vibronic spacings and intensities much like those seen for 12SB (Figure 2) and 12HSB (Figure 3). The emission spectrum given in 4 shows relative vibronic intensities somewhat different from those observed for 12SB and 12HSB. Preliminary *corrected* emission spectra, on the other hand, greatly reduce these differences and indicate very similar vibronic patterns for the three species. These similarities as well as the all-important separation between the electronic origins lead us to retain the "$1^1B_u^+$" > "$2^1A_g^-$" assignments found for 12SB and 12HSB.

One additional point to consider is the possibility that in the emission spectra given in Figures 2–4 the electronic origins might be too weak to be properly assigned. For example, it might be argued that for the 5:1 complex (Figure 4) the (0–0) lies not at 477 nm but somewhere within the weak emission seen at 450–460 nm. Excitation spectra monitored in this region, however, show little resemblance to those monitored at λ's $\geq$ 477 nm. This indicates that the 450–460 nm emission is due to other 12SB species and/or impurities. In addition, the *corrected* emission spectra of 12SB, the 1:1 complex, and the 5:1 complex are very similar to the vibronically resolved, 77 K emission spectra of polyene hydrocarbons.[8] Even in these more symmetric species the electronic origins are readily seen. Solvent perturbations can reduce molecular symmetries and relax selection rules.[38] Even for those molecules in which an inversion center is maintained (clearly not the case for 12SB and its complexes), vibronic coupling via low-frequency (<200 cm^{-1}) modes[9,10,38] would make the low-resolution ($\Delta(1/\lambda) > 200$ cm^{-1}) origins appear to be allowed and relatively intense.

The existence of an anomolously weak, undetected emission origin in either 12SB, the 1:1 complex, or the 5:1 complex is thus

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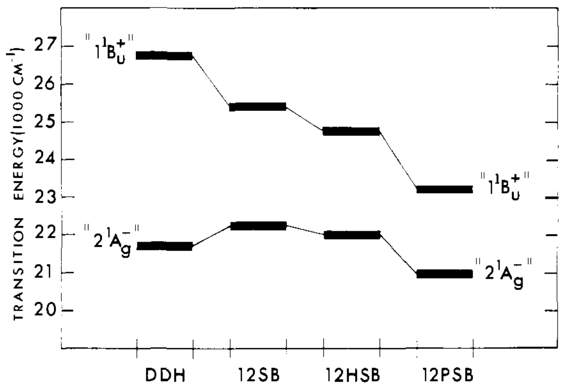

Figure 5. Comparison of "$2^1A_g^-$" → "$1^1A_g^-$" and "$1^1A_g^-$" → "$1^1B_u^+$" transition energies of dodecahexaene (DDH)[8], 12SB, 1:1 perfluoro-*tert*-butyl alcohol:12SB ("12PSB"), and 5:1 perfluoro-*tert*-butyl alcohol:12SB ("12PSB"). All transition energies are in 77 K PMH (isopentane:methylcyclohexane 3/1(v/v)).

Table I. (0-0)'s for Absorption and Fluorescence of Polyenes with Six Double Bonds (in 77 K PMH)

	absorption,[b] nm ($1^1A_g^- \rightarrow 1^1B_u^+$)	emission,[b] nm ($2^1A_g^- \rightarrow 1^1A_g^-$)	energy difference,[b] cm^{-1} ($1^1B_u^+ - 2^1A_g^-$)
dodecahexaene[a]	374	461	5045
12SB	394	449	3109
12SB + perfluoro-*tert*-butyl alcohol (1:1)=12HSB	404	455	2774
12HSB + perfluoro-*tert*-butyl alcohol (1:4)	431	477	2238

[a] From D'Amico et al.[8] [b] All values refer to spectra taken at 77 K in a PMH glass (isopentane/methylcyclohexane 3/1).

seen to be extremely unlikely. With particular reference to the 5:1 complex (Figure 4), it is important to note that even if the 477-nm peak has been incorrectly assigned, the general conclusions of this paper ("$1^1B_u^+$") > "$2^1A_g^-$" for all three species) would not be changed. If the 477-nm peak is not the (0-1), then it would have to be assigned as (0-1), i.e., an electronic transition into a ground state which retains one quantum of the dominant C=C stretch ($\nu \sim 1600^{-1}$ cm^{-1}).[9,10,38] This would place the (0-0) at 443 nm, still well below the 431-nm origin of the allowed absorption.

