Electronic Energy Levels in all-*trans* Long Linear Polyenes: The Case of the 3,20-Di(*tert*-butyl)-2,2,21,21-tetramethyl-all-*trans*-3,5,7,9,11,13,15,17,19-docosanonaen (ttbp9) Conforming to Kasha's Rule

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Abstract: The absorption, fluorescence and fluorescence excitation spectra for 3,20-di(*tert*-butyl)-2,2,21,21-tetramethyl-all-*trans*-3,5,7,9,11,13,15,17,19-docosanonaen (ttbP9) in dilute solutions of 2-methylbutane were recorded at temperatures over the range 120–280 K. The high photostability of this nonaene allows us to assert that it exhibits a single fluorescence and that this can be unequivocally assigned to emission from its 1^1B_u excited state, it being the first excited electronic state. Available photophysical data for this polyene and the wealth of information reported for shorter all-*trans* polyenes allow us to conclude that if the first excited electronic state for the chromophore possessed 2^1A_g symmetry, then the energy of such a state might have been so close to that of the 1^1B_u state that: 1) the radiationless internal conversion mechanism would preclude the observation of the emission from the 1^1B_u state reported in this work and 2) the 2^1A_g state reached through internal conversion would be vibrationally coupled to 1^1B_u and would facilitate the detection of the emission from 2^1A_g, which was not observed in any of the solvents used in this work. The spectroscopic and photochemical implications of these findings for other polyenes are discussed.

Keywords: absorption · fluorescence spectroscopy · Kasha's rule · photochemistry · polyenes

Introduction

Although the spectroscopic behaviour of polyenes has been widely studied,[1–5] a number of questions remain unanswered that are addressed in this paper. This may have been the result of the experimental difficulties posed by the high instability of polyenes, which very often prevent recording of the spectroscopic data required to reliably elucidate their photophysical behaviour. The photolability of these unsubstituted hydrocarbons is substantially reduced by the presence of substituents such as β-ionylidene or phenyl groups at the terminal carbon atoms, constituting the well-known carotinoid or diphenylpolyene families; however, the interaction between the π-electrons in the polyene structure and such substituents may conceal or alter the actual photophysical properties of the polyene chain. The use of methyl substituents to stabilise polyenes[6,7] has provided some results of a high photophysical significance that are commented on below.

Polyene chromophores occur in such prominent structures as visual pigments,[8] the carotenoid antenna of photosynthesis[9] and vitamins A[10] and D.[11] By virtue of their molecular structure, with alternate double and single carbon bonds, they are prototypes for such important structural transformations as *cis–trans* isomerisations.[12] Also, their potential metallic character makes them candidates for constructing molecular nanostructures capable of conducting charge along the linear polyene chain.[5] For all these reasons, polyenes continue to be a priority research topic.

The currently accepted photophysical model for unsubstituted polyenes, which has been extended to their derivatives, was developed by Hudson and Kohler[13] and establishes the following energy sequence for electronic states in the poly-

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enes beyond octatetraene: $1^1A_g \ll 2^1A_g < 1^1B_u$, in which 1^1A_g is the ground electronic state, and 2^1A_g and 1^1B_u are the first two excited singlet states. While the transition $1^1A_g \rightarrow 2^1A_g$ is forbidden, $1^1A_g \rightarrow 1^1B_u$ is strongly dipole-allowed. As a result, Hudson and Kohler believe that $1^1A_g \rightarrow 1^1B_u$ gives the first absorption band and $1^1A_g \rightarrow 2^1A_g$ the emission band, the energy gap between the excited electronic states 1^1B_u and 2^1A_g increasing with increasing length of the polyene chain. Most experimental evidence for octatetraene, pentaene and hexaene is consistent with the assumptions of this model. However, there exist conflicts with it as well:

