

# The Photophysics of Diphenyl Polyenes Analyzed by Their Solvatochromism

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**Abstract:** The solvent-dependent intensity changes in the first UV/Vis absorption band of the three polyenes DPH, DPHb, and ttbP3 dissolved in a hydrocarbon solvent with temperature allow for the conclusion that, at temperatures above 233 K, the two phenyl groups of DPH are rotated out-of-plane to yield a non-coplanar molecular structure. This leads to the conclusion that DPH becomes increasingly less coplanar as the temperature rises above 233 K. When the phenyl groups rotate out-of-plane, the polarizability decreases, and the energy of the first electronic transition increases by an extra value. Therefore, below 233 K, the correlation lines between the absorption energy of the 0–0 component of the UV/Vis absorption band and the solvent polarizability, as measured by the *SP* values, show bilinear behavior. The unexpected behavior shown by DPH dissolved in tetrachloro- and dichloromethane is discussed. We dedicate this research as a tribute to the very important contribution to the solvent effect made by Prof. Christian Reichardt and also to his generous and altruistic scientific help that he has always shown.

**Keywords:** solvent effect on the spectra of organic compounds; solvatochromism of diphenylpolyenes; on the polarizability of diphenylpolyenes in Cl<sub>4</sub>C and in Cl<sub>2</sub>CH<sub>2</sub>



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## 1. Introduction

Polyene compounds are part of the chromophores involved in important biochemical processes such as vision, the coloration of relevant fruits and vegetables, the generation of vitamins, and protection mechanisms against sunlight. In these biochemical processes, the photophysics of these compounds plays a very important role, and therefore, it has been imperative to know their photophysical functioning.

Thus, Hausser et al. [1,2] synthesized in 1935 seven diphenylpolyenes, [C<sub>6</sub>H<sub>5</sub>-(CH=CH)<sub>n</sub>-C<sub>6</sub>H<sub>5</sub> with n = 1–7]. From their photophysical studies, carried out at 293 and 77 K, they established for the first time a series of guidelines on the photophysical properties of these compounds [2,3]. From these studies, the authors were able to conclude that the bathochromic shift of the first UV/Vis absorption band of these vinylogous diphenyl polyenes by the successive addition of a vinylene group is significantly large. They also found that this band shift does not depend on (a) the solvent's dipole moment or (b) the solvent's relative permittivity, but (c) it does depend on the solvent's refractive index. In summary, these authors established in 1935 that the vinylogous bathochromism of diphenylpolyenes depends only on the solvent's polarizability.

Hausser et al. also confirmed that (a) the solvatochromism of the emission band of these diphenylpolyenes is almost negligible, as compared to that shown by their UV/Vis absorption, and (b) that these compounds show a significant Stokes band shift, which increases with increasing polyene chain length. These findings supported the hypothesis, which was later widespread, that the electronic states involved in the UV/vis absorption and the emission process in these compounds must be of a different nature.

On the other hand, it is important to point out that from theoretical calculations [4–6] obtained at a temperature of 0 K, it was assumed that these diphenylpolyenes have a coplanar molecular structure in their fundamental electronic state. The evidence obtained by X-ray diffraction [7–9] allowed for the conclusion that all these compounds have flat polyene chains.

However, Drente et al. [9,10] already indicated that, although in a crystalline state these polyenes adopt a coplanar conformation with their phenyl rings, in the case of 1,8-diphenyl-1,3,5,7-octatetraene (DPO), the phenyl groups appear rotated by 7.5° and 5.4° at 293 K and 173 K, respectively [10]. On the other hand, Hall et al. [11] found that for 1,6-diphenyl-1,3,5-hexatriene (DPH) in crystal form at 293 K, its phenyl groups are rotated by only 1.9° with respect to its coplanar polyene chain.

One should keep in mind that in a crystalline state, the diphenylpolyene molecules are arranged in a way that forces the molecules to adopt a coplanar structure, particularly at very low temperatures. However, it cannot be ruled out that this coplanar arrangement can change in solutions at higher temperatures.

There is also evidence from the <sup>13</sup>C NMR spectra of diphenylpolyenes, measured in a thermotropic liquid crystal ZLI-1167 between 354 and 307 K, showing a loss of planarity due to the rotation of the two phenyl groups, as reported by Benzi et al. [12], and the spectra of DPH, dissolved in 2-methyl-tetrahydrofuran and measured at 323, 293, 268, 238, 208, and 188 K, as reported by Catalán et al. [13].

Let us now focus on the solvatochromism of diphenylpolyenes, which, according to Hausser et al. [1,2], depends solely on the polarizability of the dissolving medium. It is already accepted that the polarizability of  $\alpha$ - $\omega$ -diphenylpolyenes increases with the elongation of their flat molecular structure. In addition, Bramley and Fèbre [14] indicate that this increase in polarizability is larger than expected by applying the additivity rule to these compounds.

It should be noted that, upon raising the temperature and the connected out-of-plane rotation of the two phenyl groups of  $\alpha$ - $\omega$ -diphenylpolyene, a decrease in the size of the planar area of the compound would inevitably lead to a significant reduction in its sensitivity to the solvent's polarizability.

