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High-Resolution Optical Spectroscopy of Polyenes Related to the Visual Chromophore

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High-resolution optical spectroscopy has been used to elucidate several features of polyene excited states. Spectra at 4.2 K of 2,10-dimethylundecapentaene in n-nonane and 2,12-dimethylundecapentaene in n-undecane are presented. Vibrational analyses of these spectra support the ^1A_g assignment for the lowest excited singlet states in these and other linear polyenes. The energy gap between the ^1A_g and the higher lying ^1B_u state increases from 3000 cm^{-1} in the pentaene to almost 4000 cm^{-1} in the hexaene. The tridecahexaene can be produced in several distinct n-undecane crystal sites. Differences in the spectra of these sites provide indications of the extreme sensitivity of polyene electronic structure to the details of local environments. The extension of these findings toward an understanding of the spectra of polyenes related to the visual chromophore is discussed.

1. Introduction

We previously have reported studies in which high-resolution optical spectroscopy has been used to gain a more detailed description of linear polyene electronic states.[1,2] Our initial work has concentrated on simple linear polyenes which are taken as models for the more complicated isoprenoid structures used in visual systems (Figure 1).[3] So far, the optical spectra of the model compounds have been more susceptible to unambiguous interpretation than have the corresponding spectra of the retinals. This can be illustrated by comparing the absorption and fluorescence spectra of *all-trans*-retinal and 2,10-dimethylundecapentaene (Figure 2) in 77-K glass. Even under such low-resolution conditions, the vibronic features in the undecapentaene spectra prove sufficiently distinct to allow the location of the origin of a forbidden electronic state (^1A_g) approximately 3000 cm^{-1} below the origin of the strongly allowed ^1B_u state.[4] An even more significant advantage of the model compounds is seen in the 4.2-K spectra of the undecapentaene substitutionally dispersed into an n-nonane host crystal (Figure 3a). These spectra are rich in vibrational structure with line widths of only a few reciprocal centimeters. Analysis of the vibronic details showed that for the undecapentaene the transitions between the ground and first excited states are induced by low-frequency, nontotally symmetric vibrations.[2] This provided direct proof that these transitions are electronically forbidden ($^1A_g \leftarrow {}^1A_g$) and are made allowed through vibronic mixing.

In addition to their relevance to retinal's electronic structure, the simple model compounds discussed here are interesting from a theoretical point of view. Thus the diphenyl and the dimethyl polyenes provide smoothly varying molecular systems with symmetries that are sufficient to test various theoretical predictions. One of the important milestones in the development of π-electron theories was the ability of the simple Hückel and free-electron treatments to account for the excitation energies of the strongly allowed $^1B_u \leftarrow {}^1A_g$ transitions.[5] The recent discoveries of low-lying forbidden $^1A_g \leftarrow {}^1A_g$ transitions in the linear polyenes[1,2,4,6] present new theoretical challenges. For example, the $^1B_u \leftarrow {}^1A_g$ transition converges to a constant excitation energy, but the dependence of the ^1A_g energy on polyene length is not yet clear. This problem is particularly intriguing with regard to the infinitely

long polyenes which might serve as models for one-dimensional superconductors.

In this paper, we present preliminary high-resolution spectra of 2,12-dimethyltridecahexaene in polycrystalline matrices of n-undecane. Preliminary analysis of the highly detailed vibronic structure is consistent with the ^1A_g assignment for the lowest excited singlet state. By varying experimental conditions we have been able to place the hexaene in different sites in the n-undecane host. Comparison of the spectra from these sites provides some indication of the influence which the environment has on polyene electronic structure. Insights into the problems encountered in the low-resolution spectroscopy of the retinyl polyenes as well as impetus for future high-resolution efforts follow from these observations.

2. Experimental Section

a. Samples. Both the 2,10-dimethylundecapentaene and the 2,12-dimethyltridecahexaene were gifts from Professor T. S. Sorenson.[7] The pentaene had a melting point in agreement with that previously reported[7] and was used without further purification. The hexaene was at most 25% pure and was, therefore, subjected to chromatography on Woelm alumina (activity grade I). The hexaene was eluted with petroleum ether, benzene, and diethyl ether. The predominant and as yet unidentified impurity came off the column first, giving a clean separation from the desired hexaene. The absorption spectra taken of the hexaene from the leading and tailing fractions off the column gave no evidence that our preparation was not homogeneous. After chromatography, the solvents were vacuum-evaporated and the hexaene was dissolved in small amounts of alkanes. The alkanes were used as obtained from Eastman. The alkane solutions when stored at -15 °C appear to be quite stable over a time period of several weeks. Sample solutions for spectroscopy were degassed by repeated freeze–pump–thaw cycles before being sealed off under vacuum.

