

Polarized Electronic Spectroscopy and Photophysical Properties of 9,10-Bis(phenylethynyl)anthracene

Marcia Levitus and Miguel A. Garcia-Garibay*

Department of Chemistry and Biochemistry, University of California, 405 Hilgard Avenue, Los Angeles, California 90095

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The photophysics and electronic spectroscopy of 9,10-bis(phenylethynyl)anthracene (BPEA) were studied using absorption spectroscopy with polarized light, fluorescence anisotropy, and simple semiempirical calculations. The UV–vis spectrum of BPEA in fluid media shows a diminished vibrational resolution as compared to the fluorescence spectrum, whereas this resolution is recovered when a polyethylene film is used as the solvent. By comparison with the results of the semiempirical calculations, we conclude that the behavior in fluid media is a result of the coexistence of several conformations. In contrast, only the planar conformation exists in the polymer, giving a well-resolved spectrum. Dichroic UV–vis spectra show that the lowest energy transition is polarized along the long axis of the molecule (short axis of the anthracene frame) and shows the existence of an overlapping blue-shifted band with perpendicular polarization, which has null oscillator strength in pristine anthracene. The spectral overlap is also evidenced in both the excitation wavelength dependence of the limiting fluorescence anisotropy and the results of the semiempirical calculations.

1. Introduction

The title compound, 9,10-bis(phenylethynyl)anthracene (BPEA, see Figure 1) is one of the most efficient fluorescent compounds. BPEA has been widely used as fluorescer in chemiluminescent formulations such as the popular green lightstick Cyalume.^{1–3} Due to its remarkably high emission efficiency in the visible, good solubility in a variety of solvents, and chemical and thermal stability, BPEA has been proposed as a good molecular probe to study translational and rotational motions in diverse media such as organic glasses, polymers,^{4–7} and supercritical fluids.⁸ A variety of spectroscopic and photophysical techniques have been used to carry out these studies, including time-resolved and steady-state fluorescence anisotropy,^{4,5} fluorescence non-radiative energy transfer,⁹ Taylor dispersion,¹⁰ and holographic fluorescence recovery after photobleaching.⁶ The physicochemical principles on which these applications are based indicate the need of a good understanding of the photophysics and electronic spectroscopy of BPEA. It is usually assumed that 9,10-substitution leaves the UV–vis absorption spectrum of the anthracene core nearly unperturbed, and hence it is generally believed that the longest wavelength absorption band of the title compound is polarized along the short axis of the anthracene moiety.^{7,8,11}

In this work, we seek to gain a deeper insight into the photophysics and electronic spectroscopy of the title compound by using polarized spectroscopy combined with a theoretical analysis. The “stretched film” method,^{12,13} was used to determine the orientation of the absorption transition dipole moments, while the polarization of the fluorescence was studied through fluorescence anisotropy experiments. Results show that the lowest energy transition is polarized along the long axis of the molecule (short axis of the anthracene frame), overlapping with a blue-shifted transition with perpendicular polarization that is forbidden in pristine anthracene. This spectral overlap is also

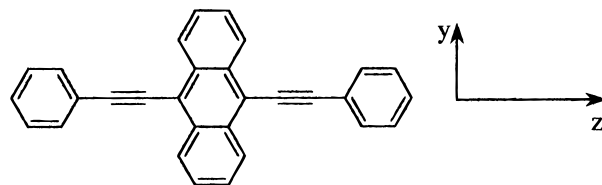


Figure 1. Structure of 9,10-Bis(phenylethynyl)anthracene (BPEA). The arrows indicate the direction of the principal axis of the molecule. The label *z* is assigned to the longest axis (short axis of the anthracene frame).

evident from the measured dependence of the fundamental fluorescence anisotropy with the excitation wavelength, and the results of the semiempirical calculations.

2. Experimental Section

2.1. Materials. BPEA was purchased from Aldrich and used as received. Chloroform, ethanol, cyclohexane, and methylcyclohexane were either HPLC or spectroscopic grade. Mineral oil (heavy paraffin oil) was purchased from Fischer. The polymer used in the dichroic spectra measurements was a linear low-density polyolefin (Sclairfilm SL-1, 4 mils) from DuPont Canada.

2.2. UV–Vis and Steady-State Fluorescence Spectra. Absorption spectra were obtained with a Shimadzu 3101-PC UV–Vis–NIR spectrophotometer. Fluorescence spectra were recorded in a Spex-Fluorolog II spectrofluorometer and corrected for nonlinear instrumental response.