At low temperatures, the electronic transition energy of the first UV/Vis absorption band should follow a linear correlation with the corresponding values of the solvent's polarizability. But this linear behavior should change with the increasing rotation of the two phenyl groups, causing a loss of planarity and of the polarizability of the diphenylpolyene.

It is well established by the Mulliken–Rieke rule [15] that the intensity of an electronic transition is independent of temperature, and if the intensity is not kept constant with temperature, it must be concluded that the compound under consideration is changing its molecular structure. We already showed [13,16] that by raising the solution temperature, there comes a point at which the intensity of the first UV/Vis absorption band of the diphenylpolyenes decreases.

The aforementioned behavior can be confirmed using a solution of the corresponding DPP in a solvent that allows us to measure the absorption band of the compound over a wide range of temperatures. For this, a suitable solvent is a 1/1 mixture by volume of decaline and methylcyclohexane, which we will call DEMCH. We have shown that in this solvent, we can measure the absorption of these compounds even at 77 K.

It seems logical to expect that if a diphenylpolyene, above a certain temperature, rotates its phenyl groups, not only will its polarizability decrease, but if not, it will also cease to be nonpolar. Consequently, at high temperatures, its solvatochromism will decrease with the polarizability of the solvent and increase with the dipolarity of the solvent. This would allow us to understand why Ponder and Mathies [17] found that diphenylpolyenes had a non-zero dipole moment in 1,4-dioxane at a temperature of 20.5 °C.

In this work, we will also show the thermochromic behavior of diphenylpolyenes, which are considered non-acidic and non-basic compounds, when dissolving them in a solvent such as Cl<sub>4</sub>C, which only shows polarizability (*SP*) (*SP* = 0.768, *SdP* = 0.00) [18],

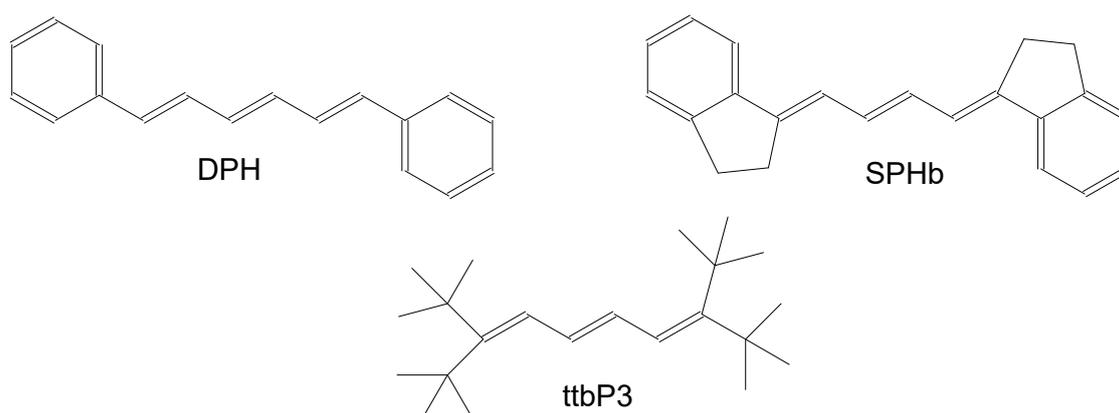
and in  $\text{Cl}_2\text{CH}_2$ , which shows both polarizability ( $SP$ ) and dipolarity ( $SP$ ) ( $SP = 761$  and  $SdP = 0.769$ ) [19].

Consequently, the peaks of the first absorption band of the polyene compound dissolved in  $\text{Cl}_4\text{C}$  should show linear behavior at low temperatures, and when reaching temperatures at which the diphenylpolyene compound rotates its phenyl groups, it should follow another type of linear behavior as the polarizability of the diphenylpolyene compound decreases. That is to say, in the wide range of temperatures studied, the energy of one of its peaks in the first absorption band should show bilinear behavior with temperature [20].

However, when dissolved in  $\text{Cl}_2\text{CH}_2$ , the behavior will be different since, while the polarizability contribution will decrease as the compound rotates its phenyl groups, the contribution due to the dipolarity of the compound will increase, possibly compensating for the previous effect caused by the polarizability of the solvent. Consequently, in these compounds, the energy of their peaks will tend to remain linear with temperature.

All this will be analyzed from the corresponding spectroscopic data obtained with DPH, ttbP3, and DPHb in the solvents indicated above. It is interesting to note that a thorough and critical review of the knowledge of the photophysics of diphenylpolyenes has been recently published [21].

In Scheme 1, the molecular structures of the polyenes used in the present work and available in our laboratory are shown: *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH), *all-trans*-diindanylidene-2-butene (DPHb), and 3,8-di-*tert*-butyl-2,2,9,9-tetramethyl-1,3,5,7-decatriene (ttbP3).



**Scheme 1.** Molecular structures of the polyenes utilized in this work.

## 2. Experimental Section

Spectrophotometric-grade methylcyclohexane and decaline from Sigma-Aldrich (St. Louis, MO, USA) are of 99 and 98% purity. Di- and tetrachloromethane are Uvasol for Spectroscopy solvents from Merck Uvasol (Rahway, NJ, USA) with purities larger than 99.9%.

