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On the temperature-dependent isomerization of all-*trans*-1,6-diphenyl-1,3,5-hexatriene in solution: A reappraisal

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Abstract

In this work, we present absorption, emission, and excitation of emission spectra of all-*trans*-DPH obtained in solution between 77 and 363 K. The analysis of these spectra allows to evaluate that this molecular probe, widely used in biophysics, does not isomerizes in solution to *s-cis*-DPH at the temperatures explored. These results are in contradiction to those reported by previous studies that emphasize that (a) all-*trans*-DPH isomerizes to *s-cis*-DPH when dissolved and the temperature ranges from 283 to 373 K and (b) the molar fraction of *s-cis*-conformer equals, or even exceeds, the molar fraction of the all-*trans*-conformer at the highest temperature studied. In this work, we show how we can infer the changes taking place in the molecular structure of DPH looking at the wavenumber (ν) shift of the peaks on the absorption and emission spectra as a function of temperature. The analysis of these band shifts allows us to corroborate the change, determined by Ogawa et al. by X-ray diffraction, that occurs in the structure of DPH in the crystalline phase through a bicycle pedal process with temperature.

KEYWORDS

cis-peak, isomerization to *s-cis*-DPH, wavenumber shift

1 | INTRODUCTION

The role played by polyenes in the photophysical processes of vision[1–3] drives the investigation of torsional processes in organic compounds with unsaturated chains. It is remarkable that these torsional processes in polyene chains take place in a very effective way in spatially restricted environments such as the bacteriorhodopsin cavity.

The studies carried out provided such interesting photophysical models such as the bicycle pedal[4] or the hula-twist process.[5–7] These models show that the torsion of the polyene chain in the retinal pigments is possible within the bacteriorhodopsin cavity through the proposed mechanism for vision.[8–10]

It is also interesting to mention that the bicycle pedal model has been used by Ogawa et al.[11–14] to explain the interconversion of molecular structures in a crystal as the temperature increases. According to Ogawa, these interconversions generate disordered crystal structures that are detectable by X-ray diffraction. The most interesting outcome of Ogawa's proposal is that transformations occur in crystals of polyene molecules depending on the temperature of the crystal.

Along these lines, Turek et al.[15] inform us that: "All-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) exists in

solution as a mixture of *s-trans,s-trans* and *s-cis,s-trans* conformers. The latter is higher in energy, and its contribution increases with increasing temperature." Later these authors[16] conclude also that in a DPH solution, the fluorescence consists of emissions from the $S_1(2^1Ag)$ and $S_2(1^1Bu)$ states of the *s-trans,s-trans* conformer (*s-t*-DPH) and of emission from the S_1 state of the *s-cis,s-cis*-conformer (*s-c*-DPH), which is generated by torsion around a simple C—C bond.

It is important to note that DPH has been widely used as a probe in membrane biology,[17–23] allowing measurements of phase separations, phase transitions, and the relative fluidity of membranes. Given this profuse use of DPH, it seems necessary to clarify whether, when dissolving pure *s-t*-DPH in that solution, when the temperature increases the conformer *s-cis*-DPH is generated; see Scheme 1. It is important to indicate that previous studies[15] do not report the temperature at which the formation of the *s-c*-DPH conformer begins, neither in its ground nor excited electronic state.

In their studies, Turek et al.[15,16] measure UV absorption spectra of DPH in *n*-dodecane and emission spectra in *n*-octane by heating the originally formed solutions from room temperature up to 90°C. Because the melting point of *n*-dodecane is −9.3°C, the spectra cannot be recorded below that temperature. Thus, Turek et al. experiments are limited to a temperature range of only 90°C.

In order to significantly expand the temperature range analyzed, in our study, we use a decalin/methylcyclohexane mixture, 1:1 in volume, as a solvent. We have verified that these are transparent up to 77 K. In the present work, we present the UV absorption, emission, and excitation spectra of the emission from 363 to 113 K. In other words, we will be able to analyze the spectral behavior of absorption, emission, and emission excitation in a much wider range of 250°C.

In this work, we will also analyze the existence of the so-called "*cis*-peak"[24–27] in the UV absorption spectrum of the solutions studied in order to discard/confirm the generation of *cis*-conformers in the solutions studied.