A summary of our results is given in Table I and in Figure 5. We also have included comparable information on dodecahexaene (DDH), a polyene hydrocarbon with the same degree of π-electron delocalization as 12SB.[8] The data on DDH thus provide a point of reference for our discussion of the electronic states of the various perfluoro-*tert*-butyl alcohol:12SB complexes.

We have tentatively identified the 5:1 (perfluoro-*tert*-butyl alcohol:12SB) complex as a protonated Schiff base (12HSB$^+$ ≡ 12PSB). This assignment is based, to a great extent, on the spectral similarities between our complex and 12 PSB prepared by more conventional means. Adding a few drops of an HCl-saturated solution of EPA (diethyl ether/isopentane/ethanol, 5/5/2) to an EPA solution of 12SB gives the spectra shown in Figure 6. Compared with the other spectra presented in this paper, the 12HSB$^+$Cl$^-$ spectra are rather broad and do not allow a unique assignment of electronic origins. Nevertheless, the similarities between the spectra seen in Figure 4 and those of 12HSB$^+$Cl$^-$ (Figure 6) support our conclusion that the two sets of spectra arise from very similar species. These similarities are particularly evident in comparing the corrected excitation spectra (Figures 4 and 6). The small discrepancies (e.g., small red shift of 12HSB$^+$Cl$^-$) can be attributed to the differences in counterions and solvents between 12HSB$^+$Cl$^-$ in EPA and the 5:1 H bonder:12SB complex in PMH. It also is important to note that both sets of spectra (Figures 4 and 6) are quite comparable with the unresolved 77 K spectra of the protonated retinylidene Schiff base (PRSB).[22,23] Indeed, the 440-nm λ_{max} of PRSB is the classic half-way point in understanding the bathochromic shift between free retinal (λ_{max} 380 nm) and retinal bound to human opsin (λ_{max} 498 nm).[3]

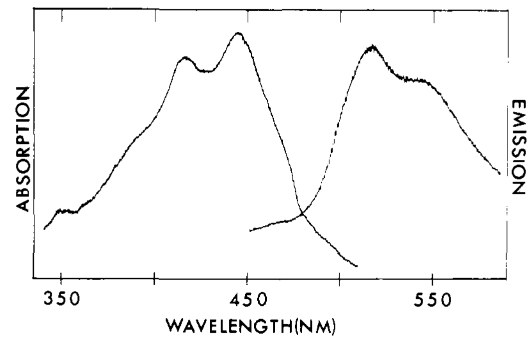

Figure 6. Fluorescence and fluorescence excitation spectra of 12SB in presence of excess HCl in 77 K EPA. Fluorescence (uncorrected): excited at 440 nm (7-nm bandwidth), detected with 2.5-nm bandwidth. Fluorescence excitation (corrected): monitored at 550 nm (2.5-nm bandwidth), excitation scanned with 3-nm bandwidth.

Spectra of 12HSB$^+$Cl$^-$ and PRSB provide very little information on the location of electronic origins. For 12HSB$^+$Cl$^-$ the diminution of vibronic structure presumably is due to the strength of interaction between the protonated solute and the polar glass (EPA) required to support this ionic species.[17] The nonhomogeneity of these strong interactions greatly reduces the resolution normally seen in spectra of nonionic, model polyenes in nonpolar environments. For PRSB there are additional effects[18] which ensure the diffuseness of its optical spectra.

It also would be useful to compare the spectra of the 5:1 complex with spectra of protonated Schiff bases in nonpolar solvents. For example, trichloroacetic acid (pK_a = 2) has been used to protonate retinylidene Schiff bases (RSB's) in hydrocarbon environments both in room-temperature solutions[39] and 77 K glasses.[23] We have carried out parallel experiments with 12SB in PMH. As in the case of the RSB's,[23] however, a large (~ 100-fold) excess of trichloroacetic acid is needed in order to obtain 77 K spectra. Under these conditions the protonated species tend to aggregate and precipitate from the solution as it is cooled. The 12SB species that remain show completely unresolved spectra with λ_{max}'s comparable to those of the 5:1 complex (Figure 4) and 12HSB$^+$Cl$^-$ in EPA (Figure 6). The results with trichloroacetic acid thus confirm the expected, unfavorable thermodynamics in maintaining ionic species in nonpolar media at low temperatures, even at the low concentrations (10^{-5}–10^{-6}M) required in our experiments. Perfluoro-*tert*-butyl alcohol appears to strike a better compromise between the high acidity required for protonation and the high solubility required to obtain spectra in low-temperature, hydrocarbon glasses.