1) Thus, in 1978 Gavin et al.[14] showed that, consistent with the model of Hudson and Kohler, octatetraene in the condensed phase exhibits emission with a large Stokes shift (3500 cm^{-1}) in *n*-hexane, but no shift in the gas phase (i.e., the emission originates from the 1^1B_u state), which is not consistent with the model. In 1984, Heimbrook et al.[15] reported that octatetraene in a free jet only exhibits $1^1B_u \rightarrow 1^1A_g$ emission, which is also inconsistent with the model. In 1990, Bowman et al.[6] found octatetraene in the gas phase to additionally exhibit slight emission resulting from the transition $2^1A_g \rightarrow 1^1A_g$, and in 1991, Petek et al.[16] observed both octatetraene emissions also in a free jet.
2) Gavin et al.[14] reported also relevant experimental facts: the emission $1^1B_u \rightarrow 1^1A_g$ of octatetraene in the gas phase at 295 K exhibits a quantum yield of 0.10 ± 0.05[14,15] and a lifetime of 14.8 ± 0.4 ns; on the other hand, the emission $2^1A_g \rightarrow 1^1A_g$ of this compound in *n*-hexane at the same temperature exhibits a quantum yield of 0.02 ± 0.01[14,15] and a lifetime of 4.4 ± 0.4 ns. As a result, the radiation constants for the two emissions, namely, 6.7 $(\pm 3.5) \times 10^6$ and 4.6 $(\pm 2.7) \times 10^6\ s^{-1}$, can be assumed to be identical within experimental error.
3) Snyder et al.[17] noted an abrupt fluorescence change from hexaene to heptaene in EPA (diethyl ether/L-methylbutane/ethanol = 5:5:2) matrix at 77 K: while hexaene only exhibited the emission $2^1A_g \rightarrow 1^1A_g$, heptaene exhibited the additional emission $1^1B_u \rightarrow 1^1A_g$, which was the stronger. This evidence allowed heptaene to be deemed an anti-Kasha compound.[18] It should be emphasised that no comparable change occurs in the corresponding dimethyl derivatives; in fact, deca-2,4,6,8-tetraene,[19] 2,10-dimethyl-1,3,5,7,9-undecapentaene,[20] 2,13-dimethyl-1,3,5,7,9,11-tridecahexaene,[20] and 2,4,6,8,10,12,14-hexadecaheptaene[7] all exhibit the typical behaviour modelled by Hudson and Kohler (namely, $2^1A_g \rightarrow 1^1A_g$ emission that is strongly shifted from the $1^1A_g \rightarrow 1^1B_u$ absorption).

A hypothetical prediction of the Hudson and Kohler model as the polyene chain is lengthened would lead to non-fluorescent all-*trans* polyenes, since the 2^1A_g state would quench the 1^1B_u state by internal conversion, and, in addition, the 2^1A_g state would not emit because it would not be coupled to 1^1B_u.

Also worth noting is the differential behaviour of α,ω-diphenylpolyenes. According to Bachilo et al.,[21] derivatives with polyene chains that contain three or more double bonds are doubly fluorescent in the condensed phase.

In this work, we synthesised and elucidated the structure and photophysics of the longest polyene (3,20-di(*tert*-butyl)-2,2,21,21-tetramethyl-all-*trans*-3,5,7,9,11,13,15,17,19-docosanonaen (ttbP9)) bearing only alkyl groups on its terminal carbon atoms studied so far. The compound consists of a chain that contains nine double bonds in an all-*trans* configuration and four *tert*-butyl groups that not only make the compound photophysically highly stable, but also result in the presence of a large number of vibrational modes and in a dramatically reduced energy gap between the electronic state 1^1B_u—which can be populated by direct excitation—and the potential state 2^1A_g. This is bound to enormously facilitate radiationless internal conversion mechanisms deactivating the 1^1B_u state to other, potentially lower energy states. This in turn should allow one to expose previously obscure states below 1^1B_u, which can be readily populated by absorption from the 1^1A_g the ground state.

The polyene structure studied, which has nine double bonds, must be regarded as a good photophysical model for carotenoid compounds, which play an important role in photosynthesis and many other important biological processes.