2 | EXPERIMENTAL SECTION

Methylcyclohexane and anhydrous decalin were purchased from Aldrich and possess a purity higher than 99%.
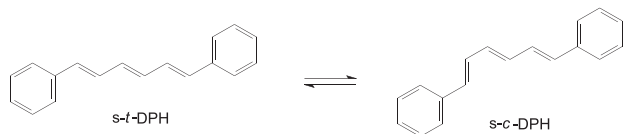
SCHEME 1 Equilibrium between *s-t*-DPH and *s-c*-DPH conformers in solution proposed by Turek et al

A mixture 1:1 by volume of both solvents (called DEMCH) will be used as solvent in this work. The anhydrous *n*-dodecane was purchased from Aldrich with a purity larger than 99%. 1,6-Diphenyl-1,3,5-hexatriene (DPH) is also from Aldrich, 98% pure, and was recrystallized three times from methylcyclohexane before being used.

For measurements below 298 K, the solution temperatures were controlled with an Oxford DN1704 cryostat that was purged with dried nitrogen (99.99% pure) and equipped with an ITC4 controller interfaced to the spectrometers. Solution temperatures over the range 293–370 K were controlled within ±0.1°C with a Fisons-Haake D8 GH thermostat.

All UV/Vis absorption spectra were recorded on a Cary-5 spectrophotometer, using suprasil quartz cells with 1-cm path length that were fixed to the cryostat or to a normal support when temperatures are above 298 K. Corrected fluorescence spectra were obtained on a calibrated Aminco–Bowman AB2 spectrofluorimeter. The sensitivity factors for the emission channel, which included not only those depending on the detector but also those related to the emission monochromator and optical arrangement (channel emission included), were obtained by using the FP-123 correction kit from SLM Instruments. This required mounting a standard lamp in a channel at right angles to the emission channel in an OL 254 M spectral irradiance lamp from Optronic Laboratories. The lamp was operated at a constant voltage supplied by an SP-270 power source and its light output driven into an integrating sphere with a pinhole leading to the fluorimeter emission channel. The conversion factors thus obtained were used to convert the measured spectra into absolute spectra, which are independent of the particular instrument used.

Corrected excitation spectra were directly obtained on the AB2 spectrofluorimeter. The small fraction of the light intensity used for excitation was switched to a Hamamatsu S1336-8BQ photodiode by means of a beam splitter. Plotting the photodiode sensitivity as a function of wavelength allowed changes in incident light intensity at each excitation wavelength to be characterized. Absolute excitation spectra were constructed from the ratio of emission intensity at the monitored wavelength to the corresponding excitation intensity at each excitation wavelength.

3 | RESULTS AND DISCUSSION

We will start by analyzing the UV/Vis absorption spectra of DPH in DEMCH obtained in 10-K increases for the temperature range between 363 and 113 K and continue with the emission obtained in the same solvent, exciting at two wavelengths 338 and 355 nm. The excitation of the emission spectra of the same solution between

363 and 133 K, monitoring the emission light at 450 nm, will also be analyzed. Finally, we will also analyze the excitation spectra obtained by monitoring light from 400 and 550 nm in 25-nm intervals of a solution of DPH in DEMCH at a temperature of 80°C.

We decided to include for the analysis some of the spectra previously obtained from solutions of all-*trans*-DPH in *n*-dodecane[15,16] that we consider to be of interest. The existence of the so-called "*cis*-peak"[27] will be investigated in the most relevant solutions to confirm the absence of the isomerization reaction.[15,16]

Finally, we will expose the causes that in our opinion lead these authors[15,16] to propose the isomerization of all-*trans*-DPH in *n*-dodecane solution at temperatures between 283 and 373 K.

3.1 | UV/Vis absorption spectra of DPH in DEMCH

Given that the most stable molecular structure of DPH is the all-*trans* isomer, called *s-t*-DPH in Scheme 1, it is coherent to expect that a dissolution of the *s-t*-DPH in DEMCH at low temperatures will only contain dissolved *s-t*-DPH. According to what is proposed in Turek et al.,[15] increasing the temperature of the solution the *s-c*-DPH conformer could be generated. Consequently, by continuing to raise the temperature, the solution would gradually enrich in the new conformer, reaching a point where the *s-c*-DPH conformer will be the majority (around 90°C).

