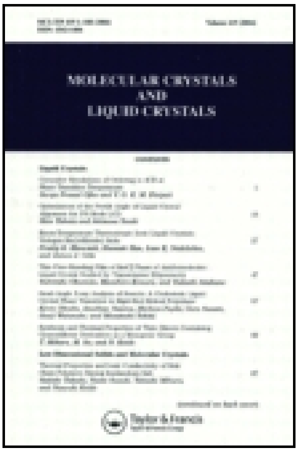

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Urea and Thiourea Inclusion Complexes of Conjugated Polyenes: Polarized Fluorescence Excitation and Resonance Raman Studies

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UREA AND THIOUREA INCLUSION COMPLEXES OF CONJUGATED POLYENES: POLARIZED FLUORESCENCE EXCITATION AND RESONANCE RAMAN STUDIES

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Abstract Urea and thiourea inclusion complexes have been prepared containing conjugated polyene chromophores. Dialkylpolyenes with n-alkane tails form complexes with urea; carotenoids and diphenylpolyenes form complexes with thiourea. In some cases the chromophoric groups are diluted by incorporation of saturated hydrocarbons into the inclusion complexes. The resulting crystals are highly dichroic with their maximum absorption along the crystallographic hexagonal c-axis. Polarized fluorescence excitation studies (of the urea n-alkylpolyene complexes) and polarized single crystal resonance Raman studies (of the thiourea carotenoid and diphenylpolyene complexes) have been performed and are interpreted in terms of the orientation of the transition dipole of these polyenes with respect to the molecular axis.

Keywords: urea inclusion compound, polarized fluorescence excitation, resonance raman spectroscopy, thiourea inclusion compound, n-alkylpolyene, carotenoids, diphenylpolyene

INTRODUCTION

It is well-known that urea forms hexagonal inclusion complexes with many long chain molecules such as n-alkanes and several of their derivatives, and that thiourea, with a larger linear channel space, forms complexes with a similar structure with branched alkanes and a variety of cyclic compounds such as cyclohexane derivatives.[1-6] A complex between urea and butadiene forms at low temperature[7] but other studies of the formation of these complexes with unsaturated compounds, e.g., alkynes[8], have indicated that no complexation occurs under the usual conditions. Thus, no inclusion complexes involving conjugated polyenes have previously been reported.

Urea and thiourea inclusion complexes are useful for spectroscopic studies because they present the included molecule in an easily oriented and, in the case of n-alkane urea complexes, primarily in an extended conformation. Such complexes have previously been used for vibrational spectroscopic studies of the included molecule.[9] There have been no previous reports of the use of such complexes for electronic spectroscopic studies except for a recent study of the host molecule electronic transitions[10] and our recent studies.[11,12]

Linear conjugated polyenes, including the carotenoids widely distributed in nature, have been the subject of investigation by electronic spectroscopy for many years.[13-23] Many of the early theories of electronic structure and spectroscopy have been applied to this class of compounds and some theories have been developed specifically for these compounds. Their color can be understood in terms of refinements of particle-in-a-box-like theories or, alternatively, in terms of excitation exchange between units viewed as ethylenic groups. Simple calculations reproduce the dependence of the maximum wavelength absorption and the intensity of these compounds. The description of electronic excited states that give rise to forbidden electronic transitions requires considerably more effort so that electron correlation is properly taken into account. Overall, there is good agreement between the more advanced theoretical models and experimental observations.

One of the few fundamental properties of the electronic spectroscopy of linear conjugated polyene chains that has never been determined with any precision is the polarization of the electronic transition dipole moment for the strongly allowed transition from the ground electronic state (with 1^1A_g symmetry) and the 1^1B_u excited state. This excitation is primarily described as the HOMO to LUMO promotion in molecular orbital terminology. In order to determine the spatial orientation of this transition dipole relative to the axis of the polyene molecule we have prepared urea and thiourea inclusion complexes of polyenes and performed polarized single crystal optical experiments on these complexes. For spectroscopic study these crystals must be made dilute so that several complications associated with high optical density crystals are avoided. One of the major advantages of inclusion crystals as a class of materials from the point of view of optical spectroscopy is that they can be prepared with variable concentration of the included compound by co-inclusion of a non-chromophoric molecule.