For the pentaene, highly resolved optical spectra were obtained by freezing as quickly as possible concentrated n-nonane solutions. This was best accomplished by quickly lowering room-temperature solutions into a liquid helium cryostat. A similar technique also worked for obtaining spectra
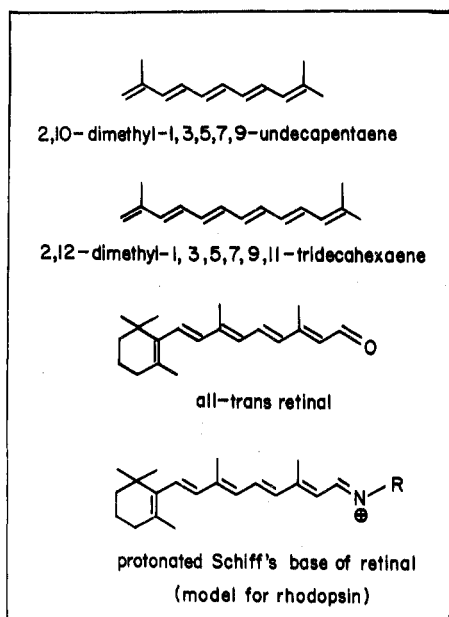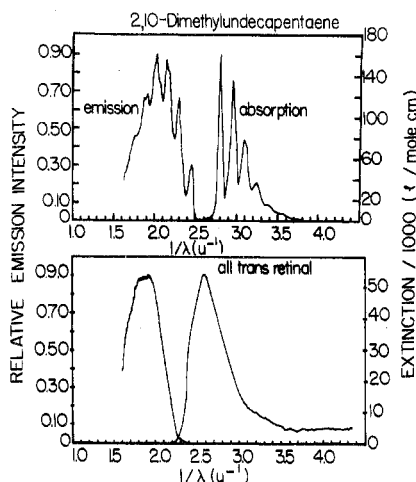
Figure 1. Polyenes related to the visual pigment.

Figure 2. The 77-K absorption and emission of *all-trans*-retinal and 2,10-dimethylundecapentaene in EPA (ether–isopentane–ethanol, 5:5:2 by volume). The emissions are corrected for the spectral sensitivities of the monochromator and photomultiplier. (1 μ^{-1} = 10 000 cm^{-1}).

of the hexaene. For the hexaene–undecane system, however, well-resolved spectra also could be obtained by slow cooling of room-temperature samples. This was done in most instances by placing the sample in the liquid helium cryostat before liquid nitrogen was placed in the outer jacket for precooling. The sample was thus cooled from room temperature to 77 K in about 2–3 h.

Emission spectra of both the slowly grown and quickly grown samples consist of sharp (minimum line widths ~4 cm^{-1}) peaks on top of a broad continuous background. The background emission could be reduced, but never completely eliminated, by adjusting the rate of cooling and the concentration of the samples. The background is presumably due to aggregation of solute molecules into microcyrstallites and/or individual solute molecules which find themselves in a broad distribution of solvent environments. The spectra of those molecules which do end up in well-defined environments indicate that, unlike many other such Shpol'skii systems,[8] only a few predominant sites are occupied. This had been noted before in the undecapentaene–nonane system and, of course,
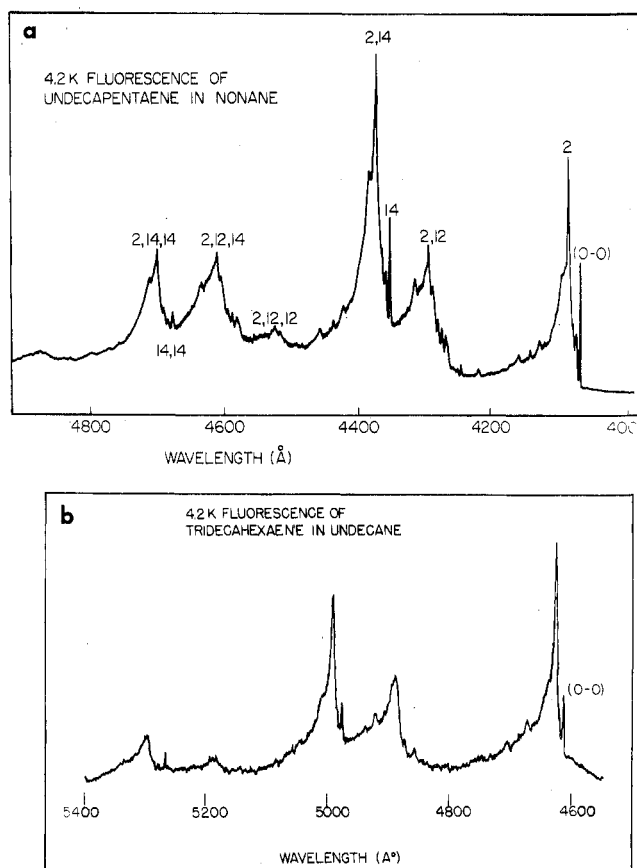

