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On the Photophysics of Polyenes. 1. Bathochromic Shifts in Their 1Ag → 1Bu Electronic Transitions Caused by the Polarizability of the Medium

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As shown in this study, the solvatochromic behavior of polyenes depends exclusively on the polarizability of the medium and, even more interestingly, their solvatochromism increases markedly with increasing length of the polyene chain. By virtue of the electronic nature of the interaction of polyenes with the medium, their solvatochromic response to a polarizability change is instantaneous, making these compounds extremely effective polarizability probes for molecular environments. The extreme sensitivity of polyenes to the polarizability of their environment is consistent with the fact that changes in molecular architecture such as those occurring in photosynthetic systems can give rise to polarizability gradients resulting in red shifts in the 1Ag → 1Bu transition, thereby opening up new channels directing the energy transfer involved to energy trapping sites in such systems.

Introduction

Unraveling the photophysical behavior of such biochemically significant structures such as the visual pigments[1] and the carotinoid antennae of photophynthesis[2,3] inevitably entails elucidating the photophysics of their polyenic chromophores. The highly dipole-allowed 1Ag → 1Bu transition in such chromophores plays a central role in the detection of visible light and the transfer of the resulting electronic excitation in these systems. As shown long ago by Hausser et al.,[4] the most salient photophysical feature of polyenes is their strong first absorption band, the envelope of which exhibits a sharp 0−0 component that can thus be precisely measured. Also, the energy of this absorption band is extremely sensitive to the polarizability of the medium;[5–10] even more interesting, however, in relation to the solvatochromic behavior of this electronic transition in polyenes is the fact that both the position and structure of the band are absolutely independent of the polarity and acid−base properties of the medium.[9] In summary, the behavior of the 1Ag → 1Bu transition in these compounds has facilitated the establishment of an empirical polarizability scale for molecular environments[9] and also the theory of color in organic chemistry.[11]

The polarizability features of polyenes have aroused interest among researchers for a long time. Thus, in 1952, Davies[12] established a theoretical relationship between the polarizability of an *all-trans*-polyene chain containing 1−20 double bonds to the chain length cubed (i.e., he found the polarizability of *all-trans* -polyenes to increase more markedly than it would in a simply additive manner with increase in chain length). In 1960, Bramley and Le Fébre[13] determined the polarizability of α,*ω*-diphenylpolyenes with 1−4 double bonds and found it to grow to a greater-than-additive extent. In 2003, one of the authors[14] showed in theoretical terms that this polarizability trend is shared by α,*ω*-diphenylpolyenes with 1−7 double bonds in the chain.

In 1983, Ponder and Mathies[15] examined changes in the absorption spectra for α,*ω*-diphenylpolyenes with 2−5 double bonds induced by the presence of an electric field and found their polarizability in the ground and first excited electronic states to increase with increasing chain length, the increase growing with the size of the chain to a greater extent in the excited state than in the ground state. The increased polarizability observed in various electronically excited α,*ω*-diphenylpolyenes (viz. DPB, DPH, DPO and DPD) by Ponder and Mathies[15] was confirmed by theoretical computations at the TDDFT level performed by Grozema et al.[16] and Ye et al.[17]

Because unsubstituted and symmetrically substituted all-*trans*-polyenes are centrosymmetric structures, their electronic states are nonpolar, so any transitions between them will be exclusively influenced by dispersive interactions of the states involved with their environment. As a result, their absorption bands retain their spectral envelope and only change in terms of energy, in a way depending on the balance of the interaction of the polarizability of the electronic states concerned with that of the surrounding molecular environment. Because the polarizability in the 1Bu excited electronic state is higher than that in the ground electronic state, 1Ag, the 1Ag → 1Bu transition will undergo a red shift as the polarizability of the medium increases.