Experimental Section

Preparation of 3,20-di(*tert*-butyl)-2,2,21,21-tetramethyl-all-*trans*-3,5,7,9,11,13,15,17,19-docosanonaen (ttbP9): Zinc dust (1.04 g, 15.83 mmol) and anhydrous pyridine (0.56 g, 7.08 mmol, 0.57 mL) were added to a solution of $TiCl_4$ (1.80 g, 9.48 mmol, 1.04 mL) in anhydrous THF (100 mL) at 0 °C under nitrogen. The mixture was stirred for 30 min at 0 °C and 9-*tert*-butyl-10,10-dimethyl-undeca-2,4,6,8-tetraenal (250 mg, 1.02 mmol) dissolved in anhydrous THF (30 mL) was added. After stirring the suspension for 1 h at 0 °C, ice water, diethyl ether and finally 2 N HCl were added until the aqueous phase became clear. The organic phase was separated, the aqueous layer was extracted carefully with diethyl ether and the organic layers were combined, neutralised ($NaHCO_3$), and dried with sodium sulfate. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel with pentane providing 194 mg (83 %) of the nonaene as a dark-red solid, m. p. 172 °C. Crystals suitable for X-ray structural analysis were obtained by recrystallisation from chlorobenzene. ^1H NMR (400.1 MHz, $CDCl_3$, int. TMS): $\delta = 1.23$ (s, 18 H; *t*Bu), 1.37 (s, 18 H; *t*Bu), 6.07 (d, $^3J = 11.7$ Hz, 2 H; 4-, 19-H), 6.11–6.17 (dd, $^3J = 10.72$, $^3J = 14.29$ Hz, 2 H; 6-, 17-H), 6.29–6.38 (m, 10 H; 7-, 8-, 9-, 10-, 11-, 12-, 13-, 14-, 15-, 16-H), 6.81–6.88 ppm (dd, $^3J = 11.80$, $^3J = 14.16$ Hz, 2 H; 5-, 18-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 31.74$, 33.72 (q, CH_3 of *t*Bu), 37.92, 38.98 (C of *t*Bu), 124.04 (d, C-4, −19), 132.41 (d, C-6, −17), 132.96 (d, C-5, −18), 132.35, 132.91, 133.23, 133.45, 133.92 (d, C-7, −8, −9, −10, −11, −12, −13, −14, −15, −16), 157.91 ppm (C-3, −20); IR (KBr): $\tilde{\nu} = 2954$ (m), 1215 (m), 1005 cm^{-1} (vs); UV/Vis (acetonitrile): λ_{max} ($\log \varepsilon$) = 460 (4.97), 432 (4.98), 408 (4.79), 390 (4.48, sh), 372 (4.15, sh), 330 (3.76), 266 nm (4.02); MS (EI, 70 eV): m/z: 460 (100) [M^+], 403 (14), 346 (22), 57 (76); HRMS: calcd: 460.407; found: 460.406. The all-*trans*-configuration of the hydrocarbon was established by X-ray structural analysis.[22]

Spectroscopic measurements: Absorption and emission spectroscopic measurements were made on solutions containing a ttbP9 concentration of approximately 4×10^{-6} M in 2-methylbutane (2-MB), by using Suprasil quartz cells of 1 cm path length. The sample temperature, which ranged from 120 to 280 K, was controlled by an Oxford DNI1704 cryostat equipped with an ITC4 controller and interfaced to the spectrophotometers. UV/Vis and emission spectra were recorded on a Cary-5 spectrophotometer and an Aminco-Bowman AB2 spectrofluorimeter, respectively.

Corrected fluorescence and excitation spectra were obtained on a precalibrated Aminco-Bowman spectrofluorimeter. Samples of ttbP9 were excited to the third peak of the first absorption band (ca. 404 nm) by using light from a continuous wave (CW) 150 W xenon lamp for steady-state spectra. Emission excitation spectra were obtained by monitoring light at 520 nm. The slit widths used in the excitation and emission monochromators were 16 and 2 nm, respectively, for emission measurements, and 2 and 16 nm for excitation measurements.

Quantum yields were calculated from spectra for freshly prepared samples at 298 K recorded on the Aminco-Bowman instrument. The absorbances used correspond to the third peak of the first absorption band for both the standard DPO (DPO = α,ω-diphenyloctatetraene; for which the ϕ_f values at 298 K in cyclohexane and benzene are 0.09[23] and 0.15,[24] respectively) and ttbP9, and are 0.20.

The benzene, cyclohexane and 2-MB used were Merck Uvasol grade and contained less than 0.005 % water.

Fluorescence lifetimes were determined relative to glycogen scattering solutions, using modulation measurements made with excitation at frequencies over the range 90–250 MHz on an SLM 48000 spectrofluorimeter furnished with solid Pockels cells.

Results and Discussion

Figure 1 shows the absorption spectra for ttbP9 in 2-MB at temperatures between 120 and 280 K. The figure exposes the amazing thermochromism of this linear polyene. As shown in Figure 2 the position of the 0–0 transition for this band is strongly correlated with the sample temperature [Eq. (1)], with $n = 12$, $r = 0.99986$ and sd = 0.1 nm (n = number of points, r = correlation coefficient, sd = standard deviation).