Figure 3. The 4.2-K fluorescence of 2,10-dimethylundecapentaene in *n*-nonane and 2,12-dimethyltridecahexaene in *n*-undecane. Note difference in wavelength scales.

greatly facilitates analyses of the spectra.

b. Spectral Measurements. The emission spectra were recorded using a Jarrell-Ash 1-m Czerny–Turner monochromator which was operated in second order with typical instrumental resolution of 2–3 cm^{-1}. The fluorescence was induced by ~1–2 mW of uv light (λ 364, 351 nm) from a Spectra Physics Model 171-05 argon ion laser. Background light from the laser was filtered by a Corning 9863 glass filter. The resulting fluorescence passed through a Corning 3389 filter before being focused on the entrance slit of the monochromator. The light was detected with an EMI 6256 B photomultiplier operating in a photon-counting configuration. The high-resolution fluorescence spectra reported here are not corrected for the sensitivities of the monochromator and photomultiplier but these are relatively flat over the wavelength region studied.

3. Results and Discussion

a. Comparison of the Fluorescence of 2,10-Dimethylundecapentaene with that of 2,12-Dimethyltridecahexaene. The fluorescence from a quickly frozen sample of the undecapentaene in *n*-nonane is compared with the fluorescence from a slowly grown sample of the tridecahexaene in *n*-undecane in Figure 3. The assignments indicated in the pentaene spectrum have been discussed in detail in an earlier paper.[2] The overlap between the absorption and emission spectra enabled features due to different crystal sites to be distinguished from those due to true vibrations of the undecapentaene. These studies showed that the bulk of the fluorescence was built not on the origin but on a quantum of a low-frequency, nontotally symmetric promoting mode (mode 2 in

Figure 3a). The undecapentaene fluorescence spectrum thus was seen to agree with Herzberg–Teller expectations for a forbidden transition and furnished strong proof for the ^1A_g assignment of the lowest excited singlet state.

Figure 3 shows that there is a remarkable similarity between the vibronic details seen in the emissions from the undecapentaene and the tridecahexaene. Preliminary absorption measurements indicate the tentative assignment of the electronic origin shown in Figure 3b. We again see evidence of Herzberg–Teller vibronic coupling with most of the intensity being built not on the sharp, forbidden origin but on a low-frequency inducing vibration. The tridecahexaene spectra thus provide further support for the A_g assignment for the lowest excited singlet state in these and other linear polyenes.[1,2,6]

The difference in energy between the origin of the ^1A_g state and the origin of the strongly allowed ^1B_u state seen in room-temperature absorption spectra is for the hexaene about 4000 cm^{-1}. The corresponding energy gap in the undecapentaene is closer to 3000 cm^{-1}. It appears, therefore, that the ^1B_u state converges more rapidly to its long ("infinite") polyene energy limit than the ^1A_g state. This is in accord with previous observations.[6] It is, of course, of theoretical interest to consider the ^1A_g energy of an infinitely long polyene. Because the longer polyenes (e.g., β-carotene) are not fluorescent, the weakly absorbing, low-lying states in these systems have not yet been located. A related problem for which experimental data are available is to account for the energy trends in the shorter molecules. We presently are studying the high-resolution spectra of 2,8-dimethylnonatetraene. The data gained from this molecule along with those from the undecapentaene and tridecahexaene should provide a reasonable calibration for various theoretical treatments.