EXPERIMENTAL METHODS AND BASIC ASSUMPTIONS OF THE ANALYSIS

Inclusion complexes of urea or thiourea were grown from solution, usually with 2-propanol as solvent, by slow cooling. The crystals were thoroughly washed. For the fluorescence excitation studies the hexagonal crystals were mounted on a post. The polarized fluorescence excitation experiments were performed using a standard SLM fluorometer with a Glan-Thompson polarizer for the excitation radiation. The intensity of the polarized fluorescence was monitored as a function of the angle of the incident polarization relative to the c-axis of the crystal. Further details are given elsewhere.[11,12] For resonance Raman studies the crystals were simply placed on a microscope slide. The Raman experiments were performed using a laser Raman microscope in the laboratory of Professor Warner Peticolas of the University of Oregon. In this case the crystals were oriented using the microscope rotation stage and a videcon image of the microscope field. Laser Raman spectra were obtained with ca. 20 mW of power from an argon ion laser. The spectra were recorded with an optical multichannel analyzer.

The basic structural assumptions on which the analysis of the spectral data rests are that the polyene chains lie along the c-axis of the crystal and that the molecular plane is randomly distributed in all six equivalent directions. Figure 1 shows a view of the packing of an n-alkane chain in the urea inclusion complex based on the crystal structure determination of Smith.[24] The presumption of a high degree of axial orientation is based on the absence of any void space in the complex that would be necessary for angular deviation away from the c-axis. The random orientation of the molecular plane is based on the interpretation of the diffuse scattering from these crystals and the observation that rotation about the long molecular axis occurs on a MHz time scale. Given these structural assumptions it is possible to derive an expression relating the intensity of fluorescence with c-axis or a-axis polarization as a function of the angle between the excitation polarization and the c-axis with the transition dipole orientation angle

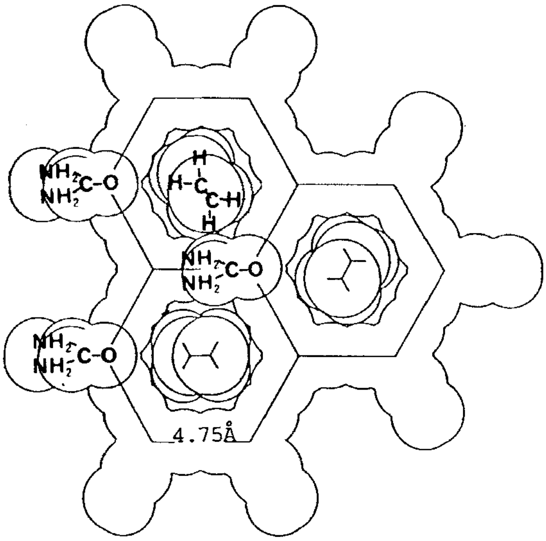

Figure 1. End view of the structure of the inclusion complex of urea and n-hexadecane.

as a parameter. These expressions simplify considerably for optically dilute crystals. The major point is that any off-axis component of the transition dipole will result in a finite intensity for excitation polarization along the a-axis.

RESULTS

Dialkylpolyenes in Urea: Polarized Fluorescence Excitation

Figure 2 shows the structures of the dialkylpolyenes that have been successfully incorporated into urea inclusion compounds. Parinaric acid is a naturally occuring 18-carbon fatty acid with a conjugated tetraene chromophore.[25] In most cases the crystals prepared were predominantly hexadecane with ca. 1% or less of the polyene added. Figure 3 shows the geometry of the spectroscopic experiments.

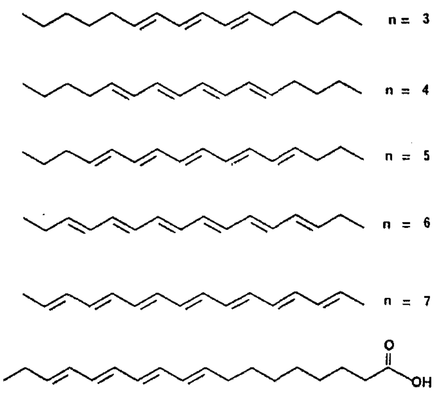

Figure 2. Structures of the dialkylpolyenes from which urea inclusion crystals have been made.