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 spectrometer. All UV/Vis absorption spectra were recorded on a Cary-5 spectrophotometer at variable temperatures, using suprasil quartz cells with a 1 cm path length that were fixed to the cryostat.

## 3. Results and Discussion

### 3.1. Changes in the Polyene's Molecular Structure with Temperature

In Figures 1–3, we present the first UV/Vis absorption band, respectively, of the three polyenes studied dissolved in decaline/methylcyclohexane (1:1 by volume; a solvent which we will call DEMCHEM), obtained in a temperature range between 93 and 363 K.

Figure 4 represents the areas of the first UV/Vis absorption bands of the three polyenes studied dissolved in DEMCHEM and measured at constant concentrations between 93 and 363 K; all areas are referred to as the area values measured at 93 K.

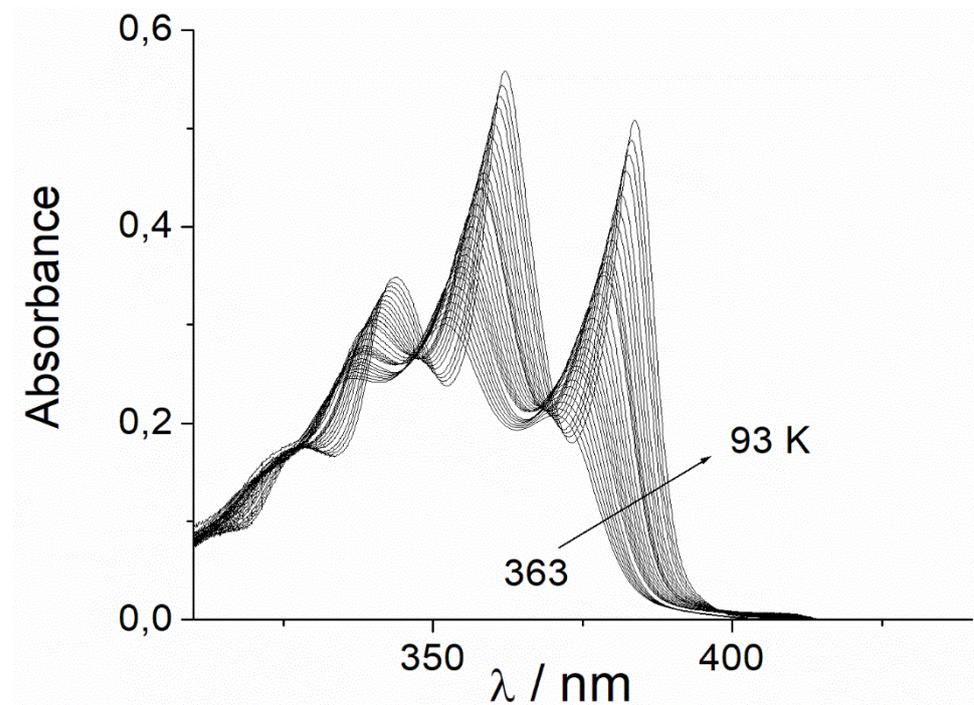


Figure 1. First UV/Vis absorption band of a solution of DPH dissolved in DEMCHEM at temperatures from 363 K to 93 K.