The increased separation between the lowest lying ^1A_g and ^1B_u states in the longer polyenes has one other important consequence. We previously had found from the absorption work on the undecapentaene that the predominant C=C double-bond stretching frequency increases from a ground-state value of 1598 cm^{-1} to 1737 cm^{-1} in the lowest excited ^1A_g state.[2] This was quite unexpected in view of the overall decreases in carbon–carbon double-bond orders predicted by molecular orbital calculations.[9] This discrepancy could be rationalized by postulating substantial mixings of excited-state vibrations. However, such effects have not been noted before in polyene spectroscopy. Unambiguous assignments for such large molecules are quite difficult to obtain. This is especially true for the undecapentaene where the 3000-cm^{-1} gap between the ^1A_g and ^1B_u states prevents the observation of overtones of the interesting peak 1737 cm^{-1} above the origin. This shortcoming is absent in the longer tridecahexaene. The 4000-cm^{-1} separation provides a wider window for observing the ^1A_g vibronic states and thus for confirming the unusual frequency changes observed for the undecapentaene. These experiments are in progress and will be reported in a subsequent paper.

b. Comparison of the Fluorescence of 2,12-Dimethyltridecahexaene in Different n-Undecane Crystal Sites. The fluorescences from the quickly grown and slowly grown undecane samples are compared in Figure 4. Assignments of the electronic origins are based on their overlap with corresponding peaks in the absorption spectrum. In the quickly grown site, the emission intensity is built on the origin rather than on a Herzberg–Teller promoting vibration. This implies that the tridecahexaene is distorted significantly along the coordinates of the promoting mode such that the π-electron
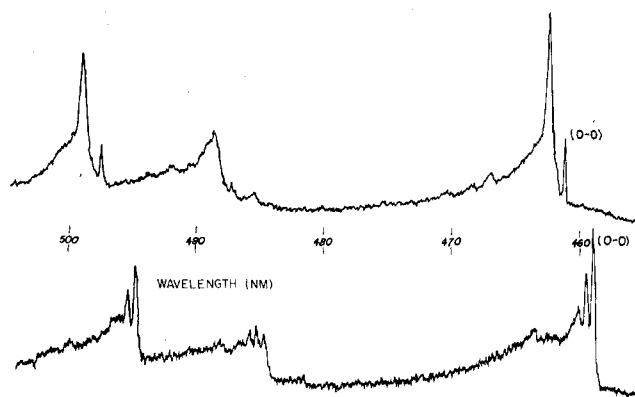

Figure 4. The 4.2-K fluorescence of 2,12-dimethyltridecahexaene in *n*-undecane. The upper spectrum is of a sample which was slowly cooled; the lower spectrum is of a quickly frozen sample.

system no longer contains even an approximate center of symmetry. This emphasizes the point that, unlike aromatic and cyclic polyene systems, the linear polyenes are quite flexible and are particularly sensitive to nonbonded interactions with the local solvent environment.

Experiments on polyenes for which the solvent environment is not well defined, therefore, may be extremely difficult to interpret. In low-resolution spectra such as those seen in Figure 2, the molecules are in a random distribution of environments. This gives rise not only to nonhomogeneous spectral shifts but also, as we have seen for electronically forbidden transitions, to a *nonhomogeneous distribution of vibronic coupling*. In a solution or glass, one must deal with a complex superposition of spectra of which those indicated in Figure 4 represent a very small sample.

These complications are magnified in retinal. This is illustrated in the comparison between the low-resolution optical spectra of retinal and the undecapentaene (Figure 2). The sources of retinal's broad spectra have been considered before.[4] Nonbonded intramolecular repulsions arising from the isoprenoid structure of retinal's ring and side chain are relieved by rotations about single polyene bonds. As a consequence, there may be multiple closely lying minima in a plot of energy vs. conformation. The interaction between conformational and solvent effects means that many different conformers are populated in a solution or glass. Furthermore, the equilibrium torsional angles will be different in each electronic state. These effects not only lead to broad optical spectra but also must result in a nonhomogeneous distributions of other excited-state properties such as fluorescent lifetimes and fluorescent and photochemical quantum yields.

In conclusion, we wish to stress the importance of high-resolution techniques in studying the electronic properties of the linear polyenes. Restricting our experimental attention to a finite number of molecular sites is essential in order to untangle effects due to the local solvent environments from those due to intramolecular properties. Further details gained from these high-resolution systems will be reported later.