2.3. Determination of Transition Dipole Moment Orientations. Preparation of Polymer Films. The polymer films were first washed with chloroform to remove additives and impurities. Films were stretched to about 3.5 times their initial length prior to the incorporation of the substrate. The doping was performed by swelling the stretched films with a chloroform solution containing the substrate and evaporating the solvent. To remove all crystalline residues from the surface of the sample, the films

* Corresponding author. E-mail: mgg@chem.ucla.edu.

were subsequently washed with ethanol, a solvent that does not swell the polymer.

Measurement of Spectra. Dichroic spectra were determined in a Shimadzu 3101-PC UV–Vis–NIR spectrophotometer equipped with a Glan–Taylor calcite polarizer in the sample beam. Absorbances were measured with light polarized parallel, $E'_Z(\lambda)$, and perpendicular, $E'_Y(\lambda)$, to the stretching direction. The absorbances corresponding to the baselines, $E^0_Z(\lambda)$ and $E^0_Y(\lambda)$ were recorded under the same conditions after extracting the solute from the polymer. Final dichroic spectra $E_U(\lambda)$ were obtained by baseline subtraction from the total absorbances $E'_U(\lambda)$.

$$E_U(\lambda) = E'_U(\lambda) - E^0_U(\lambda) \quad U = Z, Y \quad (1)$$

Identical parallel and perpendicular spectra ($E_Z(\lambda)$ and $E_Y(\lambda)$, respectively) were obtained for an isotropic liquid solution, ruling out the possibility of artifacts derived from polarization biases introduced by monochromators and other optical elements. In the remainder of the manuscript, lowercase subscripts (x, y, z) are used for molecular axes, and uppercase subscripts (X, Y, Z) refer to laboratory axes.

2.4. Time-Resolved Fluorescence Decays. The fluorescence decays were measured with a time-correlated single photon counting fluorometer (Edinburgh Instruments, model FL900CDT) equipped with a pulsed H_2 discharge lamp operating at 0.4 bar (fwhm ~ 0.7 ns). When necessary, the fluorescence intensity was attenuated to obtain an average number of detected fluorescence photons lower than 1% of the excitation source repetition rate (40 kHz). The experimentally measured emission was deconvoluted from the instrumental response to obtain the emission decay. The instrumental response was measured using a LUDOX suspension as a scattering sample, setting both monochromators at the emission wavelength of the sample. Measurements at 77 K were carried out by exciting the sample with vertically polarized light and setting the emission polarizer at the magic angle to eliminate polarization effects.

2.5. Time-Resolved Fluorescence Anisotropy Measurements. Time-resolved fluorescence anisotropy studies were performed at room temperature using mineral oil as the solvent (kinematic viscosity larger than 34.5 cSt at 40 °C). The fluorescence anisotropy, $r(t)$, was calculated from the time-resolved fluorescence data using eq 2. The subscripts V and H

$$r(t) = \frac{I_{VV}(t) - I_{VH}(t)}{I_{VV}(t) + 2I_{VH}(t)} \quad (2)$$

refer to the position of the excitation and emission monochromators ($V = 0^\circ$, $H = 90^\circ$), respectively. The two decays, $I_{VV}(t)$ and $I_{VH}(t)$, were normalized on the tail to account for the difference in sensitivities of the detection system for vertically and horizontally polarized light.

3. Results

The UV–vis absorption and fluorescence emission spectra of BPEA in cyclohexane are shown in Figure 2. The shape and position of both spectra were shown to be almost identical in a variety of solvents including benzene, *tert*-butyl alcohol, dibutyl phthalate¹⁴ and supercritical CO_2 .⁸ The inset shows the UV–vis spectrum in a nonstretched film for comparison. A fluorescence quantum yield of 0.87 was measured in cyclohexane at room temperature using quinine sulfate as a standard. This result is in accordance with literature values.^{1,14}