$$\lambda_{0-0} = (-0.086 \pm 0.0005)T + 481.2 \pm 0.99 \qquad (1)$$

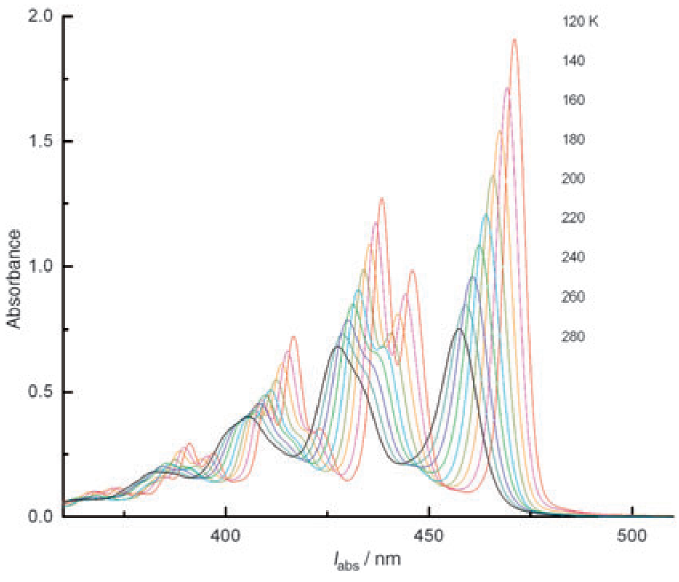

Figure 1. UV-visible absorption spectra of a solution of ttbP9 in 2-MB (4×10^{-6} M) between 280 and 120 K.

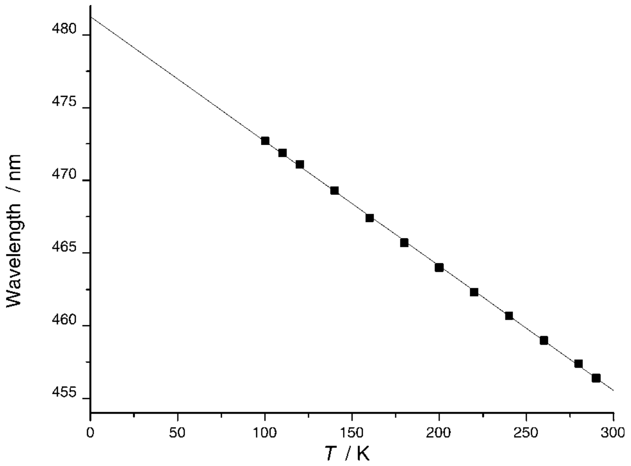

Figure 2. Wavelength of the 0–0 transition $1^1A_g \rightarrow 1^1B_u$ of ttbP9 in 2-MB versus experimental temperature.

Extrapolation to 0 K gives 481.2 ± 0.09 nm for the position of the 0–0 component, which must, therefore, correspond to the totally planar conformation of the compound. Also, because the 0–0 component of ttbP9 can be measured precisely in any type of medium, the compound can in principle be used as an accurate molecular thermometer.[25]

As can be seen from Figure 1, the electronic transition $1^1A_g \rightarrow 1^1B_u$ in ttbP9 is highly structured and spans a broad spectral range (360–490 nm).

The emission of ttbP9 in 2-MB upon excitation to its third vibronic peak (404 nm, Figure 3) exhibits no Stokes shift; nor does it change appreciably upon direct excitation of the 0–0 component. The excitation spectra (Figure 3) acceptably match the corresponding absorption spectra (Figure 1). Consequently, the emission can only be produced by a pure sample of ttbP9. In fact, no trace of emissions subject to large Stokes shifts was found over the spectral range examined.

Figure 3 shows the excitation and emission spectra for ttbP9 in 2-MB at 280, 220 and 120 K. For easier comparison, they were normalised with respect to their second peaks. The emission spectra clearly reveal the absence of a 0–0 component. This is highly significant as it indicates that 1) any Stokes shift is negligible and 2) the process is extremely efficient as the emission of the 0–0 component is virtually completely quenched by the bulk solution; this is particularly remarkable on account of the high dilution used. The spectra exhibit acceptable mirror symmetry at the three temperatures studied.

As with the absorption spectra (Figure 1), lowering the temperature resulted in bathochromic shifts in the emission excitation spectra (Figure 3). Thus, the second excitation peak was shifted by $-158\,\text{cm}^{-1}$ from 280 to 220 K and by $-477\,\text{cm}^{-1}$ from 280 to 120 K. Interestingly, the corresponding emission spectra (Figure 3) exhibited similar bathochromic shifts; thus, the second emission peak was shifted by $-182\,\text{cm}^{-1}$ from 280 to 120 K and by $-484\,\text{cm}^{-1}$ from 280 to 120 K. This confirms that the transition that gives the first