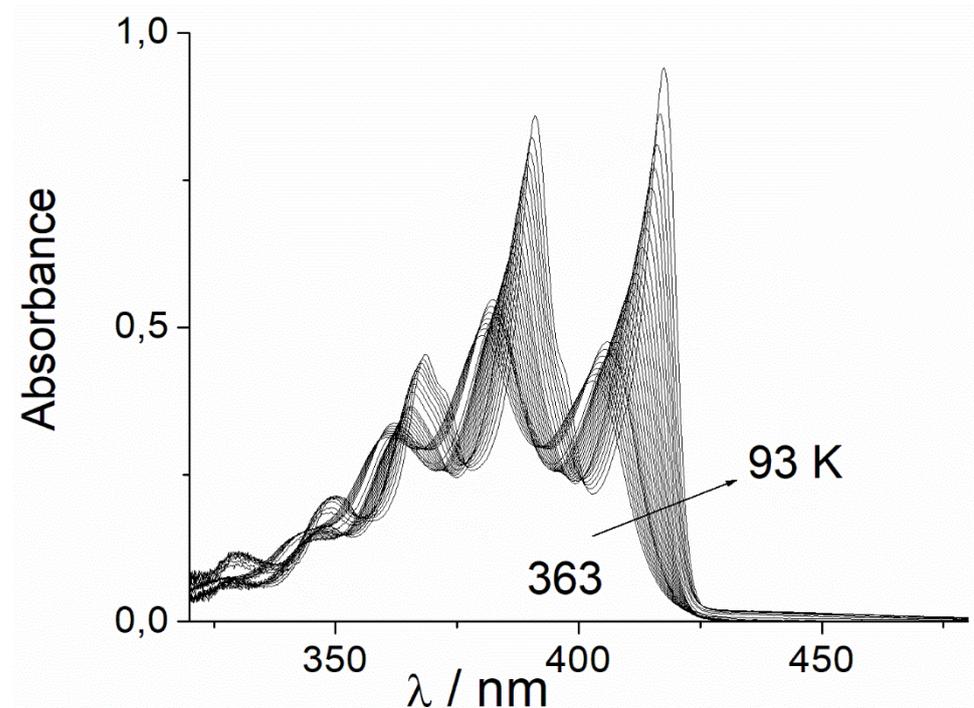
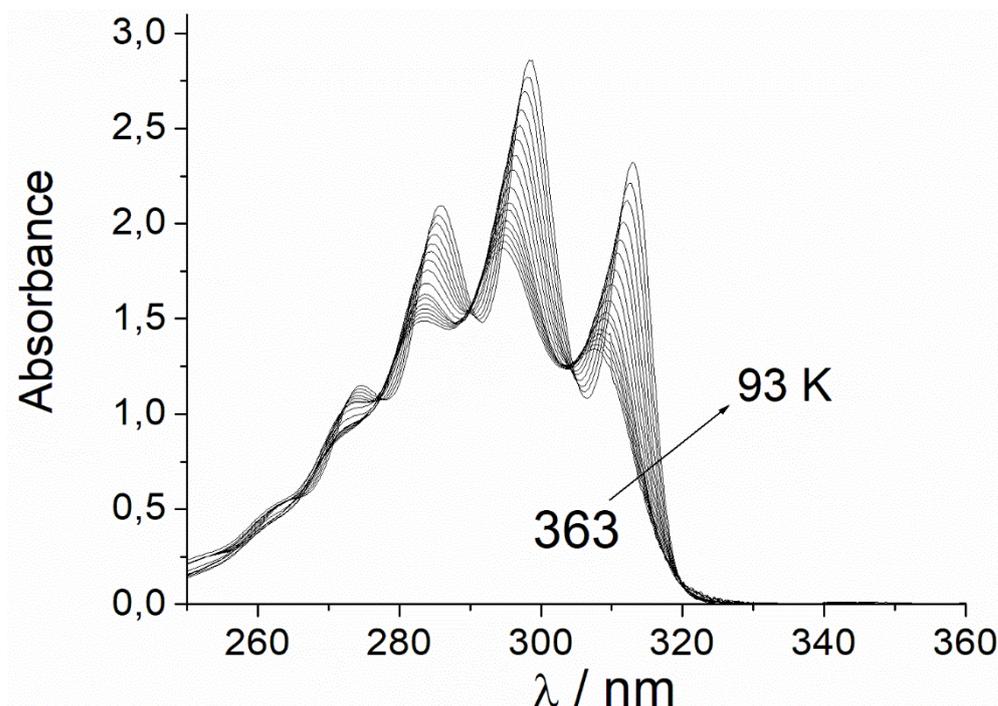


Figure 2. First UV/Vis absorption band of a solution of DPHb dissolved in DEMCHEM at temperatures from 363 K to 93 K.



**Figure 3.** First UV/Vis absorption band of a solution of ttbP3 dissolved in DEMCHEM at temperatures from 363 K to 93 K.

The data for DPH shown in Figure 4a allow for the clear conclusion that (a) DPH studied in a temperature range of 93 to 223 K maintains its molecular structure, and (b) above 223 K, its molecular structure experiences increasing deformation with increasing temperature.

The data for DPHb shown in Figure 4b exhibit that hardly any molecular structure deformation occurs within the temperature range studied. The area of this first absorption band measured between 93 and 363 K maintains its values, referring to the corresponding value at 93 K within  $1 \pm 0.01$ .

This behavior of DPH and DPHb dissolved in DEMCHEM is in incontestable agreement with the supposition that DPH experiences a twisting of its two phenyl groups, whereas this twisting does not occur in DPHb because its two phenyl groups are blocked and cannot rotate (see Scheme 1).

The corresponding areas of the first absorption band of ttbP3 dissolved in DEMCHEM are shown in Figure 4c, clearly confirming the previously mentioned supposition.