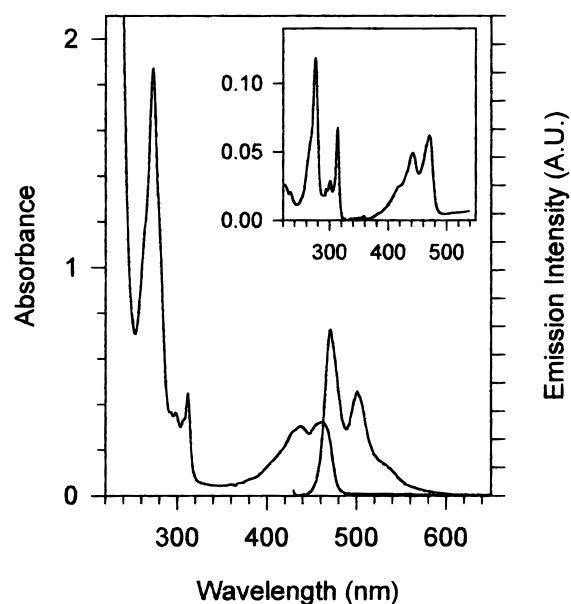


Figure 2. UV–vis and fluorescence spectra of BPEA in cyclohexane at room temperature. Inset: UV–vis absorption spectrum of BPEA in a nonstretched polyolefin film.

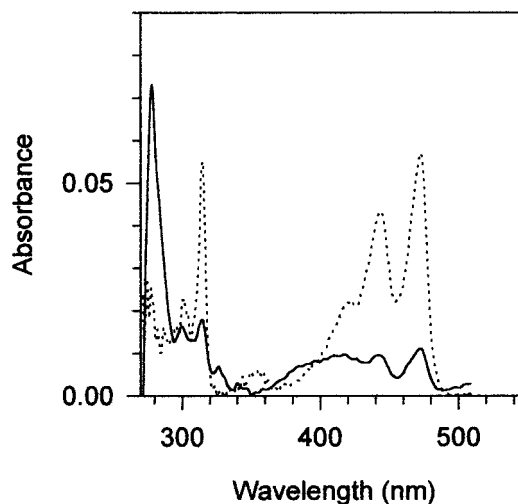


Figure 3. Dichroic spectra of BPEA in a polyolefin stretched film. Solid line: E_Y , spectrum measured with the polarizer axis perpendicular to the stretching direction. Dotted line: E_Z , spectrum measured with the polarizer axis parallel to the stretching direction.

The fluorescence decay in methylcyclohexane was adequately fitted by a monoexponential with a lifetime of 3.2 ± 0.1 ns at room temperature, and 3.8 ± 0.1 ns at 77 K. The ratio of these values equals the fluorescence quantum yield obtained at room temperature within experimental error. Assuming that internal conversion is the only temperature-dependent process, this result suggests that intersystem crossing does not play a significant role on the photophysics of this compound.

The dichroic UV–vis absorption spectrum of BPEA in a stretched film is shown in Figure 3. The dotted line shows the spectrum obtained when the polarizer axis was set parallel to the stretching direction of the film (Z -axis), while the solid line is the spectrum obtained when the polarizer was rotated 90° . A first examination of the two spectra reveals that the dichroic ratio, E_Z/E_Y , is not constant throughout the band in the visible, indicating the contribution of spectral features with mixed polarization to the total absorbance. Because of the high symmetry of the molecule, the transition dipole moments are expected to lie along one of the principal axis of the molecule.

A general equation that relates the measured spectra (E_X , E_Y , E_Z) with the purely polarized spectra (A_x , A_y , A_z) is given below.⁸

$$\begin{pmatrix} E_X(\lambda) \\ E_Y(\lambda) \\ E_Z(\lambda) \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(1-K_x) & \frac{1}{2}(1-K_y) & \frac{1}{2}(1-K_z) \\ \frac{1}{2}(1-K_x) & \frac{1}{2}(1-K_y) & \frac{1}{2}(1-K_z) \\ K_x & K_y & K_z \end{pmatrix} \begin{pmatrix} A_x(\lambda) \\ A_y(\lambda) \\ A_z(\lambda) \end{pmatrix} \quad (3)$$

In the film, E_X cannot be measured and it is usually assumed that $E_X = E_Y$. This assumption is supported by studies which show equivalence of the X and Y directions in stretched polyethylene.¹⁵ In eq 3, the subscripts x , y , z represent each of the three principal axis of the molecule, and $K_{x,y,z}$ denotes the orientation factors, which are a measure of the degree of alignment of each molecular axis with the unique sample direction Z (coincident with the stretching direction).