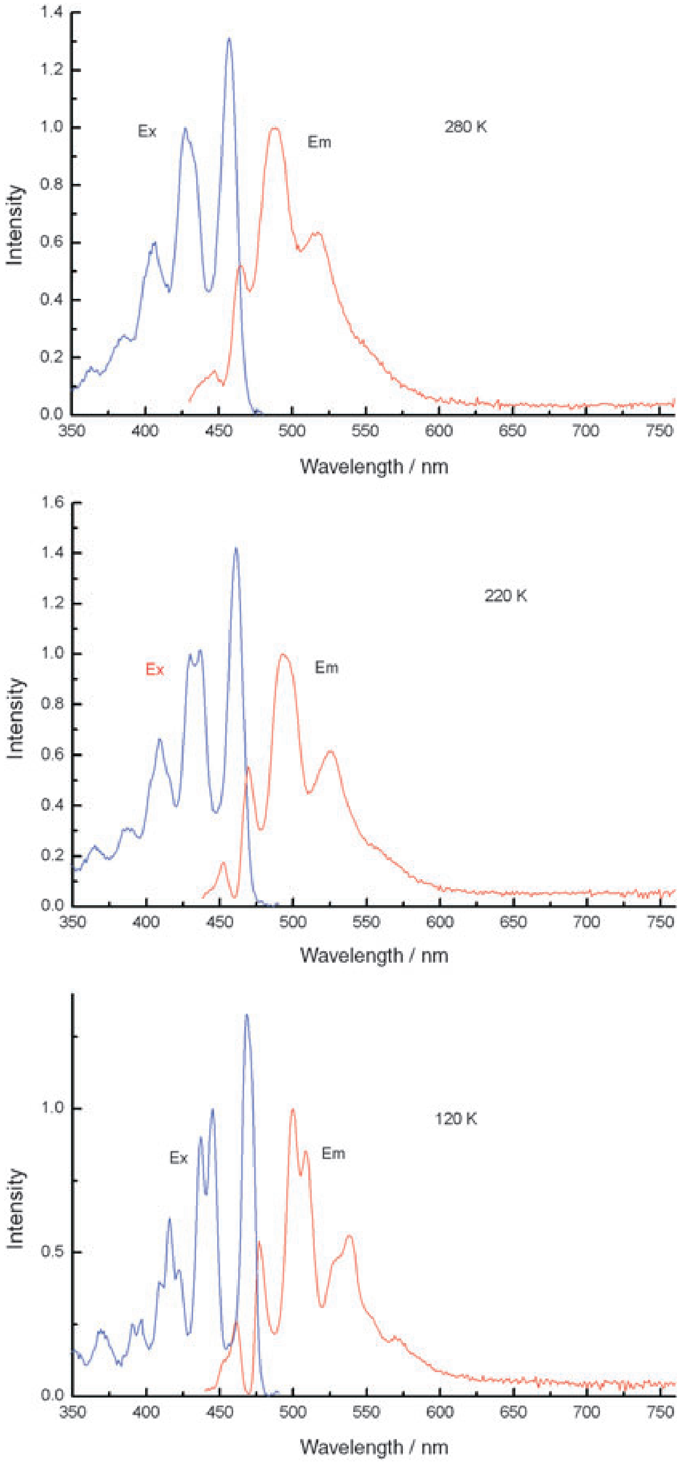

Figure 3. Corrected excitation (blue) and emission (red) spectra of a solution of ttbP9 in 2-MB (4×10^{-6} M) measured at 280 (top), 220 (middle) and 120 K (bottom).

absorption band for these compounds, $1^1A_g\rightarrow1^1B_u$, is also responsible for their emission (i.e., that the absorption leads to 1^1B_u and the emission originates from this state as well). The emission has $\phi_f=0.0004$ and $\tau_f=133$ ps, hence $k_f=3\times10^6$ s^{-1}.

The spectra of Figure 3 contain no band for any other fluorescence exhibiting a large Stokes shift. The absence of the $2^1A_g\rightarrow1^1A_g$ emission postulated by the Hudson and Kohler model cannot be explained by means of a self-absorption process, for the reason that no absorption band appears in the spectral region in which the $2^1A_g\rightarrow1^1A_g$ transition would have to be located. That is, the Hudson and Kohler model predicts that the 0–0 component of the $2^1A_g\rightarrow1^1A_g$ transition would be located at 555 nm (i.e., 18034 cm^{-1}, see Table 1 and the corresponding comments in text).

Table 1. Transition energies [cm^{-1}] for $1^1A_g\rightarrow1^1B_u$ and $2^1A_g\rightarrow1^1A_g$ for the unsubstituted polyenes (octatetraene, pentaene, hexaene, heptaene) in 2-MB, estimated from the solvatochromic relationships established by Snyder et al.[17] and their corresponding energy gaps.