If we take into consideration the absorption spectra corresponding to the pure conformers of DPH, that is, *s-t*-DPH and *s-c*-DPH, see figs. 2a and 16b of Turek et al.,[15] and the recent theoretical results reported by Küpper et al.[28] at the DFT/MRCI[29] level, the band bathochromic shift between the absorption spectra corresponding to *s-t*-DPH and *s-c*-DPH can be estimated to be of 1048 cm^{-1}. This behavior can be easily observed spectroscopically analyzing the shift of the corresponding maxima of these spectra with temperature.

Figure 1 shows the UV absorption spectra obtained every 10 K: (a) between 293 and 77 K and (b) between 293 and 363 K. A first analysis of the spectra collected in Figure 1 is not consistent with the idea proposed by Turek et al.[15] that for the low temperature range, the solution contains only *s-t*-DPH isomer while from a certain temperature, the solution contains both isomers: *s-t*-DPH and *s-c*-DPH.

These spectra present two well-defined peaks in the entire temperature range studied, which displace when the temperature of the solution changes, the first peak between 370 and 384 nm and the second one more intense that shifts from 351 to 362 nm. It seems reasonable to think that the position of these peaks shows the possible conformer composition changes in the solution of pure *s-t*-DPH in DEMCH with temperature.

Figure 2 show the hypsochromic band shift of these peaks for temperatures between 93 and 363 K. The linearity of the data presented is not consistent with the presence of a zone of low temperature range where only the
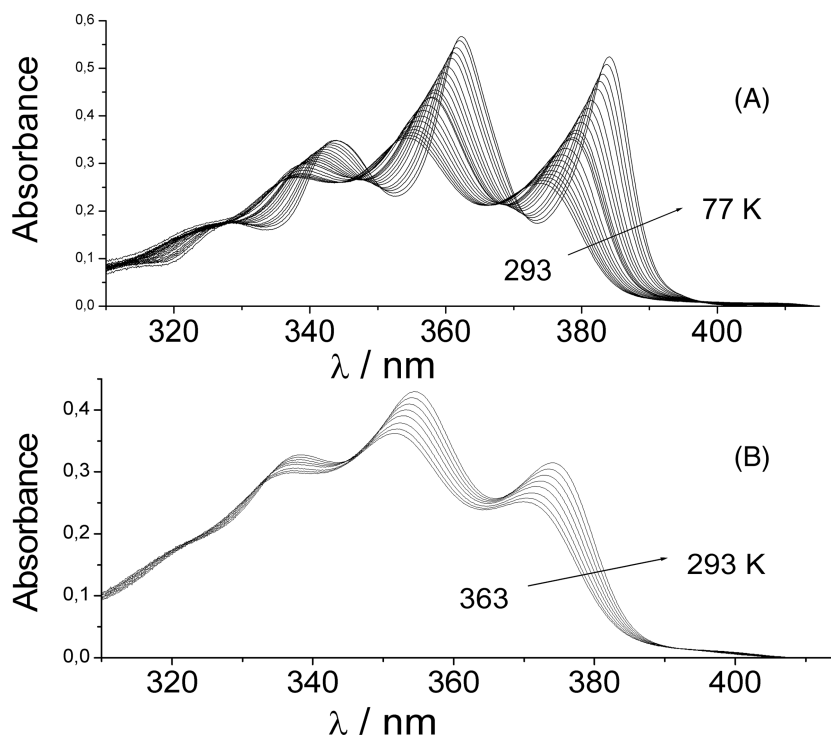