$$K_u = \langle \cos^2 \theta_u \rangle \quad u = x, y, z \quad (4)$$

Equation 3 serves as a basis for the analysis of experimental data. Linear combinations of the form $E_Z(\lambda) - cE_Y(\lambda)$ over the entire spectrum will contain the features of different polarizations to different degrees, and in some of them, one of the purely polarized spectra (A_x , A_y , A_z) will be absent altogether. Such linear combinations can be found by trial and error (stepwise reduction, see ref 12). If a set of peaks $A_u(\lambda)$, polarized along the axis u , disappears from the linear combination (i.e., the coefficient at $A_u(\lambda)$ vanishes), we have from eq 3.

$$c = \frac{2K_u}{1-K_u} \quad (5)$$

Results show that the dichroic ratio (E_Z/E_Y) is fairly constant in the 450–480 nm range, indicating that this band is purely polarized along the molecular axis that aligns better with the stretching direction Z . However, it is evident from Figure 3 that spectral features with different polarization contribute to the absorbance around 370–450 nm. The assumption that the long axis in BPEA (z -axis) aligns better with the stretching direction than any other axis in the molecule (see discussion below) leads to the assignment of the lowest energy transition as being z -axis polarized. As it will be discussed in detail in the next section, this result is in agreement with what is expected for anthracene derivatives, and with the results of simple semiempirical calculations. The use of the stepwise reduction procedure described above gives the purely polarized spectra A_z and A_y shown in Figure 4. The corresponding orientation factors are $K_z = 0.72$ and $K_y = 0.22$.

The previous analysis relies on the assumption that molecular shape determines how the molecule is oriented in the film. Although this was found not to be true in some cases, including indole, tryptophan, and purine derivatives in poly(vinyl alcohol),¹⁶ a comprehensive study on the orientation of aromatic molecules in stretched polyethylene¹³ shows that the longest axis of the molecule tends to align with the stretching direction. This was shown to be true for numerous molecules, including several aromatic hydrocarbons with similar size and shape as BPEA [for example naphthalene, dibenzo-1,2,7,8-anthracene, 1,4-diphenyl 1,3-butadiene, 9-benzo[*rst*]pentaphene and indeno-(1,2,3-*c,d*)fluoranthrene].^{12,13}

Time-resolved fluorescence anisotropy decays were measured at different excitation and emission wavelengths. In all cases, a monoexponential decay was observed, which is in accordance with results reported by Maroncelli et al. in a variety of

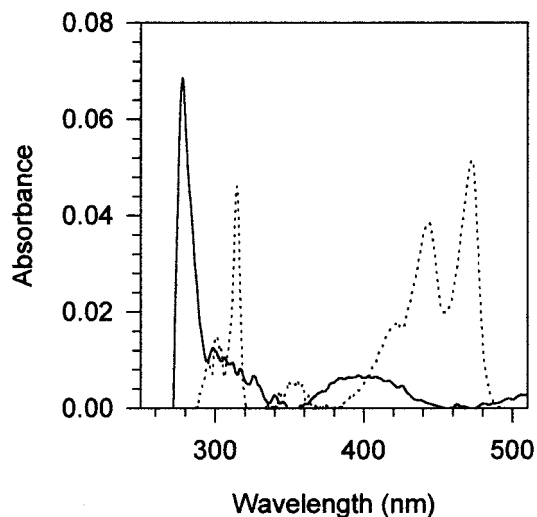


Figure 4. Purely polarized spectra obtained from the stepwise reduction procedure discussed in the text. Solid line: A_y , spectrum polarized along the y -axis. Dotted line: A_z , spectrum polarized along the z -axis.

TABLE 1: Measured Fundamental Anisotropy, r_0 , as a Function of the Excitation and Emission Wavelengths

	excitation wavelength (nm)	emission wavelength (nm)	r_0
1	270	470	-0.19
2	312	470	0.38
3	312	500	0.39
4	312	520	0.37
5	385	500	0.30
6	440	500	0.36
7	475	500	0.38

solvents.⁸ Extrapolation to zero time gives the fundamental anisotropy, r_0 , which depends on the angle formed between the absorption and emission dipole moments (β) according to eq 6. The extrapolated values of r_0 are shown in Table 1 for

$$r_0(\beta) = \frac{2}{5} \left(\frac{3}{2} \cos^2 \beta - \frac{1}{2} \right) \quad (6)$$

different excitation and emission wavelengths. Comparison of rows 2–4 shows that r_0 is independent of the emission wavelength, while rows 1–2 and 5–7 show that there is a strong dependence of r_0 with the excitation wavelength. This dependence is illustrated in Figure 5, where the r_0 values are superimposed on the measured UV–vis spectrum in mineral oil.