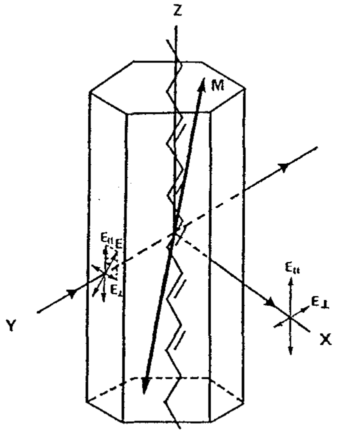

Figure 3. Schematic diagram of a hexagonal urea inclusion complex with an incorporated polyene chain.

A typical pair of fluorescence excitation spectra for an alkyl polyene in a urea complex is shown in Figure 4. The important feature is the lack of complete extinction of the fluorescence with excitation perpendicular to the c-axis. This indicates that the transition dipole is not oriented along this axis. The complete angular dependence of the fluorescence intensity as a function of the angle between the excitation polarization and the c-axis is shown in Figure 5. The curve drawn through the data shows the optimized fit of the expected behavior with the off-axis angle of the transition dipole being the only adjustable parameter. The degree of goodness of fit as a function of this angle is shown in Figure 6. A correction has to be applied to these experimentally determined numbers if they are to be compared to theoretical calculations that refer to the isolated molecule.[11,12]

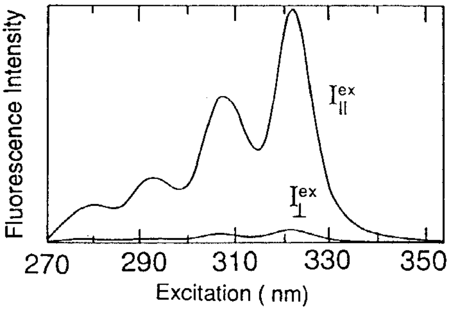

Figure 4. Fluorescence spectra of a urea/hexadecane inclusion complex crystal containing parinaric acid at a low concentration obtained with excitation light polarized parallel and perpendicular to the c-axis.

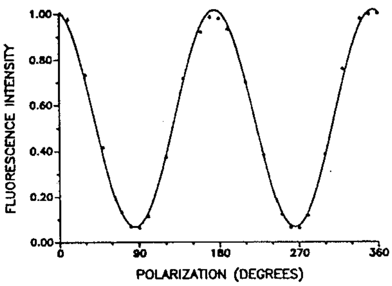

Figure 5. The angular dependence of the fluorescence of an inclusion complex containing parinaric acid. The angle is that between the c-axis and the polarization of the excitation light.

This has been done using a uniform continuum dielectric model with an elliptical cavity approximating the chromophore in the urea crystal. The resulting transition dipole angle after this correction has been applied is shown as a function of number of double bonds in Figure 7.

The curves drawn on Figure 7 are from Huckel calculations with various values of the bond alternation parameter β_S/β_D. If this parameter is adjusted to fit the observed transition energies for simple linear polyenes it is found that the optimum value is near $\beta_S/\beta_D = 0.72$.[11,12] However, as seen in Figure 7, this value of the parameter does not result in adequate agreement with the polarization data. The values obtained from our experiments when corrected for the elliptical cavity effect are in excellent agreement with theoretical calculations that include electron repulsion interactions between the π-electrons.[26] In the case of the tetraene chromophore we have made an independent measurement of the transition dipole orientation based on analysis of the time-dependence of the anisotropy of the fluorescence.[27,28] Very good agreement is found for the values obtained by these two very different methods.

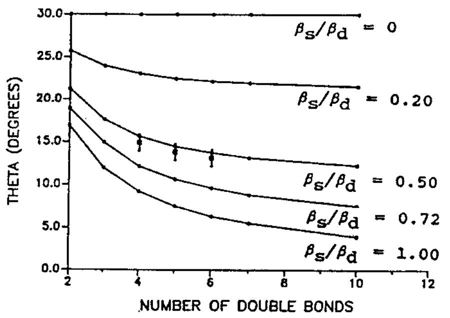

Figure 6. The dependence of the χ^2 of the fit of observed and calculated fluorescence intensity as a function of the off-axis orientation angle for parinaric acid in urea.