FIGURE 1 UV absorption spectra of DPH dissolved in DEMCH, obtained (A) between 77 and 293 K and (B) between 293 and 363 K
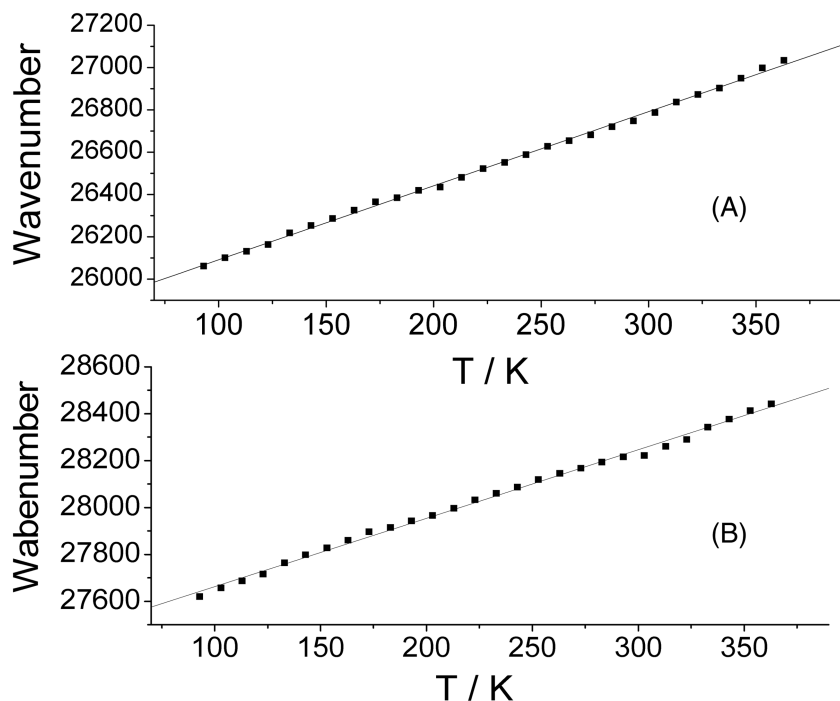
s-t-DPH exists and a higher temperature range where the two proposed conformers of DPH would coexist.

3.2 | Emission spectra of DPH in DEMCH

Figures 3 and 4 show the DPH emission spectra exciting the sample at $\lambda = 355$ nm and $\lambda = 338$ nm, respectively.

Figure 5 shows the corresponding excitation spectra obtained by monitoring light at 450 nm. Figure 6 shows the excitation spectra obtained at 80°C and monitoring light from 400 to 550 nm at 25-nm intervals.

Taking into account the shape of the spectral envelopes that *s-t*-DPH and *s-c*-DPH pure emissions should have, see figs. 10 and 12 of Turek et al.,[16] we must conclude that the spectral envelopes of the corresponding emissions and excitations determined in the present work