Equation 6 predicts a maximum possible value of $r_0 = 0.4$ in isotropic solutions, obtained when the absorption and emission dipole moments are parallel ($\beta = 0^\circ$), whereas the minimum value $r_0 = -0.2$ is obtained when the transition moments are perpendicular ($\beta = 90^\circ$). Results show that excitation at 475 and 312 nm yield r_0 values very close to the theoretical maximum, while excitation at 270 nm yields a value very close to the minimum. The limiting anisotropy exhibits a dependence with the excitation wavelength throughout the band in the visible (440–385 nm), indicating the existence of overlapped transitions of different polarizations. As the excitation wavelength is shifted to the blue, the limiting fluorescence anisotropy decreases, suggesting that there is a transition polarized perpendicular to the fluorescence whose contribution to the total absorbance is increasing.

To explore the nature of the two transitions overlapping in the region between 350 and 480 nm, we performed semiempirical calculations of the electronic spectra and transition

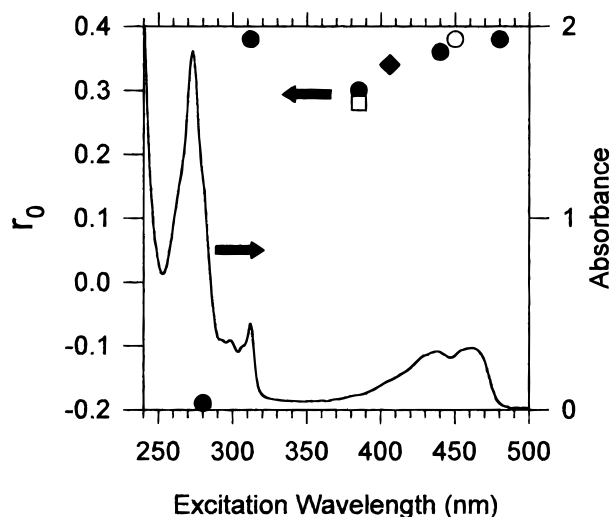


Figure 5. Fundamental anisotropy (r_0) as a function of the excitation wavelength. The UV-vis spectrum in mineral oil is superimposed for clarity. ● This work. ○ From ref 8, in several polar and nonpolar solvents. □ From ref 8, in *n*-decane and Decalin. ◆ from ref 4, in a solution of polystyrene in THF.

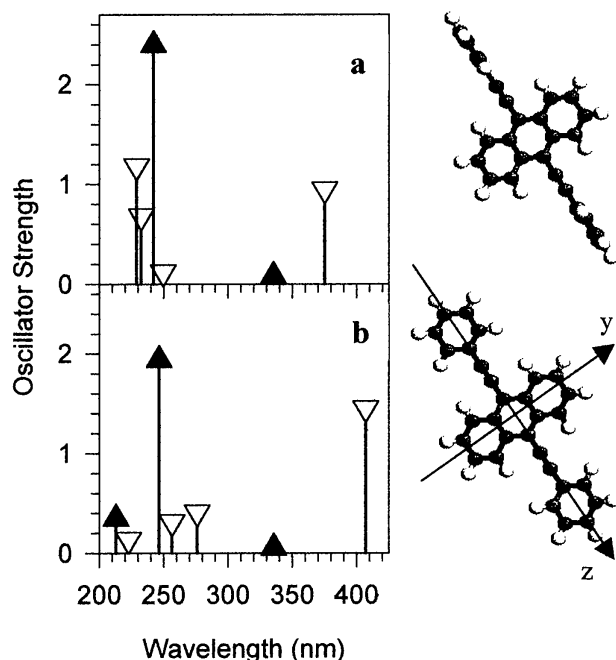


Figure 6. Calculated UV-vis spectrum for the two conformations shown on the right. ▽: *z*-axis polarized transition. ▲: *y*-axis polarized transition.

moment directions of BPEA. The geometry of BPEA was optimized using the AM1 method, and the electronic spectrum and transition moment directions were computed using the ZINDO/S method as implemented in the Hyperchem package.¹⁷ The CI matrix was computed using 201 lowest, single excited configurations. Figure 6 and Table 2 show the results obtained for the two conformations. According to the calculations, the planar conformation is the most stable, although the conformation where the two phenyl rings are perpendicular to the anthracene plane (**a** in Figure 6) is only 0.34 kcal/mol higher in energy. This indicates that the phenyl groups can rotate almost freely at room temperature and both conformations should be present in a fluid solution. For all calculated transitions, the transition dipole moment lies parallel to one of the principal axis of the molecule. In some cases, the energy of the transition and the corresponding calculated oscillator strengths depends