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Discussion

G. A. CROSBY. What is the experimental evidence supporting the assignment of the lowest singlet state?

R. L. CHRISTENSEN. The most direct evidence is that in the optical spectra of both the pentaene and the hexaene there are weak absorptions with origins coincident with the origins of fluorescence. In neither of these molecules are there emissions coincident with the origin of the higher energy ^1B_u state. Thus, by Kasha's rule, the lowest excited singlet state is not the ^1B_u state.

A. El-BAYOUMI. What is the experimental evidence that the weak long wavelength bands are due to an electronically forbidden transition to a ^1A_g state rather than due to highly Franck–Condon forbiddenness or conformers of different geometries?

R. L. CHRISTENSEN. The high resolution spectra provide us with a very detailed picture of the vibronic states. The analyses of these spectra lend no support to the idea that the weak absorptions are due to Franck–Condon forbiddenness (ref 2). That the spectra are not due to different conformers is seen in the insensitivity of the fluorescence spectra to the wavelength of excitation. Thus, excitation into the strongly allowed ^1B_u state results in the same emission as excitation into the weak, long wavelength absorption.

R. M. HOCHSTRASSER. I suggest that your 1700-cm^{-1} mode frequency increase may be due to the fact that the total vibronic "symmetry" of that level may be the *same* as that of the ground state of a noncentrosymmetric molecule. In the two-photon spectra of benzene and naphthalene the strongest bands (all having the same *symmetry* as the ground state and not allowed in one-photon absorption) go up in frequency on excitation. Vibronic mixing with the ground state is a reasonable interpretation of this. Why don't you study the two-photon spectrum of these polyenes? You would thereby get all the odd vibrations of the "g" state.

R. L. CHRISTENSEN. Two-photon spectra certainly would be very interesting, particularly if done under high resolution conditions such as those I have described here. Both one photon and two photon spectra of low resolution systems suffer from the inability to distinguish different cases of vibronic coupling, e.g., vibronically allowed components of electronically forbidden transitions vs. purely electronically allowed transitions.

Pressure Tuning of the Fluorescence Spectra Due to Deep Traps in Anthracene and Naphthalene Crystals[1a]

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At low pressures and room temperature, excitation of relatively pure melt-grown anthracene crystals by the 458-nm line of an argon-ion laser yields a relatively weak structured fluorescence which has about the same intensity as the Raman spectrum of the crystal.[2-5] This emission is assigned to anthracene deep traps which are thought to be located near defects and can be directly excited by absorption of a single 458-nm photon. Compression of anthracene crystals at either room (nominally 20 °C) or liquid helium temperatures, however, drastically change the nature and intensity of this fluorescence.[6] At pressures as low as 2 kbars, the spectrum broadens to an excimer-like emission, the fluorescence intensity increases dramatically for fixed excitation wavelength, and the excitation spectrum dramatically shifts to lower wave numbers (by ~ -160 cm^{-1} kbar^{-1}). Thus, when a crystal at 15 kbars is excited at 514.5 nm, the broad fluorescence swamps the Raman spectrum; and 632.8-nm excitation at 30 kbars yields a broad fluorescence extending beyond 700 nm. At room temperature, the broad fluorescence extends to higher wave numbers of the excitation by several hundred cm^{-1}, but this hot-band emission is quenched upon cooling. Similarly broad fluorescence can be observed for naphthalene crystals at 30 kbars with 458-nm excitation. These spectral effects are completely reversible to compression.

Support for this assignment of the emission is obtained by observation of the appearence of a similar broad emission background in Raman spectra of powdered crystals of dianthracene compressed to 10 kbars and excited at 458, 488, 514.5, or 632.8 nm.[7] This fluorescence is believed to arise from pairs of anthracene molecules occluded in the crystal during the growth of the photodimer crystals, since the intensity of this fluorescence is sensitive to the degree of purification of the dianthracene.

References and Notes

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Discussion

R. KOPELMAN. What is the pressure effect on the vibrational exciton bands (factor group splitting) in your crystals?

M. NICOL. We see no changes in the Raman spectra that would indicate a change of crystal structure. There obviously is compression of the crystal; the lattice phonon frequencies increase by large amounts and some factor group splittings of the internal phonons increase. We have not been able to model the pressure dependence of the internal phonons; we are able to model that of the lattice phonons [*J. Chem. Phys.*, **61**, 1380 (1974); **63**, 1992 (1975)]. When we begin