Therefore, the solvatochromism of a polyene must be proportional to the polarizability difference between the states involved in the electronic transition, which, based on the results of Ponder and Mathies,[15] should increase with increasing length of the polyene chain. However, reported results have led to a somewhat confusing situation. Thus, in 1977, Sklar et al.[6] studied the solvatochromic behavior of α,*ω*-diphenylpolyenes with 1, 2, 3, 4, 5, 6 and 8 double bonds in the polyene chain and obtained the following solvatochromic slopes: -6700 ± 300,-9700 ± 500, -10600 ± 500, -10900 ± 500, -9000 ± 900, -9300 ± 700 and -9700 ± 1200 cm^{-1}. Thus, the slope increases with the increasing number of double bonds up to four, but then it seems to keep constant for the molecules containing 5, 6 and 8 doubles bonds in the polyene structure. In 1978, Gavin et al.[5] studied the solvatochromism of octatetraene in ten different solvents (methanol, pentane, hexane, heptane, isooctane, hexadecane, chloroform, tetrachloromethane, benzene and *o*-dichlorobenzene) and found a good linear relationship between the 0−0 component of the 1Ag → 1Bu

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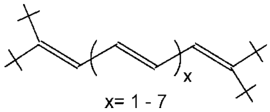
SCHEME 1



transition in octatetraene and the polarizability of the solvent, with a slope of $-10\,909 \pm 1000$ cm^{-1}. In 1980, D'Amico et al.[7] conducted a similar study on decapentaene and decahexaene in five different solvents (methanol, hexane, isooctane, chloroform and benzene) and obtained a slope of -9640 ± 1290 cm^{-1} for the former polyene and -9260 ± 1140 cm^{-1} for the latter (i.e., the slope seemingly decreased with increasing chain length if compared with the previous result for octatetraene). In 1985, Snyder et al.[8] studied tetradecaheptaene in four different solvents (*n*-pentane, *n*-hexane, *n*-hexadecane and benzene) and obtained a slope of -12110 ± 600 cm^{-1}, which was thus substantially greater than the previous ones. In summary, available results do not allow one to unambiguously state that the solvatochromism of polyenes increases monotonically with increasing chain length as one would expect.

In this paper, we revisit the solvatochromism of polyenes by studying ttbPn (3,8-di-*tert*-butyl-2,2,9,9-tetramethyl-3,5,7-decatriene, 3,10-di-*tert*-butyl-2,2,11,11-tetramethyl-3,5,7,9-dodecatetraene, 3,12-di-*tert*-butyl-2,2,13,13-tetramethyl-3,5,7,9,11-tetradecapentaene, 3,14-di-*tert*-butyl-2,2,15,15-tetramethyl-3,5,7,9,11,13-hexadecahexaene, 3,16-di-*tert*-butyl-2,2,17,17-tetramethyl-3,5,7,9,11,13,15-octadecaheptaene, 3,18-di-*tert*-butyl-2,2,19,19-tetramethyl-3,5,7,9,11,13,17-icosaoctaene, 3,20-di-*tert*-butyl-2,2,21,21-tetramethyl-3,5,7,9,11,13,15,17,19-docosanonaene) with $n = 3-9$ double bonds (Scheme 1) to demonstrate that the spectral envelope of the first absorption band for these compounds is insensitive to the natural order of the solvent and that shifts in this band are consistent with changes in the polarizability of the medium. Also, we discuss a potential relationship between solvatochromic shifts in these compounds and the length of their polyene chain.

Experimental Section

The polyenes ttbPn with $n = 3-9$ were prepared by McMurry coupling of the corresponding unsaturated aldehydes (uneven number of double bonds) and by Witting olefination of appropriate aldehydes with the respective ylides (even number of double bonds) and chromatographed and recrystallized several times prior to use. On the basis of spectroscopic and chromatographic evidence, the products thus obtained contained no impurities. The synthesis and spectroscopic properties of these compounds, and the preparation of polyenes with up to 13 consecutive double bonds, will be described in a future paper.

UV−visible spectra were recorded on a Cary-5 spectrophotometer using Suprasil quartz cells of 1 cm light path for dissolved samples at 293 K and 10 cm for gaseous samples at 353 K. Both temperatures were controlled to within ±0.1 °C by means of a Fisons Haake D8 GH thermostat. The solvents used, all in a high purity, were carefully chosen to span a wide range of polarizability (SP)[9] and included *n*-hexane (nHex), *n*-heptane (nHep), tetrachloromethane (CCl$_4$), chloroform (CHCl$_3$), 2-methylbutane (2MB), methanol (MeOH), benzene (ph) and dimethyl sulfoxide (DMSO), all Merck Uvasol-grade, in addition to perfluoro-*n*-hexane (pFnH), 1,2-dichlorobenzene (1,2Clph) and squalane (SQ), all Aldrich and over 99% pure. Squalane was passed through an SiO$_2$ column prior to use. All solvents were previously checked to contain no substances potentially interfering with the spectra for the ttbPn compounds.