FIGURE 4 Emission spectra of DPH, dissolved in DEMCH, obtained after exciting at 388 nm: (A) between 153 and 293 K and (B) between 293 and 363 K
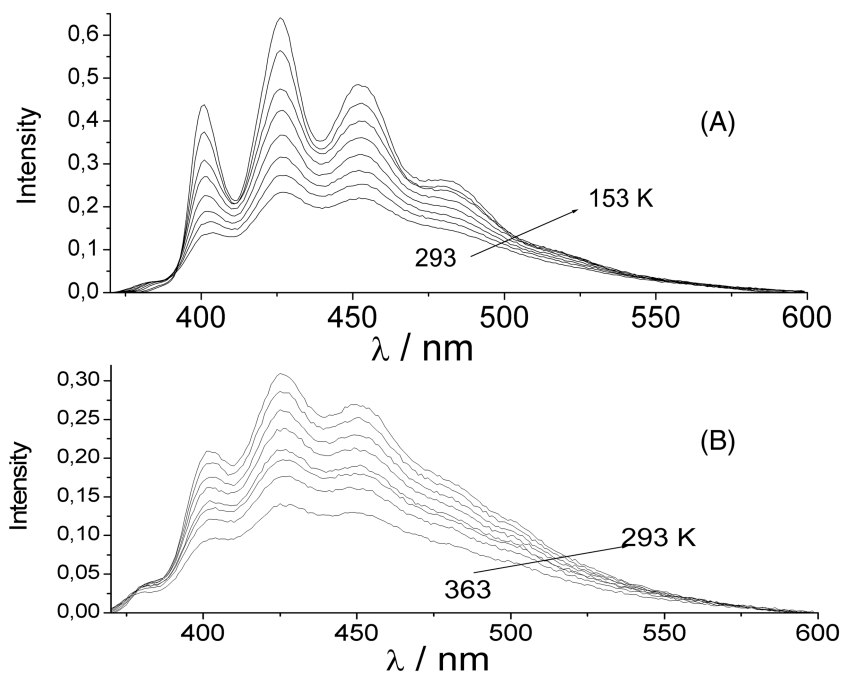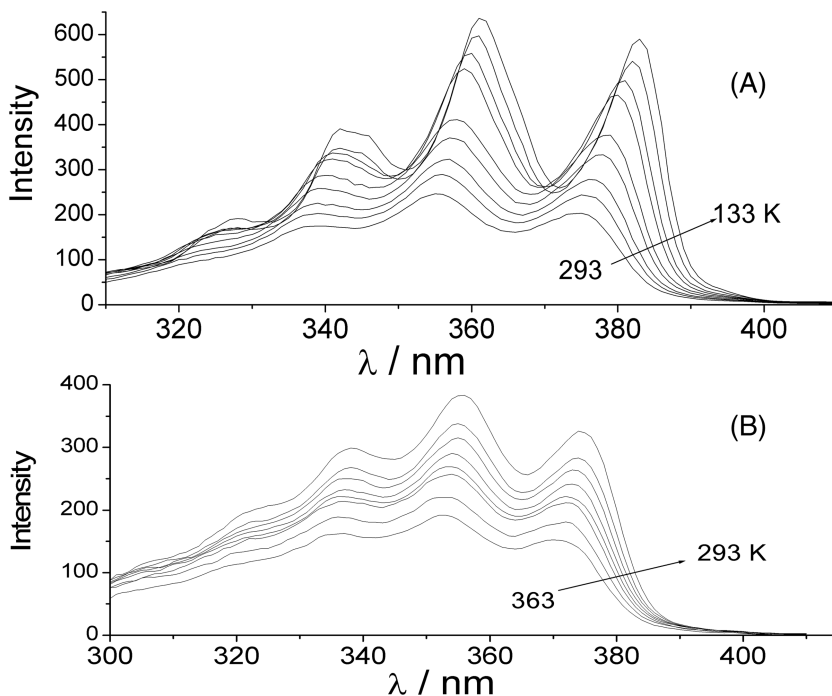
FIGURE 5 Excitation spectra of DPH, dissolved in DEMCH, obtained by monitoring light at 450 nm: (A) obtained between 133 and 293 K and (B) between 293 and 363 K

do not show a change significant enough to make us think that from a certain temperature, the *s-t*-DPH conformer begins to disappear, generating the *s-c*-DPH conformer.

In Figure 7, we show as an example the behavior of the band shift of the first emission peak obtained between 153 and 253 K after exciting at 355 nm.

Consequently, we can also conclude, as for the absorption spectra of DPH in DEMCH, that the spectral

data do not support the existence of the isomerization process in the 100-363 K temperature range.

3.3 | UV/Vis absorption of a DPH glass

In 2008, Harada et al.[12] provided evidence through X-ray diffraction measurements of single DPH crystals, at low temperature, 90 K, and above room temperature,
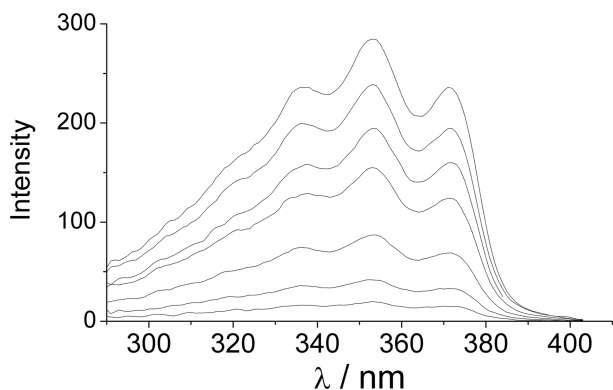
FIGURE 6   Excitation spectra of DPH, dissolved in DEMCH, obtained at a temperature of 80°C, monitoring light from 400 to 550 nm with 25-nm intervals
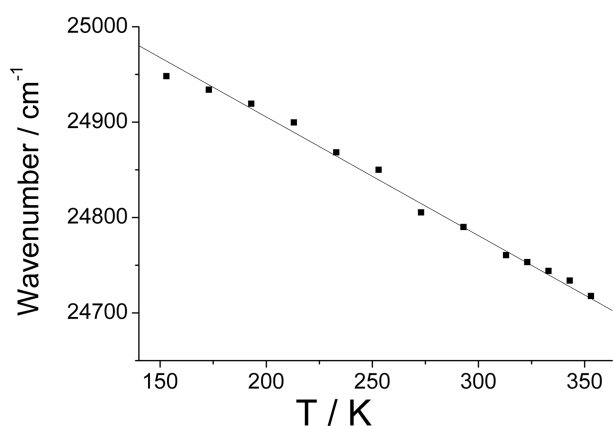