	Absorption ($1^1A_g\rightarrow1^1B_u$) [ttbP]	Emission ($2^1A_g\rightarrow1^1A_g$)	ΔE
octatetraene	32978	28602	4376
decapentaene	29984	24550	5434
dodecahexaene	27437	21689	5748
tetradecaheptaene	25897	19472	6425
nonaene	24746[a] [21925][b]	18034[a]	6712

[a] Transition energies for absorption of the unsubstituted nonaene, extrapolated from the corresponding energy values of octatetraene, pentaene, hexaene, and heptaene. [b] 0–0 energy component for the transition $1^1A_g\rightarrow1^1B_u$ of ttbP9.

In 1950, Kasha[18] envisaged the photophysical significance of the radiationless internal conversion mechanism and wrote [that] "the phenomenon of internal conversion is manifested by the appearance of a unique luminescence, regardless of which state of a given multiplicity is excited. It yields a most useful spectroscopic criterion: *The emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity*." This criterion has come to be known as Kasha's rule. Fifty years on, few molecular systems have been found to contradict it. The best-known exception is no doubt azulene, the fluorescence of which starts from its second excited singlet and thus corresponds to an $S_2\rightarrow S_0$ transition. Recently, Christensen et al.[7,17] studied the fluorescence of heptaene and identified anti-Kasha behaviour in longer polyenes; according to these authors, heptaene exhibits double fluorescence due to an $S_1\rightarrow S_0$ transition ($2^1A_g\rightarrow1^1A_g$) and an $S_2\rightarrow S_0$ transition ($1^1B_u\rightarrow1^1A_g$).

Based on the solvatochromic behaviour of unsubstituted polyenes (octatetraene, pentaene, hexaene and heptaene) established by Snyder et al.,[17] we estimated the energies for the 0–0 components of the transitions $1^1B_u\rightarrow1^1A_g$ and $2^1A_g\rightarrow1^1A_g$ in 2-MB at room temperature (see Table 1). The data for all-*trans* polyenes containing 4–7 double bonds in their chains allows us to extrapolate the values for the 0–0 components in nonaene (also shown in Table 1). This in turn allows us to estimate the energy gap between the 1^1B_u and 2^1A_g states in nonaene: 6712 cm^{-1}.

Let us now estimate the energy gap for ttbP9. D'Amico et al.[26] reported that the presence of two methyl groups at the α- and ω-positions in a polyene decreased the energy gap by about 1000 cm^{-1}, as the exclusive result of a red shift by approximately 1000 cm^{-1} in the transition $1^1B_u \rightarrow 1^1A_g$, since, according to these authors, "the $2^1A_g \rightarrow 1^1A_g$ transition is almost unaffected by these substitutions". Table 1 includes the position of the 0–0 component for ttbP9 in 2-MB; the results expose an increased red shift for the transition $1^1B_u \rightarrow 1^1A_g$ by effect of the substitution with four *tert*-butyl groups at the α- and ω-positions in the polyene. The shift, which can be estimated to be about 2800 cm^{-1} for ttbP9, would reduce the hypothetical energy gap for this compound in 2-MB at room temperature to only 3900 cm^{-1}.

If an electronic state (2^1A_g) were present only 3900 cm^{-1} below 1^1B_u in the Jablonski diagram for ttbP9, then one could estimate the radiationless internal conversion constant for the transformation of the state reached through absorption (1^1B_u) into the forbidden state 2^1A_g. This is one of the molecular systems in which, similar to the particle-in-a-box model, the stability of the electronic states increases with increasing chain length; this is also the case with linear polyacenes, with which polyenes have frequently been compared in spectral terms. Let us use the $S_1 \rightarrow S_0$ internal conversion constants of the linear polyacenes benzene, naphthalene, anthracene, pentacene and hexacene, all in cyclohexane at 293 K, recently obtained by Nijegorodov et al.[27] with a view to establishing the energy-gap law. As can be seen from Figure 4, the logarithm of the corresponding k_{IC} values varies linearly with the energy gap between S_1 and S_0, which facilitates extrapolation of this behaviour.