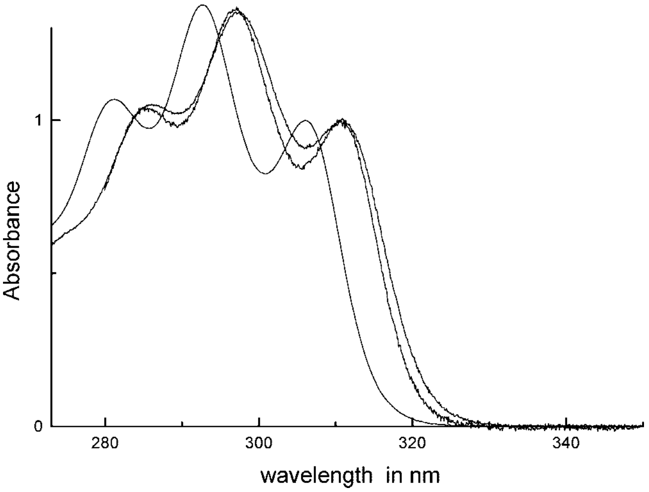


Figure 1. First electronic transition of ttbP3 in chloroform (solid line), benzene (dash line) and 2-methylbutane (dot line), all at 293 K.

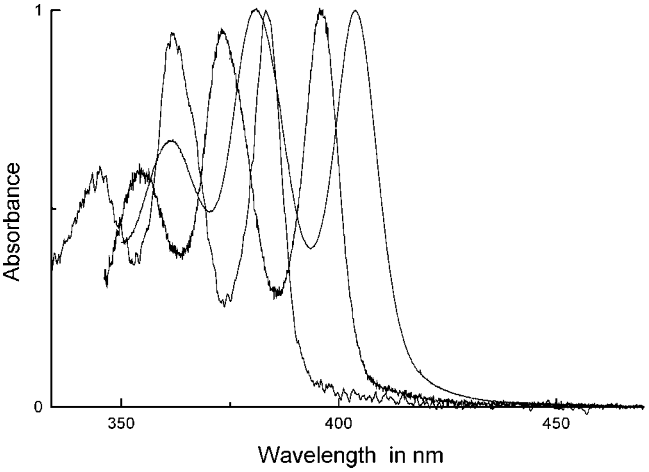


Figure 2. First electronic transition of ttbP6 in terachloromethane (solid line), *n*-hexane (dash line) and *n*-perfluorohexane (dot line), all at 293 K .

Results and Discussion

We shall first confirm that the studied polyenes are only affected by the polarizability of the medium, so they retain the envelope of their first absorption band from solvent to solvent, and then examine the solvatochromic behavior of these polyenes containing 3−9 double bonds to ascertain whether, as expected, it depends on the length of the chain.

Spectral Envelope of the 1Ag → 1Bu Transition in ttbPn. Figures 1–3 show the spectral envelopes for the 1Ag → 1Bu transition of ttbP3 in 2MB, Cl$_3$CH and ph; ttbP6 in nHex, CCl$_4$ and pFHex; and ttbP9 in MeOH, SQ and 1,2Clph; all as normalized with respect to the 0−0 component. As can be seen, the envelope for each polyene changes little with the nature of the solvent. Figure 1 in ref 9 shows the spectral envelopes for the 1Ag → 1Bu transition of ttbP9 in perfluorohexane, carbon disulfide, hexafluorobenzene, aniline, 2MB, DMSO, acetic acid and tetramethylguanidine. Taking into account that the envelope for ttbP9 is virtually identical in solvents despite the high basicity of tetramethylguanidine, high polarity of DMSO or high acidity of acetic acid, for example, one can conclude that the polyenes respond to perturbations of their polarizability but are completely insensitive to the dipolarity, acidity and basicity of the medium.