FIGURE 7   Behavior of the position of the first emission peak of DPH, dissolved in DEMCH, obtained between 153 and 253 K exciting at 355 nm
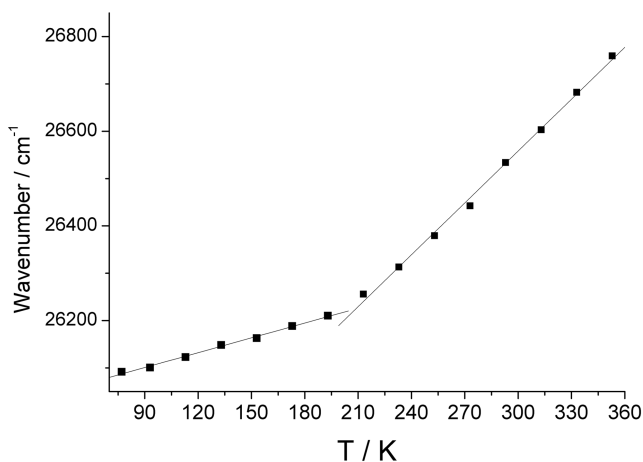

FIGURE 8   Wavenumbers of the first peak of the UV absorption band of a monoclinic single crystal of DPH by changing the temperature

370 K. At low temperature, they found that all-*trans*-DPH molecules were arranged in the crystal in agreement with previous studies,[30–33] while at above room temperature, they found signals evidencing the presence of a fraction of DPH molecules in the single crystal that had changed their all-*trans* structure, generating new conformer cells in the crystalline phase. They called it the misoriented conformer of the DPH.

Figure 8 shows the wavenumber of the first peak of the absorption band of a monoclinic single crystal of DPH. Clearly, this shift follows two different behaviors depending on whether it is below or above 205 K. Below 205 K, the shift of the wavenumber corresponds to the expected behavior of DPH single crystal. Above 205 K, the shift of the wavenumber changes its slope showing that the single crystal transforms into what Ogawa et al. called misoriented conformer of DPH.

3.4 | Isomerization of DPH according to Lunde and Zechmeister

In 1954, Lunde and Zechmeister[27] synthesized three of the five possible *cis*-isomers generated from all-*trans*-DPH and measured their UV spectra between 200 and 410 nm; see figs. 1–4 of their work. These UV spectra of the *cis*-isomers present an intense band centered between 334 and 349 nm and a structured band but of less intensity in the zone of 260 nm. For all-*trans*-DPH, this last band has no structure in the area of 240 nm.

It is important to note that the UV absorption spectrum of the *cis*-conformers, see figs. 2–4 of the work by Lunde and Zechmeister,[27] clearly presents the so-called *cis*-peak with a maximum at 268 nm in the cases of *cis*-1 and *cis*-2 and less clearly around 250 in the case of *cis*-3. In the same figures, the authors show that if these compounds are illuminated for 60 min in the presence of iodine, the corresponding spectrum is transformed into the spectrum of all-*trans*-DPH that no longer presents the *cis*-peak but the typical band without structure centered around at 240 nm belonging to all-*trans*-DPH.

Thus, this contribution by Lunde and Zechmeister makes it possible to elucidate whether the *s-c*-DPH proposed by Turek et al. is generated by heating the solution of all-*trans*-DPH from 283 to 373 K.