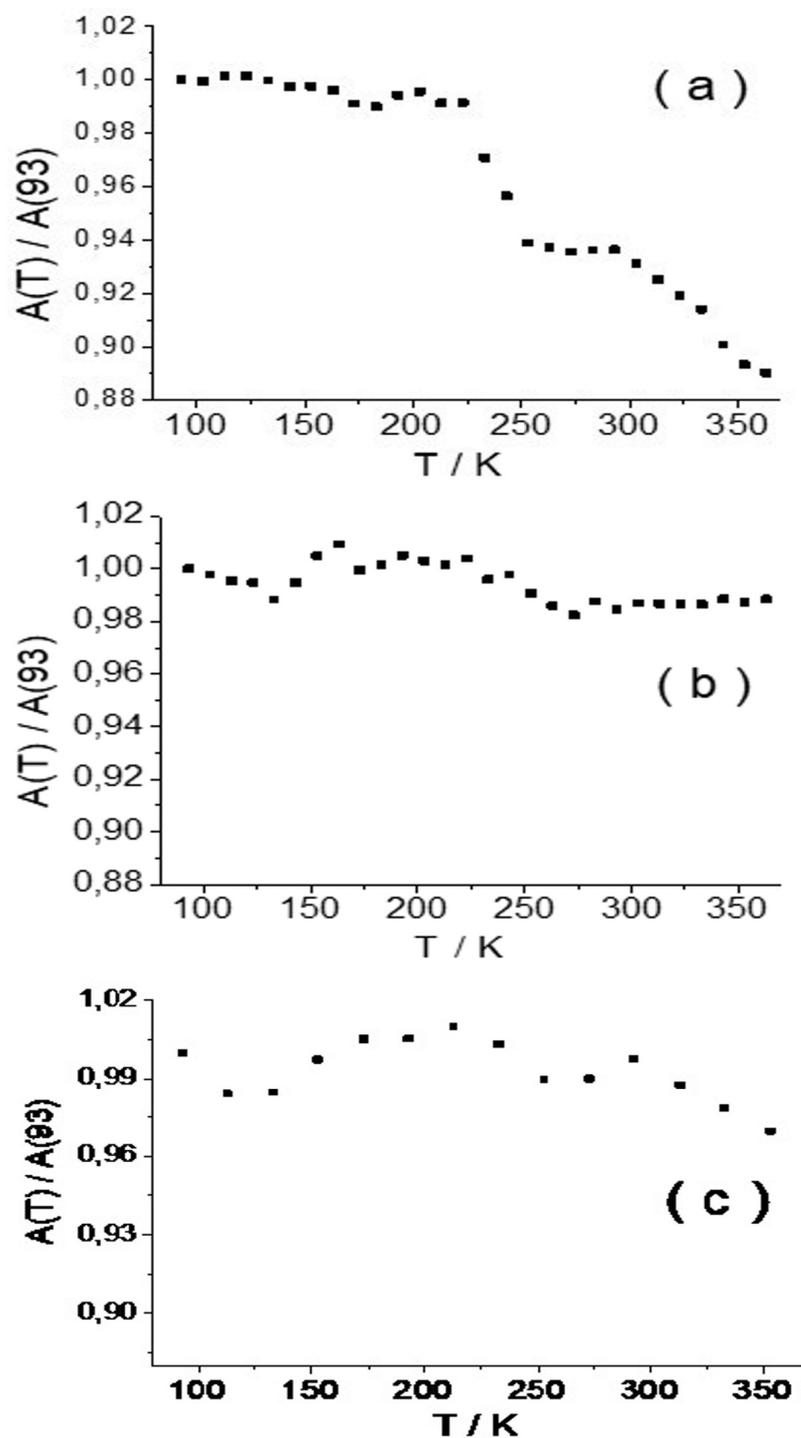
The results achieved in ttbP3 indicate that in this triene, the small temperature-induced deformations, which may be due to small changes in the *tert*-butyl groups, will barely be translated into small changes in the intensity of its first absorption band. The measured values of the corresponding band areas, referring to the corresponding value at 93 K, are within  $1 \pm 0.02$  throughout the whole temperature range studied.

### 3.2. Temperature-Dependent Solvatochromic Changes in Polyenes

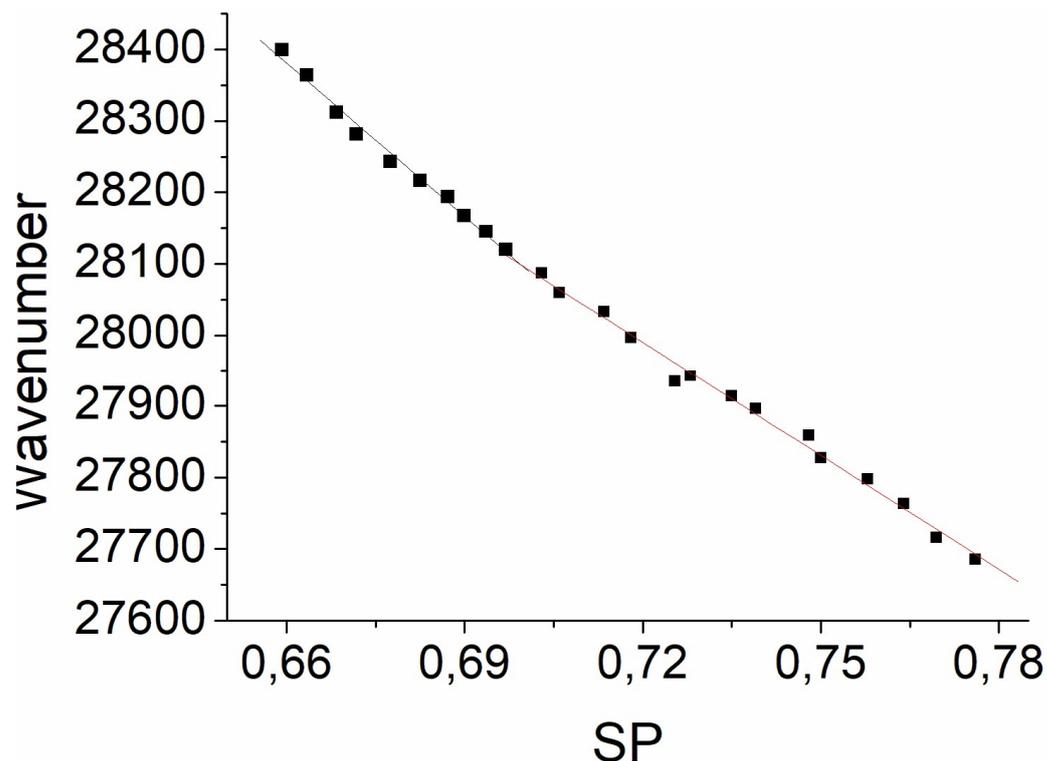
As was previously shown (see Figure 4a), by increasing the temperature of the DPH solution in DEMCHEM above 233 K, as shown in Figure 4a, the compound begins to rotate its phenyl groups, and the rotation of these groups will increase with an increase in the temperature of the solution. As a consequence of this rotational movement, the coplanar surface of the DPH will begin to decrease, and therefore, its polarizability will decrease below an *SP* of 0.71.