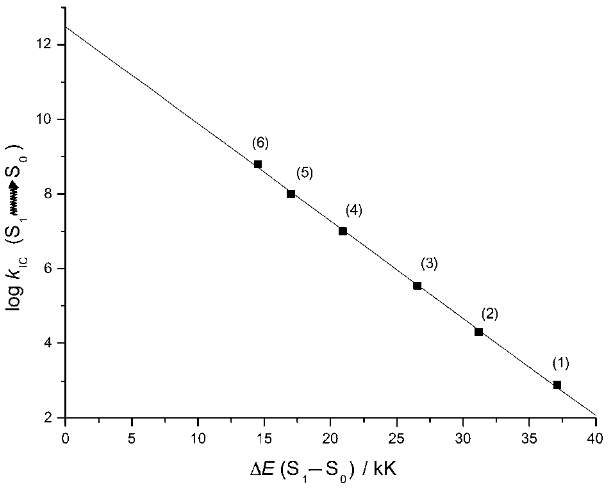

Figure 4. Logarithm of the internal conversion constant ($S_1 \rightarrow S_o$) versus the corresponding energy gap (S_1–S_o) for the polyacenic compounds: (1) benzene, (2) naphthalene, (3) anthracene, (4) tetracene, (5) pentacene, and (6) hexacene, all of them measured by Nijegorodov et al.[27] ($\log k_{IC} = -0.260 \pm 0.003)\Delta E + 12.48 \pm 0.09$; $r = 0.9996$ and sd = 0.074 kK).

Based on this figure, a gap of 3900 cm^{-1} results in $k_{IC} = 2.9 \times 10^{11}$ s^{-1}. This should only be taken as a lower limit for k_{IC} as internal conversion is a radiationless process, so it must obey Fermi's golden rule [Eq. (2)] in which φ_1 and φ_2 are the electronic wave functions of S_1 and S_2, respectively; θ_{1l} and θ_{2k} the nuclear wave functions for the appropriate vibrational levels of S_1 and S_2, respectively; **J** is the nuclear energy operator and ρ the number of isoenergetic levels present in S_1 relative to the S_2 levels involved in the internal conversion process.

$$k_{CI} \propto \langle \varphi_2|\mathbf{J}|\varphi_1\rangle^2 \sum\nolimits_k \sum\nolimits_l \langle \theta_{2k}|\theta_{1l}\rangle^2 \rho \quad (2)$$

As previously shown for acenes, the vibrations involved in this process are of the C–H type and their number increases substantially with the presence of the *tert*-butyl substituents. For this reason, the number of available isoenergetic states in ttbP9 must be quite large, as must k_{IC} as determined from the energy-gap law as a result. Therefore, if ttbP9 possessed a state 3900 cm^{-1} below 1^1B_u in the Jablonski diagram, the latter would be deactivated at room temperature by internal conversion, with a rate constant above 10^{12} s^{-1}; this would contradict the experimentally observed fluorescence of this compound from its 1^1B_u state, for which $k_f = 3 \times 10^6$ s^{-1}. Also, lowering the temperature from 280 to 120 K shifts the 0–0 component for the transition $1^1A_g \rightarrow 1^1B_u$ of ttbP9 in 2-MB hypsochromically by about 700 cm^{-1}, so the energy gap for the compound at 120 K must be 3200 cm^{-1} and its emission cannot change significantly. One other interesting fact is that the quantum yield changes little from cyclohexane to benzene (ϕ_f is 0.00043 in the former and 0.00041 in the latter); by contrast, the energy gap can be about 700 cm^{-1} smaller, consistent with the red shift in the 0–0 component for ttbP9 between the two solvents.[25]

We should bear in mind that for azulene, Kasha's rule breaks down because it exhibits an unusually large energy gap between its S_2 and S_1 states (13 980 cm^{-1}) with $k_{IC} = 7\text{x}10^8$ s^{-1};[28] however, this is not the case with ttbP9, for which the gap as small as 3900 cm^{-1} yields a large $k_{IC} = 10^{12}$ s^{-1}. Accordingly, if the forbidden state 2^1A_g is closer to 1^1B_u in ttbP9 than in octatetraene, why do 2^1A_g and 1^1B_u not couple one with another in ttbP9 thus allowing 2^1A_g to emit, as they supposedly do in octatetraene?

Based on the aforementioned, the first singlet state in the Jablonski diagram for ttbP9 must be 1^1B_u, which can be directly reached by absorption of light, so the emission must also correspond to the transition $1^1B_u \rightarrow 1^1A_g$ and the compound obeys Kasha's rule. This, however, does not exclude the potential generation of other molecular structures of ttbP9 from the 1^1B_u state; however, it is rather inconsistent with the presence of an excited electronic state only 3900 cm^{-1} below 1^1B_u and usurping the assignation of the S_1 state in the Jablonski diagram for the photophysical processes of ttbP9.