Figure 9 shows the corresponding UV absorption spectra obtained for a solution of DPH in DEMCH when maintaining the temperature at 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, and 90°C. The band centered at 240 nm is clearly seen but not the band corresponding to the *cis*-peak that should be located slightly red shifted from the 268 nm. Therefore, we can conclude that the isomerization of all-*trans*-DPH does not occur.

Figure 10 shows the excitation spectra monitoring light at 435 nm at temperatures of 20°C, 55°C, and 90°C. These spectra confirm that the excitation of these
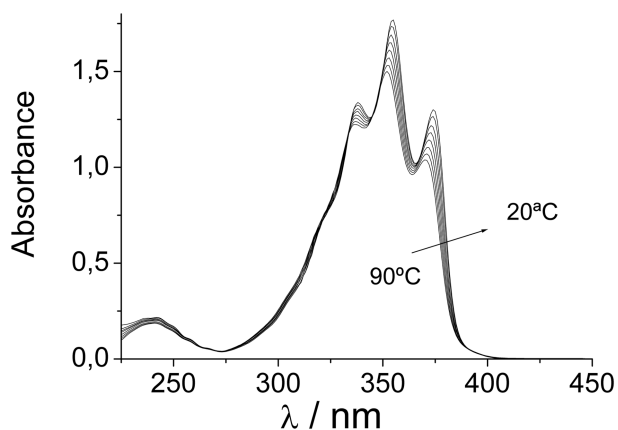
FIGURE 9 UV absorption spectra of all-*trans*-DPH, dissolved in DEMCH, obtained at 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, and 90°C
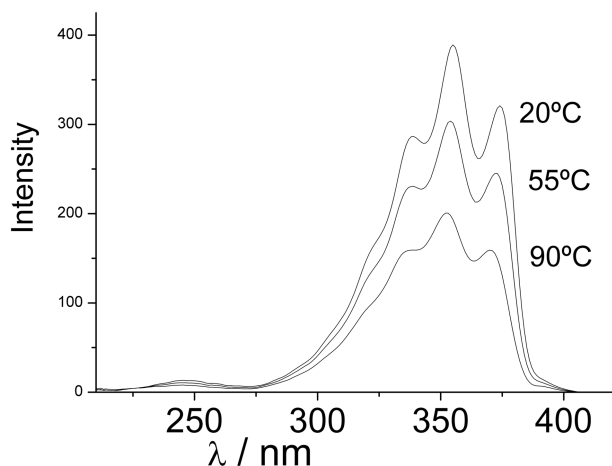

FIGURE 10 Excitation spectra of all-*trans*-DPH, dissolved in DEMCH, obtained by monitoring light at 435 nm at temperatures of 20°C, 55°C, and 90°C

FIGURE 11 UV absorption spectra of DPH, dissolved in *n*-dodecane, obtained between 263 and 363 K

solutions does not contain the *s-c*-DPH proposed in Turek et al.[15]

The sharpness with which the spectral envelope corresponding to the all-*trans*-DPH structure is maintained in the spectra shown in Figures 9 and 10 clearly indicates that the isomerization proposed in Turek et al.[15] does not occur upon raising temperature from 20°C to 90°C.

3.5 | On the possible causes that allow understanding the different proposals on the isomerization of DPH in solution

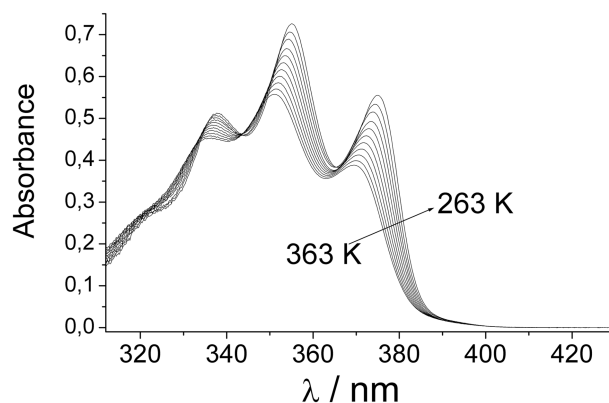At this time, we must start by considering that diphenylpolyenes are apolar compounds, not acidic and not

basic but very polarizable; consequently, its solvatochromism, at a given temperature, is only a function of the changes in the polarizability of the medium. But Turek et al.[15] base their isopolarizability method on the fact that the solvatochromic changes that these compounds undergo when the temperature changes are the consequence only of the changes in the polarizability that the medium undergoes with temperature.