Solvatochromism of ttbPn. The facts that polarizability is significantly higher in the 1Bu state than in the ground state

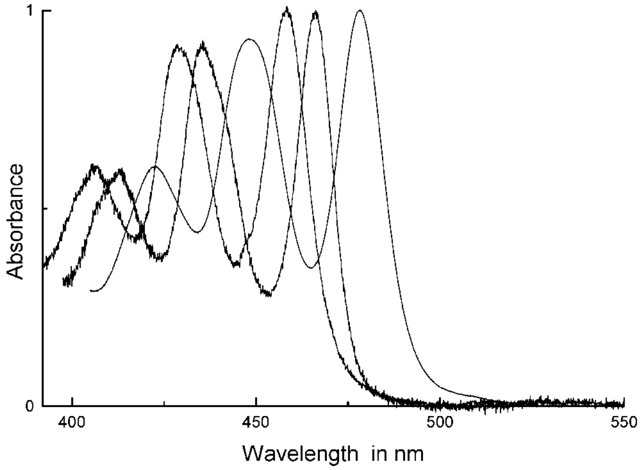


Figure 3. First electronic transition of ttbP9 in 1,2-dichlorobenzene (solid line), squalane (dash line) and methanol (dot line), all at 293 K.

TABLE 1: Wavelengths for the 0−0 Component Corresponding to the Transition 1Ag → 1Bu of the ttbPn in Eleven Solvents at 20 C

solvent	ttbP3	ttbP4	ttbP5	ttbP6	ttbP7	ttbP8	ttbP9
pFHex	301.0	332.4	359.6	383.4	404.9	422.1	439.3
2MB	306.0	339.2	367.4	394.3	417.0	436.4	456.1
MeOH	306.0	339.7	369.2	395.6	418.8	437.5	458.1
n-Hex	306.3	340.0	369.4	395.6	419.4	437.9	458.8
n-Hept	306.7	340.5	370.1	396.6	419.9	439.1	460.1
SQ	308.1	342.4	373.1	399.9	424.8	444.8	466.1
Cl_4C	310.6	345.2	376.4	403.9	428.2	448.4	470.2
Cl_3CH	310.2	345.9	376.5	403.9	429.3	449.7	471.4
Ph	310.9	345.5	376.8	404.6	429.5	449.8	472.2
DMSO	311.6	346.3	377.2	406.0	431.2	452.0	475.9
12Clph	312.5	348.0	379.7	408.7	434.2	455.2	478.3

(1Ag), i.e., that $\Delta\alpha > 0$, and that the difference between the two increases with increasing length of the polyene chain,[10,14–16] are quite consistent with the first absorption band for ttbPn compounds undergoing a red shift as the polarizability of the medium increases, but not with the above-described behavior of unsubstituted *all-trans*-polyenes[5,7,8] and α,ω-diphenylpolyenes.[6] To our minds, this inconsistency has no easy explanation. For this reason, in this work we examined the solvatochromic behavior of a wide range of *all-trans*-ttbPn compounds in 11 solvents spanning an also wide range of polarizability, as formerly done with octatetraene by Gavin et al.[5] The solvents used to this end were as follows, arranged according to polarizability: pFHex (SP = 0.3388), 2MB (SP = 0.5813), MeOH (0.6079), *n*-Hex (SP = 0.6164), *n*-Hept (SP = 0.6354), SQ (SP = 0.7139), Cl_4C (SP = 0.7677), Cl_3CH (SP= 0.7833), ph (SP = 0.7929), DMSO (SP = 0.8295) and 12Clph (SP = 0.8686). The wavelengths for the 0−0 components of the ttbPn molecules in eleven solvents are gathered in Table 1.

Figure 4 illustrates the solvatochromic behavior of the studied compounds by a plot of the frequency of the 0−0 component for the 1Ag → 1Bu transition against the solvent polarizability expressed in terms of SP.[9] As expected, lengthening the polyene chain (i.e., expanding the molecular box) decreases the energy of the transition; as a result, the distance between the curves describing the solvatochromism of consecutive polyenes decreases with increasing chain length.