Figure 5 presents the correlation between the temperature-dependent energy of the 0–0 component of the first UV/Vis absorption band of DPH dissolved in DEMCHEM and the corresponding values of the empirically determined solvent polarizability parameter *SP* of DEMCHEM. The correlation clearly shows bilinear behavior with respect to *SP*: for *SP* values

larger than 0.7, a correlation line corresponding to  $\bar{v}_{\text{abs}} = (-5300 \pm 135) SP + (31,806 \pm 99)$  with  $n = 14$  and  $r = 0.996$  can be seen, and for  $SP$  values smaller than 0.7, a correlation line of  $\bar{v}_{\text{abs}} = (-5671 \pm 89) SP + (32,081 \pm 63)$  with  $n = 10$  and  $r = 0.997$  is found.

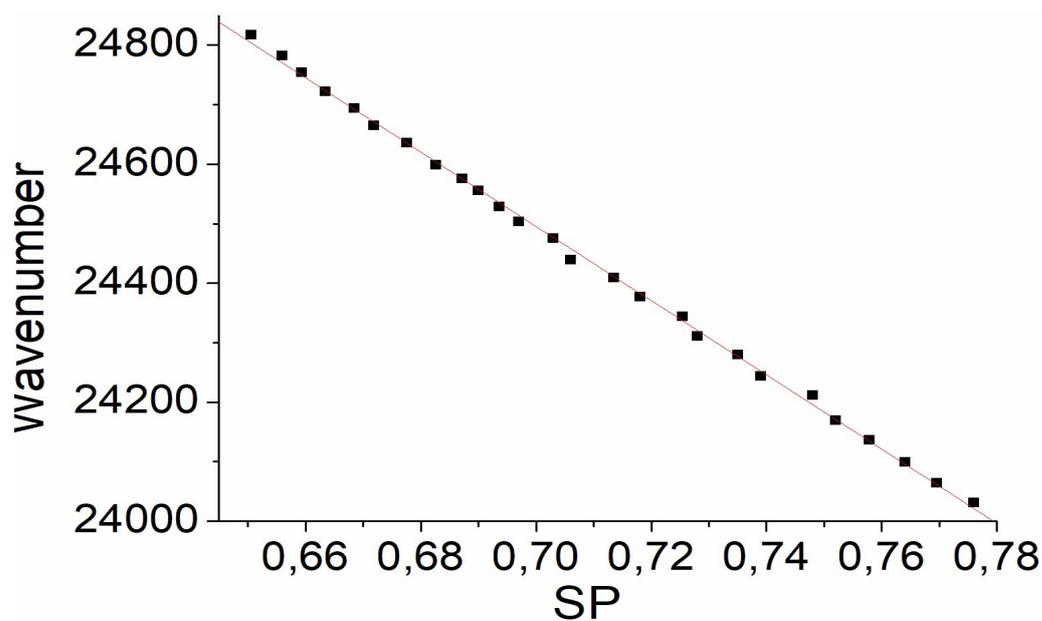


**Figure 4.** Temperature-dependent areas of the first UV/Vis absorption band of (a) DPH, (b) DPHb, and (c) ttbP3 dissolved in DEMCHEM at a constant concentration divided by the respective area measured at 93 K.