In 2008, we showed[34] that diphenylpolyenes present different solvatochromic than thermochromic behavior with respect to the polarizability of the medium; see figs. 1–4 of our work. We also showed that if the polyene has a rigid structure, the solvatochromic and thermochromic behaviors of these compounds show the same behavior against changes in the polarizability of the medium.

In several publications,[35–38] we have shown that the UV/Vis absorption spectra of diphenylpolyenes in solution obtained at different temperatures do not comply with the Mulliken–Rieke rule,[39] and consequently, these compounds change their molecular structure with temperature. Therefore, the changes in their spectral absorption envelope cannot be assigned only to changes in the polarizability of the medium as Turek et al.[15] do. In principle, they arise from the sum of both contributions.

We measured the UV/Vis absorption spectra of DPH dissolved in liquid *n*-dodecane, as reported by Turek et al.[15] (Figure 11). If the areas enclosed in these spectra are divided by the corresponding values of the density of the liquid *n*-dodecane measured by Caudwel et al.[40] of these temperatures, and normalized these results to the value of the corrected area of the corresponding lowest analyzed temperature, 263 K, we obtain the results shown in Figure 12.

Figure 12 indicates that when the temperature increases between 263 and 283, the area hardly changes; in contrast, increasing the temperature above 293 K, the
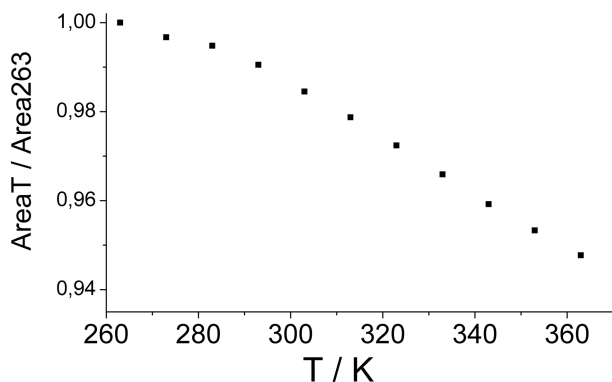
FIGURE 12 Areas of the UV spectra of DPH shown in Figure 11, corrected to constant concentration divided by the respective area at 263 K

area decreases notably. According to the Mulliken–Rieke rule, this fact indicates that the molecular structure of all-*trans*-DPH is changing. In principle, one would attribute this change to an increase in the torsional movement of all-*trans*-DPH phenyl groups with increasing temperature.[38,41]

Turek et al.[16] in their work on the fluorescence of DPH in *n*-dodecane gave special importance to the fact that their results, see fig. 10 of their work, present a clear situation of mirror symmetry with respect to the corresponding absorption spectrum of the compounds, following the proposition formulated by Levshin.[42] The subsequent contributions by Stepanov,[43] Birks and Dyson,[44] and Catalán[45] on the subject allow to conclude that if a compound rigorously complies with what is proposed by Levshin, as Turek et al.[16] say it happens with the spectra of the compound, they should not present a clear situation of mirror symmetry.

4 | CONCLUSIONS

Figures 2A and 8 show clear evidence that if new DPH conformers are generated when increasing temperature, it would be clearly detectable spectroscopically.

The UV/Vis absorption and emission spectroscopic information provided in the present work allows us to conclude that when pure all-*trans*-DPH is dissolved, it does not isomerize to *cis*-DPH in the temperature range between 113 and 363 K. This contradicts the conclusions of Turek et al.[15,16] that pure all-*trans*-DPH when dissolved in an *n*-alkane isomerizes to *cis*-DPH above room temperature (up to 100°C).

Our results show that all-*trans*-DPH can be used as a probe without structural problems in the studied temperature range. The shift in the wavenumber of the peaks of

the DPH spectra with temperature is a clear indication of structural changes in the DPH samples.

The absence of the *cis*-peak in the absorption spectra, see Figure 9, and the emission excitation spectra, Figure 10, strictly rules out the isomerization of all-*trans*-DPH.

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