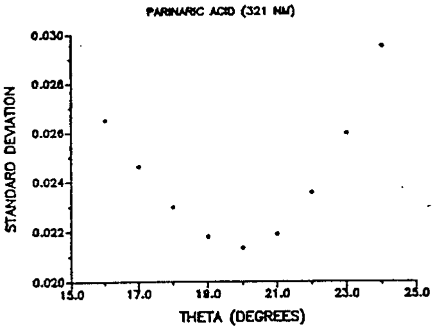

Figure 7. The variation of the off-axis transition dipole angle as a function of the number of double bonds for linear polyenes.

Carotenoids and Diphenylpolyenes in Thiourea: Resonance Raman Studies

We have found that certain carotenoids and diphenylpolyenes can be incorporated into thiourea inclusion compounds, especially if "helper molecules" which are themselves good complex formers are included. Specifically, thiourea complexes have been prepared containing the carotenoids lycopene and canthaxanthin and the diphenylpolyenes diphenyl-1,3,5,7-octatetraene and diphenyl-1,3,5,7,9-decapentaene. The helper molecules used were squalane or dicyclohexylethane. The resulting carotenoid crystals are orange or red in color and are highly dichroic. Polarized single crystal resonance Raman spectra have been obtained from many of these crystals. An example is shown in Figure 8. The resonance enhanced Raman transitions of lycopene seen for excitation parallel to the c-axis are at exactly the same frequencies as those observed for lycopene in solution.[29]

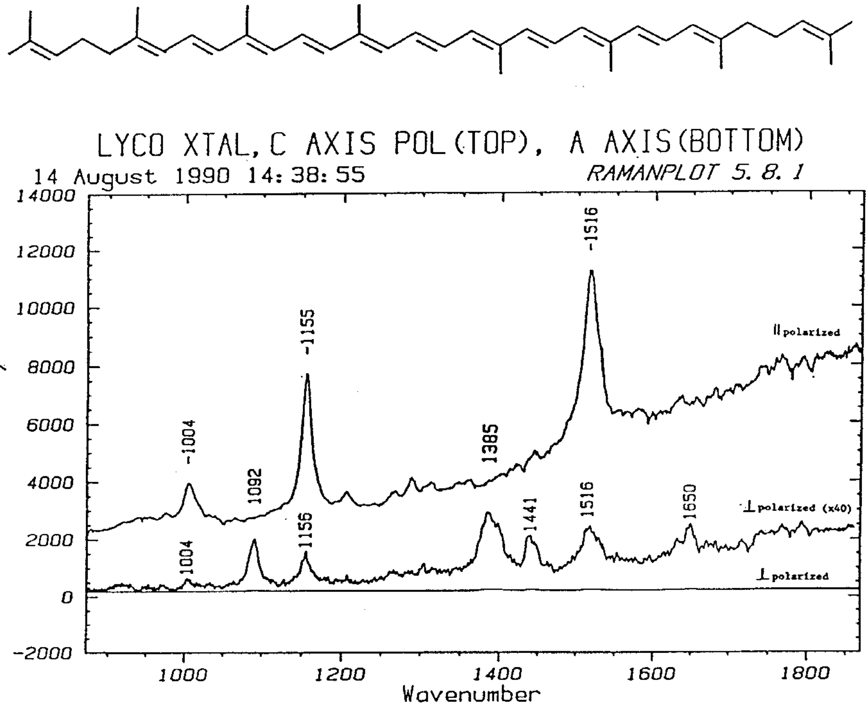

Figure 8. The resonance Raman spectrum of lycopene in a thiourea inclusion crystal. The structure of lycopene is shown at the top of the figure. Two scans of the resonance Raman spectrum resulting from perpendicular polarization are shown; the upper one is expanded by a factor of 40.

With excitation polarization perpendicular to the c-axis the lycopene bands become roughly 200 times weaker and some transitions due to the thiourea host can be seen. The angular dependence of the Raman intensity is consistent with the dependence of the transition orientation shown in Figure 7 extrapolated to a chain of 11 double bonds.

CONCLUSIONS

We have shown that urea and thiourea inclusion crystals can provide excellent systems for studies of the electronic spectroscopy of linear conjugated polyenes. In the present study this crystal system has been used to determine the orientation of the transition dipole of these chromophores. Future possible studies include the observation of exciton effects as the concentration of chromophores is raised, the examination of spectra at low temperatures to see if well-resolved emission is observed permitting polarized studies of weak transitions and the examination of A_g to A_g transitions using two-photon spectroscopy with these oriented samples.

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