

Photophysics of the electronic states S_0 and S_1 for the coplanar molecular structures of the α,ω -diphenylpolyenes DPH and DPO

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Abstract

Spectroscopy of the monoclinic and orthorhombic crystalline forms of all-*trans*-diphenylhexatriene (DPH) and all-*trans*-diphenyloctatetraene (DPO) show absorption and emission bands that do not generate the widely known Stokes shift of the polyene compounds, discovered by Hausser et al. in 1953 and repeatedly studied over the last 60 years. It can be concluded from our study that the crystallization system, whether in a monoclinic or orthorhombic system, does not significantly influence the photophysics of DPH and DPO in the crystal phase.

KEYWORDS

absorption and emission spectra of single crystals of DPH and DPO, photophysics of coplanar structures of diphenylpolyenes, Stokes shift of diphenylpolyenes

1 | INTRODUCTION

Research on the spectroscopy of polyene compounds has grown substantially over the last century for several reasons: (a) the central role played by retinal chromophores in the biochemistry of vision,^[1,2] (b) by the role played by carotenoid antennas in the photosynthesis process,^[3,4] (c) because β -carotene is the molecular structure of provitamin A,^[5] and (d) because the spectral behavior of polyenes was essential both for Lewis^[6] to establish the theory of color in organic chemistry and for Maccoll^[7] to develop his reasoning about the resonance effect.

It is noteworthy to emphasize the importance of these compounds in the construction of volume-conserving models for the mechanism of *cis*-*trans* photoisomerization in the bicycle-pedal^[8] or hula-twist^[9,10] process, which are crucial to understand the photoisomerization of 11-*cis*-retinal to all-*trans*-retinal that

occurs within the rhodopsin cavity in the phenomenon of vision.^[11,12]

Photophysical studies carried out in 1935 by Hausser et al.^[13–15] in a series of α,ω -diphenylpolyenes of formula $C_6H_5-(CH=CH)_n-C_6H_5$ ($n = 1-7$) allowed them to conclude the following: (a) The bathochromic shift shown by the absorption of these compounds depended solely on the refractive index of the medium, whereas the solvatochromism of its emission hardly depended on the properties of the medium. Furthermore, (b) compounds with a polyene chain with more than two double bonds present an unexpected Stokes shift (SS), that is, an energy difference between the 0–0 components of their first absorption and emission band, which increases significantly as the length of the polyene chain increases.

The contributions made by Hausser et al.^[13–15] will focus the investigation of the photophysics of polyene compounds on the study of α,ω -diphenylpolyenes as a

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prototype of these compounds. This will also be influenced by the fact that unsubstituted polyenes normally present high photochemical and thermal instability,^[16] which makes it extremely difficult to properly establish their photophysics. As a priority, the research effort on the photophysics of α,ω -diphenylpolyenes focused on reaching an explanation for the SS presented by these compounds, and even today, this explanation is not definitive.^[17]

Thus, in 1939, on the basis that the molecular structures of both the ground and first excited electronic states are coplanar, Mulliken^[18] explained the SS based on the non-detection of the 0–0 component of the intense first absorption band of the compound due to its cancellation by a low-frequency vibration present in the polyenes.

In 1951, Förster^[19] suggested that for 1,4-diphenyl-1,3,5,7-octatetraene (DPO), the SS must be generated by a significant change in the nuclear configuration of the compound when it is electronically excited. Later, in 1963, Birks and Dyson^[20] concluded that for the molecules 1,3-diphenyl-1,3,5-hexatriene (DPH) and DPO, “the nuclear configurations corresponding to the ground electronic state and to the excited electronic state of these compounds should differ considerably.” In 1970, Berlman^[21] concluded that for DPH and DPO, the nuclear conformation in its ground electronic state must be flat, whereas in their first excited electronic state, it must be nonplanar.