As can be seen from Table 2, all curves were fitted with coefficients better than 0.99 and small standard deviations, less than 45 cm^{-1}. It should be noted that the zero polarizability value in each fitted curve would correspond to the 0−0 component of the transition as measured in the absence of solvent (i.e., in the gas phase). Interestingly, the solvatochromically calculated 0−0 component for ttbP3 was 34 072 ± 66 cm^{-1}, which is quite consistent with the measured value in the gas phase at 353 K (see Figure 5): 34100 cm^{-1}. The corresponding value for ttbP4, 30976 ± 51 cm^{-1}, is also consistent with that in the gas phase at 353 K: 31104 cm^{-1}.[18]

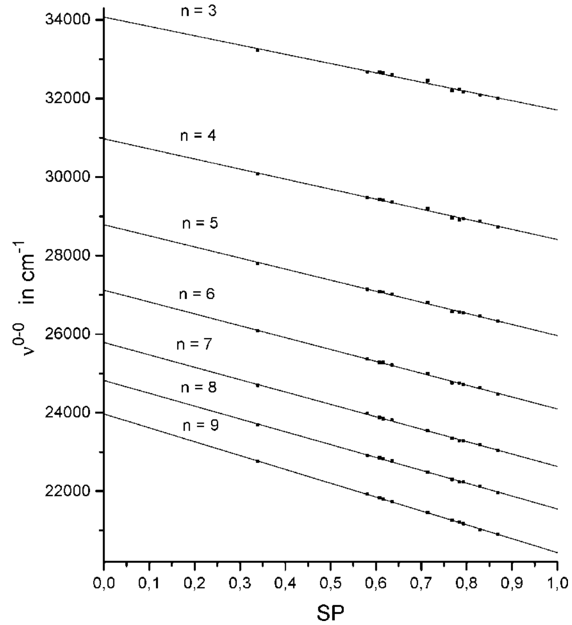


Figure 4. Solvatochromic behavior of ttbPn with $n = 3-9$ as established by plotting the 0−0 component for their 1Ag → 1Bu transition against the empirical polarizability[9] of the following solvents: pFHex (SP = 0.3388), 2MB (SP = 0.5813), MeOH (SP = 0.6079), *n*-Hex (SP = 0.6164), *n*-Hept (SP = 0.6354), SQ (SP = 0.7139), Cl_4C (SP = 0.7677), Cl_3CH (SP = 0.7833), ph (SP = 0.7929), DMSO (SP = 0.8295) and 12Clph (SP = 0.8686).

TABLE 2: Statistical Correlations for the v^{0-0} of the Electronic Transition 1Ag → 1Bu vs the Empirical Solvent Polarizability (SP)[9] or vs the Polarizability Equation $(n^2 - 1)/(n^2 + 2)(\alpha)$ for the Eleven Solvents Employed

compound	polarizability	slope (cm^{-1})	intercept (cm^{-1})	r	sd (cm^{-1})
ttbP3	SP	−2364 ± 94	34072 ± 66	0.993	45
	α	−7553 ± 654	34341 ± 166	0.968	95
ttbP4	SP	−2564 ± 73	30976 ± 51	0.996	35
	α	−8106 ± 781	31245 ± 190	0.961	113
ttbP5	SP	−2822 ± 55	28787 ± 39	0.998	26
	α	−8902 ± 914	29071 ± 231	0.956	132
ttbP6	SP	−3023 ± 53	27122 ± 37	0.999	25
	α	−9595 ± 844	27449 ± 214	0.967	123
ttbP7	SP	−3155 ± 41	25790 ± 28	0.999	20
	α	−9963 ± 1000	26110 ± 253	0.957	145
ttbP8	SP	−3279 ± 44	24824 ± 31	0.999	21
	α	−10395 ± 884	25182 ± 224	0.969	129
ttbP9	SP	−3527 ± 25	23968 ± 17	0.999	12
	α	−11110 ± 1006	24344 ± 255	0.965	146

The consistency of the solvatochromically predicted 0−0 components for the 1Ag ± 1Bu electronic transition with available measured data in the gas phase (see Table 2) allows one to adopt these solvatochromic predictions for longer ttbPn compounds, where obtaining a measurable sample by raising the temperature in the gas phase is impossible. Determining the corresponding 0−0 components enables a deeper analysis of these compounds in light of the one-dimensional box model. As shown by available XRD data,[19] *all-trans*-ttbP compounds are elongated molecules resembling a one-dimensional box; this can facilitate rationalization of their spectral behavior in terms