In the 5:1 complex between perfluoro-*tert*-butyl alcohol and 12SB, we apparently have realized a route to a protonated polyene in an essentially nonpolar medium. This preserves much of the vibronic structure seen in the 77 K PMH spectra of 12SB and 12HSB. We hypothesize that in the 5:1 complex, the four extra perflouro-*tert*-butyl alcohols form a localized, hydrogen-bonded network which stabilizes the charge separation required to completely transfer 12HSB's proton to the Schiff base nitrogen. Such H-bonding networks often are invoked to explain the intermolecular associations of other organic alcohols.[40,41] Of particular significance are association studies on dilute solutions of the parent alcohol, ("perhydro") *tert*-butyl alcohol.[42] These studies indicate

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the dominance of a linear trimer and higher polymers (tetramers, pentamers, etc.) with cyclic structures. Similar cooperative effects should be present in the more acidic perfluoro-*tert*-butyl alcohol. A complex between 12SB and several molecules of perfluoro-*tert*-butyl alcohol would allow the counter-anionic charge of 12PSB to be delocalized over the extended H-bonded network. This delocalized charge can therefore be stabilized in an essentially nonpolar solvent environment. In effect, we have developed a solvent system in which the polar component (perfluoro-*tert*-butyl alcohol network) is restricted to the nitrogen end of the polyene, while the nonpolar component (PMH glass) surrounds the rest of the polyene chain. The net result is a minimization of solute–solvent interactions and the retention of enough vibronic structure to locate and identify the electronic origins.

The structural details of the 5:1 complex remain a matter of conjecture. Previous studied of the parent *tert*-butyl alcohol[42] and steric considerations may suggest a preference for linear H-bonded networks in the fluorinated alcohol. It also should be noted that the "5:1" complex may well represent a distribution of H-bonded networks in terms of stoichiometry as well as geometry. The predominance of H-bonded networks in many other alcohols strongly supports the hypothesis that the perfluoro-*tert*-butyl alcohol solvent "cages" are both well organized and localized around the Schiff base nitrogen. Lack of interaction between the H bonder and the polyene chain is supported by separate experiments in which a 10-fold molar excess of perfluoro-*tert*-butyl alcohol was added to dilute solutions of dodecahexaene and dodecapentaenal.[8] The 77 K spectra showed no evidence of interaction in contrast to the large spectral changes observed when the H bonder is added to 12SB.

Summary and Conclusions

Our results have been summarized in Figure 5. It should be reemphasized that our ability to accurately measure the energies of the "$1^1B_u^{+}$" and "$2^1A_g^{-}$" states requires (1) model polyene Schiff bases that do not possess the extensive substitutions (e.g., methyl groups and cyclohexenylidene rings) that are responsible for the unresolved optical spectra of the retinyl polyenes[18] and (2) in the case of 12PSB, a method for stabilizing it and its counterion in a nonpolar medium. This critical step has been realized by using excess perfluoro-*tert*-butyl alcohol to form a small, localized polar "cage" around the Schiff base nitrogen while leaving the polyene backbone in an essentially hydrocarbon environment.

Our data (Figure 5) show that 12SB, 12HSB, and 12PSB all exhibit the "$1^1B_u^{+}$" > "$2^1A_g^{-}$" state ordering previously observed for the parent polyene hydrocarbon, dodecahexaene.[8] The "$1^1B_u^{+}$" state undergoes a large bathochromic shift (~2200 cm^{-1}) in changing from 12SB to 12PSB. The "$2^1A_g^{-}$" state, however, also experiences a significant shift (~1300 cm^{-1}) to lower energy. The net effect is a narrowing of the "$1^1B_u^{+}$" – "$2^1A_g^{-}$" energy difference from 3100 cm^{-1} in 12SB to 2200 cm^{-1} in 12PSB. The large red shift in the "$1^1B_u^{+}$" state upon protonation of 12SB is comparable with that seen in the Schiff bases of retinal. It previously had been supposed that the "$2^1A_g^{-}$" state did not experience such a shift and that in protonated Schiff bases such as rhodopsin the ordering of the two lowest lying singlets was inverted. For example, both the INDO—CISD calculations of Birge and Hubbard[4,27] and the similar CNDO/S calculations of Schulten et al.[28] on demethyl-12PSB ("11PSB" in our nomenclature) place "$1^1B_u^{+}$" ~10,000 cm^{-1} *below* "$2^1A_g^{-}$". This proposed level inversion has been rationalized by the strong stabilization experienced by the "ionic" $1^1B_u^{+}$ upon protonation. The "covalent" $2^1A_g^{-}$ state is thought to be largely unaffected by the addition of a proton. The present work indicates that while there is a large bathochromic shift of "$1^1B_u^{+}$", it is not nearly as large as calculated. Furthermore, the "$2^1A_g^{-}$" state also undergoes its own shift to lower energy and its not overtaken by the "$1^1B_u^{+}$".