In 1972, Hudson and Kohler^[22] proposed as an explanation of their photophysics that in these compounds, there is a first phantom excited electronic state, 2^1A_g , which would be responsible for the emission of the polyene compound. That is, the intense first absorption band of the compound would be assignable to the second excited electronic state, the 1^1B_u state. In support of this explanation, Schulten and Karplus^[23] reasoned that “the phantom state proposed by Hudson and Kohler could only be excited from the ground electronic state of the compound, the 1^1A_g state, by means of a two-photon excitation, and therefore, it being not detectable in the allowed absorption spectrum.” However, in 1975, Cehelnik et al.^[24] studying the fluorescence of DPH in various solvents and at various temperatures concluded that the model raised by Hudson and Kohler was inconsistent with their evidence. However, “we must state that despite all this above-mentioned criticism, at this point in time the accepted photophysical model for polyene compounds is the one proposed by Hudson and Kohler.”^[22,25,26]

In the last 4 years, our laboratory has provided photophysical evidence of α,ω -diphenylpolyenes,^[17,27–33] which has left unsubstantiated the main arguments by Hudson and Kohler. Our contributions lead inexorably to a

photophysical model based on structural changes that starts, under normal conditions, with the excitation of a molecular structure of the nonplanar polyene compound.^[31,33] In contrast, the emission is generated from a planar structure, which makes up the SS monitored.

This starting point for the photophysics of diphenylpolyenes is undoubtedly novel based on the previous reasoning presented by other authors. Furthermore, in a recent publication,^[17] we have shown that dilute solutions of DPH and DPO in CS_2 show absorption and emission that do not present the usual SS when they solidify. This interesting experimental evidence leads us to propose that it is a consequence of starting in both transitions from flat molecular structures. For this, we see it necessary to study the photophysics of these compounds in their crystalline structures in which for the moment it is assumed that they are under all-*trans* flat forms. The experimental verification of this hypothesis is, therefore, central to establish the photophysical behavior of polyene compounds, and it will be the main reason for this work.

Thus, in 1930, Hengstenberg and Kuhn^[34] analyzed the crystalline structures of a series of α,ω -diphenylpolyenes and concluded that the first four ($n = 1–4$) crystallize in the monoclinic system and that those with the highest chain ($n = 5–7$) crystallize in the orthorhombic system. In 1940, Krishnan et al.^[35,36] showed that diphenyloctatetraene also crystallizes in the orthorhombic system. In 1953, Drenth and Wiebenga^[37] characterized by X-rays the monoclinic and orthorhombic crystals of DPH and DPO at room temperature and concluded that they are thermally stable even when heated to 100°C. Subsequently, these same authors^[38] determine the molecular structure of DPO at –100°C and concluded that “the centrosymmetrical molecules have the all-*trans* configuration; they are not perfectly planar. The carbon atoms of polyene chain are located in a plane, making an angle of 5,4° with the plane of the benzene rings.” In 1989, Hall et al.^[39] determined the structure of DPH and concluded that the structure of DPH is nearly planar—“the phenyl ring makes an angle of only 1.9° with the least-squares plane defined by the hexatriene chain.” In 2008, Harada et al.^[40] determined the crystal structure by X-ray diffraction analysis at two temperatures as extreme as 90 and 300 K and concluded that the torsion angle of the phenyl rings is 3.90 at 90 K and 4.4 at 300 K.

The most striking thing to our understanding of the study by Harada et al.^[40] is that all-*trans*-DPH crystals present “a misoriented minor conformer was observed at higher temperatures, and it disappear at lower temperature. The temperatures dependence of the crystal structure was accounted for in terms of a conformational change through pedal motions in crystals.”

Consequently, in this work, we propose to study for the first time the single-crystal photophysics of these compounds, where we have seen there is bibliographic evidence that the structures of the polyenes in the single crystals are very close to the required coplanar structural situation.

2 | EXPERIMENTAL SECTION

Ethyl acetate was purchased from Merck Uvasol grade. The molecule 1,6-diphenyl-1,3,5-hexatriene (DPH) is from Aldrich (98% pure) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO) from Lancaster Synthesis.

The crystallization of DPH and DPO is carried out in the dark, allowing a very slow evaporation of the solvent ethyl acetate. In both molecules, we detected that single crystals are generated in both monoclinic and orthorhombic forms. These small single crystals are selected using a Leica GZ6 optical microscope. It is found that DPO generates crystals significantly smaller than those of DPH.

The UV/Vis absorption spectra were recorded on a Cary-5 spectrophotometer, and those of emission on an Aminco-Bowman AB2 spectrofluorometer. The single crystals of these compounds are mounted in a sample holder that was fixed to the cryostat. In our experiments, the sample temperatures were controlled with an Oxford DN1704 cryostat.