The stability of ttbP9 and its photophysical evidence compel extended studies to longer polyenes in order to check whether they also exhibit a single fluorescence due to the transition $1^1B_u \rightarrow 1^1A_g$ and to examine its behaviour, and also to shorter polyenes with a view to checking whether they behave like ttbP9 or why they do otherwise.

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[1] B. Hudson, B. Kohler, *Annu. Rev. Phys. Chem.* **1974**, *25*, 437–460.
[2] B. Hudson, B. Kohler, K. Schulten in *Excited States Vol. 6* (Ed.: E. C. Lim), Academic Press, New York, **1982**, pp. 1–85, and references therein.
[3] R. Christensen in *Photochemistry of Carotenoids* (Eds.: H. A. Frank, A. J. Yong, G. Briton, R. Codgell), Kluwer Academic, Dordrecht (The Netherlands), **1999**, p. 137.
[4] J. Catalán, *J. Chem. Phys.* **2003**, *119*, 1373–1385, and references therein.
[5] J. Catalán, J. L. G. de Paz, *J. Chem. Phys.* **2004**, *120*, 1864–1872, and references therein.
[6] W. G. Bowman, A. C. Jones, D. Phillips, P. Thibodeau, C. Friel, R. L. Christensen, *J. Phys. Chem.* **1990**, *94*, 7429–7434.
[7] S. A. Cosgrave, M. A. Guite, T. B. Burnell, R. L. Christensen, *J. Phys. Chem.* **1990**, *94*, 8118–8124.
[8] "The Photochemical Macromolecular Aspects of Vision": E. W. Abrahamson, S. E. Ostroy in *Progress in Biophysics and Molecular Biology*, *Vol. 7* (Eds.: J. A. Butler, H. E. Huxley), Pergamon, Oxford, **1967**.
[9] Govindjee in *Photochemistry of Carotinoids* (Eds.: H. A. Frank, A. J. Yong, G. Briton, R. Codgell), Kluwer Academic, Dordrecht (The Netherlands), **1999**, p. 1.
[10] "The biosynthesis of Carotinoids and Vitamin A": C. O. Chichester, T. O. M. Nakayama in *Biogenesis of Natural Products* (Ed.: P. Bernfeld), Pergamon, Oxford, **1963**.
[11] H. J. C. Jacob, E. Havinga, *Adv. Photochem.* **1979**, *11*, 305–373.
[12] C. Dugade, L. Demange, *Chem. Rev.* **2003**, *103*, 2475–2532.
[13] B. Hudson, B. Kohler, *Chem. Phys. Lett.* **1972**, *14*, 299–304.
[14] R. M. Gavin, Jr., C. Weisman, J. K. McVey, S. A. Rice, *J. Chem. Phys.* **1978**, *68*, 522–529.
[15] L. A. Heimbrook, B. E. Kohler, I. J. Levy, *J. Chem. Phys.* **1984**, *81*, 1592–1597.
[16] H. Petek, A. J. Bell, K. Yoshihara, R. L. Christensen, *J. Chem. Phys.* **1991**, *95*, 4739–4750.
[17] R. Snyder, E. Arvidson, C. Foote, L. Harrigan, R. L. Christensen, *J. Am. Chem. Soc.* **1985**, *107*, 4117–4122.
[18] M. Kasha, *Discuss. Faraday Soc.* **1950**, *9*, 14–19.
[19] J. R. Andrews, B. S. Hudson, *Chem. Phys. Lett.* **1978**, *57*, 600–604.
[20] R. L. Christensen, B. E. Kohler, *J. Phys. Chem.* **1976**, *80*, 2197–2200.
[21] S. M. Bachilo, C. W. Spangler, T. Gillbro, *Chem. Phys. Lett.* **1998**, *283*, 235–242.
[22] D. Klein, Ph.D. dissertation, Braunschweig, **2000**.
[23] I. B. Berlman, *J. Phys. Chem.* **1970**, *74*, 3085–3093.
[24] J. B. Birks, D. J. Dyson, *Proc. R. Soc. London Ser. A* **1963**, *275*, 135–148.
[25] J. Catalán, H. Hopf, *Eur. J. Org. Chem.* **2004**, *22*, 4694–4702.
[26] K. L. D′Amico, C. Manos, R. L. Christensen, *J. Am. Chem. Soc.* **1980**, *102*, 1777–1782.
[27] N. Nijegorodov, V. Ramachandran, D. P. Winkoun, *Spectrochim Acta Part A* **1997**, *53*, 1813–1824.
[28] N. J. Turro, V. Ramamurty, W. Cherry, W. Farnet, *Chem. Rev.* **1978**, *78*, 125–145.

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