Our spectra also suggest a reconsideration of the fluorescent lifetimes and quantum yields of the retinylidene Schiff bases (RSB).[23] As discussed previously, such data, when combined with the determination of the integrated intensity of the strong "$1^1A_g^{-}$" → "$1^1B_u^{+}$" absorption band ($\tau = \tau_0\phi_f$), can be useful, if not conclusive, in assigning the lowest excited (fluorescent) singlet.[24] For all-trans RSB the discrepancy between the observed lifetime (τ 5–6 ns) and that calculated from the fluorescent quantum yield and integration of the strong absorption (τ = 0.1–0.3 ns) indicate a weak, "$2^1A_g^{-}$" → "$1^1A_g^{-}$" fluorescence transition.[23] This conclusion is totally supported by the resolved spectra of 12SB (see Figures 2 and 5). For the protonated RSB(PRSB) the difference between the observed and calculated lifetimes (1 ns vs. 0.2 ns)[23] is not as large as RSB but, again, is certainly consistent with our spectroscopic conclusions. The shorter observed lifetime for excited PRSB may reflect increased mixing between the more energetically similar "$1^1B_u^{+}$" and "$2^1A_g^{-}$" states, as previously suggested.[23]

Our identification of the 5:1 complex as 12PSB, i.e., as a protonated Schiff base, is based on the following: (1) the high acidity (pK_a = 5.2[32]) of perfluoro-*tert*-butyl alcohol and its ability to hydrogen bond to 12SB in a 1:1 complex—this positions the proton for subsequent transfer; (2) the spectral similarities (e.g., λ(0–0) of 431 nm for the 5:1 complex vs. ~ λ(0–0) of 440 nm for 12HSB$^+$Cl$^-$) between the 5:1 complex and 12SB protonated in polar solvents by addition of excess HCl (cf. Figures 4 and 6); (3) the ability of *tert*-butyl alcohol (and therefore perfluoro-*tert*-butyl alcohol) to form extended hydrogen-bonded networks in dilute solutions;[42] (4) the potential for such hydrogen-bonded networks to cooperatively support the charge separation required for protonation. These arguments do not eliminate the possibility that the 5:1 complex represents an intermediate species somewhere between 12HSB and 12PSB or perhaps just 12HSB which is strongly red shifted by the excess alcohol in its solvent cage. Similar possibilities have been raised concerning rhodopsin itself, and, in spite of extensive resonance Raman, ^{13}C NMR, and theoretical effort, the extent of protonation in rhodopsin remains a subject of debate.[43,44]

Our spectra clearly indicate that "$2^1A_g^{-}$" has lower energy than "$1^1B_u^{+}$" in 12SB, 12HSB, and 12PSB (5:1 complex) and that both states can undergo substantial energy changes, depending on their solvent environment (see Figure 5). These findings bear on the relative role of the two states in the photodynamics of rhodopsin and bacteriorhodopsin. Rhodopsin's absorption (λ_{max} 498 nm) is bathochromically shifted from the absorptions of PRSB (λ_{max} 440 nm) and the 5:1 complex (λ(0–0) 431 nm) in nonpolar solvents. If, in comparing the electronic energies of the 5:1 complex with those of rhodopsin, the 3100-cm^{-1} red shift of "$1^1B_u^{+}$" is accompanied by a 1000-cm^{-1} red shift in "$2^1A_g^{-}$", then the state orderings observed for the 5:1 complex would be retained in rhodopsin. Extrapolation of the data summarized in Figure 5 suggests that a 1000-cm^{-1} shift in "$2^1A_g^{-}$" is quite reasonable. For rhodopsin and other pigments and intermediates with λ_{max} < 500 nm, we therefore propose that "$1^1B_u^{+}$" > "$2^1A_g^{-}$". It is important to note that this extrapolation does not require the 5:1 complex or rhodopsin itself to contain fully protonated Schiff bases. The arguments listed above and previous work on rhodopsin,[43] however, favor the protonated forms.