3 | RESULTS AND DISCUSSION

We will start by obtaining the monoclinic and orthorhombic single crystals of these α,ω -diphenylpolyenes. We will continue to determine the absorption and emission spectra of these single crystals at two extreme temperatures as 293 and 77 K. Then, we will compare the corresponding absorption and emission spectra of these compounds obtained at 77 K, in order to establish whether the spectral behavior found is consistent with two planar structures in these compounds, as we propose in our recent work.^[17]

Finally, we will analyze the behavior of the absorption spectra obtained between 77 and 295 K of 3mC in order to check the interesting proposal made by Harada et al.^[40] that there are two different structures of DPH as a function of temperature.

4 | DPH AND DPO SINGLE CRYSTALS

When evaporating slowly, in the dark, a saturated solution of DPH or DPO in ethyl acetate ends up depositing

crystalline forms of DPH or DPO among which one detects, with the help of a Leica GZ6 optical microscope, crystalline structures in the system monoclinic and also in the orthorhombic system. These single crystals are carefully removed and mounted on the cryostat accessory to measure their absorption and emission spectroscopy at various temperatures. It should be noted that the crystals achieved with DPO are significantly smaller than those achieved in the case of DPH.

Because it is well established that the structures of α,ω -diphenylpolyenes in their crystalline forms present an all-*trans* configuration and that these are not perfectly planar molecular structures due in large part to the torsion that their phenyl groups exhibit, this torsion appears to increase with the length of the polyene chain of the compound.^[30,41] We believe it is interesting to determine both the absorption and emission spectra of DPH and DPO at temperatures of 293 and 77 K in order to detect possible spectral differences that are assignable to a greater planarity of the molecular structures involved in their spectroscopy.

4.1 | Spectroscopy of the DPH single crystals

In Figure 1, we show the absorption spectra obtained at 293 and 77 K of the monoclinic 1a and orthorhombic 1b single crystals of DPH. These spectra clearly show a gain in structure and significant bathochromic shift as the temperature drops, which is the typical behavior of polyene compounds.

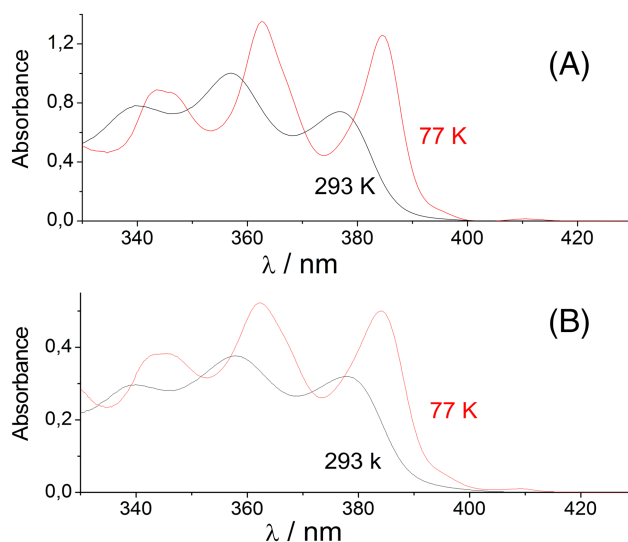


FIGURE 1 Absorption spectra obtained at 293 and 77 K of the monoclinic 1a and orthorhombic 1b single crystals of DPH

It is noteworthy that the first intense peak of the absorption spectrum obtained at 293 K, in both monoclinic 1a and orthorhombic 1b single crystals, exactly coincides at 377.8 nm, whereas for the spectra obtained at 77 K, they show up respectively at 384.5 and 384.0 nm. This indicates that the thermochromism suffered by these spectra is in the monoclinic system of 467 cm^{-1} and in the orthorhombic system of 433 cm^{-1} . A bathochromism on the order of 450 cm^{-1} when going from 293 to 77 K in the single crystals of DPH should be considered small if we take into account that for this change in temperature, the DPH presents a thermochromism of 813 cm^{-1} dissolved in chlorobutane, that is, it is almost twice the value corresponding to the single crystal.

We should also note that the onset in the absorption spectra obtained at 293 K in the monoclinic crystal is located at 400 nm, whereas it shifts at 407 nm in the orthorhombic crystal. It is also interesting that the onset of this first peak in both single crystals moves to 415 nm in the corresponding spectra obtained at 77 K.