TABLE 2: Calculated UV-Vis Spectrum for the Two Conformations Shown in Figure 6^a

<i>a</i>			<i>b</i>		
λ (nm)	<i>f</i>	<i>p</i>	λ (nm)	<i>f</i>	<i>p</i>
375.2	0.95	<i>z</i>	407.1	1.45	<i>z</i>
335.3	0.08	<i>y</i>	335.7	0.05	<i>y</i>
249.7	0.12	<i>z</i>	276.1	0.41	<i>z</i>
242.1	2.39	<i>y</i>	256.5	0.32	<i>z</i>
232.6	0.68	<i>z</i>	246.6	1.94	<i>y</i>
229.0	1.19	<i>z</i>	222.7	0.14	<i>z</i>

^a *f* and *p* represent the oscillator strength and polarization of the transition, respectively.

on the dihedral angle formed by the anthracene plane and the planes containing the phenyl groups. This is especially true for the lowest energy transition, for which calculations predict a smooth blue shift of 32 nm when rotating both phenyl groups from conformation **b** to obtain conformation **a** (see Figure 6). In this hypothetical process, the oscillator strength decreases by 35%.

4. Discussion

The electronic excited states of anthracene have been extensively studied. Various anisotropic media and techniques for dichroic measurements applied to anthracene have shown consistent results.^{16,18–21} Polarization experiments permit an unambiguous assignment of the intense B_b transition near 255 nm as long-axis polarized, and the assignment of the 0–0 component of the L_a band as in-plane, short-axis polarized. Linear dichroism in stretched polyethylene shows mixed polarization in the 1L_a band with long-axis polarized spectral features. However, this was assigned to vibronic mixing with the 1B_b band, and no evidence for the presence of a 1L_b state (which would be polarized along the long axis) was found.²² Theoretical calculations predict a zero oscillator strength for the 1L_b transition in anthracene; however, it was shown that methoxy substitution at the 9,10 position causes a new transition to appear, which was identified as the 1L_b band.²³

Our results in polyethylene for BPEA show that there is mixed polarization throughout the band in the visible region of the spectrum. The dichroic spectra in a stretched polymer film show the overlap of a vibronically resolved electronic transition polarized along the *z*-axis (short axis of the anthracene moiety, long axis of the BPEA molecule) with a *y*-axis broad polarized transition of higher energy.

The values of r_0 obtained by fluorescence anisotropy are consistent with these results. The fact that r_0 is independent of the emission wavelength suggests that the emission is exclusively from the S_1 state, giving a vibronically resolved fluorescence spectrum, which is practically the mirror image of the purely *z*-axis polarized absorption obtained in the dichroic measurements.

A value of r_0 very close to 0.4 is obtained when an isotropic solution is excited at 475 nm, a region where the *y*-axis polarized band does not contribute to the absorption in the visible. However, as the excitation wavelength is shifted to lower values, the observed anisotropy decreases, indicating the contribution of transitions of mixed polarizations to the absorption. This is consistent with the results obtained in stretched polyethylene, which shows that the two transitions with perpendicular polarizations overlap in the 350–450 nm range. Fluorescence anisotropy results show that the bands at 312 and 270 nm are purely polarized along the *z*-axis and *y*-axis, respectively, which are in good agreement with the stretched film results. From

Figure 4, a negative r_0 value would be expected when exciting at 385 nm, in contrast with the positive value obtained experimentally. This suggests that direct comparison between the results obtained in the polymer and the ones obtained in solution is not straightforward. The fact that the lowest energy transition of the different conformations in solution span a range of nearly 30 nm, and the extinction coefficient of the bands in the visible depends on the conformation, and possibly on the solvent, complicates the comparison between the two media to a large extent.