The ability of "$2^1A_g^{-}$" to shift to lower energy in Schiff base systems with strong absorptions comparable to rhodospin's (λ_{max} ~ 500 nm) could be substantiated by obtaining resolved spectra of the 5:1 complex in a range of polar and polarizable solvents.[45,46] Fluorescent quantum yields and lifetime measurements on the 5:1 complex and on 12HSB$^+$Cl$^-$ also would be useful. This information would help in establishing the extent of protonation in the complex (cf. τ(obsd)/ϕ_f with that of 12HSB$^+$Cl$^-$) and in providing a more rigorous assignment of the fluorescent state. These ex-

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periments would further exploit the structured spectra and nonnegligible fluorescence yields of our model Schiff bases. Neither of these advantages is found in rhodopsin.

The relative positions of the "$2^1B_u^{+}$" and "$1^1A_g^{-}$" states should influence the mechanisms by which rhodopsin disposes of its absorbed photons. Previous models of the 11-cis→trans isomerization have relied on excited-state potential surfaces calculated for a lowest excited singlet of "^1B_u" character.[4,27,47,48] Since the distribution of electrons is predicted to be much different in "$2^1A_g^{-}$", the applicable potential energy surfaces (e.g., those describing the torsion about the bond corresponding to C_{11}–C_{12} in retinal) may lead to qualitatively different photochemical events. Our work indicates that the nature of rhodopsin's first excited state is, at least from an experimental point of view, very much an open question.

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Spectroscopic Studies of the Thermal Rearrangement Reaction of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate in the Solid State

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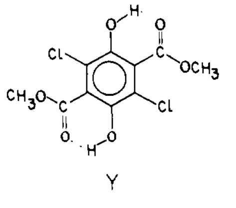
Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received March 29, 1982*

Abstract: The thermal rearrangement of the yellow (Y) isomer of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate in the solid state, which yields a white (W) isomer, has been investigated by a combination of Raman phonon spectroscopy and electronic emission spectroscopy. The rearrangement is found to start as a homogeneous process but becomes heterogeneous as the product forms. The Raman spectra of the Y and the W isomers both in the phonon and in the internal vibration region show differences that relate to the difference in the nature of the hydrogen bonds of these two isomers in the solid state. A rigid-motion analysis of the published X-ray thermal parameters has been used to make assignments of the molecular nature of the phonon transitions observed in the Raman spectra. A temperature-dependence study of the Raman phonon spectra suggests that the rearrangement may be defect controlled rather than phonon assisted.

The thermal rearrangement of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate, which leads to the conversion of a yellow crystal to a white crystalline form, was reported by Hantszch[1] in the beginning of this century. This rearrangement process in the solid state was more thoroughly investigated by Curtin and Byrn[2] and by Byrn, Curtin, and Paul.[3] They used the X-ray diffraction technique to determine the detailed crystal structures of both the yellow and the white crystalline forms. In solutions, this compound also exhibits yellow and white forms.[4] A yellow solution is obtained in weakly interacting solvents such as chloroform. On the other hand, a white solution results in a solvent like methanol, which forms strong hydrogen bonds. The spectroscopic studies of these solutions reveal an equilibrium between two limiting structures.[4] The two forms differ in the nature of the hydrogen bond. The Y form (yellow) involves a hydrogen bond to the carbonyl oxygen atoms at each end of the molecule. The W form (white) has two intramolecular hydrogen bonds to the chlorine atoms. The molecular structures of the Y and W forms in the solid state differ in the conformation of the carboxymethyl groups with respect to the benzene ring. They are coplanar in the Y form but are distinctly out of the plane of the benzene ring in the W form. In the solid state, the Y form still contains the hydrogen bonding, which is predominantly intramolecular and of a chelate type. A detailed structural analysis[3] of the W crystalline form, however, suggests a bifurcated hydrogen bond involving an intermolecular O–H···O bond and an intramolecular H···Cl bond. Since there are differences in both the molecular conformation and the nature of the hydrogen bond, the two forms have been classified as chemical isomers.[3]



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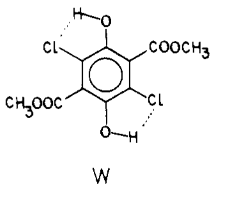

W

Although both isomers crystallize in the same space group, $P\bar{1}$, the unit cell of the Y isomer contains one one-half molecule per asymmetric unit while that of the W isomer contains two one-half molecules per asymmetric unit. In other words, the conversion of the Y form to the W form leads to a doubling of the unit cell. A closer inspection of the spatial arrangement of the W structures reveals that it can be generated from the Y structure if a considerably large reorientation of the molecule is assumed. Specifically, a reorientation of nearly 180°, of half of the molecules, around the Cl–Cl axis is required in addition to the conformational change.[3]

[†] On leave from the Institute of Organic and Physical Chemistry, Technical University of Wroclaw, Poland.

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