In Figure 2, we show the fluorescence emission spectra corresponding to monoclinic 2a and orthorhombic 2b single crystals of DPH obtained at 293 and 77 K. These spectra show a clear gain in structure and very little spectral shift when the temperature drops, which is the typical behavior of polyene compounds. It is important to note that its first emission peak appears very sharp and intense but only at 77 K.

It is interesting to note that the system in which DPH crystallizes does not appear to influence either absorption or emission of the compound.

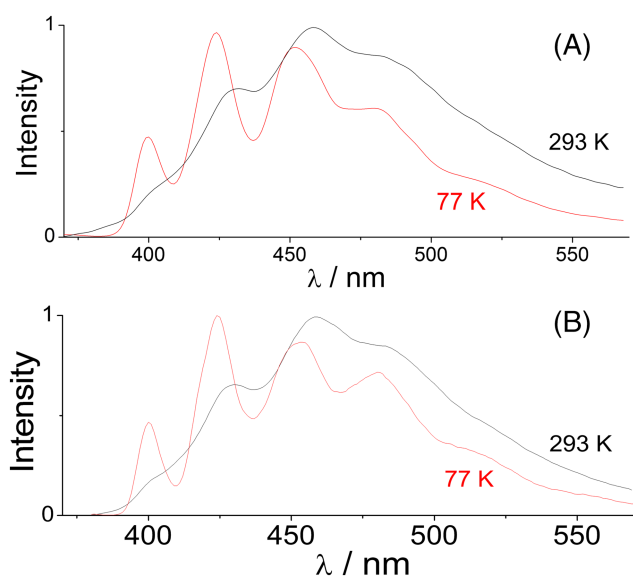


FIGURE 2 Fluorescence emission spectra corresponding to monoclinic 2a and orthorhombic 2b single crystals of DPH obtained at 293 and 77 K

4.2 | Spectroscopy of the DPO single crystals

In Figure 3, we show the absorption spectra of the monoclinic 3a and orthorhombic 3b crystals of DPO obtained at 293 and 77 K. These spectra show, as well as for DPH, a clear gain in structure and a significant bathochromic shift when lowering the temperature.

The first intense peak of the DPO absorption spectrum obtained at 293 K in both monoclinic 3a and orthorhombic 3b single crystals only shifts by 1 nm (402.0 vs. 401.0 nm, respectively), and the same situation occurs at 77 K where the first intense peak appears at 408.1 and 407.1 nm, respectively. This fact indicates that the thermochromism experimented by these spectra in the monoclinic system is 370.4 cm^{-1} and 373.0 cm^{-1} in the orthorhombic system. A bathochromism in the single crystals of the DPO on the order of 370 cm^{-1} on going from 293 to 77 K should also be considered small if we take into account that for this temperature change, the DPO solution in chlorobutane exhibits a thermochromism of 803 cm^{-1} , that is, more than double the value determined in the single crystal. We should also note that the onset of the first absorption band in the DPO invariably appears around 460 nm.

In Figure 4, we show the fluorescence emission spectra corresponding to monoclinic 4a and orthorhombic 4b single crystals of DPO obtained at 293 and 77 K. These spectra also show a clear gain in structure and a slight hypsochromic shift as the temperature drops. It is also important to note that its first emission peak appears only well resolved at 77 K.

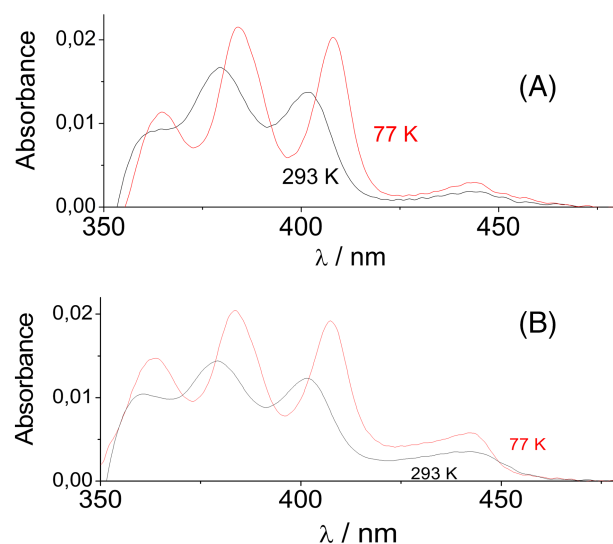


FIGURE 3 Absorption spectra obtained at 293 and 77 K of the monoclinic 3a and orthorhombic 3b single crystals of DPO

It is interesting to note that the system in which the DPO crystallizes does not seem to influence either the absorption or the emission of the compound.