The results discussed above would explain in part why the visible band in the UV-vis spectrum of BPEA in solution lacks the vibrational resolution seen in the fluorescence spectrum. In the polymer, once the y-axis polarized band is subtracted, the remaining z-axis polarized spectrum shows the same features as the fluorescence spectrum. However, the existence of a variety of conformations in solution may contribute even further to a decrease in the vibrational resolution. The calculated UV-vis spectra are in good agreement with the experimental data. The position of the calculated bands are 30–50 nm shifted to the blue with respect to the measured spectrum, but the relative position of the transitions give satisfactory results. Independently of the conformation of the molecule, theory predicts the lowest energy transition to be polarized along the long axis of the molecule (short axis of the anthracene moiety). The same result is observed in pristine anthracene and many 9,10-disubstituted anthracenes such as dimethyl,²⁴ diphenyl, dibromo,²⁰ and several 9-acetoxy-10 phenylanthracenes.²⁵ Our calculations predict the presence of a y-axis polarized transition located 40–70 nm to the blue, depending on the torsion of the phenyl groups with respect to the anthracene plane. This result is in agreement with the dichroic experiments and the fluorescence anisotropy results that show the contribution of a y-axis polarized transition to the absorbance in the visible. However, the calculated oscillator strength of this transition is too small to account for the experimental observations, indicating that either the calculations do not give accurate values for the oscillator strengths, or vibronic mixing with the y-axis polarized band around 270 nm contributes to this absorption.

The intense y-polarized transition calculated around 270 nm is clearly seen in the dichroic spectra and fluorescence anisotropy experiments, and it is analogous to the B_b transition of anthracene. However, a new z-axis polarized transition that is not present in either anthracene nor 9,10-diphenyl anthracene appears around 312 nm and is also predicted by the calculations.

Figure 2 shows a remarkable difference between the UV-vis spectrum in solution and the one measured in the polymer film (shown in the inset). As stated previously, the UV-vis spectrum measured in cyclohexane is relatively broad and is identical to those published in the literature for a variety of solvents of different polarities and viscosities. However, when polyethylene is used as a solvent, the visible region of the spectrum is more resolved and is very similar to the z-polarized band obtained in the dichroic experiments (see Figure 4). Furthermore, the relative intensity of the 270 nm band with respect to the bands at 312 and 470 nm is much higher in solution than in the polymer. A possible explanation for these observations becomes apparent by examination of the predicted influence of the conformation of the phenyl rings on the UV-vis spectrum.

It is well-known that the main locations of guest molecules in unstretched polyethylene are the amorphous parts and the interfacial regions between crystalline and amorphous domains.²⁶ It is reasonable to assume that the planar conformation of BPEA

is preferred in this environment²⁷ in contrast to the situation in fluid media where all conformations are expected to be present in similar proportions. According to the calculations, the overlap between the z-polarized and y-polarized transitions in the visible is smaller in the totally planar conformation, which would explain why the visible region of the UV-vis spectrum in the polymer shows better vibrational resolution. Furthermore, the fact that the position of the z-axis polarized transition in the visible spans a range of ca. 30 nm when the phenyl groups are rotated with respect to the anthracene plane is also consistent with the fact that the visible bands in solution are broader. According to the calculations, the energy difference between the two conformations of Figure 6 increases from 0.34 kcal/mol in the ground state to 6.3 kcal/mol in the excited state, suggesting that emission occurs mainly from the planar configuration even in solution. Finally, calculations predict the relative absorption at 270 nm with respect to the bands at 312 and 470 nm to be smaller for the more planar structure. This would explain the differences observed in the polymer with respect to the spectrum in fluid media.

5. Conclusions

In this paper, we have examined the photophysics and electronic spectroscopy of BPEA. The results obtained from the UV-vis measurements can be explained with the aid of semiempirical calculations, which show that the energy of the well resolved band in the visible depends on the dihedral angles formed by the anthracene plane and the two phenyl rings.²⁸ The measured absorption spectrum in fluid media would then result by convolution of the individual spectra for each present conformer, while the measured absorbance in the polymer film would correspond to the spectrum of the planar form, which is expected to be dominant in the polymer. Dichroic UV-vis spectra in stretched films of polyethylene show that the lowest energy transition is polarized along the long axis of the molecule, and the existence of an overlapping blue-shifted transition with perpendicular polarization. This overlap is confirmed in the fluorescence anisotropy experiments, where the fundamental anisotropy shows a marked dependence on the excitation wavelength where the two transitions overlap. These results suggest that the 9,10-substitution has a great influence on the oscillator strength of the 1L_b band, which is forbidden for pristine anthracene.

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Supporting Information Available: Representative polarized fluorescence decays and time-resolved fluorescence anisotropy of BPEA in mineral oil. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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