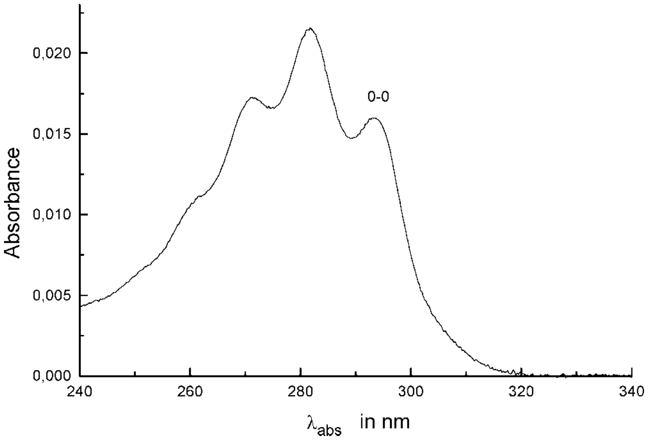


Figure 5. 1Ag → 1Bu electronic transition for ttbP3 in the gas phase at 353 K.

of this quantum model. The treatment involved implicitly considers all π electrons in the compound and assumes the box length to coincide with the distance between the terminal carbon in the polyene chain and be $L = r(C_1 - C'_1)$ as inferred from X-ray data.[19]

The energy levels available within a one-dimensional box can be quantified as

$$E = h^2n^2/8mL^2 \tag{1}$$

where h is the Planck constant, m is the mass of the particle held in the box, L is the box length and $\boldsymbol{n}$ is an integer (1, 2, 3, ...).

The first electronic transition of interest to this study on ttbPn is 1Ag → 1Bu, known to involve an electronic transition between the HOMO and LUMO (i.e., between levels n and $n + 1$ in the box, n coinciding with the number of double bonds in the compound). Let us evaluate the energy of this $n \rightarrow n + 1$ transition from the energy levels available for a particle in a box:

$$\Delta E_{(n\rightarrow n+1)} = (h^2/8m)(2n + 1)/L^2 \tag{2}$$

which can be rewritten as

$$\lambda_{(n\rightarrow n+1)} = (8cm/h)[L^2/(2n + 1)] \tag{3}$$

Based on eq 3, the wavelength of the electronic transition must change linearly with $L^2/(2n + 1)$ in these compounds. Figure 6 illustrates the excellent correlation between the transition wavelength as evaluated solvatochromically (see Table 2) and the term $L^2/(2n + 1)$ in all studied compounds.

Worth special note is the fact that the slopes of the fitted solvatochromic curves increase significantly with increasing chain length (see Table 2 and Figure 7). As can clearly be seen from Figure 7, the solvatochromism of the studied polyenes increases linearly with the increasing length of their chain, as expected.

Essentially identical conclusions can be drawn by expressing the solvent polarizability in terms of $(n^2 - 1)/(n^2 + 2)$ instead of the empirical SP values used. Table 2 shows the results for the corresponding fitted curves. The sole difference from the previous ones is that the fitting was somewhat poorer than with SP. Thus, r was in the region of 0.96 and the errors significantly greater. On the other hand, the predictions for the gas phase were quite good but subject to higher uncertainty for ttbP3 (34341 ± 166 cm^{-1}) and ttbP4 (31245 ± 190 cm^{-1}). The solvatochromic slopes also increased with increasing chain length (see Table 2). Such slopes were considerably smaller than those for unsubstituted polyenes. At this point, one may wonder whether the sensitivity of the different polyenes to the solvent polarizability is shared by the polyene structure, in which case, the slopes of the corresponding v versus polarizability plots should be identical for all polyene derivatives; otherwise, they would reflect the intrinsic variation of polarizability with electronic excitation, $\Delta\alpha$,[10] and be proportional to $\Delta\alpha$ for the polyene type. One further question is whether the solvatochromic slope may also be influenced by some interaction between the substituent and solvent.