4.3 | On the SS in the DPH and DPO single crystals

In Figure 5, we show the normalized absorption and emission spectra obtained at 77 K in the monoclinic crystal 5a and in the orthorhombic crystal 5b of DPH. These

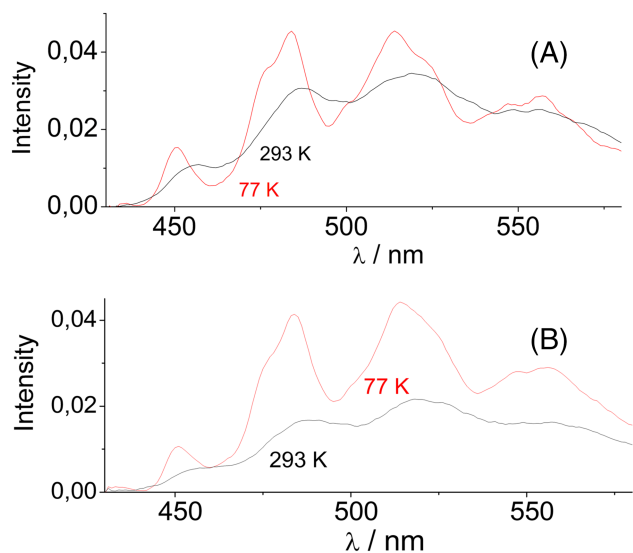


FIGURE 4 Fluorescence emission spectra corresponding to monoclinic 4a and orthorhombic 4b single crystals of DPO obtained at 293 and 77 K

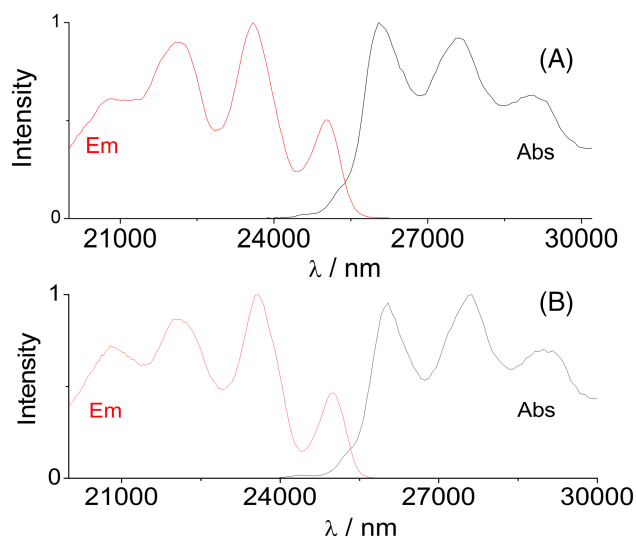


FIGURE 5 Normalized absorption and emission spectra obtained at 77 K in the monoclinic crystal 5a, and in the orthorhombic crystal 5b of DPH

spectra, as they are both significantly overlapping in the area of the 0–0 components, rule out the existence of an SS in the DPH. However, it is important to note that the peak corresponding to the 0–0 component in the absorption spectra is practically disappeared.

In Figure 6, we show the normalized absorption and emission spectra obtained at 77 K in the monoclinic crystal 6a and in the orthorhombic crystal 6b of DPO. These spectra also rule out the existence of an SS in the DPO, because they are both overlapping in the region of the 0–0 components. However, it is important to note that the peak corresponding to the 0–0 component in the absorption spectra also seems to exhibit a significant decrease of its absorbance in the area where it is located the 0–0 component of its emission.

In principle, the striking loss of intensity observed in the absorption spectrum in the area corresponding to the 0–0 component could be consistent with the existence in these compounds of flat molecular structures that that would propitiate absorption and emission transitions so similar between their fundamental and first excited electronic states. Consequently, as Einstein^[42] showed, when light passes through the sample, it will induce absorption, but with equal probability it will induce emission of the form that was excited, which would lead to a decrease in the absorbed intensity with the consequent decay of absorbance in this zone of the absorption spectrum. This is hopefully not happening if we excite at higher energetic levels of the compound because this level will relax and it is no longer likely that the excitation light can induce emission from this level as it has already depopulated.