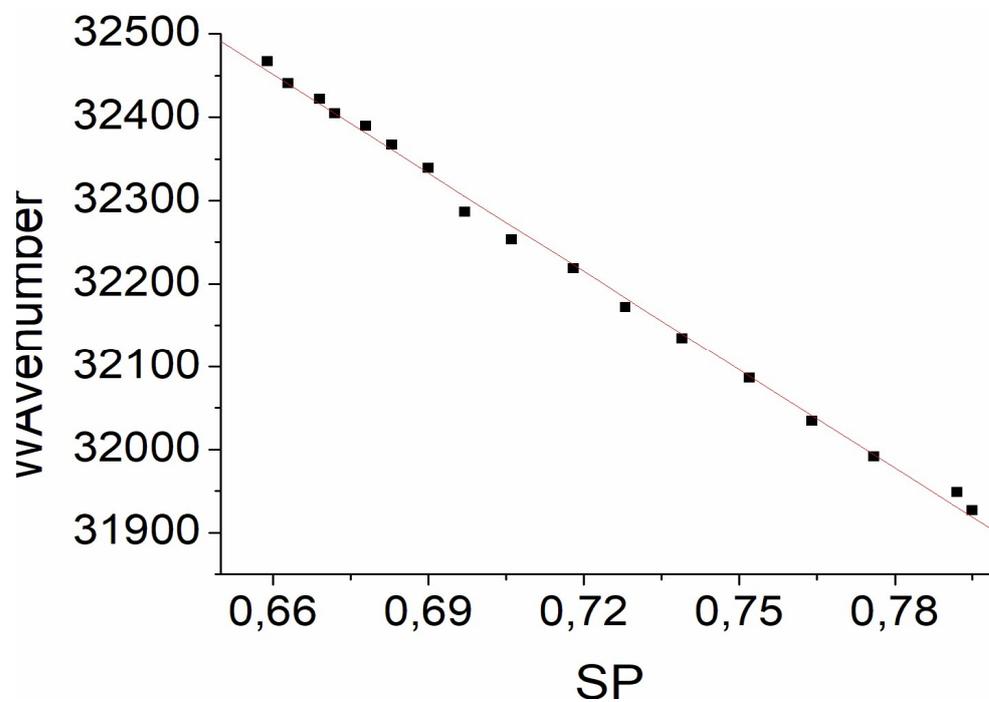
**Figure 5.** Wavenumber (in  $\text{cm}^{-1}$ ) of the 0–0 component of DPH in DEMCHEM versus the polarizability ( $SP$ ) of the solvent.

Figure 6 shows the correlation between the temperature-dependent energy of the 0–0 component of the first UV/Vis absorption band of DPHb dissolved in DEMCHEM and the corresponding  $SP$  values. The results show a clear linear correlation line for the entire  $SP$  range, which can be adjusted by  $\bar{\nu}_{\text{abs}} = (-6229 \pm 43) SP + (28,856 \pm 30)$ , with  $n = 26$  and  $r = 0.999$ .



**Figure 6.** Wavenumber (in  $\text{cm}^{-1}$ ) of the 0–0 component of DPHb in DEMCHEM versus the polarizability ( $SP$ ) of the solvent.

Figure 7 presents the correlation between the temperature-dependent energy of the 0–0 component of the first UV/Vis absorption band of ttbP3 in DEMCHEM and the corresponding  $SP$  values. Again, a clear linear correlation line for the entire  $SP$  range is found, which can be described by the correlation equation  $\bar{\nu}_{\text{abs}} = (-3946 \pm 56) SP + (35,055 \pm 40)$ , with  $n = 17$  and  $r = 0.998$ .

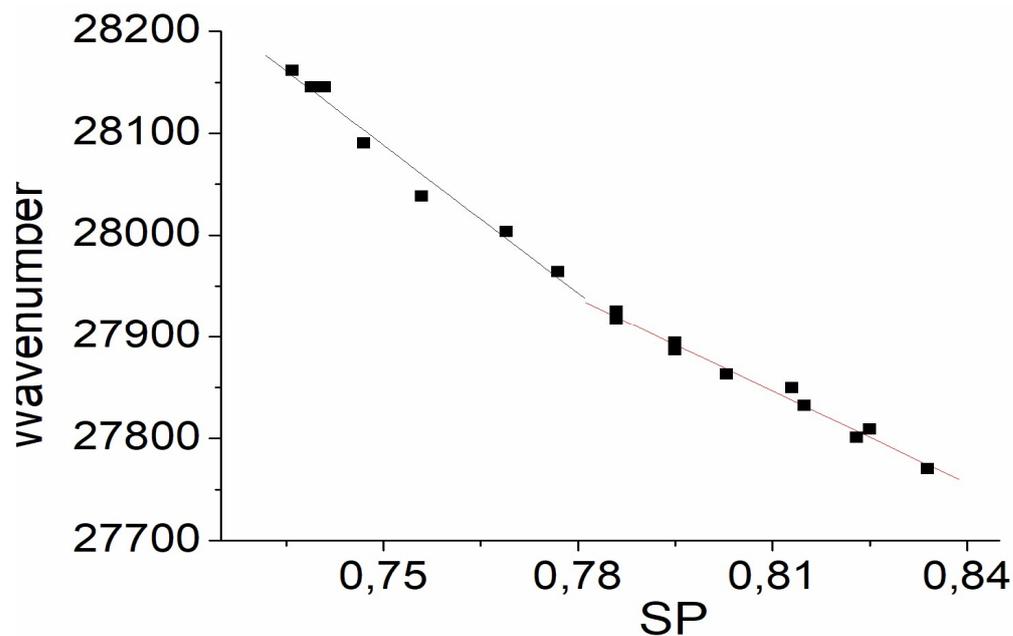


**Figure 7.** Wavenumber (in  $\text{cm}^{-1}$ ) of the 0–0 component of ttbP3 in DEMCHEM versus the polarizability ( $SP$ ) of the solvent.