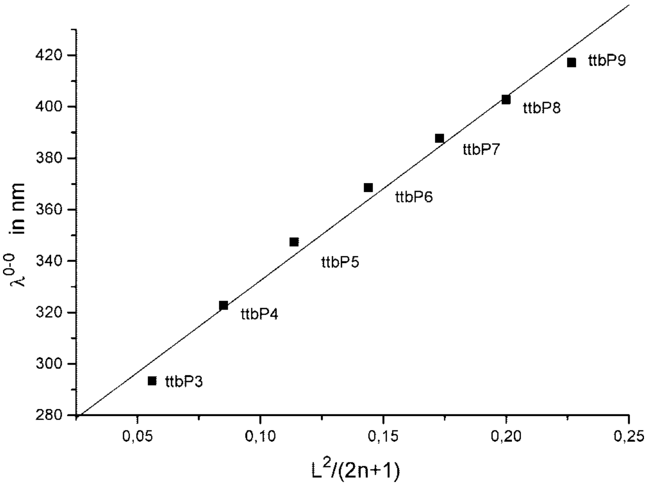


Figure 6. Variation of the wavelength of the 0−0 component for the ttbP compounds studied with the term $L^2/(2n + 1)$, which is assigned to the one-dimensional model for a particle in a potential energy box (see text).

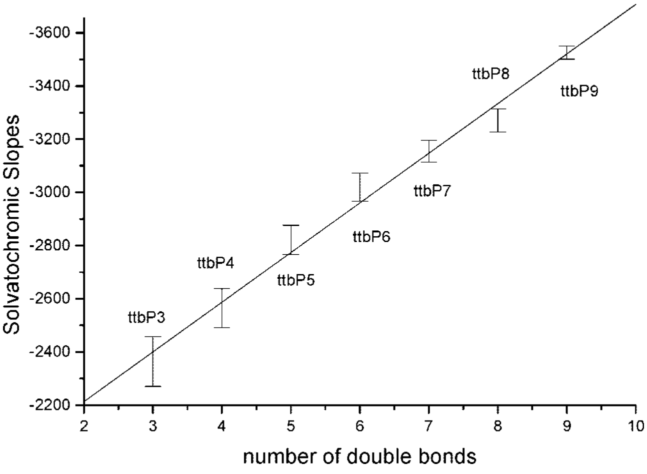


Figure 7. Variation of the solvatochromic sensitivity of ttbPn (see Table 2) with the length of the polyene chain.

By way of example, let us focus on the solvatochromic behavior of octatetraenes. In 1977, Sklar et al.[6] found the absorption maximum for the 1Ag → 1Bu transition in α,ω-diphenyloctatetraene to vary linearly as a function of the solvent polarizability, with a slope of −10900 ± 1000 cm^{-1}. In 1978, Gavin et al.[5] showed that the 0−0 component for the 1Ag → 1Bu transition in octatetraene in ten different solvents also varied linearly with solvent polarizability, with a slope of −10909 ± 1000 cm^{-1}. These results suggest that the slope is insensitive to the polarizability change in the octatetraene and hence that the slope for the phenylated octatetraene should be greater than that for unsubstituted octatetraene. However, in 1978, Andrews[20] showed α,ω-dimethyloctatetraene to exhibit a slope of −10150

± 150 cm^{-1} against the solvent polarizability. At most, such a slope can be assimilated to that for unsubstituted octatetraene; more probably, however, it is smaller because, on the basis of its $\Delta\alpha$ value, it should exceed that for octatetraene. Recently, our group measured the solvatochromism of ttbP4,[17] which has a $\Delta\alpha$ value between those for octatetraene and α,ω-diphenyloctatetraene, and found a slope of only -8049 ± 772 cm^{-1}, which is markedly smaller than even that for octatetraene. These results can be ascribed to alkyl substituents, hindering access of solvent molecules to the polyene system and reducing its solvatochromism via the solvent polarizability as a result. Also, they warrant further investigation, which, however, should be conducted by the same group, using an appropriate body of methyl and *tert*-butyl derivatives of the same polyene structure.

Conclusions

All-trans-polyenes exhibit a strong absorption band for their 1Ag → 1Bu transition that is red-shifted as the polarizability of the medium increases. The transition, however, is insensitive to other properties of the medium such as dipolarity, acidity of basicity. The sensitivity of the transition to the polarizability of the medium increases linearly with increasing length of the polyene chain.

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