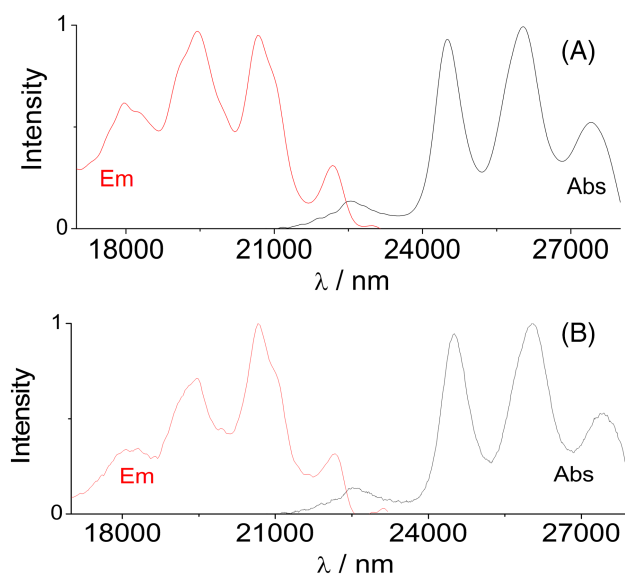


FIGURE 6 Normalized absorption and emission spectra obtained at 77 K in the monoclinic crystal 6a, and in the orthorhombic crystal 6b of DPO

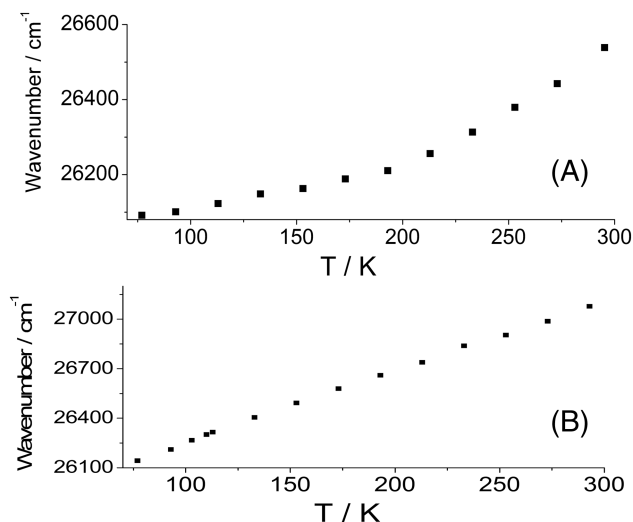


FIGURE 7 Behavior of the wavenumber of the first peak of the absorption spectra obtained between 77 and 293 K: (A) from 3mC and (B) from a solution of DPH in 3-methylpentane

4.4 | On the misoriented minor conformer in the crystal of DPH

In Figure 7A, we show the behavior of the wavenumber corresponding to the first peak of the 3mC absorption spectra obtained in the temperature range between 77 and 293 K. It is interesting to note the existence of a rectilinear behavior of the wavenumber for the data obtained below 200 K and a different one for the data obtained above 200 K.

In Figure 7B, we present the corresponding data obtained in a solution of DPH in a solvent such as 3-methylpentane, which allows us to measure well the corresponding absorption spectra in this entire temperature range because we are in a solvent that has its melting point located at 110.3 K. As can be seen, the corresponding data now show a single linear behavior.

Consequently, the data shown in Figure 7 allow us to sustain that a structural change is taking place in the DPH crystal in the range of temperatures studied, as reported by Harada et al.^[40] However, this interesting behavior deserves a more detailed and extensive spectroscopic investigation considering different polyene compounds.

5 | CONCLUSIONS

The systems in which the α,ω -diphenylpolyenes crystallize do not appear to influence either the absorption or the emission of these compounds.

In this work, we have verified that if polyene compounds absorb and emit from coplanar all-*trans*

molecular structures, their spectral behavior does not present, at 77 or 293 K, the anomalous SS that characterizes these compounds. Consequently, it must be admitted that under common noncrystalline conditions, polyenes are excited from significantly nonplanar conformations of the compound, whereas their emission is generated from practically planar all-*trans* structures.

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