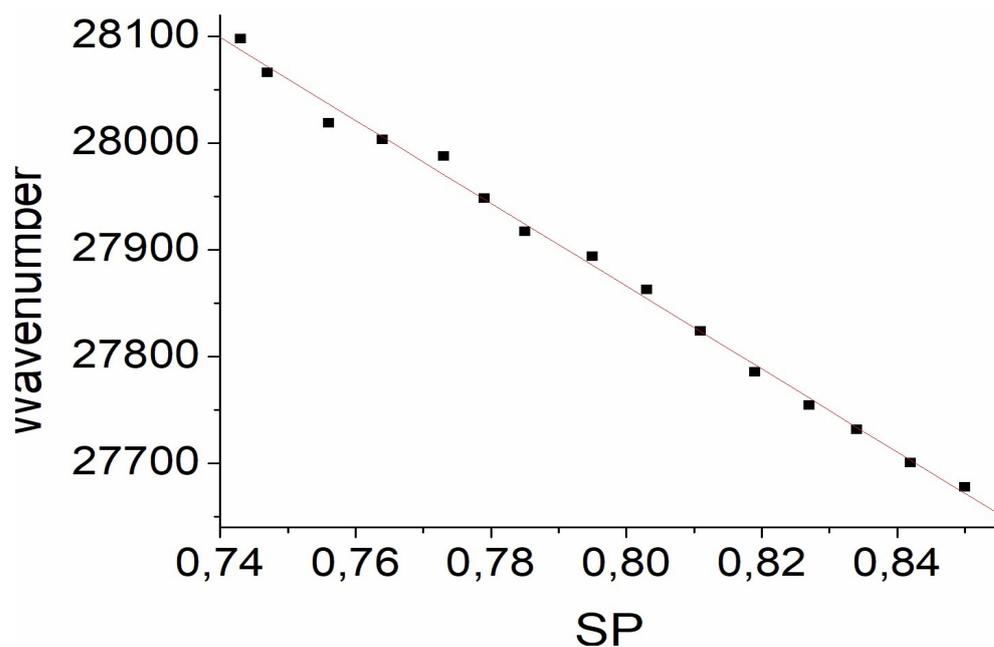
Figure 8 describes the correlation between the temperature-dependent energy of the 0–0 component of the first UV/Vis absorption band of DPH dissolved in  $\text{Cl}_4\text{C}$  and the corresponding  $SP$  values. A clearly bilinear behavior is shown for  $SP$  values larger than 0.78, with a corresponding correlation of  $\bar{\nu}_{\text{abs}} = (-3023 \pm 127) SP + (30,295 \pm 103)$  with  $n = 11$  and  $r = 0.992$ , and for  $SP$  values smaller than 0.78, the fitting is expressed by  $\bar{\nu}_{\text{abs}} = (-4848 \pm 352) SP + (31,724 \pm 265)$  with  $n = 7$  and  $r = 0.987$ .

Finally, Figure 6 shows the correlation between the temperature-dependent energy of the 0–0 component of the first UV/Vis absorption band of DPH dissolved in  $\text{Cl}_2\text{CH}_2$  and the corresponding  $SP$  values. A clear linear behavior is evident, in agreement with the correlation equation  $\bar{\nu}_{\text{abs}} = (-3882 \pm 69) SP + (30,971 \pm 56)$ , with  $n = 15$  and  $r = 0.998$ .

The results given in Figures 8 and 9 do not only highlight the particular solvatochromic influence of these two solvents, apolar  $\text{Cl}_4\text{C}$  and dipolar  $\text{Cl}_2\text{CH}_2$ , but they are also in agreement with the accepted model for the solvatochromism of diphenylpolyenes. As already mentioned in the Introduction, it is commonly accepted that diphenylpolyenes are polarizable planar compounds which are non-polar, non-acidic, and non-basic.  $\text{Cl}_4\text{C}$  and  $\text{Cl}_2\text{CH}_2$  are solvents with high polarizability and have, with  $SP = 0.768$  and  $0.761$ , nearly the same polarizability  $SP$  values. However, they differ in their other empirical solvatochromic parameters: for  $\text{Cl}_4\text{C}$ , the solvent dipolarity parameter  $SdP = 0.000$ , the solvent basicity parameter  $SB = 0.044$ , and the solvent acidity parameter  $SA = 0.000$  [19], whereas for  $\text{Cl}_2\text{CH}_2$ , the corresponding solvent parameters are  $SdP = 0.769$ ,  $SB = 0.0178$ , and  $SA = 0.040$  [19].



**Figure 8.** Wavenumber (in  $\text{cm}^{-1}$ ) of the 0-0 component of DPH in  $\text{CL}_4\text{C}$  versus the polarizability ( $SP$ ) of the solvent.



**Figure 9.** Wavenumber (in  $\text{cm}^{-1}$ ) of the 0-0 component of DPH in  $\text{CL}_2\text{CH}_2$  versus the polarizability ( $SP$ ) of the solvent.

Consequently, DPH sees its bilinear behavior revealed when dissolved in  $\text{CL}_4\text{C}$  due to its high polarizability (see Figure 8), while in  $\text{CL}_2\text{CH}_2$ , the destabilization created by its polarizability is practically compensated for by the stabilization generated by its dipolarity, thus explaining the linear correlation behavior shown in Figure 9.

#### 4. Conclusions

In this work, an adequate analysis of the solvatochromism of three carefully selected polyene compounds, measured in well-selected suitable solvents, was carried out, allowing for a better understanding of their photophysical behavior.

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